

Secondary Chemistry Student's Book

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The book comprehensively covers the Secondary 3 syllabus as developed by Ministry **o**f General Education and Instruction.

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Secondary Chemistry

Student's Book



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Chemistry Student's Book 3

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FOREWORD

I am delighted to present to you this textbook, which is developed by the Ministry of General Education and Instruction based on the new South Sudan National Curriculum. The National Curriculum is a learner-centered curriculum that aims to meet the needs and aspirations of the new nation. In particular, it aims to develop (a) Good citizens; (b) successful lifelong learners; (c) creative, active and productive individuals; and (d) Environmentally responsible members of our society. This textbook, like many others, has been designed to contribute to achievement of these noble aims. It has been revised thoroughly by our Subject Panels, is deemed to be fit for the purpose and has been recommended to me for approval. Therefore, I hereby grant my approval. This textbook shall be used to facilitate learning for learners in all schools of the Republic of South Sudan, except international schools, with effect from 4th February, 2019.

I am deeply grateful to the staff of the Ministry of General Education and Instruction, especially Mr Michael Lopuke Lotyam Longolio, the Undersecretary of the Ministry, the staff of the Curriculum Development Centre, under the supervision of Mr Omot Okony Olok, the Director General for Quality Assurance and Standards, the Subject Panelists, the Curriculum Foundation (UK), under the able leadership of Dr Brian Male, for providing professional guidance throughout the process of the development of National Curriculum and school textbooks for the Republic of South Sudan since 2013. I wish to thank UNICEF South Sudan for managing the project funded by the Global Partnership in Education so well and funding the development of the National Curriculum and the new textbooks. I am equally grateful for the support provided by Mr Tony Calderbank, the former Country Director of the British Council, South Sudan; Sir Richard Arden, Senior Education Advisor of DflD, South Sudan. I thank Longhorn and Mountain Top publishers in Kenya for working closely with the Ministry, the Subject Panels, UNICEF and the Curriculum Foundation UK to write the new textbooks. Finally, I thank the former Ministers of Education, Hon. Joseph Ukel Abango and Hon. Dr John Gai Nyuot Yoh, for supporting me, in my previous role as the Undersecretary of the Ministry, to lead the Technical Committee to develop and complete the consultations on the new National Curriculum Framework by 29 November 2013.

The Ministry of General Education and Instruction, Republic of South Sudan, is most grateful to all these key stakeholders for their overwhelming support to the design and development of this historic South Sudan National Curriculum. This historic reform in South Sudan's education system is intended to benefit the people of South Sudan, especially the children and youth and the future generations. It shall enhance the quality of education in the country to promote peace, justice, liberty and prosperity for all. I urge all Teachers to put this textbook to good use.

May God bless South Sudan. May He help our Teachers to inspire, educate and transform the lives of all the children and youth of South Sudan.

ashi Noutra

Deng Deng Hoc Yai, (Hon.) Minister of General Education and Instruction, Republic of South Sudan

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Learning Outcomes				
Knowledge and understanding	Skills	Attitudes		
 Understand volumetric analysis and identify various gases. Understand molarity, standard solutions, concentration, neutralisation, end point, equivalent points, and titration. 	 Investigate what is meant by concentration and how it might be determined through volumetric analysis. Design investigations to accurately make solutions. Investigate the practical implications and applications of volumetric analysis in the formation of compounds and overcoming conditions such as 'hard water.' Carry out practical tests to identify 	• Appreciate the importance of gases in life.		
	 Carry out practical tests to identify gases/ 			

1.1 Introduction

Volumetric analysis is the application used in most chemical laboratories to determine the concentration and molarity of substances. The substance may include; acids, bases, cleaning detergents, soft drinks and water analysis. This helps to determine their components and purity levels for safe usage.

In your previous Chemistry lessons and laboratory activities, for example, you have come across information such as:

- use dilute hydrochloric acid or concentrated nitric acid
- 1. What does such information bring to your mind?
- 2. If you are instructed to use dilute acid and not concentrated acid. Have you ever wondered what difference it makes? If so, why?

Activity 1.1

Work in groups of three

- 1. Differentiate between the strength of acid and bases and their concentrations.
- 2. Using books and the internet, find out and write an outline on how you would find out the concentration of an acid in a given sample of soft drink.

List all the necessary materials you will need and discuss your plan with your group members.

3. Take about 10cm³ of carbonated soft drink or lemon juice and put in two separate beakers. To the first beaker add some broken biscuits and record your observations.

To the second beaker, add a solution of wood ash followed by some broken biscuits and record your observations.

Compare and discuss your results with students from other groups.

Discussion corner!

- 1. What do you think makes carbonated and other soft drinks acidic?
- 2. Discuss the observations made when broken biscuits were added to the soft drink.
- 3. Explain the role of wood ash in the second beaker.

The Facts

The soft drinks are carbonated, so a freshly-opened bottled drink should have a lot of dissolved carbonic acid, but among the other ingredients may also include other acids such as phosphoric acid and citric acid . Biscuits contain sodium hydrogen carbonate that reacts with acidic coke to produce bubbles of a gas (carbon (IV) oxide). In the second beaker wood ash being base therefore neutralizes the acid in the soft drink. When biscuits are added there is no production of a gas.

The concentration of the acid can be determined through volumetric analysis.

Volumetric analysis takes place in a wide variety of situations such as in industrial laboratories, hospital laboratories and forensic science laboratories.

Discussion corner!

In pairs, think about these everyday reactions:

- Baking: an acid base reaction: how does this reaction make dough to rise?
- Alkalis: are used to remove grease. Why?
- Tooth paste: neutralises acids which attack teeth. How?
- Magnesium hydroxide: used to cure stomach upsets and ulcer wounds. How?
- Bee sting: Applying wood ash reduces the pain. Why?

1.2 Standard solutions

Discussion corner

In groups of three

1. The following are some of the apparatus used in volumetric analysis. Identify them and their uses.



Fig 1.1

2. Research about the main steps to be followed in preparing standard solutions. Write a report and share with other class members.



Volumetric analysis involves the use of solutions of known concentrations. A common task in every chemical laboratory is the preparation of solutions of known concentrations. Solutions are usually prepared from liquids or solids and occasionally gases or solutes. A solution is called a **standard solution** when its concentration is accurately known. Standard volumetric flasks marked with volumes are used in preparation of standard solutions. Also, pippettes and conical flasks are used during titration.

1.3 Making standard solutions

Activity 1.2

In pairs;

Suppose your teacher asks you to prepare 250 cm³ of 1 mol dm⁻³ (1M) of sodium hydroxide for a chemistry lesson. How would you prepare this solution?

Procedure

- 1. Get a clean and dry 1 dm³ standard volumetric flask, 25 cm³ beaker and a funnel. *Why should all apparatus be clean dry?*
- 2. Calculate the mass of sodium hydroxide to be weighed to prepare 0.1M sodium hydroxide. Use the following formula or first principle method to get the required mass.

Solution

First Principle method

Step 1: Work out the moles needed.

1 M means 1000 cm³ contain 1 mole 250 cm³ contain *x* moles Cross multiply then solve for *x* $\therefore x$ moles = $\frac{1 \text{ mole} \times 250 \text{ cm}^3}{1000 \text{ cm}^3} = 0.25$ moles

Step 2: Write the formula of sodium hydroxide and work out the R.F.M Sodium hydroxide NaOH

 $1 \times Na = 1 \times 23 = 23$

 $1 \times O = 1 \times 16 = 16$ $1 \times H = 1 \times 1 = 1$ R.F.M = 40This means that1 moles of NaOH = 40 g0.25 moles of NaOH = y gCross multiply and solve for y

1 moles $\times y$ g = 40 g \times 0.25 moles

$$\therefore y = \frac{40 \text{ g} \times 0.25 \text{ moles}}{1 \text{ mole}} = 10 \text{ g}$$

This means you weigh 10 g of sodium hydroxide pellets and put in a 250 cm³ volumetric flask, dissolve in distilled water. Make it up to 250 cm³ mark with distilled water.

Formula method

Step 1

Molarity
$$= \frac{\text{number of moles of solute}}{\text{volume of solution (in dm}^3)}$$

Substitute the values

1

$$= \frac{\text{number of moles of solute}}{0.25}$$

Cross multiply

Number of moles = 1×0.25

$$= 0.25$$
 moles

Step 2

Number of moles = $\frac{\text{number of grams}}{\text{mass of 1 mole}}$ 0.25 = $\frac{\text{number of grams}}{40}$

Number of grams = 0.25×40

= 10 g

Note that masses from the two methods are the same.

- 3. Weigh the mass of sodium hydroxide obtained from your calculation in step 2 above and put into the beaker. *Can the mass of air above the solid in the beaker affect your weighing?*
- 4. Using a funnel and a wash bottle containing distilled water, transfer quantitatively all the solid into 1 dm³ volumetric flask. *What is quantitative transfer?*
- 5. Close the flask tightly, swirl and shake the contents. Carefully add distilled water to a level slightly below the graduated mark. Now use a teat pipette to add distilled water drop by drop to the mark. Shake well and label the flask with the concentration. Why should the flask be tightly closed?

Using First principle method to get the mass of substance.

Check your progress 1.1

- 1. List three ways in which concentrations of solutions can be expressed.
- 2. Explain the meaning of the following terms;
 - (a) Molarity
 - (b) Standard solution
 - (c) Concentration
- 3. Express the following concentrations of solutions in grams per dm³.
 - (a) 1 dm³ solution containing 10 grams of sodium chloride.
 - (b) 0.5 dm³ solution containing 11.1 grams of calcium chloride.
- 4. 5g of NaOH in 250 cm³ of solution and the solution made upto 1000 cm³. Calculate the concentration of the resulting solution.

1.4 Preparation of molar solutions

The Facts

A molar solution is a solution containing 1 mole of a substance made up to one litre. Concentration of a solution is often referred to as its molarity. *Molarity refers to the number of moles per litre of a solution*. When one mole of a solid is dissolved in water and the volume of the solution is made to one litre, the resulting solution is a **molar solution** and the molarity is 1M. Two moles in a litre give 2 molar solution.

For example mass of one mole of sodium hydroxide is 40grams. When this mass is dissolved in water and the volume of the solution is made to one litre, the resulting solution is 1molar sodium hydroxide i.e. 1M NaOH. 80g of sodium hydroxide in a litre solution is 2M NaOH.

Give reason why 80g of NaOH in 2 litre of solution is 1M NaOH.

Molarity is expressed in moles per litre or moles per cubic decimetre. Concentration may sometimes be expressed in grams per dm³.

How to Prepare Molar Solutions

Activity 1.3

In groups of four;

To prepare 1M solution of sodium chloride (1M NaCl)

You are provided with the following apparatus and reagents to prepare 1M solution of sodium chloride.

 In your working groups, before carrying out the activity, identify wrong apparatus included in the list and propose (suggest) its suitable replacement. Which reagents do you not need in that activity.

Apparatus and chemicals

- Beam balance
- 1 dm³ volumetric flask
- Stirrer/glass rod
- Wash bottle
- Distilled water
- Dilute hydrochloric acid
- Beaker
- Funnel
- Sodium chloride
- 2. Using hints from Activity 1.2 and subsequent discussions below, proceed to conduct activity. It may be helpful to refer to Unit 2 on how to calculate mass of sodium chloride required in case you do not know.

3. Suggest some possible sources of error or common mistakes likely to be committed by the learners. How can they be minimised or avoided.

Calculations of molarity of ions in molar solutions

Examples 2

Calculate the molarity of calcium, Ca²⁺ ions and chloride, (Cl⁻) ions in 2M CaCl₂ solution.

CaCl ₂ (aq) —	→ Ca ²⁺ (aq)	+	2 Cl-(aq)
1 mole	1 mole		2 moles
2 moles	2 moles		4 moles

Since the mole ratio of Ca^{2+} : Cl^{-} is 1:2

Molarity of Ca^{2+} ions = 2M

 \therefore Molarity Cl⁻ ions = 4M

Examples 3

In example 2, what is the concentration of calcium ions and chloride ions in g dm^{-3} ?

(Ca = 40, Cl = 35.5).

2M means 2 mol in 1000 cm3 (1dm3)

But 1 mol of $Ca^{2+} = 40 g$

Molarity of Ca²⁺ ions in g per dm³ = $2 \times 40 = 80$ g dm⁻³

4 M means 4 moles in 1000 cm³ (1dm³)

Note: Loss or gain of electrons has negligible change in mass of an atom. This is why for example irrespective of Ca²⁺ having lost 2 electrons, the mass still remains the same. The same applies to Cl and Cl⁻.



Check your progress 1.2

- 1. Calculate the mass of H_2SO_4 acid whose concentration is 0.25M in a volume of 50 cm³.
- 2. Calculate the concentration of the following solutions in g/dm^3 .
 - (i) A solution containing 3.9 g of sodium carbonate in 0.25 dm^3 of solution.
 - (ii) A solution of containing 74.5 g of potassium chloride in 2 dm^3 of solution.
- 3. Calculate the molarity of magnesium, Mg^{2+} ions and chloride, Cl^{-} ions in 0.5 moles dm⁻³ solution of magnesium chloride (Mg = 24, Cl = 35.3).
- 4. What is the concentration in g dm⁻³ of ammonium and sulphate ions in 0.4 M solution of ammonium sulphate? (Na = 23, H = 1, S = 32, O = 16).

1.5 Dilution of standard solutions

Activity 1.4

To demonstrate dilution

Apparatus and chemicals

- copper(II) sulphate crystals or potassium manganate(Vll)
- beaker
- stirring rod

Procedure

1. Label four 250 cm³ beakers A, B, C and D respectively.

- 2. Place equal amounts of crystals (either copper(II) sulphate or potassium manganate(VII) into each beaker.
- 3. Place 50 cm³ of water into beaker A, 100 cm³ into beaker B, 150 cm³ into beaker C and 200 cm³ into beaker D as illustrated in Fig. 1.2



Fig 1.2 Demonstrating the dilution

- 4. Stir the mixture thoroughly.
 - What do you observe? What conclusions can you make from your observations?
 - Record your observations and conclusions in your notebook.

The Facts

Standard solutions can be diluted to lower the concentration by adding solvent e.g. water. The process is called **dilution**. Dilution is a common practice in laboratories since most solutions are often purchased when already prepared in high concentration. The highly concentrated solutions are known as **stock solutions**.

During the dilution, the amount of solute remains the same while the volume of the solution increases. The concentration of the new solution is calculated using the dilution law as follows;

$$C_1 V_1 = C_2 V_2$$

Where:

C₁ - Concentration of 1st solution

 V_1 – Volume of 1st solution

C₂ – Concentration of 2nd solution

 V_2 – Volume of 2^{nd} solution

Dilute acids, bases and solutions or pure liquids of other substances can be prepared from concentrated solutions (stock solutions) obtained from chemical shops.

Worked Example I

Calculate the volume of 0.5M $H_2SO_{4(aq)}$ solution that will be required to make 1000 cm³ of 0.05M $H_2SO_{4(aq)}$.

$$C_1 = 0.5, C_2 = 0.05, V_1 = ?, V_2 = 1000$$

 $0.5 \times V_1 = 0.05 \times 1000$
 $\frac{0.5V_1}{0.5} = \frac{50}{0.5} = V_1 = 100 \text{ cm}^3$

Worked Example 2

250 cm³ of 2M NaOH is diluted to 2000 cm³. Calculate the new concentration of the solution.

$$C_1 = 2M$$
, $V_1 = 250 \text{ cm}^3$, $C^2 = ?$, $V_2 = 2000 \text{ cm}^3$
 $2 \times 250 \text{ cm}^3 = C_2 \times 2000 \text{ cm}^3$
 $500 \text{ cm}^3 = 2000 \text{ cm}^3 \times C_2$
 $C_2 = 0.25M$

Check your progress 1.3

- If 10 g of sodium hydroxide is dissolved in pure water and made up to 1 dm³ of solution, when 10 cm³ of this solution is taken will its concentration remains 10 g/dm³. What is the concentration of smaller solution taken?
- 2. During dilution process does the number of moles of solute change? Does the mass of solute change or not?
- 3. What aspect of the solution changes?
- 4. Choose the correct answers from the choices given.
 - (a) 20 cm³ of 4M sodium hydroxide is diluted to 400 cm³. What is the concentration of the final solution?

A.	0.8M	С.	0.6M
B.	0.2M	D.	0.5M

(b) A solution is said to be one molar (1M) when:

A. 1 mole of solution is present in 1 litre of solvent

B. 1 mole of solute is present in 1 litre of solution

- C. 1 cm^3 of solute is added to 999 cm³ of solvent
- D. 1 g of solute is added to 999g of solvent
- (c) You are given sulphuric acid of 10 molarity. How will you obtain from it 100cm³ of 0.1M sulphuric acid?
 - A. Take 1 cm³ of the acid and dilute it to 100 cm³
 - B. Take 1 cm³ of the acid and add to it 100 cm³ of distilled water
 - C. Take 10 cm³ of the acid and dilute it to 100 cm³ with water
 - D. Take 10 cm³ of the acid and add to it 100 cm³ of distilled water

1.6 Volumetric Analysis

In practical chemistry, sometimes you will be required to establish the concentration of solutions or amount of solutes in a substance; to ascertain its quality or accuracies of the specified ingredients in a substance. This is what volumetric analysis is all about. In everyday volumetric analysis, there are three common types of titrations: acid-base titration, redox titration and back titration.

The Facts

Volumetric analysis is a quantitative analytical method of determining unknown concentration of a substance using another substance whose concentration is known, usually, in a chemical reaction for which the equation is known. The process involves measuring accurately the volumes of two solutions which react with each other. One standard solution is reacted with another solution of unknown concentration to determine the reacting volumes. This process is also called *titrimetric analysis* or *titration*. This is because it is based on the measurement of exact volumes. The standard solution is called **titrant**. A known volume of titrant reacts with a solution of unknown concentration. The point in titration at which all the analyte has

reacted is called the **end point**. This is indicated by the colour change of the indicator. The moles of acid are equivalent to the moles of base reacting, according to the reaction equation. Acid-base titrations are very commonly use in titrimetric analysis because they are *fast*, *essentially complete and the endpoint is easily detected by the indicator*. The other types of fitration include redox titration and back titration.

Handling of titration apparatus

Activity 1.5

Practising correct use of burettes and pipettes

Work in pairs:

- Fill 50 cm³ burette with distilled water. Hold it horizontally and shake well. Open the tap and drain water out of the burette.
- 2. Using the same technique rinse the burette with distilled water. Using a filter funnel fill the burette with water to near the zero mark. Check to ensure the tap is not leaking and open the tap to flush out any air bubbles. Allow the water level to steady and estimate the volume to two decimal places and record.
- 3. Release a small volume of water, allow the level to steady and record as the final reading. Ask the teacher to check at least one of your readings.
- 4. Dip the tip of a 25 cm³ pipette into water in a beaker. Suck carefully until its three quarter full. Rinse out and repeat three times.
- 5. Pipette accurately measures 25 cm³ of water. Repeat several times and ask your teacher to observe.

My Environment, My Life

Used acidic and basic solutions causes yellowing of plants. Let them always be treated before disposal. Do not pour out on open ground.

The Facts

Burettes and pipettes are expensive apparatus and must be handled with a lot of care to avoid breakage.

(a) 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, from a tilted conical flask as shown in Fig. 1.3 and to use a pipette filler to fill the pipette.



Fig 1.3 How to fill a pipette

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 up right and read below the meniscus. See Fig. 1.3 (c).

• 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.

Note: A burette and pipette are read correctly by viewing the bottom of the meniscus at an horizontal eye level.

(b) Filling a burette

A burette is calibrated from top downwards i.e. 0 cm^3 at the top and 50 cm³ at the bottom near the tap. Examine the burette and note that the divisions are 1 cm³.

- Wash the burette with water, 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 solution to above the 0cm³ graduation mark, holding the funnel with one hand. See Fig. 1.4.



Fig 1.4: Correct filling of burette

My Safety, My responsibility

Always make sure there is no spillage when filling burette since this may cause corrosion on your skin, clothes and unprotected surfaces.

Discussion corner!

- 1. Give reasons for the following during filling of pipette or burette.
 - (a) It is recommended to suck solution from tilted flask.
 - (b) When filling the burette, hold the funnel with one hand.

- 2. Why is the correct filling of pipette and burette important in volumetric analysis?
- 3. Suggest when the use of pipette filler in the filling is most needful.

1.7 Understanding the titration process

- 1. Clean the burette and rinse it with the solution it is going to contain(titrant).
- 2. Fill the burette with the given reagent to the zero mark.
- 3. Pipette any stated volume of the alkali into a conical flask.
- 4. Add one or two drops of the indicator to the alkali in the conical flask and note the colour.



Fig 1.5 Titration process

- 5. Flush out air bubbles from the jet of the burette.
- 6. Adjust the level of the burette so that the tip is almost inside the mouth of the conical flask. Carefully estimate and record the initial burette reading. With the neck of the flask in one hand use the other hand to operate the tap to drain the acid from the burette in small volumes until the new colour begins to show and disappears. This shows that the end point is near. Now add the liquid from the burette drop wise until a single drop permanently changes the colour. Carefully estimate and record the final burette reading. Use a white tile, if necessary, to make the meniscus more readable.
- 7. Carry out two more titrations and average any two consistent volumes to get the volume of an acid which reacts with the pipette alkali.

Discussion corner!

In pairs, discuss these questions:

- 1. Suggest another material that can be used instead of a white tile.
- 2. What are consistent volumes in titration process?

Recording and Treatment of Titration Data

Titration data is recorded in a table like the one below.

Volume of pipette used _____ cm³

Table 1.1

Titre Titrant	1	2	3
Final burette reading (cm ³)			
Initial burette reading (cm ³)			
Volume of acid used (cm ³)			

After titration, average titre is obtained using the formula:

 $Average \ volume = \frac{Sum \ of \ consistent \ values}{Number \ of \ consistent \ values}$

Discussion corner!

Differentiate between titre and titrant.

Choice of indicators on titration

In Form 2 you learn tabout indicators and their uses. Different acid-base indicators are used in titration of strong and weak acids and bases. The choice of indicator depends on the pH at endpoint and the pH range over which the indicator changes colour. The table below gives guidelines on how to choose an indicator to use in different titrations. *Table 1.2*

Reactions	Acid-base Indicator	Example
Strong acid	Methyl orange,	
+ strong	phenolphthalein	$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$
base	or litmus	
Strong acid	Methyl orange	UCl(ag) + NUOU(ag) NUCl(ag) + UO(1)
+ weak base		$\operatorname{IICI}(\operatorname{aq}) + \operatorname{III}_4 \operatorname{OII}(\operatorname{aq}) \longrightarrow \operatorname{III}_4 \operatorname{OII}(\operatorname{aq}) + \operatorname{II}_2 \operatorname{O}(\operatorname{I})$
Weak acid +	Phenolphthalein	$CH COOU(a_2) + N_2OU(a_2)$
strong base		CH_{3} COONa(aq) + NaOII(aq) \longrightarrow CH_{3} COONa(aq) + H_{2} O(l)
Weak acid +	No indicator	$CH COOH(a_2) + NH OH(a_2) $ $CH COONH (a_2) + H O(1)$
weak base		$CH_3COONH(aq) + NH_4OH(aq) \longrightarrow CH_3COONH_4(aq) + H_2O(l)$

Discussion corner!

Give a reason why no indicator is used when titrating weak acid against a weak base.

Acid-base titrations

Experiment

Aim

To standardize a solution of Hydrochloric acid using anhydrous Sodium carbonate.

Reagents and apparatus

Anhydrous Sodium carbonate, Hydrochloric acid, phenolphthalein, burette, conical flask, beaker, glass rod and weighing balance.

Procedure

- 1. Weigh exactly 1.45g of Sodium Carbonate and transfer into 100 cm³ of distilled water in a beaker.
- 2. Stir the mixture using a glass rod to dissolve, transfer the solution to

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250 cm³ volumetric flask, rinse the beaker with distilled water and transfer all the washings to the volumetric flask. Top up the solution to the 250 cm³ mark, swirl, then label.

- 3. Fill the burette with the acid solution, pipette 25 cm³ of the Sodium carbonate solution into a conical flask and add 3 drops of phenolphthalein indicator.
- 4. Titrate the Sodium carbonate against the acid from the burette. Record your results in a table. Repeat the titration two more times.

Table 1.3: Specimen results

	Ι	II	III
Final burette reading (cm ³)			
Initial burette reading (cm ³)			
Volume of solution used (cm ³)			

Questions

- 1. Calculate the concentration of Sodium Carbonate solution in mol dm^{-3}
- 2. Calculate the number of moles of the base used.
- 3. Calculate the number of moles of the acid that reacted.
- 4. Calculate the concentration of acid in mol dm⁻³.

Solution

Average volume of acid used =
$$\frac{23.00 \text{ cm}^3 + 23.10 \text{ cm}^3 + 23.00 \text{ cm}^3}{3} = 23.03 \text{ cm}^3$$

Solution

- 1. 250 cm^3 of solution contain 1.45 g
 - 1000 cm^3 solution contain X

$$X = \frac{1000 \times 1.45 \text{ g}}{250}$$

= 5.8 g/dm³

Relative formula mass of Na₂CO₃

$$= (2 \times 23) + (1 \times 12) + (3 \times 16)$$
$$= 106$$

1 mole of Na₂CO₃ = 106g y mole of NaCO₃ = 5.8 g/dm³ $\frac{5.8 \text{ g/dm}^3 \times 1}{106 \text{g/mol}}$ y = 0.05mol/dm³

2. 1000 cm^3 of Na₂CO₃ contains 0.05 mole

 $\frac{25 \text{ cm}^3 \text{ of } \text{Na}_2\text{CO}_3 \text{ contains } \text{Z mole}}{1000}$ Z = 0.00125 mole.

Therefore, 0.00125 mole of Sodium Carbonate is reacting.

3. $Na_2CO_3(aq) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$ Reacting mole ration is 1:2 hence moles of acid reacted

 $= 0.00125 \times 2$

= 0.0025 moles

23.03 cm³ of the acid contain 0.0025 mole

1000 cm³ of the acid will contain X moles

 1000×0.0025 moles

23.03

 $= 0.1086 \text{ mol/dm}^3$

Activity 1.6

To standardize aqueous sodium carbonate

Work in groups:

A standard solution of 0.1M hydrochloric acid is used to standardize sodium carbonate.

- 1. Suggest apparatus and suitable indicator required to carry out this activity.
- 2. Prepare a sodium carbonate solution by dissolving about 10 grams of hydrated crystals in a litre of solution. The concentration of sodium carbonate in grams per litre can now be found by titrating portions of this solution with

hydrochloric acid.

- 3. Proceed to carry out the titration.
 - (i) Which solution is placed in the burette?
 - (ii) Which solution is placed in the flask?
- 4. Record your results in a table such as the one shown below. *Table 1.4*

Titre Titrant	1	2	3
Final burette reading (cm ³)			
Initial burette reading (cm ³)			
Volume of acid used (cm ³)			

Activity Questions

- 1. Calculate the concentration of the alkali in grams of sodium carbonate per litre. (H = 1, Cl =35.5, Na = 23, C = 12, O = 16)
- 2. Compare your titre value with the one supplied by your teacher. In case they are different, suggest possible sources of error in this activity.
- 3. How do you know that the reactions has reached end-point.

Sample results

When the following sample results were obtained 25 cm^3 of sodium carbonate solution were titrated with 0.1M sulphuric (VI) acid using a suitable indicator.

Titre	1	2	3
Final burette reading (cm ³)	18.4	17.9	17.7
Initial burette reading (cm ³)	0.0	0.0	0.0
Volume of acid used (cm ³)	18.4	17.9	17.7

Calculate the molarity of sodium carbonate and its concentration in grams per litre.

Average volume of acid used =
$$\frac{17.9 + 17.8}{2} = 17.85 \text{ cm}^3$$

Moles of acid reacting = $\frac{0.1 \times 17.85}{1000}$ = 0.001785 moles Na₂CO₃(s) + H₂SO₄ (aq) \longrightarrow CO₂(g) + Na₂SO₄(aq) + H₂O(l) Mole ratio = 1:1 Therefore, moles of sodium carbonate reacted = 0.001785 moles Molarity of sodium carbonate = $\frac{0.001785 \times 1000}{25}$ = 0.0714M Concentration in grams per litre = molarity × molar mass = 106 × 0.0714

= 7.568 grams per litre

Back titration

Experiment

Example of a back titration.

Example I

You are provided with, Solution A, which was made by dissolving 5.3 g dm⁻³ of sodium carbonate Na_2CO_3 .

Solution B, which is hydrochloric acid in 1 dm3 solution.

You are required to:

- (i) calculate the molarity of the sodium carbonate solution.
- (ii) standardise solution B using solution A, i.e find its concentration.

(Na = 23; O = 16; C = 12)

Procedure

- Fill the burette with dilute hydrochloric acid provided.
- Pipette 25.0 cm³ of solution A and transfer 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 consistent values.
- Record your values as in Table 1.5 below

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.

Table 1.5: Burette reading

Burette reading	1	2	3
Final burette reading (cm ³)			
Initial burette reading (cm ³)			
Volume of solution B used (cm ³)			

- Find the volume of the acid that reacted.
- Standardize solution B using solution A.
- Find the molarity of the sodium carbonate.

The following is a sample practical titration data and detailed calculation that shows you how to use your results after titration.

Table 1.6: Specimen results

Burette reading	1	2	3
Final burette reading	22.5	44.4	21.8
Initial burette reading	0.0	22.5	0.0
Volume of solution B used (cm ³)	22.5	21.9	21.8

(i) Calculate the average volume of solution B used. Show how you get your average.

$$=\frac{21.9+21.8}{2}=21.85 \text{ cm}^3$$

(ii) Write an equation for the reaction.

$$Na_2CO_3(aq) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

The equation gives us the mole ratio of the reactants i.e. moles of the sodium carbonate (solution A) and acid (solution B).

We should start by calculating the moles of solution A because it is the one whose volume (25.0 cm³) and concentration (5.3 g dm⁻³) are known. This is done as follows:

(i) 1 mole of $Na_2 CO_3 = 2(23) + 12 + 3(16) = 106g$

= 5.3 g

x moles

....

Cross multiply and solve for x

$$x = \frac{5.3 \text{ g}}{106 \text{ g}} = 0.05 \text{ mole}$$

The molarity of solution A is 0.05 mol dm^{-3} (0.05 M)

(ii) From part(i) we can say that:

1000 cm³ of solution A contained 0.05 mole

 \therefore 25 cm³ that we took in the pipette contained x moles

Cross multiply and solve for x

$$x = \frac{0.05 \text{ mole} \times 25 \text{ cm}^3}{1000 \text{ cm}^3} \text{ mole}$$

= 0.00125 mole of Na₂CO₃
Since mol ratio of Na₂CO₃ : HCl is 1 : 2
moles of HCl = 0.00125 × 2 = 0.0025 mole
This means, from our average volume
21.85 cm³ contained 0.0025 mole of HCl
 $\therefore 1000 \text{ cm}^3$ contained x moles
Cross multiply and solve for x
$$x = \frac{0.0025 \text{ mole} \times 1000 \text{ cm}^3}{21.85 \text{ cm}^3} = 0.114 \text{ moles}$$

= 0.114 moles

The concentration of HCl = $0.114 \text{ mol dm}^{-3}$

Activity 1.7

To determine the atomic mass of X in the formula, XCO₃

Apparatus: Solid XCO_3 , weighing balance, wash bottle, standard hydrochloric acid, glass rod, 250ml volumetric flask, two conical flasks, burette, pipette, white tile.

Procedure

- 1. Weigh exactly 1.5g of metal carbonate XCO₃ provided in a conical flask.
- 2. Using a pipette, measure 50 cm³ of standard hydrochloric acid and add to the insoluble carbonate and allow the substances to react. Make up the resulting solution to 250 cm³ using distilled water.
- 3. Titrate 25 cm³ of this solution with standard sodium hydroxide using methyl orange indicator. Record your results in a table 1.7.

Table 1.7

Titre Titrant	1	2	3
Final burette reading (cm ³)			
Initial burette reading (cm ³)			
Volume of alkali used (cm ³)			

Activity Questions

- 1. Calculate the average volume of the alkali used to neutralise excess acid.
- 2. Determine:
 - (a) The number of moles of base used.
 - (b) The volume of the acid that neutralised the base.
 - (c) Moles of the acid that reacted with the carbonate.
- 3. (a) Write equation for the reaction between the acid and the carbonate.
 - (b) Determine the number of moles of the carbonate in the sample.
 - (c) Determine the formula mass of the carbonate.
 - (d) Determine the relative atomic mass of X.



Sodium hydroxide, sodium carbonate and other bases and acids mentioned so far are soluble in water. It is therefore possible to prepare their standard solutions and use the solutions in volumetric analysis. However, there are some insoluble substances whose standard solutions cannot be prepared for direct use in volumetric analysis.

Therefore in back titration, the insoluble substances are added to excess of a standard solution which reacts with them, and the amount of standard solution which does not react can be determined by titration against a second standard solution. For example, a known mass of calcium carbonate is added to a known volume of hydrochloric acid, the acid being in excess. When the reaction is over, some of the acid remains, and the amount of unreacted acid then can be determined by titrating against standard alkali. Hence the amount used by the carbonate can be calculated.

Sample results

Mass of $XCO_3 = 1.5g$. This mass reacted with 50 cm³ of 1.16M hydrochloric acid and the resulting made to 250 cm³. 25 cm³ of this solution required 28.2 cm³ of 0.092M sodium hydroxide.

Moles of the base used = $\frac{28.2 \times 0.092}{1000}$ = 0.0025944 moles Equation for the reaction is HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H₂O(l) Moles of the acid that reacted = 0.0025944 moles Number of moles in 250 cm³ = $\frac{250 \times 0.0025944}{1000}$ = 0.025944 moles

Moles of the acid in the initial 50 cm³ = $\frac{50 \times 1.16}{1000}$ = 0.058 moles

Moles of the acid that reacted with the carbonate =0.058 - 0.025944 = 0.02856Equation for the reaction is

$$XCO_3(s) + 2HCl(aq) \longrightarrow XCl_2(aq) + CO_2(g) + H_2O(l)$$

Moles of the carbonate used = $0.02856 \div 2 = 0.01428$ Molar mass = $\frac{1.5}{0.01428} = 105.0$ g X + 12 + 48 = 105 X = 45

Caution

Carbon (IV) oxide emitted must be neutralized. When emitted directly to the atmosphere, the long term effect is global warming. It is a greenhouse gas.

Redox titration

In redox titration the commonly used oxidising agents are acidified solutions of the following compounds.

- (i) Potassium manganese (VII), KMnO₄
- (ii) Potassium dichromate (VI), $K_2 Cr_2 O_7$

They are referred to as acidified KMnO₄ and K₂Cr₂O₇ respectively.

In these titration there is no need of indicator because they change colour a follows:

- Potassium manganate which is purple turns colourless
- Potassium dichromate which is orange turns green

Activity 1.8

Work in groups of four:

To standardize potassium manganate (VII) solution using ammonium iron (II) sulphate

1. You are provided with the following apparatus and chemicals.

Apparatus and chemicals: two conical flasks, burette, pipette, white tile, acidified potassium manganate (VII), ammonium iron (II) sulphate.

- 2. Proceed to carry out the standardization (titration) in your working groups.
 - (i) Which substance is put in the conical flask?
 - (ii) Which substance is filled in the burette? Why is this so?
- 3. Record your results in a table like the one shown below.

Table 1.8

Titre Titrant	1	2	3
Final burette reading (cm ³)			
Initial burette reading (cm ³)			
Volume of KMnO ₄ used (cm ³)			



Activity Questions

- 1. State the colour change observed.
- 2. Calculate the average volume of $KMnO_4$ solution used.
- 3. Calculate the molarity of iron (II) salt solution.
- 4. Calculate the number of moles of iron (II) salt.
- 5. Given the equation for the reaction as

 $MnO_4^{-}(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$ Determine the molarity of potassium manganate (VII) solution.

Experimental example

You are provided with solutions P and Q.

Solution P is acidified potassium manganate(VII)

Solution Q was prepared by dissolving 23.5g of ammonium iron(II) sulphate, $(NH_4)_2$ Fe(SO₄)₂ . $6H_2O$, per dm³.

You are required to standardize i.e find the concentration of solution P.

Procedure

- 1. Fill the burette with solution P.
- 2. Adjust the volume to exactly zero mark.
- 3. Pipette 25.0 cm^3 of solution Q, and transfer into a 250 cm^3 conical flask.
- 4. Titrate solution P against solution Q until a permanent pink colour just appears.
- 5. Record your results in a table as shown below.
- 6. Repeat the procedure two more times.
- **Note:** The values in Table 1.9 below are just sample results. You may get different values when you perform the experiment. Make sure you are accurate.

Table 1.9: Specimen results

Burette readings	1	2	3
Final burette reading (cm ³)	16.9	32.9	16.1
Initial burette reading (cm ³)	0.0	16.9	0.0
Volume of solution P added (cm ³)	16.0	16.1	16.9

Average any two readings that are within \pm 0.2 of each other. Show your working.

$$=\frac{16.0+16.1}{2}=\frac{32.1}{2}=16.05 \text{ cm}^3$$

(a) 1 mol of $(NH_4)_2 Fe(SO_4)_2 \cdot 6H_2O$

 $= (14 + 4)2 + 56 + (32 + 16 \times 4)2 + 6(18) = 392$

1 mole of $(NH_4)_2$ Fe $(SO_4)_2$. $6H_2O = 392$ g

x moles of $(NH_4)_2$ Fe $(SO_4)_2$. $6H_2O$ =23.5 g

Cross multiply and solve for x

$$\therefore x = \frac{23.5 \times 1}{392} = 0.0599 \text{ moles}$$

0.0599 moles was dissolved in 1 dm³

 \therefore The molarity is 0.0599 mol dm⁻³ (or 0.0599 M)

(b) When 1 mole of ammonium iron(II) sulphate was dissolved, it formed the following ions:

$$(NH_4)_2 Fe(SO_4)_2 \cdot 6H_2O(aq) \longrightarrow 2NH_4^+(aq) + Fe^{2+}(aq) + 2SO_4^{2-}(aq)$$

1 mole of ammonium iron(II) sulphate produces 1 mole of iron(II) ion

But from answer (b)

1000 cm³ of $(NH_4)_2$ Fe $(SO_4)_2$. 6H₂O contained 0.0599 moles

25 cm³ (pipette volume) contained x moles

Cross multiply and solve for x $\therefore x = \frac{0.0599 \text{ moles} \times 25 \text{ cm}^3}{1000 \text{ cm}^3} = 0.00149 \text{ moles}$

 \therefore 25 cm³ that was pipetted contained about 0.0015 moles.

(c)
$$MnO_4^{-}(aq) + 5Fe^{2+}(aq) + 8H^{+}(aq) - Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$

Mole ratio of MnO_4^{-1} ions to Fe^{2+1} ions is 1 : 5

: We require about 0.0003 mole of MnO_4^{-1} ions (i.e 0.0015 \div 5).

From the average volume obtained in (a), it implies that

16.05 cm³ contained 0.0003 moles of MnO_4^{-} ions

 \therefore 1000 cm³ would contain x moles of MnO₄⁻ ions

Cross multiply and solve for x $x = \frac{0.0003 \text{ mol} + 1000 \text{ cm}^3}{16.05 \text{ cm}^3} = 0.01869$ $= 0.019 \text{ mol dm}^{-3}$

 \therefore The concentration MnO₄⁻⁻ ions is 0.019 mol dm⁻³ or 0.019 M.

1.8 Water of crystallisation

Activity 1.9

Work in groups of three:

Investigating the percentage of water of crystallization in hydrated sodium carbonate

Select the apparatus and reagents needed for this activity. You are to use 5g of the reagent to be standardized and 0.2M of the acid.

Procedure

- 1. Prepare 250 cm^3 of the reagent to be standardized.
- 2. Pipette about 25 ml of this solution into a clean conical flask followed by two drops of the indicator.
- 3. Fill the burette with the standard solution and adjust the level to zero mark. What precautions must you take as you fill the burette.
- 4. Titrate in the usual manner until there is permanent colour change.
- 5. Record your results in suitable format.

Table 1.10

Titre Titrant	1	2	3
Final burette reading (cm ³)			
Initial burette reading (cm ³)			
Volume of acid used (cm ³)			

From the results, calculate the value of \mathbf{x} . The number of moles of water of crystallization.


Water has the property of chemically uniting with salts to form hydrated substances. Water of crystallization is the water which is found as part of the structure of a crystalline substance. It has nothing to do with the substance being wet. The water molecules referred occupy positions in the crystal lattice of the substance. This water of crystallization is generally represented in the chemical formulae of such compounds toward the end of the formula.

We can determine the percentage of water of crystallization in a substance by titration.

Activity1.10

To determine the number of molecules of water of crystallisation in hydrated sodium carbonate (Na₂CO.₃XH₂O) using 0.2M HCl acid.

You are provided with 5g hydrated sodium carbonate. Select the appropriate apparatus and other reagents and proceed to carry out the activity.

Record your results accordingly.

Titre	Ι	II	III
Final burette reading (cm ³)			
Initial burette reading (cm ³)			
Volume of solution used (cm ³)			

Activity Questions

- 1. Determine the concentration of sodium carbonate in Mol/dm³
- 2. Calculate the value of X in the formula.

 $Na_{2}CO_{3}.XH_{2}O$ (Na = 23, C = 12, O = 16)

3. Explain why the beaker should be rinsed and the waste water added to the beaker.

We can now calculate the values of 'x' is the formula.

Na₂CO₃.xH₂O

We already, know that there are 0.0235 moles of sodium carbonate present in the crystals.

We also know that there are 4.239g of water present. This is equivalent to

```
\frac{4.239}{18} \text{ moles} = 0.2355 \text{ moles}
Moles of Na<sub>2</sub>CO<sub>3</sub> : Moles of H<sub>2</sub>O
0.0235 : 0.2355
1 : 10
x = 10
```

Real life applications of titration

Medical Uses: Titration is used in medical laboratories to determine unknown concentrations of chemicals of interest in blood and urine. Pharmacists also use titration to achieve a desired mix of compound drugs.

Food Industry: Titration may also be used to determine the amount of a certain chemical in food substances. Often titration is used to determine fat content, water content, and concentrations of vitamins. Titration is also used to tell if cheeses and wines have aged enough for distribution to supermarkets and shops.

Bioscience: Titration can be employed in biology labs, where it is used to determine the proper concentration of chemicals to anesthecitize test animals.

Education: In high school chemistry classes, titration is often used as a test of students' practical aptitude. It is a standard procedure for determining unknown concentration.

Check your progress 1.4

- 1. What volume of 0.1M H_2SO_4 will neutralize completely 250 cm³ of 0.2M NaOH?
- 2. Define equivalent point and molar solution. Describe with full practical details how you would determine the concentration in grammes per litre of a solution of hydrochloric acid using, 0.1M solution of sodium hydroxide.
- 25 cm³ of 2M hydrochloric acid is required to neutralize a solution containing
 2.1g of a soluble base. What is the molar mass of the base?
- 4. 25 cm³ of a solution of sodium carbonate were neutralized by 20 cm³ of 0.1 M hydrochloric acid using methyl orange as indicator. Calculate the concentration in grammes per litre of the sodium carbonate solution (C = 12, O = 16, Na = 23).

5. 20 cm^3 of a solution of sulphuric (VI) acid were neutralized by 35 cm³. 1M sodium hydroxide. Calculate the concentration of the acid solution. (H = 1, O = 16, S = 32.

1.9 Qualitative test for gases

Activity 1.11

Work in groups of three:

Test identification of various gases (Oxygen, hydrogen and carbon dioxide)

Apparatus and materials

Two test tubes, calcium grain, 40 cm³ beakers, wooden splint, 2M ethanoic acid, small piece of calcium carbonate, two boiling tubes, calcium hydroxide, hydrogen peroxide (30 volumes), rubber stopper and glass beads.

Safety precaution

Handle the acid and hydrogen peroxide carefully. If there is spillage on your skin rinse immediately with a lot of clean water. Wear goggles and an apron all the times.

Test 1 Identification test for oxygen

- 1. Using your previous knowledge, prepare some amount of oxygen using the reagents provided and perform the identification.
- 2. When the test tube is about $\frac{3}{4}$ full with the gas (after about 10 minutes), prepare a glowing splint.
- 3. Remove the test tube from the water and quickly insert the glowing splint into the test tube and record your observations.
- 4. You are required to use glass beads in this test. At what stage of the investigation is it used? Why is the use of the glass beads important?



Fig 1.6 Testing for oxygen gas relighting glowing splint

5. Rinse out the beaker, clean and return the glass beads.

Test 2 Identification fo carbon dioxide

Using the set up below, prepare carbon dioxide and conduct its identification test.



Fig 1.7 Testing for carbon dioxide gas

Test 3 Identification of hydrogen gas

- 1. Obtain 40 cm^3 of water and put into a beaker.
- 2. Fill a test tube with water and quickly invert into the water.
- 3. Place a calcium nodule into the water and let the mouth of the test tube be directly above the nodule to collect the gas.

- 4. When the test tube is about $\frac{3}{4}$ full with the gas (after about 10 minutes), prepare a burning splint.
- 5. Remove the test tube from the water and quickly insert the burning splint into the test tube and record your observations.
- 6. Make sure that all the calcium has reacted and then rinse well the beaker.



Sulphur dioxide (SO₂)

To test for this gas, dip a filter paper in acidified potassium dichromate (VI) and then drop the paper in a gas jar of sulphur dioxide.

Observation

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



- 3. Explain reason(s) for ensuring that all calcium has reacted before rinsing the beaker. How do you all the calcium has reacted?
- 4. What was the importance of use of glass beads in Test 1.



Qualitative analysis is a method by which constituent parts of a substance are identified. Here the changes that take place and products formed are observed closely without making precise measurements as in titration.

There are common laboratory tests for identifying gases. The general guiding principles include:

- (i) **Basic gas tests** look for colour, smell, effect on litmus solutions or papers and effect on splints (glowing and burning). Ammonia gas is the only known alkaline gas; it turns damp red litmus paper blue.
- (ii) Acidic gases (SO₂, HCl, H₂S, HBr, HI) are evolved when dilute mineral acids or concentrated sulphuric acid reacts with SO₃²⁻, Cl⁻, S²⁻, Br⁻, I⁻ respectively. The gases turn damp blue litmus red. Carbon (IV) oxide from CO₃²⁻ is a weak acid in aqueous solution and usually does not affect blue litmus papers. Nitrogen dioxide is brown and turns blue litmus red.
- (iii) All other **gases including oxygen** and hydrogen are colourless. These gases do not affect litmus papers. Nitrogen (I) oxide and carbon (II) oxide are also neutral gases.

Guide to the identification of gases

The table below gives guidelines on how to identify the various gases.

Gas	Appearance	Test
Hydrogen	Colourless	A lighted wooden splint goes off pop
Oxygen	Colourless	A glowing splint relights
Carbon (IV) oxide	Colourless	Forms a white precipitate with lime water
Ammonia	Colourless	Forms dense white fumes with hydrogen
		chloride gas
Chlorine	Green yellow	Damp blue litmus paper turns red then
		white

Table 1.11

Remember

Smell gases by holding the mouth of the test tube about 20 cm³ from the nose. The gas is then waved or wafted towards the nose and sniffed carefully.

For successful results;

- That litmus papers must be damp for use in tests.
- When testing for gases using litmus paper do not touch the mouth of the inner walls of the test tube.
- That all the litmus paper, delivery tube and any other necessary apparatus must be ready before the reagent is poured into a test substance.

Discussion corner!

- 1. Give reasons why litmus papers must be damp when testing for gases.
- 2. Why must one assemble all apparatus ready before pouring reagent in test tube during testing of gases?

Check your progress 1.5

- 1. Iron II ammonium sulphate solution was reacted with acidified potassium manganate (VII) solution. 25.0 cm³ of the Fe²⁺ ion solution required 24.8 cm³ of 0.02 M KMnO₄ solution. Calculate the molarity of Iron II ammonium sulphate solution.
- 2. 12.17g of oxalic acid (COOH)₂.nH₂O were dissolved in water to make 1 litre of solution. 25 cm³ of this solution needed 22 cm³ of 16g/litre sodium hydroxide solution for complete neutralisation. Determine the value n.

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UNIT 2

Learning Outcomes		
Knowledge and understanding	Skills	Attitudes
• Understand the mole concept and the application of gas laws	 Investigate and understand the mole concept, relative atomic mass and molecular mass 	Appreciate the importance of the gas laws.
• Understand chemical and ionic equations	 Measure accurately masses, volumes, pressure and temperature of sample substances. Calculate masses from stoichiometry equations Carry out inter conversion of moles to mass, atoms, and molecules Construct full balance equations 	Appreciate the importance of the gas laws.

Introduction

Activity 2.1

Work in pairs:

Study the substances below. Are you able to identify them? What are they made of?





Discussion corner!

- 1. Do you believe that the substances are made up of tiny invisible particles? Explain your answer.
- 2. Have you ever heard of the term "mole" in Chemistry? What do you think it means?
- 3. Think about the following terms people use everyday: a pair, dozens, fortnight and decade. How did they come about?

The Facts

The above some of the substances that we interact with daily. All substances are made of atoms, molecules and ions bound together to make the total matter of the substance. The details of the particles that make up the above are learnt under mole concept.

2.1 The mole concept

Mole is a very important unit of measurement for Chemists. It is an important tool in stoichiometry and balancing chemical reactions which plays critical role in manufacturing of drugs, dyes and chemical substances for safe use. All calculations in Chemistry are based on the smallest unit of any compound or element called moles. Moles can be converted to mass vice versa.

Activity 2.2

To count the number particles in table salt and rice.

Work in pairs

Apparatus: Table salt, rice, saucers and weighing balance.

Procedure

- 1. Place approximately the same amount of table salt and rice each in a saucer.
- 2. Weigh each sample and record the masses in a table like the one shown below.

Table 2.1

Substance	Mass (grams)
Table salt	
Rice	

3. Try to count the particles from each of the substances.

Study Questions

- (a) Was it easy to count the particles in each sample?
- (b) How can we know the number of particles in each sample without necessarily counting?

The Facts

You may have realized that it is nearly impossible to physically count the particles in a sample of salt? You may count the particles of rice but with difficulties. However, by weighing, it can be possible to find out the number of particles in a sample of a substance. When few particles are in a sample they weigh less, when more particles are in a given sample, it weighs more. Therefore it can be concluded that every particle contributes to the total weight of any given amount of substance.

Chemists for a long time were interested in knowing the quantities of substances they are dealing with. For example how many atoms, molecules, mass of compounds or ratios in which atoms or substances combine. These particles are generally so small and their mass value equally very neglible e.g. the mass of hydrogen is 1.4×10^{-24} g.

Because it would be quite cumbersome counting individually these number of particles involved in a reaction, Amedeo Avogadro came up with unit measurement called *mole* for representing these count of particles after a series of experiments and much study. It is important to bear in mind that the term *mole* simply represents a number just as a dozen is used to denote 12 items.

Therefore chemists found it convenient to use the unit *mole*. The mole is the chemist's measure of the *amount of substance*. Amount of substance relates directly to the particles making up the matter and can be calculated even though the particles themselves cannot be seen wth naked eyes or easily counted.

One mole of any substance is the amount of that substance that contains as many particles as there are in 12g of the isotope carbon-12.

When amount of substance is measured in moles, the nature of particles must be stated either as atoms, molecules or ions. For example whether two moles of hydrogen refer to moles of hydrogen atoms or one mole of hydrogen molecules.

Note that mole is an SI unit of measuring the amount of substance, which is a physical quantity. The mole is a counting unit similar to familiar units like pair (two items), dozen (12), gross (144) and a ream (500).

2.2 Avogadro's constant, (L)

Activity 2.3

Individually:

Calculate the number of hydrogen atoms present in 0.5 moles of hydrogen gas, H_2 .

Solution

1 mole of hydrogen gas contains 6.022×10^{23} hydrogen molecules.

Therefore 0.5 mole of hydrogen gas $=\frac{0.5 \times 6.022 \times 10^{23}}{1} = 3.011 \times 10^{23}$

But one molecule of $H_2 = 2$ hydrogen atoms

Therefore, the number of hydrogen atoms present

 $= 2 \times 3.011 \times 10^{23}$

= 6.022×10^{23} hydrogen atoms.

The Facts

Mole is defined according to the number of particles that a substance contains. One mole of any chemical substance contains the same number of particles as there are atoms in 12g of carbon-12. It then follows that if we have 12g of carbon-12, we must have one mole of it. Experiments have shown that the number of atoms in this quantity of carbon-12 is approximately **6.022 x 10**²³. This number is called **Avogadro's constant**, denoted by **'L'**. The number was established after a series of experiments, an effort greatly contributed to by Italian physicist called Amedeo Avogadro. It is a fixed and constant number. It is represented as $L = 6.022 \times 10^{23}$.

The Avogadro's constant has units of 'per mole' or 'mol⁻¹' and can be stated as $L = 6.022 \times 10^{23}$ particles per mole.

Hence: • One mole of any substance contain 6.022×10^{23} particles

- Two moles of any substance contain $2 \times 6.022 \times 10^{23}$ particles
- Three moles of any substance contain $3 \times 6.022 \times 10^{23}$ particles
- Half a mole of any substance contain $0.5 \times 6.022 \times 10^{23}$ particles

It is important to note that one mole of atoms contain 6.022×10^{23} atoms, one mole of molecules contain 6.022×10^{23} molecules, one mole of formula units contain 6.022×10^{23} formula units, one mole of ions contain 6.022×10^{23} ions.

2.3 Relative Atomic Mass (R.A.M)

Activity 2.4

In pairs:

We have already seen that a pair is made up 2 items whereas one dozen consists of 12 items, and 1 mole consists of 6.023×10^{23} particles. Let us find out whether 1 pair of different items weigh the same.

Apparatus

Beam balance, potatoes, tomatoes, oranges

Procedure

- 1. Choose one pair of potatoes and one pair of tomatoes or oranges of the same size as the potatoes.
- 2. Place the pair of tomatoes/oranges on one side of the beam balance and the pair of potatoes on the other. Do they balance? If not, which pair is heavier than the other?
- 3. Repeat procedure 2 using other items such as earrings, pens and pencils. What do you observe?
- 4. Record your observations in your notebook. What do you conclude?

A student was supplied with a dozen chicken feathers of the same size. Explain briefly how the student would find the number of pieces of paper each measuring $6 \text{ cm} \times 2 \text{ cm}$ that have the same mass as the feathers.

You may have observed that, although a pair consists of two items, the items may have different masses. In the same way, though a dozen has twelve items, the items may have different masses. Do you expect 1 mole of different particles to have different or similar masses?

If we weigh 12g of carbon atoms and 1g of hydrogen atoms, they will contain the same number of atoms. 24g of magnesium will also contain the same number of atoms as 1 g of hydrogen atoms. In other words, the relative atomic mass of all elements expressed in grams contain the same number of atoms. Experiments

have shown this number to be 6.023×102^3 . It means that if we placed these number of atoms on a balance, they would weigh the same as the relative atomic mass.

How do bank clerks count large amounts of coins in the banking hall or pharmacists package exact number of large quantities of tablet medicine? We have also seen in Activity 2.2 how tedious it is to count small particles. In deed, manual counting of these items can be very tiring and cumbersome. Therefore there are automatic counting machines designed for such counting by weighing. Examples are the ones given above i.e. A - ATM machine and B - mass spectrometer.

Discussion corner!

Work in groups:

- 1. In your groups discuss why the masses of atoms are called relative masses.
- 2. Why are there no units for relative masses.

The Facts

Atoms too can be counted by weighing, but atoms are so light that millions are needed to reach a mass that can be recognized. Therefore the mass of one atom can be compared with that of another atom and so easier to determine the **relative masses** of the atoms in comparison with each other. Whereas hydrogen served for a long time as the reference element, the carbon isotope ${}^{12}_{6}C$ is used today as a reference element used to get masses of other atoms indirectly. All atomic masses are compared to $\frac{1}{12}$ of the mass of carbon ${}^{12}_{6}C$, which is now taken as a reference mass for measurement of masses. The instrument used for weighing and comparison of atomic masses is called **mass spectrometer**

Definition of Relative Atomic Mass

Relative atomic mass can be defined as average mass of one atom compared to $\frac{1}{12}$ the mass of one atom of ¹²C. It tell us, on average how many times heavier or lighter an atom of an element is compared to $\frac{1}{12}$ the mass of carbon-12. Carbon was chosen as the standard atom to which other atoms are measured against because of its abundance in a large number of compounds.

Looking at the table of relative atomic masses we see some statements like Mg = 24, or Cl = 35.5. This, to a chemist, is a way of saying the relative atomic mass of magnesium is 24 and chlorine 35.5; that is every atom of magnesium has a mass of 24 times more than that of atom of carbon.

Element	Symbol	Relative Atomic Mass
Hydrogen	Η	1
Sodium	Na	23
Zinc	Zn	64.5
Copper	Cu	63
Aluminium	Al	27
Potassium	K	39
Iron	Fe	56
Calcium	Ca	40
Sulphur	S	32
Iodine	Ι	53
Oxygen	0	16
Nitrogen	N	14
Lead	Pb	207

Table 2.2 Relative atomic masses of some common elements

Activity 2.5

Work in pairs

Investigating if pairs of different items have the same mass

Requirements: beam balance, onions, lemon, potato, eggs.

Procedure

- 1. Set up a beam balance.
- 2. Choose one pair onions and one pair of lemon of the same size as onions.
- 3. Place one pair of onions on one side of the beam balance and the pair of potato on the other side of the balance.
- 4. Repeat procedure 2 using onions and potato and record your observations.
- 5. How do the pairs of the items compare.

In groups of two, discuss your observations and draw own conclusions.

The Facts

From Activity 2.5 you may have observed that a pair of two items may have different masses. This also applies for atoms of different elements. For example,



23g of sodium atoms and 14g of nitrogen atoms though of different masses, they contain the same number of atoms, that is, 6.022×10^{23} atoms.

Elements have same number of particles in one mole but different relative atomic masses.

2.4 Relative Molecular Mass

Discussion corner!

Work in groups:

- 1. In your groups, discuss the following terms and make class presentations.
 - (a) Are the relative masses of atoms and their ions the same or different?
 - (b) Why are these measurements referred to as relative masses?
 - (c) What is Relative Molecular Mass (R.M.M)?
- 2. Classify the following as atoms or molecules.



The Facts

When atoms combine, they form molecules. So the molecular mass of a compound is the sum of all the atomic masses of each atom in the formula. Some compounds are made up of ions rather than atoms, hence we use the term **Formula Mass** which incorporates atomic, molecular and ionic compounds.

Relative Molecular Mass is defined as the mass of one molecule of an element or a compound compared to the mass of an atom of carbon, carbon-12. Relative molecular mass of any substance contains amount of that substance as there are in 12g of C-12. See the table 2.2.

Table 2.3: Relative molecular mass (R.M.M).

Molecule	Number of moles	Number of particles	Relative molecular mass
H ₂	1	$6.02\ 2 \times 10^{23}$	2
CO ₂	1	6.022×10^{23}	44
NO_2	1	6.022×10^{23}	46
H ₂ O	1	6.022×10^{23}	18
Al ₂ O ₃	1	6.022×10^{23}	102
H_2SO_4	1	6.022×10^{23}	98

Calculation of Relative Molecular Mass

Calculate the relative molecular mass of the following.

(Relative Atomic Mass, S = 32, H = 1, O = 16, Na -23, Cl = 35.5)

1. H_2SO_4 2. HCl 3. Na_2SO_4

Solution

- 1. $H_2SO_4 = 2 \times 1(H) + 1 \times 32(S) + 4 \times 16(O) = 98$
- 2. $HCl = 1 \times 1(H) + 1 \times 35.5(Cl) = 36.5$
- 3. $Na_2SO_4 = 2 \times 23(Na) + 1 \times 32(S) + 4 \times 16(O) = 142$

Molar mass (M)

Discussion corner!

In Pairs answer these questions:

- 1. Why do RAM, RMM and RFM have no measurement units?
- 2. What is molar mass and why is it important?

The Facts

Molar mass is the measurement unit that enables scientists to calculate the weight of any chemical substance, be it an element or a compound. It is defined as the mass of one mole of a substance. It contains the Avogadro's number of particles with units grams per mole.

The relative atomic mass, relative molecular mass and relative formula mass are numerically equal to their molar mass but they have no units.

For example RAM of chlorine is 35.5 and the molar mass of chlorine is 35.5 g.

Steps in calculating molar mass

For example: calculate the molar mass of sulphuric (VI) acid.

- 1. List each of the element and the number of atoms of the element present in the substance e.g. H = 2, S = 1, O = 4.
- 2. Determine the atomic mass of each element. H = 1, S = 32, O = 16 These are often provided.
- 3. Multiply each atomic mass by the number of atoms in the formula, e.g.
- 4. H($1 \times 2 = 2$), S ($32 \times 1 = 32$), O ($16 \times 4 = 64$)
- 5. Sum up the atomic masses obtained in step 3 (2+32+64) = 98g Therefore, the molar mass of H₂SO₄ is 98g.

2.5 Calculations involving conversion of moles

Discussion corner!

Work in groups:

In your groups, discuss how the knowledge of moles is used in the preparation of solutions.

The Facts

In unit one you learnt how number of moles can be calculated using volumes and concentrations of solutions. For solid substances the total number of atoms in a substance can also be determined by using the relationship between grams, moles, and atoms.

If given the mass of a substance and asked to find the number of atoms in the substance, one must first convert the mass of the substance, in grams, to moles, as chemical substances are weighed in grams.

The following formulas help us in calculations involving moles and its conversion into mass or molar mass.

Number of moles = $\frac{\text{Mass in grams}}{\text{Molar mass}}$

Mass in grams = number of moles × molar mass Molar mass = $\frac{Mass \text{ in grams}}{Number \text{ of moles}}$

Worked example I

Calculate the number of moles present in 7g of nitrogen atoms. (N = 14)

Solution

Mass = 7g Molar mass = 14g Remember, Number of moles = $\frac{\text{Mass in grams}}{\text{Molar mass}}$ Therefore, moles = $\frac{7}{14}$ = 0.5 moles

Worked example 2

What is the mass of 0.4 moles of sodium carbonate?

Solution

Write the correct formula of sodium carbonate, Na₂CO₃

Moles of sodium carbonate = 0.4 mol

Molar mass of sodium carbonate = 2×23 (Na) + 12(C) + 3×16 (O) = 106

Mass of 0.4 moles = $0.4 \times 106g = 42.4g$

Worked example 3

How many moles of atoms of oxygen are there in 0.2 mole of sulphur (IV) oxide (SO_2) ?

Solution

Formula of the substances, SO_2

1mole of sulphur (IV) oxide contains 1 mole of sulphur atoms and 2 moles of oxygen atoms.

 \therefore 0.2 mole of sulphur (IV) oxide contain (0.2 × 2) = 0.4 moles of oxygen atoms

Worked example 4

How many atoms are there in 4g of $PbSO_4$?

Solution

1 mole of any substance contains the Avogadro constant number of particles.

The relative molecular mass in grams of $PbSO_4 = (207 + 32 + 64) = 303g$

303 g contains = 6.022 × 10²³ atoms ∴ 4g of PbSO₄ contains = $\frac{4 \times 6.022 \times 10^{23}}{303}$ atoms

 $= 7.95 \times 10^{21}$ atoms

Worked examples 5

How many moles are there in 10 g of H_2SO_4 ?

Molar mass of $H_2SO_4 = (2 + 32 + 64) g = 98g$

10g of H₂SO₄ = $\frac{10}{98}$ mole = 0.102 moles

2.6 Molar gas volume

Activity 2.6

Work in groups:

Investigating the volume of one mole of hydrogen gas?

Apparatus and chemicals (per group): burette, burette stand, water bath, 2M hydrochloric acid, magnesium ribbon 3.5 cm long

Safety Precaution: Wear eye protection equipment.

Procedure

Set apparatus as shown below.



Figure 2.2

- 1. Clean a piece of magnesium ribbon about 3.5 cm long and weigh accurately.
- 2. Measure 25 cm³ of dilute hydrochloric acid into the burette. Carefully add 25 cm³ of water on top of this.
- 3. Push the magnesium into the end of the burette so it will stay in position with its own tension.
- 4. Add 50 cm^3 of water to a 250 cm^3 beaker.
- 5. Quickly invert the burette into the water. If this is done quickly and carefully very little is lost. It is important that the liquid level in the burette starts on the graduated scale. If it is not on the scale; momentarily open the tap, this allows the level to drop). Clamp the burette vertically.
- 6. Take the burette reading note: it is upside down.
- 7. Observe the magnesium ribbon react as the acid diffuses downwards, wait until all the magnesium has reacted.

Results

The equation for the reaction is

 $Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$

The relative atomic mass of magnesium is 24.

Volume of hydrogen produced = $\ cm^3$

Mass of magnesium used = _____ g

Calculate the moles of Mg used (Mg = 24)

Calculate the volume of hydrogen gas produced when 1 mole of Mg is used.



Avogadro's law of gases states that equal volume of gases under the same conditions of temperature and pressure contain equal number of molecules. From this law we can conclude that one mole of any gas contain equal number of molecules and therefore would occupy the same volume under the same conditions.

Molar gas volume is the volume occupied by one mole of a gas. At Standard temperature and pressure (S.T.P) one mole of an ideal gas will occupy a volume of 22.4dm³ and at room temperature and pressure (R.T.P) the volume is 24.0dm³

One mole of any gas contains Avogadro's constant, $6.022 \ge 10^{23}$ molecules. Mole of the gas = $\frac{\text{Volume}}{\text{Molar gas mass}}$

Worked example I

Calculate the number of gas molecules in 5.6 dm³ of CO₂ at stp.

Solution

Moles of the gas = $\frac{\text{Volume of given}}{\text{Molar gas volume}} = \frac{5.6}{22.4} = 0.25 \text{ moles}$

1 mole of CO₂ contains = 6.022×10^{23} molecules

0.25 mole of CO_2 contains = $0.25 \times 6.022 \times 10^{23}$ =1.5055 × 10²³ molecules

Standard conditions for measuring gas volumes

The unending changes in the temperature and the pressure of a gas make it necessary to choose suitable standards of temperature and pressure under which volumes of gases can be referred to.

The standards fixed are:

- 0°C or 273K and 760mm pressure. These are known as **Standard temperature** and pressure (S.T.P).
- 25°C or 298K and 760mm pressure. These are known as **Room temperature** and pressure (**R.T.P**).

Check your progress 2.1

- 1. Why is relative atomic mass of some elements not whole numbers?
- 2. Calculate the relative formula mass of the following compounds.
 - (a) Na_2SO_4
 - (b) $Ca(HCO_3)_2$ (Na = 23, S = 32, O = 16, C = 12, H = 1, Ca = 40)
- 3. Find the relative molecular mass of:
 - (a) HCl (b) O_2 (c) $C_6H_2O_6$
- 4. Differentiate between relative molecular mass and relative formula mass.
- 5. Distinguish between mole of a gas and molar gas volume.
- 6. Briefly explain the relationship between molar mass and the mole.
- 7. Calculate the mass of:
 - (i) 0.23 moles of carbon (Zn = 65)
 - (ii) 3.5 moles of potassium atoms
 - (iii) 0.4 moles of sulphur (VI) oxide
- 8. How many moles of atoms are there in:
 - (i) 32.5g of Zinc atoms (Zn = 65)
 - (ii) 46.5g of phosphorus atom (P = 31)
 - (iii) 16.4g of sodium phosphate, Na_3PO_4 (Na = 23, P = 31 and O = 16)
- 9. Calculate the number of atoms in:
 - (i) 0.2 moles of Zn (ii) 0.25 moles of Al (Zn = 65, Al = 27)

2.7 Determination of chemical formulae In pairs, discuss the question below:

What important chemical information do we obtain from empirical and molecular formulae?

The Facts

In the previous sections, we discussed the relationship between the mass of a substance and the number of atoms or molecules it contains (moles). Given the

chemical formula of the substance, you were able to determine the amount of the substance (moles) from its mass, and vice versa. But what if the chemical formula of a substance is unknown? In this section, we will explore how to apply these very same principles in order to derive the chemical formulas of unknown substances from experimental mass measurements.

Determination of Empirical and Molecular Formulae

The Facts

- **Empirical Formula** is the formula which shows the simplest whole number ratios of the different types of atoms combining, that is the simplest ratio of the atoms present in a compound.
- **Molecular formula** is the formula which shows the actual number of different atoms in a molecule or compound, that is, the actual formula for a molecule or compound.

The molecular formula represents the compound in the way it exists. The empirical formula for many compounds is not the same as molecular formula. Empirical formula does not show the actual form in which the molecule exists naturally. For example, there are six possible CH empirical formula units for the molecule C_6H_6 .

Molecular formula	Empirical formula
H ₂ O ₂	НО
Na ₂ O ₂	NaO
$C_{6}H_{12}O_{6}$	CH ₂ O
C_4H_8	CH ₂

Table 2.4: Molecular and empirical formula of some compounds

Empirical formula

Find the empirical formula of a compound that has 48.38% carbon, 8.12% hydrogen, and 53.5% oxygen by mass.

The following steps are followed:

1. Note the mass of each element or use the percentage composition given e.g.

Carbon = 48.38%, Hydrogen = 8.12%, Oxygen = 53.5%

2. Convert the mass or percentage composition of each element to moles of each element using their atomic masses. In most cases, the atomic masses are given.

$$C = \frac{48.38}{12} = 4.028 \text{ mole } H = \frac{8.12}{1} = 8.12 \text{ mol } O = \frac{53.38}{16} = 3.336 \text{ mol}$$

3. Find the mole ratio of each element by dividing using the smallest number of the moles obtained in step 2 above. In this example, there are fewer moles of oxygen than any other element, so we use the mole of oxygen to establish the ratios.

$$C = \frac{4.028}{3.336} = 4.028 \text{ mole} \quad H = \frac{8.12}{3.336} = 2.4 \qquad O = \frac{3.336}{3.336}$$

4. Use the mole ratios obtained in step 3 above to write the empirical formula.

Note that some mole ratios are not whole numbers. Since we cannot have partial atoms in the empirical formula, a multiplication factor must be applied to get whole numbers. In this case, 5 is the factor we need.

 $C = 1.2 \times 5 = 6; H = 2.4 \times 5 = 12; O = 1 \times 5 = 5.$

Now the ratios are whole numbers, and we can write the empirical formula, which is: $C_6H_{12}O_5$

Calculations involving empirical formula

Worked example I

Find the empirical formula of a compound containing 0.2g hydrogen and 0.16g oxygen.

Solution

The procedure above can be simplified by use of a table as follows:

Table 2.5

Atoms	Н	0
Mass	0.2	1.6
Molar mass	1	16
Moles	$\frac{0.2}{1} = 0.2$	$\frac{1.6}{16} = 0.1$
Mole ratios (divide by the smallest amount to get the smallest whole number)	$\frac{0.2}{0.1} = 2$	$\frac{0.1}{0.1} = 1$



 \therefore Empirical formula = H₂O

Activity 2.7

Determining empirical formula of magnesium oxide

As a class

Apparatus and materials: Crucible and lid, magnesium ribbon, weighing balance, bunsen burner, emery paper/sand paper, tripod stand (or clay triangle).

My safety, my responsibility

Eye protection is essential. Do not breathe the fumes generated. Do not touch the crucible, lid, triangle, ring, or stand during or after heating. Never place anything hot on a balance. Do not look into the crucible directly during heating.

Procedure

Before placing the folded magnesium ribbon into the crucible, there are two steps or activities you must carry out. Identify them and carry them out before you start the heating.

Place the crucible securely on the clay triangle. Place the Bunsen burner under the crucible, light it, and heat strongly until all the magnesium turns into greywhite powder (probably after about 10 minutes).



Stop heating and allow the crucible, lid and contents to cool. Add a few drops of water directly to the solid powder. Carefully waft some of the gas that is generated toward your nose and record any odour. Why was the water added? Also, use

tongs to carefully hold a piece of moist red litmus paper over the crucible. Record your observations.

Heat the crucible and contents, gently for about 2 minutes and then strongly for about another 5 minutes. Allow the crucible to cool and then record the mass of the crucible and contents, M_3 .

My environment, My life
Follow instructions for oxide disposal given by your teacher. Clean all equipment thoroughly and keep them safely.
Record your results as follows:
(a) Mass of Mg metal used (a) = \g
(b) Mass of oxide product formed (b) =g
(c) Mass of combined $O_2 = (b - a) = \g$
(d) Moles of magnesium =
(e) Moles of oxygen =
(f) Mole ratio of Mg and O =
(g) Empirical formula of the oxide (lowest whole-number as subscripts) =
(h) Percent by mass of Mg and O in the oxide =
(i) Percent yield of Mg + $\frac{1}{2}O_2 \longrightarrow MgO\left(\frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%\right)$
Activity Questions
1. How does your experimental empirical formula compare to the theoretical empirical formula. Do they match?
2. What could be the primary sources of experimental error?
3. Does this method appear to be a valid way to determine the formula of metal oxides?
Calculations involving molecular formula
Worked example 2
An organic compound was found to contain 40% carbon, 53.33% oxygen and 6.67% hydrogen. Given the relative molecular mass of the compound is be 60, calculate its molecular formula. (C = 12, H = 1, $O = 16$)

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Solution

Atoms	С	Н	0
% by mass	40	6.67	53.33
Molar mass	12	1	16
Moles	$\frac{40}{12} = 3.33$	$\frac{6.67}{1} = 6.67$	$\frac{53.33}{16} = 3.31$
Mole ratios (divide by the smallest amount to get the smallest whole number)	$\frac{3.33}{3.31} = 1$	$\frac{6.67}{3.31} = 2$	$\frac{3.31}{3.3} = 1$
	1	2	1

: Empirical formula CH₂O

Relative molecular mass of $(CH_2O)n = 60$

 $= C_2 H_4 O_2$

Therefore,

 $n = (1 \times 12) + (2 \times 1) + (1 \times 16)n = 60$ (30)n = 60 n = 2 Molecular formula = (EF)n = (CH₂O) × 2

Activity 2.8

Determining empirical formula of hydrated copper (II) sulphate, $CuSO_4 xH_2O$

Work as a class:

In this experiment, the water of crystallization is removed from hydrated copper (II) sulphate. The mass of water is found by weighing before and after heating. This activity is used to find x in the formula: $CuSO_4$.xH₂O, using **mole calculations**.



1. You are provided with the following set up. Using your knowledge obtained from Activity 2.7, proceed to carry out this activity.

First, identify two things that are wrong with this set up. Suggest how they should be corrected.

2. Outline the procedure to use.

3. Hint:

Heat the crucible and contents, gently at first, over a medium Bunsen flame, then slightly strong. But avoid over-heating and immediately stop heating when the colour starts to turn black.

- 4. Record your observations and results in a suitable format.
- 5. (a) During the heating some changes were observed. Explain the occurance of these changes.
 - (b) Why were the following necessary during the activity.
 - (i) Gentle heating at the start
 - (ii) Avoiding over-heating
 - (c) Weighing before the start and after heating.

Activity Questions

- 1. Calculate the molar masses of H_2O and $CuSO_4$ (Relative atomic masses: H = 1, O = 16, S = 32, Cu = 64).
- 2. Find the mass of water driven off and the mass of anhydrous copper(II) sulphate formed in activity.

- 3. Calculate the number of moles of anhydrous copper (II) sulphate formed.
- 4. Calculate the number of moles of water driven off.
- 5. Calculate how many moles of water of crystallization would have been driven off if 1 mole of anhydrous copper(II) sulphate had been formed.
- 6. Write down the formula for hydrated copper(II) sulphate.

Calculating Percentage Composition

Percentage composition is the term used to describe the percentage by mass of each element in a compound. It is typically found using the molar mass values for both the elements in the compound and that of the compound.



Worked example 3

Calculate the percentage by mass of hydrogen and oxygen in water.

Solution

Step 1: Find the molar mass of water (H_2O)

 $H = 1 \times 2 = 2$, $O = 16 \times 1 = 16$, $H_2O = 2 + 16 = 18$.

Step 2: Calculate the percentage composition of each element

Hydrogen = $\frac{2}{18} \times 100 = 11.1\%$ Oxygen = $\frac{16}{18} \times 100 = 88.9\%$

Check your progress 2.2

- 1. 14.4g of magnesium metal was reacted completely in a closed container of pure nitrogen gas to form 18.6g of a compound of these two elements. Calculate the empirical formula of the compound. (Mg = 24, N = 14)
- 2. Calculate the percentage by mass of calcium, nitrogen and oxygen in calcium nitrate, $Ca(NO_3)_2$. (Ca = 40, N = 14, O = 16)

- Calculate the percentage by mass of sodium, carbon, oxygen and water of crystallization in sodium carbonate decahydrate. (Na = 23, C = 12, O = 16, H = 1)
- 4. Calculate the percentage composition of each elements in the following compounds.
 - (i) $CaCO_3$ (ii) $Mg(OH)_2$ (iii) C_2H_5OH (H = 1, C = 12, O = 16, Mg = 24, Ca = 40)
- 5. Calculate the percentage composition of nitrogen in following compounds.
 - (i) NH₄NO₃ (ii) HNO₃
 - (H = 4, N = 14, O = 16)

2.8 Percentage yield and percentage purity

Research work

In pairs:

Percentage yield and percentage purity are important consideration in many industrial productions. Identify some of the industrial processes in which they impact greatly and support their causes.

The Facts

The percentage yield is the amount of product obtained from a chemical reaction. Percentage purity is the percentage of the material which is the actual desired chemical in amount of substance or product.

Calculating percentage yield and percentage purity of a product

The following activities will help us understand how to determine percentage yield of reaction and percentage purity of substances.

Percentage purity

- Useful in extraction of table salt, crude oil refinery.
- Extraction and purification of metals.

Activity 2.9

Determination of percentage purity

Apparatus and chemicals: 30 cm³1M sodium hydroxide, 30 cm³1M hydrochloric acid, conical flask, evaporating dish, filter paper.

Procedure

- 1. To 30 cm³ of 1M hydrochloric acid provided, add directly 30cm³ of sodium hydroxide.
- 2. Gently heat the resulting solution to evaporate excess water and allow the solution to cool and form crystals.
- 3. Filter to separate the crystals from any remaining solution and dry them on a filter paper.
- 4. Weigh an evaporating dish and transfer the crystals into the dish. Then reweigh the dish and its content.
- 5. Now heat the crystals strongly to drive off any water that remained.
- 6. Weigh the contents of the evaporating dish and record your results.
 - Mass of empty evaporating dish = _____g
 - Mass of impure salt + dish = _____g
 - Mass of dish + salt after heating = _____g
 - Using your results, calculate the percentage purity of the salt formed.

Sample results

The salt that was prepared was analyzed for its water content by heating to remove any residual water.

mass of evaporating dish empty = 51.32g

mass of impure salt + dish = 56.47g

mass of dish + salt after heating = 56.15g

mass of impure salt = 56.47 - 51.32 = 5.15g

mass of pure salt = 56.15 - 51.32 = 4.83g

Percentage purity of the salt = -	mass of pure salt \times 100	
	mass of impure salt	
= -	$\frac{4.83 \times 100}{5.15} = 93.8\%$	

Worked example 4

30g of impure calcium carbonate was reacted with an excess of dilute hydrochloric acid to produce 2240 cm³ of carbon (IV) oxide gas at standard temperature and pressure. Calculate the percentage purity of calcium carbonate. (Ca = 40, C = 12, O = 16 Molar gas volume at STP = 22.4 dm³.

Solution

The equation for the reaction is

 $CaCO_3$ (s) + 2HCl (aq) \longrightarrow $CaCl_2$ (aq) + H₂O (l) + CO₂ (g)

Step 1: Find molar mass of $CaCO_3 = 100$

Step 2: Calculate moles of CO₂ produced = $\frac{2240}{22400}$ = 0.1 moles

Mole of $CaCO_3$ that reacted = mole of CO_2 produced = 0.1 moles

Mass of CaCO₃ that reacted = moles x molar mass = $0.1 \times 100 = 10g$

Remember, 22.4 litres of gas is produced by 100 g (1 mole) of calcium carbonate

Because only 10g of calcium carbonate reacted out of the 30g of impure carbonate;

Percent purity of calcium carbonate used = $\frac{10}{30} \times 100\%$ = 33.33%

Determining percentage yield of a reaction

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? (Cu = 63.5, S = 32).

Solution

We calculate percentage yield using the following formula.

Percentage yield = $\frac{\text{Actual yield}}{\text{Theoretical}} \times 100\%$

 $2Cu(s) + S(s) Cu_{2}S(s)$

From the equation,

= _____ mass of copper given Moles of copper that reacted molar mass of copper

$$\frac{2.4}{63.5} = 0.0378$$
 moles

Mole ratio in the equation can be used to calculate the expected number of moles of the product.

Moles of Cu: $Cu_2S = 2:1$

Expected moles of $Cu_2S = \frac{1}{2} \times 0.0378$ mole

= 0.0189 mole R.M.F of Cu₂S $= (2 \times 63.5) + 32 = 159$ Expected yield of Cu₂S $= 159 \text{ g} \times 0.0189 = 3.0051 \text{ g}$ Percentage yield of $Cu_2S = \frac{2.25}{3.0051} \times 100\% = 74.87\%$

Check your progress 2.3

- 1. 3g of impure sample of iron was reacted with dilute nitric acid to give 1240 cm³ of hydrogen gas at room temperature and pressure. Calculate the percentage yield of the product. (Fe = 56, molar gas volume at $RTP = 24 \text{ dm}^3$).
- 2. During extraction of iron from its ore, haematite, 60 kg of a sample was reduced to iron using carbon monoxide. The mass of iron obtained was 33.6 kg. Calculate the percentage purity of the ore. (C = 12, O = 16, Fe₂ = 56)
- 3. It has been established, in practice, that most chemical reactions do not yield the total amount expected or predicted by stoichiometric reaction equations. The amount of product often produced is found to be less than what was expected. Validate this statement with good argument.
- 4. 2.34g of aluminium reacted with excess copper (II) sulphate solution to produce 3.89g of copper according to the equations:

 $2Al(s) + 3CuSO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 3Cu(s)$

What was the percentage yield of copper? (Al = 27, Cu = 63.5)

5. When 54.8g of silicon(IV) oxide is heated with an excess of carbon, 32.5g of silicon carbide is produced besides the carbon monoxide gas. What is the percentage yield of this reaction? (Si = 28)

 $SiO_2(s) + 3C(s)$ heating SiC(s) + 2CO(s)

2.9 Chemical equations and mole ratio

The Facts

Chemical reaction represents the change in which one or more substances act alone or on each other to produce one or more new substances. The substances which change are called **reactants** (always represented on the left) and the new substances formed are called **products** (always represented on the right) of the equation. A chemical equation is a convenient means of representing a chemical reaction by using symbols and formulae.

A chemical equation is an expression, in symbols, of the relative amounts of substances taking part in reaction. A Chemical equation can be derived from an experiment.

The simplest forms in which the reactants and products can exist are atoms, molecules, ions and formula units. Each particle has a name, symbol or formula to represent it. The actual (practical) measurement of quantity of reactants and products occur in various units e.g. mass units of grams, volume units of dm³ or cm³. These can in turn be converted into other units such as moles.

The simplest form of an equation is to represent it by the names of the reactants and products. This is called **word equation**. For example, if we wish to represent a reaction between zinc and dilute sulphuric (VI) acid to form zinc sulphate and hydrogen, it is written as follows:

Zinc + sulphuric acid _____ zinc sulphate + hydrogen gas

Work To Do

Write word equations for the reactions.

- 1. Reaction of dilute hydrochloric acid and sodium hydroxide
- 2. Combustion of carbon in limited air.

In Chemistry the standard practice and convenient way is to represent reaction using chemical symbols and formulae. This is referred to as chemical equation. It must always be balanced.

Writing correct chemical equations

A correct chemical equation is written using:

- correct names or symbols and formulae of substances involved in the reaction.
- showing the physical state of each substance involved in the reaction.
- amounts of reactants and products involved in the reaction.

The following signs and symbols are used in writing equations.

s – solid or precipitate

l – liquid

Note that state symbols are usually placed in parenthesis (brackets), e.g (s)

g – gas

aq – aqueous solution

+, on reactant side means reacts with and +, on products side means and

→ Forms or produces (in the forward direction)

The relative amounts of reactants and products can be obtained by experiment or predicted by balancing the equation.

Remember

The simplest form in which a substance exists is used in an equation. For example, oxygen is written as O_2 because it exists freely as a molecule, and not as an atom. Magnesium exists as an atom and not as an ion or molecule, and therefore must be presented as Mg. Calcium oxide exists as ions and must be represented as a formula unit, CaO with right mole ratios of the combining elements.

Discussion corner!

- 1. Write the chemical symbols and state for the following substances.
 - (i) Carbon (II) oxide (iv) Phosphorous pentaoxide
 - (ii) Flourine (v) Bromine
 - (iii) Sodium peroxide (vi) Hydrogen sulphide
- 2. Did you find difficulty in writing chemical symbols for the substances in 1 above? What do you learn from this exercise?

Balancing equations (Stoichiometry)

It is very important in Chemistry now and for the future to learn to know to write correct chemical symbols and formula for elements and compounds and their status. Without this, it would be very challenging to write balanced chemical equations.

Activity 2.10

Work in pairs:

1. Study the two photographs below.



Figure 2.5

2. Comment on what is going on in the photographs.

The Facts

A chemical equation, must be balanced, that is, there must be same number of atoms of each kind of atom on each side of the equation.

Think Tank

Support the statement "chemical equation must always be balanced." In your opinion, do you think this is a mere assertion or it is scientifically valid? You can use sample chemical equation to prove your argument.

The following steps are used as a guide in balancing of equations:

- 1. Write down the unbalanced equation leaving spaces before each formulae or symbol in order to fix the numbers later.
- 2. Write down the total number of the different atoms on each side of the equation.
- 3. Check which atoms are not equal? Fix suitable numbers in front of the symbol or formula to make the atoms on both sides equal.
- 4. Include the state symbols to show the physical states of reactants and products.
Remember

A formula of a compound must never be altered to balance an equation since any particular compound has a fixed formula.

How to balance equations

Lets consider Sodium reacting with water to form sodium hydroxide and liberating hydrogen gas.

In this reaction;

Reactants are: sodium, Na and water, H₂O.

Products are: sodium hydroxide, NaOH, and hydrogen gas, H₂.

Steps

- (i) Na + $H_2O \longrightarrow NaOH + H_2$ (Unbalanced because hydrogen atoms are not equal on both side)
- (ii) There can only be even number of hydrogen atoms on each side, so we write 2 in front of NaOH e.g.

 $Na + H_2O \longrightarrow 2NaOH + H_2$

(iii) Now make sodium atoms equals by adding 2 in front of Na on the left hand side of the equation, e.g.

 $2Na + 2H_2O \longrightarrow 2NaOH + H_2$

Now the equation is balanced.

(iv) Include the state symbols of the reactants and products

 $2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$

Writing balanced equations is important. In fact, unbalanced equations are unacceptable in Chemistry. Balanced equations help to indicate the mole ratios. Note that it does not show the amount of reacting substances and products formed. It is also essential to be able to assign correct formula to substances and then balance the equations. Though some equations may become familiar due to frequent use, it is unwise to memorise equations. Always construct from knowledge of the formula.

Discussion corner

In pairs:

- 1. List all the information one can obtain from analysing a chemical equation.
- 2. Discuss the importance of balanced chemical equations.
- 3. Suggest some crucial information about reactions one cannot learn from the reactions.

Reading chemical equations

Activity 2.11

Work in pairs.

1. With your partner, read out these chemical equations.

	Zn(s)	+ 2HCl(g)	\longrightarrow ZnCl ₂ (s)	+ H ₂ (g)
Reacting				
particles	1 atom Zn	+ 2 molecules	→ 1formula	+ 1 molecule
		HCl	unit, ZnCl ₂	H_2
Amount of substance/mol	1 mol Zn	+ 2 mol HCl	\longrightarrow 1 mol ZnCl ₂	+ 1 mol H_2
	65.4g	$2 \times 36.5g$	136.4g	2g
ions and volume at stp	1 mol Zn	$2 \times 22.4 \text{dm}^3$	\longrightarrow 1 mol Zn ²⁺	+ 22.4dm ³
		HCl gas		H_2 gas
Number of				
particles	L atoms Zn	2L molecule	$s \longrightarrow L$ formula	+ L molecules
		HCl	units ZnCl ₂	H_2
2. Did you re	ealise some p	atterns during y	our reading?	

The Facts

Chemical equations can be read in many ways as illustrated above.

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Calculation of quantities of substances in chemical reactions

The equation as it is written does not indicate only one possible set of amounts of reactants and products. Different amounts of substance can react and be formed, but the relative amount (i.e the proportions) is always the same as shown in the balanced equation.

The relative amounts of any two substance involved in a chemical reaction is known as the **mole ratio**.

Take the reaction between sodium metal and oxygen gas to give sodium oxide. Various amounts of sodium and oxygen can react to give various amounts sodium chloride, but the mole ratio between any of the two substances involved is constant.

That is:

4Na (s) -	+ O ₂ (g)	>	$2Na_{2}O(s)$
4mol	+ 1mol		2mol
2 mol	+ 0.5mol		1 mol
5 mol	+ 1.25 mol		2.5mol
0.1mol +	- 0.025mol		0.05mol
Mole rat	io = $\frac{n(Na)}{n(O_2)}$ =	$\frac{4}{1} = \frac{2}{0.5} =$	$\frac{5}{1.25} = \frac{0.1}{0.025}$

It is evident that not only four moles of sodium which can react with one mole of oxygen to produce two moles of sodium oxide, many other amounts can react but the mole ratio is always constant and equal.

Having learnt about mole ratios, let us look at how mole ratios can be used to calculate the unknown quantities e.g. volumes, concentrations, moles and mass.

Steps in calculating quantities

- 1. Write a balanced equation for the reaction.
- 2. Find out the mole ratios of all the substances involved.
- 3. Equate mole ratios and calculate the required quantity.

Worked example

6.54g of zinc metal reacted completely with dilute hydrochloric acid at standard temperature and pressure. Calculate:

- (i) The number of moles of hydrochloric acid that reacted.
- (ii) The volume of hydrogen gas produced. (Zn = 65.4, H = 1, Molar gas volume at s.t.p = 22.4dm³)

Solution

(i) The equation for the reaction is

 $Zn(s) + 2HCl (aq) \longrightarrow ZnCl_2(aq) + H_2 (g)$ Moles of zinc reacting = $\frac{6.54}{65.4} = 0.1$ moles

Mole ratios = Δ Zn:HCl = 1:2

Therefore moles of HCl that reacted = $0.1 \times 2 = 0.2$ mole

(ii) Mole ratios =
$$\Delta Zn:H_2 = 1:1$$

Therefore moles of hydrogen = 0.1 moles

Volume of hydrogen gas produced = $0.1 \times 22.4 = 2.24$ dm³

Ionic equations

Discussion corner

In pairs:

1. Look at the following reaction between dilute hydrochloric acid and aqueous sodium hydroxide.

 $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l) \dots I$

 $H^{+}(aq) + Ch^{+}(aq) + Na^{\pm}(aq) + OH^{-}(aq) \longrightarrow Na^{\pm}(aq) + Ch^{-}(aq) + H_{2}O(l) \dots II$

2. What is happening in equation II?

The Facts

Chemical reactions taking place in aqueous solutions involve at least one ionic species either as reactants or products. When ionic solids are dissolved in water, the ions become separated and move freely in the solution. These ionic species can be used in writing equations, called an *ionic equations*.

During reactions involving ions or ionic compounds, some of the ions may not take part in the reaction. Ions which exists in a chemical reaction process but do not take part are known as **spectator ions**. Spectator ions cancel out and are therefore not shown in ionic equation. For example, in the equation considered in the discussion corner above;

Cl⁻(aq) and Na⁺(aq) ions are spectator ions (present in both sides of the equation) and therefore cancel out from the equation. Therefore, the ionic equation is

 $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$

Remember:

In writing ionic equations:

- 1. Balance the equation in terms of charges or/and moles.
- 2. Include state symbols of reactants and products.
- 3. Show formula unit of ionic solid.
- 4. Identify substances containing free ions and those that do not.
 - **Hint** Containing free ions *aqueous solutions of salts, acids and bases.*
 - Do not contain free ions- insoluble salts, gases, molecular substances, insoluble bases.

Worked example of ionic equations of some reactions:

- 1. An aqueous solution of barium nitrate and sulphuric (VI) acid reacting to form a precipitate of barium sulphate and nitric (V) acid.
- 2. Solid copper (II) oxide and hydrochloric acid to form soluble copper (II) chloride and water.

Solution

3. $Ba(NO_3)_2(aq) + H_2SO_4(aq) \longrightarrow BaSO_4(s) + 2HNO_3(aq)$ (Full equation)

 $Ba^{2+}(aq) + 2NO_{3}(aq) + 2H^{+}(aq) + SO^{2-}_{4}(aq) \longrightarrow BaSO_{4}(s) + 2H^{+}(aq) + 2NO_{3}(aq)$ (Total ionic equation)

 $Ba^{2+}(aq) + SO^{2-}_{4}(aq) \longrightarrow BaSO_{4}(s)$

4. $CuO(s) + 2HCl(aq) \longrightarrow CuCl_2(aq) + H_2O(l)$ (Full equation)

 $CuO(s) + 2H^{+}(aq) + 2ef(aq) \longrightarrow Cu^{2+(aq)} + 2ef(aq) + H_2O(l)$ (Total ionic equation)

 $CuO(s) + 2H^+(aq) \longrightarrow Cu^{2+(aq)} + H_2O(l)$

Check your progress 2.4

- 1. Balance the following chemical equations.
 - (a) $Cu(s) + O_2(g) \longrightarrow CuO(s)$
 - (b) CaO (s) + NH₄Cl (aq) \longrightarrow CaCl₂ (aq) + NH₃(g) + H₂O (l)

2. Write the ionic equations for the following reactions.

- (i) $AgNO_3(aq) + NaCl(aq) \longrightarrow AgCl(s) + NaNO_3(aq)$
- (ii) $2NaOH(aq) + CuCl_2(aq) \longrightarrow Cu(OH)_2(s) + 2NaCl(aq)$
- (iii) $2\text{NaOH}(aq) + H_2\text{SO}_4(aq) \longrightarrow \text{Na}_2\text{SO}_4(aq) + 2H_2O(l)$

2.10 The gas laws

Activity 2.12

Work in groups:

- 1. Discuss the particulate nature of gases. Design a demonstration to show that gases are in continuous random motion.
- 2. Discuss the following questions:
 - (a) Do gases have fixed volume? Do gases have same mass?
 - (b) Do you think temperature and pressure have any effect on gases? Think and design experiments that help explain your answers to some of these questions.

The Facts

Kinetic theory of gases states that the gas molecules are very small, relative to the distance between molecules. That the molecules are in constant, random motion and frequently collide with each other and with the walls of the container. Gases expand and contract with changes of temperature and pressure. This theory is summarised in three gas laws namely:

- Boyle's law
- Charles' law
- Combined gas law

Boyle's law

Activity 2.13

Investigating the relationship between volume and pressure of a gas.

Materials: Balloon, 50 ml syringe

Procedure

- 1. Blow some little amount of air into the balloon and tie the balloon.
- 2. Fix the balloon onto a syringe connected to a plunger. Push in the plunger i.e. moving the piston towards the balloon. Write down your observations.
- 3. Now, place a finger over the opening of the syringe and push the piston towards the balloon.



Figure 2.6

4. Write down your observations.

Activity Questions

1. Explain the observations made above.



In 1662, a scientist called Robert Boyle discovered that when volume of a fixed mass of a gas is decreased the pressure of the gas increases and when volume is increased, pressure decreases. He expressed his results into law named after him. Boyle's law states that "the volume of a fixed mass of dry gas at constant temperature is inversely proportional to its pressure." Diagrammatically it can be represented as;



Figure 2.7

This law expressed mathematically gives the following equation;

Volume, V
$$\alpha \frac{1}{pressure}$$
 : or
V = $\frac{k}{P}$ or

PV = constant (k) for any fixed mass of a dry gas at constant temperature.

When pressure changes from P_1 to P_2 and volume changes from V_1 to V_2 , therefore,

The general equation becomes, $P_1V_1 = P_2V_2$

Where: $P_1 = Original pressure$ $V_1 = Original volume$ $P_2 = Final pressure$ $V_2 = Final volume$

Using your mathematical knowledge and the Boyle's law concept, sketch how a graph of pressure against volume would look like. From your diagram, justify why the curve should not touch the axes.

From your sketched graph;

- I What happens to the volume of the gas if:
 - (a) pressure is increased?
 - (b) pressure is decreased?
- II What happens to the pressure of the gas if:
 - (a) volume is increased?
 - (b) volume is decreased?

III The following graph is obtained when one of the data is manipulated. Study the graph carefully then answer the questions that follow.



Figure 2.8

- (a) Identify the variable data manipualted and the action relation.
- (b) Label the axes appropriately assigning each axis its relevant measurement quantity.
- (c) Give the graph suitable title.

Calcualtions involving Boyle's law

Worked example I

The volume of a gas is 375 cm³ at a pressure of 20 atm. What would be the new volume of the gas if the pressure is reduced to 15 atm?

Solution

$$P_{1} = 20 \text{ atm },$$

$$V_{1} = 375 \text{ cm}^{3},$$

$$P_{2} = 15 \text{ atm,}$$

$$V_{2} = ?$$

$$P_{1}V_{1} = P_{2}V_{2}$$

$$V_{2} = \frac{P_{1}V_{1}}{P_{2}} = \frac{20 \times 375}{15}$$

$$V_{2} = 500 \text{ cm}^{3}$$

Worked example 2

-

A given mass of a gas occupies a volume of 200cm³ at a pressure of 5atm.What would be its new pressure if the volume of the gas changes to 800cm³?

$$P_{1} = 5 \text{ atm,}$$

$$V_{1} = 200 \text{ cm}^{3},$$

$$P_{2} = ?$$

$$V_{2} = 800 \text{ cm}^{3}$$

$$P_{1}V_{1} = P_{2}V_{2}$$

$$P_{2} = \frac{P_{1}V_{1}}{V_{2}}$$

$$P_{2} = \frac{5 \times 200}{800} = 1.25 \text{ atm}$$

Remember

The SI-unit for pressure is Pascal (Pa). One pascal is equivalent to a force of one newton exerted on an area of one square metre. That is, 1 Pascal (Pa) = $1N/m^2$. Other units used to express pressure are standard atmosphere (atm).

1 atm is equal to 760 mm of mercury. 1 atm = 101325 Pa or 1.01325×10^6 Nm⁻² The SI unit of volume is cubic metres (m³). 1m³ is equal to 1.0×10^6 cm.

Remember

Boyle's law have important real life application which includes the following:

- (i) Filling of gas cylinders.
- (ii) popping of corns.

Discuss how pressure and volume relationships is utilized in these applications.

Charles's law

Activity: 2.14

Investigating the relationship between volume and temperature of a gas

What happens to the volume of a gas system when the temperature is increased at constant pressure?

Work in groups

Materials: Goggles, hot plate, graduated cylinder, conical flask, balloon.

The following set up can be used to investigate effect of changes in temperature on volume of a gas. In your groups, carry out the investigation.





Figure 2.9

Activity Questions

- 1. Why did the balloon size change when water was heated?
- 2. Account for the results in this experiment.
- 3. How can you make your measurements quantitative? Why could this be important?
- 4. Why is direct heating not recommended in this investigation?
- 5. If you repeated the activity, do you think you would get the same results? If not, why?

In 1782, Jacques Charles investigated the relationship between the volume of a fixed mass of a dry gas and the changes in temperature. He discovered that as temperature increases the volume of gas molecules expanded.

The Facts

From the experiment above, it should be observed that as water heats up, the balloon expands. Therefore, an increase in temperature of a gas causes increase of gas volume. This is summarized by Charles' law which *states that at constant* pressure, the volume of a fixed mass of a gas is directly proportional to its absolute temperature.

Absolute temperature is a temperature measured with respect to absolute zero on Kelvin scale. If the absolute temperature is decreased at constant pressure, the volume consequently decreases. This relationship can be represented diagrammatically as shown below.



Fig 2.10.Charles'Law

Mathematically, Charles' law is expressed as follows:

Volume is directly proportional absolute temperature at constant pressure

 $V \alpha T$ or V = kT where k is a constant

$$\frac{V}{T} = k$$

In general, when the volume changes from V_1 to V_2 and temperature changes from T_1 to T_2 , the equation becomes $\frac{V_1}{T_1} = k$

$$\frac{V_2}{T_2}$$
 = k and therefore,

 $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ for a fixed mass of a gas at constant pressure.

Where

 $T_1 = Original temperature$

 $V_1 = Original volume$

 T_2 = Final temperature

 V_2 = Final volume

When the volumes occupied by a fixed mass of gas at different temperatures are plotted on a graph, the graph obtained is a straight line.



Fig 2.11 Graphical representatation of Charles' law

The graph above implies that the volume of a fixed mass of dry gas increase or decrease by 1/273 of its volume at 0°C for every 1°C rise or fall in temperature provided the pressure remains constant. The graph also shows that the volume of gas would be zero at -273°C. However gases liquefy or solidify before this temperature therefore no gas volume can be measured at this temperature. However, when volumes are measured at different temperatures, and the graph extrapolated backwards, it will be found that it cuts the x-axis, i.e. the volume is theoretically zero when the temperature is -273°C.

The temperature at which the volume of any gas is theoretically zero is called **absolute zero**, and it forms a useful bottom limit to a new scale of temperature – the Absolute Scale – whose unit of temperature is **Kelvin**.

Any temperature on the Celsius scale is converted into absolute temperature simply by adding 273, i.e. $T^{o}C = (273 + t)K$.

-273°C would be zero or 0K 0° C would be, 0 + 273 = 273K 100° C would be, 100 + 273 = 373K

Remember:

The temperature readings or values used in the calculation must be converted to Kelvin scale.

Calculation involving Charle's law

Worked example I

A sample of gas occupies 60cm³ at 35^oC, at what temperature would it occupy 96cm³ if the pressure remains constant.

Solution

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_1 = 60 \text{ cm}^3, V_2 = 96 \text{ cm}^3$$

$$T_1 = 35^{\circ}\text{C} (35 + 273)\text{K} = 308\text{K}$$

$$T_2 = \frac{V_2 T_1}{V_1}$$

$$T_2 = \frac{96 \times 308}{60}$$

 $T_2 = 492.8 \text{K}$

Worked example 2

The volume of fixed mass of a gas was found to be 224cm³ at 288K. What would be the temperature in K for the same gas if its volume increased to 280cm³.

$$V_1 = 224 \text{ cm}^3$$
, $T_1 = 288 \text{ K}$, $V_2 = 280 \text{ cm}^3$
 $T_2 = ?$
 $T_2 = \frac{V_2 \times T_1}{V_1} = \frac{280 \times 288}{224} = 360 \text{ K}$

Discussion corner

In pairs, identify real life applications of Charle's law. Evaluate the usefulness of these applications.

- 1. A gas occupies 500 cm³ at 24°C and 750mmHg pressure. At what temperature will it occupy at 200 cm³ volume of air at the same pressure?
- 2. The volume of a given mass of dry gas at 0°C is 150 cm³. At what temperature will its volume be doubled; assuming the pressure on the gas remains the same?
- 3. A certain gas occupies 800 cm³ at 18°C and 760mmHg pressure. What volume will it occupy at 29°C at the same pressure?

The combined gas law

By combining Boyle's law and Charles' law, a single equation expressing the relationship between temperature, volume and pressure of a fixed mass of any dry gas is obtained. That is:

 $V \alpha - \frac{1}{pressure}$ at constant temperature (Boyle's law)

 $V \alpha T$ at constant pressure (Charles' law)

Combining the two equations we get

$$V \alpha - \frac{T}{pressure}$$
 and so $V = \frac{kT}{pressure}$

Therefore:

 $\frac{PV}{T}$ = constant for any fixed mass of a gas.

Hence



where P_1 and P_2 are the two different pressures, T_1 and T_2 the two different absolute temperatures, and V_1 and V_2 the volumes under the two sets of conditions respectively. This equation is useful in calculating the volume of a fixed mass of any dry gas under any conditions provided we know its volume at any one temperature and pressure.

Worked examples I

A gas occupies 100 cm³ at 15^oC and 750mmHg pressure. What would be its volume at s.t.p?

Solution

Remember standard pressure is equal to 760 mmHg, standard temperature is O°C.

 $P_{1} = 750 \text{ mmHg} \qquad P_{2} = 760 \text{ mmHg}$ $V_{1} = 100 \text{ cm}^{3} \qquad V_{2} = ?$ $T_{1} = 273 + 15 = 288 \text{K} \qquad T_{2} = 273 \text{K}$ $\frac{P_{1}V_{1}}{T_{1}} = \frac{P_{2}V_{2}}{T_{2}}$ $\frac{750 \times 100}{288} = \frac{760 \text{V}_{2}}{273}$ $V_{2} = \frac{750 \times 100 \times 273}{760 \times 288} \text{ cm}^{3}$

= 93.54 cm³

Worked example 2

A gas occupies 78cm³ at 17^oC and 740mmHg pressure, at what temperature will it occupy 100 cm³ at 790mmHg pressure.

 $P_{1} = 740 \text{mmHg} \qquad P_{2} = 790 \text{mmHg}$ $V_{1} = 78 \text{ cm}^{3} \qquad V_{2} = 100 \text{ cm}^{3}$ $T_{1} = 17 + 273 = 290 \text{K} \qquad T_{2} = ?$ $\frac{P_{1}V_{1}}{T_{1}} = \frac{P_{2}V_{2}}{T_{2}}$ $\frac{740 \times 78}{290} = \frac{790 \times 100}{T_{2}}$ $T_{2} = \frac{790 \times 100 \times 290}{740 \times 78} \text{K} = 397 \text{K}$

Worked example 3

273

A gas occupies 200 cm³ at 0°C and 740mmHg pressure. What volume will it occupy at 47°C at the same pressure?

$$V_1 = 200 \text{ cm}^3$$
, $T_1 = 0^{\circ}\text{C} (0 + 273 = 273\text{K})$, $T_2 = 47^{\circ}\text{C} (47 + 273 = 320\text{K})$
 $V_2 = \frac{320 \times 200}{272}$ Thus $V_2 = 234.43 \text{ cm}^3$

Check your progress 2.6

- 1. A certain mass of gas occupied 250 cm³ at 25^oC and 750 mmHg. Calculate its volume at 25°C and a pressure of 760 mmHg in SI units.
- 2. At constant temperature, agas at 540 mmHgoccupies a volume of 300 litres. The gas is made to expand and occupy a volume of 600 litres. What is the new gas pressure?
- 3. A fixed mass of a gas has a volume of 250 cm^3 at a temperature of 27°C and 750mmHg pressure. Calculate the volume the gas would occupy at 42°C and 750mmHg. $(0^{\circ}C = 273K)$

2.11: Graham's Law of diffusion

Have you ever been in a room when someone walks in and after sometime you detect the smell of their perfume without moving closer to that person? What about walking past a house and a sweet smell of delicious food compound your nose? Think about it, how did that smell reach you?

These observations prompted English chemist Thomas Graham to study how fast gases travel through the air. Particles of gases and liquids move from areas of their high concentration to areas of low concentration until they are uniformly spread out. This process is called **diffusion**. Diffusion is defined as the movement of molecules from regions of high concentration to regions of low concentration.

Activity 2.15

Work as a Class

To investigate diffusion of nitrogen (IV) oxide fumes

You are provided with the following apparatus and chemicals to carry out this investigation.

Apparatus and chemicals: clamp stand, two gas jars, concentrated HNO_3 , copper turnings.

- Using the set up shown carry out the activity to demonstrate diffusion of nitrogen (IV) oxide.
- Use 1g of copper turnings and 1cm³ of concentrated nitric acid.
- What precautions do you need to take in this experiment?
- Predict the outcome of this activity if dilute nitric acid was to be used. Justify your statement.
- What other apparatus do you need for this activity not provided in the list of apparatus given above?
- Once the reaction has stopped, invert a second gas jar over the clamped gas jar containing the gas, and observe for 20 minutes what happens.



Figure 2.12

- Record your observations and draw your conclusion.
- How would you dispose the nitrogen dioxide?

Activity Question

- 1. Write chemical equation for the reaction that took place.
- 2. Suggest how this activity can be conducted where there is no fume cupboard.
- 3. Differentiate between diffusion and osmosis.

Diffusion is a daily phenomenon experience. Diffusion is important in a number of real life situations such as: use of perfume by people to avoid the bad body odour during sweating, diffusion of tea bags in tea preparation and gaseous exchange in lungs and plant leaves.

Diffusion of liquids

Activity 2.16

Investigating diffusion in liquids

Work in groups.

Apparatus and chemicals: eye protection, petri-dish, white tile or pieces of white paper, two glass tubes, distilled water, lead nitrate crystal (toxic), potassium iodide crystals.

Procedure

- 1. Place petri dish on a white tile and add to it distilled water.
- 2. Place a glass tube at the opposite ends of the petri dish holding it firmly to avoid disturbance.
- 3. Place white crystals of potassium iodide and lead nitrate separately at the opposite sides of the petri dish using the glass tubes.
- 4. Leave the set up to stand for about 10 minutes and record your observations.

Study Questions

- 1. What did you observe after some time?
- 2. Write an equation for the possible reaction that took place
- 3. Explain the role of diffusion in the reaction that occurred.

Liquids are made up particles with spaces between them. Diffusion occurs between the particles of liquids. In the above experiment, lead nitrate and potassium iodide dissolve to form ions which move from a region of high concentration to a region of low concentration. When lead and iodide ions collided a reaction took place to form yellow substance called lead iodide.

Rate of diffusion of gases

Experiments have established that different gases diffuse at different rates. Chemists refer to a gas travelling through air as diffusion in air, and the speed with which this happens is referred to as its rate.

Activity 2.17

Investigating rates of diffusion of hydrogen chloride and ammonia gases

Work as a class

• You have been provided with the following apparatus and chemicals. Organise yourselves in suitable groups if the class is very big and carry out this investigation.

Apparatus and chemicals: 2 clamp stands, cotton wool, two pair of tongs, goggles, gloves, long glass tube, stoppers, concentrated hydrochloric acid and concentrated aqueous ammonia.

• What safety should be taken during this activity?

Precaution

Wear safety goggles and gloves to protect the eyes and hands from the strong acid and base used in this demonstration. Keep the containers of concentrated hydrochloric acid and aqueous ammonia covered except when using the reagents. Work in a well ventilated area and avoid breathing the concentrated vapours of either reagents.

Activity Questions

- 1. Discuss your observations at the start and the end of the activity.
- 2. What do you conclude from the experiment?
- 3. Suppose the experiment was repeated with the glass tube in a vertical position and the concentrated hydrochloric acid soaked wool placed at the top tube end, estimate where the position of the white ring is likely to be formed? Give reasons for your answers.





Rate of diffusion of
$$NH_3(g) = \frac{Distance}{Time} = \frac{12 \text{ cm}}{5 \text{ sec}} = 2.4 \text{ cm/sec}$$

Rate of diffusion HCl = $\frac{Distance}{Time} = \frac{8 cm}{5 sec} = 1.6 cm/sec$

The rates of diffusion of gases depend on the molecular mass and density of a gas. This relationship was discovered by Graham who compared the densities of different gases and their rates of diffusion. He found out that a less dense gas diffuse through a medium faster than a denser gas. Based on this observation, he formulated a law, Graham's law which states that: the rate of diffusion of a gas is inversely proportional to the square root of its density provided temperature and pressure remains constant. Expressed mathematically as

Rate of diffusion
$$\alpha \frac{1}{\sqrt{Density}}$$

R $\alpha \frac{1}{\sqrt{\rho}}$ Where R is rate and ρ = density
R = $\frac{k}{\sqrt{\rho}}$ Where k is a constant

Comparing the rate of diffusion of two gases, their rates are inversely proportional to the square roots of their densities.

Rate of diffusion of gas A = $\frac{constant}{\sqrt{density of gas A}} = R_A = \frac{k}{\sqrt{P_A}}$

Therefore $R_A \sqrt{P_A} = k$ Rate of diffusion of gas $B = \frac{constant}{\sqrt{density of gas B}} = R_B = \frac{k}{\sqrt{P_B}}$ therefore $R_B \sqrt{P_B} = k$

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Since $R_A \sqrt{P_A} = k$ and $R_B \sqrt{P_B} = k$ For two gases A and B the equation becomes $\frac{R_A}{R_B} = \frac{\sqrt{P_B}}{\sqrt{P_A}}$

Where $R_A =$ rate of diffusion of gas A

$$R_{B}$$
 = rate of diffusion of gas B
 ρ_{A} = density of gas A
 ρ_{B} = density of gas B

Since density is directly proportional to molecular mass (M), the equation becomes $\frac{R_A}{R_B} = \frac{\sqrt{M_B}}{\sqrt{M_A}}$

Considering the time of diffusion, it was discovered that the rate of diffusion is inversely proportional to time.

(Rate) R $\alpha \frac{1}{Time(T)}$

$$R = \frac{k}{T}$$

Therefore RT = k

Compassing two gases with equal volumes

 $R_A T_A = k$ for gas A and $R_B T_B = k$ for gas B

Combining the two equations, $R_A T_A = R_B T_B$ $\frac{R_A}{R_B} = \frac{T_B}{T_A}$

$$\frac{R_A}{R_B} = \frac{T_B}{T_A} = \sqrt{\frac{M_B}{M_A}}$$
$$\frac{T_B}{T_A} = \sqrt{\frac{M_B}{M_A}}$$

Worked example I

Equal volumes of carbon (II) oxide (CO) and carbon (IV) oxide (CO_2) were allowed to diffuse through the same medium, calculate the relative rate of diffusion of CO. (C=12 O=16)

Mass of CO = 12 + 16 = 28g



 \therefore CO (g) diffuses 1.254 times faster than CO₂ (g)

Worked example 2

If it takes 40 seconds for 400 cm³ of oxygen gas to diffuse across a porous plug, how long will it take an equal volume of sulphur (VI) oxide gas to diffuse across the same plug? (O = 16.0, S = 32.0)

Mass of $O_2(g) = (16 \times 2) = 32g$

Mass of $SO_2(g) = 32 + (16 \times 2) = 64g$

$$\frac{T_B}{T_A} = \sqrt{\frac{M_B}{M_A}}$$
$$\frac{TSO_2}{TO_2} = \sqrt{\frac{64}{32}}$$
$$\frac{TSO_2}{40} = \sqrt{2} = 1.414$$

 $TSO_2 = 1.414 \times 40$ $TSO_2 = 56.56$

It takes 56.56 seconds for sulphur (IV) oxide to diffuse.

Check your progress 2.7

1. Hydrogen gas diffuses eight times faster than gas A under same conditions of temperature and pressure. Calculate the relative molecular mass of A if that of hydrogen is 2.

- 2. 140 cm³ of nitrogen gas diffuse through a porous pot in 35 seconds, how long will it take 400 cm³ of carbon (IV) oxide to diffuse through the same pot.
- 3. Briefly explain how Charles' law is applied in hot air ballon operations.
- 4. Filling a hypodermic syringe and spray paint is an important application of Boyle's law. Describe how the processes use Boyle's law principle.
- 5. Two gases X and Y have molar masses 72g and 2g respectively. How much faster does Gas Y diffuse from a porous pot than Gas X at the same temperature and pressure?
- 6. A given volume of nitrogen gas, N(g), reignites 68.3 seconds to diffuse through a tiny hole in a chamber. Under the same conditions, another unknown gas reignites 85.6 seconds for the same volume of diffuse. What is the molecular mass of the gas?
- 7. The relative molecular masses of ammonia and hydrogen chloride gases are 17 and 36.5 respectively. If the two gases are subjected to the same conditions of temperature and pressure, find the rate at which ammonia will diffuse faster than hydrogen chloride.
- 8. A student wants to find out whether a balloon would burst. The balloon can hold a maximum of 1000 cm³ of air. The ballon contain 980 cm³ of air at 10°C. Will the balloon burst if the student gets into a room with a temperature of 25°C? Assume the pressure of the air remains constant.
- 9. To what temperature must two litres of air at 17°C be heated at constant pressure in order to double the volume of the gas?
- 10. Imagine you are traveling on a long journey from Juba to Rumbek. Before you start the journey, your tyre pressure in 3×10^4 Pa and the temperature is 16° C. At the end of the journey, the pressure has increased to 3.2×10^4 Pa. Calculate the temperature of the air in the tyre at the end of the journey. Assume the volume of the tyre remains constant.



Learning Outcomes							
Knowledge and understanding	Skills	Attitudes					
 Understand volumetric analysis and identification of gases Understand molarity, standard solutions, concentration, neutralization, end point, equivalent points, and titration 	 Investigate what is meant by concentration and how it might be determined through volumetric analysis Design investigations to accurately make solutions Investigate the practical implications and applications of volumetric analysis in the formation of compounds and overcoming conditions such as 'hard water'. Carry out practical tests to identify gases 	Appreciate the importance of the gases to life.					

Introduction

You learnt in Secondary 2 about Period Table and how elements are arranged in it. Periodic table is a very useful tool helping chemists to arrange elements into prospective chemical families and even predicting existence of unknown elements yet to be discovered. In the unit, we are going to study about Period 3 element to help us understand how properties across a period varies with the properties of elements within a group.

3.1 Period 3 elements

The modern periodic table is arranged into periods (rows) and groups (columns).

All elements within a period have the same number of energy levels.

All elements within a group have same number of electrons in their outermost energy level, which is why they have similar chemical properties.

Activity 3.1

Study the photographs below.



Fig 3.1 Some elements of a Periodic 3 elements

- 1. What is common among these elements?
- 2. Give any economic importance of these elements?

Research work

Research from books, journals and internet. What are the differences and similarities among the Period 3 elements.

The Facts

The third period contains eight elements: sodium, magnesium, aluminium, silicon, phosphorus, sulphur, chlorine and argon.

Aluminium is heavily used in the making of power transmission cables and major aircraft components due to its light weight. Chlorine is used in water treatment and making of bleaching reagents. Magnesium is a major constituent of chlorophyll in plants. Sulphur and nitrogen have both wide industrial applications as well as a major nutritional requirement in most crops and livestock.

Did you know?

The element in sulphur drugs that reacts with some patients is the same one present in the egg yolk known for allergic reactions in some people.

3.2 **Properties of Period 3 elements**

Electronic Configuration of Period 3 elements

In Secondary 2, you learnt how to distribute electrons in their respective energy levels. The number of energy levels is used to identify the period (row) of elements in the periodic table. Table 3.1 shows elements that have their electrons distributed in the first three energy levels.

Element	Symbol	Atomic Number	Electronic Configuration
Sodium	Na	11	2:8:1
Magnesium	Mg	12	2:8:2
Aluminium	Al	13	2:8:3
Silicon	S	14	2:8:4
Phosphorous	Р	15	2:8:5
Sulphur	S	16	2:8:6
Chlorine	Cl	17	2:8:7
Argon	Ar	18	2:8:8

Table 3.1: Atomic number and electronic configuration of period 3 elements

Same and Different

In pairs, point out or debate any similarities and differences between atomic and electronic configuration.

Work To Do

Individually;

- 1. Construct a simple periodic table and put the period 3 elements in their correct positions.
- 2. From your periodic table, what other information can you deduce from it?

.....

Trend in Physical properties of Period 3 elements

Discussion corner!

- 1. Discuss with your friend the physical appearance of each element shown in fig 3.1 and compare them to the ones provided by your teacher.
- 2. Relate the state of the elements and their electronic configuration.

The Facts

Physical appearance

The elements of period 3 vary in appearance, showing metallic and non metallic properties from the extreme ends of the period respectively. Sodium, magnesium and aluminium show the bright lustre typical of metals when freshly cut. Silicon which is much harder than magnesium and aluminium depicting both metallic and non metallic properties. Phosphorus is a waxy solid with distinctly non-metallic appearance. White phosphorus is yellowish while red phosphorus is red in colour. Chlorine and argon are gases.

Work To Do Individually research using books and from internet reasons why silicon is much harder than the metals yet it is a semi-metal (metalloid). In groups of three discuss the trend in the physical states of elements across period three of the Periodic table.



Period 3 of the periodic table consists of metal and non-metal elements, and that silicon is a semi-metal.

Melting point and Boiling point



Fig 3.2 Bar chart showing comparative melting points and boilings of period 3 elements

Discussion corner!

- 1. Discuss why melting points generally increases from sodium to silicon, and decrease going to argon.
- 2. Discuss why boiling point generally increases from sodium to aluminium, and thereafter decrease moing towards argon.
- 3. Explain the following in terms of structure and bonding.
 - (a) Magnesium has a higher melting point than sodium.
 - (b) Silicon has a high melting point.
 - (c) Sulphur has a lower melting point than aluminium.
 - (d) Chlorine has a higher melting point than argon.

Using the previous knowledge,

- 1. Describe the nature of bonding of the elements across period 3.
- 2. Fromtheknowledgeofthebondingofperiod3elements,predictthetrendofmelting andboilingpointsacrossperiod3.Evaluatetherelationshipbetweenthestructure and type of bonding, and the melting and boiling points.



Sodium, magnesium and aluminium have giant metallic structures which are maintained by strong metallic bonds. The metallic bond becomes stronger as the valence electrons per atom increase and also increased overall nuclear charge pulling strongly the valence electrons. That explains why sodium with one valency electron has a lower boiling and melting points while aluminium with three valency electrons has much higher melting and boiling points.

Silicon atoms are covalently bonded to four other silicon atoms. These covalent bonds are very strong giving the silicon crystals giant atomic structure. A lot of energy is required to break this structure hence its very high melting and boiling points.

Phosphorus, sulphur and chlorine are made up of simple molecular structure. The atoms of these elements are joined together by strong covalent bonds to form discrete molecules which are held together by weakVan der Waal's forces, therefore resulting into their general lower melting points and boiling points. Sulphur has a higher melting point and boiling point than the rest of non metals, in period 3. This is because sulphur exists as S_8 molecules while phosphorus exist as P_4 molecules, chlorine exist as Cl_2 molecules while argon exists as individual atoms. The strength of the van der Waal's forces decrease as the size of the molecules decreases.

$S_8 > P_4 > Cl_{2>}Ar$

Atomic radii

Study the table below which shows the atomic radii of period 3 elements.

Discussion corner!

Table 3.2: Atomic radii of period 3 elements

Element	Na	Mg	Al	Si	Р	S	Cl	Ar
Atomic radius (nm)	0.157	0.136	0.125	0.117	0.110	0.104	0.099	0.094

1. In your groups discuss the trend of atomic radii across period three in relation to the increase in their atomic number. How does the trend in atomic radii influence the reactivity?

The atomic radii generally decrease from left to right across period 3 as seen in the table 3.2.

Think Tank

In pairs, analyse and link the relationship between the net effective nuclear i.e increase in atomic number with the decrease in melting and boiling points of elements across the period.



Fig 3.3: Trend in atomic radii of period 3 elements

Ionization energy

Discussion corner!

In your groups, using books and from the internet determine the values of 1st and 2nd ionization energy of each of the listed elements. Compare the values across the period. Why ionisation energy of argon is the highest in the period despite being in gaseous state.

Ionization energy is the energy or work required to remove an electron from gaseous atom. The ionization energy of the Period 3 elements generally shows an increase moving across the period. However, there are exceptions or interruption in the trend as shown in the table.

Table 3.3 Ionisation energies of period 3 elements

Element	Na	Mg	Al	Si	Р	S	Cl	Ar
Ionization	496	740	584	793	1017	1006	1257	1520
energy kJ/mol								

The few irregularities in the general trend are related to the extra stabilities shown by sub energy levels that are either empty or half-filled. This is the case with aluminium having lower first ionization energy than magnesium.

The first ionisation energy is affected by a number of factors:

- 1. The charge in the nucleus.
- 2. The distance of the outer electrons from the nucleus.
- 3. The amount of screening by inner electrons.
- 4. Whether the electron is alone in a sub energy level (orbital) or in pair.



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3p orbital subshell in Sulfur
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Fig 3.4 Trend in ionisation energy of Period 3 elements

The trend in the ionisation energy is broken by falls between magnesium and alluminium and between phosphorus and sulphur.

Fall at the aluminium and sulphur

It is expected that aluminium with an extra proton than magnesium, should have a higher ionization energy value, though this is not the case. The electron to be lost in aluminium is located in the second sub energy level which is slightly far from the nucleus compared to magnesium whose electron is in the first sub energy level. Aluminium electron in the second sub energy level which should be first removed is partially screened by those electrons in first sub energy level and by those in the inner energy levels. Both of these factors offset the effect of the extra proton in aluminium. As one moves from phosphorus to sulphur, the screening is identical in both phosphorus and sulphur and the electron to be lost are in same sub energy level. The difference is that the sulphur electron to be lost has paired with another. The pairing between the two electrons increase repulsion making it easier to remove an electron in sulphur than it would have been predicted.

Check your progress 3.1

- 1. How does the ionisation energy change across a period?
- 2. Name three factors that affect the size of ionisation energies.

Valency

The number of electrons to be lost or gained when an element reacts determine the valency of the element. Electrons in the outermost energy level of an atom are referred to as **valence electrons**. Valency can be said to be the combining power of an element.

Discussion corner!

1. Discuss how the valency electrons affect properties of period three metal elements.

The number of valency electrons increases from sodium to aluminium metals. The metallic bond becomes stronger as the number of valency electrons in the metals increases, which in turn increases the ionization energy of these metals across the period.

The increasing number of valency electrons across the period explains the trend in the ionization energy across period three and other physical properties of period 3 metal elements.

Metal elements sodium, magnesium and aluminium have few number of electrons in the outmost energy level (few valency electrons) and thus low ionization energy.

The valency electrons in sodium, magnesium and aluminium occupy some subenergy levels leaving others empty. Note that the third energy level is divided into three other sub energy levels.

Find out

- 1. Establish the influence of the valency electrons of period 3 elements and the physical properties of the elements.
- 2. Does the valency of elements impact on their reactivity? Explain your answer.

Electrical conductivity

Discussion corner!

- 1. Using a simple cell investigate which of the period 3 elements would allow electricity to pass through them, and group them as either conductors or non -conductors.
- 2. Silicon is a poor conductor of electricity yet it shows some metallic properties. Explain why.
- 3. Consider the number of electrons occupying the outer energy level, among the elements that conducted electricity. Do you think the number of valence electrons have any role in their conductivity.

Sodium, magnesium and aluminium are good conductors of electricity, the conductivity increasing from sodium to aluminium.

The valency electrons in sodium, magnesium and aluminium metals are free to move throughout the metallic surface (delocalised) and thus responsible for ease of conduction of heat and electricity.

Silicon is a semi-conductor. The valence electrons in silicon are not free to move throughout the solid. But a few of the valence electrons acquire enough energy to break from covalent bonds and move freely accounting for small noticeable electrical conductivity in silicon. Phosphorus, sulphur, chlorine, and argon are non conductors.



Fig 3.5 Trend in electrical conductivity of Period 3 Elements

1. Explain why electrical conductivity decrease across period 3 from sodium to phosphorus.

Element	Na	Mg	Al	Si	Р	S	C1	Ar
Electronic	2:8:1	2:8:2	2:8:3	2:8:4	2:8:5	2:8:6	2:8:7	2:8:8
Valency	1	2	3	4	3	2	1	0
Atomic radius(nm)	0.157	0.136	0.125	0.117	0.110	0.104	0.099	0.094
Ionization energy kJ/mol	496	740	584	793	1017	1006	1257	1520
Melting point °C	98	650	660	1410	44	113	-102	-189
Boiling point °C	883	1110	2467	2680	280	445	-35	-186

Table 3.4: General properties and trend of period 3 elements

Oxides and chlorides of period 3 elements

Activity 3.2

- 1. Your teacher to provide you with the following period 3 chlorides if available in the school laboratory: sodium chloride, magnesium chloride and aluminium chloride. Study their appearance carefully.
- 2. Did you notice any variation in physical appearance?
- 3. Dissolve a spatulaful of each salt in a boiling tube containing 10cm³ of distilled water.
- 4. Test the resulting solution using both blue and red litmus papers. What was your observation?
- 5. Explain how the oxides of period 3 elements can be prepared? Discuss the type of bonding between period three elements with oxygen and with chlorine.


Discussion corner!

- 1. Predict the thermal conductivity of period 3 elements.
- 2. Does the valency of the elements in period 3 have influence on their structure and atomic radii.

The Facts

Elements in period 3, except argon, when ignited and lowered in a gas jar of chlorine would continue to burn to form chloride compounds.

Sodium and magnesium form neutral chloride compounds. The chlorides of aluminium, silicon, phosphorus and sulphur react with water exothermically forming acidic solutions. This explains why these chlorides fume in moist air.

The bond types of period 3 compounds vary across the period. Sodium, magnesium and aluminium have strong ionic bonds that require a lot of energy to break. This explains why they have high melting points and boiling points.

All elements across period 3 except chlorine and argon burn in oxygen to form their oxides. Sodium oxide and magnesium oxide are ionic compounds that dissolves in water with evolution of heat to give an alkaline solution. Both white aluminium oxide powder and silicon (IV) oxide do not dissolve in water.

Silicon (IV) oxide is a giant atomic structure with a high melting point and boiling point due to the large network of strong covalent bonds.

Oxides of phosphorus, sulphur and chlorine exhibit covalent bonds with weak intermolecular forces between the molecules that is why they have lower melting points and boiling points. Sulphur (IV) oxide gas dissolves in water forming sulphuric (IV) acid, phosphorus (V) oxide dissolves readily in water to form a solution of phosphoric (V) acid.

Remember

The change in structure and bond type across each period from ionic oxides and chlorides to simple molecular oxides and chloride is related to changes in electro– negativity across the period. Values are low on the left and high on the right. Thus the bonding in the oxides and chlorides become less ionic and more covalent as we move from atoms of low electronegativity to atoms of high electronegativity across a period.

Did you know...

Anhydrous aluminium chloride is a covalent compound which sublimes at $180^{\circ}C$ to form vapour consisting of dimer molecules, Al_2Cl_6 .

Check your progress 3.3

Study the table below.

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P_4O_{10}	SO ₂
Melting point °K	1548	3125	2345	1883	573	200
Bonding						
Structure						

- 1. Complete the table above using reference textbooks and the Internet.
- 2. Explain the changes in melting points.
- 3. Describe the reactions of the oxides with water.
- 4. Describe the reactions of the chlorides with water.

Research Work

Research from books, journals and internet the boiling points and electrical conductivity of the chlorides and oxides of period three elements. Describe type of bonding and structure of these chloride and oxides.

3.3 Group II and VII elements

Activity 3.3

1. You are provided with the following simple structure of periodic table. Study it carefully.



- 2. Place the group II elements in their correct positions in the above periodic table.
- 3. Place the group VII elements in their correct positions in the above periodic table.
- 4. Discuss with your friend why these elements are put together in the same groups.

Group II Elements

These elements are also known as alkaline earth metals. They include: beryllium, magnesium, calcium, strontium, barium and radium. For our study at this level, only first three elements of the group will be considered.

Discussion corner!

- 1. Based on the electronic configurations and positions in the periodic table, predict whether
 - (a) The elements are metals or non-metals.
 - (b) Calcium is likely to resemble magnesium or potassium in its chemistry?
 - (c) Calcium is likely to have a higher or a lower melting and boiling point as compared to magnesium?
- 2. Predict the trend in atomic and ionic radii of the group II elements.
- 3. Discuss with your friend and predict the trend in the ionisation energy of the elements down the group.

The Facts

Trends in the properties of the elements in a group are influenced by their atomic sizes. The similarities in chemical properties and behaviours of elements are determined by the valence electrons. For instance, it is expected that magnesium and calcium will share a lot of similarity than with elements in the adjacent groups.

Electronic configuration of Group II elements

Group II elements all have two electrons in their outermost energy level. That is, they have two valence electrons. They attain stability by losing the two outermost electrons to form a cation with a charge of +2.

Table 3.5 Electronic configuration of some group II elements and their ions.

Element	Symbol	Electronic configuration	Ion
Beryllium	Be	2:2	Be ²⁺
Magnesium	Mg	2:8:2	Mg ²⁺
Calcium	Ca	2:8:8:2	Ca ²⁺

Trends in physical properties of group II elements

Atomic radius

Atomic radius is the distance between the centre of the nucleus and the outermost energy level of an atom. Of the first three alkaline earth metals, beryllium has the smallest atomic radius followed by magnesium and then calcium.



The atomic radius increases down the group.

Ionic radius

The group II elements have smaller ionic radius than atomic radius. This is because they react by losing outer electrons.

During ion formation the group two elements lose the two electrons in their outer most energy level, making the ion to have more protons than electrons. The resulting ion has effective increased positive nucleus charge that strongly pulls inward the remaining electrons. Hence the smaller ionic sizes compared to the atomic sizes.



Fig 3.8 Ionic radii of the alkaline earth metals

Ionic radius of the group II elements increase down the group.

Discussion corner!

Justify the increases of atomic and ionic radii of group II elements down the group.

Ionization energy

Ionization is the removal of an electron from an atom in gaseous state. Alkaline earth metals ionize by losing the first electron and then the second electron in their outermost energy level.

The amount of energy required to remove the first electron is called first ionization energy while the energy required to remove a second electron is called the second ionization energy.

Table 3.6: 1st and 2nd ionization energy of some group II elements

Element	First ionization energy (E_1)	Second ionization energy E_2
Beryllium	900	1800
Magnesium	740	1450
Calcium	590	1150

Discussion corner!

In groups of three, explain why the ionization energies of the group II elements decrease down the group. Why are the second ionization energies much higher than the first ones?

- 1. Use the electron configurations of both magnesium and calcium to compare their difference in ionisation energies.
- 2. Explain the factors that affect the trend of the atomic size of group II elements.

Chemical properties of Group II Elements

Activity 3.4

Investigate reactions of magnesium and calcium with air and water

1. Reaction of magnesium and calcium with air

You are provided with the following apparatus and chemicals. In your working groups, design plan and carry out activity.

Apparatus and chemicals

- Bunsen burner
- Pair of scissor
- Pair of tongs
- Deflagrating spoon
- Magnesium ribbon

- Distilled water
- Calcium granules
- 10ml measuring cylinder
- Sand paper or emery paper
- Litmus paper

Hints

- Use 6 cm magnesium ribbon. Ensure it is cleaned before using it.
- Do not look directly at the magnesium when burning.

Activity Questions

- 1. Describe the appearance of the magnesium ribbon before cleaning and after cleaning.
- 2. Observe the colour of the burning magnesium.
- 3. Compare the reactions of magnesium and calcium with air.
- 4. From your observations, predict reactivity of beryllium with air.

2. Reaction of magnesium and calcium with water

In your groups, select the apparatus and materials required to demonstrate the reactions of group II elements with water.

- 1. Test the gas collected by introducing a burning splint to the mouth of the boiling tube.
- 2. Compare the rate at which the water is being displaced in the reactions of magnesium and calcium.
- 3. Heat the water to near boiling and observe any change in the rate of gas production with calcium now. Account for these observations made.
- 4. Predict reactivity of the other members of group II elements.

Discussion corner!

- 1. Why are the group II elements preferably first cleaned before using them in reactions?
- 2. Between magnesium and calcium, which one was more reactive?
- 3. Predict the reactivity of beryllium.

The Facts

Magnesium burns readily with an intense white flame to produce a white powder of magnesium oxide.

Magnesium	+	Oxygen>	Magnesium oxide
2Mg(s)	+	$O_2(s)$ \longrightarrow	2MgO(s)

Magnesium oxide dissolves sparingly in water to form an alkaline solution of magnesium hydroxide. The solution turns red litmus paper blue.

Magnesium ox	xide	+	water	>	Magnesium hydroxide
Mg O(s)	+	H ₂ O (1)	>	Mg(OH) ₂ (aq)

Calcium, at first, is reluctant to burn because of the oxide coating, but then bursts into intense white flame to form a white solid of calcium oxide.

Calcium	+	Oxygen —	 Calcium oxide
2Ca(s)	+	O ₂ (g)	 2CaO(s)

The white solid of calcium oxide dissolves sparingly in water to form an alkaline solution of calcium hydroxide. The solution turns red litmus paper blue.

Calcium oxide	+	water —	> calcium hydroxide
CaO(s)	+	H ₂ O(g) —	\rightarrow Ca(OH), (aq)

It might not be very clear to see the trend of reactivity of alkaline earth metals with air due to the oxide coating on the metal surface. However the reactivity increases as you go down the group due to increasingly ease of removing the electrons in the outermost energy level.

Due to their reactive nature, group II elements react with air to form a dull oxide coating on their surfaces. This oxide coating prevents the elements from any further reaction. The coat is removed by polishing the surface of an alkaline earth metal. A polished metal has a shiny metallic lustre.

Reactions of calcium and magnesium with water

Calcium metal remained at the bottom of the beaker, because it is denser than water. A stream of colourless gas displaced the water inside the boiling tube.

The gas collected produced a "pop" sound when a burning splint was introduced at the mouth of the tube, confirming it is hydrogen gas. The resulting calcium hydroxide solution turns red litmus to blue, showing it is an alkaline solution.

Calcium	+	water	Calcium hy	droxide	+	Hydrogen
Ca(s) +	2 H ₂ O)(1)	\rightarrow Ca(OH) ₂ (aq)	+	$H_2(g)$	

Reaction of magnesium with water is slow. When water was heated to boiling point the reaction proceeded much faster, but not enough to displace all the water in the boiling tube. Magnesium metal does however react with steam to give magnesium oxide and hydrogen gas.

Magnesium +	water —	→ Magnesium oxide + Hydrogen
Mg(s) +	H2O(g)	\longrightarrow MgO + H ₂ (s)

A white suspension forms in the beaker as the reaction progresses.

Magnesium react with excess steam to form magnesium hydroxide and hydrogen gas.

The resulting solution is magnesium hydroxide which turns red litmus paper to blue, showing it is alkaline.

Magnesium	+ water (steam excess)	→	Magnesium hydrox	xide + 1	hydrogen
Mg(s) +	2H ₂ O(s)	→	Mg(OH) ₂ (aq)	+	H ₂ (g)

Work to do

The table shows the atomic radii of three group 2 elements

Element	Atomic radius(nm)
Р	0.089
Q	0.198
R	0.176

Predict and explain which element would react vigorously with water.

(a) Write an equation for the reaction of the element.

Activity 3.5

To demonstrate reactions of magnesium and calcium with chlorine

Apparatus and chemicals

- 1. Select the apparatus and chemicals required for this activity.
- 2. Note the precaution to take while carrying out this activity.
- 3. In your groups, discuss and outline the procedure needed and proceed to conduct the activity.

Discussion corner!

- 1. Discuss the observations made in the above activity.
- 2. Compare reactivity of magnesium and calcium with chlorine.



Calcium appears to burn less vigorously in chlorine to form a white solid of calcium chloride.

 $Ca(s) + Cl_2(g) \longrightarrow CaCl_2(s)$

Magnesium burns in chlorine with a bright light to form a white solid of magnesium chloride.

Magnesium + Chlorine — Magnesium chloride

 $Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$

Reactivity of group II elements with chlorine increases as you go down the group. It may appear from the above experiments that magnesium is more reactive than calcium but this is not true. Calcium is the more reactive one only that a coat of calcium chloride forms very fast such that the inner silvery calcium metal cannot be easily reached by the chlorine.

Reaction of magnesium and calcium with dilute acids

Discussion corner!

- 1. Predicthowreactivityofacidwithcalciumandmagnesiummetalswouldcompare to that of reaction of water with calcium and magnesium metals.
- 2. Discuss how the gas generated when metals react with acids can be tested.

Activity 3.6

Investigating reactions of magnesium and calcium with dilute acids

Apparatus and chemicals: Test tubes, test tube rack, wooden splints, 10cm³ measuring cylinder, dilute sulphuric acid, dilute nitric (V) acid, dilute hydrochloric acid.

Procedure

1. Place in one test tube, a strip of 2 cm of cleaned magnesium ribbon and into a second test tube a few granules of calcium metal.

- 2. Transfer 5 cm^3 of dilute hydrochloric acid into each of the test tubes and observe the reactions.
- 3. Cover the mouth of the two test tubes until the gas builds up. Test the gas produced by introducing a burning splint near the mouth of the test tube.
- 4. Repeat the procedures using 5 cm³ of dilute nitric acid and dilute sulphuric acid. Discuss the observations made.

The Facts

Magnesium reacts vigorously with the dilute acids and production of a lot of effervescence. The effervescence is as a result of hydrogen gas evolution.

Magnesium	+ Hydrochloric acid — Magnesium chloride + Hydrogen
Mg(s)	+ 2HCl(aq) \longrightarrow MgCl ₂ (aq) + H ₂ (g)
Magnesium	+ Sulphuric acid — Magnesium sulphate + Hydrogen
Mg(s) +	$H_2SO_4(aq) \longrightarrow MgSO_4(aq) + H_2(g)$
Magnesium	+ Nitric acid — Magnesium nitrate + Hydrogen
Mg(s)	+ $HNO_3(aq) \longrightarrow Mg(NO_3)(aq) + H_2(g)$

Calcium reacts very vigorously with dilute nitric acid and dilute hydrochloric acid to form a compound of the respective salt and hydrogen gas. Effervescence is seen due to production of the hydrogen gas.

Calcium + Hydrochloric acid \longrightarrow Calcium chloride + Hydrogen Ca(s) + 2HCl (aq) \longrightarrow CaCl₂(aq) + H₂(g) Calcium + Nitric acid \longrightarrow Calcium nitrate + Hydrogen Ca(s) + 2HNO₃(aq) \longrightarrow Ca(NO₃)₂ (aq) + H₂ (g)

Calcium metal reaction with dilute sulphuric acid starts and then quickly stops. This is because an insoluble calcium sulphate coating formed on the surface of calcium metal prevents any further reaction with the acid. In writing reaction equations involving dilute acids, they are indicated as aqueous (aq). The concentrated acids are indicated as liquid (l).

Precaution

The reaction of calcium and acids is very explosive. Always use very dilute acids. NEVER attempt any reaction of the metals with concentrated hydrochloric and sulphuric acids in school laboratory without supervision of your teacher. It is explosive and fatal.

Group VII elements

These elements are also called halogens. They include: fluorine, chlorine, bromine, iodine and astatine.

Activity 3.7

- 1. Let your teacher provide you with group VII elements available in the school laboratory or a chart of group VII elements. Can you identify these elements using their colours?
- 2. Discuss the reasons why the more reactive VII elements are used as sterilising and bleaching agents.
- 3. Explain why flouride is used in toothpaste yet its higher quantities in domestic water causes browning of teeth.

Electronic configuration

Group VII elements all have 7 electrons in their outermost energy level. They gain an electron to form stable anions with a charge of -1.

Element	Symbol	Electron configuration
Fluorine	F	2:7
Chlorine	Cl	2:8:7
Bromine	Br	2:8:18:7
Iodine	Ι	2:8:18:18:7

 Table 3.7 Electronic configuration of halogens

Trends in physical properties

Electronegativity

Halogens are highly reactive elements. They have the highest electron affinity as compared to the other elements in the periodic table. This is because they readily gain electrons. But the larger atoms tend to have less attractive affinity for electrons



than their smaller counterpart. Electron affinity decreases down the group from fluorine to iodine, thus the reactivity decrease down the group.

Oxidising power

Because halogens react by gaining an electron, it means they themselves get reduced as they oxidize other elements. They are good oxidising agents. In fact fluorine and chlorine are very powerful oxidizing agents. Because the reactivity decreases down the group, and so the oxidising power decreases down the group. As you move down the group, the atoms become larger due to increasing number of energy levels and in addition to the outer electrons get further away from the nucleus. The outer energy levels also get increasingly shielded by electrons in the other inner energy levels preventing the strong attraction by the positive nucleus. This makes it harder for the larger atoms to easily attract the electrons needed to form an ion, therefore larger atoms are less reactive.

Fluorine is the smallest halogen, and the most reactive of all the non-metal elements. It is rarely found occurring in free state. Fluorine is so dangerous to be use in school, but its properties are predicted by looking at those of the other halogens. Astatine is a solid, you would expect it to be the least reactive halogen, but its properties have not been studied because it is highly radioactive and decays quickly.

Get your Facts Straight

- Most of group VII elements are oxidising agents and not reducing agents. Justify that statement.
- Atomic radius affects the reactivity the halogens but not their electronegativity. Think about.

Atomic radii of halogens

Atomic radii of halogens increases down the group. This is because of successful addition of an extra energy level down the group.



Fig 3.9 Diagramatical representation of atomic radii of halogens

Ionic radii of halogens

Ionic radius of halogens is larger than the corresponding atomic radius. There is general increase in ionic radii moving down the group.

Discussion corner!

- 1. Research using books and from internet the ionic radii of halogens.
- 2. Give explanation why the ionic radii of halogens are greater their atomic radii.

Halogen atoms are very reactive to exist as single atoms. Fluorine and chlorine are diatomic gases (F_2 , Cl_2) at room temperature. Fluorine is a pale yellow gas; chlorine is a pale green gas. Bromine gas is a red-brown liquid (Br_2), while iodine (I_2) is a shiny dark purple solid at a room temperature.

Because they are covalently bonded, they have low solubility in water. Iodine gives a brown colour in water and a pink-violet colour in hexane.

Boiling points and melting points

The melting and boiling points of halogens increase down the group, this is due to the increasing strength of Van der Waals forces as the size and relative mass of the atoms increases. These forces are responsible for trend in the changes of physical state from fluorine (gas) to iodine (solid).

Element	Melting point (°C)	Boiling point (°C)	Colour	Physicalstate
Fluorine	-220	-188	Pale yellow	Gas
Chlorine	-102	-35	Pale green	Gas
Bromine	-7	59	Red-brown	Liquid
Iodine	114	184	Black	Solid

Table 3.8	Some	physical	properties	of group	VII	elements
1 4010 5.0	001110	physical	properties	oj group		ciententis

Reaction of halogens with water

Activity 3.8

To prepare solutions of halogen and investigate some of their properties.

In groups of three,

- 1. Design an experiment to prepare chlorine water and investigate some its properties.
- 2. Prepare bromine water, and iodine solution, and investigate their properties.

Caution! Do not inhale the gases directly. Carry out the experiments in the open air or in a fume chamber.

- (i) Suggested apparatus and chemicals
 - A gas jar of chlorine
 Water
 - Bromine liquid
 - Crystals of iodine solid

Spatula

Cork

Stirring rod

Boiling tube

• Beakers

- Litmus paper (red and blue)
- (ii) Test solubility and acidic properties of the halogens dissolved in water.
- (iii) Did you notice the bleaching properties of chlorine water. What was the evidence of bleaching action. Name the substance responsible for the bleaching action.

The Facts

Chlorine dissolves in water turning blue litmus red forming green-yellow solution. The resulting solution has acidic properties. Both hydrochloric acid (HCL) and chloric (I) acid (HOCL) are formed in the solution. Chloric (I) acid has bleaching properties, it bleaches both red and blue litmus papers. The solution first turns blue paper red then bleaches it (i.e turns white).

Coloured		colour	less	
Dye +	HOCl(aq)	 HCl(aq) +	(dye +O)	
$H_2O(l)$	+ $\operatorname{Cl}_2(s)$	 HCl(ac	l) +	HOCl(aq)

Bromine liquid dissolves in water, to form hydrobromic acid (HBr) and Bromic (I) acid. The resulting mixture is orange-yellow and has both acidic and bleaching properties.

Iodine is almost insoluble in water, the resulting mixture is brown. Fluorine reacts with water to form hydrogen fluoride and oxygen gas.

Fluorine	+	Water -		Hydrogen fluoride+	oxygen
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 $2HF(aq) + O_{2}(g)$ $F_2(g) + H_2O(l)$

Discussion corner!

Chemical properties of Halogens

- 1. Research using books, journals and from the internet some of the reactions of halogens.
- 2. Identify common halogen compounds you are aware of.

Activity 3.9

Group Work

Investigating reaction of chlorine with alkaline solution

- 1. Design the procedure and carry out this experiment (investigation). Your teacher will provide necessary help.
- 2. Suggest the apparatus and chemicals needed for this activity.
- 3. Give some precautions one needs to take during this activity.
- 4. Compare your list of apparatus and chemicals with the one your teacher shall give.

The Facts

Chlorine reacts with cold dilute sodium hydroxide solution to form a yellow solution of sodium hypochlorite and sodium chloride. Sodium hypochlorite has bleaching properties.

Sodium hydroxide + chlorine ----- sodium hypochlorite + sodium chloride + water

 $Cl_2(g) \longrightarrow NaOCl(aq) + NaCl(aq) + H_2O(l)$ 2NaOH(aq) +

Chlorine reacts with hot concentrated sodium hydroxide solution to form sodium chlorate and sodium chloride solutions. Sodium chlorate has bleaching properties

Sodium	т	chlorine	sodium	sodium + water
hydroxide	т	gas	chlorate	chloride + water
6NaOH(aq)	+	$3Cl_2(g)$	→ NaClO ₃ (aq) +	5NaCl(aq) + 3 H ₂ O(l)

Check your progress 3.5

- 1. When red litmus paper is placed in chlorine water, it turns white. Explain the observation.
- 2. Write an equation of how sodium hypochlorite would bleach a dye.

Reaction of halogens with metal iron

Activity 3.10

Investigating reaction of halogens with iron

Apparatus and chemicals

- Dropping funnel
- Round bottomed flask
- Boiling tubes
- Delivering tubes
- Clamp and stand
- Source of chlorine
- Bromine liquid
- Iodine
- Iron wool
- Combustion tube with side arm

Procedure

1. Generate chlorine gas as illustrated in fig 3.10a.









Fig 3.10 (b) Passing a stream of chlorine gas over heated iron

2. Arrange the apparatus as shown in the diagram. Your teacher or laboratory technician will help.

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3. Heat the iron wool strongly.

- 4. Pass a steady stream of chlorine gas over the heated iron.
- 5. Discuss observations made. Predict the reactivity of iron wool with bromine.
- 6. Repeat the procedure by passing a steady stream of bromine gas over heated iron wool as shown in Fig 3.11. Discuss the observations made.



Fig 3.11 Passing stream of bromine vapour over heated iron

- 7. Place crystals of iodine in a boiling tube.
- 8. Position the iron powder a few centimetres away.
- 9. Heat the iron wool strongly after which iodine crystals are to be heated. Note and discuss observations made.



Fig 3.12 Iodine over heated iron

10. Compare the resulting products in terms of oxidation strength of the halogens.

Being responsible and cooperative is fantastic

To successfully carry out experiments individually or in groups, team work and respect for others count. Listen to instructions given and use apparatus and chemicals carefully. They cost a lot of money. If you are not sure of anything, seek help from your teacher or lab technician.

The Facts

Iron wool continues to burn and react with chlorine producing brown fumes of iron (III) chloride. The brown fumes condense on the cooler part of the delivery tube to form red-brown crystals.

Iron +	chlorine		iron(III) chloride
2Fe(s) +	$3\text{Cl}_2(g)$	>	$2\text{FeCl}_{3}(s)$

Hot iron wool reacts with bromine vapour to form red crystals of iron (III) bromide. The reaction is not as vigorous as the one with chlorine and you can predict the reactivity of iron with iodine to be the least reactive.

Iron +	bromine	i:	ron (III) bromide
2Fe(s) +	$3Br_2(g)$		$2\text{FeBr}_{3}(s)$

Iodine crystals sublime to give a purple vapour of iodine, which reacts slowly with the heated iron wool forming iron (II) iodide. Iodine is a weaker oxidizing agent, it oxidises iron to iron (II) ions unlike bromine and chlorine that oxidises iron to iron (III).

Iron	+	iodine —	\rightarrow	Iron (II) iodide
Fe _(s)	+	I ₂ (g)	→	$\operatorname{FeI}_2(s)$

Check your progress 3.6

- 1. Explain why chlorine reacts with iron to form iron(III) salts, but when iodine reacts with iron it forms iron(II) salts.
- 2. Differentiate between the electronegativity and oxidizing power of halogens.
- 3. Describe the trend in melting and boiling points of the group VII elements.

Displacement reactions of halogens

Activity 3.11

To demonstrate the displacing power of the halogens

Apparatus and chemicals

- Source of chlorine
- Boiling tube

- Potassium bromide solution
- Potassium iodide solution

• Distilled water

Procedure

- 1. What precaution do you need to take during the activity.
- 2. Bubble chlorine gas into a solution of potassium bromide in a boiling tube as shown.



Fig 3.13 Chlorine displacing bromine from bromide solution

- 3. Repeat the experiment using potassium iodide in place of potassium bromide.
- 4. Predict displacement reaction of fluorine with the rest of halides solution.

Activity Question

- 1. Describe the oxidising strengths of the halogens.
- 2. Explain the observation in the trend of oxidising strengths og halogens.

The Facts

A halogen will displace the one below it in the group from its halide solution. Fluorine will displace chlorine, bromine and iodine ions from their halide solutions. While bromine displaces iodine from its aqueous solution.

$\operatorname{Cl}_{2(g)}$ + $2\operatorname{Br}_{(aq)}$	\longrightarrow	$2\text{Cl}_{aq} + \text{Br}_{2(aq)}$
$Cl_{2(g)} + 2I_{(aq)}$		2Cl_{aq}^{-} + $I_{2(s)}$
$Br_{2(aq)} + 2I_{(aq)}$	>	$2\mathrm{Br}_{\mathrm{aq}}^{-}$ + I _{2 (s)}

Table 3.9 Displacement reactions of halogens

	Potassium chloride solution KCl ⁻ (aq) colourless	Potassium bromide solution KBr-(aq) colourless	Potassium iodide solution KI ⁻ (aq) colourless
Chlorine water Cl ⁻ (aq) colourless	No observable reaction	Orange solution formed	Brown solution (I_2) formed
Bromine water Br ₂ (aq) orange	No observable reaction	No reaction	Brown solution (I_2) formed
Iodine solution I-2(aq) brown	No observable reaction	No reaction	No reaction

Check your progress 3.7

- 1. Explain the occurences of colour change during displacement reactions of halogens yet the halide solutions are colourless.
- 2. How does electronegativity between chlorine and iodine compare?

3.4 Nitrogen and its compounds

Discussion corner!

- 1. Write the electronic configuration of nitrogen and use it to predict its group and period in the periodic table.
- 2. Describe how nitrogen gas can be obtained in large scale from air.

Composition of the Atmospheric Air

Table 3.10 Air components by percentages

Gas	Percentage by volume
Nitrogen	78 %
Oxygen	21 %
Carbon dioxide	0.0318 %
Argon	0.93 %
Other noble gases	0.002428 %
Water vapour	varies

Remember

Nitrogen is the most abundant gas in the atmosphere yet it does not support most life processes such as respiration and combustion.

Preparation of Nitrogen

Activity 3.12

Laboratory preparation of nitrogen from the air

Apparatus and chemicals

- Aspirator
- Tap water
- Wash bottle
- Combustion tube
- Copper turnings
- Bunsen Burner

- Gas jars
- Trough
- Delivery tube
- Clamp stand
- Glass tubings

Procedure

1. In your groups, arrange the apparatus as shown in Fig 3.14:



Fig 3.14 Preparing nitrogen from atmospheric air

- 2. Heat the copper turnings strongly.
- 3. Force air out of the aspirator by passing a stream of tap water slowly into the aspirator.

Discussion corner!

- 1. Discuss with your friend the changes expected in the combustion tube and the role of potassium hydroxide solution.
- 2. Which other reagent can be used in place of potassium hydroxide?
- 3. Give reason why water should be slowly ran into the aspirator.
- 4. Write the chemical equations for the reactions taking place at the combustion tube and wash bottle.

Activity 3.13

Laboratory preparation of nitrogen from a mixture of sodium nitrite and ammonium chloride

- 1. You are required to prepare nitrogen from a mixture of sodium nitrate and ammonium chloride.
- 2. In groups of three, identify all the apparatus and chemicals required for this experiment. Each group should comprise of at least one female where possible. Mention any precaution you require to take during this activity.



- 3. Outline the procedure you would use to carry out this experiment. Research from relevant text books and internet sources and even consulting your laboratory technician.
- 4. Collect many gas jars of this gas and carry out the following tests.
 - (i) Smell the gas from one of the gas jar by wafting the gas towards your nose. Did you detect any smell of the gas?
 - (ii) Insert a burning splint in one of the gas jar.
 - (iii) Drop pieces of wet red and blue litmus pass into one of the gas jar. Discuss your observations.

The Facts

The mixture should be moderately heated. The effervescence may be too fast if the liquid is strongly heated. The equations for the reactions:

$\operatorname{NaNO}_{2}(\operatorname{aq}) + \operatorname{NH}_{4}\operatorname{Cl}(\operatorname{aq}) \longrightarrow \operatorname{NaCl}(\operatorname{aq}) + \operatorname{NH}_{4}\operatorname{NO}_{2}(\operatorname{aq})$	$NaNO_{2}(aq) +$	$NH_{A}Cl(aq)$	→ NaCl(aq) +	NH_ANO_2 (aq)
---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------	------------------	----------------	--------------	-----------------

Ammonium nitrite then decomposes to produce nitrogen.

Ammonium nitrite — Nitrogen + Water

 NH_4NO_2 (aq) \longrightarrow $N_2(g)+2H_2O(l)$

My Safety and Environmental check

Ammonium nitrite heated in small quantities can be explosive.

Discussion corner!

- 1. What difference would there be between a sample of nitrogen prepared from ammonium nitrite and one got from atmospheric air in the laboratory?
- 2. Nitrogen can be prepared by heating solid ammonium nitrite only, however this is not advisable. Explain why.

Physical properties of nitrogen

Nitrogen gas is

- Odourless
- Colourless
- Insoluble in water

Chemical properties of nitrogen

Combustion

Nitrogen does not burn or support combustion. This is why a glowing or burning splint is put off once inserted in a gas jar of nitrogen.

Activity 3.14

Using one of the jars of nitrogen collected, introduce a burning magnesium ribbon? What do you observe? Give reason for your observation remembering that nitrogen does not support combustion.

The Facts

Because magnesium burns with intense heat, the heat energy produced is capable of breaking the nitrogen triple covalent bond (N=N) of the nitrogen molecules to form single atoms of nitrogen which now is able to react with magnesium.

Magnesium + Nitrogen \longrightarrow Magnesium nitride 3Mg(s)+ N₂(g) \longrightarrow Mg₂N₂(s)

Effect on litmus

Nitrogen is neutral gas and does not change the colour of moist litmus papers.

Compounds of Nitrogen

- 1. In groups of two, list compounds of nitrogen you are aware of.
- 2. Identify common substances where some of these compounds are found in.
- 3. Discuss uses of these compounds you have come across or are aware of.

The Facts

Some of the common compounds of nitrogen include:



- (i) Oxides of nitrogen
- (ii) Ammonia
- (iii) Nitric acids
- (iv) Nitrates

Oxides of Nitrogen

The following are the common oxides of nitrogen:

- (i) Nitrogen (I) oxide, N₂O (dinitrogen monoxide or nitrous oxide)
- (ii) Nitrogen (II) oxide, NO (nitric oxide)
- (iii) Nitrogen (IV) oxide NO₂(nitrogen dioxide)
- (iv) Ammonia

For the purposes of our study in this unit, we shall discuss in details nitrogen (IV) oxide and ammonia only.

Research Work

- 1. In groups of three, with assistance of your teacher, research from books and internet about nitrogen (I) oxide and nitrogen (II) oxide. Use the following guideline provided.
 - (i) Their properties (physical and chemical)
 - (ii) Preparation methods
 - (iii) Their uses and pollution effects.
- 2. Write a report of your findings and make a presentation to the rest of the class.

Ammonia

It is considered probably as the principal compound of nitrogen available.

Activity 3.15

Laboratory preparation of ammonia gas

Apparatus and chemicals

- Round bottomed flask
- Glass tubings
- Mortar and a pestle

- Cardboard cover
- Ammonium chloride (8g)
- Calcium hydroxide (12g)

- Litmus paper
- Several gas jars

- Drying tower
- Calcium oxide

Procedure

- 1. Place the calcium hydroxide and ammonium chloride in a mortar.
- 2. Grind the mixture using a pestle and transfer it into a round bottomed flask.
- 3. Arrange the apparatus as shown in the Fig 3.15



Fig 3.15 Preparing and collecting ammonia gas in the laboratory

4. Heat the mixture. Collect several gas jars of the gas and store well for the next activity.

Activity Question

1. Explain how you can determine the gas jar is full.



Ammonia gas is usually prepared by reacting an alkali with an ammonium salt. For example:

Calcium hydroxide + Ammonium chloride ----> Calcium Chloride + Water + Ammonia

 $Ca(OH)_{2}(aq) + 2NH_{4}Cl(s) \longrightarrow CaCl_{2}(aq) + 2H_{2}O(l) + 2NH_{4}(g)$

Properties of ammonia

Activity 3.16

Investigating some properties of ammonia

Apparatus and chemicals

- Wooden splint
- Distilled water
- Trough
- Conc. hydrochloric acid
- 4 gas jars of ammonia

- Round bottomed flask
- Litmus papers (blue and red) •
- Glass tubing
- Litmus indicator
- Cork

Procedure

- 1. Introduce a burning splint into a gas jar of ammonia. Record your observation. State and explain the observation made.
- 2. Dip the end of a glass rod into a concentrated hydrochloric acid and hold it in a jar of ammonia. Explain observation made.
- 3. Dip wet red and blue litmus papers into a gas jar of ammonia.
- 4. Invert a gas jar full of ammonia in a trough of water. Note the water level in 3 minutes.
- 5. (a) fill a dry round bottomed flask with ammonia gas and connect a glass tubing.
 - (b) Put water in a trough and add 5 drops of litmus solution.
 - (c) Invert the flask into the trough.
 - (d) Close the tube with your finger and remove the whole flask from the trough and invert it.
 - (e) Remove the finger to allow the little solution that rose into the tube to enter into the flask.
 - (f) Close the tube with the finger again and quickly dip it into the solution as shown in Fig 3.16.





Fig 3.16: Fountain experiment

Activity Question

- 1. Explain what happens after sometime. What is demonstrated in the experiment?
- 2. From the activity, indicate some of the physical and chemical properties of ammonia.

The Facts

When glass tubing connected to a round bottomed flask containing ammonia is placed into litmus solution, water that gets into the tube dissolves so much ammonia creating a partial vacuum in the flask. Water is then forced rapidly up the tube and forms a blue fountain. The fountain experiment is a test to show that ammonia gas is very soluble.

Physical properties of ammonia gas

- Has a pungent choking smell
- It is a colourless gas
- It is highly soluble in water and water will rise fast to fill the gas jar full of ammonia gas.

Chemical properties of ammonia gas

- Ammonia gas does not burn in air neither supports combustion.
- Ammonia gas turns moist red litmus paper to blue showing it is alkaline in nature.
- Ammonia reacts with hydrogen chloride gas to form white fumes of ammonium chloride.

Ammonia	+	Hydrogen chloride	 Ammonium Chloride.
$NH_3(g)$	+	HCl(g)	 $NH_4Cl(s)$

Remember

Ammonia is the common known alkaline gas. Do you remember what gives the gas its characteristics basic property.

Reaction of ammonia with air or oxygen

Activity 3.17

To show the reaction of ammonia with oxygen

Apparatus and chemicals

- Open glass tube 10 cm long and 3 cm in diameter.
- Delivery tube, glass wool or cotton wool, wooden splint, cork/rubber bung
- Source of oxygen
- Source of ammonia

Procedure

- 1. Prepare concentrated ammonia solution.
- 2. Pour about 15 cm^3 of concentrated ammonia solution into a boiling tube.
- 3. Warm the ammonia solution gently (or add sodium hydroxide pellets to it).
- 4. Pass oxygen into the wide tube.
- 5. Put a burning splint near the end of the delivery tube carrying ammonia. Does the gas burn? Describe the colour of the flame if the gas burns.

Discussion corner!

- 1. Discuss the role of cotton wool or glass wool.
- 2. Why did ammonia gas burn in this experiment?

The ammonia gas diffuses rapidly. The cotton wool helps to spread the oxygen through the whole tube. Ammonia burns with a yellow–brown flame when in the presence of oxygen.

Ammonia gas can only burn in air enriched with oxygen.

Ammonia	+	Oxygen -		Nitrogen	+	Water
$4\mathrm{NH}_{\mathrm{3(g)}}$	+	30 _{2(g)} —	>	$2N_{_{2(g)}}$ +	6H ₂ O	(1)

Activity 3.18

As a class or in groups;

- Design and carry out catalytic oxidation of ammonia. List the apparatus and chemicals.
- The diagram below can help you with your experiment setup.

Catalytic oxidation of ammonia



A reaction takes place when oxygen bubbles through ammonia solution and a redhot platinum coil lowered into the gas mixture. The red brown fumes turn blue litmus paper red.

Ammonia	+	Oxygen —		Nitric oxide	+	Water
$4\mathrm{NH}_{\mathrm{3(g)}}$	+	50 _{2(g)}		$4\mathrm{NO}_{(\mathrm{g})}$	+	6H ₂ O ₍₁₎
			(124)			



Red brown fumes

If only white fumes form, it is an indication of too much ammonia in the gas above the liquid. Reduce the amount of ammonia by raising the delivery tube so that the oxygen bubbles through less ammonium hydroxide.

Scientific mind

What do you think will happen in the absence of platinum coil?

Reaction of ammonia with copper (II) oxide

Activity 3.19

To show the reaction of ammonia with copper (II) oxide

Apparatus and chemicals

- Delivery tube
- Source of ammonia
- Copper (II) oxide
- Beaker
- U-tube

Procedure

1. Set up the apparatus as shown in Fig 3.18.



Fig 3.18 Reaction of copper (II) oxides and ammonia

- Ice cold water
- Combustion tube
- Source of heat
- Anhydrous copper (II) sulphate

- 2. Heat strongly copper (II) oxide in the combustion tube.
- 3. Pass dry ammonia over the hot metal oxide.
- 4. Test the liquid in the U-tube by using the anhydrous copper (II) sulphate.
- 5. Test the gas in the jar with a burning splint, litmus and lime water. Why are all these used in testing of the gas?

Activity Questions

- 1. What was formed in the cooled U-tube?
- 2. What happens to the black copper oxide? Explain
- 3. What gas was produced during this activity?
- 4. Identify the reducing and oxidising agents in the reaction.

The Facts

When copper (II) oxide is heated strongly and dry ammonia passed over it, the black oxide is reduced to red-brown copper. Ammonia itself gets oxidised to form a colourless gas and a colourless liquid collects in the U-tube. The colourless liquid turns white anhydrous copper (II) sulphate blue confirming it is water.

The tests show that the gas in the jar is nitrogen because it does not relight a glowing splint, it does not produce a 'pop' sound when a burning splint is introduced, it does not burn and has no effect on lime water.

Copper (II) oxide + ammonia ------ Copper + water + nitrogen

 $3CuO(S) + 2NH_3(g) \rightarrow 3Cu(s) + 3H_2O(l) + N_2(g)$

In this reaction copper (II) oxide is the oxidizing agent and ammonia is the reducing agent.

Work to Do

1. Ammonia is very soluble in water and less dense than air, how do these properties influence the preparation and collection of the gas.

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- 2. Describe the reactions that occur between ammonia gas and
 - (a) Chlorine gas.
 - (b) Dilute hydrochloric acid.

Nitric acid

It can be prepared in the laboratory as well as by industrial method called Ostwald process.

Activity 3.20

Laboratory preparation of nitric(v)acid and investigating its properties

Apparatus and chemicals

- Retort flask about 200ml
- Sulphur powder
- Round bottomed flask
- Copper turning
- Concentrated sulphuric acid
- Deflagrating spoon

- Carbon (activated charcoal)
- Two stands and clamps
- Bunsen burner
- Water glass
- Iron(II) sulphate
- Dilute sulphuric acid

• Potassium nitrate (20g)

Do you think there is any precaution involved in this activity? Explain your answer.

Procedure

- 1. Slide powdered potassium nitrate down a small paper funnel into a retort flask. Why is the sliding and not dropping important in this step?
- 2. Arrange the apparatus as shown in Figure 3.19.



Fig 3.19 Laboratoy preparation of nitric acid

- 3. Add concentrated sulphuric acid to cover potassium nitrate.
- 4. Heat the retort flask gently and observe all the changes that occur. Open tap water to cool the round bottomed flask.
- 5. Continue heating for 5-10 minutes until the liquid in the retort flask no longer appear to boil and no more liquid distills over it.
- 6. Remove the flask and use the fuming nitric acid for the following tests. Note the colour and the smell of the acid. Is it easy mobile or viscous liquid, that is, does it run easily like water or slowly like syrup?
- (i) Pour concentrated nitric acid to a depth of about 1cm in a test tube. Add pieces of copper turnings. What happens? What is the colour of any gas produced and of the solution formed?
- (ii) Place a small lump of sulphur powder (about 1g) in a test tube. Add about 5cm³ of concentrated nitric acid. Warm gently for one minute. What do you observe?
- (iii) Place a water glass on a sheet of white paper and place into it 5 or 6 drops of concentrated nitric acid. Heat activated charcoal in a deflagrating spoon over a burner flame. Plunge the red hot carbon into the acid. What do you observe?
- (iv) Dissolve a few crystals of iron (II) sulphate in dilute sulphuric acid. Add a little concentrated nitric acid to the solution and warm. Record the observations made.


- 1. In regard to step 4 of the activity;
 - (i) Did the solid dissolve?
 - (ii) Was there any effervescence? What was the colour of the fumes evolved?
 - (iii) What colour was the distillate which collected in the flask? (Pure nitric acid is colourless. Give reason for the colour of this nitric acid?)
- 2. Describe how the retort mixture should be handled after the experiment.



When concentrated sulphuric acid is added to potassium nitrate then heated, the potassium nitrate gradually dissolves and effervescence occurs.

Nitric acid is formed and it distils because it is more volatile than concentrated sulphuric acid. This is concentrated nitric acid. Its vapours condense to form a yellow liquid.

Potassium nitrate + Sulphuric acid ----> Potassium hydrogen sulphate + Nitric acid

 $KNO_3(s) + H_2SO_4(s) \longrightarrow KHSO_4(aq) + HNO_3(aq)$

Red-brown vapours of nitrogen dioxide are seen in the retort flask as a result of heat decomposing nitric acid.

Nitric acid -	heat	water +	nitro	ogen dioxide	+	oyvgen
	lesst	water	mui	gen dioxide		oxygen
4HNO _a (aq)	neat	 $2H_{O}(1)$	+	$4NO_{a}(g)$	+	$O_{a}(g)$
3 1		2		2(0)		2(0)

The nitrogen dioxide dissolves in nitric acid giving it a yellow colour. The yellow colour can be removed by bubbling air through the acid. Retort apparatus used for preparation of nitric acid is made entirely of glass. Hot nitric acid vapours attack cork or rubber stoppers.

Properties of fuming nitric acid

1. Concentrated nitric acid reacts with copper forming brown fumes of nitrogen dioxide, copper nitrate and water.

 $Cu(s) + 4HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$

2. Concentrated nitric acid reacts with sulphur forming nitrogen dioxide and sulphuric acid.

Sulphur + Nitric acid ----> Sulphuric acid + Nitrogen dioxide + Water

 $S(s) + 6HNO_3(aq) \longrightarrow H_2SO_4(aq) + 6NO_2(g) + 2H_2O(l)$

3. Concentrated nitric acid reacts with charcoal forming brown nitrogen dioxide gas, carbon dioxide and water.

Carbon + Nitric acid ----- Carbon dioxide + Nitrogen dioxide + Water

 $C(s) + 4HNO_3(l) \longrightarrow CO_2(g) + 4NO_2(g) + 2H_2O(l)$

 Nitric acid oxidises green iron (II) salts to brown iron (III) salts and itself reduced to nitric oxide. Nitric oxide is readily oxidised to nitrogen dioxide. Water is formed as a by product.

 $6FeSO_4(aq) + 3H_2SO_4(aq) + 2HNO_3(aq) \longrightarrow 3Fe_2(SO_4)_3(aq) + 2NO(g) + 4H_2O(l)$

 $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

Colourless

Brown

Properties of dilute nitric acid

Activity 3.21

Investigating properties of dilute nitric acid

1. You are provided with the following:

Apparatus and chemical

- Test tubes
- Sodium carbonate
- Copper (II) oxide
- Wooden splint
- Sodium hydroxide
- Magnesium ribbon

• Dilute nitric acid

- Blue and red litmus papers
- Measuring cylinder
- Spatula
- Lime water in a test tube
- Bunsen burner
- Dropper
- 2. In your groups, suggest and plan an investigation on properties of nitric acid using the provided materials.

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- 3. Measurement of quantities of reagents.
 - 2 cm³ of dilute nitric acid when using with blue and red litmus paper
 - 20 cm³ of nitric acid when using with copper (II) oxide.

Activity Question

- 1. Account for the observations made in the activity above.
- 2. Suggest other metal oxides that can be used in place of copper (II) oxide.
- 3. What gas was produced in one of the investigation?

The Facts

Complete the following reactions.

 $NaOH(aq) + HNO_{3}(aq)$

(ii) Dilute nitric acid reacts with metal oxide to form a corresponding metal nitrate and water only. The reaction is called a neutralization reaction.

CuO(s) +HNO₃(aq)

(iii) Dilute nitric acid reacts with carbonates and hydrogen carbonates producing corresponding metal nitrate, carbon dioxide and water.

 $Na_2CO_3(s) + HNO_3(aq) \longrightarrow$

(iv) Magnesium + Nitric acid

 $Mg(s) + HNO_3(aq) \longrightarrow$

Because of its oxidizing properties, nitric acid does not usually give off hydrogen with other metals. The hydrogen produced is immediately oxidised to form water.

Work To Do

In group of two research and;

- (i) Write the chemical equations for the reactions of dilute and concentrated nitric acid with calcium, zinc and copper.
- (ii) State the physical properties of nitric (V) acid.
- (iii) Explain why pure nitric acid does not affect metals and their carbonates.
- (iv) Explain the reaction of concentrated nitric acid with sulphur.

Check your progress 3.8

- 1. Describe how you would produce nitrogen (II) oxide and nitrogen (IV) oxide when provided with concentrated nitric (V) acid, water and copper.
- 2. Nitric acid is prepared in the laboratory by the action of concentrated sulphuric acid and a suitable nitrate.
 - (a) Why does nitric acid distill off and not the sulphuric acid?
 - (b) Pure nitric (V) acid is colourless but the one obtained during distilling is yellow. Explain.
 - (c) How can you obtain a colourless sample of nitric acid?

Nitrogen (IV) oxide (Nitrogen dioxide)

This is a brown gas with irritating pungent smell. The gas is very poisonous.

Safety awareness check

Always carry out all reactions involving the nitrogen (IV) oxide in fume cupboard.

Activity 3.22

Laboratory preparation of nitrogen (IV) oxide

Apparatus and chemicals

Copper turnings

- Eight gas jars and covers
- Concentrated nitric acid
- Seven boiling tubes and corks

- Beaker
- Litmus papers (red and blue)
- Deflagrating spoon
- Bunsen burner

- Magnesium ribbon
- Red phosphorus
- Carbon
- Sulphur
- Test tubes and test tube holders

Procedure

1. Place about 10g of copper turnings (enough for 6 litres of gas) into a flask and arrange the apparatus as shown in Fig 3.20



Fig 3.20 Preparation of nitrogen (IV) oxide

- 2. Add concentrated nitric acid so that the end of the dropping funnel is covered with the acid. What happens? When the reaction becomes very vigorous, do not add more acid until it slows and then only add about 5 cm³ at a time. Collect the gas by downward delivery.
- 3. Note the colour and the smell of the gas.
- 4. Invert a boiling tube full of nitrogen dioxide in a beaker of water.
- 5. Put wet red litmus paper and blue litmus papers into one of the boiling tube containing nitrogen (IV)oxide gas. Record your observations.

- 6. (a) Place a little sulphur on a deflagrating spoon, heat until it just starts to burn and plunge the feebly burning sulphur into a jar of nitrogen (IV) oxide. What happens?
 - (a) Remove the spoon and heat the sulphur until it is burning brightly. Insert it again into the gas jar. What happens?
 - (b) Repeat the test with carbon and red phosphorus.
- 7. (a) Put some copper turnings in a deflagrating spoon. Heat copper until red-hot and insert into a jar with the gas. What happens?
 - (b) Repeat the test using burning magnesium ribbon. What happens?

Discussion corner!

- 1. What happens:
 - (i) when feebly burning sulphur was put into a jar of nitrogen dioxide?
 - (ii) red hot copper turnings and burning magnesium ribbon were introduced into the jar containing the gas?
 - (iii) bright burning sulphur is inserted into the gas jar?
- 2. Write chemical equations for the reactions (observations made)?

The Facts

Concentrated nitric acid reacts immediately with copper turnings to form redbrown fumes of nitrogen IV oxide. These fumes fill the flask and the gas jar. A blue solution of copper (II) nitrate is left in the flask.

 $Cu(s) + 4HNO_3(l) \longrightarrow Cu(NO_3)_2(aq) + 2H_2O(l) + 2NO_2(g)$

Properties of nitrogen dioxide

Physical properties

- It is a red-brown gas
- It has an irritating smell
- It is denser than air
- It is soluble in water

Chemical properties

• Nitrogen dioxide reacts with water to form nitric acid and nitrous acid.

Nitrogen dioxide + Water \longrightarrow Nitric acid + Nitrous acid 2NO₂(g) + H₂O(l) \longrightarrow HNO₃(aq) + HNO₂(aq)

The gas is acidic. The solution formed turns wet blue litmus paper red.

• Burning magnesium continues to burn in nitrogen dioxide forming magnesium oxide and nitrogen.

 $4Mg(s) + 2NO_2(g) \rightarrow 4MgO(s) + N_2(g)$

The heat from burning magnesium decomposes this gas into nitrogen and oxygen. Oxygen supports the burning of magnesium.

Vigorously burning phosphorus and sulphur continue to burn in nitrogen dioxide.

Phosphorous + Nitrogen dioxide — Phosphorous pentoxide + nitrogen

 $8P(s) + 10NO_2(g) \longrightarrow 4P_2O_5(s) + 5N_2(g)$

 $2S(s) + 2NO_2(g) \longrightarrow 2SO_2(g) + N_2(g)$

Burning carbon do not produce enough heat to decompose nitrogen dioxide.

Nitrogen dioxide oxidises red hot copper into black copper (II) oxide and itself reduces to nitrogen.

Copper + Nitrogen dioxide — Copper oxide + Nitrogen

 $4Cu_{(s)} + 2NO_{2(g)} \longrightarrow 4CuO_{(s)} + N_{2(g)}$

Pollution effects of nitrogen compounds on the environment

(a) Oxides of nitrogen

Nitrogen (II) oxide combines with oxygen in the atmosphere to form nitrogen (IV) oxide. Nitrogen (IV) oxide is also found in the atmosphere as a result of industrial processes or automobile exhaust gases. Nitrogen (IV) oxide is toxic and cause respiratory diseases.

Nitrogen (IV) oxide also reacts with water vapour in the air and or rain water to form dilute nitric acid. Rain containing this acid or other acids is called "*acid rain*". Acid rain causes chemical imbalance of aquatic bodies which may adversely aquatic animals and plants. The acid rain lowers the pH of soil and water making it difficult for some organisms to survive. Acid rain also attacks most metallic objects and building surfaces corroding iron sheet roofs, car bodies and painted surfaces.

Discussion corner!

What is formed when "acid rain" containing nitric acid reacts with rust-free iron sheets?

(b) Nitrate fertilisers

Prolonged and excessive use of large quantities of nitrate fertilisers pollute the environment. This is because excess nitrates in the soil are washed down into rivers, lakes and other water bodies. In water bodies, nitrates cause aquatic plants (e.g. planktons and algae) to grow in large quantities. The plankton and algae support higher plants and fish. Dead plants and animal materials accumulate faster than can be decomposed by bacteria and they settle to the bottom of the water bodies. Dead plant matter has a high biological oxygen demand (BOD) and some water bodies give up nearly all their dissolved oxygen in order to allow natural decay (oxidation) of the dead plant material to take place.

It is obvious that any substance which has a high BOD or which results in the formation of something with a high BOD is a potential pollutant in water. Such substances decrease the concentration of dissolved oxygen in water and this leads to death of aquatic animals such as fish.

- Due to large masses of dead plants and animals, the penetration of light in water decreases thereby affecting photosynthesis in aquatic plants.
- If nitrates are consumed in drinking water, they are converted by bacteria in the intestines to more toxic nitrites. After absorption into the blood stream, the nitrites combine with haemoglobin forming *metahaemoglobin*. As a result the oxygen carrying capacity of blood is reduced. Babies suffering from excess intake of nitrates have been known to go "blue" due to lack of oxygen in their blood, a condition referred to as 'blue babies'.

Nitrates pollution effects can be reduced by use organic manure which releases nitrates very slowly giving time for crops to use efficiently the nitrates released.

Check your progress 3.9

1. Study the flow diagram below for the preparation of nitrogen and answer the questions that follow.



State the use of each of the following:

- (i) Aqueous NaOH
- (ii) Copper turnings
- (iii) Write the equation for the reaction in step 3.
- (iv) Name gas X
- (v) Name a major impurity in gas X.
- 2. Awhitesaltproducesared-browngasandacolourlessgasthatre-lightsaglowing splint. The residue is red-brown when hot but yellow when cold.
 - (i) Write the formulae of the ions in the white salt.
 - (ii) Write the chemical equation for the reaction.
 - (iii) Namethetwoproductsformedwhenthered-browngasisdissolvedinwater.
- 3. If 50 percent concentrated nitric acid is dropped into copper turnings, a colourless gas and later a red-brown gas is produced.
 - (i) Name the colourless gas.
 - (ii) Name the red-brown gas.
 - (iii) Write a chemical equation for the reaction which leads to the formation of the red-brown gas.
 - (iv) Why is it not possible to identify the smell of the colourless gas?
- 4. A concentrated acid A, is added to copper turnings and water in a flask. A red-brown gas B, is liberated. In a second experiment, air is removed by filling the flask with nitrogen before adding the acid. A colourless gas C, is produced.



- (i) State and explain what is observed when burning magnesium is lowered into a gas jar full of the colourless gas.
- (ii) State and explain what happens when a glowing splint is inserted in a test tube which had previously heated nitrogen(IV) oxide.
- 5. Ammonia is prepared in the laboratory by reacting an ammonium salt and an alkali.
 - (a) (i) Give an example of an ammonium salt and an alkali that we can use to prepare ammonia.
 - (ii) Name the drying agent used.
 - (b) Explain briefly the following properties of ammonia
 - (i) It is collected by upward delivery
 - (ii) It is not dried by concentrated sulphuric acid
 - (c) A student collected 120 cm³ of ammonia at r.t.p.
 - (i) How many moles did the student collect?
 - (ii) How many grams of the gas were collected? (Molar gas volume at r.t.p =24 dm³ N = 14, H = 1)

3.5 Sulphur and its compounds

Study the photographs below





В







Fig 3.21 Some uses of sulphur

Discuss with your friend how sulphur or its compound is important in the use or production of items shown in the photographs above.

Occurence and extraction of sulphur

Sulphur occurs as free element in the earth's crust. It is found in large deposits in South Susdan at: Juba, Yei and Torit zone.

It can also occur as combined in compounds such as:

- (i) Hydrogen sulphide found in petroleum, coal and natural gas.
- (ii) Metal sulphides e.g. zinc blende(ZnS), iron pyrites(FeS₂), copper pyrites (CuFeS₂), galena (PbSO₄ e.t.c)
- (iii) Metal sulphates e.g. gypsum ($CaSO_4.2H_20$)

Sulphur deposits are extracted by pumping superheated water at about 170°C down the sulphur bed. This help to melt the sulphur and blowing it to the surface with compressed air. The product obtained is about 99.5% pure and it can be used without purification for most commercial purposes.

The method used to extract sulphur was invented by Frasch, hence it is called also Frasch process. It preferred because sulphur has far low melting point (113°C).

A hole about 1 foot diameter is bored down through the clay, sand and limestone to the sulphur beds. This boring is lined with an iron pipe and inside the pipe is sunk a device called the sulphur pump which consists of three concentric tubes terminating in a pipe reservoir of larger diameter. The three pipes have diameters of about 2, 8 and 15cm. The superheated water is forced down the outermost of

the three pipes at high pressure of 10 atmospheres to maintain it in liquid form. The molten sulphur flows into the reservoir at the base of the pump and is forced up to the surface through the second of the three tubes by means of a blast of hot compressed air at a high pressure which is delivered by the narrowest tube.



Fig 3.22 Extraction of sulphur by Frasch process

Allotropes of sulphur

Research work

In groups of two, using books and from internet describe the allotropes of sulphur.

Crystalline allotropes of sulphur

Activity 3.23

To prepare rhombic and monoclinic allotropes of sulphur

Apparatus and chemicals

Sulphur powder

- Beaker
- Test tube and test tube holder
- Carbon disulphide

• Watch glass

Filter paper

(150)

- Tongs
- Metal rod

- Beaker
- Bunsen burner

I. Preparing rhombic or octahedral (α-sulphur)

- 1. Before starting, make sure that all flames are extinguished, as carbon disulphide is very inflammable. Add powdered sulphur to a depth of about 2 cm into a test tube and then cover with about 10 cm³ carbon disulphide. Shake vigorously. Does sulphur dissolve easily?
- 2. Filter the mixture through a dry filter paper held in the fingers and collect the filtrate in a beaker. Carbon disulphide does not pass through wet filter paper. It is better not to use a funnel, as some sulphur crystallizes in the stem and is not easily removed.
- 3. (a) To obtain some crystals quickly, pour a little of the solution in a watch glass and leave it to evaporate in a fume cupboard or near an open window. The crystals are small.
 - (b) To obtain larger crystals, cover the beaker with paper, make a few pin-holes in the paper so that disulphide can only evaporate very slowly, and leave the beaker and solution in a fume cupboard until next lesson.
- 4. Examine the crystals formed, and make a drawing of one of the best.

II. Preparing monoclinic or prismatic or ß -sulphur

- 1. Fold a filter paper into a cone in the usual way. Heat some sulphur powder in a test tube until it just melts, then pour it into the dry filter paper held in tongs.
- 2. Let the sulphur cool. When a crust forms, make two holes in it and pour away any liquid sulphur into water.
- 3. Open the filter paper and look for crystals.

Discussion corner!

- 1. Draw a diagram of one of the crystals observed above.
- 2. Describe the shape of the crystal you have drawn.
- 3. Explain the differences between the two shapes of sulphur obtained.





Rhombic sulphur or alpha sulphur (α -sulphur)

Rhombic sulphur which is also known as alpha sulphur. It is a yellow crystalline solid with an octahedral shape. It crystallizes from a solution of carbon disulphide. Rhombic sulphur is stable at below 96°C. Above this temperature, needle shaped crystals of monoclinic sulphur are slowly formed.

Monoclinic sulphur or Beta sulphur (ß -sulphur)

Monoclinic sulphur also known as beta sulphur (β) is a yellow crystalline solid. It is obtained by allowing molten sulphur to solidify. Forming long prism shaped needles as shown in fig 3.23 (b). If monoclinic sulphur is kept at room temperature for a few days, it gradually changes to rhombic sulphur.



Fig 3.23 (a) Rhombic sulphur

Melting point

(b) Monoclinic sulphur

119°C

Table 5.11 Properties of rhomoic and monoclinic autoropes of suprir				
Characteristics	Rhombic sulphur	Monoclinic sulphur		
Shape of the crystals	Octahedral	Long prism needle like shaped		
Colour of the crystal	Yellow	Yellow		
Stability	Stable below 96ºC	Stable above 96ºC upto 119ºC		
Density	2.07 g/cm ³	1.96g/cm ³		

Table 3.11 Proper	rties of rhon	nbic and mon	oclinic allotro	pes of sulphur

113°C



Transition temperature between the allotropes is 96°C.

Rhombic $\xrightarrow{\text{Above 96°C}}$ monoclinic sulphur Below 96°C

The other allotrope of sulphur is amorphous sulphur. It is non-crystalline and colloidal in appearance. It is finely divided and therefore difficult to filter. It is insoluble in carbon disulphide. In water, it forms a colloidal solution called 'milk of sulphur'.

[•]Research work

In pairs;

- (i) Research using books and from internet how one can prepare amorphous sulphur in the laboratory.
- (ii) Indicate all the apparatus and chemicals needed and design the procedure for its preparation.
- (iii) With the help of your teacher, carry out the preparation of amorphous sulphur.

The chemical equation for the reaction responsible for preparation of amorphous sulphur is;

Sodium + hydrochloric ______ sodium + sulphur (IV) + water + sulphur thiosulphate + acid ______ oxide + water + sulphur

 $Na_2S_2O_3(aq) + 2HCl(aq) \longrightarrow 2NaCl(aq) + SO_2(g) + H_2O(l) + S(s)$

Physical and chemical properties of sulphur

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

Chemical properties of sulphur

(i) Reaction of sulphur with oxygen

Activity 3.24

To show reaction of sulphur with oxygen

Apparatus and chemicals

Deflagrating spoon, source of heat, sulphur powder.

Procedure

- 1. Place a small amount of sulphur in a deflagrating spoon and heat.
- 2. What do you observe?
- 3. Record your observation.

Discussion corner!

- 1. What product was formed when sulphur burnt in the air?
- 2. Discuss all the observations made.
- 3. Predict the reaction of sulphur with hydrogen.

Reaction of sulphur with metals

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.

Iron + sulphur \longrightarrow Iron (II) sulphide + heat

 $Fe(s) + S(s) \longrightarrow FeS(s) + heat$

Other metals such as zinc and copper combine with sulphur to form respective metal sulphides.

Work to Do

Write the equations for the reactions of copper and zinc with sulphur.

Reaction of sulphur with dilute and concentrated acids

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



 $S(s) + 2H_2SO_4(l) \longrightarrow 3SO_2(g) + 2H_2O(g)$

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

 $S(s) + 6HNO_3(l) \longrightarrow H_2SO_4(l) + 6NO_2(g) + 2H_2O(g)$

Uses of sulphur

Sulphur is used in many ways. Some of these include:

- 1. In the manufacture of sulphuric acid (H_2SO_4) which is used in the manufacture of many other compounds. such as detergents, plastics, etc.
- 2. For making gun powder, matches e.t.c.
- 3. For manufacture of fire works.
- 4. In the vulcanization (hardening) of rubber.
- 5. For manufacturing germicides, fungicides.
- 6. In manufacture of medicines.
- 7. In photographic development.
- 8. For making bleaching agents.
- 9. In making artificial hair colours or dyes.

Compounds of Sulphur

(i) Hydrogen sulphide

Activity 3.25

Preparation of hydrogen sulphide gas in the laboratory

Apparatus and chemicals

- 16g of iron sulphide (enough for 4 litres of gas)
- Concentrated hydrochloric acid
- Gas jars and covers
- Boiling tubes and corks
- Beaker



- Litmus solution
- Test tubes and holder
- Concentrated nitric acid, concentrated sulphuric acid
- Potassium permanganate solution
- Potassium dichromate solution
- Iron (II) sulphide
- Chlorine water or jar of chlorine gas
- Sulphur dioxide solution or gas jar of sulphuric dioxide
- Lead acetate, filter paper, bromine water, dilute sulphuric acid
- Solutions of: lead nitrate, copper sulphate, zinc sulphate, iron chloride.

Caution: Hydrogen sulphide is poisonous, do not breathe the gas. Prepare it in a fume cupboard or a well ventilated laboratory.

Procedure

1. Add iron (II) sulphide to a flask and arrange the apparatus as shown in Fig 3.24 below.



Fig 3.24 Preparation of hydrogen sulphide

2. Add sufficient water to cover the sulphide and then add 30cm³ of concentrated hydrochloric acid in small quantities at a time. Collect the gas over warm water. The number of gas jars and boiling tubes to be collected depends on how many the properties of the gas are to be examined.

 $FeS(s) + 2HCl (aq) \longrightarrow FeCl_2 (aq) + H_2S (g)$

- 3. Bubble the hydrogen sulphide through a wash bottle containing water, which removes spray of hydrochloric acid, and collect as many gas jars and test tubes of gas as required.
- 4. Note its colour and smell (do not smell it directly).
- 5. Determine solubility of the gas in water by inverting a test tube with hydrogen sulphide gas into a beaker of distilled water.
- 6. Drop wet blue and red litmus papers in a gas jar of hydrogen sulphide gas.
- 7. Test the combustion of the gas using:
 - (a) Plentiful air supply. Put a light at the end of the delivery tube giving out the gas. Does the gas burn?
 - (b) Limited air supply. Push a burning splint into a jar containing the gas. What happens to the splint and what happens to the gas? A second way of doing the test is to place a test tube in the flame at the end of the delivery tube. What forms on the test tube?
- 8. Test the reducing reactions as follows.
 - (a) Bubble gas through water in a beaker and then leave the solution until next lesson to interact with air. What do you observe? Name the product formed.
 - (b) Bubble the gas through about 3 cm³ concentrated nitric acid in a test tube. What do you observe? Feel the tube in the palm of your hands. What do you feel?
 - (c) Bubble the gas through about 3 cm³ concentrated sulphuric acid.
 - (d) (i) To a test tube add about 5 cm³ dilute potassium (VII) manganate solution and about the same volume of dilute sulphuric acid. Bubble hydrogen sulphide through the mixture, which is called acidified potassium permanganate. What do you observe?
 - (ii) Repeat the test but this time do not add any sulphuric acid. What happens? Why is the use of acid necessary?

- (e) To a test tube add about 5 cm³ dilute potassium dichromate solution and about the same volume of dilute sulphuric acid. Bubble hydrogen sulphide through the mixture, which is called acidified potassium dichromate. What do you observe?
- (f) Repeat the test but this time do not add any sulphuric acid. What happens? Why is the use of acid necessary?
- (g) Bubble hydrogen sulphide through about 10 cm³ of iron (II) chloride solution in a test tube. What do you observe? Heat to boiling to coagulate the precipitate and filter the hot mixture. What colour is the filtrate? (It may be difficult to observe the colour of a small quantity in a test -tube.)
- (h) Bubble hydrogen sulphide through about 10 cm³ of hydrogen peroxide solution in a test tube. What do you observe?
- (i) Bubble hydrogen sulphide through about 10 cm³ of iron (III) sulphate solution in a test tube. What do you observe?
- (j) I. Bubble hydrogen sulphide through about 10 cm³ of chlorine water and bromine water in two test tubes. What do you observe?
 - II. If a jar of chlorine gas is available, invert it over a jar of hydrogen sulphide. What do you observe? Separate the two jars. Blow over the mouth of one and hold the moist stopper of an ammonium hydroxide bottle in the other. What do you see? What gas was formed in the jars?
- (k) Invert a jar of sulphur dioxide over a jar of hydrogen sulphide and press the vase lined surfaces of the two jars together firmly. What do you see? Try to separate the two jars. What happens and what does this show? (The reaction is slow if the gases are dry.)



- (1) Precipitate the metallic sulphides by:
 - (i) Dipping a strip of filter paper in lead acetate (or lead nitrate) solution and hold it in the gas. What happens?

Test for hydrogen sulphide. The gas has a repulsive smell of bad (rotten) eggs, and turns lead acetate or lead nitrate paper a shiny, brownish-black colour.

(ii) Bubble the gas through about 10 cm³ of lead nitrate, copper sulphate and zinc nitrate in three separate tubes. What do you observe?

Discussion corner!

- 1. What is common in all above observations? Explain your answer.
- 2. Write balanced equations for the above reactions.

The Facts

Hydrogen sulphide is generally prepared in the laboratory by the action of a dilute acid on metal sulphide.

Metal sulphide + dilute acid _____ metal salt + hydrogen sulphide

In this activity, dilute hydrochloric acid and iron (II) sulphide have been used.

Iron (II) sulphide + hydrochloric acid ------- Iron(II) chloride + hydrogen sulphide

 $FeS(s) + 2HCl (aq) \longrightarrow FeCl_2(aq) + H_2S(g)$

Hydrogen sulphide gas is bubbled through distilled water to remove any hydrogen chloride gas present and then the gas is collected by downward delivery because hydrogen sulphide is denser than air. The gas is then collected over warm water. It is fairly soluble in water.

Hydrogen sulphide is tested by a strip of filter paper soaked in lead (II) ethanoate solution. The paper turns black. The colour change is caused by precipitation of black lead (II) sulphide.

Lead (II) ethanoate + hydrogen sulphide \longrightarrow lead sulphide + ethanoic acid Pb(C₂H₃O₂)₂(aq) + H₂S(g) \longrightarrow PbS(s) + 2C₂H₄O₂(aq) Lead (II) nitrate + hydrogen sulphide \longrightarrow lead sulphide + nitric acid Pb(NO₃)₂(aq) + H₂S(g) \longrightarrow PbS(s) + HNO₃(aq)

Physical properties of hydrogen sulphide

Hydrogen sulphide gas

- Is colourless
- Has a repulsive rotten egg smell
- Is denser than air
- Is fairly soluble in water.

Chemical properties of hydrogen sulphide

(i) Reducing property of hydrogen sulphide

Hydrogen sulphide is readily oxidised and therefore acts as a very powerful reducing agent. The table below shows what is observed when hydrogen sulphide gas is bubbled through various solutions.

Table 3.12 Reactions of hydrogen sulphide with various reagents

Solution	Observation			
1. Concentrated nitric acid	 A red-brown gas is produced 			
	• A yellow solid is formed			
2. Concentrated sulphuric acid	• A yellow solid is formed.			
3. Acidified potassium	• Solution turns from purple to colourless.			
manganate (VII) solution	• A yellow solid is formed.			
4. Acidified potassium	Solution turns from orange to green			
dichromate (VI) solution	 A yellow solid formed. 			
5. Iron (III) chloride solution	• Solution turns from yellow to pale green.			
	• A yellow solid is formed.			
6. Hydrogen peroxide solution	• A yellow solid is formed.			
7. Iron (III) sulphate solution	• Solution turns from yellow to pale green.			
	• A yellow solid is formed.			
8. Chlorine water	• A yellow solid is formed.			
	• Solution turns from green to colourless.			
9. Bromine water	• Solution turns from orange to colourless.			
	 A yellow solid is formed. 			

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In all the reactions above, some yellow deposits of sulphur are observed.

The equations for the above reactions are as follows

Bromine water + Hydrogen sulphide \longrightarrow Hydrogen bromide + sulphur Br₂(aq) + H₂S(g) \longrightarrow 2HBr(aq) + S(s) Bromine has been reduced to bromide ions.



Chlorine water + hydrogen sulphide \longrightarrow hydrogen chloride + sulphur Cl₂(aq) + H₂S(g) \longrightarrow 2HCl(aq) + S(s)

Chlorine has been reduced to chloride ions.



Hydrogen sulphide reduces iron (III) ions to iron (II) ions.

Iron (III)
chloridehydrogen
sulphideIron (II)
chloridehydrochloric
acid+ sulphur2 FeCl₃(aq) + H₂S(g)
$$\longrightarrow$$
 2FeCl₂(aq) + 2HCl(aq) + S(s)
(pale green)(yellow solid)

Hydrogen sulphide reduces acidified manganate (VII) ions to manganese (II) ions. That is why the colour changes from purple to colourless. In the process, hydrogen sulphide is oxidized to sulphur (yellow solid).

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Hydrogen sulphide reduces hydrogen peroxide (which is colourless) to water which is colourless. This results in formation of sulphur.

Hydrogen peroxide + hydrogen sulphide — water + sulphur

 $\begin{array}{cccc} H_2O_2(aq) & + & H_2S(g) & \longrightarrow & 2H_2O(l) & + & S(s) \\ (colourless) & & (colourless) & (yellow solid) \end{array}$

Hydrog sulphide reduces concentrated nitric acid to nitrogen (IV) oxide gas. This is evident by the red-brown fumes. In the process, hydrogen sulphide is oxidized to sulphur which is a yellow solid.

Nitric acid + hydrogen sulphide _____ nitrogen (IV) oxide + sulphur + water

$$2 \text{ HNO}_{3}(\text{aq}) + \text{H}_{2}\text{S}(\text{g}) \longrightarrow 2\text{NO}_{2}(\text{g}) + \text{S}(\text{s}) + 2\text{H}_{2}\text{O}(1)$$
(red-brown) (yellow solid)

Work To Do

- 1. Write the equations for the following reduction reactions of hydrogen sulphide.
 - (i) Iron (III) sulphate + hydrogen sulphide
 - (ii) Reduction of acidified orange dichromate (VI) ions to green chromium (III) ions.
 - (iii) Reaction between hydrogen sulphide and concentrated sulphuric acid
- 2. Why was dilute sulphuric acid used in the case of potassium manganate (VII) and potassium dichromate solutions?

Hydrogen sulphide being a stronger reducing agent, it reduces sulphur (IV) oxide in solution to form yellow solid of sulphur. Sulphur (IV) oxide in solution forms sulphite ion (SO_3^{-2}) and hydrogen ion (H^+) .

 $2H_2S(g) + SO_3^{2-}(aq) + 2H^+(aq) \longrightarrow 3H_2O(l) + 3S(S)$

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(Yellow solid)

Sulphur (IV) oxide

Activity 3.26

Laboratory preparation of sulphur (IV) oxide

1. You are provided with the following

Apparatus and chemicals

- 12g copper turnings (enough for about 3 litres of gas)
- Concentrated sulphuric acid
- Gas jars and covers

- Round bottomed flask
- Boiling tubes and corks
- Bunsen burner
- 2. Using the set up below as an aid, plan and carry out the activity in your groups.
- 3. Two things are wrong with the following set up. Identify and correct them before proceeding with the experiment.





- 4. Measurement of quantities of reagents use about 30 cm³ concentrated sulphuric acid. It must cover the bottom of the thistle funnel.
- 5. Hints
 - Heat the mixture gently with small flame, and take care that the reaction does not become too vigorous. The reaction is usually slow at first, but remove the flame as soon as the first bubbles of gas are formed. If heating is continued, the reaction may become too violent in a short time. Judge the rate of reaction by watching how fast the gas bubbles through the acid in the wash bottle.

Activity Questions

- 1. Why must the thistle funnel bottom be covered with acid?
- 2. Dilute sulphuric acid is not recommended for use in this activity. Give reasons.
- 3. Suggest another way the gas can be collected and stored.

Research work

In pairs; design, plan and carry out preparation of sulphur (IV) oxide using sodium sulphite or sodium hydrogen sulphite with dilute hydrochloric acid. Arrange as a class to perform this experiment with the help of your teacher or laboratory technician.

The Facts

Sulphur (IV) oxide is prepared in the laboratory by heating copper turnings with concentrated sulphuric acid. Concentrated sulphuric acid is used and not dilute sulphuric acid because dilute sulphuric acid does not react with copper, since copper is lower in the reactivity series than hydrogen. The reaction with concentrated sulphuric acid will not occur without heating. When it is heated, sulphur (IV) oxide is evolved.

 $Cu(s) + 2H_2SO_4(l) \longrightarrow CuSO_4(aq) + 2H_2O(l) + SO_2(g)$

Physical properties of sulphur (IV) oxide

- It is a colourless gas
- It has a pungent choking smell. It is a poisonous gas and can cause respiratory disorders.

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- It is denser than air and that is why it is collected by downward delivery.
- It is highly soluble in water. Therefore the filter funnel is used to prevent "sucking back" when dissolving sulphur (IV) oxide in water.



Fig 3.27 Dissolving sulphur dioxide in water using inverted funnel

Chemical properties of sulphur (IV) oxide

(i) Forms acidic solution with water

Sulphur (IV) oxide actually reacts with water to form a solution of sulphurous acid. Sulphurous acid is a weak acid.

 $SO_2(g)$ + $H_2O(l)$ \longrightarrow $H_2SO_3(aq)$

The sulphurous acid is responsible for the colour change of the blue litmus paper to red. This shows the acid nature of the gas.

(ii) Bleaching action of sulphur dioxide

The coloured flowers placed in a gas jar of sulphur (IV) oxide are bleached. The wet blue and red litmus papers are also bleached but there would be no effect on the dry blue and red litmus papers. For bleaching to take place, there must be presence of water.

Sulphur (IV) oxide first reacts with water to form sulphurous acid.

The sulphurous acid formed then reduces the dye by removing an oxygen atom hence the dye is bleached. Sulphurous acid bleaches by reduction.

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Dye + sulphurous acid \longrightarrow	(dye – oxygen ato	om) + sulphuric acid	
$Dye + H_2SO_3(aq) \longrightarrow$	(dye - O) + H	$I_2SO_4(aq)$	
(coloured)	(colourless)		

The sulphite (SO_3^{2-}) ion readily accepts an oxygen atom from the substance being bleached or reduced (flowers, or wet litmus papers). It is then readily oxidized to sulphate ion (SO_4^{2-}) .

Sulphite ion + 'O' _____ sulphate ion

 $SO_3^{2-}(aq) + O' \longrightarrow SO_4^{2-}(aq)$

When some dilute hydrochloric acid and barium nitrate solution are added to sulphurous acid, white precipitate of barium sulphate proves the presence of sulphate ion.

(iii) Action of sulphur (IV) oxide with nitric (v)acid

Brown fumes of nitrogen (IV) oxide evolves and the liquid becomes warm. When some dilute hydrochloric acid and barium chloride are added to the resulting liquid, white precipitate of barium sulphate proves the presence of sulphuric acid.

 $BaCl_2(aq) + H_2SO_4(aq) \longrightarrow BaSO_4(s) + 2HCl(aq)_1$

The concentrated nitric acid oxidises the sulphur (IV) oxide in presence of water to sulphuric acid and has itself reduced to nitrogen (IV) oxide.

 $SO_2(g)$ + $2HNO_3(aq) \longrightarrow H_2SO_4(aq) + NO_2(g)$

(iv) Action of sulphur (IV) oxide with iron(III) chloride solution

Brown colour of the solution is rapidly converted to pale green. The sulphur (IV) oxide reduce the brown iron (III) to iron (II) and is itself oxidised to sulphuric acid.

 $2\operatorname{FeCl}_{3}(\operatorname{aq}) + 2\operatorname{H}_{2}O(1) + SO_{2}(g) \longrightarrow \operatorname{H}_{2}SO_{4}(\operatorname{aq}) + 2\operatorname{FeCl}_{2}(\operatorname{aq}) + 2\operatorname{HCl}(\operatorname{aq})$

When some dilute hydrochloric acid and barium chloride solution are added to the resulting liquid, white precipitate of barium sulphate forms which proves the presence of sulphate ion.

(v) Reaction of sulphur dioxide with potassium dichromate (VI), $(K_2Cr_2O_7)$

As sulphur dioxide is bubbled through acidified orange potassium dichromate (VI) solution, it turns green. The dichromate (VI), $(Cr_2O_7)^{2-}$ ions are reduced to chromium ions (Cr^{3+}) which are green. The ionic equation for this reaction is as follows.



The complete equation for the reaction is as follows:





- 1. Predict and write the reaction equations for the following:
 - (i) Action of sulphur (IV) oxide with chlorine.
 - (ii) Action of sulphur (IV) oxide with potassium manganate VII.
 - (iii) Reaction of sulphur (IV) oxide with oxygen.
- 2. Describe tests for sulphites and sulpahtes.
- 3. Carry out an experiment to demonstrate the bleaching action of sulphur (IV) oxide on coloured flowers.

Tests for sulphur (IV) oxide

- Sulphur (IV) oxide is a colourless gas which bleaches moist litmus papers.
- Sulphur (IV) oxide decolourises an acidified solution of potassium manganate(VII).
- Sulphur (IV) oxide changes the colour of acidified solution of potassium dichromate (VI) from orange to green.
- Sulphur (IV) oxide changes the colour of a solution of iron (III) chloride from brown to green. It reduces iron (III) chloride (yellow) to iron (II) chloride (green)

Uses of Sulphur (IV) oxide

- 1. It is used for bleaching, as a fumigant and as food preservatives.
- 2. Large quantities of sulphur (IV) oxide are used in the Contact process for the manufacture of sulphuric acid.
- 3. Sulphur (IV) oxide is used in industries in bleaching of sponges and straws.
- 4. Sulphur (IV) oxide is used as disinfectant.
- 5. Liquid sulphur (IV) oxide has been used in purifying petroleum products.

Most chemical industries release sulphur (IV) oxide as a by-product during manufacture of some products.

- (i) Name some of the industries you know including any present in the country that produce sulphur (IV) oxide.
- (ii) What are some of the pollution effects of sulphur (IV) oxide in the environment?
- (iii) Suggest and outline some methods suitable for use in removing sulphur (IV) oxide from waste gases escaping from a factory chimney.

Sulphur (VI) oxide

Activity 3.27

Laboratory preparation of sulphur (VI) oxide and investigating its properties

Caution!

Sulphur (VI) oxide in any form is corrosive to eyes, skin, mucous membranes and respiratory tract. Do not inhale sulphur (IV) oxide. It may cause damage to the respiratory tract and even lung tissue.

- 1. Apparatus and chemicals
- Source of sulphur (IV) oxide.
- Source of oxygen.
- Flask fitted with 3 holed stoppers
- Glass tubes

- Concentrated sulphuric acid
- Flask
- Beaker
- Ice

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• Two stands and clamps

Test tube

Bunsen burner

- Glass rod.
- Combustion tube with two 1-holed stoppers and wide delivery tubes
- Platinised asbestos with a volume of about 1 cm³
- 2. What risk assessment do you need to take in this activity?
- 3. Procedure
 - (i) In your groups or as a class, arrange the apparatus as shown in Fig 3.32. All parts of it must be dry, Why? Place the apparatus in a fume cupboard.
 - (ii) Pass sulphur dioxide from a siphon at the rate of about one bubble a second, and oxygen from a cylinder at two bubbles a second i.e. use excess oxygen.



Fig 3.28 Laboratory preparation of Sulphur (VI) oxide

- 4. Warm the asbestos with an almost luminous flame. The best temperature for the reaction is about 50°C and a non luminous flame is too hot. What happens near the platinum? Continue to pass the gases for 10-15 minutes .
- 5. Remove the flask and examine the crystals in it. Describe their appearance.
- 6. Action on water. Remove a small part of the crystals on a glass rod and drop into water in a test tube. What changes do you observe?





Sulphur (VI) oxide is prepared by passing a mixture of dry sulphur (IV) oxide and dry air, or oxygen, over heated platinised asbestos or vanadium (V) oxide.

The sulphur (VI) oxide is seen as dense white fumes and may solidify in a freezing mixture forming white crystals. Sulphur (VI) oxide combines vigorously with water, producing sulphuric acid. Platinum is used as catalyst.

Physical properties of sulphur (VI) oxide

- It is a white crystalline solid which is hygroscopic.
- It can also occur as a colourless liquid.
- It has a sharp irritating smell.
- It reacts vigorously with water producing sulphuric acid. The reaction is highly exothermic.

Chemical properties of sulphur (VI) oxide

(i) Reaction of sulphur (VI) oxide with water

Sulphur (VI) oxide reacts vigorously with water to form sulphuric acid. The reaction can be very dangerous if not handled with care. It is extremely vigorous and occurs with a hissing sound giving out corrosive vapour i.e. white fumes of sulphuric acid spray (i.e. tiny droplets) as shown in the figure below.



Fig 3.29 Dissolving sulphur (VI) oxide bubbling in water using inverted funnel

Sulphur (VI) oxide + water \longrightarrow sulphuric acid + heat SO_{3 (g)} + H₂O (I) \longrightarrow H₂SO_{4(aq)} + heat Sulphur (VI) oxide produced is directly passed into water via an inverted funnel. Sulphuric acid cannot be prepared directly by inserting the delivery tube into the water because sulphur (VI) oxide is very soluble in water. This may cause water 'suck back' through the delivery tube into the heated combustion tube causing the tube to crack.

(ii) Reaction of sulphur (VI) oxide with basic oxides

Sulphur (VI) oxide easily reacts with basic oxides to form sulphates.

 $CaO_{(s)}$ + $SO_{3(g)}$ \longrightarrow $CaSO_{4(s)}$

Uses of sulphur (VI) oxide

Sulphur (VI) oxide is used in industrial manufacture of sulphuric acid.

Industrial manufacture of sulphur (VI) oxide (Contact Process)

There is no convenient laboratory method of preparing sulphuric acid.

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

Stage 1: Production of sulphur (IV) oxide

Sulphur (IV) oxide is produced by burning sulphur or roasting metal sulphides in the air.

• Sulphurisburnedinafurnaceinpresenceofpurifiedairtoformsulphur(IV) oxide.

Sulphur + Oxygen ———> Sulphur (IV) oxide

 $S(s) + O_2(g) \longrightarrow SO_2(g)$

• Sulphur (IV) oxide produced from heating of metal sulphides e.g.

Zinc sulphide + oxygen ------> zinc oxide + sulphur (IV) oxide

 $2ZnS(S) + 3O_2(g) \longrightarrow 2ZnO(s) + 2SO_2(g)$

Therefore, the raw materials required are sulphur, air and water.

Stage 2: Conversion of sulphur (IV) oxide to sulphur (VI) oxide

Sulphur (IV) oxide is dried in a drying tower and cooled to an optimum temperature of 450°C -500°C and a pressure of about 2-3 atmospheres.

More air is continued pass to through the reactor packed with vanadium (V) oxide (V_2O_5) catalyst. The reaction is exothermic and no external heating is required. Sulphur (IV) oxide is converted to sulphur (VI) oxide.

Sulphur (IV) oxide + oxygen Sulphur (VI) oxide + heat

 $2SO_2(g) + O_2(g) \implies 2SO_3(g)$

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

Any sulphur (IV) oxide, (SO_2) , not converted to sulphur (VI) oxide, SO_3 , might be released to the atmosphere. This causes pollution of the atmosphere. Hence all measures must be taken to make sure that no sulphur (IV) oxide (SO_2) or very little if any gas goes into the atmosphere. This is done by reacting the unreacted sulphur (IV) oxide, SO_2 , being with calcium hydroxide in the chimneys forming salt and water. This process is called **scrubbing** of the gas.

Calcium hydroxide + Sulphur (IV) oxide \longrightarrow Calcium sulphite + Water Ca(OH)₂(s) + SO₂(g) \longrightarrow CaSO₃(aq) + H₂O(l)



Fig 3.30 Contact process

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 (VI) oxide to sulphuric acid

Finally the sulphur (VI) oxide is absorbed in concentrated sulphuric acid. An oily liquid called oleum is formed.



Fig 3.31 Flow chart for contact process

Optimum conditions for contact process are

- Catalyst, vanadium (V) oxide.
- Temperature of 450 °C -500 °C
- Pressure of about 2-3 atmospheres.

Activity 3.28

To investigate some of the properties of concentrated sulphuric acid Apparatus and chemicals

I. Oxidizing properties

- Concentrated sulphuric acid
- Beaker
- Gummed label
- Copper
- Zinc
- Aluminium or iron,
- Filter paper
- II. Dehydrating properties
 - Test tubes and holders
 - Beaker
 - Copper sulphate crystals
 - Sugar
 - Filter paper
 - Cloth

- Sulphur
- Acidified potassium manganate (VII) solution
- Acidified potassium dichromate (VI) solution
- Wood charcoal
- lime water
- Splint
- Glass tube or rod
- Oxalic acid
- Formic acid
- Bunsen burner
- **Caution!** Concentrated sulphuric acid is dangerous i.e. highly corrosive. Never boil the acid and never use more than the stated quantities. In case of spill over on the skin, immediately wash with plenty of water. Then rinse with dilute alkali.

Procedure

Observing physical properties of the acid

- 1. Note the colour and the smell, if any, of the acid. Lift a bottle of the acid; does it appear to be more or less dense than water? Shake a bottle of the acid gently so that the liquid moves from side to side; is the acid easily mobile or viscous?
- (a) Add about 30 cm³ of water to a beaker and then carefully pour 5 cm³ of concentrated acid into the water. What do you observe? Feel the outside of the beaker. What do you notice?


(b) Pour concentrated acid into a beaker to a depth of about 3 cm, mark the level of the acid with a gummed label. Leave for a few days. What change do you observe, and what does this show?

Oxidizing reactions

- 1. Pour about 3 cm³ of concentrated acid into a test tube held in a test tube holder, preferably over a sink or trough. Add a few small pieces of the metal being tested *(be prepared for a sudden and vigorous reaction)*. What happens? If necessary, warm the acid but do not boil. Repeat the test with each metal provided.
- 2. Sulphur. Slide a small lump of sulphur into a test tube containing about 5 cm³ of the acid. Heat the mixture gently. What do you observe? Test any gas formed with a strip of filter paper dipped in potassium (VII) manganate solution and another dipped in acidified potassium dichromate solution. What gas was formed?
- (a) Add about 1g of wood charcoal to a test tube and cover the charcoal with about 5 cm³ of concentrated sulphuric acid. Warm the mixture gently with the tip of a small flame, clamp the tube upright and collect any gas formed.
 - (b) Watch the bubbles of the gas as they pass up the water into the gas jar. Do they seem to dissolve partly?
 - (c) When there is enough gas in the gas jar, remove the flame. Test the gas with lime water. What is this the gas? (Why cannot the test be done by holding a drop of lime water at the end of a glass rod in the gas at the mouth of the reaction tube?)
- (a) Pour about 2 cm³ concentrated acid into a dry test tube. Slide into it a crystal of copper sulphate, large enough so that partly is in the acid and partly outside it. Examine the crystal at the end of the lesson and after a few days. What change do you observe?
 - (b) Place a crystal copper sulphate in a test tube and cover it with acid. Warm gently. What changes in the colour and appearance of the crystal do you observe?
- 5. (a) Place about 1g of sugar in each of two test tubes. Cover the sugar with acid. Leave one test tube and warm the other gently. What action has cold and hot acid has on sugar?

- (b) A second way of doing the test is to add about 10g sugar to a beaker and just cover it with water. Stand the beaker in a trough or sink. Carefully pour about 20 cm³ of concentrated acid into the beaker with water. What happens? Can you explain your observations?
- 6. (a) Use a glass tube or rod to 'write' or make marks on some filter paper and on a piece of dry cloth. What do you observe?
 - (b) Repeat the test with a piece of damp cloth. What happens? Can you explain?
 - (c) Dip the end of a wooden splint in some concentrated sulphuric acid. What happens?
- 7. Oxalic and formic acids.
 - (a) Place about 1g oxalic acid crystals in a boiling tube, cover with 5 cm³ of the acid, and warm until a gas is given off steadily. Put a burning splint near the mouth of the tube. Does the gas burn? What is this gas?
 - (b) Repeat the test with about 3 cm³ of methanoic acid. Does reaction occur in the cold?
- (a) Carefully add 2 cm³ of concentrated sulphuric (VI) acid to potassium nitrate crystals in a test tube. Warm the mixture gently and test the gas produced with wet litmus paper.
 - (b) Repeat using sodium chloride crystals. Discuss the type of salt formed.

Properties of concentrated sulphuric acid

Physical properties

- Concentrated sulphuric acid is a colourless liquid.
- It is a viscous, dense oily liquid whose density is 1.83g/cm³.
- It is a non volatile acid.
- It has a high boiling point of 338°C.

Chemical properties

(i) Concentrated sulphuric acid affinity for water

When concentrated acid is mixed with water, it produces a lot of heat. That is why when you touch the sides of the test tubes, it feels hot.

When diluting concentrated sulphuric acid never add water to the acid. The acid should be added to a large volume of water carefully and slowly down the sides of the container.

(ii) Concentrated sulphuric as a dehydrating agent

Concentrated sulphuric acid removes water molecules or elements that make water from other substances. Its thus a dehydrating agent.

(iii) Reaction of concentrated sulphuric acid and hydrated copper(II)sulphate 5 water ($CuSO_4.5H_2O$) It removes the water of crystallization turning the blue hydrated copper (II) sulphate to white anhydrous copper (II) sulphate powder.

Hydrated copper (II) sulphate $\xrightarrow{\text{Conc. H}_2\text{SO}_4}$ (II) sulphate + water

 $CuSO_4. 5H_2O(s) \xrightarrow{Conc. H_2SO_4} CuSO_4(s) + 5 H_2O(l)$ blue white

Because of its great affinity for water the acid can absorb water from the atmosphere, and increase in volume and becoming diluted. Because of that, concentrated sulphuric acid is said to be hygroscopic hence used for drying of gases. However the concentrated sulphuric acid is not used to dry gases that react with it such as alkaline ammonia gas.

(iv) Concentrated sulphuric acid also dehydrates sucrose. The mixture turns brown then black and the beaker becomes very hot. A black spongy substance is formed. This black solid is **carbon**. This black spongy carbon swells and fills the container. Steam is also produced.

Sucrose $\xrightarrow{\text{Conc. H}_2\text{SO}_4}$ carbon + water $C_{12}H_{22}O_{11}(s) \xrightarrow{\text{Conc. H}_2\text{SO}_4} 12C(s) + 11H_2O(g)$

- (v) Concentrated sulphuric acid dehydrates sucrose by removing hydrogen and oxygen to form water leaving behind a black spongy mass of carbon.
- (vi) Ethanol is dehydrated by concentrated sulphuric acid at about 170°C to produce a colourless gas ethene. That is why production of bubbles of colourless gas is observed.

Ethanol $Conc. H_2SO_4$ ethene + water

 $CH_{3}CH_{2}OH(aq) \xrightarrow{Conc. H_{2}SO_{4}} CH_{2} = CH_{2}(g) + H_{2}O(l)$

(vii) Concentrated sulphuric acid reacts with oxalic acid giving effervescence, The gas produced burns with a blue flame, showing carbon (II) oxide gas is formed. When the gas produced is bubbled in lime water, a white precipitate forms showing carbon (IV) oxide gas is also formed.

 $H_2C_2O_4(s)$ Conc. H_2SO_4 CO(g) + CO₂(g) + $H_2O(g)$

Oxalic acid

Dehydrating properties of concentrated sulphuric acid explains why concentrated sulphuric acid attack organic substances such as clothes, wood, paper.

Concentrated sulphuric acid as an oxidizing agent

Concentrated sulphuric acid oxidises all metals except those that are very low in the reactivity series such as gold and platinum.

Copper turnings (red-brown solid) is oxidized by concentrated sulphuric acid to form copper (II) sulphate which is a blue solution.

 $Cu(s) + 2 H_2 SO_4(l) \longrightarrow CuSO_4(s) + SO_2(g) + 2 H_2O(l)$ (brown) (blue)

Zinc and aluminium react in the same way as copper with concentrated sulphuric acid producing respective metal sulphates, sulphur (IV) oxide and water.

Concentrated sulphuric acid oxidises the potassium dichromate (VI) paper or solution turning it from orange to green because of the presence of sulphur (IV) oxide which is produced when sulphuric acid is reduced. When the filter paper soaked in solution of potassium manganate(VII) is used, it is decolourised.

Concentrated sulphuric acid also oxidizes non metals like sulphur and carbon .





$$C(s) + 2 H_2 SO_4(l) \longrightarrow 2SO_2(g) + 2 H_2 O(l) + CO_2(g)$$

Oxidation

Displacement reactions of concentrated sulphuric acid

Concentrated sulphuric acid has a higher boiling point than concentrated solutions of nitric acid and hydrochloric acid. It is therefore a non-volatile acid. Hydrochloric and nitric acid are more volatile than sulphuric acid. They are displaced from the reaction mixture as vapour more easily. Concentrated sulphuric acid therefore displaces more volatile acids such as nitric and hydrochloric acids from their salts. The vapour turns blue litmus to red. Usually an acid salt is formed.

Potassium nitrate + Conc. sulphuric acid -> potassium hydrogen sulphate + nitric acid

 $\text{KNO}_3(s) + \text{H}_2\text{SO}_4(l) \longrightarrow \text{KHSO}_4(aq) + \text{HNO}_3(aq)$

Sodium chloride + Conc. sulphuric acid -> sodium hydrogen sulphate + hydrogen chloride

 $NaCl(s) + H_2SO_4(l) \longrightarrow NaHSO_4(aq) + HCl(g)$

The flask cannot stand the temperature at which a normal salt would be formed. The high temperature would melt the glass. The type of salt formed is thus an acid salt.

Properties of dilute sulphuric acid

Activity 3.29

Investigating the properties of dilute sulphuric acid

Follow the procedures indicated in table 3.12 and write correct observations made and draw appropriate conclusions. Write balanced chemical equations for each reaction.

Observation and conclusion of reactions of dilute sulphuric acid.



Table 3.12 Tests for properties of dilute sulphuric acid				
Procedure	Observation	Conclusion		
 Take three test tubes. In each of the test tubes, place small amount of magnesium ribbon, zinc granules and copper turnings respectively. Add about 2-3 cm³ of dilute sulphuric acid. Test the gas evolved with a burning splint. Did all the metals used react with the dilute sulphuric acid? Take another three test tubes. In 				
each of the test tubes, place small amounts of potassium carbonate, sodium hydrogen carbonate and calcium carbonate respectively. Add to each test tube 5 cm ³ of dilute sulphuric acid. Test for any gas produced with a burning splint and aqueous calcium hydroxide. Identify soluble and insoluble sulphates.				
• Predict from which compounds they are formed (consider only carbonates and hydrogen carbonates reacting with dilute sulphuric acid).				
 Place small amount of copper (II) oxide powder in a test tube. Add about 10cm³ of dilute sulphuric acid and warm. Repeat with copper (II) hydroxide. 				

(180)

Physical properties of dilute sulphuric acid

- It has a sour taste.
- It turns blue litmus red.
- It is a colourless solution.

Chemical properties of dilute sulphuric acid

(i) Reaction of dilute sulphuric acid with metals

Dilute sulphuric acid will react with most metals to produce hydrogen gas and a salt. As you go down the reactivity series the reaction is less vigorous. Metals like copper, silver and gold do not react with dilute sulphuric acid.

Sulphuric acid + magnesium ----- magnesium sulphate + hydrogen gas

 $H_2SO_4(aq) + Mg(s) \longrightarrow MgSO_4(aq) + H_2(g)$

 $H_2SO_4(aq) + Zn(s) \longrightarrow ZnSO_4(aq) + H_2(g)$

(ii) Reaction of dilute sulphuric acid with carbonates and hydrogen carbonates

Dilute sulphuric acid reacts with metal carbonates and hydrogen carbonates to form a salt, carbon (IV) oxide and water. The general reaction equation is:

The gas produced extinguishes a burning splint and forms a white precipitate with aqueous calcium hydroxide. This is the test for carbon (IV) oxide gas.

Potassium carbonate and sodium hydrogen carbonate react with dilute sulphuric acids to produce soluble salts, carbon (IV) oxide and water.

Potassium + sulphuric
$$\longrightarrow$$
 Potassium + carbon (IV)
sulphate + $oxide$ + water
 $K_2CO_3(s) + H_2SO_4(aq) \longrightarrow K_2SO_4(aq) + CO_2(g) + H_2O(l)$
Sodium hydrogen + sulphuric \longrightarrow Sodium + carbon (IV)
carbonate + acid \longrightarrow Sulphate + $oxide$ + water
 $2NaHCO_3(s) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + 2CO_2(g) + 2H_2O(l)$

When dilute sulphuric acid reacts with calcium carbonate, the reaction starts and soon stops. This is evident by the evolution of carbon (IV) oxide for some time. The calcium sulphate produced is a slightly soluble salt which forms an impervious coating on the surface of the unreacted calcium carbonate. This prevents any further reaction from taking place. Dilute sulphuric acid therefore reacts with both calcium carbonate and hydrogen carbonates to form a slightly soluble salt, water and carbon (IV) oxide.

Calcium + sulphuric \rightarrow calcium + carbon (IV) + water CaCO₃(s) + H₂SO₄(aq) \rightarrow CaSO₄(s) + CO₂(g) + H₂O(l)

(iii) Reaction of dilute sulphuric acid with oxides and hydroxides

Basic oxides and hydroxides react with dilute sulphuric acid to form neutral solutions of salt and water. The reactions are known as neutralization reactions. The general equation for the reaction is:

Acid + metal oxide — a salt + water

Acid + metal hydroxide — a salt + water

When a warm dilute sulphuric acid is reacted with copper (II) oxide powder, the solid dissolves and a blue solution of copper (II) sulphate is formed. Dilute sulphuric acid also neutralizes sodium hydroxide to form salt and water only.

 $CuO(s) + H_2SO_4(aq) \longrightarrow CuSO_4(aq) + H_2O(l)$

2NaOH (aq) + $H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O(l)$

Same and different

In pairs, discuss the similarities and differences between dilute sulphuric acid and concentrate sulphuric acid.

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Uses of sulphuric acid

Sulphuric acid is used in many ways.

- 1. To manufacture fertilisers like ammonium sulphate.
- 2. In production of synthetic fibres.
- 3. In petroleum refining.
- 4. In car batteries (lead acid accumulators).

- 5. In cleaning of metals.
- 6. To make soaps and detergents.
- 7. To make dyes, drugs, paints, explosives and many other compounds.

Radio Talk Show

- (i) You and your group members, have been invited to make presentation on economic importance of sulphur and its compound. Prepare a 30 minutes to your listeners,
- (ii) It is said that "The tonnes of sulphuric acid consumed by a country indicates the level of its industrialization" support or dispute against this statement.

Testing for sulphates and sulphites

Activity 3.30

Apparatus and chemicals

Test tubes

• Dilute sulphuric acid

- Copper (II) sulphate solution
- Iron (II)sulphate solution
- Dilute nitric acid or dilute hydrochloric acid
- Barium chloride or barium nitrate solution
- Copper(II) sulphite solution
- Iron (II) sulphite solution

Procedure

- 1. Add spatulaful of the sulphate and sulphite salt each to a separate test tube, then add 5 cm³ of distilled water. Shake to dissolve to form a solution.
- 2. (a) To three drops of the sulphate solution, add six drops of dilute hydrochloric acid or dilute nitric acid and then barium chloride solution or barium nitrate solution. What do you observe? What can you conclude from the above observations?
 - (b) To three drops of the sulphite solution, add six drops of dilute hydrochloric acid or nitric acid, then three drops of barium chloride solution or barium nitrate solution. What do you observe? What can you conclude from the above observations?

The Facts

Test	Sulphites	Sulphates
Action of barium nitrate or barium chloride solution	A white precipitate is formed when barium chloride or barium nitrate is added. No precipitate when added to an acidified sulphite solution.	A white precipitate is formed when barium chloride or barium nitrate is added to an acidified sulphate solution.
$Ba^{2+}(aq) + SO_3^{2-}(aq) -$	\rightarrow BaSO ₃ (s)	$\operatorname{Ba}^{2+}(\operatorname{aq})+\operatorname{SO}_4^{2-}(\operatorname{aq})\longrightarrow \operatorname{Ba}^{2-}(\operatorname{aq})$
Note: the precipitate acid.	dissolves in excess	Note: the precipitate is insoluble in excess acid.

Table 3.13 Tests identification for sulphites and sulphate

Pollution of the environment by compounds of sulphur

The presence of hydrogen sulphide, sulphur (IV)oxide and sulphur (VI) oxide in the air cause serious air pollution.

Most fossil fuels contain sulphur as an impurity. When the fuels such as petrol, diesel and coal are burnt, sulphur is oxidized to sulphur (IV)oxide and sulphur(VI) oxide. Power stations and industries especially those processing sulphide ores are major contributors of sulphur (IV) oxide (SO₂) and sulphur (VI)oxide (SO₃) into the atmosphere. When sulphur (IV) oxide and sulphur (VI) oxide are released into the atmosphere, they dissolve in rain water to form acidic solutions, known **acid rain**.

 $SO_2(g) + H_2O(l) \longrightarrow H_2SO_3(aq)$

Sulphurous acid + oxygen — sulphuric acid

 $2 H_2 SO_3(aq) + O_2(g) \longrightarrow 2 H_2 SO_4(aq)$

Acid rain has a number of devastating environmental degradation effects.

• On human health

The pollutants that cause acid rain e.g. sulphur (IV) oxide and sulphur (VI) oxide are injurious to human health. These gases can be transported long distance by wind. When inhaled into people's lungs, the effect is increased illness and can even result in death from lung disorders such as asthma and bronchitis.

• On useful materials

Acid rain contributes to the corrosion of metals and deterioration of paint and stone. These effects seriously reduce the value of building, bridges, statues, cultural objects and cars. This can be observed in towns that are near sulphuric acid factories, due to sulphur (IV) oxide released to the atmosphere.

On coating vehicles

Acid rain damages coating in vehicles so that their surfaces appear as irregularly shaped and permanently etched. It occurs after evaporation of moisture droplet. Usually the damage is permanent; once it has occurred, the only solution is to repaint the vehicle.

Aluminium compounds in the soil

The action of acid rain on insoluble aluminium compounds in the soil makes them soluble. Insoluble aluminium compounds are fairly harmless to plants and animals, but with increased acidity, the compounds become soluble and seep into the soil. Plants then absorb the aluminium ions through the roots, become poisoned and die. Plant roots are also weakened and trees often fall. Acid rain can pass through the soil and end up in rivers and lakes. Fish living in such kind of water die or become poorly developed.

Control measures

These include:

- Recycling of unreacted sulphur (IV) oxide back to the catalyst chambers.
- Solid calcium hydroxide or calcium carbonate can be used to neutralise sulphur (IV) oxide before it leaves the factory chimney. In the process calcium sulphate is formed which can be used in the building industry to make plaster.
- Burn less fossil fuels that contain sulphur by using energy more efficiently. Pollutants like sulphur should be removed from fuels before they are burned. We should use alternative forms energy.

- Sulphur (IV) oxide and sulphur (VI) oxide can be converted into harmless compounds before they leave the power stations or industries. For example, a mixture of calcium carbonate and water neutralises the sulphur (IV) oxide.
- There should be strict laws in the country to limit the amount of oxides of sulphur and hydrogen sulphide released to the environment from industries.

Hydrogen sulphide

• Small quantities of hydrogen sulphide are common in the environment. It is found dissolved in mineral springs, water bodies, waste water and in natural gases. Much of the gas is produced in marshes, standing water, rotting vegetables and sewage treatment plants. It is also produced in various processes in industries such as in the manufacture of chemical fibres and oil refineries.

Effects of hydrogen sulphide

• On humans and animals

Hydrogen sulphide is an irritant. It is toxic to the nerves and cells of human and animals. It may cause irritation of the eye and respiratory organs, nausea, malfunction of nerves, numbress and finally death due to respiratory paralysis. Illness caused by hydrogen sulphide must be reported immediately to the doctor once detected.

Plants

Hydrogen sulphide causes only slight damage to plants. The most sensitive plants to the gas are tomatoes, cucumbers and soya beans.

Discussion corner!

- 1. Outline ways to reduce pollution caused by oxides of sulphur and hydrogen sulphide?
- 2. Discuss effect of acid rain on the environment.

Check your progress 3.10

- 1. Powder 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 blue litmus paper was dipped to the product found in (c) above, what colour would be observed.
- (e) Write an equation for the reaction that will occur between the solution formed in (c) above and sodium hydroxide solution.
- 2. Describe some of the uses of sulphur (IV) oxide and dilute sulphuric acid.
- 3. Suggest some of the ways through which pollution effects of sulphur and its compounds can be mitigated in African countries.
- 4. Describe an experiment to show action of hydrogen sulphide:
 - (a) as a combustible substance.
 - (b) as a reducing agent.
- 5. Discuss any useful applications of hydrogen sulphide.
- 6. (a) With the aid of a fully labelled diagram, describe briefly how dry sulphur (IV) gas can be prepared in the laboratory using copper turnings.
 - (b) Write the equation for the reaction in (a) above.
 - (c) Describe one test that can be used in the laboratory to identify sulphur (IV) oxide.
 - (d) (i) What would be observed if sulphur (IV) oxide was bubbled through aqueous hydrogen sulphide?
 - (ii) Write an equation for the reaction.
 - (e) The reaction in (d) above is a redox reaction. Name the oxidising agent in the reaction. Explain how it oxidises hydrogen sulphide.

3.6 Chlorine and its compounds

Activity 3.31

Laboratory preparation of chlorine

Apparatus and chemicals

• 18 g solid potassium manganate (VII) (enough for 6 litres of chlorine)

- 130 ml concentrated hydrochloric acid.
- 40g bleaching powder (enough for 6 litres of chlorine).
- Gas jars and boiling tubes as required.
- Beaker of ice-cold water.
- Granular calcium chloride.
- 24gm lumps of manganese (IV) oxide (enough for 6 litres of chlorine).
- Dilute hydrochloric acid.
- Sodium hydroxide or potassium hydroxide solution.
- Bunsen burner.
- **Caution!** Chlorine is a very poisonous gas. It should be prepared in a fume cupboard or an open verandah. If large amounts do escape into the laboratory sprinkle ammonium hydroxide on the bench and floor. If anyone is affected by chlorine, inhale the vapour from cotton wool dipped in alcohol or gargle 1 per cent sodium bicarbonate solution.)

Method I: Using potassium manganate (VII) or bleaching powder

Procedure

1. Arrange the apparatus to prepare chlorine as shown in Fig 3.32.



Fig 3.32 Laboratory preparation of chlorine using potassium manganate (VII)

- 2. Drop hydrochloric acid from a dropping funnel onto the solid; use concentrated acid for potassium manganate (VII) and dilute acid for bleaching powder. What do you see?
- 3. Collect the gas over brine or hot water. Collect gas jars and boiling tubes of the chlorine as required. If the gas is required dry, bubble it through two

wash bottles, one containing water and the other concentrated sulphuric acid, and collect by upward displacement of air (downward delivery).

4. As soon as enough jars and tubes of chlorine have been collected bubble the gas into water (preferably containing ice) to form chlorine water, which is used quite a lot in the laboratory.

Method II: Preparing chlorine using solid manganese (IV) oxide

Using hints from methods I, suggest apparatus and chemicals you need. Set up the apparatus shown in Fig 3.33 and proceed to carry out the production of chlorine gas.



Fig 3.33 Laboratory preparation of chlorine using manganese (IV) oxide

Hints

- Heat the flask gently. Collect jars and tubes of chlorine as required, and make chlorine water.
- Note the colour of the gas formed.

Method III: Further practical

Chlorine can also be prepared from sodium chloride using manganese (IV) oxide powder and cold dilute sulphuric acid. Research using books and from internet and outline the procedure for its preparation by use of these ingredients. You can organise with the class teacher to carry out this practical.

Same and different

1. Highlight what is common in all the three possible methods for laboratory

preparation of chlorine.

- 2. Identify the difference.
- 3. In your opinion, of the three methods which one do you consider most suitable? Justify.

The Facts

Chlorine is prepared by oxidation of hydrochloric acid using a suitable oxidising agent. The common oxidising agents used are potassium manganate (VII) or manganese (IV) oxide. When potassium manganate (VII) is used as an oxidising agent, no heating is required.

But with manganese (IV) oxide heating is required for oxidation to take place. The oxidising agents provide the oxygen atoms needed to oxidise hydrochloric acid. After heating the mixture of concentrated hydrochloric acid and manganese (IV) oxide, effervescence occurs and a yellow- green gas is given out. Hydrogen chloride gas which is an impurity dissolves in the water in the first wash bottle. Chlorine is then dried by passing it through concentrated sulphuric acid. It is collected by downward delivery because it is denser than air.

Investigating some properties of chlorine

Activity 3.32

Caution!

Chlorine is very poisonous and therefore most of its properties should be demonstrated using a fume cupboard or open air.

Using the collected chlorine gas from Activity 3.32, carry out the following investigation/actions.

- 1. Observe colour and smell of the gas, by placing a sheet of white paper behind a jar of chlorine, and noting the colour of the gas. What is its smell? (Caution! there is no need to smell it directly as there is usually sufficient of the gas in the air already in the laboratory during its preparation.
- 2. Determine solubility in water by inverting a tube of chlorine in a beaker of distilled water.
- 3. Hold a jar of chlorine mouth upwards, and another with the mouth

downwards for 30seconds. Replace the covers and judge by their colours which jar still contains most chlorine. Is chlorine more or less dense than air?

- 4. (a) Drop a small piece of coloured cloth and red or blue flowers into a jar of moist chlorine. What happens?
 - (b) Write in ordinary ink on a piece of newspaper and drop the paper into moist chlorine. What happens to the ordinary ink and the printer's ink? Can you explain the difference noticed?
 - (c) Drop a piece of coloured cloth, a flower, and paper with ink on it into the jar of chlorine dried with calcium chloride. What happens? Leave for several days. Do the colours change? Add a few drops of water to the jar. What happens? Explain the steps moist blue litmus paper takes before being bleached by chlorine.
- 5. Fill a long glass tube with chlorine water and invert it over a beaker of chlorine water. Clamp the tube and place it in bright sunlight. Can you observe any change? Leave it for several hours. What happens to the colour of the solution? Test any gas formed with a glowing splint; what is it?
- 6. (a) Add a few drops of concentrated ammonium hydroxide to a test tube containing chlorine water. What happens?
 - (b) Pour 10 cm³ of concentrated ammonium hydroxide into a test tube fitted with a stopper carrying a glass tube bent at right angles. Drop five sodium hydroxide pellets into the liquid; ammonia gas comes off at once (if liquid is heated, both ammonia and steam come off). When the ammonia gas is coming off quickly, lower the end of the glass tube into a jar of chlorine. What happens? Are the fumes formed at once or only after some time. Can you explain?
- 7. Lower a piece of burning sodium (size of rice grain) on a deflagrating spoon into a jar of chlorine. What happens? Repeat test with magnesium ribbon.
- 8. Crumple one fine sheet of brass, hold it in tongs, and drop it into a jar of chlorine. What happens?
- 9. Lower cold dry white phosphorus on a gas jar spoon into a jar of chlorine. Repeat with burning red phosphorus. What do you observe?
- 10. (a) Make 10cm³ of a saturated solution of potassium bromide in a test tube and bubble chlorine gas slowly through it (or add chlorine water). What colour changes occur? Is any liquid formed at the bottom of the tube? (Note that it may not be formed by chlorine water)

(b) Repeat the test with potassium iodide solution. What changes occur?

- 11. Bubble chlorine gas slowly for 3 minutes through 10 cm³ cold dilute sodium hydroxide or potassium hydroxide solution in a test tube. Smell the product cautiously. What is its action on moist litmus paper? To the solution add excess dilute hydrochloric acid; what do you observe?
- 12. Add a spoonful of finely powdered calcium hydroxide to a jar of chlorine standing in front of a sheet of white paper. What change do you notice? Smell the jar cautiously after a few minutes; is any chlorine left?

The Facts

Reaction equations for chlorine preparation

Hydrochloric acid + $\underset{(IV) \text{ oxide}}{\text{manganese}}$ + $\underset{(II) \text{chloride}}{\text{manganese}}$ + water + chlorine 4HCl (aq) + $\underset{(Arrow MnO_2(s))}{\text{manganese}}$ + $\underset{(Arrow MnCl_2(aq))}{\text{manganese}}$ + water + chlorine

If potassium manganate (VII) is used, heating is not required. This is because it is a stronger oxidising agent that releases oxygen readily than manganese (IV) oxide.

 $\begin{array}{l} \text{Hydrochloric} \\ \text{acid} \end{array} + \begin{array}{c} \text{potassium} \\ \text{manganate} \\ (VII) \end{array} \rightarrow \begin{array}{c} \text{potassium} \\ \text{chloride} \end{array} + \begin{array}{c} \text{manganese} \\ (II) \text{chloride} \end{array} + \text{water + chlorine} \\ 16\text{HCl}(aq) + 2\text{KMnO}_4(s) \longrightarrow 2\text{KCl}(aq) + 2\text{MnCl}_2(aq) + 8\text{H}_2\text{O}(l) + 5\text{Cl}_2(g) \end{array}$

Preparation of chlorine from bleaching powder uses the same set up as that of potassium manganate (VII), where dilute acid (e.g. hydrochloric acid ornitric (V) acid) is dropped on to the bleaching powder.

 $CaOCl_{2}(s) + 2HCl(aq) \longrightarrow Cl_{2}(g) + CaCl_{2}(aq) + H_{2}O(l)$

Bleaching powder + dil hydrochloric acid --> calcium chloride + water + chlorine

 $CaOCl_{2}(s) + 2HNO_{3}(aq) \longrightarrow Cl_{2}(g) + Ca(NO_{3})_{2}(aq) + H_{2}O(l)$

Bleaching powder + dil. nitric acid — calcium nitrate + water + chlorine Another method of preparing chlorine is by reaction of sodium chloride with concentrated sulphuric acid and manganese (IV) oxide. In this reaction, hydrogen chloride gas is produced and then oxidised by manganese (IV) oxide to chlorine.

Note that heat is required in this reaction.

Conc. sodium sodium Hydrogen heat +sulphuric hydrogen chloride chloride acid suphate heat HCl (g) + NaHSO₄(aq) $H_2SO_4(l)$ + NaCl (aq) Hydrogen + manganese (IV) oxide manganese heat + water + chlorine chloride (II) chloride gas 4HCl (g) + MnO₂(s) $\xrightarrow{\text{heat}}$ MnCl₂ (aq) + 2 H₂O(l) + Cl₂(g)

Hydrogen chloride gas is then oxidised to chlorine gas.

Properties of chlorine

Physical properties of chlorine

- Is a yellow-green gas.
- Has unpleasant, pungent and irritating smell.
- Is fairly soluble in water.
- Is denser than air.
- Is easily liquified under pressure. This makes it easy to store and transport chlorine in liquid state in steel cylinders.

Chemical properties of chlorine

When chlorine is dissolved in water, some of it reacts with water to form chlorine water, which is a mixture of hydrochloric acid (HCl) and chloric (I) acid (HOCl). Chlorine water is a yellow-green solution. This water bleaches blue and red litmus papers. Blue litmus first turns to red due to the acidic properties of the solution and then bleaches to white due to oxidation by chloric (I) acid. The resulting solution in the beaker is colourless. Coloured materials such as coloured flowers and litmus paper contain dyes and can be bleached by chlorine. Chloric (I) acid gives up its oxygen atoms to these dye molecules. In the process the flower petals and litmus papers are bleached.

Water + chlorine _____ hydrochloric acid + chloric (I) acid





Water must be present before any bleaching action by chlorine can take place. If absent no chloric (I) acid can be formed and therefore no bleaching occurs. If wet newsprint is inserted into a gas jar of chlorine, the newsprint is not affected because writings on it are not dyes.

Bleaching by chlorine cannot occur in the dark despite the presence of water, because energy is required to release oxygen atoms from chloric (I) acid (HOCl). Light provides this energy. The bleaching property can be used as a test for chlorine.



Fig 3.34 Investigating action of sunlight on chlorine water

Chlorine + water \longrightarrow hydrochloric acid + chloric (I) acid Cl₂(g) + H₂O(l) \longrightarrow HCl (aq) + HOCl (aq)

When chlorine water is left for two days, a gas that re-lights a glowing splint is produced. This gas is oxygen. The resulting solution in the beaker becomes colourless because of the formation of hydrochloric acid and oxygen. It turns blue litmus paper red showing that it is acidic.

Chloric (I) acid is a very unstable acid and light energy from the sun decomposes it to form hydrochloric acid and an oxygen atom.

HOCl(aq) \longrightarrow HCl (aq) + [O]

Since oxygen is a diatomic gas, the atoms join to form molecules.

 $[O] + [O] \longrightarrow O_2(g)$

Overall equation

2 HOCl (aq) \longrightarrow 2 HCl (aq) + O₂ (g)

The chloride ions (Cl⁻) from hydrochloric acid give a white precipitate of silver chloride with silver nitrate solution.

Silver nitrate + hydrochloric acid ------ silver chloride + nitric acid

 $AgNO_3(aq) + HCl(aq) \longrightarrow AgCl(s) + HNO_3(aq)$ white precipitate

Action of chlorine on magnesium

When burning magnesium ribbon in a deflagrating spoon is lowered into a gas jar of chlorine gas, magnesium continues to burn in dry chlorine with a sputtering sound forming white fumes of magnesium chloride.

Magnesium + chlorine — magnesium chloride

 $Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$

Action of chlorine on iron

A red hot glowing iron wire reacts with a stream of pure dry chlorine, forming black crystals of iron (III) chloride on the cooler sides of the combustion tube.



Fig 3.35 Reaction of chlorine with iron



When the end combustion tube near the receiver is warmed, the black crystals of iron (III) chloride sublime to form brown fumes and are deposited in the receiver, where they can be collected. When exposed to air, iron (III) chloride slightly fumes. This is because the iron (III) combines with water vapour in the atmosphere to form white fumes of hydrogen chloride gas. This gas dissolves in water vapour to form hydrochloric acid.

Iron (III) chloride + water ------ iron (III) hydroxide + hydrochloric

 $FeCl_3(s) + 3H_2O(l) \longrightarrow Fe(OH)_3(s) + 3HCl(g)$

Therefore, in the preparation of iron (III) chloride, the whole apparatus should be dry.

Remember:

Chlorine combines with magnesium or iron to form salts. A lot of heat energy is required for these reactions to take place. This energy is provided by the burning magnesium or red-hot iron.

Action of chlorine on sodium

When a piece of burning sodium on a deflagrating spoon, is lowered into a gas jar of chlorine, it continues to burn, giving off white clouds of sodium chloride.

Sodium + chlorine -----> sodium chloride

 $2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$

Action of chlorine on brass

When brass (an alloy of copper and zinc) is dropped in a gas jar of chlorine, it burns spontaneously with a green flame to form copper chloride and a little zinc chloride.



Remember:

The copper and zinc on the hot deflagrating spoon also react and the fumes formed make the product coloured.

Action of chlorine on phosphorus

Caution: Use red phosphorus in place of white phosphorous whenever possible. Red phosphorus is less reactive hence less risky.

When lowered into a jar full of dry chlorine, warm phosphorus chloride is formed.

Phosphorus +	chlorine>	Phosphorus (III) chloride
P ₄ (s) +	$6Cl_2(g) \longrightarrow$	$4PCl_{3}(s)$
Phosphorus	+ chlorine —	Phosphorus (V) chloride
$P_4(s)$ +	$10Cl_2(g) \longrightarrow$	$4PCl_5(s)$

If cold white phosphorus is used, it catches fire spontaneously forming the white fumes of chlorides of phosphorus. Phosphorus is very reactive towards chlorine. White phosphorus is even more reactive towards chlorine than red phosphorus.

Action of chlorine on hydrogen

Hydrogen gas burns in a gas jar of chlorine to form hydrogen chloride gas.

Hydrogen + chlorine \longrightarrow hydrogen chloride H₂(g) + Cl₂(g) \longrightarrow 2 HCl(g)

Action of chlorine on hydrogen sulphide

When dry hydrogen sulphide gas reacts with dry chlorine gas, a yellow solid of sulphur is seen on the sides of the lower gas jar. Chlorine oxidises hydrogen sulphide gas to sulphur at a room temperature. Chlorine is reduced by hydrogen sulphide to hydrogen chloride. Therefore, chlorine is the oxidising agent and hydrogen sulphide is the reducing agent.



Action of chlorine with ammonia

When ammonia gas is mixed with chlorine gas, it catches fire and burns for sometime. The flame goes off after a few minutes. White fumes of ammonium chloride fill the gas jar. The chemical reactions which take place are:



The hydrogen chloride gas formed reacts with the unreacted ammonia to form dense white fumes of ammonium chloride.



More hydrogen chloride is formed only to react with the unreacted ammonia gas. The overall reaction is :

Ammonia + chlorine \longrightarrow ammonium chloride + nitrogen 8 NH₃(g) + 3Cl₂(s) \longrightarrow 6NH₄Cl(s) + N₂(g)

Here, chlorine is reduced to hydrogen chloride and ammonia is oxidised to nitrogen. Chlorine is the oxidising agent while ammonia is the reducing agent. Ammonia and chlorine gas should be dry because hydrogen chloride gas formed is very soluble.

Action of chlorine on alkali

Chlorine reacts with cold dilute sodium hydroxide solution or potassium hydroxide to form hypochlorite solution and chloride of the metal.

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Potassium hydroxide + chlorine	>	potassium hypochlorite + potassium chloride + water
$2KOH(aq) + Cl_{a}(aq)$	>	$KOCl(aq) + KCl(aq) + H_{a}O(l)$

Chlorine reacts with hot concentrated sodium hydroxide or potassium hydroxide solution to form chlorate and chloride of the metal.

Sodium hydroxide + chlorine	\longrightarrow	sodium potassium chlorate + chloride + water
6NaOH (aq) + 3 Cl ₂ (g)		$NaClO_3(aq) + 5NaCl(aq) + 3H_2O(l)$
Potassium hydroxide + chlorine		potassium chlorate + potassium chloride + water
6KOH (aq) + 3 Cl ₂ (aq)	>	$\mathrm{KClO}_{3}(\mathrm{aq}) + 5\mathrm{KCl}(\mathrm{aq}) + 3\mathrm{H}_{2}\mathrm{O}(\mathrm{l})$

Both chlorate and hypochlorus solution bleach the litmus papers. When hydrochloric acid is added to them, they liberate chlorine gas.

Action of chlorine on calcium hydroxide

When a gas jar full of chlorine is added a tea spoonful of freshly prepared calcium hydroxide, the green – yellow colour of chlorine disappears immediately.

Calcium hydroxide	+	chlorine		bleaching powder
$Ca(OH)_2(aq) + Cl_2(aq)$	g)	>	CaOCl ₂ .H ₂ O((s)

Displacement reactions of chlorine

The trend in the oxidising power of halogens is most easily seen in their displacement reactions as studied under group VII elements earlier. Chlorine displaces bromine and iodine from solutions of their salts.

For example when chlorine water or chlorine gas is added to colourless potassium bromide solution, the solution turns red due to the formation of bromine water. Chlorine oxidises bromide ions to bromine. Chlorine gas is reduced to chloride ions.

Potassium bromide + chlorine ----- potassium chloride + bromine

 $2KCl(aq) + Br_2(aq)$

2KBr (aq) + Cl₂(g)

Ionically, the reaction between potassium bromide and chlorine can be represented as follows:

 $2Br(aq) + Cl_2(g) \rightarrow 2Cl(aq) + Br_2(aq)$

Chlorine is more reactive than bromine hence it displaces bromine from potassium bromide solution. Similarly chlorine would displace iodide ions from potassium iodide solution. The formation of iodine is seen when the clear solution of potassium iodide turns dark brown (a characteristic of iodine colour) and finally a black solid (iodine) is deposited.

Potassium iodide + Chlorine \longrightarrow potassium chloride + iodine 2KI(aq) + Cl₂(g) \longrightarrow 2KCl(aq) + I₂(aq)

Ionically:

 $2I^{-}(aq) + Br_{2}(l) \longrightarrow 2Br^{-}(aq) + I_{2}(aq)$

Chlorine is, therefore more reactive than iodine. We can also prove that bromine displaces iodide ions from potassium iodide solution. Iodine is deposited as a result.

Potassium io	dide +	bromine	potassiui	n brom	nide + iodine
2KI (aq)	+	$\operatorname{Br}_2(l)$	2KBr(aq)	+	I ₂ (aq)
Ionically:					
2I ⁻ (aq)	+	$Br_2(aq) \longrightarrow$	2Br ⁻ (aq)	+	I ₂ (aq)

From these observations, we can conclude that the order of reactivity is chlorine being more reactive than bromine which in turn more reactive than iodine.

Test for chlorides in solid form or in aqueous solution

All solid chlorides produce hydrogen chloride gas when reacted with concentrated sulphuric acid. The gas forms white fumes of ammonium chloride when ammonia solution on the glass rod is brought near the mouth of the test tube containing gas. Hydrogen chloride gas also forms a white precipitate with acidified silver nitrate solution on the glass rod. This is the test for chlorides.

To about 5cm³ of the chloride solutions, add an equal volume of dilute nitric acid and then a few drops of silver nitrate solution. A white precipitate is formed when acidified aqueous silver nitrate is added to any soluble chloride.

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Remember:

Silver nitrate should be acidified with dilute nitric acid. A precipitate of silver chloride can be confused with that of silver carbonate. When the acid is present, silver carbonate reacts with it and therefore no precipitate will be observed.

Ionically:

 $Ag^{+}(aq) + Cl^{-}(aq) \longrightarrow AgCl(s)$ (white precipitate)

When lead (II) nitrate solution is added to a chloride in aqueous solution, a white precipitate which is soluble on heating is formed.

Ionically

 $Pb^{2+}(aq)$

+

Discussion corner!

PbCl₂(s) (white precipitate)

Also all chlorides in solution form a white precipitate with acidified silver nitrate solution. But lead (II) chloride is soluble in hot water.

Why is silver nitrate solution is not acidified with hydrochloric acid?

Silver nitrate	+	hydrochloric ac	id			silver chl	oride + nitric acid
AgNO ₃ (aq)	+	HCl(aq)		•	AgCl(s)) +	HNO ₃ (aq)

Ionically:

Ag⁺(aq) + Cl⁻(aq) ----> AgCl(s) (from hydrochloric acid) (white precipitate)

 $2Cl^{-}(aq)$

Uses of chlorine

- 1. Sterilization of drinking water or swimming pools. Due to its poisonous nature, chlorine kills germs.
- 2. In the manufacture of antiseptics.
- 3. In the manufacture of herbicides, such as sodium and potassium chlorates.

- 4. Manufacture of bleaching agents, though chlorine can also be used directly as a bleach. For example, the wood pulp used in paper mills to make paper is initially bleached by chlorine and other bleaching agent such as sulphur (IV) oxide and calcium hydrogen sulphite.
- 5. Manufacture of plastics like polychloroethane (polyvinyl chloride, PVC).
- 6. In the manufacture of anaesthetic such as trichloromethane($CHCl_3$).
- 7. In the manufacture of dry cleaning solvents such as carbon (IV) chloride.
- 8. Chlorine compounds as nutrients help in digestion of food in our bodies and maintenance of water balance in body cells. They are found in, table salt and foods such as meat, milk and eggs.

Hydrogen chloride

Activity 3.33

To prepare hydrogen chloride in the laboratory and investigate its properties

1. In your groups, select your apparatus and chemicals required for preparation of hydrogen chloride.

The reaction equation is;

 $NaCl(s) + H_2SO_4(aq) \longrightarrow NaHSO_4(aq) + HCl(g)$

2. Design, plan and carry out the preparation of hydrogen chloride.

Hints

- Add 20cm³ of the liquid reagent to cover the solid reagent. Gently heat the mixture. If powdered salt is used then use cold diluted acid (2 volumes of acid to 1 volume of water).
- Collect five gas jars and four boiling tubes of gas, and also fill a thick-walled round bottomed flask for the fountain experiment.

Discussion corner!

- 1. What is the purpose of concentrated sulphuric in the wash bottle?
- 2. Give reasons why use of cold diluted acid is important in this experiment when powdered salt is used.
- 3. Write the chemical equation for the reaction.

Investigating properties of hydrogen chloride

Note: Use the collected gas for the following investigations.

- 1. Note the colour and smell of the gas (**Caution!** There is no need to smell it directly.) Open one tube and blow across its mouth, what happens?
- 2. Determine solubility in water by inverting a tube or gas jar containing the hydrogen chloride in a beaker containing distilled water.
- 3. Drop a small piece of coloured cloth and red or blue flower into a jar of moist hydrogen chloride. What happens?
- 4. Density. Hold one gas jar of the gas with its mouth downwards and a second jar of gas with the mouth upwards. What happens? Is hydrogen chloride more or less dense than air?
- 5. (a) Fill a dry round bottomed flask with hydrogen chloride gas and connect to a glass tubing.
 - (b) Put water in a trough and add 5 drops of litmus solution.
 - (c) Invert the tubing in a trough of the litmus solution.
 - (d) Close the tube with your finger and remove the whole flask from the trough and invert it.
 - (e) Remove the finger to allow the little solution that rose into the tube to enter into the flask.
 - (f) Close the tube with the finger again and quickly dip it into the solution as shown in Fig 3.36.



Fig 3.36 Fountain experiment demonstrating high solubility of hydrogen chloride gas

Explain what happens after sometime. What is demonstrated in the experiment?

- 6. Dip the end of a glass rod into a concentrated hydrochloric acid and hold it in a gas jar of ammonia. Explain observation made.
- 7. (a) Dip a glass rod into a solution of silver nitrate acidified with dilute nitric acid and take out one drop. Hold the drop in the gas, what happens?
 - (b) Mix 5 cm³ dilute nitric acid with 5cm³ silver nitrate solution and add to a jar of hydrogen chloride. What happens?

When powdered salt is used, the reaction is very vigorous and much frothing occurs even in the cold. Therefore, the use of cold acid gives a steady evolution of gas.

To carry out the tests for chlorides

Procedure

I. Test for a soluble chloride

- (a) Dissolve a pinch of sodium chloride in 5ml distilled water. Add 5ml dilute nitric acid and a few drops of silver nitrate solution. What happens?
- (b) Divide the product into two parts. To one part add ammonium hydroxide until it is present in excess. What happens?
- (c) Leave the other part in the light for a few minutes. What change occurs?
- (d) Repeat the test on other chlorides, if required.

II. Action of concentrated sulphuric acid

- (a) Place 0.5 g of solid sodium chloride in a dry test tube and add 2ml concentrated sulphuric acid. Test any gas formed by blowing gently across the mouth of the tube and by bringing the stopper of an ammonium hydroxide bottle near. What is the gas?
- (b) Repeat the test on other chlorides. Warm only if necessary.

II. Manganese (IV) oxide and concentrated sulphuric acid

- (a) mix ¹/₂ g sodium chloride with an equal volume of manganese dioxide powder in a dry test tube. Just cover the mixture with concentrated sulphuric acid and warm gently. What do you see?
- (b) Hold a piece of damp neutral litmus in the mouth of the test tube (do not touch the glass with it, why?). What happens to the litmus?

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(c) Repeat with other chlorides, as required.

When the mixture of sodium chloride and concentrated sulphuric acid is heated, colourless hydrogen chloride gas which has a pungent irritating smell is produced. The gas forms white fumes of ammonium chloride with ammonia gas. This is the test for hydrogen chloride gas.

 $NaCl(s) + H_2SO_4(aq) \longrightarrow NaHSO_4(aq) + HCl(g)$

Hydrogen chloride gas is dried by passing it through concentrated sulphuric acid. The temperature used in this experiment is not enough to produce sodium sulphate (normal salt) but, only sodium hydrogen sulphate (acid salt). Sulphuric acid does not distill off because the temperature used in the experiment is below the boiling point of this acid.

Physical properties of hydrogen chloride gas

- It is a colourless gas with a pungent irritating smell.
- It is very soluble in water. The water rapidly fills the gas jar, if the jar is full of hydrogen chloride.
- It is denser than air. It can therefore be poured down to extinguish a burning candle.
- It turns moist blue litmus red.
- It is collected by downward delivery.

Chemical properties of hydrogen chloride gas

Combustion

Hydrogen chloride does not burn neither does it support burning. This is why it extinguishes a burning splint.

Effect on litmus

Hydrogen chloride turns moist blue litmus paper red. Therefore the gas is acidic.

Reaction with ammonia

Concentrated ammonia solution on a glass rod reacts with hydrogen chloride gas to form white fumes of ammonium chloride.

 $NH_{4}Cl(s)$

Ammonia + hydrogen chloride

→ ammonium chloride

 $NH_{3}(g) + HCl(g)$

(white fumes)

This is the test for hydrogen chloride gas.

Reaction with acidified silver nitrate solution

Hydrogen chloride gas forms white precipitate of silver chloride with acidified silver nitrate solution. The gas first forms hydrochloric acid with water in the silver nitrate solution then reacts with silver ions to form white precipitate of silver chloride and nitric acid.

Hydrogen chloride	+	Water	>	Hydrochlor	ic acid
HCl(g)	+	H ₂ O		HCl(aq)	
Silver nitrate + H	Iydroc	hloric acid		silver chloride	+ nitric acid
$AgNO_{3}(aq) +$	HCl((aq)	>	AgCl(s) +	HNO ₃ (aq)

Effect of water on the properties of hydrogen chloride

When dissolved in water, hydrogen chloride gas forms hydrochloric acid which ionises to form hydrogen ions (H^+) and chloride ions (Cl^-). These hydrogen ions gives the aqueous solution its acidic properties.

Hydrochloric acid

- Has sour taste and turns blue litmus paper red.
- Reacts with some metals to give salt and hydrogen gas. For example:

Magnesium + hydrochloric acid — magnesium chloride + hydrogen

 $Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$

• Reacts with carbonates and hydrogen carbonates to give salt, water and carbon (IV)oxide. For example:

Sodium carbonate +	Hydrochloric acid		Sodium chloride	+Water	+	Carbon (IV) oxide
$Na_2CO_3(s) +$	2HCl(aq)	>	2NaCl(a	q) + H_2O	(1)	+ $CO_2(g)$

- Reacts with strong oxidising agents like manganese (IV) oxide to give off chlorine gas. Chlorine gas is the one that bleaches moist litmus papers.
- Neutralises alkalis (soluble bases) to form a salt and water only. For example.

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Sodium hydroxide + Hydrochloric acid — Sodium chloride + water

Potassium + hydroxide +	Hydrochloric acid		Potassium chloride	+	water
KOH(aq) +	HCl (aq)	>	KCl(aq)	+	$H_2O(l)$

• Reacts with insoluble basic oxides to form salt and water only. For example black copper (II) oxide reacts with hydrochloric acid to form a green solution of copper (II) chloride.

Copper (II) oxide + hydrochloric acid \longrightarrow copper (II)chloride + water CuO(s) + 2HCl(aq) \longrightarrow CuCl₂(aq) + H₂O(l)

Like in the preparation of aqueous ammonia, a filter funnel is used when dissolving hydrogen chloride gas in water. This is to prevent "sucking back" of water from the beaker to the preparation flask. This preparation flask is hot and contains hot concentrated sulphuric acid. Water can react explosively with the hot acid.

Uses of hydrogen chloride gas

- 1. The major use of this gas is in the manufacture of hydrochloric acid.
- 2. To standardize pH of beers and wines.
- 3. In the pickling of metals.
- 4. In the manufacture of dyes, drugs e.t.c.
- 5. In the manufacture of photographic materials.
- 6. In school and research laboratories.

Pollution effects of Chlorine and its compounds

1. Chlorine

We said earlier that chlorine is useful in sterilizing drinking water and water in swimming pools, manufacturing antiseptics and insecticides, among other uses. Chlorine, however, has some bad effects on the environment as well. Chlorine was used as the first chemical weapon in the first weapon in the First World War that killed millions of people. It was used in Tanzania during the First World War (1914-1918).

All Human Life is important. Value other people's lives as is important as ours. Lets respect others and their culture for peaceful co-existence. No man

is an island. Do we live to fight or enjoy life with others around us? Use of chemical weapons is strictly prohibited by United Nations.

2. Chlorofluorohydrocarbons (CFCs)

CFCs are non toxic, not flammable chemicals which are almost inert. A CFC molecule contains atoms of carbon, chlorine and fluorine. CFCs are used in the manufacture of aerosol sprays, foams (e.g mattresses), coolants and solvents. CFCs are safe to use in most appliances. However, they are harmful when released into the atmosphere.

CFCs are harmful because they destroy the ozone layer (O_3) that protects us from the harmful ultra violet (uv) rays from the sun. Ozone is found in the upper part of the atmosphere (10 to 50km) above the earth's surface.

When CFCs get to the atmosphere, the chlorine atom (CI) is released from CFC molecule. The chlorine atom split ozone molecule (O_3) , layer.

Ozone	Chlor	ine atom	oxygen m	olecule	e +	oxygen atom
O ₃ (g)		• $O_2(g) + C$) (g)			
Ozone	+	oxygen atom			oxygen n	nolecule
O ₃ (g)	+	(O)		2 O ₂ (§	g)	

With destruction of the ozone layer more harmful ultra-violent (U.V) rays now reach the earth's surface. Even a low concentration of these rays are harmful. Ultra-violet rays are responsible for some skin cancers and eye cataracts. They damage the lungs and reduce crop yields.

Discussion corner!

Your class has been requested to conduct a debate on the importance of sulphur and chlorine in growing the economy of South Sudan. Prepare adequately to make a convincing presentation on how the economic benefits of these substances outweightheir environmental harmful effects.

Sources of CFCs into the atmosphere

CFCs are released to the atmosphere during the manufacture and disposal of substances such as:

- (i) Coolants that contain (CFCs) used in refrigerators and air conditioners.
- (ii) Certain aerosols where CFCs are used as propellants.
- (iii) Foam containing CFCs used in the manufacture of mattress among other things.

Check your progress 3.11

- 1. When chlorine gas is bubbled through dilute sodium hydroxide solution, the resulting solution acts as a bleaching agent.
 - (a) Write an equation for the reaction between chlorine gas and sodium hydroxide solution.
 - (b) Explain how the resulting solution acts as a bleaching agent.
- 2. Study the following flow chart and answer the questions that follow:



- (a) Name:
 - (i) Gas X
 - (ii) SolutionY
 - (iii) Gas Q
- (b) Name the substance used in drying gas X.
- (c) Name the method used in collecting dry:
 - (i) Gas X
 - (ii) Gas Q
- (d) In the preparation of gas X, sodium sulphate is not formed. Give a reason for this.
- 3. (a) What is observed when moist hydrogen chloride gas is bubbled in aqueous silver nitrate in a test tube?
 - (b) Write the chemical equation for the reaction in 3(a).
 - (c) Write the ionic equation for the reaction in 3(a).

- (d) Silver chloride and silver carbonate are insoluble in water. How can you differentiate them?
- 4. (a) Explain why a solution of hydrogen chloride in methlybenzene has no effect on carbonates.
 - (b) Which gas is produced when aqueous hydrogen chloride is reacted with
 - (i) a hydrogencarbonate salt.
 - (ii) potassium manganate(VII).
 - (c) Give the test of each gas.
 - (d) In the manufacture of hydrochloric acid name the two gases which are used.
 - (e) Write the chemical equations of the reactions taking place in 4 (d) above.
 - (f) In the manufacture of hydrochloric acid, the gases are dissolved in water over glass beads. What is the use of the beads?
 - (g) In the laboratory preparation of hydrogen chloride using concentrated sulphuric acid, it is not advisable to use solid barium chloride or lead(II) chloride or calcium chloride. Explain why.


Learning Outcomes					
Knowledge and	Skills	Attitudes			
understanding					
 Explain the properties of transitional metals. Know the uses of some transition metals. 	• Carry out practical investigations to identify the characteristics of transition metals.	 Appreciate the importance of transition metals. 			

4.1 Introduction



Fig 4.1 Section of periodic table

- 1. Study the periodic table above. Then carry out the following:
 - (i) Identify elements in row 4. Which of these elements are familiar to you?
 - (ii) Why do you think these elements are not put in the main groups of the periodic table you studied earlier.

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- 2. Write the electronic configuration of vanadium, copper and iron.
- 3. Obtain coloured substances from your chemistry and biology laboratories. Which transition metals form the constituents of these coloured substances in their solid and aqueous states?

Research work

In groups of two, research from books and internet:

- 1. Which transition metals show,
 - (a) The same oxidation state in different compounds.
 - (b) Different oxidation state in different compounds.
- 2. Common properties of transition elements.
- 3. Reasons why they are called transition elements.

The Facts

Between group 2 and group 3 of the periodic table are found sub group of elements arranged without assigned universal group numbers. Why do think this is the case?

The first row of these elements is found in period 4 and has 10 elements. The elements are scandium(Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese(Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu) and zinc (Zn). Each of these ten elements heads a sub group which consists of other elements below it. The elements with atomic numbers from 57 to 71 are called the **lanthanides** while those with 89 to 103 are called the **actinides**.

These elements are usually referred to as the transition elements because chemists once believed that some elements behaved in a way intermediate between the extremes represented by the elements in the left and right sides of the periodic table.

Element	Symbol	Atomic number
Scandium	Sc	21
Titanium	Ti	22
Vanadium	V	23

Atomic number of transition elements in the fourth row

Chromium	Cr	24
Manganese	Mn	25
Iron	Fe	26
Cobalt	Co	27
Nickel	Ni	28
Copper	Cu	29
Zinc	Zn	30

4.2 **Properties of transition elements**

Discussion corner!

Using your previously acquired knowledge;

- 1. Define oxidation state.
- 2. How is the knowledge of oxidation state of elements helpful in Chemistry?
- 3. Give the oxidation state or numbers of the following.
 - (i) H_2, O_2
 - (ii) Cl-
 - (iii) Hydrogen in NaH (Sodium hydride)

Much of the properties of transition elements are attributed to their variable oxidation states.

General properties

- (i) They are hard and have high densities.
- (ii) They have high melting and boiling points.
- (iii) They form compounds which are often paramagnetic.
- (iv) Show variable oxidation states.
- (v) Form coloured ions and compounds.
- (vi) Form compounds with catalyst characteristics.
- (vii) Form stable complexes.

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Abundance of transition elements in the earth crust

All elements in the first transition row are relatively scarce except iron which is very abundant, and titanium which is moderately abundant.

4.3 Trend in physical properties

	Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
First ionization energy. kJ/mole	637	663	657	659	723	766	765	743	751	912
Melting point °C	1540	1670	1900	1890	1250	1540	1490	1450	1083	419
Boiling point °C	2730	3260	3450	2642	2100	3000	2900	2730	2600	906
Density g/cm ³ at 20°C	3.0	4.5	5.8	7.19	7.43	7.86	8.9	8.9	8.96	7.14
Atomic radius (nm)	0.161	0.145	0.131	0.129	0.137	0.124	0.125	0.125	0.128	0.133
Ionic radius (nm) M ²⁺	-	0.090	0.088	0.084	0.081	0.076	0.074	0.073	0.070	0.074
M ³⁺	0.081	0.076	0.074	0.069	0.065	0.065	0.064	0.064	-	-
Common oxidation state	3	2,3,4	2,3,4,5	2,3,6	2,3,4,6,7	2,3	2,3	2	1,2	2

Table 4.2 Trend in physical properties of transition elements

Atomic mass

The atomic masses, of transition metals increases gradually across the fourth row with exception for cobalt and nickel, see table 4.2 above. The reason for this change is due to how naturally occurring isotopes of the two elements are distributed. Natural cobalt consists in greater proportion of the isotopes ⁵⁹/₂Co, while natural nickel consists of the isotopes ⁵⁸/₂Ni and ⁶⁹/₂₈Ni where the 58 – isotopes is about 3 times as abundant as the 60-Ni isotopes. Hence natural nickel though coming after cobalt has smaller atomic mass.

Melting and boiling points

The first transition row elements have quite high melting and boiling points except for zinc. See table 4.2. These could be attributed to the elements having a large number of valence electrons and a large number of unfilled up units (orbitals) in the valence sub energy level. For zinc, it has all sub energy levels (orbitals) filled up causing drop in the melting points. The first row of transition elements have strong metallic bonds due to ability of the elements to release electrons from inner third sub energy levels and outer fourth sub energy level to form bonds. Zinc has lower melting point because only the electrons in outer fourth sub energy level are used in metallic bonding. The electrons in third energy level of zinc are not involved in bonding because the energy level is full.

Density

There is a steady increase in densities across the fourth row of transition elements but the trend changes from iron onwards. See table 4.2. This trend is closely related to the almost constant size of the atoms such that the main effect producing density change is the increasing nuclear mass.

Variation in the densities is caused by decreasing atomic volume and increasing atomic mass moving from scandium to copper. The forces between transition metals ions in the metal lattice are strong and the ions are packed closely. This gives the metals high densities, and high melting and boiling points.

Ionization energy

Transition elements do not show much difference in the ionization energy. They neither have very high nor very low ionisation energy. This is because even though there is general increase in the nucleus charge which should cause an increase in ionization energy, such effect is neutralized by increased screening of the nucleus by the added electrons.

Successful ionisation energy increases from scandium to manganese, after which it decreases again. This is because from scandium to manganese the highest oxidation state is simply sum of electrons in the last third sub energy level, and in the first fourth sub energy level. After manganese the highest oxidation state becomes lower and less stable as more protons in the nucleus result in higher positive charge attracting electrons strongly.

Did you know that

In every energy level of atom there are sub energy levels called sub shells or orbitals where electrons occupy or arranged at most two according to energy requirements of the given orbitals.

Atomic radii

The metallic radii show a decrease moving from scandium to copper. The decrease is steeped up to vanadium then levels out. The decrease is due to the very poor screening (shielding) of the electrons in fourth sub energy level by the inner third sub energy level which allows the outer electrons to be strongly pulled closer to the nucleus. But the successive filling up of third sub energy level electrons shields electrons in fourth sub energy level from the much nucleus pull. This makes the difference in metallic radius from one metal to the other relatively small. It is the



increased shielding of electrons in the outer fourth sub energy level as the third energy level continues to be filled up that leads to small increase in the metallic radius of the copper atoms and a larger increase for the zinc atoms.

Ionic radius

Ionic radii across the row do not show significant change. The electrons added in the third sub energy levels repel each other which counter the effect of increased nuclear charge hence the increased size.

Ions of the same element with a higher oxidation state are smaller than those with a lower oxidation state. This is because nuclear charge is constant while removal of one additional electron from inner third sub energy level reduces repulsion between the remaining electrons thus are pulled much closer to the nucleus.

Check your progress 4.1

- 1. Describe the trend in the boiling points of transition as shown in Table 4.2.
- 2. Discuss some of the differences between transition metals and main group metals.
- 3. How does the sub shell filling affects the trend in atomic radii and ionization energy of transition metals?
- 4. Explain why transition metals have high melting and boiling points. Briefly describe this trend.

Oxidation state

Valences of the first row transition elements are variable and their ions undergo oxidation or reduction readily. This change makes them good catalysts.

From titanium to copper, the metals show two or more oxidation states in their compounds. This is due to the third sub energy level and the fourth sub energy levels being very close in their energies and their electrons are available for bond formation.

There is a small increase in ionisation energies as electrons are removed from these sub energy levels. The elements toward the centre of the row show more oxidation states than those toward both ends. The stability of particular oxidation state depends on ability of electrons in the inner energy levels to screen the bonding electrons from the nucleus charges. The following generalizations emerge from a study of the oxidation states:

- 1. The common oxidation states for each element at the beginning of the corresponding series correspond to the maximum oxidation available, which involves the loss of possible electrons to attain a noble gas structure.
- 2. The common oxidation states for each element towards the end of the series is +2. As the nuclear charge increases progressively across the period, electrons are more firmly held, making the removal of all electrons in third energy level practically impossible.
- 3. Elements rarely form simple ions with oxidation state greater than +3, since this would result in ions of extremely high charge density. Compounds with higher oxidation states are usually found in oxides, fluorides and oxy-anions, all of which are highly electronegative and less likely to be polarized.

Metals with lower oxidation states usually form simple ionic compounds e.g. Cu^{2+} in copper sulphate while metals with higher oxidation states are usually bonded covalently to oxygen or fluorine e.g. manganate (VII) ion, MnO_{4}^{-} .

4. Both scandium and zinc have only one oxidation state in their compounds. In fact, their properties differ so much from the typical transition elements with metallic properties that they are usually not regarded as transition elements.

	Check	vour	progress	4.2
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- 1. Explain why transition metals show two or more stable oxidation state.
- 2. Give all the possible oxidation states of:
 - (i) Copper (ii) Manganese (iii) Iron
- 3. In your opinion, does the variable oxidation states have effect on some properties of the transition metals?

Electrical conductivity

The transition metals show high electrical conductivity attributed to the delocalization of the sub energy levels electrons similar to what occurs in alkaline earth metals. Those with filled up third energy level and with a single electron in the fourth energy level are better conductors than those with two electrons in the fourth energy level with filled up third energy level or half filled sub energy levels. Thus copper is better conductor of electricity than zinc, and chromium is better conductor than manganese.

Hardness

Unlike alkaline earth metals, transition metals are hard, brittle and have fairly high melting points. This is because they are relatively small sized atoms. They have strong interatomic bonding giving them high tensile strength.

Ductility and malleability

Transition metals can be drawn into wires and beaten into sheets of metals.

Appearance

Except copper, the rest of the row 4 transition metals are silvery with bright lustre.



Fig 4.2 various metals

Catalytic properties

The transition metals and their compounds show catalytic activity in a variety of chemical processes. This important activity is assumed on their ability to show multiple oxidation states and to form complexes, alloys and interstitial compounds.

Transition metals whose third energy level have *empty lower sub energy levels* may accept electrons to fill the empty sub energy levels, and by accepting electrons form temporary bonds between catalysts and reactants, thus bringing reactants particles closer enough to result in successful reactions or collisions. One such common days is the heterogeneous catalyst used in car exhausts which contains a platinum/rhodium alloy that converts the mixture of oxygen, carbon (II) oxide, nitrogen oxides and hydrocarbons in the exhaust gases to form water, carbon (IV) oxide and nitrogen. Other examples are the use of V_2O_5 in Contact process for manufacture of sulphuric acid, finely divided iron in Haber's process for manufacture of ammonia gas and use of nickel in hydrogenation of oils.



Fig 4.3: Catalytic converter in car exhaust system

An example of homogeneous catalyst is the use of rhodium compound $[Rh(CO)_2I_2]^$ in catalysing a reaction, which results in the addition of carbon(II)oxide (CO) to methanoic acid(CH₃OH) to form ethanoic acid (CH₃COOH).

- 1. Transition metals are much harder than alkali or alkaline earth metals. Explain why.
- 2. In your judgment, between transition metals and alkali/alkaline earth metals which ones have higher electrical conductivity? Give reasons for your answer.
- 3. Scandium and zinc have only one oxidation state yet they are grouped transition elements. Suggest reason(s) for this.
- 4. What characteristics of some transition metals give them good catalytic properties.

Coloured ion formation

The energy absorbed by transition atom move electrons from a lower sub energy level to a higher sub energy level within an energy level. That energy corresponds to the frequency which generally lies in the visible region of light. Thus colour observed corresponds to the complementary colour of the light absorbed. When light interacts with a substance giving rise to colour, there is absorption of part of spectrum. E.g, if the blue portion of white light is absorbed, then the remainder appears red, likewise if red frequencies are absorbed, the substance appears blue.

A substance appears white when light falls on it is totally reflected. It appears black when the light is totally absorbed. Coloured substances absorb certain wavelengths of light and reflect others. The reflected wavelengths give rise to colour of the substance.

Therefore most transition elements are coloured because they use some of the visible light energy to move electrons from lower sub energy level to higher sub energy levels in an energy level. The frequency of light absorbed is determined by the nature of ions or molecules (ligands), that bond to the metal ion.

Electrons may exist in pairs. It is the unpaired electrons in the higher energy level of the transition ions that cause the absorption of light. Where the higher sub energy levels are either completely empty (e.g. Sc^{3+}) or completely full (e.g. Zn^{2+} , Cu^+) their compounds are not coloured. The unpaired electrons absorb light energy by becoming promoted from their normal low energy levels to higher energy levels.

Table 4.3 shows colours for some aqua species of the first row transition metal ions bonded with water in their oxidation states of +2 and +3.

Table 4.3 Example of coloured transition metals ions

Element	+2	+3
Sc		$[Sc(H_2O)_6]^{3+}$ colourless
Ti		$[Ti(H_2O)_6]^{3+}$ violet
V	$[V(H_2O)_6]^{2+}$ violet	$[V(H_2O)_6]^{3+}$ green
Cr	$[Cr(H_2O)_6]^{2+}$ Blue	$[Cr(H_2O)_6]^{3+}$ violet/green
Mn	$[Mn(H_2O)_6)]^{2+}$ pink	$[Mn(H_2O)_6)]^{3+}$ violet
Fe	$[Fe((H_2O)_6)]^{2+}$ pale green	$[Fe(H_2O)_6)]^{3+}$ yellow/brown
Co	$[Co(H_2O)_6)]^{2+}$ pink	$[Mn((H_2O)_6)]^{3+}$ blue
Ni	$[Ni(H_2O)_6)]^{2+}$ green	
Cu	$[Cu(H_2O)_6)]^{2+}$ blue	
Zn	$[Zn(H_2O)_6)]^{2+}$ colourless	



Fig 4.4: Various salts

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Some transition elements' compounds / ions and their colours

- (v) $[Fe(CN)_6]^{4-}$, yellow (ix) $K_2Cr_2O_7$ orange TiO₂ white (i)
- $[Ti(H_2O)_6]^{3+}$, violet (vi) $[Fe(CN)_6]^{2-}$, green (x) $[V(H_2O)_6]^{3+}$, green (ii)
- (iii) Fe_3O_3 brown (vii) $KMnO_4$ purple (xi) $[V(H_2O_6)]^{2+}$, violet
- (iv) FeO, black
- CoCl₂.6H₂O blue
- ZnCO₃ white
- $CuSO_4.5H_2O_5$ blue
- CuO, black ٠
- $[Cu(H_2O)_{\epsilon}]^{2+}$ colourless

Most of the hydrated compounds above are complexes. Transition metals and some group three elements (e.g. aluminium and boron) have the ability to form complex ions.

Check your progress 4.4

- 1. Describe briefly how the colour formation comes about in compounds of some transition metals.
- 2. Try to explain why some compounds of transition metals show different colours in different oxidation states e.g. Cu⁺/Cu²⁺, Fe²⁺/Fe²⁺.

Formation of complex ions 4.4

Complex ions are composed of a central metal ion surrounded by anions or molecules called ligands. Lone-pair electrons on the ligand form co-ordinate bonds (dative covalent bonds) with the central metal ion which provides the empty sub energy levels to accommodate these electron pairs.

Name	Formula of complex ion	Colour of solution
Tetraamminezinc(II)ion	$[Zn(NH_3)_4]^{2+}$	Colourless
Tetraamminecopper(II)ion	[Cu(NH ₃) ₄] ²⁺	Deep blue

Table 4.4 Some complex ions formed with aqueous ammonium solution

- (viii) MnO₂, black (xii) $[Ni(H_2O)_6]^{2+}$ green

Uses of complex ions

- 1. Detection of metal ion by the colour of its complex, e.g. Fe^{3+} in [Fe (SCN)] ²⁺ appears blood red, Cu^{2+} in $[Cu(NH_3)_4]^{2+}$ appears deep blue. The complex must have an intense and characteristic colour so that the metal ion can be readily identified.
- 2. Extraction of metals

Aluminium and silver are extracted from their formation of soluble complexes, AF_6^{3-} and Al (CN)₂.

3. Softening of hard water

When hard water, containing Ca^{2+} and Mg^{2+} ions, is mixed with soap, it reacts with the anions in these salts, producing insoluble compounds which we see as 'scum' on the surface of water. Various ligands form complex salts with Ca^{2+} and Mg^{2+} ions, thus preventing them from reacting with the anions in soap and thus the water is said to be 'softened'.

4. Formation of essential biological macromolecules, e.g. chlorophyll (complex of Mg^{2+}) and haemoglobin (complex of Fe^{2+}).

Remember:

The chemistry of a complex ion is, in most cases, entirely different from that of the free metal ion.

Activity 4.2

Group work

Procedure

1. Place 5 cm³ of distilled water in three test tubes, another 5 cm³ of dilute hydrochloric acid into three other test tubes and another 5 cm³ of dilute sulphuric acid into three more test tubes as shown.



Fig 4.5

- 2. Drop some pieces of iron fillings into one of each set of the test tubes. What do you observe after 5 minutes?
- 3. Repeat the above procedure using copper turnings and about 4 cm of magnesium ribbon in turns in place of the iron fillings.
- 4. Trying cutting a piece of zinc and copper metals using knife. Now take a piece of sodium and aluminium metal and try cutting.
- 5. Discuss the observations.

Activity Questions

- 1. What was the colour of the products or solutions formed in each case?
- 2. Was there colour change in some of the products after some time? If so, give reasons.
- 3. Compare the ease of cutting transition metals with that of main group metals. Explain differences in your observations.

4.5 Chemical properties

The small, highly charged cations cause greater polarization of associated anions, resulting in the following chemical properties of transition metal compounds.

(i) Their oxides and hydroxides in oxidation state +2 and +3 are less basic and less soluble.

- (ii) Their salts are less ionic and less thermally stable;
- (iii) Their salts and aqueous ions are more hydrated and more readily hydrolyzed forming acidic solutions.
- (iv) Their ions are more easily reduced than main group metal ions.
- (v) Most transition metals react slowly with dilute acids, as compared with the main group metals, because:
 - They are less electropositive than the main group metals;
 - The presence of a thin, unreactive layer of oxide protects the metal from chemical attack (similar to the case of aluminium).
 - The variety of oxidation states causing successive ionisation energies.

Activity 4.3

Group work

An investigation of some transition metal compounds

Most transition metal compounds are coloured.

Some of them are used as dyes and pigments.

A dye is a soluble coloured compound.

A pigment is an insoluble coloured compound.

Both dyes and pigments have to be resistant to chemical change.

Three solutions, labelled \mathbf{P} , \mathbf{Q} and \mathbf{R} , have been provided by a supplier as possible dyes.

- You will carry out tests on these solutions.
- You will record what you observe for each test.
- Where no visible change is observed, write 'no visible change'.

In this task, you are not required to identify any of the solutions or any of the reaction products.

Requirements

- chromium(III) sulphate solution labelled 'Solution P'.
- iron(III) nitrate solution labelled 'Solution Q'.

- copper(II) chloride solution labelled 'Solution R'.
- sodium hydroxide solution.
- sodium carbonate solution.
- silver nitrate solution.
- 9 test tubes.
- 6 dropping pipettes.
- test tube rack.
- 250 cm³ beaker.
- access to hot water.
- plentiful supply of distilled or deionised water.

Procedure

Test 1(a)

- 1. Place about 10 drops of solution P in a test tube.
- 2. Add sodium hydroxide solution, drop wise with gentle shaking, until in excess.
- 3. Do not discard this mixture.
- 4. Repeat this test with solution Q and then solution R.

Test 1(b)

- 1. Half fill a 250 cm³ beaker with the freshly boiled water provided.
- 2. Allow the three test tubes containing the mixtures from Test 1(a) to stand in the beaker of hot water for about 10 minutes.
- 3. While you are waiting, begin Test 2.

Test 2

- 1. Place about 10 drops of sodium carbonate solution in a test-tube.
- 2. Add about 10 drops of solution P and shake the mixture gently.
- 3. Repeat this procedure with solution Q and then with solution R.

Test 3

- 1. Place about 10 drops of solution P in a test tube.
- 2. Add about 10 drops of silver nitrate solution and shake the mixture gently.
- 3. Repeat this procedure with solution Q and then with solution R.
- 4. Allow the three test tubes to stand for about 10 minutes.

Record your results in a table format.

What is your conclusion about the experiment?

Uses of transition metals

- 1. Some transition metals and their compounds are used as catalysts in many industrial and chemical reactions such as Haber process and contact process.
- 2. Iron and its alloys are heavily used in building and construction industry for bridges, roofing, locomotive rails and automobile parts; making of many cutting tools such as panga, knife, axes e.t.c.
- 3. Copper is used in domestic water system since it is effective at stopping growth of many micro-organisms. It is also used in making of pipes, electrical cables and radiators.
- 4. Zinc is used in dry cells and roofing cladding.
- 5. Iron catalyst used in Haber process in industrial manufacture of ammonia.
- 6. Platinum catalyst used in Oswald process (industrial manufacture of nitric acid)
- 7. Vanadium (V) oxide catalyst is used in contact process to produce sulphuric acid.
- 8. Manganese (IV) oxide used in laboratory preparation of chloride.

Research Project

In groups of three, using textbooks and from internet research on the uses and properties of the transition metals linked to its particular use. Write a report and present to the class. Your teacher will guide you accordingly.

Acids, Bases, Amphoteric oxides and Hydroxides and the Solubility of Salts

Learning Outcomes					
Knowledge and	Skills	Attitudes			
understanding					
 Further explain the properties of acids, bases and salts Understand the properties of amphoteric oxides and hydroxides Explain the hardness of water and solubility of salts in water 	 Design practical investigation to identify the properties of amphoteric oxides and hydroxides Design practical investigation to identify the causes of hardness of water and methods of removing it Investigate solubility of some salts and interpret and suggest application of solubility curves 	 Appreciate the importance of the solubility of salts 			

5.1 Introduction

In Form one, you learnt about characteristics of acids and bases and what is responsible for the acidic and basic property of substance. In this unit, you shall learn about a number of definitions of acids and bases and why is so. It is important to know that there are some substances that behave as acids and bases. How are such substances chemically referred to? You will also learn about solubility of salts, solubility curves and their applications as well as causes of water hardness due to solubility of some salts in it.

5.2 Definitions of acids and bases

Discussion corner!

In pairs;

1. What properties of acids and bases do you remember from your study in Secondary One?

- 2. Give examples of strong and weak acids/bases. Differentiate between strong and weak acids/bases.
- 3. Research from books and internet about the various definitions of acids and bases. Write the report and present it to the class.

There are several definitions of acids and bases commonly in use. It is important to know that there has never been one universally adopted standard definition i.e. which definition is regarded as most useful. It is therefore necessary for a chemist to be familiar with all these several definitions. But in our study here, we shall consider only the following two definitions.

Arrhenius definition of acids and bases

In defining acids and bases, Arrhenius described acids as substances which dissociate to produce hydrogen ions (H⁺), and bases as substances which dissociate to give hydroxyl or hydroxide ions (OH⁻), in water or aqueous solutions. The definition is recommended because of its simplicity and wide use. Arrhenius accounted for the acidic properties such as sour taste, turning litmus to red, reactions with metals to produce hydrogen gas. He assumed that all acids have the formula HX and can dissociate to give H⁺ and X⁻.

For example when the acids are dissolved in water, they dissociates as follows.

H_2SO_4 (aq) \longrightarrow	2H+ (aq)	+	SO ₄ ²⁻ (aq)
HCl (aq)	H ⁺ (aq)	+	Cl ⁻ (aq)
CH ₃ COOH (aq)	H ⁺ (aq)	+	CH ₃ COO ⁻ (aq)

He also assumed that all bases have the formula MOH and can dissociate to give $M^{\scriptscriptstyle +}$ and $OH^{\scriptscriptstyle -}$.

For example, soluble bases dissolve in water to dissociate as follows.

KOH(aq) →	K ⁺ (aq)	+	OH-(aq)
NaOH(aq)>	Na ⁺ (aq)	+	OH ⁻ (aq)
$Ca(OH)_2(aq) \longrightarrow$	Ca ²⁺ (aq)	+	2OH ⁻ (aq)

Arrhenius definition system was further modified by chemists since it was established that solvents also dissociate into positive and negative ions. For example water can also dissociate as follows. $H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$

From the above equation it shows that water molecules dissociate giving equal concentration of hydrogen ions and hydroxide ions. This equilibrium of hydrogen ion to hydroxide ions is changed when some substances are added to water.

Those substances which will increase the hydrogen ions concentration are called acids, while those substances which will increase the hydroxide ions concentration are called bases.

Example

Carbon (IV) oxide is an acid gas because its addition to water increases the hydrogen ions concentration so that the resulting solution has acidic properties.

 $CO_2(g) + H_2O(l) \longrightarrow H^+(aq) + HCO_3^-(aq)$

Similarly ammonia is a base because its dissolution in water increases the hydroxide ion concentration.

 $NH_3(g) + H_2O(l) \longrightarrow NH_4^+(aq) + OH^-(aq)$

Bronsted Lowry definition of acid and bases

It defines an acid as a proton donor and a base as a proton acceptor. The definition matches the Arrhenius definition of an acid, but is more general of base.

For example, not only is hydroxyl ion (OH⁻) a base but so is water (H₂O) since it can accept a proton to form hydroxonium ion (H₃O⁺). Similarly, ammonia (NH₃) is base because it can accept a proton to form ammonium ion (NH₄⁺).

HX (aq) + H₂O(l) \longrightarrow H₃O⁺ + X⁻ H₂O (l) + NH₃(g) \longrightarrow NH₄⁺(aq) + OH⁻(aq)

Generally, every substance that donates a proton gives a substance that can accept a proton back, to the original substance.

Le,

[#]Research work

Using books and from the internet, explain what are conjugate acid-base pairs and give examples. State the Lewis definition of acids and bases. Explain the relevance and usefulness of these definitions.

- 1. What is the basicity of acids?
- 2. Why are there a number of definitions of acids and bases generally accepted?

5.3 Amphoteric oxides and Hydroxides

Before getting into the study of amphoteric oxides and hydroxides, let us briefly look at what oxides are and the other types of oxides. This will help us to fully appreciate what are amphoteric oxides and amphoteric hydroxides.

What is an oxide?

An oxide is a binary compound of oxygen and other elements. It is formed when an element burns in sufficient air (or oxygen). For example, magnesium and carbon if burnt in sufficient air forms magnesium oxide and carbon dioxide respectively.

Mg(s)	+	$O_2(g)$	 MgO(s)
C(s)	+	$O_2(g)$	 $CO_2(g)$

Types of oxides

There are four common types of oxides

- (i) Acidic oxides
- (ii) Basic oxides
- (iii) Neutral oxides
- (iv) Amphoteric oxides

Research and Discussion Corner

- 1. In suitable group size, using books and from internet explain:
 - (a) meaning and how acidic, basic and neutral oxides are formed.
 - (b) give examples of acidic, basic and neutral oxides.
 - (c) the difference between oxides and peroxides.
- 2. Design, investigate and demonstrate the type of oxide formed when the following elements burn in air.
 - (a) Sulphur.
 - (b) Sodium.

- (c) Aluminium.
- 3. In your opinion, is there a difference between basic oxides and hydroxides. Explain your answer.

The Facts

From your research, you must have established that amphoteric oxides and hydroxides are able to react with both acids and bases. This is a unique property of amphoteric substances. Examples of these amphoteric oxides and hydroxides are: zinc oxide, lead (II) oxide, aluminium oxide, zinc hydroxide, lead (II) hydroxide and aluminium hydroxide.

Activity 5.1

To Investigate properties of amphoteric oxides and hydroxides with acids and alkalis

In pairs

Instructions:

- 1. Be in groups of four or five. Select a group leader and a secretary.
- 2. Identify the apparatus and chemicals you need to carry out this investigation. List them down.
- 3. Develop a fair test plan procedure for this investigation. Share the plan with other groups and your teacher. Your teacher will correct your investigation plan as is appropriate.
- 4. With the guidance of your teacher or laboratory technician proceed to carry out the investigation.
- 5. Record your observation/results appropriately.

Activity Questions

- 1. How would you ensure fair test results?
- 2. What control experiment must you include in the above investigation?
- 3. In the investigation, which substances;
 - (i) reacted with both acids and bases?

- (ii) did not react with both bases and acids?
- 4. In your judgment, why do you think substances reacted with both acids and bases and other did not?
- 5. Write chemical equations for the reactions that took place.

The Facts

I. Reactions of oxides of zinc, lead and aluminium with acids

These reactions you are familiar with. Complete their equations below.

ZnO (s)	+	$2HNO_3$ (aq)	>
PbO (s)	+	2HNO ₃ (aq)	
$Al_2O_3(s)$	+	6HNO ₃ (aq)	>

In the above reactions, the amphoteric oxides are showing basic property by reacting with an acid (nitric (V) acid) to form simple salts and water only. The hydroxides of the zinc, lead and aluminium also react in similar way as the oxides to form simple salts and water.

II. Reactions of the following metal oxides with a base (hydroxides)

Amphoteric oxides are capable of reacting with bases as well.



In metal oxides, they are showing acidic property. They react with a base forming a complex salt. They react with strong bases. The hydroxides of zinc, lead and

aluminium react with a strong base to form complex salts like their oxides counterpart above.

Same and Different

In your groups,

- (i) discuss the similar characteristics for acids, bases and amphoteric oxides.
- (ii) What are the differences, if any, between amphoteric oxides/hydroxides and acid or bases.

Activity 5.2

Work in groups

- Add a few drops of sodium hydroxide to a 2cm³ of aluminium nitrate, what do you observe? Continue adding more sodium hydroxide till excess, what do you observe?
- In another separate test tube, add a few drops of sodium hydroxide to a 2cm³ of aluminium nitrate, what do you observe? Add dilute nitric (V) acid, what do you observe?
- Predict the outcome if lead nitrate and zinc nitrate were used in place of aluminium nitrate. Explain your observations above and expected outcomes for the last step to the class.

Amphoteric oxides are metallic oxides which exhibit both acidic and basic properties in different reactions or media. That is, they can react with acid as a base and also able to react with a base as acid. Amphoteric hydroxides are also capable of reacting with both acids and bases. Zinc hydroxide, $Zn(OH)_2$, lead hydroxide, $Pb(OH)_2$, aluminium hydroxide and chromium hydroxide $Cr(OH)_3$ are examples of other common amphoteric hydroxides. Oxides of zinc, lead and aluminium are also regarded as amphoteric oxides.

Discussion corner!

- 1. In your Activity 5.2 above, you were required not to use a particular acid.
- 2. Name the acid.
- 3. Give reasons why you are not suppose to use the named acid.
- 4. Potassium hydroxide solution is not recommended for use in cleaning aluminium utensils. Using your knowledge and understanding from the above Activity 5.2, why is this the case?

- 1. Give examples of amphoteric oxides and hydroxides you are aware of.
- 2. Write the reaction equations for amphoteric oxides and hydroxides named in 1 above with the following reagents:
 - (i) Aqueous potassium hydroxide.
 - (ii) Dilute sulphuric acid.
- 3. Youareprovided with unidentified substances which consist of acidic oxides, basic oxides and amphoteric oxides. How can you distinguish the identity of each oxide?

5.4 Solubility of salts in water

Amphoteric oxides and hydroxides react with acids where possible to form a salt and water only. Amphoteric oxides and hydroxides are also able to react with strong alkali forming a complex compound.

Activity 5.3

- List some substances that dissolve in water.
- Ask your Chemistry teacher to provide you with some salts that are stored in the laboratory, try to dissolve them in water.
- Describe nature of their solubility. You should carry out experiment to establish whether the salts are soluble or insoluble.
- For the salts which are completely soluble, compare the amount that dissolve to saturate equal volumes of cold and warm water. Discuss your observations.

Activity Questions

- 1. List the apparatus and chemicals required to test the solubility of salts above.
- 2. Describe the solubility of the various salts in regards to in cold and warm waters. Explain the difference observed.
- 3. Suggest how the dissolved salts can be recovered from the solutions.



The Facts

Some salts completely dissolved (completely disappear) in water, some slightly dissolved causing suspension of particles in the solvent (water) and other do not dissolve at all. Different types of salts dissolved in different amounts in the same amount of solvent i.e. water and also at different temperatures.

When a salt completely dissolves in water to form a uniform mixture, we say that the resulting solution is homogeneous (that is, it is the same throughout). In other words, the particles of the salt have been "shared out" evenly to all parts of the liquid. Water is considered a universal solvent because it is known to dissolve most of the substances in the world.

Substances that do not dissolve completely form suspension. A solid is said to be in suspension in a liquid when small particles of it remain in the liquid undissolved. If the mixture is left undisturbed the solid particles will slowly settle to the bottom of the containing vessel, leaving the pure liquid above them.

Saturated solution

When a salt is added in small quantities at a time in a given volume of water then stirring vigorously between each addition, it brings about dissolution of the salt. Finally, it reaches a time that no more salt when added would dissolve. When this happens the solution is then said to be **saturated** with that salt at that particular temperature.

Therefore a saturated solution of a solute at a particular temperature is one which contains as much solute as it can dissolve at that temperature, in the presence of the crystals of the solute.

The concentration of a saturated solution varies with the solutes, the amount of solvent and also with the temperature. Thus, sulphur is almost insoluble in water yet readily dissolves in carbon disulphide and a rise in temperature will cause more to dissolve.

This is generally true for a number of solids; for example, lead nitrate is at least seven times more soluble in water at 80° C than it is in the same amount of water at 10° C.

The knowledge of solubility is of great importance to chemists in a number of applications such as fractional crystallisation method used in extraction of table salts (sodium chlorides) and soda ash and preparation of metals of different types of salts.

Activity 5.4

To investigate the solubility of lead (II) nitrate in water at 30°C in the laboratory

- (i) In groups of four, carry out the activity. You are provided with the following apparatus and chemicals. Discuss in your group, the procedure plan and then carry out the activity.
 - Evaporating dish
 - Watch glass
 - Measuring cylinder
 - Thermometer
 - Beaker
 - Tripod stand

- Filter paper
- Filter funnel
- Wire gauze
- Distilled water
- Bunsen burner
- Lead (II) nitrate

• Stirring rod

- Electronic balance
- (ii) Record the results of the activity in a suitable manner. You can use some of the hints from the sample results below.

Activity Questions

- 1. Give reasons why it is not suitable to strongly heat the solid obtained during the activity.
- 2. You were supposed to add the salt until some remains undissolved. Why is this important during the activity?

Sample results

Weight of evaporating dish + watch glass = 60g

Weight of evaporating dish + watch glass + solution = 89g

Weight of evaporating dish + watch glass + solid salt = 69g

Mass of saturated solution = 29g

Mass of solvent = 20g

Mass of solute = 9g

Temperature of saturated solution = 30° C

Thus, 20g of water dissolve 9g of lead (II) nitrate.

Therefore 100g of water will dissolve $\frac{9}{20} \times 100 = 45$ g of the solute at 30°C

Remember that

To give a quantitative meaning to solubility, it is necessary to fix the amount of the solvent and to state the temperature under consideration. The amount of solvent is usually fixed at 100g. It denotes a limit, that is, the maximum amount which can normally be held in that solution. Solubility is also sometimes expressed in grams of solute per litre of a solution at given a temperature.

The Facts

The solubility of a solute in a solvent at a particular temperature is the number of grams of the solute necessary to saturate 100 grams of the solvent at that temperature. The solubility of most substances increases with increase in temperature, however there are some substances whose solubility decreases with increase in temperature such as, calcium sulphate, sodium sulphate and calcium hydroxide.

By finding the solubility of a solute at varying temperatures a graph can be plotted to show how the solubility alters with increase of temperature, with many interesting results. This is called a **solubility curve** of the solute.

Worked example 5.1

Calculate the solubility of potassium chlorate if 5grams of it saturates 10 cm^3 of water at 90°C . (Density of water =1g/cm³)

First principle method

 10cm^3 of water = 10 grams

If 10 g of water dissolve 5g of KNO_3

100 g of water dissolve = ?

$$= \frac{100 \times 5}{10}$$
$$= 50g$$

Formula method

Solubility = $\frac{100 \text{ cm}^3 \times \text{mass of solute in grams}}{\text{Volume of solvent in cm}^3}$

$$\frac{100 \text{ cm}^3 \times 5g}{10 \text{ cm}^3} = 50g$$

Therefore, the solubility of KClO_3 is 50g/100grams of water at 90°C.

Worked example 5.2

Calculate the solubility of potassium nitrate if 5 grams of it saturate 40 cm³ of water at $8^{\circ}C$

First principle method

 $40 \text{ cm}^3 \text{ of water} = 40 \text{ grams}$

If 40 g of water dissolve 5g of KClO₃

100g of water dissolve ?

$$= \frac{100 \times 5}{10}$$
$$= 12.5g$$

Formula method

Solubility = $\frac{100 \text{ cm}^3 \times \text{mass of solute in grams}}{Volume \text{ of solvent in cm}^3}$ $\frac{100 \text{ cm}^3 \times 5g}{40 \text{ cm}^3} = 12.5g$

Therefore, the solubility of KNO_3 is 12.5g/100g water at 8°C.

5.5 Solubility curves

Activity 5.5

Group work

To investigate the solubility of potassium chlorate and potassium nitrate

Apparatus and chemicals

- Boiling tubes
- Thermometer $(-10^{\circ}\text{C} 110^{\circ}\text{C})$
- 10cm³ measuring cylinder
- 250cm³ beaker

- Potassium chlorate
- Potassium nitrate
- Graph papers

Caution: Potassium chlorate is a strong oxidising agent and highly corrosive.

Procedure

- 1. Weigh 5g of potassium chlorate and put into a boiling tube.
- 2. Measure 10 cm³ of distilled water and add it to the boiling tube containing potassium chlorate.
- 3. Insert a thermometer into the boiling tube and heat the mixture while stirring until all the solid dissolves. The thermometer bulb is fragile; so handle it gently.
- 4. Allow the solution to cool while stirring gently with the thermometer. Observe the solution as it cools. As soon as crystallisation begins, note and record the temperature of the solution.
- 5. Add 5cm³ of water to the solution and repeat the procedure and note the temperature at which the crystals start forming.
- 6. Continue adding 5 cm³ portions of water until 40 cm³ of water has been added, noting the temperature at which crystallisation occurs in each case.

Draw the table below in your notebook and record your results.

Total volume of water added to 5g of KClO_3 (cm ³)	10	15	20	25	30	35	40
Mass of KClO ₃ in grams per 100g of water							
Crystallisation temperature ^o C							

- 7. Repeat the whole experiment with potassium nitrate and record your data in a table similar to the one shown above.
- 8. Convert your grams in 10cm³ of water to grams in 100cm³ of water.

Activity Questions

- 1. From the two tables, draw a graph of solubility of potassium chlorate and potassium nitrate in grams per 100grams of water against crystallisation temperature (on x-axis) using the same axes.
- 2. Describe how the solubility of these two salts vary with temperature:
 - From your solubility curve, predict

- (a) The solubility of KNO_3 at $30^{\circ}C$
- (b) The solubility of KNO_3 at $10^{\circ}C$.
- (c) The mass of KNO_3 in its saturated solution at 50°C.
- (d) The percentage of KNO_3 that will crystallise out when its saturated solution at 100° C is cooled to 10° C.
- (e) Do the same four predictions for $KClO_3$.

The Facts

The amount of solute which dissolves in a solvent e.g. water at a particular temperature is different for different substances. A graph of solubility against temperature is called **solubility curve**.

The graph below shows the solubility curves of potassium chlorate and potassium nitrate.



Fig 5.1 Solubility curves of potassium chlorate and potassium nitrate

When the two graphs are drawn on the same axes it becomes possible to compare the solubility of the two salts easily. It does not mean that they were both dissolved together in the same solution.

Discussion corner!

Study the above solubility curves and discuss the following questions.

- 1. For which salt does the solubility increase most rapidly with increase in temperature?
- 2. Given a mixture of equal masses of potassium nitrate and potassium chlorate, how would you compare their crystallisation?
- 3. Predict the outcome of cooling or heating a solution using solubility curves.

The Facts

The solubility of potassium nitrate and potassium chlorate vary with temperature rise. The solubility of potassium nitrate rises steeply (rapidly) as the temperature increases while that of potassium chlorate shows moderate increase.

Remember that: Any point on the solubility line represents a saturated solution at that temperature. Any part below the solubility line represents unsaturated solutions at that temperature. It is possible to predict using the solubility curves, what will happen when the solution is cooled or heated. The curves are also useful because they can be used to show temperature when crystals are obtained from saturated solutions.

Worked example 5.3

(Use the graph in Fig 5.1 to help you answer the following questions)

- 1. If 110g of a saturated solution of potassium chlorate at 30°C containing 10g of salt is cooled to 10°C, determine the amount of salt that crystallises.
- 2. Which salt will crystallise the most?

Solution

1. From the graph above, at 10°C, the solubility of potassium chlorate is 6g/100g of water, at 30°C it is approximately 10g/100g of water. To obtain the amount of salt that will crystallise, we subtract the solubility at 10°C from that at 30°C.

=(10-6)g

= 4g of potassium chlorate will crystallise.

2. At 10°C the solubility of potassium nitrate is 22g/100g of water as shown in the graph. At 30°C, it is about 62g/100g of water.

Amount of salt that will crystallise = (62 - 22)g

= 40g

Therefore, Potassium nitrate crystallises the most, with 40g compared to potassium chlorate with only 4g.

Solubility curves of some common substances

Activity 5.6

- 1. In groups of four, investigate the solubility of the following salts of varying temperature upto 100°C:
- 2. Sodium chloride, calcium sulphate, potassium chlorate and potassium.
- 3. Plot the solubility curves for the salts investigated above.
- 4. Analyse the suitability curves of these salts.

Research work

Propose how a mixture of salts with different solubility can be separated.

5.6 Fractional crystallisation

The separation of different salts dissolved in the same solution is made possible by use of the differences in their solubility, a method known as **fractional crystallisation**.

A mixture of soluble solids can be separated by dissolving them in suitable hot solvent and then lowering the temperature slowly. The least soluble component will crystallise out first, leaving the other components in the solution. By controlling the temperature, it is sometimes possible to remove each component in turn.

Discussion corner!

- 1. In Secondary 1, you learnt about crystallisation. What is crystallisation?
- 2. Differentiate between crystallisation and fractional crystallisation.

Conserve a mixture of two salts which contains 20g of potassium chlorate and 30g of potassium nitrate in 100g of water at 50° C, separation of the two salts can be done very easily using fractional crystallisation. Let us consider the following example below.

Name of the salt	Solubility at various temperatures		
	50°C	25°C	
Potassium chlorate	18g	10g	
Potassium nitrate	85g	32g	

Table 5.2 Solubility of potassium chlorate and potassium nitrate

If the mixture is slowly cooled from 50°C to 25°C, 8g of pure potassium chlorate will crystallise out. Potassium nitrate will still be in solution form as its solubility is higher. These crystals can be filtered off. If two substances in a mixture are present in comparable proportion, they can be separated by fractional crystallisation using information from solubility curves.

Applications of Fractional Crystallisation

Some lakes contain some dissolved salts such as trona, Na_2CO_3 . $NaHCO_3.2H_2O$ and common salt NaCl. The existence of trona in such lakes is as a result of the process of natural fractional crystallisation. During the day when temperatures are high, sodium carbonate crystallises out because its solubility is low at high temperatures while common salt remains in solution. At night when the temperatures are low, sodium chloride crystallises out while sodium carbonate remains in solution.

The process of fractional crystallisation is applied to obtain sodium chloride from ocean water. Ocean water is collected into a series of shallow ponds during high tides. In these ponds, the concentration of sodium chloride increases from one pond to another as evaporation due to sun's heat continues. In the final pond, sodium chloride crystals, crystallises out and are scrapped together, piled in a heap and washed with concentrated sodium chloride solution. During the washing clean water is not used since it will dissolve the sodium chloride already obtained. Instead, it is washed with a salty solution. After it is clean, it is dried and finally packed for use of table salt. This salt has impurities of magnesium chloride and calcium chloride which also crystallise from ocean water but they removed during washing with concentrated sodium chloride solution (brine). Sodium chloride is almost insoluble in brine.

Apart from using solubility curves to predict what happens when the solution is cooled or heated, you can also calculate, using given data, the amount of salt dissolved or deposited. Below are worked examples to explain how this is done.

Worked example 5.4

Salt X and Y are mixed together and dissolved to saturate 100g of water at 100° C. The solution was then filtered. This solution was then cooled to 30° C. The solubility of X at 100° C is 80g/100g of water and at 30° C it is 36g/100g of water. The solubility of Y at 100° C is 100g/100g of water and at 30° C it is 50g/100g of water. What is the composition of the mixture at 30° C?

Solution

At 30° C, the mass of X deposited = (80 - 36)

$$= 44g$$

At 30° C, the mass of Y deposited = (100 - 50)g

Therefore, the mixture contains

- (i) 36g of X in solution and 44g of X undissolved
- (ii) 50g of Y in solution and 50g of Y undissolved.

Uses of solubility curves

We have seen that solubility curves help us to:

- Know the effect of temperature on the solubility of salts.
- Know how to separate a mixture of salts in solid or solution form using differences in solubilities of the salts in the mixture.
- Determine the mass of crystals that would be obtained by cooling a given volume of hot saturated solution from one known temperature to another.

Check your progress 5.3

- 1. Describe two types of solubility.
- 2. Explain how solubility curve is useful in the extraction of common salt.
- At 100°C, the solubility of a salt X is 80g/100g of water. At 20°C its solubility is 42g/100g of water. How much salt X will be deposited if initially it was saturated and the solution filtered at 100°C in 100g of water and then cooled to 20°C.



5.7 Water hardness

Experiments on this topic will require the following reagents: soap solution, samples of temporary hard water and permanent hard water. These substances for use can be made as follows.

Activity 5.7

Work in groups

- To prepare some soap solution.
- To prepare some temporary hard water.
- To prepare some permanent hard water.

Preparing soap solution

- (a) Using the knowledge of concentration, in your group prepare 1 percent soap solution. This solution goes cloudy on standing and therefore should be made just before when needed. The cloudy solution can be filtered off if necessary.
- (b) Using internet and from textbooks, describe how to prepare soap solution that can be stored for a long time.

Preparing temporary hard water

You are provided with calcium hydroxide and distilled water, in your groups proceed to prepare water with temporary hardness. Research from books and internet.

Preparing permanent hard water

Add about 1g of powdered calcium sulphate to a half-litre bottle full of distilled water. Shake and leave for a day or so, and decant or filter off the clear solution. Add distilled water to the solid if more hard water is required.

Activity 5.8

Work in groups

To compare the different hardness of various water.

You are provided with the following apparatus and some reagents. Using your knowledge of titration process, proceed to analyse the different kinds of water hardness.
Apparatus and chemicals

- Burette and its stand.
- Soap solution.
- Conical flasks and one cork to fit.
- Measuring cylinder, 20 or 50 cm³.
- Distilled water.
- Any natural hard waters or artificially prepared hard waters as carried out in activity 5.4.

The following will guide you.

- (i) Title of experience will guide you.
- (ii) Procedure:
 - clearly indicate the essentials steps
 - set up a control experiment.
- (iii) Recording data
- (iv) Provide the precautions that must be observed to obtain consistent and fair test results.
- (v) Conclusions and inferences.

The table below is a suggested format to help you with your data recording.

Type of water	Burette readings (cm ³)	Volume of soap solution used (cm ³)
20 cm ³ distilled water		cm ³
20 cm ³ tap water		cm ³
20 cm ³ sea water or river water e.t.c)		cm ³
20 cm ³ temporarily hard water		cm ³
20 cm ³ permanently hard water		cm ³

Activity Questions

- 1. Give reasons why it would be advisable to put the burette in sloping position and run in the soap solution slowly
- 2. What other visible change other than lathering, occurs when soap solution is added to the hard water? Explain this occurrence.
- 3. Suggest control experiment for this activity.

The Facts

Water hardness

Distilled or rain water forms lather very easily with soap. Tap water, water from wells, river, lake and sea waters will vary in the amount of soap used depending on the location of your school. Solutions containing sulphates of calcium and magnesium ions do not produce lather easily.

Distilled water or rain water contains no dissolved solid impurities. They lather easily with soap. The water that readily forms lather with soap is known as **soft water**. Hard water does not readily form lather with soap.

How water becomes hard

Rain dissolves carbon(IV) dioxide as it falls to form carbonic acid. Therefore rain water is very dilute carbonic acid.

Water + Carbon(IV) oxide _____ Carbonic acid

H2O(l) + CO₂(g) \longrightarrow H₂CO₃(aq)

If this water passes through rocks containing calcium and Magnesium carbonates, some of it dissolves to form respective hydrogen carbonates and the water is said to be hard because the hydrogen carbonates (HCO_3^{-}) reacts with soap to form a complex.

 $CaCO_3(s) + HCO_3(aq) \longrightarrow Ca(HCO_3)_2(aq)$

Magnesium carbonate + Hydrogen carbonate -->Magnesium hydrogen carbonate

 $MgCO_3(s)$ + $H_2CO_3(aq)$ \longrightarrow $Mg(HCO_3)_2(aq)$

When rain-water passes through rocks containing sulphates of magnesium

and calcium (CaSO₄. $2H_2O$, gypsum), portions of the rocks dissolve into the rain water. Thus the water contains sulphate ions. These ions react with the ions in soap forming white insoluble substances called scum.

Temporary water hardness

It is caused by the presence of soluble hydrogen carbonates of calcium or magnesium or both hydrogen carbonates in water. Water which exhibits such hardness include well and some borehole water depending on the location. It is called temporary hardness because it can be removed by boiling.

Permanent water hardness

It is caused by the presence of dissolved calcium sulphate and magnesium sulphate. This occurs when water dissolves small amounts of calcium and magnesium sulphate from ground rocks as it seeps on its way to reservoirs, lakes, rivers or to the sea. This type of hardness cannot be removed by boiling. It can however be removed through chemical treatment or distillation.

Effects of water hardness

As earlier mentioned, hard water does not form lather easily with soap. Instead a grey-white suspension or scum is formed with water.

Discussion corner!

In your groups,

- 1. Conduct research and write a report on why hard water does not easily form lather with soap?
- 2. Water containing calcium carbonate is not hard water yet containing calcium hydrogen carbonate is hard water. Justify the occurences.

Methods of removing water hardness

Activity 5.9

To demonstrate the effect of sodium carbonate (soda ash) and of boiling on water hardness

Apparatus and chemicals

Burette

Soap solution

- Measuring cylinder
- Tap water
- Temporarily hard water
- Permanently hard water

- Three conical flasks and one cork
- Sodium carbonate
- Tripod and gauze
- Bunsen burner.

Procedure

- 1. Fill a burette with soap solution and note the reading.
- 2. Measure 20 cm³ of tap water into three conical flasks (if the tap water in your district is not hard, omit this part of the experiment and just use the temporarily and permanently hard waters).
- 3. To one flask add a crystal of sodium carbonate about the size of a pea, shake until it dissolves, and allow to stand for at least 5 minutes. Place the second flask on a tripod and gauze and boil the water gently for at least 10 minutes.
- 4. Find out as shown in activity 5.4 how much soap solution is required to form a permanent lather (one lasting at least 2 minutes) with the contents of the three flasks.
- 5. Wash the flask. Repeat the whole experiment with temporarily hard water and then with permanently hard water. Do any visible changes occur when these solutions are boiled?

Type of water	Burette readings	Volume of soap solution used cm ³
20 cm ³ tap water	<u> </u>	cm ³
20 cm ³ tap water		
after boiling	$_$ cm ³	<u> </u>
20 cm ³ water		
and sodium		
carbonate	$ cm^3$	<u> </u>

The Facts

When the temporarily hard water was boiled i.e water containing calcium hydrogen carbonate the boiled water formed lather easily. This is so because the calcium hydrogen carbonate decomposed into calcium carbonate which precipitated from the solution. The remaining solution (water) now is able to form lather easily.

Calcium hydrogencarbonate <u>heat</u> calcium carbonate + water + carbon (IV) oxide

 $Ca(HCO_3)_2(aq) \longrightarrow CaCO_3(s) + H_2O(l) + CO_2(g)$

The permanently hard water (containing magnesium sulphate solution) even after being heated did not form lather easily. This is because magnesium sulphate does not decompose on heating.

Removal of Temporary water hardness

Temporary water hardness can be removed by:

(a) Boiling

Boiling decomposes the soluble hydrogen carbonates to insoluble carbonates, carbon (IV) oxide and water.

Calcium hydrogen carbonate \longrightarrow Calcium carbonate + water + carbon (IV) oxide Ca(HCO₃)₂(aq) \longrightarrow CaCO₃(s) + H₂O(1) + CO₂(g) Magnesium hydrogen \longrightarrow Magnesium carbonate + water + carbon (IV) oxide

 $Mg(HCO_3)_2(aq) \longrightarrow MgCO_3(s) + H_2O(l) + CO_2(g)$

The insoluble carbonates formed remove the calcium and magnesium ions from the water hence the water becomes soft.

(b) Addition of calcium hydroxide or sodium carbonate

The method of removing temporary hardness by boiling is too expensive to be used on a large scale. Temporary water hardness removal can be done on large scale inexpensively by adding calculated amounts of calcium hydroxide or sodium carbonate. This causes precipitation of calcium and magnesium ions as carbonates.

Calcium hydrogen carbonate + calcium hydroxide \longrightarrow calcium carbonate + water Ca(HCO₃)₂(aq) + Ca(OH)₂(aq) \longrightarrow 2CaCO₃(s) + 2 H₂O(l) Calcium hydrogen + Sodium carbonate \longrightarrow Calcium carbonate + sodium hydrogen carbonate Ca(HCO₃)₂(aq) + Na₂CO₃(aq) \longrightarrow CaCO₃(s) + 2NaHCO₃(aq) (251) It is important to know that the sodium ions from sodium hydrogen carbonate present in water as seen in the above equation does not cause water hardness.

Removal of permanent water hardness

Permanent water hardness can be removed by;

(a) Addition of sodium carbonate

Addition of sodium carbonate causes the precipitation of calcium and magnesium ions as insoluble carbonates.

Calcium sulphate + sodium carbonate -----> calcium carbonate + sodium sulphate

 $CaSO_4(aq) + Na_2CO_3(aq) \longrightarrow CaCO_3(s) + Na_2SO_4(aq)$

(b) Distillation

This method removes both permanent and temporary hardness because it removes all the dissolved solids. However, it is expensive to use it to soften large amounts of water. It can, however be used in the laboratory to make distilled water for analytical work or for batteries.

(c) Use of ion exchange method

This method involves use of a resin made of an insoluble complex of a sodium salt known as **sodium permutit.** This method is also referred to as permutit process. Permutit releases sodium ions which exchange with the calcium and magnesium ions in the hard water. Calcium and magnesium ions now become part of the insoluble complex compound.





Fig 5.2 (a): Permutit process

Sodium ions (Na⁺(aq)) in water do not cause water hardness. When all the sodium ions on the permutit column have been exchanged with calcium or magnesium ions. i.e. resin contains ions of calcium and magnesium, it is said to be discharged. The permutit, can be "regenerated" or "recharged" by passing concentrated sodium chloride solution (brine) through it. Another ion-exchange process takes place. The calcium or magnesium ions are washed away or leaving the permutit now full of sodium ready for use again.



Fig 5.2 (b): Ion-exchange column during regeneration

Advantages and disadvantages of hard water

Adv	antages	Disa	advanta	iges			
1.	The calcium compound present	1.	Waste	of	soap	during	scum
	in hard water is good for teeth		format	ion			
	and bone formation.						
2.	Helps to form a lead carbonate	2.	Scum	leav	ves di	rty mar	ks on
	coat in water pipes made of		clothes	afte	r washi	ing.	
	lead. This prevents some lead						
	from dissolving in water which						
	otherwise could give rise to lead						
	poisoning.						

3.	Good for formation of shells of animals. Snails obtain calcium for their shell formation from hard water.	3.	Deposits carbonates of calcium and magnesium as "fur"on electrical appliances e.g. kettles, boilers thereby making them
			inefficient i.e using more fuel,
			hence increasing power costs.
4.	Calcium and magnesium are	4.	The deposits of carbonates can
	necessary for both plant and		block pipes boilers pipes reducing
	animal growth. Hard water is a		efficiency to heat conductivity,
	source of this.		water flow and even accelerated
			rusting

Remember that

Methods used to remove permanent hardness in water can also be applied in removing temporary water hardness.

Further Activity

- 1. Find out if the water in your locality is hard water. If so, analyse if the hardness is temporary or permanent.
- 2. Your Chemistry class has been requested to come up with simple inexpensive project to help a community disadvantage with very salty hard water. In your groups, design and devise such equipment that can be used to solve this community's water problem.

The following outline cab guide you.

- (i) Project title
- (ii) Feasibility study
- (iii) Processed water treatment stage
- (iv) Equipment and reagents needed
- (v) Challenges likely to be encountered and suggested solutions.

- 1. Describe the importance of hard water treatment and purification.
- 2. State two disadvantages of using hard water in industries.
- 3. It is not advisable to use excess calcium hydroxide solution in water purification. Explain.

Glossary

A

Absolute temperature:

It is the temperature measured with respect to absolute zero on the Kelvin scale.

Absolute zero:

This is the lowest possible temperature that can be achieved. It is the starting point of absolute temperature scale (Kelvin scale). It is -273° C.

Addition polymer:

A polymer formed by an addition reaction-the monomer molecules must contain C = C double bond or $C \equiv C$ triple bond; for example polythene is formed from ethene.

Alkane

A series of hydrocarbons with the general formula (C_nH_{2n+2}) . They are saturated compounds as they have only single bonds between carbon atoms in their structure.

Alkenes:

A series of hydrocarbons with the general formula (C_nH_{2n}) . They are unsaturated molecules as they have a C = C (double bond) somewhere in the chain.

Alkynes:

A series of hydrocarbons with the general formula (C_nH_{2n-2}) . They are unsaturated molecules as have a $C \equiv C$ triple bond somewhere in the chain.

Artificial fertiliser:

A substance added to soil to increase the amount of elements such as nitrogen, potassium and phosphorus (NPK fertilisers). This enables crops to grow more healthy and produces higher yields.

Avogadro number or constant:

The number of particles (atoms, molecules, ions or electrons) in one mole of a substance. It is usually 6.023×10^{23} .

B

Bleaching:

The process by which colour is partially or wholly removed from a coloured substance. **Bleaching powder:**

A chlorine - containing substance used in bleaching textiles or sterilising water. It is made from solid calcium hydroxide and chlorine. Its chemical name is calcium hypochlorite.

Boyle's Law:

The volume of a given mass of a gas is inversely proportional to its pressure provided that the temperature remains constant.

Bromination:

The addition of bromine to an unsaturated organic compound e.g. ethene plus bromine

С

Charles Law:

The volume of a given mass of a gas at constant pressure is directly proportional to its absolute temperature.

Chloride test:

A chloride ion is present in a substance if it forms a white precipitate when dilute nitric acid and silver nitrate solution are added to a solution of the substance.

Chlorination:

Addition of chlorine to an unsaturated organic compound or the treatment of water with chlorine to destroy germs.

Constant

A magnitude that does not change in value e.g Avogadro's constant (6.023×10^{23}).

Contact process

The industrial manufacture of sulphuric acid in which the sulphur(IV) oxide and oxygen come in contact with vanadium(V) oxide catalyst.

Cracking:

The breaking down of long hydrocarbon molecules with heat and/or a catalyst to produce short hydrocarbon molecule and alkene.

D

Diffusion:

The process by which particles spread out as a result of the random motion.

Displacement reactions:

A reaction in which a more reactive element displaces a less reactive element from a solution of its salt.

E

Empirical formula

A chemical formula for a compound which shows the simplest ratio of atoms present. It does not give the actual number of each atoms in most cases e.g. the empirical formula of ethane (C_2H_6) is CH_3 .

Excess:

In a chemical reaction there is a connection between the quantities of substances reacting. In practice if one of the reactants is present in larger quantities than is required for the reaction it is said to be in excess.

Exothermic reaction:

A reaction that gives out heat e.g. burning of magnesium.

F

Frasch process:

The process of obtaining sulphur from sulphur beds below the earth's surface. Superheated water is pumped down a shaft to liquefy the sulphur, which is then forced to the surface.

Free radicals:

Atoms or groups of atoms with unpaired electrons and therefore highly reactive. They can be produced in high-energy radiation such as ultra-violet light in photochemical reactions.

Functional group:

Refers to the site of a chemical reaction in an organic compound.

Η

Homologous series.

The name given to a family of organic compounds e.g. alkane. Members of the series conform to a general formula and show similar chemical reactions, varying only in their reactivity.

Hydrocarbons:

Compounds which contains carbon and hydrogen only, e.g. methane (CH_{4}) .

Hydrogenation:

The chemical addition of hydrogen to a substance, e.g. ethene (C_2H_4) to give ethane (C_2H_6) . Oil plus hydrogen to give margarine is also called **hydrogenation**.



Ι

Inert substance:

A substance that reacts passively with other substances, e.g. nitrogen reacts with air only at very high temperatures.

Isomers:

Compounds which have the same molecular formula but different structural arrangements of the atoms i.e they have different structural formulae.

Isomerism

It is the occurrence of two or more compounds with the same molecular formula but different structural formula

Κ

Kelvin scale

Is a scale of temperature with absolute zero as the starting point.

L

Law:

A statement of scientific fact concerning natural phenomena, e.g. Boyle's law.

Liquefaction:

The process of converting a gas to a liquid.

Μ

Molar gas volume

The volume of one mole of a gas at specified temperature and pressure e.g. the molar gas volume of any gas at s.t.p is 22.4 dm³

Morality:

The concentration of a solution expressed in moles of solute per one dm³ of solution.

Mole:

The measure of amount of substance in chemistry. One mole of a substance has a mass equal to its relative formula mass in grams. This amount of substance contain 6.023×10^{23} (Avogadro's constant) of atoms, molecules, ions or formula unit depending on the substance considered.

Molecular formula

A formula which shows the actual number of atoms of element present in a molecule of a compound.

Monomer:

A small molecule, such as ethene, which can be polymerised to make a polymer. Many monomers are joined together to make a polymer. For example ethene can be polymerised to make polythene.

Ν

Nitride:

A compound of nitrogen and an electropositive element e.g. Magnesium nitride (Mg_3N_2) .

0

Organic chemistry:

The study of carbon compounds, both natural and synthetic.

Organic matter:

Plant and animal material containing carbon as one of the elements, e.g. starch.

Ozone: (trioxygen)

A colourless gas (O_3) . It is produced in the upper atmosphere (10 to 50 km) above earth's surface by the action of high– energy ultraviolet radiation on oxygen gas, producing oxygen atoms. These oxygen atoms then react to produce the ozone gas.

Ozone depletion:

This is the production of a "hole" in the ozone layer by the action of certain compounds, mostly CFCs.

Ozone layer:

A layer of ozone in the atmosphere which prevents harmful ultra-violet radiation reaching the earth's surface.

Ρ

Petroleum:

A liquid mixture of hydrocarbons obtained from beneath the surface of the ground.

Phenomenon:

A situation or an event of scientific interest susceptible of scientific description and explanation.

Polymer:

Alongchainmoleculebuiltup of a number of repeating units or monomerse.g (polyethene) is a polymer made up from ethene molecules linked together.

Polymerisation:

The chemical reaction in which molecules (monomers) join together to form a long-chain polymer.

Polar solvent:

The molecules of some solvent, such as water contain slight positive and negative charges due to different strengths of attraction of shared electrons making bonds. A polar solvent dissolves substances containing ionic bonds. Solvents without these charges are called non-polar solvents, e.g methylbenzene.

Q

Qualitative:

A qualitative study or analysis is one which depends upon changes in appearance only.

Quantitative:

This involves a study or analysis of quantities e.g. mass, volume among others.

R

Relative atomic mass (A_r) :

The average mass of an atom of an element, taking account of the isotopes of the element on a scale where a carbon -12 atoms has a mass of exactly 12.00.

Relative molecular mass (RMM):

The sum, of the relative atomic mass of atoms present in the molecule or one mole of a compound. It is also called relative formula mass (R.F.M)

S

Saturated organic compound:

A compound which have all the carbon atoms in its molecules linked with another by a single covalent bond, e.g. ethane, propane.

Standard pressure:

The pressure exerted by a column of mercury exactly 760 mm (76 cm) at $O^{\circ}C$ (273 K).

Standard solution

A solution whose concentration is known.

Standard temperature:

O $^{\rm o}C$ or 273 K

Stoichiometric equation:

A normal balanced chemical equation which shows the reactants and products and their physical states.

Substitution reaction

A reaction in which an atom (or atoms) of a hydrocarbon molecule is (are) replaced by different atoms (s), without changing the molecules general structure.

Sulphate test:

If a white precipitate is produced when dilute hydrochloric acid or nitric acid and barium chloride or nitrate solution are added to a solution of a substance, sulphate ions are present.

Systematic naming

Describes a way of naming compounds based on a special international agreed system, the IUPAC system. For example C_2H_6 is called **ethane**. It has two carbons. The **-ane** shows the absence of double or triple bond i.e. It is a saturated hydrocarbon.

Т

Titration

A method of quantitative analysis using solutions. A volume of one solution is slowly added to known volume of another solution using a burette until an end-point is reached. If an acid and alkali are used then an indicator is used to show that the end point has been reached.

Titre: The volume in cm³ of solution run from the burette during titration. It is also called titration value.

u

Unsaturated organic compound.

A compound which has the carbon atoms linked by two (double) or three (triple) covalent bonds e.g. ethene ($H_2C = CH_2$), ethyne (HC = CH).

V

Vulcanisation

The process of converting weak plastic inelastic raw rubber into a strong elastic non-plastic material. For example heating of rubber with sulphur.

Appendix I

Element	Symbol	Atomic number	Relative atomic mass
Aluminium	Al	13	27
Argon	Ar	18	40
Barium	Ba	56	127
Beryllium	Be	4	9
Boron	В	5	11
Bromine	Br	35	80
Calcium	Ca	20	40
Carbon	С	6	12
Chlorine	CI	17	35.5
Chromium	Cr	24	52
Copper	Cu	29	63.5
Fluorine	F	9	19
Gold	Au	79	197
Helium	He	2	4
Hydrogen	Н	1	1
Iodine	Ι	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	200
Neon	Ne	10	20
Nickel	Ni	28	59
Nitrogen	Ν	7	14
Oxygen	0	8	16
Phosphorus	Р	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

Atomic numbers and relative atomic masses of some elements



Appendix II

Periodic Table

