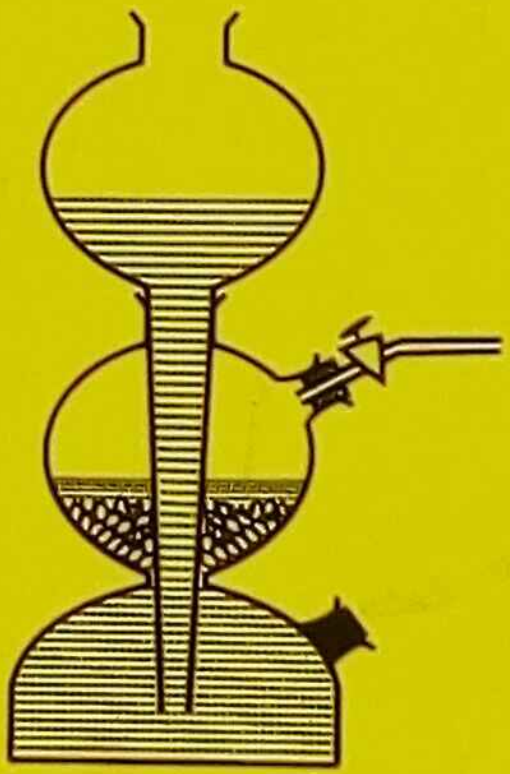
Second Revised Edition

# UNDERSTANDING CHEMISTRY

For Schools and Colleges



Godwin O. OJOKUKU

I

(SECOND REVISED EDITION)

# UNDERSTANDING CHEMISTRY

## For

## Schools and Colleges

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**PRESS-ON CHEMBOOKS**

# Preface

*Understanding Chemistry* has been written to meet the requirements of the 2009 revised chemistry curriculum and needs of students preparing for the West African Examinations Council (WAEC) and National Examinations Council (NECO) examinations. The topics covered are also sufficient to prepare candidates for the Universities Matriculation Examination (UME) of the Joint Admissions and Matriculation Board (JAMB) in Nigeria.

In order to conform to the Examinations Councils' desire that practical experiments should be the basis of teaching chemistry, much stress has been placed on practical work. Most of the experiments included are those that can be performed by the students, or used as demonstration by the teacher using simple laboratory set-ups. The book is intended to complement practical work.

I have tried to ensure that *Understanding Chemistry* will be suitable for use by Senior Secondary students of all abilities. Consequently, each chapter is divided into sections with many worked examples, where necessary, to illustrate the applications of chemical concepts and theories. The revision exercises at the end of each section are such that they will encourage the students to read more carefully and promote their *higher order thinking skills*. Most of these exercises (multiple-choice and short-structured) have been carefully selected from past WAEC, NECO and JAMB examinations. Many of them are designed to test understanding and applications of chemical concepts rather than factual recall. It is very important that efforts should be made to answer these questions. They can be used in classroom discussions, in tests, or for homework. Answers to multiple-choice and numerical questions are provided at the *end of each chapter*.

Every effort has been made in *Understanding Chemistry* to enable students to develop laboratory skills needed for laboratory work and prepare them adequately for chemistry practical and alternative to practical examinations.

In order to stimulate the interest of students in chemistry in particular and in science in general, the inter-relationships between chemistry and other branches of science, mathematics and technology have been mentioned where necessary, and the applications of chemistry in everyday life and in the industry emphasized.

The order in which the topics are presented is not necessarily the order in which they should be taught; it is simply a convenient arrangement of topics within a single-volume textbook.

Care has been taken to use simple English, when necessary, to avoid ambiguity, and to present the topics using the down-to-earth approach.

Godwin O. Ojokuku,
Government Science Secondary School,
Dutsin-Ma, Katsina State.
31st July, 2010.

# Preface to the Revised Edition

The book has been fully revised Understanding Chemistry has been found suitable for Students studying Chemistry and related courses in the tertiary institutions – hence, the change in the title.

September, 2012 G.O.O.

# Preface to the Second Revised Edition

Understanding Chemistry has been fully revised. Some of the sub-topics in the book have been rearranged, in order to improve on the sequencing, and hence, provide a better understanding of the concepts involved.

Many of the solved problems and revision exercises (multiple-choice and short-structured) have been carefully selected from past and up to July 2017 WAEC, NECO and JAMB examinations.

GSSS. Faskari.
July, 2017 G.O.O.

## Acknowledgements

I wish to express my heartfelt thanks and lifelong indebtedness to the following:

• The past and present Executive Secretaries of the Katsina State Science and Technical Education Board, STEB, from year -2002 to date, namely: Alhaji Bishir M. Daku, Alhaji Aliyu Abubakar Mashi and Alhaji Bala Isyaku Mashi, for their kindness, understanding and hospitality, and for giving me the opportunity to develop and use the materials in this book to teach at Government Science Secondary School, Dutsin-Ma, Katsina State;

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• My wife, Comfort; children, Adeola and Ayoola and grand-child, Oludara, for their patience and understanding during the course of this work.

During the course of writing this book, I consulted and gathered relevant information from numerous chemistry textbooks, journal articles and other publications, that it is impossible to acknowledge their authors by name. I am especially grateful the Science Teachers Association of Nigeria, STAN, and the Chemistry Panel of the association, for organizing annual conferences and workshops. Their current publications served as sources of information in the areas of teaching and learning of chemistry.

Most of the questions used as worked examples, solved problems and revision exercises in this book are past questions from examinations conducted WAEC, NECO and JAMB.

I sincerely acknowledge the efforts of the Managing Director of MacChin Multimedia Designers, Mr. Gideon L. Dine and his staff in conjunction with the Publishers of Press-on Chembooks, for working hard to see this book published.

Finally, To God be the Glory.

September, 2010

Godwin O. Ojokuku

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• The former and present students of Government Science Secondary School, Faskari, from year 2010 to date, for their cooperation.

• Finally, To God be the Glory.

GSSS, Faskari,
July, 2017

Godwin O. Ojokuku

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# 1

# •INTRODUCTION TO CHEMISTRY•

## 1.0 What this Chapter is All About

- The Chemical World
- Chemistry and Enviroment.
- Chemistry of Life.
- Chemistry and Industry.

## 1.1 Introduction

### What is Matter?

Things that are regarded as *matter* surround us. *Matter is anything that has mass and occupies space*. The houses we live in; the clothes we wear; the food we eat; the air we breathe; the water we drink; stone, wood, plants, animals – including the person reading this book – are examples of *matter*.

### What is Chemistry?

**Chemistry** is a branch of **science** that deals with the study of *matter*: its structure, composition, properties, and the changes it undergoes. It involves the study of material substances that occur on earth and in the universe. Other branches of science are **biology** and **physics**.

### What are Chemicals?

All forms of *matter* – whether *natural* or *artificial* (*man-made*) are **chemical substances**.

### Why Study Chemistry?

We study chemistry in order to understand the way *matter* behaves and reacts under different conditions, and to device ways in which *it* can be used to improve our life. Chemistry concerns with the utilization of *natural* substances and the creation of *artificial* ones.

A study of chemistry enables those who study it to acquire certain *scientific skills* such as handling of laboratory apparatus, performing experiments with ease, and thinking scientifically. The *application of knowledge and skills gathered through the study of science* is called **technology**. **Scientists** in the field of chemistry are called **chemists**.

### Contents of Chemistry

Chemistry is a relevant and developing science, which is making essential contributions towards human life, society, industry and civilization. Its contents can be divided into four broad categories:

### Revision Exercises

1. Define the term matter.
2. Give two examples of matter.
3. What is chemistry? Why is the study of chemistry so important?
4. The following are chemical substances except
   A. cold sweat  B. powdered starch.
   C. sweet smell.  D. dry leaf.

## 1.2 The Scientific Method

### Law, Theory and Hypothesis

Chemistry, like other branches of science, has developed through a logical scientific method of working. A **scientific law** is a statement that *describes experimental facts*. For instance: Experiments have shown that *all gases are compressible*. How can this *fact* be explained?

A **theory** is *an idea suggested to explain* an *experimental fact*. For instance: *Compressibility in gases* is explained on the assumption that *gases are made up of small particles that are far apart*.

A *theory* must be testable. During the process of testing, it may be modified or rejected and a new one is formulated. When an *idea* is still in the testing stage, it is called a **hypothesis**; and when other scientists universally accept it, it becomes a *theory*.

*Scientific methods of analysis* involve the following steps:

1. Identifying a problem;
2. Collecting facts (or data) on the problem;
3. Formulating hypothesis;
4. Testing the hypothesis;
5. Rejecting, modifying, or formulating new hypothesis;
6. Continuing testing, until a theory is formed.

*Scientific method* can be applied to everyday problems.

**Guided Discovery: Reporting Experiments**

*As a chemist-in-training, you will be guided when carrying out experiments in the chemistry laboratory. Such hands-on experiments should be reported logically, using the following format:*

**Date and Title:** *Date and title to be written clearly on top of the page.*

**Aim:** *States what is to be done or the purpose.*

**Objective:** *Gives what is to be achieved.*

(Aim and objective of an experiment may be identical)

**Materials:** *Chemical substances and laboratory apparatus required for the experiment.*

**Method** or **Procedure:** *Step-by-step description on how to carry out the experiment.*

**Diagram:** *Shows the arrangement of the apparatus – the set-up – to be used.*

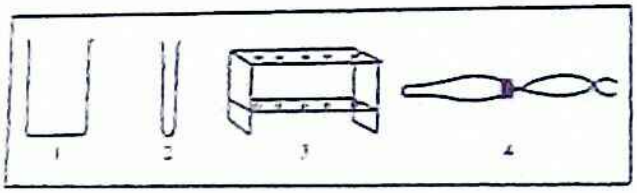
**Observation** or **Result:** *What you see or notice; readings or data you obtain during the course of the experiment.*

**Discussion** or **Inference:** *What can be deduced from the observation or result?*

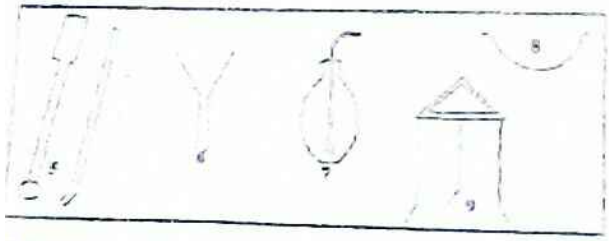
**Conclusion:** *Summary of findings.*

## Chemistry Laboratory Apparatus

Some of the commonly used chemistry laboratory pieces of apparatus are drawn below. They are of different shapes and sizes. You should be able to identify them by their names, draw them, and be familiar with their uses. Most of these apparatus are made of glass; they should be handled with care to avoid damages.

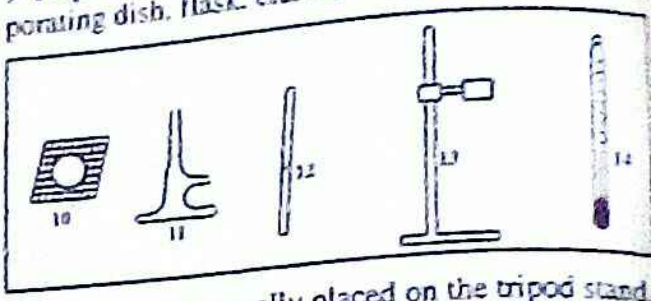



1 **Beaker:** To hold solids and liquids.
2 **Test-tube:** To hold reactants.
3 **Test-tube rack:** In keeping the test-tubes
4 **Test-tube holder:** In holding the test-tube when heating is required.

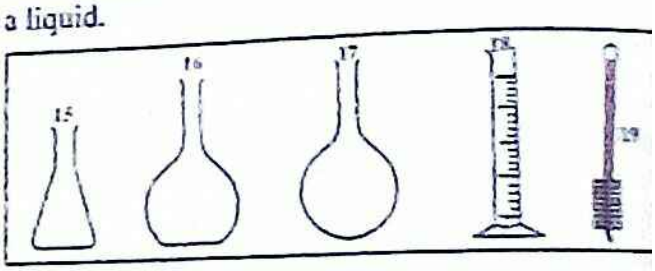



5 **Spatula:** In transferring a solid into a test-tube.
6 **Filter funnel:** For filtration and for transferring a liquid into an apparatus with a narrow neck.

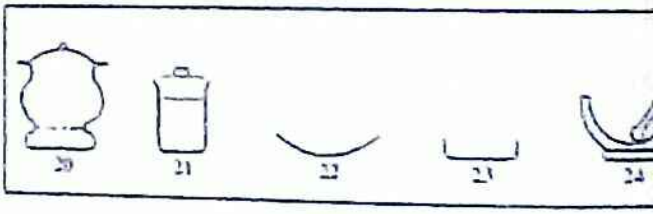
7 **Wash bottle:** It is made of flexible plastic; used in holding distilled water for rinsing glassware such as a test-tube.
8 **Evaporating dish:** To hold a liquid to be evaporated.
9 **Tripod stand with wire-gauze:** To support evaporating dish, flask, etc. when heating is required.




10 **Wire gauze:** usually placed on the tripod stand
11 **Bunsen burner:** in providing high temperatur
for heating by the combustion of liquefied gas.
12 **Glass rod:** for stirring a mixture, or as
support when pouring a liquid from a beaker.
13 **Retort stand with clamp:** Generally used as
support for thermometer, funnel, etc.
14 **Thermometer:** in measuring the temperature
a liquid.




15 **Conical flask:** in holding reactants.
16 **Flat-bottomed flask:** for holding reactants t
require heating.
17 **Round-bottomed flask:** for holding reactan
that require heating.
18 **Measuring cylinder:** to measure the volume
a liquid.
19 **Brush:** For cleaning the interior part of t
tubes, beakers, etc.




20 **Desiccator:** Used in keeping a solid dry.
21 **Weighing bottle:** For weighing small qua
of a solid.
22 **Watch glass:** is circular, shallow and w
round bottom. It is used in keeping solids
drying and as a cover for a beaker.

23 **Petri dish:** is circular, shallow and with a flat bottom. It is used in keeping solids for drying.
24 **Mortar and pestle:** used in grinding coarse solids into fine powder.

**Revision Exercises**
5. What is a scientific law?
6. Give the difference between theory and hypothesis.
7. List five laboratory apparatus and their uses.

## 1.3 Chemistry in Everyday Activities

### Chemical Processes

*Experiments in chemistry are not magic*; they are everyday activities, observations and experiences outside the school.

**Daily Activities**

- Striking of match.
- Cooking with firewood, kerosene or cooking gas.
- Bathing with *toilet* soap;
- Washing clothes with *laundry* soap or detergent;
- Burning of a candle;
- Breathing in and out, etc.

**Observations and Experiences**

- Honey is *sweet* to taste, but unripe mango is sour.
- Coca-cola drink releases gas when opened;
- Vapour of onion makes you shed tears;
- Fresh palmwine *foams*, while stale one does not;
- Iron nails rust when exposed to the atmosphere;
- Kerosene and water are *immiscible* liquids.

### Kitchen-Chemistry

It is not only in the school laboratory that experiments are performed. In homes, it is in the kitchen that controlled chemical processes and changes take place.

Cooking in the kitchen involves sorting, estimating, measuring, weighing, pounding, washing, sieving, grinding, observing, boiling, frying, roasting, refluxing, diluting, concentrating, titrating, etc.

### Products of Chemistry

The *products of chemistry* are too numerous to mention, and are being used in everyday life.

**Our daily needs** are products of chemistry: Soap, detergent, toothpaste, toothbrush, plate, spoon, cup, pair of sandals, clothes, plastics, kerosene, etc.

**Household materials:** Kitchen utensils; chairs, tables, carpets, boxes, bags, etc; mattresses and pillows; creams; matches; batteries; camphor; razor blade; air fresheners; insecticides (with trade names such as *Mobil*, *Rambo*, etc), etc.

**Clothing materials:** Man-made textile fibres such as polyesters and nylon, dyes, buttons, zips, etc.

**Agricultural materials:** Fertilizers (NPK, urea, super phosphate) and herbicides (weed-killers).

**Construction and Building materials:** Cement, iron and steel; roofing sheets, plastic pipes, paints.

**Drugs:** *Panadol*, *aspirin*, etc.

**Explosives:** Dynamites and TNT.

**Poisons:** Mercury, chlorine, etc.

**Revision Exercises**
8. Which of the following is not kitchen-chemistry?
   A. Boiling of water. B. Roasting of groundnuts.
   C. Tasting of soup. D. Raising of yam.
9. Which of the following is not a product of chemistry?
   A. Plastic cup. B. Bicycle tyre. C. Rain water.
   D. Local soap. E. Air freshener.
10. Which of the following is not true?
   A. Experiments in chemistry are magic.
   B. Chemistry is life.
   C. Detergent foams readily in water than soap.
   D. Spatula is a laboratory apparatus.
11. List four pieces of protective apparatus in the lab.

## 1.4 Applications of Chemistry

Chemistry plays a major role towards the provision of the basic necessities of life. Its applications in various fields cannot be quantified. Chemical processes, products of chemistry, chemical research and technology are put into use in the following fields:

**Agriculture:** Production of fertilizers, insecticides and herbicides; Preservatives; Soil analysis; Agricultural implements.

**Hospital:** Drugs (pharmaceuticals), Anaesthetics in surgery; surgical equipment are made of stainless steel; Sterilization of hospital equipment.

**Industry:** Manufacturing of goods, food processing, Industrial equipment, tools.

**Transportation:** Structural materials for the constructions of vehicles, trains, planes etc; fuels.

**Military:** Arms and ammunitions, Camouflages, Bullet-proof wears; Helmets.

**Teaching:** Laboratory chemicals, School chalks, Nurturing and training of future scientists.

**Engineering:** Structural materials, chips, insulators, etc.

**Space Science:** Production of structural materials for the constructions of rockets, rocket fuels.

**Revision Exercises**

12 Which of the following is *not* a product of application of chemistry?
A. Soap B. Air C. Paint D. Plastic E. Candle

13 State three applications of chemistry in each of the following:
a. Hospital b. Agriculture c. Military

## 1.5 Hazardous and Adverse Effects of Chemical Products

When chemical substances are being produced and put into use, living and non-living things are adversely affected by the production of hazardous materials.

### Environmental Pollution

Pollution is caused by the following:

- Vehicle exhausts emit hazardous gases into the atmosphere, thereby, causing air pollution;
- Effluents and toxic wastes from chemical and petro-chemical industries are dumped on land or discharged into rivers, thereby causing water, soil and air pollutions;
- Plastic containers litter the surrounding; they are not biodegradable (not decomposed by bacteria) thereby, causing soil pollution.
- Crude oil spillage causes water and soil pollution.

### Corrosion

Iron and steel objects exposed to the atmosphere rust when in contact with water and air. These objects are either protected or replaced; this is additional cost.

### Drug Abuse

Drugs are chemical substances that are supposed to be used to cure diseases. However, some drugs, like aspirin, morphine and cocaine, when *abused (wrongly used)*, can cause damages in the body.

**Revision Exercises**

14 List three adverse effects of chemical substances.
15 State two causes of environmental pollution.
16 What is drug abuse?
17 State the effect of drug abuse.

## 1.6 Career Prospects in Chemistry

### Courses of Study

Chemistry is one of the subjects that must be offered and passed at credit level, in the Senior Secondary School examinations by students aspiring to read science-related courses in the higher institutions: university, polytechnic and college of education.

The following courses are linked to chemistry: Agriculture; Human medicine, Pharmacy; Nursing; Veterinary medicine; Engineering; Pure Sciences; Textile Science; Food technology.

### Careers Linked to Chemistry

The following careers are linked to chemistry: Agriculturist; Chemical engineer; Medical doctor; Veterinary doctor; Nurse; Pharmacist; Biochemist; Microbiologist; Industrial chemist; Soil chemist;

### Job Opportunities

There are numerous job opportunities in public and private sectors of the economy available to anyone who is able to complete an educational career in chemistry in the university, polytechnic or college of education:

**Teaching sector:** Chemistry teacher in the secondary school; Chemistry lecturer in the university, polytechnic or college of education; Laboratory assistant in the secondary school; Technologist in the university, polytechnic or college of education.

**Industrial sector:** Chemists and laboratory technologists are required in all goods-manufacturing industries – chemicals; petroleum and petrochemicals; pharmaceutical; foods and beverages; textiles; glass; paints; cement; soap and detergents; etc.

**An Entrepreneur:** A trained-chemist should be able to utilize the knowledge and skills acquired and become a successful *entrepreneur* – in goods manufacturing, sales of goods, consultancy services, laboratory services, etc – once the *government is able to provide the enabling environment.*

**Revision Exercises**

18 List four courses in the university that are linked to chemistry.
19 List four careers that are linked to chemistry.
20 A university-trained chemist cannot become a
A. business man B. teacher
C. lawyer D. sales representative

**Answers to Revision Exercises**

4. C 8. D 9. C 10. A 12. B 20. C

# 2

# •NATURE OF MATTER•

## 2.1 States and Classes of Matter

### Introduction

*Matter* has been defined as *anything that has mass and occupies space*, and that all forms of matter are *chemical substances*. *A chemical substance is any form of matter that is single in composition*. It has its own characteristic qualities and behaviours called ***properties***.

A *chemical substance* has two types of properties: ***physical*** and ***chemical***.

### Physical Properties

*Physical properties* are qualities or behaviours that can be determined at any time on the same substance, such as: state of the substance, its colour, odour, taste, density, melting point, boiling point and solubility.

Based on *physical properties*, matter exists in *three* distinct states: ***solid***, ***liquid*** and ***gas***. Iron, wood and sand are solids; water and kerosene are liquids; while air and smoke are gases.

### Chemical Properties

*Chemical properties* are behaviours during which a substance undergoes a permanent change. A new substance, that has different physical properties from the original substance is produced. For instance:

- A matchstick will *burn*, once and for all, to produce charcoal (a black solid), smoke (a gas), light and heat. *Combustion is a chemical process.*
- An iron nail will *rust*, when exposed to air and moisture. *Rusting is a chemical process.*
- The food we eat in the form of carbohydrates, fats, oils and proteins *decompose* in our body into *simpler substances. Decomposition is a chemical process.*

Based on *chemical properties*, the *three* classes of matter are: ***elements***, ***compounds*** and ***mixtures***.

*Any form of matter, which contains a single substance, is* ***pure***. *Elements* and *compounds* are pure substances. *A mixture is composed of two or more substances; hence, it is* ***impure***.

### Revision Exercises

1. What is a chemical substance?
2. What are *physical* properties? Give two examples.
3. What are *chemical* properties? Give two examples.
4. Mention the three states of matter.
5. What are the three classes of matter?

## 2.2 Elements

### An Element

An *element* is a substance that cannot be broken into simpler substances by any chemical method. Examples include: iron, copper, carbon and iodine.

As at now, 118 substances are classified as elements. Out of this number, 94 occur naturally; the rest are man-made or artificial. A list of some common elements is given in Table 2.1.

### Revision Exercises

6. What is an element?
7. Name two elements that you are familiar with.

### Chemical Symbols of Elements

The *names of elements* are represented by ***chemical symbols***. A Swedish chemist, Jons Berzelius (1818), suggested the use of the *letters of the alphabets* as the *chemical symbols of elements*.

In some elements, the first letters in their names, in *capital*, stand for their symbols. For instance: the symbol of hydrogen is **H**, oxygen is **O**, while carbon is **C**.

In other elements, a combination of the *first two letters* or the *first and another letter* in their names are used, written in such a way that the first letter is in capital, while the second is a small letter. For instance: the symbol of calcium is **Ca** (not ca), aluminium is **Al** (not AL), cobalt is **Co** (not co or CO), while chlorine is **Cl** (not cl or CL).

The symbols of some metals are derived from their Latin names. For instance: the symbol of iron **Fe** (not fe) is derived from the Latin word *ferrum*, that of lead, **Pb** (not pb) is from Latin *plumbum*, while sodium is **Na** (not NA or na) is derived from Latin word *natrium*.

*No two elements have the same symbol.*

The symbols of some elements are given in Table 2.1. Students are advised to master them quickly.

**Table 2.1** *Some common elements and their symbols*

| Element | Symb | Element | Sym |
|---|---|---|---|
| Hydrogen | H | Lithium | Li |
| Carbon | C | Neon | Ne |
| Oxygen | O | Nickel | Ni |
| Nitrogen | N | Silicon | Si |
| Sulphur | S | Titanium | Ti |
| Boron | B | Chlorine | Cl |
| Fluorine | F | Chromium | Cr |
| Iodine | I | Magnesium | Mg |
| Phosphorus | P | Manganese | Mn |
| Uranium | U | Zinc | Zn |
| Vanadium | V | Potassium (Kalium) | K |
| Aluminium | Al | Gold (Aurum) | Au |
| Argon | Ar | Copper (Cuprum) | Cu |
| Barium | Ba | Iron (Ferrum) | Fe |
| Beryllium | Be | Sodium (Natrium) | Na |
| Bromine | Br | Silver (Argentum) | Ag |
| Calcium | Ca | Mercury(Hydrargyrum) | Hg |
| Cobalt | Co | Lead (Plumbum) | Pb |
| Helium | He | Tin (Stannum) | Sn |

**Revision Exercises**

8 What is a chemical symbol?

9 Give the symbols of the following elements:

a. Hydrogen b. Silicon c. Carbon
d. Helium e. Sodium f. Chlorine

10 Name the elements with the following symbols:

a. F b. Sn c. Br d. B e. Co
f. Mg g. P h. Ba i. Be j. Ca

11 What term is used to describe something that has mass and can occupy space?

### Classes of Elements

The *two* general classes of elements are *metals* and *nonmetals*.

### Metals

The *general physical* properties of metals are:

1. They are elements with characteristic metallic lustre that reflects light.
2. They are good conductors of heat and electricity.
3. Some are *malleable* (can be hammered into thin sheets).
4. Some are *ductile* (can be drawn into wire).
5. They have high densities (except magnesium and aluminium; while potassium and sodium are so soft that they can be cut with a knife).
6. They are solids with high melting and boiling points (except mercury, which is a dense liquid).

### Nonmetals

The *general physical* properties of nonmetals are:

1. They are elements with no metallic lustre, hence do not reflect light (except diamond).
2. They are poor conductors of heat and electricity.
3. They are *brittle*, hence, cannot be hammered into sheets, or drawn into wire.
4. They have low densities (except iodine).
5. They have relatively low melting and boiling points (except carbon).
6. Most nonmetals are gases: oxygen and nitrogen; bromine is a liquid. Some of them are solids at room temperatures, e.g. sulphur and carbon.

### Metalloids

*Metalloids* are elements with properties that are intermediate between those of metals and non-metals. The most common metalloid is *silicon*; a *semi-conductor*. Graphite, a form of carbon, conducts electricity. Diamond, another form of carbon, has a shining metallic lustre, but a non-conductor.

The two most abundant elements on the earth's surface and in the earth's crust are *oxygen* and *silicon*. Others – such as iron, sodium, calcium, aluminium, potassium and magnesium are found in the earth's crust.

**Revision Exercises**

12 Name the two general classes of elements.

13 What are *metalloids*? Give two examples.

14 List three differences between the physical properties of a metal and a nonmetal.

15 Which element is a liquid metal?

16 Mention two of the most abundant elements on the earth's surface.

17 Which of the following is not a characteristic physical properties of metals ? They are:

A. good conductors of heat and electricity.
B. ductile C. brittle D. malleable.

## 2.3 Compounds

*A compound is a chemical substance formed when two or more elements are chemically combined in a fixed proportion by mass.* For example: Water is a compound of hydrogen and oxygen, chemically combined in the ratio 1: 8 by mass respectively.

The elements in a compound are joined together by *chemical bonds*. A *chemical bond* is a strong *attractive force* that makes it difficult to separate the elements in a compound. Some examples of compounds and their constituent elements are given below:

| Compound | Constituent Elements |
|---|---|
| Water | *Hydrogen and oxygen* |
| Common salt | *Sodium and chlorine* |
| Sand | *Silicon and oxygen* |
| Chalk or Marble | *Calcium, carbon and oxygen* |
| Petrol or Kerosene | *Carbon and hydrogen* |
| Sucrose (Sugar) | *Carbon, hydrogen and oxygen* |

The properties of a compound differ from those of the constituent elements. For instance:

- Hydrogen and oxygen are colourless and odourless gases, while, water, a compound of hydrogen and oxygen is a colourless liquid with an *insipid* taste.
- Sodium is a soft and silvery solid metal, while chlorine is a greenish-yellow gas, which is choking and poisonous. However, common salt, which is a compound of sodium and chlorine, is a white crystalline solid with a characteristic salty taste.

Based on their natural sources, compounds are broadly classified into *inorganic* and *organic*:

***Inorganic*** compounds are those that occur in the form of mineral ores, and found in the earth's crust, e.g. sand, limestone and rock salt.

***Organic*** compounds are found in plants (as carbohydrate, fats and oils); in animals (as proteins, fats and oils); and in liquid minerals (crude oil).

### Revision Exercises

18 Define the term compound.

19 Name the elements present in each of the following compounds: a. Water b. Sucrose c. Chalk

20 The most abundant element on the earth's surface is
A. aluminium B. nitrogen C. oxygen D. iron.

## 2.4 Mixtures

A *mixture* is made up of two or more substances, which can be mixed together, mechanically, in any proportion.

Most of the naturally occurring substances we see frequently are not pure; they are mixtures. A few examples are: air, soil, well-water, tap-water, sea-water, milk, palm oil, blood, sweat, and urine.

### Types of Mixtures

There are six distinct types of mixtures:

1. ***Mixture of solids***: e.g. soil, rocksalt, and brass.
2. ***Mixture of solid and liquid***: e.g. muddy water, sea-water, well-water, tincture of iodine (a solution of iodine in alcohol), milk and writing ink (a solution of dyes in water).
3. ***Mixture of solid and gas***: e.g. smoke (from cigarette, etc) and sand storm (dust in air).
4. ***Mixture of liquids***: water and alcohol (*miscible*), kerosene and water (*immiscible*) and alcoholic beverages – such as whisky or gin.
5. ***Mixture of liquid and gas***: e.g. fog, mist or dew, cloud, perfume-spray, bubble, lather, bottled drinks – such as *Coca-Cola* and *7-Up*.
6. ***Mixture of gases***: e.g. air and rotten-egg smell.

The physical properties of a mixture depend on the nature and quantities of its constituents.

### Experiments

**1. To show that Ordinary Water is a Mixture**

a. Place about 20 $cm^3$ of well-water in a beaker and heat until it boils. Allow it to cool; then taste.
***Observation***: The boiled water has an *insipid* taste, i.e. tasteless.

b. Taste an unboiled well-water sample.
***Observation***: It has a characteristic taste.
***Explanation***: The characteristic taste of unboiled water is due to the presence of dissolved gases and solids in ordinary water. Once a *water sample* is boiled, the dissolved gases are expelled, and hence, becomes tasteless.

c. Place about 50 $cm^3$ of well water in an evaporating dish; then, heat to dryness.
***Observation***: A dirty-white residue is obtained.
***Explanation***: Well-water contains dissolved solids.

**2. Sweetness of a Solution**

a. Add *one* spatula of granulated sugar into 20 $cm^3$ of water in a beaker. Stir the mixture, to obtain a solution; then, taste.
***Observation***: The solution is *sweet* to taste.

b. Add *two or three* spatula of granulated sugar into 20 $cm^3$ of water in a beaker. Stir the mixture, to obtain a solution; then, taste.
***Observation***: The solution is *sweet* to taste; but *sweeter* than the solution obtained in 2a above.
***Conclusion***: The sweetness of a solution depends on the quantity of sugar dissolved in a given volume of water.

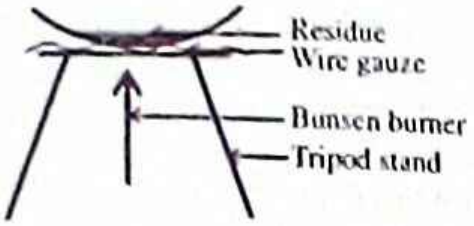
### Solved Problem 1

Describe an experiment to show that seawater is a mixture.

**Title:** *Mixture of Substances*
**Aim:** *To show that seawater is a mixture.*
**Materials:** *Seawater sample, evaporating dish, tripod stand and wire-gauze, Bunsen burner, and measuring cylinder.*
**Procedure:** *Measure 50 $cm^3$ of seawater with a measuring cylinder and transfer into a clean evaporating dish.*

*Place the dish on a tripod stand supported with wire gauze.*
*Heat the content of the dish using a Bunsen burner flame, and evaporate to dryness. Allow to cool.*

**Diagram:**




**Observation:** *A dirty-white residue is obtained.*
**Inference:** *Seawater contains dissolved solids.*
**Conclusion:** *Seawater is a mixture.*

**Revision Exercises**

**21** What is a mixture?
**22** Mention three types of mixtures. Give one example of each type.
**23** Which of the following is not a mixture?
Brine ; ink ; soil ; sucrose ; air
**24** Which class(es) of matter is/are described as
a. pure, and why? b. impure, and why?

## Classes of Mixtures

The two classes of mixtures are *homogeneous* and *heterogeneous*.

### *Homogeneous Mixtures*

A *mixture* is *homogeneous*, if its constituents are distributed uniformly or it appears to be of uniform composition.

A solution of sugar in water is an example of a *homogeneous liquid solution*. Although the proportions can be varied, the mixture will be uniformly colourless and sweet.

*Fresh air* is an example of a *homogeneous gaseous solution*; while brass, bronze and steel are *homogeneous solid solutions* called *alloys*.

### *Heterogeneous Mixtures*

A *mixture* is *heterogeneous* if its constituents are not distributed uniformly – with some parts having different *physical* properties.

Soil samples, muddy-water and smoke are examples of heterogeneous mixtures.

**Revision Exercises**

**25** Define and give one example of
a. homogeneous mixture; b. heterogeneous mixture.
**26** State *one* difference between homogeneous and heterogeneous mixtures.
**27** Classify the following into *homogeneous* and *heterogeneous* mixtures:
Brine, sweat, muddy water, table salt, sand storm, blood, rotten-egg smell.

## 2.5 Differences between Mixtures and Compounds

A *mixture* of iron filings (grey) and sulphur powder (yellow), and a *compound* of iron and sulphur – called iron(II) sulphide (a black solid) can be used to illustrate the differences between a mixture and a compound.

### *Experiments on a Mixture of Iron filings and Sulphur powder*

**1a.** Mix 5 spatulaful of each of iron filings and powdered sulphur in a beaker.
*Observations*:
- *The particles of iron filings and sulphur powder can still be seen with the naked eye.*
- *The particles of iron are still grey, while those of sulphur are still yellow.*

**b.** Stir the mixture with a magnet.
*Observation: Only the iron filings are attracted, leaving the sulphur powder.*

**c.** Add 20 $cm^3$ of carbon disulphide to the mixture in a beaker (use the *fume cupboard*).
*Observation: Particles of sulphur dissolves.*

**2.** Heat a mixture of iron filings (7.0 *g*) and sulphur powder (4.0 *g*) in a *crucible* on a *triangular pipeclay* support placed on a tripod stand. Stir the mixture continuously.
*Observations*:
- *A solid black-mass is obtained.*
- *No particles of iron or sulphur can be seen.*
- *The black mass, when ground into powder, is not attracted by a magnet.*
- *Black solid is not soluble in carbon disulphide.*

Table 2.2 gives the main differences between a mixture and a compound.

**Table 2.2**: *Differences between a mixture and a compound.*

| Mixture | Compound |
|---|---|
| 1 Constituents can be mixed in any proportion. | Constituents are present in a fixed proportion by mass. |
| 2 No chemical bonds between constituents. | Constituents are joined by chemical bonds. |
| 3 Constituents retain their identities or properties; hence, can be separated easily, e.g. a mixture of iron filings and sulphur | Constituents lose their identities or properties; hence, cannot be easily separated, e.g. sodium and chlorine in sodium chloride. |
| 4 Constituents cannot be represented by a chemical formula. | Constituents can be represented by a chemical formula. |

**Solved Problem**

1. Consider the following group of words/letters:
   A. Elements, compounds and mixtures.
   B. Metals, nonmetals and metalloids.
   C. B, Ba and Br.
   D. Iron, oxygen and tin.
   E. Gas, liquid and solid.

Identify the group representing:

a. states of matter. (*Answer*: E)
b. classes of elements. (*Answer*: B)
c. classes of matter. (*Answer*: A)
d. names of elements. (*Answer*: D)
e. symbols of elements. (*Answer*: C)

**Revision Exercises**

28 Give **THREE** differences between mixtures and compounds. [NECO]

29 Give three differences between a mixture of iron and sulphur, and a compound of iron and sulphur.

## 2.6 Solutions and Suspensions

### Solutions

A *solution* is a *homogeneous mixture of two or more substances*. It is formed when one substance *dissolves* in another substance. *A substance that dissolves another substance is the solvent* while *a substance that dissolves in another substance is the solute*.

Scientifically: **Solute + Solvent = Solution**

That is: A *solute dissolves in a solvent to give a solution*. The *dissolved solute particles in a liquid solution are called crystalloids*. *Crystalloids* are so small that they cannot be seen with the naked eye.

A *solute can be a solid, liquid, or gas*. So also, a *solvent can be a solid, liquid or gas*. Usually, the *solvent is always present in a larger proportion than the solute in a solution*.

The commonest solvent is water; it is a liquid. Others are: alcohols (e.g. ethanol and methylated spirit), petrol, kerosene, and carbon disulphide.

The following are examples of common *solutions* and their constituent solutes and solvents:

| Solution | Solute | Solvent |
|---|---|---|
| *Brine* | Common salt | Water |
| *Tincture of iodine* | Iodine | Alcohol |
| *Air* | Oxygen | Nitrogen |
| *Brass* | Zinc | Copper |
| *Bronze* | Tin | Copper |
| *Steel* | Carbon | Iron |

### Saturated and Unsaturated Solutions

When a small quantity of a solute, such as *granulated sugar*, is placed in a beaker containing a known volume of water and the mixture is stirred, the solute dissolves to give a colourless solution. As more of the solute is added to the solution with stirring, it dissolves. However, a stage is reached in which the solute no longer dissolve in the solution.

*A solution in which the solute can no longer dissolve in the presence of undissolved solute at a given temperature is said to be* ***saturated***, while *a solution, which is still capable of dissolving more solute at a given temperature is* ***unsaturated***.

*Brine is a saturated solution of common salt in water.*

### Dilute and Concentrated Solutions

*A solution which contains a small quantity of the solute dissolved in a large quantity of the solvent is said to be dilute*, while a *solution, which contains a large quantity of the solute dissolved in a small volume of the solvent is said to be* ***concentrated***.

### Properties of a Liquid Solution

A *dilute solution of common salt in water* is a typical example of a *true solution*:

1. A liquid solution is either colourless or coloured – but transparent (not opaque).
2. Its colour and composition are homogeneous.
3. The *dissolved solute particles* in a solution, called ***crystalloids***, do not settle down on standing the solution. It is a *true* solution.
4. The size of a *crystalloid* is too small to be seen with the naked eye; hence, a *true solution* will *not* scatter a beam of light that passes through it.

### Suspension

A *suspension* is a mixture in which the particles of the solute are neither soluble nor insoluble, but are suspended. Such a mixture is *heterogeneous*, e.g.

- *Muddy water* is a suspension of clay particles in water.
- ***Sandstorm*** is a suspension of dust and fine particles of sand in air.

The *particles* in a *suspension* are called ***sediments***.

### Properties of a Suspension

*Muddy water* is a typical example of a *suspension*.

1. Its colour and composition are not *uniform*.
2. The particles in a suspension, *sediments*, can be seen with the naked eye.
3. The *sediments* will settle down due to gravity, by a process called ***sedimentation***.

### Colloidal Dispersions

*A colloidal dispersion is neither a liquid solution nor a suspension*. It is a *false* solution, e.g. natural milk, blood, gum, glue, and smoke.

The particles in a *colloidal dispersion* are known as *colloids*. Their sizes are intermediate between *crystalloids and sediments*. They cannot be seen with the naked eye, but will scatter a beam of light that passes through. *The scattering of light by colloids in a colloidal solution is called* **Tyndall effect**.

### Classes of Colloidal dispersions

In a *colloidal solution*, the *solvent* is the medium of *dispersion*; the *solute* is *dispersed* in the *solvent*.

The three classes of colloidal dispersions are: *sol or gel, emulsion, and aerosol*.

#### 1. Sol and Gel

*Sol is the dispersion of a solid in a liquid*, e.g. *Starch solution consists of starch powder dispersed in water*.

When a *sol* becomes *concentrated*, it forms a *gel*, where in, the *solute* is now more *dominant* than the *solvent*, e.g. *natural honey*.

#### 2. Emulsion

***Emulsion** is the dispersion of a liquid in another liquid*, e.g. *Natural milk is a dispersion of butter-fat in a dilute sugar solution*; while *paints are liquid solutions dispersed in water or alcohols*.

#### 3. Aerosol

*Aerosol is the dispersion of a liquid or solid in a gas*:

- *Cigarette smoke is tobacco particles in air.*
- *Fog (smoke), mist, dew, or cloud is an aerosol dispersion of water vapour in air.*
- *Insecticides (Shelltox, Mobil, or Raid) and perfume-sprays are liquid solutions in air.*
- *Lather, foam or gas bubble is a dispersion of air in a liquid.*

### Membranes

***Membranes** are porous sieves*. They can be used to distinguish between a *suspension, solution, or colloidal dispersion*.

There are *three* types of membranes:

#### 1. Filter paper (non-permeable membrane)

It is a *special porous paper* used for *filtration*. A *solution or colloidal dispersion will pass through a filter paper without leaving a residue* (*crystalloids* and *colloids* are small enough to pass through). *Sediments cannot pass through; they will leave a residue on the filter paper*.

#### 2. Parchment (permeable) membrane

Only a *solution* will pass through a *parchment* (*permeable*) *membrane* by ***dialysis***. *Colloids* and *sediments* are too large in size to pass through.

***Dialysis** is the process whereby crystalloids in a true solution pass through a permeable membrane*.

#### 3. Cellophane (semi-permeable) membrane

Only the *solvent in a solution* (*e. g. water*) *will pass through a semi-permeable membrane by osmosis*. *Crystalloids* in a solution are too large to pass through.

***Osmosis** is the movement of solvent particles from a region of lower concentration to a region of higher concentration through a semi-permeable membrane*. The in-take of water in the soil by plants through the roots is by *osmosis*.

### Revision Exercises

30 Give **two** properties of a liquid solution.

31 A solution that contains as much solute as it can dissolve at a given temperature is said to be
A. concentrated. B. saturated. C. dilute.
D. unsaturated

32 State **two** *differences* between a *solution* and a *suspension*.

33 Distinguish between a *dilute* solution and a *concentrated* solutions.

34 Arrange the following in order of increasing size:
*colloids, crystalloids and sediments*.

35a. What is Tyndall effect?
b. Give **two** examples of solutions that exhibit this phenomenon. [NECO]

36 Explain the following terms:
a. Osmosis b. Dialysis.

37 Mention **three** types of membrane, and give one example of each of them.

## 2.10 Liquid Solvents and their Uses

*Water* is the *commonest* and a *universal solvent*. This is because it is the most useful of all solvents, and can dissolve more substances – solids, liquids and gases – than any other liquid solvent.

Water is *polar*; it is a solvent for *inorganic* compounds. Other liquid solvents are *organic* compounds of carbon, which are *non-polar*; hence, *immiscible* with water. They are good solvents for *organic* compounds, but poor solvents for *inorganic* compounds: *Like dissolves like*. This explains why petrol or kerosene can be used to remove palm oil-stain, paint-stain, or grease – but water cannot.

A few examples of organic solvents and their common uses are as follows:

1. *Alcohols* (e. g. *methanol* and *ethanol*) and *esters* (have characteristic sweet smell) are used as solvents for paints, nail varnishes and perfumes. A solution of iodine in an alcohol is called *tincture of iodine*; it is an antiseptic. Alcohols and water are *miscible*.

2. *Propanone (acetone), petrol, kerosene, ethers, turpentine, and tetrachloromethane* are solvents for (i.e. will dissolve) paints, nail varnishes, waxes, fats, oils and greases. *Tetrachloromethane* is used in laundry – in dry-cleaning of clothes.
3. *Benzene* dissolves rubber to give rubber solution used for vulcanizing vehicle tyres.
4. *Turpentine* is used in laundry and dry cleaning.
5. *Carbon disulphide* will dissolve sulphur powder. Its vapour is poisonous.
6. Organic solvents are used in the extraction of colours (pigments) or chlorophyll from flowering plants.

*A solution of borax in water* can be used to remove coffee or tea stain.

### Solved Problems

2. Mention a property of a colloidal dispersion, which a solution does not have. *(Tyndall effect)*

3. State the term used to describe:
a. A solution in which the solute can no longer dissolve at a given temperature. *[Saturated]*
b. A process whereby suspended particles in a liquid settle down due to gravity. *[Sedimentation]*
c. The dispersion of liquid particles in another liquid. *[Emulsion]*

4. Explain **briefly** why benzene is miscible with ethanol but immiscible with water.
*Benzene and ethanol are organic solvents, which are non-polar, while water is an inorganic solvent, which is polar. Since like dissolves like, benzene is miscible with ethanol, and immiscible with water.*

### Revision Exercises

38 What term is used to describe a substance that
a. dissolves another substance?
b. dissolves in another substance?

39 Give one use of each of the following solvents:
a. Ethanol; b. Petrol; c. Benzene; d. Water.

## 2.11 General Physical Properties of States of Matter

### Solid State

A substance is a solid if at atmospheric pressure its melting point is well above the room temperature of 25 °C. A stone is a typical solid.

1. A solid has *definite size* (or *volume*) and *shape*.
2. It cannot be compressed except at high pressure.
3. It diffuses slowly.

The *physical* properties of a solid is due to the *strong forces of attraction or cohesion between its particles*. Hence, the particles are held firmly, and fixed rigidly in definite positions, in a *highly ordered* manner. As such, there is no space between them.

Consequently, the only mode of *motion* a solid particle can perform is ***vibrational***; that is, the particle can only *vibrate* to and from its fixed position.

### Liquid State

A substance is a liquid if at atmospheric pressure it *melts* at a temperature below the room temperature of 25 °C, and boils at a temperature above the room temperature. *Water* is a typical liquid.

1. A liquid has *a definite volume, but no definite shape*; it assumes the shape of the container, since *its particles have no fixed positions.*
2. A liquid is practically *incompressible*, because, there is *no space between the particles.*
3. It diffuses slowly, and can evaporate – when placed in an open container.

The *physical* properties of a liquid is due to the fact that the forces of attraction between the particles are not as strong as those between solid particles; hence, a liquid can flow. So also, liquid state is *more disordered than the solid state*; hence, liquid particles can ***vibrate*** and ***rotate***.

### Gaseous State

A substance is a gas, if at atmospheric pressure it *boils at a temperature below* the room temperature. Air is a typical example.

1. A gas has *no definite shape and volume*; usually, it spreads to occupy any available space.
2. It has a low density and is highly compressible.
4. It expands when heated.
3. It diffuses rapidly; hence, gases are *miscible* in any proportion.

The *physical* properties of a gas is due to the fact that the particles are far from each other, move independently, and perform rapid random motion. Consequently, gas particles can ***vibrate***, ***rotate*** and ***translate*** (perform *zigzag motion*).




*Complete Order* (*Not Disordered*) *Less Order* (*More Disordered*) *No Order* (*Most Disordered*)

**Fig 2.1:** *Order and disorder in the states of matter*

The gaseous state is the simplest state of matter. It is the *least ordered* (or *most disordered*). Figure 2.1 shows the diagrammatic representations of the states of matter.

Summary:

| | State | Nature | Shape | Volume | Compressibility | Diffusion |
|---|---|---|---|---|---|---|
| 1. | Solid | Melts above room temperature, e.g. stone | Constant | Constant at room Temperature | Cannot be compressed | Very slow |
| 2. | Liquid | Melts below and boils above room temperature, e.g. water | Changes with shape of container | Definite at a given temperature | Cannot be compressed | Slowly, but can flow. |
| 3. | Gas | Boils below the room temperature | Not definite. Spread to cover any available space | Not definite. Spread to cover any available space | Can be compressed readily | Very rapid |

**Revision Exercises**

40 State three physical properties of each state of matter.

41 List two differences between the physical properties of: a. solids and liquids; b. liquids and gases; c. solids and gases.

42 Which state of matter contains particles that are:
a. readily compressed?
b. held firmly by some forces of cohesion?
c. involved in rapid random motion? [WAEC]

43 Which mode(s) of motion is/are exhibited by particles of a I. gas; II. liquid; III. solid?

44 Smoke consists of
A. solid particles dispersed in liquid;
B. solid or liquid particles dispersed in gas;
C. gas or liquid particles dispersed in liquid.
D. liquid particles dispersed in liquid. [JAMB]

## 2.12 Changes of States and Entropy

### Heating

When a *solid is heated*, the *heat absorbed* is used in increasing the *vibration* of the particles, and in breaking the various forces of cohesion between the particles. When enough heat has been absorbed by the particles, they become mobile, and eventually, turn to *liquid* (see fig 2.2).

*Any process in which heat is absorbed from the surrounding is endothermic.* The *process whereby a solid changes to liquid is called melting*, and *the temperature it occurs is called melting point.*

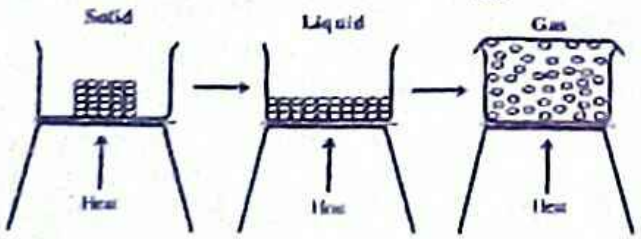



**Fig 2.2** *Changes from Solid State*

*As the liquid is being heated, the heat absorbed is used in breaking up the forces of attraction between the particles.* With time, the particles become independent and turn to *gas* (see fig 2.2). *The process whereby a liquid changes to a gas is called boiling or vapourisation, and the temperature at which it occurs is called boiling point.*

It is possible for liquid particles to turn to a gas at a temperature lower than the boiling point. When this occurs, it is called *evaporation*. It is a natural phenomenon, which occurs at the surface of a liquid at all temperatures.

### Cooling

The changes described above are *reversible*, i.e. can be made to proceed in the *opposite* direction. When a *gas* is *cooled*, the particles *lose heat* to the surrounding, come close together to reform the attractive forces, and turn to *liquid*. The process is called *liquefaction* or *condensation*. *Any process in which heat is released or lost to the surrounding is exothermic.*

Further *cooling* of a *liquid* increases the attractive forces between the particles, leading to the formation of a *solid*. The process is called *freezing* or *solidification*.

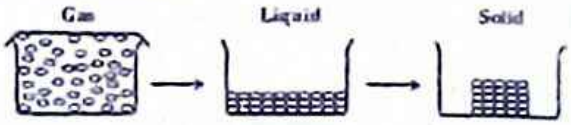



**Fig 2.3** *Changes from Solid State*

Water, a *liquid at room temperature*, is unique in that it can exist as a *solid* (*ice*) at a very low temperature, and as a *gas* (*steam* or *water vapour*) at its boiling point.

### Sublimation

Certain solids (iodine, sulphur, naphthalene and ammonium chloride), when heated, do not melt to form a liquid. Instead, their particles change directly to a gas. On cooling, the gas changes directly to a solid – without passing through the liquid state. *The change of state from a solid directly to a gas, or from a gas directly to a solid is called sublimation*. Such a solid is said to *sublime*.

Figure 2.4 illustrates changes brought about by heating and cooling.




1 melting; 2 freezing or solidification; 3 boiling or vaporisation; 4 liquefaction; 5 or 6 is sublimation.

Fig 2.4: Changes of states

### Entropy

*Changes from solid to liquid, and then, to gas represent changes of states.* During these changes, the *arrangements of the particles* are altered from a *complete ordered* state in a solid (where there is *no disorder*), to a *less ordered* state in a liquid (where there is a *little disorder*), and finally, to the *least ordered* state in a gas (where there is *complete disorder*). *The property that describes the disorderliness of a system is called* ***entropy***.

Generally, an *increase in temperature* leads to an *increase in the entropy* of a system. So also, *when a solid changes to a liquid, or a liquid changes to a gas, there is an increase in the disorderliness*; hence, *entropy increases*).

In these changes, the arrangements of the particles change from a *disordered gaseous state*, to a *less disordered liquid state*, and finally, to the *least disordered* (i.e. *most ordered*) *solid state* (see fig 2.3).

*Diffusion, evaporation, dialysis, and osmosis, which are natural phenomena, and sublimation, illustrate that matter is made up of small particles that are in a state of constant motion.*

### Revision Exercises

45a Explain each of the following changes/processes:
i. Melting, ii. Evaporation; iii. Freezing;
iv. Boiling; v. Sublimation; vi. Condensation
b What can bring about any of these changes in a above?

46 Distinguish between:
a. melting and melting point;
b. boiling and boiling point;
c. boiling and evaporation.

47a Define entropy.
b Which of the three states of matter has the
i. lowest entropy? ii. highest entropy?
c Indicate whether there is a decrease, increase, or no change in entropy in each of the following changes:
i. Boiling of water; ii. Filing of iron nail;
iii. Dissolution of common salt in water;
iv. Melting of candle wax.

48 Mention two natural phenomena which show that particles of matter are in a state of constant motion.

## 2.13 Physical and Chemical Changes

When a solid, such as ice, absorbs heat, it melts to form a liquid (water). On cooling, the liquid solidifies to ice again. Such a change or process, which is easily *reversible*, and can be repeated on the same substance again and again, is a ***physical change***. Other examples:
- Boiling of water;
- Dissolution of common salt in water;
- Removing a paint stain or grease with kerosene.

However, when a matchstick burns, it gives out heat, light and smoke, and a black solid (charcoal) is formed. The process cannot be reversed; that is, obtain the matchstick again! Such a change, which is *permanent, irreversible*, or *produces new substances*, is called a ***chemical change***.

Other examples are:
- Chemical decomposition – like digestion of food;
- All combustion processes – like burning of coal;
- Rusting of iron;
- Any process in which a gas is liberated.
- Smouldering of phosphorus in air.

A mixture of iron filings and sulphur powder can be used to illustrate the differences between physical and chemical changes (see the experiments in section 2.9). Table 2.3 gives the main differences between physical and chemical changes.

Table 2.3: *Differences between Physical and Chemical changes*

| Physical Change | Chemical Change |
|---|---|
| 1. Mixture is formed, e.g. dissolution of sugar in water. | Compound is formed, e.g. Burning of wood, rusting of iron. |
| 2. Easily reversible, e.g. boiling of water, melting of wax. | Not easily reversible or irreversible, e.g. burning of coal, digestion of food. |
| 3. No new substance is formed, e.g. melting of wax; magnetizing iron. | New substance is formed, e.g. Rusting of iron. |
| 4. No change in mass: mixing of iron filings and sulphur powder. | There is a noticeable change in mass, e.g. burning of wood or coal. |
| 5. Not accompanied by heat change, e.g. dissolving of sugar in water. | Usually accompanied by heat change, e.g. Action of an acid on a metal. |

### Revision Exercises

49 List *three* differences between physical and chemical changes.

50 Classify each of the following as a *physical* or *chemical* change:
a. Boiling of egg; b. Ripening of fruits;
c. Melting of wax; d. Filing of iron;

e. Digestion of glucose; f. Dissolving iron in an acid.

51 State with a reason in each case, whether each of the following is a physical or chemical change:

a. Dissolving common salt in water

b. Burning of petrol; c. Digestion of glucose.

## 2.14 Melting, Dissolving and Burning

*Melting occurs when a solid, held in a container, is heated and changes to a liquid.* It is a physical change (reversible) and an endothermic process, e.g. melting of ice or candle wax.

*Dissolving occurs when a solution is formed on stirring a mixture of a solid and a liquid.* The process can be a physical or chemical change; it can be exothermic or endothermic, e.g.

- When sugar dissolves in water to give a colourless solution, the change or process is physical, and neither exothermic nor endothermic.
- When a metal, such as calcium, magnesium or iron dissolves in a *dilute* acid, a gas is liberated; the change is chemical and exothermic.

*Burning occurs when a substance combines chemically with oxygen in air, usually, when a spark is applied, producing new substances.* It is a chemical change, which is irreversible and exothermic, e.g. *burning* of candlestick, wood, or kerosene.

### Solved Problems

4. Consider the following terms:

A. Exothermic; B. Dissolving; C. Colloidal; D. Evaporation; E. Endothermic; F. Cooling

Which of these terms is used to describe

a. a change from liquid to gas. **Answer** *D*.

b. a mixture which is neither a solution nor a suspension? **Answer** *C*.

c. a change in which heat is absorbed from the surrounding? **Answer** *E*.

d. the dissolution of sugar in water? **Answer** *B*.

5. State and explain whether *tincture of iodine* is a mixture or a compound.

**Answer:** *It is mixture; because the iodine and alcohol that form the solution can be mixed in any proportion, and the alcohol can be recovered by distillation.*

6. What name is given to the conversion of a solid directly into vapour without melting?

**Answer:** *Sublimation.*

### Revision Exercises

52 Explain each of the following terms:

a. Melting; b. Dissolving.

53 Distinguish between *melting* and *dissolving*.

### Answer to Revision Exercises

7. solid, liquid and gas 8. Elements, compounds and mixtures 9a. elements and compounds; b. mixtures 12a.109; b. 17; c. 92 17. Matter 18a. metals and non-metals; b. chemical symbols 22. Mercury 24. C 30. C 35 sucrose 46b. crystalloids < colloids < sediments 54a. solvent; b. solute 62a. gas; b. solid; c. gases 62. B 65c I. increase; II. no change; III. increase; IV. increase 69a. chemical; b. chemical; c. physical; d. chemical; e. chemical; f. chemical.

# 3

# •SEPARATION TECHNIQUES•

## 3.1 Introduction

*Separation techniques* are *physical methods* used for separating the *constituents* of various mixtures.

The principle of separation is based on the differences in the *physical properties of the constituents of the mixtures*. Such properties include: *physical state (solid, liquid or gas), particle size, colour, density, melting point, boiling point, solubility in common solvents, magnetic property, polarity, and degree of adsorption. Adsorption* occurs when a substance becomes attached to the surface of a liquid or a solid. It is different from *absorption*.

**Revision Exercise**

1. List five physical properties that can be used as the basis for the separation of mixtures.

## 3.2 Common Separation Techniques

The separation techniques used in the laboratory can be grouped according to the constituents of the mixtures:

### I. Separation of a Solid from a Liquid

The following separation techniques can be used for the separation of a mixture of a *solid* and a *liquid*:

### 1. Filtration

*Filtration method* is used to separate a mixture of a solid in contact with a liquid in which it is insoluble. The method is based on the differences in the physical state and the insolubility of one component of the mixture in the other.

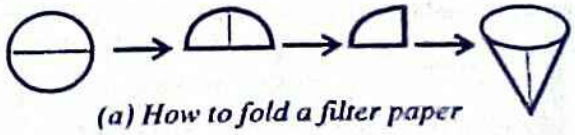
The following mixtures can be separated by filtration method:

- Suspended particles in a liquid or muddy water;
- Sediments in a sample of water;
- A saturated solution in contact with undissolved solid.

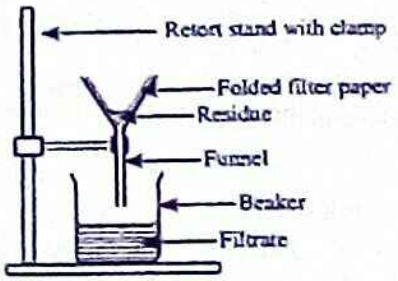
A *filter* made from a *porous paper* is used for the separation. A liquid will pass through the pores of a filter paper, while a solid will not.

**Procedure**:

- *Insert a cone-shaped filter paper into a filter funnel, and clamp on a retort stand;*
- *Pour the mixture into the filter funnel; allow to drain.*
- *The solid left on the filter paper is called residue, while the liquid that passes through the filter paper into the receiver is called filtrate, see fig 3.1.*



*(a) How to fold a filter paper*




*(b) Filtration set-up*

**Fig 3.1** *Filtration*

When filtration is used as a separation technique, the wanted pure component is the residue.

In homes, *domestic filters* are used in purifying drinking water. It has two layers: the upper layer is fitted with a *filter candle*, while the filtered water is stored in the lower layer.

*Boiled* water, on cooling, is poured into the upper layer. The water passes through the filter candle into the lower layer, where it is stored for use. The sediments are retained in the upper layer (fig. 3.2).

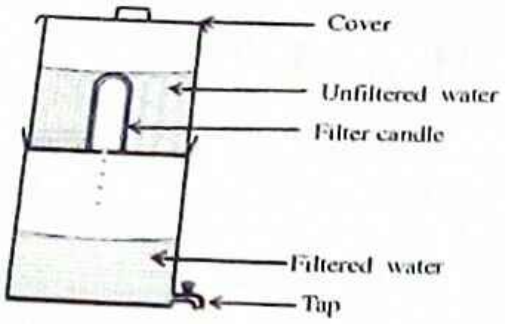



Fig 3.2 *A domestic filter*

On a large scale, a filter bed, composed of various sizes of sand and pebbles is used in the purification of water for town supply (fig 3.3).

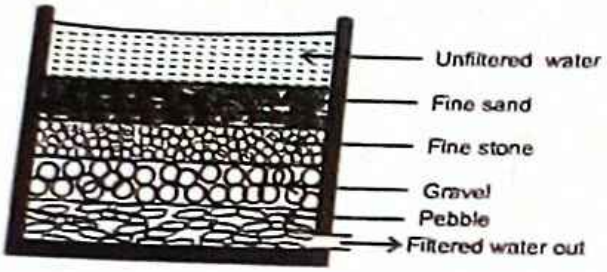



Fig 3.3 *A sand filter bed*

## 2. Decantation

*Decantation*, like *filtration*, is based on the *insolubility of a solid in a liquid*. However, in *decantation*, the solid is of greater density, hence, it sinks. An example is a mixture of sand and water.

**Procedure:**

Pour the liquid in the mixture into another container; leaving the sand in the first container.

## 3. Evaporation to dryness

*Evaporation* method is used to recover a solid from a liquid solvent in which it is soluble to give a solution. The method is suitable, if the solid has a *high* melting point, i.e. cannot be decomposed by heating.

*Evaporation* is based on the large difference between the *melting point of the solid* and the *boiling point of the solvent*. For instance: common salt can be recovered from its aqueous solution by complete evaporation of water.

**Procedure:**

- Pour the solution into an evaporating dish placed on a tripod stand with wire-gauze.
- Heat gently, using a Bunsen burner, until the solvent is completely evaporated, leaving the *residue*, (fig 3.4).

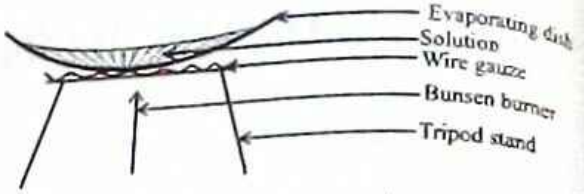



Fig 3.4 *Evaporation using a Bunsen burner flame*

**Use of Water-bath**

Unlike direct heating on the Bunsen burner flame, heating on a *water-bath* – using the steam generated from boiling water – prevents over-heating and splashing or spitting of the residue, see fig 3.5. *Water-bath* is used, when the solvent is flammable.

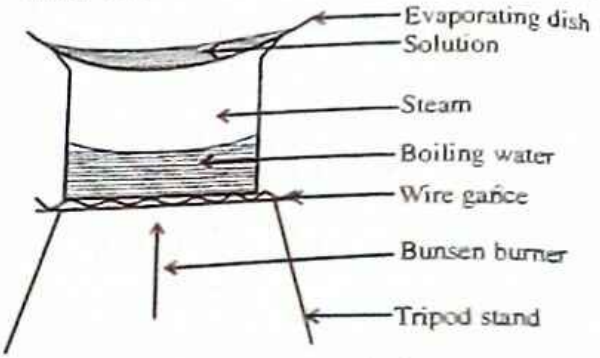



Fig 3.5 *Evaporation on a water-bath*

On a large scale, common salt is obtained from sea-water by the slow evaporation of water in the sun (by solar energy).

## 4. Crystallization

*Crystallization* is the process of obtaining crystals of a solid from its saturated solution, without evaporating the solvent completely.

**Procedure:**

- Place the solution in a beaker, and heat on a Bunsen burner flame; evaporate part of the solvent, in order to obtain a saturated solution.
- Allow the hot saturated solution to cool: the crystals appear on cooling.
- Filter the crystals, and dry between filter papers.

*Crystallization* method is better used for recovering solids that decompose or melt easily when heated directly. For instance: crystals of sugar are obtained from sugar solution by crystallization.

**Crystallization versus Evaporation to dryness**

- Crystallization process is slower than evaporation to dryness.
- All the crystals in a solution cannot be recovered by crystallization, unlike evaporation to dryness.

• Product of crystallization is purer, because the impurity remains in the solution, unlike evaporation to dryness.

**Recrystallization**

When the *crystallization process* is repeated on a given *solid sample* using a *fresh solvent*, it is called *recrystallization*. The purpose is to obtain purer crystals.

## 5. Fractional Crystallization

*Fractional crystallization* is the process whereby a mixture of two or more solid substances are crystallized, one after the other, from the same solution. It is based on the *difference in the solubility of the solids in the same liquid solvent.*

Generally, *when a hot saturated solution containing two or more different solids is cooled, the least soluble solid crystallizes first.*

## 6. Centrifuging

A *centrifuge* is a *device* used to separate fine solid particles in a colloidal solution. Such a mixture is usually difficult to filter, e.g. blood.

*Centrifuging* is based on the difference in the rates of sedimentation of different particles in a centrifugal field.

One disadvantage of *centrifuging* is that the liquid cannot be completely separated from the sediments due to the fine nature of the particles.

*Centrifuging* is used in the hospital laboratory to separate the blood cells from plasma.

## 7. Precipitation (Physical)

In *physical precipitation*, two solids that are soluble in the same solvent are separated by the addition of another solvent in which one of the solids is *insoluble*, e.g. an aqueous solution of *common salt* [sodium chloride] and *green vitriol* [a compound of iron].

**Procedure:**

• Place the aqueous solution of the mixture in a beaker and add an equal volume of *ethanol*; the *green vitriol* is *precipitated.*

• Filter the mixture, to obtain the green crystals.

Separation is possible due to the fact that *green vitriol* is *insoluble* in ethanol.

## 8. Simple Distillation

*Distillation* is the process whereby a liquid, when heated, changes into *vapour*, and the *vapour* when cooled, forms the liquid again. It is reversible.

*Simple distillation* is primarily *used to recover the solvent in a liquid solution.* The principle of separation is based on the difference in the boiling points of the constituents of the mixture, i.e. the solvent has a lower boiling point than the solute. Simple distillation can be used to obtain pure water from a sample of water from the sea, river or well.

***To obtain pure water from a sample of seawater***

**Procedure:**

• Place the sample of seawater in a distillation flask, add 2 or 3 pieces of *boiling chips*, and set up the apparatus as shown in fig. 3.6.

• Heat the solution until it starts to boil. The steam condenses as it passes through the water-cooled *Liebig condenser*, to form a *distillate*, which is *distilled water.*

• Continue the heating process until only the *residue* is left in the flask.

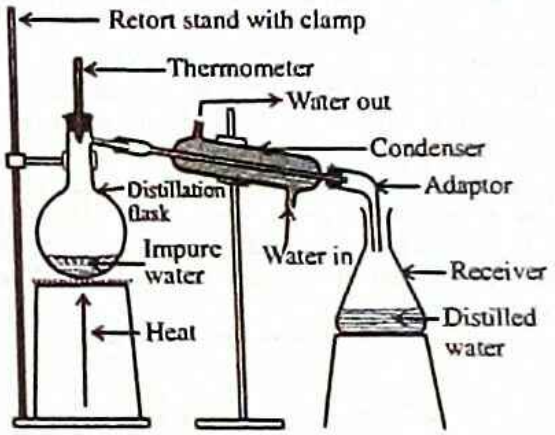



**Fig 3.6** *Simple Distillation*

**Notes:**

•*Boiling chips* (or *anti-bumping granules*) are obtained from *broken porcelain, and are used in order to prevent bumping of the liquid in the distillation flask, and hence, provide smooth boiling.*

•*The direction of flow of water through the Liebig condenser is such that it cools the vapour steadily, until it turns to a liquid. If the direction of flow of water is reversed, the vapour will not condense readily.*

On a large scale, *simple distillation* is used in the production of *distilled water*, and in the *brewery*, for the production of *alcoholic beverages.*

### Revision Exercises

2. List four separation techniques suitable for separating a mixture of a solid and a liquid.
3. State one difference between crystallization and evaporation to dryness.
4. Explain the term *recrystallization.*
5. Name five pieces of apparatus required for simple distillation.

## II. Separation of a Mixture of Solids

The following methods are for the separation of mixtures of solids.

### 9. Sublimation

*Sublimation* is the process whereby a solid, when heated, changes directly to a gas, or a gas, when cooled, changes directly to a solid, without passing through the intermediate liquid state. Such a solid is said to *sublime*.

Only a few chemical substances *sublime*: crystals of *ammonium chloride*, *iodine*, *sulphur* and *naphthalene*. They do not exist in the liquid state at atmospheric pressure.

*Sublimation* method is used to separate a mixture of two or more solids in which one of them sublimes at a temperature below the melting points of the others, e.g. a mixture of common salt and ammonium chloride.

**Procedure:**

- Place the mixture in an evaporating dish and cover it with an inverted funnel, which has been blocked with cotton wool, see fig 3.7.
- Heat on a Bunsen burner flame; the ammonium chloride decomposes to give dense white fumes, which solidifies to give white crystals, called *sublimate*, inside the inverted funnel – leaving sodium chloride in the dish, as the *residue*.

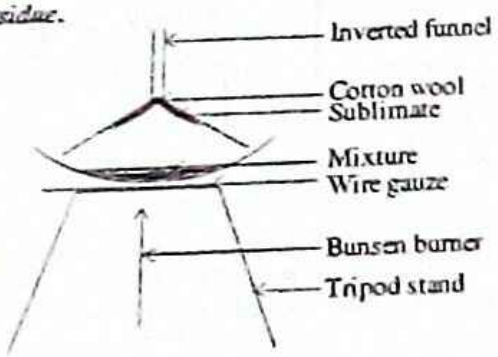



Fig 3.7 *Sublimation*

A *sublimate* is the pure solid obtained when the vapour of a substance, which sublimes solidifies.

### 10. Magnetization

*Magnetization* is used to separate a mixture of magnetic and non-magnetic solids, e.g. a mixture of iron filings and yellow sulphur powder.

**Procedure:**

Place the mixture in a petri-dish; then, use a bar magnet to stir the mixture. The iron filings are attracted by the magnetic, leaving the sulphur powder in the dish (see fig. 3.8).




Fig 3.8 *Magnetization*

*Magnetic separation* is based on the magnetic property of a constituent of the mixture. The method is used, industrially, for the separation of iron ores from impurities, or scrap iron from the scrap of other metals.

### 11. Flotation

*Floatation* method is based on the wide difference in the densities of the constituents of the mixture.

The method is used for the separation of a mixture of two solids in which one constituent is light and the other is heavy. On the addition of a liquid in which neither is soluble, one constituent sinks, while the other floats, e.g. a mixture of coarse sand and wooden cork.

**Procedure:**

Place the mixture in a beaker, and add plenty of water. The sand particles sink, while the wooden corks float.

### Froth flotation (Frostation)

This method is specifically used to separate an *ore* of a metal from earthy impurities.

**Procedure:**

- The *ore* is crushed into powder; then, mixed with water containing detergent, in order to cause *frothing* (*foaming*).
- Air is then blown into the mixture, so that the earthy impurities sink, while the ore floats and mixes with the *froth* (*foam*).
- The ore is finally recovered from the *foam*.

### 12. Sieving

*Sieving* technique is based on the difference in the particle sizes of the constituents of the mixture. Example is soil sample.

**Procedure:** Place the soil sample in a *sieve* (a container with a wire-mesh or wire-gauze at the base), and shake continuously. Particles with *fine* sizes will pass through the mesh, leaving the *coarse* particles in the sieve.

*Sieving* is used in the laboratory for soil analysis. At home, *sieving* is used to obtain fine powdered corn-flour from ground corn-flour.

On a large scale, it is used in the mining industry to sieve out various sizes of diamond or gold.

**Solved Problem**

1. List two methods that can be used to separate a mixture of iodine crystals and iron filings.[WAEC]

**Solution:**

- *Magnetization*: A magnet will attract iron filings only.
- *Sublimation*: Only iodine crystals will sublime.

**Revision Exercises**

6. Which of the following is not a separation technique?
   A. Sieving. B. Dissolution. C. Filtration
   D. Floatation. [WAEC]
7. Separation of mixtures of solids by physical methods can be based on differences in the following except
   A. melting point. B. solubility C. particle size.
   D. molar mass. E. magnetic property. [WAEC]

## III. Separation of a Mixture of Liquids

### 13. Separating Funnel

A *separating funnel* is used to separate two liquids, which do not mix (*immiscible liquids*) e.g. water and kerosene.

The use of separating funnel is based on the difference in the *polarities of the liquids*. Water is a *polar solvent*, while most *organic solvents are non-polar*; hence, *immiscible with water*.

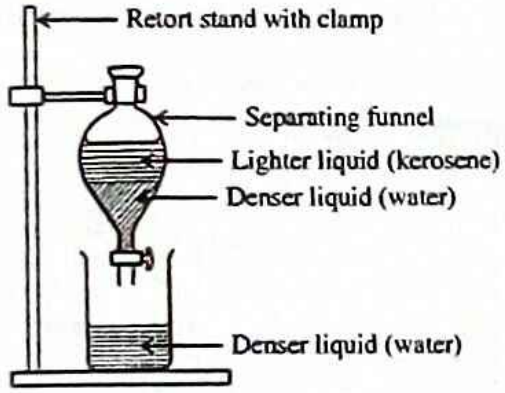



Fig 3.9 *Separating funnel*

**Procedure:**

- Clamp the separating funnel on a retort stand with the tap closed, and pour the mixture into it.
- Wait for a while, in order for the mixture to separate.
- The *denser liquid* is the *lower layer* (water). Run it off through the tap into a container, leaving the *lighter liquid*, the *upper layer* (kerosene) (fig. 3.9).

Vegetable oils, paraffin, benzene, petrol, turpentine and tetrachloromethane are examples of non-polar organic solvents that are immiscible with water.

### 14. Simple Distillation

A mixture of *miscible liquids with widely different boiling points*, can be separated by the use of *simple distillation*, e.g. mixture of ethanol (b.p. 78 °C) and water (b.p. 100 °C).

***Separation of a Mixture of Ethanol and Water***

**Procedure:**

- Place the mixture in the distillation flask, add a few small pieces of boiling chips, and set up the apparatus as in fig 3.6 above.
- Heat the mixture gradually until it starts to boil; the vapour of ethanol and a small quantity of water vapour distill at about 78 °C, leaving a large quantity of water, in the distillation flask.

One disadvantage of the use of *simple distillation* in the separation of *miscible* liquids is that the separation will not be complete. For instance: the *distilled ethanol will contain a small quantity of water*. Hence, simple distillation can be used to obtain a concentrated solution of ethanol in water.

### 15. Fractional Distillation

*Simple distillation* cannot be used to separate a mixture of *miscible liquids* with *close boiling points*; the separation will be incomplete, e.g. a mixture of petrol, kerosene and diesel oil. For such a mixture, a more refined method, called *fractional distillation* is used.

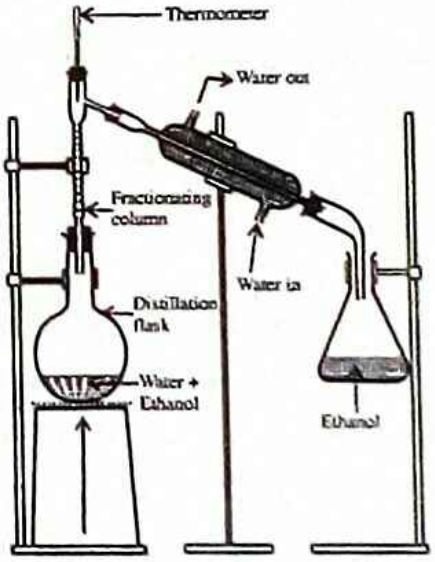



**Fig 3.10** *Fractional Distillation*

*Fractional distillation* involves the use of a *fractionating column* packed with small glass beads, to enable only the vapour of the liquid with the lowest boiling point in the mixture to ascend the column, and condense first (see fig 3.10).

On a large scale, *crude oil* (*petroleum*) is separated into its constituents in the *refinery* by *fractional distillation*.

Similarly, *liquid air*, which is mainly a mixture of nitrogen (b.p. -196 °C) and oxygen (b.p. -174 °C) is separated into its constituents by *fractional distillation*. Liquid nitrogen distils first, since it has a lower boiling point; followed by liquid oxygen.

**Revision Exercises**

8. Separating funnel is used for separating a mixture of
   A. liquids with different boiling points.
   B. sediments of a liquid.
   C. liquids with different colours.
   D. liquids that are immiscible.
9. Fractional distillation of petroleum depends on differences in
   A. molar masses B. densities
   C. boiling points D. freezing points. [WAEC]
10. The property used in obtaining oxygen and nitrogen industrially from air is the
   A. boiling point B. density
   C. rate of diffusion D. solubility [JAMB]
11. Name the most suitable physical method for:
   a. Obtaining ground-nut oil from a mixture of the oil and water;
   b. Obtaining pure water from seawater.
12. State one industrial application of each of the following methods of separation:
   a. crystallization; b. filtration;
   c. fractional distillation. [WAEC]

## IV. Separation of Coloured Mixtures

### 16. Chromatography

*Chromatography* means *colour writing*. It is a method of separating constituents of *coloured mixtures* of solids, liquids and gases – such as in *inks* and *dyes*; extracts from leaves (*chlorophyll*) and flowers (*pigments*); and petroleum fractions. It can also be used to detect coloured contaminants in food samples.

**Types of chromatography:**

- **Gas Chromatography** is used for the separation of complex gaseous mixtures.
- **Column Chromatography** is used for the separation of liquid extracts from leaves, flowers, dyes, and mixtures of proteins.
- **Paper/Thin-layer Chromatography** is used for the separation of *dyes* and mixtures of coloured substances

Separation by *chromatography* requires a *stationary phase* (a solid or a liquid) to *adsorb* the mixture to be separated, and a *mobile phase* (a liquid or a gas), which carries the mixture, and move on the *stationary phase*. *Adsorption* is the process in which a substance becomes attached to the surface of a solid or a liquid – without being *absorbed* and forms a solution.

Separation by chromatography is based on the differences in the *degree of adsorption* of the components in the mixture by the *stationary phase*, or the *degree of retention* of the components by the *mobile phase*.

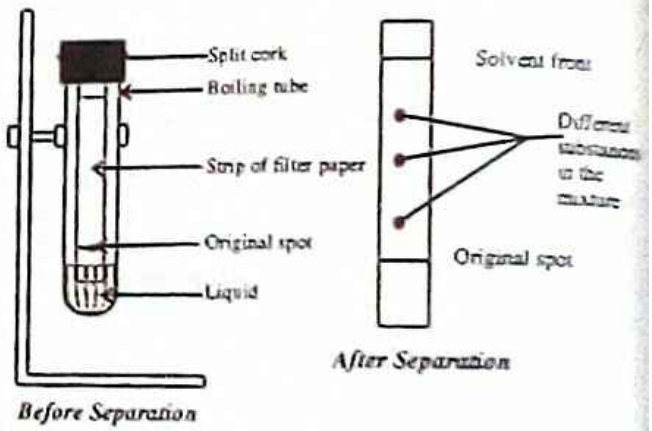
**a. Paper Chromatography**

*Paper chromatography* is the simplest form of chromatography. It is specifically used to separate mixtures of coloured solids, such as dyes.

In *paper chromatography*, a strip of chromatographic (or filter) paper (15 *cm* × 2 *cm*) is the *solid* used as the *stationary phase*, while a *liquid solvent* is the *mobile (moving) phase*. The coloured mixture is dissolved in a suitable liquid solvent.

**Procedure:**

- Introduce a drop of the *coloured mixture* (ink) into the *start-line*, with the aid of a capillary tube, on the filter paper; allow to dry. (The *start-line* represents the *original spot* or *point of application* of the mixture).
- Pour about 20 $cm^3$ of the *liquid solvent* into a moderate boiling tube. Then, suspend the strip of filter paper in a split cork and insert into the boiling tube, such that the spot is about 2 *cm* from the surface of the solvent (see fig. 3.11).




3.11 *Paper Chromatography*

- As the solvent rises on the filter paper by capillary action, it carries with it dissolved *dyes* in the *ink*, which are then deposited at various spots as the solvent rises to the *solvent front*. When or where the *constituent dyes* in the *ink* will be deposited on the paper depends on the *degree of retention of the dyes by the solvent*, or *degree of adsorption by the paper*.
- The paper, now referred to as a *chromatogram*, is removed as soon as the solvent rises to the *solvent front*. The number of spots on the *chromatogram* corresponds to the number of constituents in the mixture.

In short, paper chromatography is based on the differences in speeds of movement of the components of the mixture on the paper.

**Mixture of Methyl orange and Phenolphthalein**

A mixture of *methyl orange* and *phenolphthalein* can be separated by the use of ammonia solution as the solvent. The *chromatogram* gives two spots: methyl orange is deposited as a *yellow spot* before phenolphthalein as a *red spot*. This shows that phenolphthalein is retained by the solvent longer than methyl orange, and vice versa.

The *degree of retention* of the solute by the solvent is expressed in terms of *retention factor*, $R_f$. It is the ratio of the *distance covered by a solute* to the *distance covered by the solvent front*.

$$R_f = \frac{\text{Distance covered by the solute}}{\text{Distance covered by the solvent}}$$

The higher the $R_f$ value, the longer the solute is retained by the solvent. Phenolphthalein has a higher $R_f$ value than methyl orange.

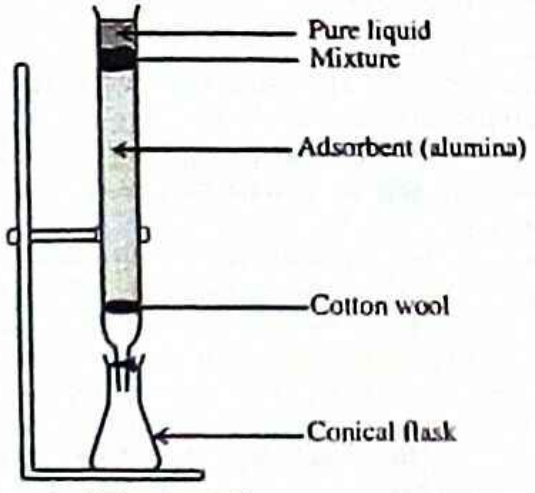
When different solvents or mixtures of solvents are used to analyze the same mixture, the solvent or mixture of solvents that gives the highest number of spots on the chromatogram is the best.

## b. Column Chromatography

In *column chromatography*, a glass tube is used as the column, while an *adsorbent*, such as powdered alumina (aluminium oxide) or an *ion-exchange resin*, is used as the *stationary phase*. A suitable solvent is used as the *mobile phase*.

**Procedure:**

- Fill the column with the *adsorbent* as in fig 3.12.




*Before separation*

**Fig 3.12** *Column Chromatography*

- Make a solution of the mixture to be separated in a suitable solvent, and pour it into the column.
- Then, pour the pure solvent alone into the column; it flows down the column. Since the various components of the mixture moves down the column at different rates in the solvent, they are separated into *bands*.
- Collect each *band* separately by the use of an appropriate solvent.

The *number of bands* in the column corresponds to the number of components in the mixture.

**Advantages of Chromatographic Separation**

- A small quantity of the mixture is needed for analysis when compared with the other separation techniques, where large quantities are required.
- Separation of the mixture into its components is always completes.

**Solved Problems**

2. Consider the following laboratory methods:
A. Crystallization B. Chromatography
C. Distillation D. Sublimation.
E. Fractional distillation
Choose from A to E one method, which is most suitable for each of the following:
a. Purifying iodine contaminated with sand.
b. Purifying 100 $cm^3$ of water contaminated with ink, which colours it blue.
c. Obtaining common salt from a sample of seawater.
d. Detecting the various colours in black ink.
e. Isolating oxygen from liquid air.
f. Separating the constituents of leaf pigment.
Solution: a. *D* b. *C* c. *A* d. *B* e. *E* f. *B*

3. Pure ethanol (b. p. 78 °C) can be obtained from a mixture of ethanol and water (b. p. 100 °C) by
A. evaporation. B. fractional distillation
C. simple distillation. D. fractional crystallization.
Solution: *B* (*Fractional distillation is best used to separate miscible liquids*)

4. A sample of orange juice is suspected to be contaminated with a yellow dye. Which of the following methods can be used to detect the dye?
A. Decantation B. Distillation.
C. Chromatography D. Evaporation. [JAMB]
Solution: *C*

5 a. Explain the following terms:
*filtrate, distillate and sublimate.*
- *Filtrate – The liquid, which passes through the filter paper during filtration.*
- *Distillate – The pure solvent obtained from the condensed vapour during distillation.*

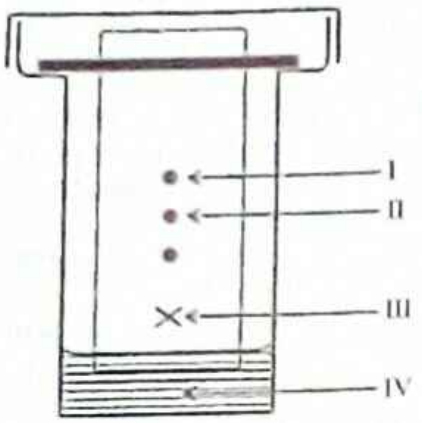
• *Sublimate – The solid formed when the vapour produced during sublimation condenses.*

b. What do these terms have in common? [WAEC]
*They are pure components of different mixtures.*

**Revision Exercises**

13 Which of the following procedures is suitable for identifying the food colouring added to a pastry sample? [WAEC]
A. Carry out some food tests.
B. Examine the pastry sample under a microscope.
C. Do a chromatogram of the colouring extract.
D. Determine the molar mass of the colouring.

14 The set-up shown in the diagram below was used to separate a drop of universal indicator into its constituent dyes, using ethylethanoate as the solvent.




a. What name is given to the separation technique illustrated in the diagram?
b. Which of the parts labeled I to IV indicates the point of application of the indicator?
c. State the
i. number of components resolved in the separation.
ii. material normally used in the laboratory as the adsorbent medium

## 3.3 Procedures for the Separation of Mixtures

### Introduction

A mixture of two or more substances can be separated by the use of the differences in the physical properties of its constituents. For instance: To separate a mixture of common salt and starch powder, use is made of the fact that common salt is soluble in water, while starch is not.

A given mixture can be separated in one single step by the use of one of the separation techniques, or by a systematic combination of two or more of these techniques. The procedure or steps to follow depend on the constituents of the mixtures.

### Physical Features

When a mixture with two constituents is provided for separation, the following steps could be taken

1. When it is a mixture of a solid and a liquid
   - If the solid is insoluble in the liquid. *Use filtration.*
   - If the solid is soluble in the liquid.
     *Use evaporation to dryness to recover the solid.*
     *(if the solid has a high melting point)*
     *or crystallization. (If its melting point is low)*
   - To recover both the solid and the liquid separately:
     *Use simple distillation.*

2. When the constituents of the mixture are solids:
   - If one of the constituents sublimes:
     *Use sublimation method.*
   - If one of the constituents is magnetic:
     *Use magnetization method.*
   - If the two constituents are soluble in the same liquid. *Use fractional crystallization.*
   - If one of the constituents is soluble in a liquid in which the other is not. *Use filtration, followed by crystallization or evaporation to dryness.*
   - If the two constituents are soluble in one liquid, and one of the constituents is soluble in another liquid in which the other is insoluble:
     *Use physical precipitation method.*

3. When the components of the mixture are liquids:
   - If they are immiscible: *Use separating funnel.*
   - If they are miscible: *Use fractional distillation.*

4. When the components of the mixture are dyes or coloured solids: *Use paper chromatography.*

Hence, it is very important to be *familiar with the physical properties of all chemical substances at different temperatures.*

### Examples

**1. Outline for the separation of a mixture of common salt and sand**

This is a mixture of solids in which one constituent is soluble in a solvent in which the other is not.

**Procedure:**

• Place the mixture in a beaker, add enough of water and stir. The salt dissolves, while the sand does not. This is *dissolution*. (*Dissolution* is not a separation technique.)

• Filter the mixture; the *colourless filtrate* is the solution of common salt in water, while the *brown residue* is sand (*filtration*).

• Heat and concentrate the filtrate on a Bunsen burner flame to obtain a saturated solution. Cool the solution to obtain the crystals of common salt (*crystallization*).

• Filter, to obtain the crystals as the residue (*filtration*), and dry between filter papers. *Or*
• Transfer the filtrate into an evaporation dish, and evaporate to dryness, to obtain the common salt (*evaporation*).

### 2. Separation of a mixture of alum, sand and ammonium chloride

This is an example of a mixture with three constituents. From common knowledge/experience:
• The three samples exist as solids at room temperatures.
• Ammonium chloride and alum are soluble in water, while sand is not.
• Only ammonium chloride sublimes.

**Procedure:**
• Place the mixture in an evaporating dish and cover it with an inverted funnel, which has been blocked with cotton wool.
• Heat with a Bunsen burner flame; ammonium chloride sublimes, and is collected as a white sublimate inside the inverted funnel.
• Transfer what is left in the evaporating dish into a beaker, and add enough of water with stirring of the mixture. Alum dissolves, while sand does not.
• Filter the mixture into another beaker; the *colourless filtrate* is the aqueous solution of alum, while the *light brown residue* is sand.
• Heat and concentrate the *filtrate* on a Bunsen burner to obtain a saturated solution. Cool the saturated solution, to obtain the crystals of alum.
• Filter, to obtain the crystals as the residue, and dry between filter paper.

**Solved Problems**

6. State *one* advantage and *one* disadvantage of evaporation to dryness over crystallization of the solution.

• *Advantage: Evaporation to dryness is faster than crystallization process.*
• *Disadvantage: The solid may decompose due to prolonged heating; the solid is impure due to the presence of solid impurities, which would have been removed by crystallization.*

7. Describe the procedure you would use to obtain pure sample of common salt from rock salt in the laboratory.

• *Grind the rock salt to powder in a mortar with pestle.*
• *Transfer the powdered rock salt into a beaker, add water, and warm while stirring the mixture.*
• *Filter off the insoluble impurities.*
• *Partly evaporate the filtrate, to concentrate it; then, allow to cool, to obtain the crystals.*
• *Filter the crystals, and dry between filter papers.*

8. The order in which a mixture of sand, ammonium chloride and sodium chloride can be separated is

A sublimation → dissolution → filtration → evaporation
B dissolution → dryness → filtration → evaporation
C filtration → sublimation → evaporation → dryness
D dissolution → filtration → sublimation → evaporation

Solution *A*. [JAMB]

**Revision Exercises**

15 Which method(s) could be used to separate the constituents of each of the following mixtures?
a. Iodine and alum b. Sulphur and naphthalene
c. Ammonium chloride and alum
d. Benzene and distilled water.
e. The colour extracts of a flower.

16 Which of these separation techniques can be used to separate an insoluble solid from a liquid?
A. Centrifugation B. Chromatography C. Distillation
D. Using a separating funnel E. Sublimation (NECO)

17 Suppose you were provided with a powdered mixture of alum and chalk. Which of the following is the best sequence of operations to obtain a sample of pure chalk?
A. Warm with water → filter → evaporate the filtrate
B. Warm with water → filter → wash with water → dry
C. Warm with water → partly evaporate → cool → filter
D. Warm with water → filter → dry

## 3.4 Pure and Impure Substances

The following are the criteria for purity of chemical substances:

• **Density**: The *density* of a *pure* substance is *definite* and *constant*, while that of an *impure substance* is higher than expected. For instance, the density of pure water is 1.0 $gcm^{-3}$ at 4.0 °C.

• **Melting point**: The *melting point* of a pure solid is *sharp, definite and with a short melting point range*. The melting point of pure sodium chloride is 801 °C. An *impurity lowers the melting point of a solid, and widens its melting point range*.

• **Freezing point**: The *freezing point* of a pure liquid is *sharp* and *definite*; the presence of an impurity *lowers* its freezing point. The freezing point of pure water is 0 °C, while water containing dissolved salt freezes at a temperature below 0 °C.

• **Boiling point**: The *boiling point* of a pure liquid is *sharp, definite, and with a short boiling point range*. The boiling point of pure ethanol is 78 °C, while that of pure water is 100 °C at atmospheric

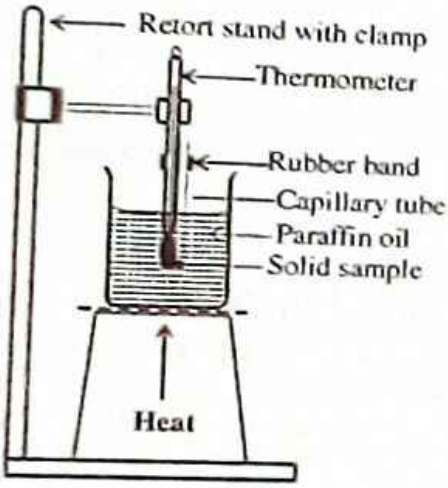
pressure. An *impurity raises the boiling point of a pure liquid, and widens its boiling point range.*

## Determination of Melting Point

The *melting point of a solid is the temperature at which it changes to liquid.* The *purity* of a *solid* sample is *best* determined by its *melting point.*

**Procedure:**

- Grind the solid sample into fine powder and force the particles down the bottom of a capillary tube sealed at one end, up to a length of about 0.5 *cm.*
- Tie the capillary tube to a thermometer using a rubber band such that the sample is directly opposite the bulb of the thermometer (fig 3.13).
- Clamp the thermometer with the sample vertically on a retort stand such that the bulb is well inside a beaker of liquid paraffin placed on a tripod stand with wire-gauze.
- Heat the paraffin slowly with constant stirring using a Bunsen burner flame, and note the temperature at which the sample just melts.
- Repeat the process with a fresh sample in another capillary tube, until two readings agree within 2.0 °C.




3.13 *Determination of Melting point*

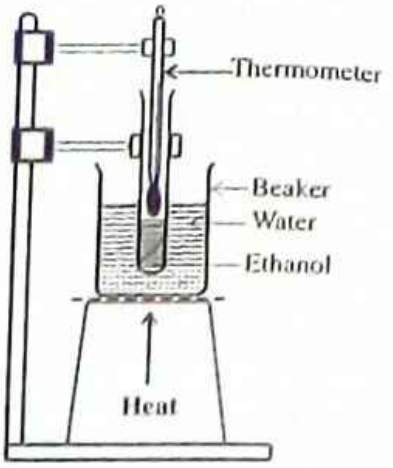
## Determination of Boiling Point

*The boiling point of a liquid is the temperature at which its vapour pressure equals atmospheric pressure.*

The *purity* of a *liquid* sample is *best* confirmed by its *boiling point.*

**Procedure:**

- Place about 10 $cm^3$ of the liquid sample in a boiling tube, and drop 2 or 3 pieces of boiling chips into it.
- Clamp on a retort stand such that the boiling tube is well inside the beaker of liquid paraffin, which is placed on a tripod stand with wire-gauze (fig. 3.14).
- Clamp a thermometer vertically inside the boiling tube such that its bulb is about 1.0 *cm* above the surface of the liquid sample.
- Heat the paraffin slowly with stirring, using a Bunsen burner flame, and note the temperature at which the sample starts to boil steadily. This is the boiling point.




3.13 *Determination of Boiling point*

## Revision Exercises

18 List **three** physical properties that are used as criteria for purity of substances. [WAEC]

19 List **five** pieces of apparatus that are common for the determination of melting and boiling points of a chemical substances

20 Explain why *boiling chips* are added to a liquid being distilled, or whose boiling point is being determined.

21 Name a physical process used in the laboratory for
- a. removing suspended matter from a sample of muddy water.
- b. showing that a dye usually contains more than one component.
- c. obtaining concentrated ethanol from dilute ethanol.
- d. separating a mixture of kerosene and diesel oil.
- e. determining whether or not, a given sample of common salt is pure.

22 State the importance of the measurement of melting and boiling points.

23 In countries where the temperature falls below 273 K salt is always sprinkled on the icy roads in order to
- A. lower the melting point of ice
- B. increase the density of the ice
- C. make the ice impure.
- D. raise the melting point of the ice. [JAMB]

24 When 25.215 g of a mixture of substances X, Y and Z was separated, 7.52 g of X and 8.48 g of Y was recovered. Assuming that there was no loss of components during the separation process, calculate the percentage by mass of Z in the mixture. [NECO]

## Answers to Revision Exercises

6. B 7. D 8. D 9. C 10. A 13. C
16. A 17. D 23. A 24. 36.5%

# 4

# •PARTICULATE NATURE OF MATTER• •ATOMIC STUCTURE•

## 4.1 Concept of Atoms

A Greek philosopher, Democritus (400 B.C.) was the first to show that matter is made up of small particles, called ***atoms***.

In order to have an idea of what an atom looks like, one has to imagine the following processes:

- A solid, such as iron nail, is cut into small pieces, until a piece can no longer be divided, i.e. to obtain powdered iron filings!
- When a cube of sugar, a solid, dissolves in water, the sugar *particles* in the solution, ***crystalloids***, become *invisible*; although, their presence can be felt from the *sweetness* of the solution.
- When the vapour of a rotten egg is allowed into a room, the odour spreads quickly and fills the entire room by a process known as ***diffusion***.

These three examples illustrate that matter is made up of small particles, which are too small to be seen with the naked eye.

**Definition:** *An atom is the smallest particle of an element, which takes part in a chemical reaction.*

The symbol of an element represents *one atom*, e.g. **Na** represents *one atom* of sodium, **O** is an atom of oxygen, and **Cl** is an atom of chlorine.

**Revision Exercises**

1. Mention two natural phenomena, which show that matter is composed of small particles.
2. Define an atom.

## 4.2 Atomic Theory of Dalton

The idea that *matter is made up of atoms* gave rise to the *atomic theory*. John Dalton (1803) presented a convincing experimental evidence to support this theory. In *Dalton's atomic theory*, the following postulates or assumptions were made:

1. Matter is made up of small or tiny indivisible particles called atoms.
2. All atoms of a particular element are exactly alike in size, shape and mass, and are different from atoms of other elements.
3. In a chemical reaction, whole atoms (never fractions) combine, separate, or change places.
4. When atoms combine with one another, they do so in small whole number ratio.

Some of the postulates of Dalton have been modified to conform to new discoveries in science, as would be seen later in Section 37.7.

**Revision Exercises**

3. Name the scientist that formulated the atomic theory.
4. List two of the postulates of the atomic theory.

## 4.3 Composition of the Atom

### Structure of an Atom

An atom has *two* main parts: the ***nucleus*** (*centre*) and the ***shells***, which surround the *nucleus* at definite distances.

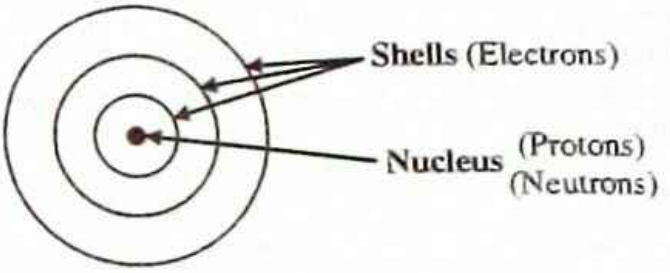



Fig 4.1 *Structure of an atom*

An atom is composed of *three subatomic* particles:

***Protons***, ***Electrons*** and ***Neutrons*** (**P.E.N.**).

The ***protons*** and ***neutrons*** are found in the ***nucleus*** while the ***electrons*** are in constant and continuous motion in the ***shells*** around the *nucleus* (see fig. 4.1).

### Relative masses and electrical charges of the sub-atomic particles

The mass of a *proton* is approximately equal to that of a *neutron*, while the mass of an *electron* is 1/1840 of that of a proton. This shows that an *electron* is extremely small; it contributes the least to the mass of an atom. In fact, the *mass of an atom is concentrated in its nucleus*.

**Table 4.2** *Charges/Relative masses of atomic particles*

| Particle | Charge | Relative Mass |
|---|---|---|
| *Proton* | + (positive) | 1 |
| *Electron* | – (negative) | 1/1840 (0.000544) |
| *Neutron* | Nil(neutral) | 1 |

In terms of electrical charge: a *proton* carries a *positive charge*, an *electron* is *negatively charged*, while a *neutron* has no charge at all – it is *neutral*. (Table 4.2).

**Revision Exercises**

5 a. Name the two main parts of an atom?
b. Mention the **three** subatomic particles in an atom.
c. Which particles are found in each part of the atom?
6. List **three** subatomic particles with their corresponding charges.

## 4.4 Nuclear Particles

*Nuclear particles* are the *protons* and *neutrons*; they are in the *nucleus* of an atom. They determine the *atomic number* and *mass number* of an atom.

### Atomic Number, Z

The ***atomic number of an element***, *Z*, is the *number of protons* in the nucleus of its atom. It is always a *whole number*. The *number of protons* in an atom is called the ***nuclear charge***. *No two elements have the same atomic number.*

An atom is electrically neutral, since the *number of protons in the nucleus* is *equal to* the *number of electrons in the shells of the atom.*

### Mass Number, A

The ***mass number of an element*** is the *sum* of the ***numbers of protons*** and ***neutrons*** in the ***nucleus*** of its atom. It is denoted by symbol *A*.

### Nuclear (Elemental) Symbol

The ***nuclear (or elemental) symbol*** of an element *X* is written as ${}^{A}_{Z}X$;

*A* is the ***mass number*** (protons + neutrons)

*Z* is the ***atomic number*** (number of protons)

For instance: the nuclear symbol of sodium atom is ${}^{23}_{11}Na$. That is: its mass number, *A* is 23, while its atomic number, Z is 11.

**Note**: The difference between the ***mass number*** and ***atomic number, (A – Z)*** gives the ***number of neutrons.***

For instance: in ${}^{23}_{11}Na$:

Mass number, *A* (protons + neutrons) = 23.

Atomic number, *Z* (number of protons) = 11.

∴ Number of neutrons, $A - Z = 23 - 11 = 12$.

Hence, there are 12 ***neutrons*** in the *nucleus* of sodium atom.

The *nuclear (elemental) symbols* of some elements are as given:

| Nuclear Symbol | Mass No. A | Atomic No. Z | Protons | Electrons | Neutrons |
|---|---|---|---|---|---|
| ${}^{1}_{1}H$ | 1 | 1 | 1 | 1 | 0 |
| ${}^{12}_{6}C$ | 12 | 6 | 6 | 6 | 6 |
| ${}^{23}_{11}Na$ | 23 | 11 | 11 | 11 | 12 |
| ${}^{39}_{19}K$ | 39 | 19 | 19 | 19 | 20 |

Note: In an atom, the *mass number, A*, is usually greater than the *atomic number, Z*, except in the hydrogen atom, ${}^{1}_{1}H$, where they are equal; because *hydrogen atom has no neutron in its nucleus.*

**Worked Examples**

**1.** The mass number of an element is 31. If its atomic number is 15, what is the composition of
a. the nucleus of its atom, b. its atom.

a. *To find the composition of the nucleus of its atom:*
*The nucleus of an atom contains protons and neutrons.*
*Mass number, A = protons + neutrons = 31 (given)*
*Atomic number, Z = number of protons = 15 (given)*
*∴Number of neutrons, A – Z = 31 – 15 = 16*
*Hence, the composition of its nucleus is 15 protons and 16 neutrons.*

b. *To find the composition of its atom:*
*An atom is composed of protons, electrons and neutrons. In a neutral atom, the number of protons equals the number of electrons.*
*∴ Number of electrons in the atom = 15*
*From a above, the number of neutrons is 16; hence, the composition of the atom of the element is:*
*15 protons, 16 neutrons and 15 electrons.*

**2.** The total number of protons and electrons in a neutral atom is 26. If its mass number is 27, calculate the number of neutrons.

*To calculate the number of neutrons:*
*Mass number = protons + neutrons.*
*First, to calculate the number of protons:*
*In a neutral atom, number of protons equals number of electrons.*
*Let x represent the number of protons,*
*∴ Number of electrons = x*
*That is: x + x = 26 (given)*
$2x = 26$
$x = 26/2 = 13$
*i.e. the number of protons = 13.*
*But mass number = protons + neutrons = 27 (given)*
*Since number of protons = 13*
*∴ Number of neutrons = 27 – 13 = 14.*
*Hence, the atom has 14 neutrons.*

**Revision Exercises**

7. What are *nuclear particles*?
8. An atom with 17 protons, 17 electrons and 18 neutrons has a mass number of
   A. 17 B. 18 C. 34 D. 35 E. 52 [WAEC]
9. If an atom of an element is represented as $^{40}_{20}Y$, this shows that it has
   A. 40 neutrons. B. mass number of 20.
   C. 20 protons. D. atomic number 40. [WAEC]
10. Fill in the following gaps:

| Atom | Mass Number | Number of Protons | Number of Neutrons |
|---|---|---|---|
| $^{?}_{1}W$ | | | |
| $^{14}_{6}X$ | | | |
| $^{35}_{17}Y$ | | | |
| $^{40}_{19}Z$ | | | |

## 4.5 Isotopy and Isotopes

### Definitions

Scientific discoveries have shown that there could *atoms of the same element with different masses*. This is contrary to one of the postulates of Dalton. Such a phenomenon is called *isotopy*, while the various atoms are known as *isotopes of the same element* or *nuclides*.

- *Isotopy is the occurrence of two or more atoms of the same elements having the same atomic number but different mass numbers.*
- *Isotopes are atoms of the same element with the same atomic number but different mass number.*

*Or*

- *Isotopes are atoms of the same element with the same number of protons but different number of neutrons.*

### Examples of Elements exhibiting Isotopy

**Hydrogen** has three isotopes: $^{1}_{1}H$ (protium); $^{2}_{1}H$ (deuterium) and $^{3}_{1}H$ (tritium). Protium, $^{1}_{1}H$ is the most abundant isotope of hydrogen. It has one proton, and hence, one electron. It has *no neutron*.

**Chlorine** has two naturally occurring isotopes with nuclear symbols $^{35}_{17}Cl$ and $^{37}_{17}Cl$. The first isotope, called chlorine-35, has 17 protons and 18 neutrons; while the second, chlorine-37, has 17 protons and 20 neutrons.

**Other examples**: **Oxygen**: $^{16}_{8}O$ and $^{17}_{8}O$;
**Carbon**: $^{12}_{6}C$ and $^{14}_{6}C$.

**Revision Exercise**

11a. What is isotopy? [WAEC]
   b. Name **two** elements that exhibit isotopy, and write the respective elemental (nuclear) symbols of the isotopes.

## 4.6 Concept of Relative Atomic Mass

Because an *atom* is so small that it cannot be seen with a microscope, chemists accepted the concept of *relative atomic mass*, which enables masses of atoms of various elements to be compared.

An atom of carbon-12 is currently the *reference standard*, and is assigned 12.0 *atomic mass unit (a.m.u.)* The *atomic masses* of other elements are estimated *relative* to that of carbon-12 by the use of *mass spectrometer*, invented by Aston in 1919.

**Definition:** *Relative atomic mass of an element is the average mass of one atom on a scale in which one atom of carbon-12 weighs 12 a.m.u.*

The *relative atomic mass* of an element has no unit; it is a ratio. The *relative atomic masses* of some elements are given in Table 4.1. The relevant values are usually provided when required. Hence, there is no need to *memorize* the values.

**Table 4.1** *Relative atomic masses of some elements*

| Element | Symbol | Relative Atomic Mass |
|---|---|---|
| Hydrogen | H | 1.0 |
| Carbon | C | 12.0 |
| Nitrogen | N | 14.0 |
| Oxygen | O | 16.0 |
| Sodium | Na | 23.0 |
| Magnesium | Mg | 24.0 |

**Revision Exercises**

12. What is relative atomic mass?
13. Which instrument can be used to measure the mass of an atom of an element?
14. Who invented the mass spectrometer?
15. State why atomic mass of an element has no unit.

### Relative atomic masses of isotopic elements

Atoms of the same isotope have the same mass number. However, the *relative atomic mass* of an element with two or more isotopes depends on the percentage (or relative) abundance of each isotope in the naturally occurring element.

The *mass spectrometer* is used to determine the number of isotopes of an element and their relative abundances.

Most elements have two or more isotopes. For an element that has no isotopes, the *mass number is* equal to its *relative atomic mass*. For example: the *mass number of sodium atom is 23*; its *relative atomic mass is exactly 23.0*. However, for an element with atoms made up of a mixture of isotopes, its *relative atomic mass is the mean or average of the isotopic masses*. This explains the fractional

value of the relative *atomic mass* of chlorine (Cl = 35.5).

Table 4.2 gives the compositions of the atoms of the elements with atomic numbers 1 to 20. Note that the composition of the nucleus of an isotopic element, such as hydrogen, carbon, and chlorine is represented by that of the most abundant isotope.

**Tables 4.2** *Compositions of the nucleus of the atoms of the first twenty element*

| Symbol | Atomic number Z | Mass Number A | Composition of the Nucleus | |
|---|---|---|---|---|
| | | | Proton | Neutron |
| H | 1 | 1 | 1 | - |
| He | 2 | 4 | 2 | 2 |
| Li | 3 | 7 | 3 | 4 |
| Be | 4 | 9 | 4 | 5 |
| B | 5 | 11 | 5 | 6 |
| C | 6 | 12 | 6 | 6 |
| N | 7 | 14 | 7 | 7 |
| O | 8 | 16 | 8 | 8 |
| F | 9 | 19 | 9 | 10 |
| Ne | 10 | 20 | 10 | 10 |
| Na | 11 | 23 | 11 | 12 |
| Mg | 12 | 24 | 12 | 12 |
| Al | 13 | 27 | 13 | 14 |
| Si | 14 | 28 | 14 | 14 |
| P | 15 | 31 | 15 | 16 |
| S | 16 | 32 | 16 | 16 |
| Cl | 17 | 35 | 17 | 18 |
| Ar | 18 | 40 | 18 | 18 |
| K | 19 | 39 | 19 | 20 |
| Ca | 20 | 40 | 20 | 20 |

**Solved Problem**

3. Give the reason why the relative atomic mass of chlorine is 35.5 and not a whole number.[WAEC]

*Chlorine is a mixture of two isotopes with different abundances. Its relative atomic mass is the mean or average of the isotopic masses.*

## Chemical calculations based on Isotopes

Consider an element with *three* isotopes. The variables involving such isotopes are:

**$M_r$** : *mean relative atomic mass of element;*

**$A_1$, $A_2$ and $A_3$** : *mass numbers of the isotopes;*

**$P_1$, $P_2$ and $P_3$** : *their percentage abundances;*

**$R_1$, $R_2$ and $R_2$** : *relative abundances in the form of a ratio.*

• When the relative abundances of the isotopes are given in percentages, it means:

$$P_1 + P_2 + P_3 = 100\%$$

i.e. Out of 100 atoms of the element, $P_1$ atoms have mass number of $A_1$ each; $P_2$ atoms have mass number of $A_2$ each; while $P_3$ atoms have mass number of $A_3$ each. Mathematically:

*Mean relative atomic mass,* $M_r$ =

$$\frac{(P_1 \times A_1) + (P_2 \times A_2) + (P_3 \times A_3)}{(P_1 + P_2 + P_3)}$$

• When the relative abundances of the isotopes are given in the form of ratio $R_1 : R_2 : R_3$ it means:

Total number of atoms = $R_1 + R_2 + R_3$

Mathematically:

*Mean relative atomic mass,* $M_r$ =

$$\frac{(R_1 \times A_1) + (R_2 \times A_2) + (R_3 \times A_3)}{(R_1 + R_2 + R_2)}$$

**Solved Problems**

**1. Using Relative Abundances in Ratio Form**

**Example 4:** An element has two isotopes, $^{20}X$ and $^{22}X$, which occur in the ratio 3 : 1, calculate the mean relative atomic mass of X.

**Solution**

Given: Ratio of $^{20}X : {}^{22}X = 3 : 1$;

Required: Relative atomic mass, $M_r$ of X.

*Method I: (From the first principle)*

*Ratio of $^{20}X : {}^{22}X = 3 : 1$ means: Out of every 4 atoms of X, 3 atoms have mass number of 20 each, while 1 atom has mass number of 22.*

*Contribution from each isotope:*

3 atoms of $^{20}X$ contributes $3 \times 20 = 60$ amu.

1 atom of $^{22}X$ contributes $1 \times 22 = 22$ amu.

Total = 82 amu.

i.e. 4 atoms of X contribute 82 amu.

The average, which corresponds to the relative atomic mass, $M_r$ of X will be:

$$M_r = 82/4 = 20.5 \text{ amu}$$

*Method 2: (Mathematical Formula)*

Given: Ratio of $^{20}X : {}^{22}X = 3 : 1$

$$M_r = \frac{(3 \times 20) + (1 \times 22)}{(3 + 1)} = \frac{60 + 22}{4} = \frac{82}{4} = 20.5$$

**2. Using Percentage Abundances**

**Example 5:** Naturally occurring chlorine atoms contain 75.0% of $^{35}Cl$ and 25.0% of $^{37}Cl$ by mass respectively. Calculate the mean relative atomic mass of chlorine.

**Solution**

Given: 75.0% of $^{35}Cl$ and 25.0% of $^{37}Cl$.

Required: Mean relative atomic mass of chlorine.

*Method I: (From the first principle)*

Contribution from each isotope:

75 atoms of $^{35}Cl$ contribute $75 \times 35 = 2165$

25 atoms of $^{37}Cl$ contribute $25 \times 37 = 965$

Total = 3550

i.e. 100 atoms of Cl contribute 3550 amu.

The average, which corresponds to the mean relative atomic mass, $M_r$ of Cl will be:

$M_r = 3550/100 = 35.5$ amu.

*Method 2: (Mathematical Formula)*

Given: 75.0% of $^{35}Cl$ and 25.0% of $^{37}Cl$.

$$M_r = \frac{(75 \times 35) + (25 \times 37)}{(75 + 25)} = \frac{(2625 + 925)}{100}$$

$$= 3550/100 = 35.5$$

6. An element X with atomic number 29 has two isotopes Y and Z. Isotopes Y and Z have 34 and 38 neutrons respectively. Calculate the

a. mass number of each isotope, and hence, write their nuclear symbols.

b. percentage abundance of each isotope, if the relative atomic mass of element X is 63.5.

a. *To calculate the mass number:*

Mass number = protons + neutrons.

Atomic number = number of protons.

Since both Y and Z are isotopes, they have the same atomic number.

*For isotope Y:*

Atomic number = no. of protons = 29 (given)

Number of neutrons = 34 (given)

∴ Mass number of Y = 29 + 34 = 63.

*For isotope Z:*

Atomic number = no. of protons = 29 (given)

Number of neutrons = 38 (given)

∴ Mass number of Z = 29 + 38 = 67

b. *To calculate the % abundance:*

Let the % abundance of Y be $a$

∴ % abundance of Z will be $(100 - a)$

Using the mathematical formula method:

$$\text{Relative atomic mass} = \frac{(a \times 63) + [(100 - a) \times 67]}{100}$$

$$= 63.5$$

i.e

$$\frac{63a + 6700 - 67a}{100} = 63.5$$

$$63a + 6700 - 67a = 6350$$

$$63a - 67a = 6350 - 6700$$

$$-4a = -350$$

$$a = \frac{-350}{-4} = \frac{350}{4} = 87.5$$

i.e. % Abundance of Y = 87.5

% Abundance of Z = 100 – 87.5 = 12.5

## Uses of the Mass Spectrometer

### 1. *Determination of the Relative Atomic Mass*

When the vapour of a naturally occurring element is introduced into the mass spectrometer, the mass spectrum produced shows one or more peaks.

The position of each peak on the *x-axis* relative to the position of that of carbon-12, gives the relative atomic mass of the element.

### 2. *Relative Abundance of Elements.*

If the mass spectrum of a naturally occurring element gives a single peak with a relative abundance of 100%, then, all its atoms are exactly alike; such an element has no isotope.

However, if two or more peaks are obtained, then, all the atoms of the element are not exactly alike; their masses differ. The *number of peaks* corresponds to the *number of isotopes*, while the *height of a peak* on the *y-axis* is directly proportional to the *relative abundance* of the isotope, e.g. When the vapour of chlorine is examined, two peaks are obtained. They correspond to the relative isotopic masses of 35 and 37, with the heights of the peaks in the ratio 3:1 (75% and 25%) respectively (see figure 4.3)

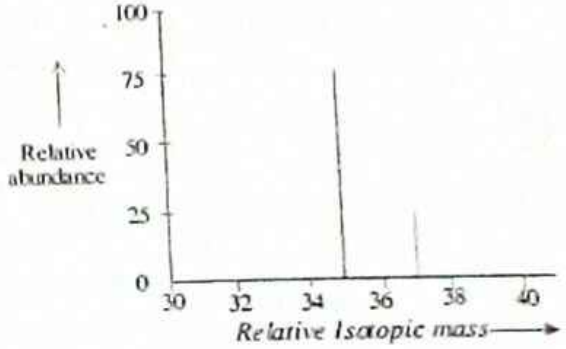
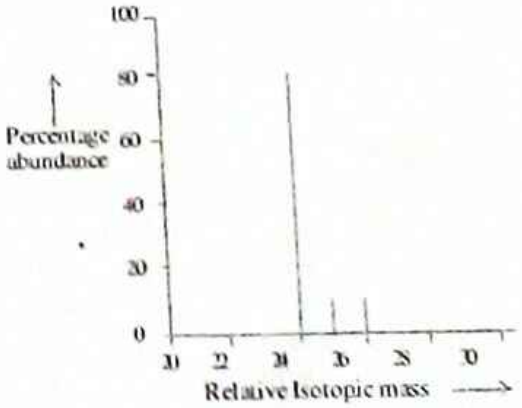



**Fig 4.3:** Mass *spectrum of chlorine.*

### Worked Example

7. The figure below shows the mass spectrum of a naturally occurring element X.




a. How many isotopes are detected in the mass spectrum of X? *•Three isotopes*

b. State the relative isotopic masses of these isotopes. *•24, 25 and 26*

c. What are the percentage abundances of the isotopes? • *80.0%, 10.0%, and 10.0% respectively*

d. What is the relative atomic mass of X?

• *Isotope with 80.0% and mass 24 give* $80 \times 24 = 1920$
• *Isotope with 10.0% and mass 25 give* $10 \times 25 = 250$
• *Isotope with 10.0% and mass 26 give* $10 \times 24 = 260$
*Total* = 2430

∴ *Relative atomic mass* =

$$\frac{(80 \times 24) + (10 \times 25) + (10 \times 26)}{100} = \frac{2430}{100} = 24.3$$

e. If the atomic number of element X is 12 identify X by name, and write the nuclear symbols for the different isotopes.

*X is magnesium;* $^{24}_{12}Mg$, $^{25}_{12}Mg$ *and* $^{26}_{12}Mg$

### Revision Exercises

16 What are isotopes? Name two elements that exhibit isotopy, and give the respective nuclear symbols of the isotopes.

17 Give the composition of the nucleus of the isotope of hydrogen, *tritium*.

18 I. $^{30}_{15}W$ II. $^{32}_{16}X$ III. $^{32}_{15}Y$ IV. $^{31}_{15}Z$
Which of the above elemental symbols are isotopes?
A. II and III only. B. I and III only.
C. III and IV only. D. I, III and IV only.

19 Two isotopes of Z with mass numbers 18 and 20 are in the ratio 1:2. Determine the relative atomic mass of Z. [WAEC]

20 An element X with relative atomic mass of 16.2 contains isotopes $^{16}_{8}X$ with relative abundance of 90% and $^{m}_{8}X$ with relative abundance of 10%. What is the value of m? [NECO]

## 4.7 Distribution of Electrons in the Atom

### Shells and Energy levels

1. The electrons in an atom are in continuous and constant motion in *shells* around the nucleus, represented by capital letters K, L, M, N, etc. The *K-shell* is the innermost and the nearest to the nucleus; followed by the *L-shell*, then, the *M-shell*, the *N-shell*, etc.

2. Each *shell* is at an *energy level*, represented by the *principal quantum number*, *n*. The K-shell is in the *first energy level*, where $n = 1$. It has the lowest energy, and hence, the most stable shell. The L-shell is in the *second energy level*, $n = 2$; the M-shell is in the *third energy level*, $n = 3$, while the N-shell is in the *fourth energy level*, $n = 4$.

| Shell | K | L | M | N |
|---|---|---|---|---|
| Energy level, *n* | 1 | 2 | 3 | 4 |

3. The higher the *principal quantum number*, *n*, the higher the energy level, and the farther away the shell from the nucleus.

### Revision Exercises

21 Which electronic shell is the innermost, and what is its energy level?

22 Which shell is a. the most stable?
b. in the third energy level?

### Shell electronic configurations of the first twenty elements

1. The electronic configuration of an element indicates the number of electrons in the shells at various energy levels of its atom.

2. The maximum number of electrons a shell can accommodate is limited by the formula $2n^2$. Hence, the K-shell ($n = 1$) accommodates a maximum of two electrons, while that of the L-shell ($n = 2$) is eight electrons. When considering the first twenty elements, the M-shell ($n = 3$) accommodates only eight electrons – instead of eighteen by calculation.

3. When filling the shells with electrons, the K-shell ($n = 1$) is filled first, with only two electrons; followed by the L-shell ($n = 2$) with eight electrons; then, the M-shell ($n = 3$) with eight electrons also; while the last two electrons enter the N-shell ($n = 4$) (Table 4.3).

**Table 4.3:** *Shell Electronic Configuration of Elements with Atomic numbers 1 to 20.*

| Symbol of Element | Atomic Number Z | Shell Electronic Configuration K | L | M | N |
|---|---|---|---|---|---|
| H | 1 | 1 | | | |
| He | 2 | 2 | | | |
| Li | 3 | 2 | 1 | | |
| Be | 4 | 2 | 2 | | |
| B | 5 | 2 | 3 | | |
| C | 6 | 2 | 4 | | |
| N | 7 | 2 | 5 | | |
| O | 8 | 2 | 6 | | |
| F | 9 | 2 | 7 | | |
| Ne | 10 | 2 | 8 | | |
| Na | 11 | 2 | 8 | 1 | |
| Mg | 12 | 2 | 8 | 2 | |
| Al | 13 | 2 | 8 | 3 | |
| Si | 14 | 2 | 8 | 4 | |
| P | 15 | 2 | 8 | 5 | |
| S | 16 | 2 | 8 | 6 | |
| Cl | 17 | 2 | 8 | 7 | |
| Ar | 18 | 2 | 8 | 8 | |
| K | 19 | 2 | 8 | 8 | 1 |
| Ca | 20 | 2 | 8 | 8 | 2 |

From Table 4.3 above:

1. The K-shell (*first energy level*) accommodates electrons from the atoms of hydrogen, $_1H$ and helium, $_2He$, i.e. at helium, the K-shell is filled completely with two electrons.

2. The *third electron* in lithium atom, $_3Li$, up to the *tenth electron* in neon atom, $_{10}Ne$, enter the L-shell in the *second energy level*; so that the electronic configuration of lithium atom, $_3Li$, is 2, 1; while that of neon, $_{10}Ne$, is 2, 8.

3. The *eleventh electron* in sodium atom, $_{11}Na$, up to the *eighteenth electron* in argon atom, $_{18}Ar$, enter the M-shell in the *third energy level*; so that the electronic configuration of sodium atom, $_{11}Na$, is 2, 8, 1; while that of argon, $_{18}Ar$, is 2, 8, 8.

4. The *last electron* in potassium atom, $_{19}K$, enters the N-shell in the *fourth energy level*, so that its shell electronic configuration is 2, 8, 8, 1; while that of calcium atom, $_{20}Ca$, is 2, 8, 8, 2.

### Shell electronic structures of some elements

The arrangement of electrons in the shells of some atoms are as shown in fig 4.5.

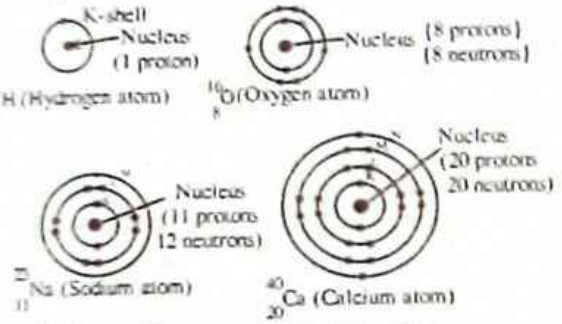



Fig 4.5 *Electronic structures of some atoms*

### Revision Exercises

23 In which electronic shell of an atom will you locate the following: a. 3rd electron? b. 10th electron? c. 16th electron? d. 20th electron?

24 Write the shell electronic configurations and draw the shell electronic structures of the atoms of elements with atomic numbers 6, 12 and 17.

25 How many electrons are in the L shell of $^{31}_{15}P$?

## Subshells and Atomic orbitals

1. Each ***shell*** has *one* or *more* ***subshells***, which are at ***energy sublevels*** represented by small letters of the alphabets ***s, p, d,*** or ***f***.

2. The number of *subshells* in a *main shell* equals the value of ***n***, the *energy level*. Hence,

- K-shell ($n = 1$), has only ***one subshell, 1s***.
- L-shell ($n = 2$), has ***two subshells, 2s and 2p***.
- M-shell (n = 3) has ***three subshells 3s, 3p and 3d***.
- N-shell, in the *fourth energy level*, ($n = 4$) has ***four subshells 4s, 4p, 4d and 4f***.

3. Each ***subshell*** has *one* or *more* ***atomic orbitals***.

*An atomic orbital is a region around the nucleus where electrons are most likely to be found.*

- An *s-subshell* has one orbital called ***s-orbital***;
- A *p-subshell* has three orbitals called ***p-orbitals***;
- A *d-subshell* has five orbitals called ***d-orbitals***;
- An *f-subshell* has seven orbitals called ***f-orbitals***.

| *Subshells* | *s* | *p* | *d* | *f* |
|---|---|---|---|---|
| *Number of Orbitals* | *1* | *3* | *5* | *7* |

4. An *s-orbital* is *spherical* in shape, and symmetrical about the nucleus (see figure 24.9).

A *p-orbital* has a *dumbbell* shape (like *figure-eight*) (see figure 24.10). The three orbitals in a p-subshell are at right angle to one another, and are designated $p_x$, $p_y$ *and* $p_z$.

5. The *total number of orbitals* in a particular *subshell* is limited by the formula $n^2$; where $n$ is the energy level:

K-shell: n = 1; number of orbitals = $n^2 = 1^2 = 1$.
L-shell: n = 2; number of orbitals = $n^2 = 2^2 = 4$.
M-shell: n = 3; number of orbitals = $n^2 = 3^2 = 9$.
N-shell: n = 4; number of orbitals = $n^2 = 4^2 = 16$.

6. An *orbital* can accommodate a *maximum* of *two electrons*. Hence, the maximum number of electrons that can be accommodated in a *shell* is represented by the formula $2n^2$; where $n$ is the *energy level*. Table 4.5 gives the distribution of *orbitals* and electrons in *shells* and *subshells*.

**Table 4.4** *Number of orbitals and electrons in the Energy levels (Shells)*

| Energy level, $n$ (Shell) | Sub-shell $n$ | No. of orbitals $n^2$ (Total) | No. of electrons per subshell | Maximum electrons per shell, $2n^2$ |
|---|---|---|---|---|
| 1 (K) | 1s | 1 (1) | 2 | 2 |
| 2 (L) | 2s | 1 | 2 | 8 |
| | 2p | 3 (4) | 6 | |
| 3 (M) | 3s | 1 | 2 | 18 |
| | 3p | 3 | 6 | |
| | 3d | 5 (9) | 10 | |
| 4 (N) | 4s | 1 | 2 | 32 |
| | 4p | 3 | 6 | |
| | 4d | 5 | 10 | |
| | 4f | 7 (16) | 14 | |

6. The order of *increasing energy of subshells* in the *same energy level*, $n$ is:

$$ns < np < nd < nf$$

7. For *similar subshells, orbital size as well as the energy increase as the energy level increases*, e.g.
   - $1s < 2s < 3s < 4s$
   - $2p < 3p < 4p$
   - $3d < 4d$

**Worked Examples**

**7.** How many subshells are in the M-shell? Name them.

*Since M-shell is in the third energy level, n = 3, it has three subshells;* namely, *3s, 3p and 3d.*

**8.** How many orbitals are in the third energy level, and what are the compositions?

*The number of orbitals in an energy level is given by the formula $n^2$. For the third energy level n = 3, the number of orbitals is $3^2 = 9$ orbitals.*

*The 9 orbitals are made up of one 3s-orbital, three of 3p-orbitals and five of 3d-orbitals.*

**Revision Exercises**

**26** Calculate the number of subshells in the fourth energy level, and name them.

**27** Which subshell is of lower energy?
   a. 1s or 2s. b. 3p or 3d.

**28a.** What is an atomic orbital?
   b. How many orbitals are in the *p*-subshell?

**29** List the various types of orbitals in the fourth energy level. Which orbital has the lowest energy?

**30** Calculate the maximum number of electrons that can occupy the following:
   a. Orbitals in the *d*-subshell. b. M-shell.

## Energy sublevel electronic configurations of the first twenty elements

The *three rules/principles* that govern the order in which electrons enter the orbitals in the various *energy sublevels* (*subshells*) of the atom are:

**1. Aufbau Principle:** ***Order of increasing energy***

***Aufbau*** *means building up.*

***Aufbau principle*** states that: *Electrons enter into orbitals in order of increasing energy.*

The order of increasing energy of some orbitals is:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p$$

**Note:** Although the 4s-orbital is in the fourth energy level, it is of lower energy than the 3d-orbitals in the third energy level.

**How to represent the positions of electrons in the subshells**

The steps to follow are:

1. Write the *energy level*, n = 1, 2, 3, 4, etc.
2. Write the *subshell (or energy sublevel* symbol) *s, p, d,* or *f;*
3. Write the *number of electrons* in the orbitals within the *subshell* as a superscript (on the top right-hand-side).

Energy level $\longrightarrow 1s^2 \longleftarrow$ number of electrons
(sublevel)

Hence:

- $1s^2$ means: In the ***first*** energy level, the *s-* ***subshell*** has ***two electrons***, or, there are ***two*** electrons in the ***s sub-level*** of the ***first energy level.***
- $3p^5$ means: In the ***third*** energy level, the ***p-subshell*** has ***five electrons***, or, there are ***five electrons*** in the ***p-sublevel*** of the ***third energy level.***

## Arrangement of electrons in the orbitals

**1. *K-shell: First Energy Level, n = 1***

The *first series of elements* corresponds to the filling of the 1s-orbital, in the K-shell with two electrons, one at a time. The two elements involved are hydrogen, $_1H$, with electron configuration $1s^1$, and helium, $_2He$, with electron configuration $1s^2$ (see Table 4.5).

**2. *L-shell: Second Energy Level, n = 2***

The *second series of elements* corresponds to the filling of the 2s- and 2p- *orbitals* in L-shell with two and six electrons respectively. The eight elements involved have atomic numbers 3 to 10:

In lithium, $_3Li$, the third electron enters the 2s-orbital, since the 1s orbital is already filled at helium. Hence, the electron configuration of $_3Li$ is $1s^2\ 2s^1$ (2, 1). The fourth electron in beryllium, $_4Be$ also enters the 2s-orbital to give $1s^2\ 2s^2$. In boron, $_5B$, the fifth electron goes into the next available 2p-orbitals to give $1s^2\ 2s^2\ 2p^1$ (2, 3). Thereafter, the three 2p-orbitals are progressively filled up to neon $_{10}Ne$, with the electronic configuration $1s^2\ 2s^2\ 2p^6$ (2, 8). L-shell is completely filled at neon.

**3. *M-shell: Third Energy Level, n = 3***

The *third series of elements* corresponds to the filling of the 3s- and 3p- *orbitals* with two and six electrons respectively. The eight elements involved have atomic numbers 11 to 18. Their electron configurations follow the same pattern as those elements from lithium, $_3Li$, to neon, $_{10}Ne$. Hence, that of sodium atom, $_{11}Na$ $1s^2\ 2s^2\ 2p^6\ 3s^1$ (2, 8, 1) is similar to that of lithium, while that of argon, $_{18}Ar$, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ (2, 8, 8) is similar to that on neon (Table 4.5).

**4. *N-shell: Fourth energy level, n = 4***

The *fourth series of elements* in the first twenty elements corresponds to the filling of the 4s-*orbital*

with two electrons. The two elements involved are potassium and calcium:

$_{19}K$ is $1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^1$ (2, 8, 8, 1)

$_{20}Ca$ is $1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2$ (2, 8, 8, 2).

When electrons occupy atomic orbitals in the various subshells according to Aufbau principle, the configuration obtained is called ***ground state electronic configuration.*** It is the *most stable state of an atom.*

Table 4.5 gives the *electronic configurations* of the first twenty elements using the *s, p and d notations*. Students are advised to master and become *addicted* to their *names, symbols, atomic numbers, as well as their electron configurations.*

**Table 4.4** *Subshell electronic configurations of the first twenty elements*

| Symbol of Element | Atomic Number | Sublevel Electronic Configuration 1s 2s 2p 3s 3p 4s |
|---|---|---|
| H | 1 | $1s^1$ |
| He | 2 | $1s^2$ |
| Li | 3 | $1s^2\ 2s^1$ |
| Be | 4 | $1s^2\ 2s^2$ |
| B | 5 | $1s^2\ 2s^2\ 2p^1$ |
| C | 6 | $1s^2\ 2s^2\ 2p^2$ |
| N | 7 | $1s^2\ 2s^2\ 2p^3$ |
| O | 8 | $1s^2\ 2s^2\ 2p^4$ |
| F | 9 | $1s^2\ 2s^2\ 2p^5$ |
| Ne | 10 | $1s^2\ 2s^2\ 2p^6$ |
| Na | 11 | $1s^2\ 2s^2\ 2p^6\ 3s^1$ |
| Mg | 12 | $1s^2\ 2s^2\ 2p^6\ 3s^2$ |
| Al | 13 | $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$ |
| Si | 14 | $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$ |
| P | 15 | $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$ |
| S | 16 | $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$ |
| Cl | 17 | $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$ |
| Ar | 18 | $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ |
| K | 19 | $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$ |
| Ca | 20 | $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$ |

**2. Pauli Exclusion Principle: *Electron-spin***

The electron in an orbital spins about its own axis either *clockwise* or *anti-clockwise*. This spinning limits the number of electrons in an orbital to two; in order to minimize electronic repulsion.

The first electron in an orbital is assumed to enter with an up-spin (clockwise), ↑, while the second electron enters the same orbital with a down-spin (anti-clockwise), ↓. This is in accordance with the ***Pauli exclusion principle***, which state that:

*An orbital accommodates two electrons of opposite spin.*

**3. Hund's rule of maximum multiplicity: *Degenerate Orbitals***

An *s-subshell* has only *one* orbital, while the *p, d and f subshells* have *three, five* and *seven* orbitals respectively.

When the *three p-orbitals*, the *five d-orbitals*, or the *seven f-orbitals* are in the *same energy level, they have the same energy.* For instance:

The *three orbitals* in the *2p (or 3p) subshell* have *the same energy. Orbitals having the same energy are called degenerate (equivalent) orbitals.*

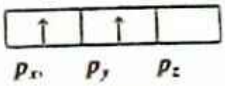
According to Hund's rule:

- *Electrons occupy degenerate (equivalent) orbitals singly, with the same spin.* Or
- *No pairing of electrons in degenerate (equivalent) orbitals until each orbital is singly occupied with parallel spin.*

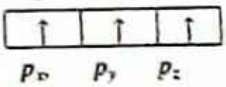
**Distribution of electrons in degenerate orbitals**

The *p-subshell* has *three degenerate orbitals* $p_x$, $p_y$ *and* $p_z$:

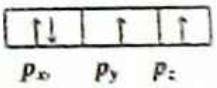
- If there are *two* electrons in the *p-subshell*, the $p_x$ *and* $p_y$ orbitals take one electron each with their spins clockwise, to give *two unpaired electrons*:




- When there are *three* electrons, each of the $p_x$, $p_y$ *and* $p_z$ accommodates one electron with the same clockwise spin, to give *three unpaired electrons.*




- When there are *four* electrons, the first orbital, $p_x$ contains two electrons with opposite spins, while the $p_y$ *and* $p_z$ contain one electron each with parallel clockwise spins, to give *two unpaired electrons*:




- When there are *five* electrons in the *p-subshell*, $p_x$ *and* $p_y$ take two electrons each of opposite spins, while the fifth electron enters $p_z$ with a clockwise spin, to give *one unpaired electron.*

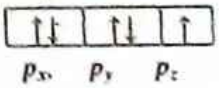



Table 4.6 gives the spins of electrons in the atomic orbitals of the first twenty elements.

**Notes:**

1. The first electron in an orbital spins clockwise ↑, while the second electron spins anti-clockwise ↓.
2. Hund's rule is applied when electrons enter the three equivalent 2p- and 3p-orbitals. Hence, $_6C$, $_8O$,

$_{14}Si$ and $_{16}S$ have two unpaired electrons; while $_{7}N$ and $_{15}P$ have three unpaired electrons.

**Table 4.6** *Electron distribution in degenerate orbitals*

| Element | Electronic Configuration | Electron Distribution in the Outer Orbitals |
|---|---|---|
| $_1H$ | $1s^1$ | ↑ |
| $_2He$ | $1s^2$ | ↑↓ |
| | | 2s 2p$_x$ 2p$_y$ 2p$_z$ |
| $_3Li$ | $1s^2\ 2s^1$ | ↑ |
| $_4Be$ | $1s^2\ 2s^2$ | ↑↓ |
| $_5B$ | $1s^2\ 2s^2\ 2p^1$ | ↑↓ ↑ |
| $_6C$ | $1s^2\ 2s^2\ 2p^2$ | ↑↓ ↑ ↑ |
| $_7N$ | $1s^2\ 2s^2\ 2p^3$ | ↑↓ ↑ ↑ ↑ |
| $_8O$ | $1s^2\ 2s^2\ 2p^4$ | ↑↓ ↑↓ ↑ ↑ |
| $_9F$ | $1s^2\ 2s^2\ 2p^5$ | ↑↓ ↑↓ ↑↓ ↑ |
| $_{10}Ne$ | $1s^2\ 2s^2\ 2p^6$ | ↑↓ ↑↓ ↑↓ ↑↓ |
| | | 3s 3p$_x$ 3p$_y$ 3p$_z$ |
| $_{11}Na$ | $1s^2 2s^2 2p^6 3s^1$ | ↑ |
| $_{12}Mg$ | $1s^2 2s^2 2p^6 3s^2$ | ↑↓ |
| $_{13}Al$ | $1s^2 2s^2 2p^6 3s^2 3p^1$ | ↑↓ ↑ |
| $_{14}Si$ | $1s^2 2s^2 2p^6 3s^2 3p^2$ | ↑↓ ↑ ↑ |
| $_{15}P$ | $1s^2 2s^2 2p^6 3s^2 3p^3$ | ↑↓ ↑ ↑ ↑ |
| $_{16}S$ | $1s^2 2s^2 2p^6 3s^2 3p^4$ | ↑↓ ↑↓ ↑ ↑ |
| $_{17}Cl$ | $1s^2 2s^2 2p^6 3s^2 3p^5$ | ↑↓ ↑↓ ↑↓ ↑ |
| $_{18}Ar$ | $1s^2 2s^2 2p^6 3s^1 3p^6$ | ↑↓ ↑↓ ↑↓ ↑↓ |
| | | 4s |
| $_{19}K$ | $1s^2 2s^2 2p^6 3s^1 3p^6 4s^1$ | ↑ |
| $_{20}Ca$ | $1s^2 2s^2 2p^6 3s^1 3p^6 4s^2$ | ↑↓ |

### Worked Examples

**9.** List the types of atomic orbitals present in the atom of element represented by $_8X$.

*First, write the subshell electron configuration of X. Its atomic number is 8; hence, it has 8 protons, and therefore, 8 electrons. Its electronic configuration is:*

$$1s^2\ 2s^2\ 2p^4$$

*From the electronic configuration, s- and p-orbitals are the two types of orbitals in element X.*

**10a.** How many orbitals are occupied by electrons in the atom of an element with atomic number 7?

**b.** How many unpaired electrons are in the atom?

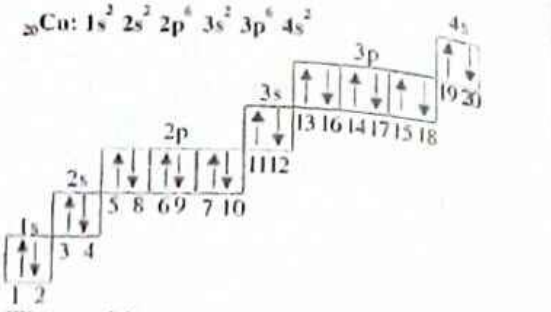
**a.** *First, write the electronic configuration of the atom with 7 electrons indicating the distribution of electrons in the p-subshell:* $1s^2\ 2s^2\ 2p_x^1 2p_y^1 2p_z^1$

*Hence, the 7 electrons are occupying 5 orbitals.*

**b.** *There are three unpaired electrons.*

### Positions and Spins of the First Twenty Electrons in the Atom

The electron configuration of calcium atom, $_{20}Ca$, can be used to indicate the positions and spins of the first twenty electrons in the orbitals of the various subshells of an atom:




**Note:** The position and spin of the last electron in the atom of an element is very important.

### Revision Exercises

**31** Arrange the following orbitals in their correct order of increasing energy level:

2p, 3s, 2s, 3d, 4s

**32** Name the element with the electron configuration

**a.** $1s^2\ 2s^2\ 2p^1$; **b.** $1s^2\ 2s^2\ 2p^6\ 3s^1\ 3p^5$

**33** Which types of orbitals are present in the element represented by $_{14}X$ ?

**34** Name the three rules/principles that are applied in writing the electronic configurations of the atoms.

**35** Mention the rule/principle that has been violated in each of the following electronic configuration, and write the correct configuration for each element:

**a.** $_5B$: $1s^2\ 2s^2\ 3p^1$ **b.** $_9F$: $1s^2\ 2s^3\ 2p^4$

**36** Which rule/principle has been violated in the electronic configuration of the element X with atomic number 7? Write the correct configuration.




**37** Write the electron configurations of the elements with atomic numbers 8 and 15, and thereafter, determine the number of unpaired electrons present in their p-orbitals.

**38** Consider the element represented by $_8X$. How many electrons are in the

**a.** 2p orbitals ? **b.** L shell ?

**39** In which subshell or orbital of an atom is the 17th electron, and what is its spin ?

**40** Which of the following elements has no unpaired electrons?

**A.** $_3Li$ **B.** $_{10}Ne$ **C.** $_{15}P$ **D.** $_{19}K$

## 4.8 Valence Shells and Valence Electrons

The *valence shell* of an atom is the outermost shell of electrons in its electronic configuration. It is the highest *occupied* energy level. The electrons in the *valence shell* are called *valence electrons*:

1. In lithium, $_3Li$, the shell configuration (2, 1) shows that L-shell, the second shell, is the *valence shell*, and has *one valence electron*. Its orbital configuration of $1s^2\ 2s^1$ shows that the valence

electron is in the second energy level. The *valence or outershell* configuration is $2s^1$ with only *one valence electron.*

2. In chlorine, $_{17}Cl$ the shell configuration (2, 8, 7) shows that the third shell is the valence shell and has seven valence electrons. Its orbital configuration of $1s^2$, $2s^2\ 2p^6$, $3s^2\ 3p^3$ shows that the *valence electrons* are in the third energy level. Its *outer shell* electron configuration is $3s^2\ 3p^3$; hence, it has seven (2 + 5) *valence electrons*. The *outer subshell* is 3p with five electrons.

### Revision Exercises

41 Which electronic shell of an atom is called the valence shell?

42a What are valence electrons?

b How many valence electrons are in each of the following elements represented by

i. $_8X$ ? ii. $_{14}Y$?

43 Write the valence shell electronic configuration of the following elements, and thereafter, determine the number of valence electrons:

a. $_{12}Mg$ b. $_9F$ c. $_{16}S$.

44 How many electrons are in the outermost subshell of an element with the electronic configuration $1s^2 2s^2 2p^3$?

## Noble (or Rare) gas configurations

*Any electron configuration in which the last electron in the atom completes the valence shell* is called *noble gas configuration*; e.g.

a. At *helium*, $_2He$, $1s^2$, the *first energy level* or *K-shell* is completely filled with two electrons.

b. At *neon*, $_{10}Ne$: $1s^2, 2s^2 2p^6$ (2, 8) the outermost L-shell is completely filled with eight electrons.

c. At *argon*, $_{18}Ar$, $1s^2 2s^2 2p^6 3s^2 3p^6$ (2, 8, 8) the *third energy level*, M-shell is completely filled.

In the atoms of He, Ne and Ar, the *outermost shells* or the *highest occupied energy levels* are completely filled with electrons. Such atoms are very *stable*, and generally *unreactive.*

Atoms of *neon* and *argon* with *eight* valence electrons have ***octet of electrons***, while that of ***helium*** is a ***duplet of electrons***.

### Revision Exercises

45a What is a noble gas configuration?

b Give the electronic configurations of two elements with noble gas configurations.

46 Which of the following atoms contain the highest number of electrons in the outermost shell?

A. $_8O$ B. $_{10}Ne$ C. $_{15}P$ D. $_{19}K$ [WAEC]

47 Which of the following electronic configurations represent that of a noble gas? [WAEC]

A. 2, 8, 8, 2 B. 2, 8, 2 C. 2, 8 D. 2, 6

48a What is an *octet of electrons*?

b Mention an element that has an *octet of electrons*.

## Answers to Revision Exercises

8. D 9. C 18. D 19. 19.3 20. m = 18
25. 8 40. B 44. 3 46. B 47. C

# 5

# •THE PERIODIC TABLE•

## 5.1 Introduction

The *Periodic Table* represents a simple systematic way of classifying elements.

A Russian Scientist, Mendeleev, in 1869, formulated the *periodic law* based on the *relative atomic masses* of the elements. However, the modern version of the *periodic law* is based on their *atomic numbers*, as suggested by Moseley (1914).

### The Periodic Law

The *periodic law* states:

• *The physical and chemical properties of elements are periodic function of their atomic numbers.*

*Or*

• *When elements are arranged in order of increasing atomic numbers, their physical and chemical properties recur periodically.*

Table 5.1 shows the ***short form*** of the Periodic Table of elements with atomic numbers 1 to 20. The elements have been arranged on the basis of the electron configurations of their *valence shells*. The *long form* of the Periodic Table is shown in Appendix 3.

### Revision Exercises

1. State the *periodic law*.
2. Name a scientist whose work could be associated with the Periodic Table.
3. On which property of the atom is the Periodic Table based?
4. Elements are arranged in the Periodic Table in the order of increasing
   A. number of neutrons. B. number of shells.
   C. atomic number. D. mass number. [WAEC]

**Table 5.1** ***Periodic Table of the First Twenty Elements***

| Group / Period | I | II | III | IV | V | VI | VII | 0 |
|---|---|---|---|---|---|---|---|---|
| 1 | 1<br>H<br>$1s^1$ | | | | | | | 2<br>He<br>$1s^2$ |
| 2 | 3<br>Li<br>$2s^1$ | 4<br>Be<br>$2s^2$ | 5<br>B<br>$2s^22p^1$ | 6<br>C<br>$2s^22p^2$ | 7<br>N<br>$2s^22p^3$ | 8<br>O<br>$2s^22p^4$ | 9<br>F<br>$2s^22p^5$ | 10<br>Ne<br>$2s^22p^6$ |
| 3 | 11<br>Na<br>$3s^1$ | 12<br>Mg<br>$3s^2$ | 13<br>Al<br>$3s^23p^1$ | 14<br>Si<br>$3s^23p^3$ | 15<br>P<br>$3s^23p^3$ | 16<br>S<br>$3s^23p^4$ | 17<br>Cl<br>$3s^23p^5$ | 18<br>Ar<br>$3s^23p^6$ |
| 4 | 19<br>K<br>$4s^1$ | 20<br>Ca<br>$4s^2$ | | | | | | |

## 5.2 The Periodic Table: Basic Features

### The Groups

1. *Elements in the same vertical column* form a ***Group.*** There are eight main groups. Each group forms a family of elements represented by Roman numerals: I, II, III, IV, V, VI, VII and 0 (or VIII), but can be represented as: 1, 2, 3, 4, 5, 6, 7 and 0.

2. *Elements in the same group have the same number of valence electrons* in their respective atoms; that is, they have similar outermost shell electronic configurations. For instance:

Li ($2s^1$), Na ($3s^1$) and K ($4s^1$) have *one valence electron* in the highest occupied orbital; therefore, they belong to group I. Those with *two valence electrons*, $ns^2$, (Be, Mg, and Ca) are in group II; those with *three valence electrons*, $ns^2np^1$, (B and

Al) belong to **group III**, and so on. In fact, the group an element belongs to corresponds to the total number of electrons in the outermost shell of its atom (except for group 0 elements).

3. Elements in which their valence shells or highest occupied energy levels in their atoms are completely filled with electrons, that is, have completed outermost shell of eight electrons $ns^2np^6$ (with the exception of He, $1s^2$) are placed in the eighth group, called **group 0** (or **VIII**).

4. Certain groups of elements have *family* names:
- *Group I* elements are called ***alkali metals***.
- *Group II* elements are the ***alkaline-earth metals***.
- *Group VII* elements are known as the ***halogens***.
- *Group 0* elements are called ***noble, inert or rare gases***.

A *family of elements* occupies a *vertical column* (or *group*) in the Periodic Table.

### The Periods

1. Elements in the same *horizontal row* form a *Period*. The first twenty elements occupy the first four periods in the Periodic Table.

2. *Atoms of elements in the same period have the same number of shells of electrons*. The highest occupied energy level in the electron configuration of an element represents its *period*. For instance: *Mg*: (2, 8, 2) or ($1s^2,2s^22p^6,3s^2$) and *Cl* (2, 8, 7) or ($1s^22s^22p^63s^23p^5$) are in *period 3*, because their electrons occupy *three shells* – K, L and M. Their *valence electrons are in the third shell* (n = 3), or the highest occupied energy level in their electron configurations in each case is $n = 3$.

3. ***Period 1*** (n = 1) contains two elements, H: $1s^1$, and He: $1s^2$; it corresponds to the filling of the 1s orbital in the first shell.

***Period 2*** (n = 2) contains eight elements, starting with Li: (2, 1) or ($1s^2$, $2s^1$) and ending with Ne: (2, 8) or ($1s^2$, $2s^22p^6$) in which its tenth electron completes the second shell.

***Period 3*** (n = 3) also contains eight elements. It corresponds to the filling of the 3s- and 3p-orbitals. It starts with Na: (2, 8, 1) or ($1s^2$, $2s^22p^6$, $3s^1$) and ends with Ar: (2, 8, 8) or ($1s^2$, $2s^2\,2p^6$, $3s^23p^6$).

***Period 4*** (n = 4) contains the last two elements among the first twenty elements. responds to the filling of 4s, 3d and 4p orbitals.

4. A *period* starts with the filling of an s-orbital, and ends with completely filled p-orbitals; both of them in the same energy level (except period 1).

### Solved Problems

1. Mention **two** criteria used for placing an element into the periodic table. [NECO]
- *The number of valence electrons in its atom – for the group.*
- *The number of electronic shells in its atom – for the period*

2. The electronic configuration of element **X** is
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$

a. What is the atomic number of element X?
*Atomic number of X is 19. (It corresponds to the number of electrons in its atom).*

b. State the period to which X belongs.
*X belongs to period 4 (The highest principal quantum number in its configuration).*

c. Give the
i. number of valence electron(s) in element X.
*X has only one valence electron (in the outer 4s).*
ii. name of element X.
*X is potassium; element with atomic number 19.*

### Revision Exercises

5. How many groups are in the periodic table?

6. In terms of electronic structure, state what is common to all the elements in the same
a. group; b. period. [WAEC]

7. State the period and the group to which each of the following elements belong:
$_4V$, $_{13}W$, $_2X$, $_{20}Y$, $_{10}Z$

8. What is the famuly name of
a. Group 2 elements? b. Group 7 elements?

9. If an atom is represented as $^{39}_{19}X$, which of the following deductions is correct? [WAEC]
A. It contains 20 protons. B. Its atomic number is 39.
C. It is an alkali metal. D. It is an alkali-earth metal.

10 "Electrons will occupy equivalent orbitals singly, as far as possible, with the same spin" is a statement of
A. Hund's rule. B. Pauli Exclusion Principle.
C. Periodic law. D. Aufbau Principle. [WAEC]

## 5.3 Blocks of Elements in the Periodic Table

Elements in the Periodic Table are in *blocks*, based on the types of their valence orbitals. There are *five blocks* of elements:

1. ***s-block elements*** have their valence electrons in the *s*-orbitals (except helium). They are in groups 1 and 2. Examples are ***Li*** ($1s^2\ 2s^1$) and ***Mg*** ($1s^2$, $2s^22p^6$, $3s^2$). They are all metals.

2. ***p-block elements*** are those in which the *outermost* electrons *partially* fill the p-orbitals. They are in groups 3, 4, 5, 6 and 7: boron, carbon, nitrogen, sulphur and chlorine respectively.

The *s*- and *p*-block *elements* are called ***representative elements***.

3. ***Noble elements*** are those in which the highest occupied energy levels are completely filled with electrons. They belong to group 0, e.g. He ($1s^2$), Ne ($2s^22p^6$) and Ar ($3s^23p^6$). They are all gases.

4. ***d-Block (transition) elements*** are those in which the outermost electrons are in the *d-orbitals*. They are all metals.

5. ***f-Block (inner-transition) elements*** have their outershell electrons in the *f-orbitals*. They are called *rare-earth elements*.

**Revision Exercises**

11 What are *representative* elements? Give two examples.

12 X is an element with a valence electron of 2. Which of the following elements will be in the same group in the Periodic table as X?

| Element | S | T | V | W |
|---|---|---|---|---|
| Atomic Number | 12 | 13 | 17 | 19 |

A. S B. T C. V D. W

13 Consider the following elements represented thus: $_5A$, $_8B$, $_{12}C$, $_{13}D$ and $_{18}E$.
State which of the elements
a. is a noble gas; b. is an alkaline-earth metal;
c. belong to group 2; d. belong to the s-block;
e. belong to the same group;
f. belong to the p-block; g. belong to period 4;
h. belong to the same period.

14 Use the form of the periodic table given below to answer the questions that follow:

| | I | II | III | IV | V | VI | VII | 0 |
|---|---|---|---|---|---|---|---|---|
| 1 | C | | | | | | | |
| 2 | | B | | | | | D | |
| 3 | E | | | | | | | A |
| 4 | | | | | | | | |

Give the letter representing:
a. a p-block element; b. a halogen
c. element with the lowest number of protons in its atom; d. an alkali metal, e. a noble gas.
f. an s-block element; g. the most stable atom.
h. an alkaline-earth metal.

15 Which of the following elements: calcium, fluorine, iodine, neon, magnesium and helium are:
a. halogens? b. noble gases? c. alkaline-earth metals?

16 If the electronic configuration of an element X is $1s^22s^22p^5$, which of the following statements about X is false? It
A. has five electrons in its valence shell.
B. has atomic number 9.
C. is a halogen. D. is a non-metal. [WAEC]

17 The electronic configuration of an element X is $1s^2\,2s^2\,2p^6\,3s^2\,3p^4$. It can be deduced that X
A. belongs to group 6 of the Periodic Table.
B. belongs to period IV of the Periodic Table.
C. has 3 unpaired electrons in its atom.
D. has relative molecular mass of 16. [WAEC]

## 5.4 Periodic Atomic Properties

*Any physical or chemical property of an element that varies with increasing atomic number is a periodic atomic property.* The following physical properties of the atoms exhibit *periodicity*:

1. Atomic size (or radius).
2. Atomic volume.
3. Ionization energy.
4. Electron affinity.
5. Electronegativity.

### 1. Atomic size (or radius)

The radius of an atom is the distance between the centre of the nucleus and the outermost electronic shell.

***Variation down the Group***

Atomic radius *increases steadily* down the group. *Reason*: Due to increase in the number of electronic shells, valence electrons are found farther from the nucleus. For instance: atomic size of potassium (2, 8, 8, 1) is more than that of lithium (2, 1).

***Variation along the Period***

Atomic size *decreases* from left to right across a period. *Reason:* Due to the steady *increase* in the number of protons in the nucleus, the outermost electrons are drawn closer to the nucleus.

### 2. Atomic volume

The *atomic volume* of an element is the relative mass per unit density. Generally, atomic volume *increases down the group*, and *decreases across the period*.

### 3. Ionization Energy

*Ionization energy is the energy absorbed in order to remove the outermost electron from a gaseous atom.*

The process is *endothermic*. Its value is a measure of the degree of attraction the nucleus has for the electron to be removed.

***Variation down the Group***

Ionization energy *decreases* steadily down the group, due to the steady *increase* in atomic size, as the electron to be removed is not strongly bound to the nucleus. Hence, it will be easier to remove the outermost electron in potassium (2, 8, 8, 1) than in the case of lithium (2, 1). Metallic properties *increase* down the group.

*Variation across the Period*

Ionization energy *increases* steadily across the period due to the *decrease* in atomic size, as the electron to be removed is strongly attracted to the nucleus. Metallic properties *decrease* across the period.

**Metals versus Nonmetals**

Generally, metals have *low ionization energies*, i.e. they lose their valence electrons with ease. On the contrary, non-metals have *high ionization energies*, i.e. they do not lose their valence electrons readily.

### 4. Electron Affinity

*Electron affinity is the energy released when a gaseous atom accepts one or more electrons.*

It is an *exothermic* process. Its value is a measure of the degree of attraction the nucleus has for the electron being added to the neutral atom.

*Variation down the Group*

Electron affinity *decreases* down the group, due to *increase* in atomic size.

*Variation across the Period*

Electron affinity *increases* from left to right across a period. The increase is due to the steady *decrease* in atomic size.

Noble gases are quite stable; hence, they do not gain or lose electrons.

### 5. Electronegativity

*Electronegativity* is a scale to predict the ability of an atom in a molecule to attract shared electrons to itself.

*Variation down the Group*

Electronegativity *decreases* down the group, due to increasing distance between the valence electrons and the nucleus.

*Variation across the Period*

There is a steady *increase* in electronegativity from the left to the right across a period, due to *decreasing distance between the valence electrons and the nucleus*.

**Metals versus Nonmetals**

In a particular period, the metals are characterized by *low electronegativity*, while the nonmetals have *high electronegativity*. Fluorine in group VII has the highest *electronegativity*, followed by oxygen in group VI.

*Electropositivity* is the opposite of *electronegativity*. It *increases* down the group, and *decreases* across the period.

*The noble gases of group zero have no electronegativity, since their atoms are quite stable.*

**Summary of Trends of Atomic Properties**

| | Atomic property | Trend down the group | Trend across the group |
|---|---|---|---|
| 1. | Atomic volume | *Increases* | *Decreases* |
| 2. | Atomic radius/size | *Increases* | *Decreases* |
| 3. | Ionization energy | *Decreases* | *Increases* |
| 4. | Electron affinity | *Decreases* | *Increases* |
| 5. | Electronegativity | *Decreases* | *Increases* |
| 6. | Electropositivity | *Increases* | *Decreases* |

**Revision Exercises**

18 List three periodic properties of elements that generally increase across the period of the periodic table.

19 Arrange the following elements in order of decreasing electronegativity: $_{16}S$, $_{13}Al$, $_{11}Na$, $_{15}P$

20 Which of the following properties increases down a group in the periodic table ?
A. Atomic radius B. Electronegativity
C. Electron affinity D. Ionization energy

21 Name a property of the atom that increases across the period and down the group in the periodic table.
A. Ionization energy B. Atomic size
C. Atomic number D. Electron affinity [WAEC]

22 What is the trend of the degree of electropositivity of elements in the periodic table?
A. Decreases across a period
B. Decreases down a group
C. Increases across a period
D. Remains constant across a period
E. Remains constant down a group [NECO]

23 Which of the following Group I elements has the highest ionization energy?
A. Li B. Na C. K D. Rb [WAEC]

## 5.4 General Relationship among the Elements

### Group Relationship

1. *Elements in the same group have the same number of valence electrons. Such a group of elements shows similarities in chemical properties.*

2. Elements in groups I, II and III are *metals*; group IV elements are *metalloids*; while those in groups V, VI, VII and VIII are *non-metals*.

3. Elements in group I, the *alkali* metals, are all reactive. Metallic character and reactivity *increase* down the group, hence, francium, Fr is the most reactive metal, followed by caesium, Cs. Elements in group II, the alkaline-earth metals, are less reactive than the alkali metals.

4. Among the *halogen family* of group VII, there is a progressive *decrease* in reactivity down the group: from the highly reactive *gaseous* fluorine, to reactive *gaseous* chlorine, to less reactive *liquid* bromine; then, to considerably less reactive iodine – which is a *solid* at room temperature.

5. All the elements in group 0 (or VIII) are called *noble, inert* or *rare gases*. They are *stable* and *unreactive* – because all the energy levels occupied by electrons in their atoms are completely filled.

### Horizontal Relationship: Elements across the Periods

1. There is a continuous variation in the electronic configurations of the atoms of elements along each period; it leads to variations in physical and chemical properties among the *representative elements*. This is because electrons enter into different s- and p-orbitals.

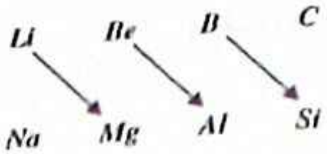
2. In going from left to right across a period, *metallic character decreases*. There is a gradual change from *metals* in groups I, II and III, through *metalloids* in group IV, to *non-metals* in groups V, VI and VII, and finally, to *noble* gases in group 0. For instance: In period 2: Lithium in group I is a soft silvery reactive metal; followed by beryllium, a silvery metal in group 2, but less reactive; then, boron in group 3 is a black and less reactive metal; followed by carbon, a *metalloid*, in group 4.

Nitrogen in group 5 is a less reactive colourless gas; followed by oxygen, a reactive colourless gas in group 6. Fluorine, a highly reactive pale-yellow gas, is in group 7; and finally, neon, an unreactive colourless noble gas is in group 0.

4. A period starts with an alkali metal and ends with a noble (inert) gas – excluding period 1.

### Diagonal Relationship

Because metallic character *increases down a group* and *decreases from left to right along a period*, there exists a ***diagonal relationship*** between the chemical properties of the first member of a group and that of the second member of the next group – as in the cases of lithium and magnesium on one hand, and beryllium and aluminium on the other (see the Periodic Table).




**Solved Problems**

1. Which of the following sets of elements are arranged in order of decreasing atomic size in the periodic table? [WAEC]

A. $_6C$, $_4Be$, $_7N$, $_8O$ B. $_4Be$, $_6C$, $_7N$, $_8O$

C. $_8O$, $_7N$, $_6C$, $_4Be$ D. $_7N$, $_8O$, $_6C$, $_4Be$

**Solution:** *B (All the elements are in the same period; atomic size decreases as atomic number increases).*

2. Which of the following statements about the elements Na, Mg, Al and Si is/are true?

I. They are all in period 3 of the periodic table.

II. Mg is more electropositive than Si.

III. Electropositivity decreases from Na to Si.

IV. Si is the most electropositive element.

A I only. B I and IV only.

C I, II and III only. D I, II, III and IV. [WAEC]

**Solution:** *C. (Si is the least electropositive)*

### Revision Exercises

24 An element, which has atomic number 11, is likely to have similar chemical properties with another element having atomic number

A. 7. B. 9. C. 18 D. 19 [WAEC]

25 Elements from left to right in a given period of the Periodic Table show

A. similarities in chemical properties.

B. steady decreases in electronegativity.

C. steady increases in atomic number.

D. similarities in electronic structures. [WAEC]

26 Li, Na and K are in the same group in the periodic table because they have the same

A. atomic radius B. electronic configuration

C. ionization energy D. number of valence electrons

### Answers to Revision Exercises

4. C 5. B 9. C 10. A 12. A 16. A
17. A 20. A 21. C 22. A 23. A 24. D
25. C 26. D

# 6

# •CHEMICAL COMBINATIONS•

## 6.1 Introduction

The atoms of noble gases, such as helium, $_2$He (2), neon, $_{10}$Ne (2,8) and argon, $_{18}$Ar (2,8,8) are *stable*; because their outermost shells are completely filled with electrons. The atoms of other elements are *unstable*. Their atoms become *stable* by forming *chemical bonds* between one another; this is the cause of ***chemical combination.***

The *attractive force between atoms when they combine chemically is called* ***chemical bond.***

**Revision Exercises**

1. Why do atoms combine?
2. What is a chemical bond.

## 6.2 Valence Electrons – Octet rule

*The electrons in an incompletely filled outer-shell of an atom are called* ***valence electrons.*** Only the *valence electrons of an atom take part in chemical combinations.*

During chemical combinations, all the valence electrons of one atom are either transferred to the valence shell of another, or shared between the combining atoms – in order to attain stable noble gas structures. This forms the basis of the **octet rule**, which states that: *An atom continues to lose, gain, or share electrons, in order to have eight electrons in the outermost shell.*

Atoms of elements in the *same group in the periodic table* and *isotopes of an element* undergo the same type of chemical combinations, and have similar chemical properties, since they have the same number of valence electrons.

**Revision Exercises**

3. State the *octet* rule.
4. The atom of an element X is represented as $^{Y}_{Z}X$. The basic chemical properties of X depend on the value of
   A. Y  B. Z  C. Y – Z  D. Z – Y (WAEC)

## 6.3 Types of Chemical Combinations

The four main types of chemical combinations are:
1. Electrovalent (or Ionic); 2. Covalent;
3. Co-ordinate covalent (or Dative); 4. Metallic.

**Revision Exercise**

5. Name **three** types of chemical combinations.

## 6.4 Electrovalent (or Ionic) Bonding

In an *electrovalent* or *ionic* bonding, *there is complete transfer of all the valence electrons of a metal atom to the valence shell of a non-metal atom, so that each atom acquires a stable noble gas electron configuration.*

### Formation of ions – Valency of an element

An atom is electrically neutral. When it ***loses*** or ***gains*** one or more electrons, it becomes an ***ion***. An atom that ***loses*** one or more of its valence electrons forms a *positively charged* ***ion*** called ***cation***, while an atom that ***gains*** one or more electrons forms a *negatively charged* ***ion*** called ***anion***.

In an *ion*, the number of protons in the nucleus is no more equal to the number of orbiting electrons. Hence, an *ion* is *not electrically neutral.*

When an atom **M** *loses one electron*, its ion carries a positive charge, written as $M^+$; this shows that the ion has ***one*** proton more than the number of electrons.

Generally, atoms of elements in groups **I**, **II** and **III** usually *lose* all their valence electrons, in order to form the most stable *cations* with noble gas configurations. They are metals.

The *number of electrons lost* by a metal atom in order to acquire an *octet* or a *duplet* of electrons corresponds to its ***group*** and its ***electrovalency*** (*combining power* or *capacity*), e.g.:

Sodium atom, $_{11}$Na, (2, 8, 1) in group I, loses its only valence electron to form sodium cation, $Na^+$, that has a neon structure (2, 8).

$$\underset{(2,\,8,\,1)}{_{11}Na} - e^- \rightarrow \underset{(2,\,8)}{_{11}Na^+}$$

Hence, the *electrovalency* of sodium atom is $+1$.

Conversely, when an atom **X** *gains* one electron, its ion carries a negative charge, written as $X^-$. This shows that the ion has ***one*** orbiting electron more than the number of protons in its nucleus.

Generally, atoms of elements in groups **V**, **VI** and **VII** in the periodic table *gain* electrons to form

anions with noble gas structure. They are non-metals. The number of electrons gained by a non-metal atom in order to acquire an octet of electrons corresponds to its *electrovalency*, i.e. its combining power or capacity. It is equal to octet minus the number of valence electrons, e.g.

Chlorine atom, $_{17}Cl$, (2,8,7) in group VII gains only one electron to form chloride anion, $Cl^-$, that has argon structure (2, 8, 8):

$$\underset{1s^2 2s^2 2p^6 3s^2 3p^5}{\underset{(2,8,7)}{Cl}} + e^- \rightarrow \underset{1s^2 2s^2 2p^6 3s^2 3p^6}{\underset{(2,8,8)}{Cl^-}}$$

Hence, its *electrovalency* is -1.

Below is a list of the most stable ions of some elements in the periodic table.

*List of stable ions of some common elements*

| I | II | III | IV | V | VI | VII | 0 |
|---|---|---|---|---|---|---|---|
| $Li^+$ | $Be^{2+}$ | $B^{3+}$ | - | $N^{3-}$ | $O^{2-}$ | $F^-$ | - |
| $Na^+$ | $Mg^{2+}$ | $Al^{3+}$ | - | $P^{3-}$ | $S^{2-}$ | $Cl^-$ | - |
| $K^+$ | $Ca^{2+}$ | | | | | $Br^-$ | - |
| | | | | | | $I^-$ | - |

**Notes:**

1. The charge of an ion is the electrovalency of the element.
2. Atoms of elements in the same group form identical ions; hence, they have the same *valency*.
3. Atoms of elements in groups IV and 0 do not gain or lose electrons.

**Solved Problems**

1. Write the electronic configuration for the most stable ion of each of the following elements:

a. $_4Be$; b. $_8O$; c. $_{13}AL$

**Note:** *First, write the electron configuration of the atom to obtain the number of valence electrons, its group, and to determine the electrovalency of the element.*

a. *$_4Be$ is $1s^2 2s^2$. Since it has only two valence electrons, it is in group II, and will lose the two valence electrons to form $Be^{2+}$ that has helium structure of $1s^2$.*

b. *$_8O$ is $1s^2 2s^2 2p^4$. Since it has six valence electrons and in group VI, it will gain two electrons, in order to form $O^{2-}$ that has neon structure of $1s^2 2s^2 2p^6$.*

c. *$_{13}Al$ is $1s^2 2s^2 2p^6 3s^2 3p^1$. It has three valence electrons, hence, in group III. It loses the three valence electrons to form $Al^{3+}$ that has neon structure of $1s^2 2s^2 2p^6$.*

2. What is the electronic configuration of the atom of an element **R** whose anion $R^{3-}$ has the electronic configuration $1s^2 2s^2 2p^6$?

*$R^{3-}$ has 3 electrons more than its neutral atom **R**, or **R** gains 3 electrons to form $R^{3-}$. Since $R^{3-}$ ($1s^2 2s^2 2p^6$) has 10 electrons, then, **R** has $10 - 3 = 7$ electrons.*
*The electron configuration of **R** is $1s^2 2s^2 2p^3$.*

3. What is the atomic number of an element whose cation $X^{2+}$ has the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6$ ?

A. 16 B. 18 C. 20 D. 22 E. 24 (NECO)

*Atomic number equals number of protons in the nucleus of an atom.*
*An atom **X** forms $X^{2+}$ on losing 2 electrons. Since $X^{2+}$ has 18 electrons, then, neutral atom **X** has $18 + 2 = 20$ electrons. The atomic number of **X** is 20.*

**Revision Exercises**

6. The atom and ion of sodium have the same
A. chemical properties. B. electrical charge.
C. electronic configuration. D. number of protons.
E. size. (NECO)

7. Write the electronic configurations for the most stable ions of each of the following elements:
a. $_9F$ b. $_{12}Mg$ c. $_{15}P$ d. $_{19}K$

8. State the atomic number an element **T** whose cation $T^{2+}$ contains 10 electrons.

9. What is the atomic number of an element whose anion $V^{2-}$ has the electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6$ ?

10 If the mass number of **X** is 24 and $X^{2+}$ contains 10 electrons, the nucleus of **X** will consist of
A. 8 protons and 16 neutrons
B. 10 protons and 15 neutrons.
C. 10 protons and 12 neutrons.
D. 12 protons and 12 neutrons. (WAEC)

## Formation of Binary Ionic Compounds

A *binary compound contains two elements only.*

**Factors that favour formation of Ionic bonds**

An *ionic bond* is usually formed between atoms of different elements in which one has ***low ionization energy*** and the other has ***high electron affinity***. In essence, ionic compounds are formed *between atoms of metals* in groups **I, II** and **III** (they *lose* electrons readily) and *atoms of non-metals* of groups **V, VI** and **VII** (they *gain* electrons readily).

In terms of ***electronegativity***: An ionic bond will be formed between atoms of elements with widely different electronegativities, i.e. between atoms of metals and non-metals.

**Stages in the Formation of Ionic bonds**

The **three** stages involved in the changes in the electronic structures of the atoms during the formation of ionic bonds are:

**I.** The metal atom *loses all its valence electrons* to form a stable *cation* that has the structure of the *nearest* noble gas. The process of *electron-loss* is called ***oxidation***. The heat energy *absorbed* during the process is called ***ionization energy***.

**II.** The nonmetal atom *gains* one or more electrons to form the most stable *anion* with the structure of

*the nearest* noble gas. The process of *electron gain* is called ***reduction***, and the energy *released* during the process is called ***electron affinity***.

**III.** The *opposite ions* combine by the *electrostatic force of attraction*, to form an extremely strong *electrovalent* (*ionic*) bond. It is *non-directional*.

The *electrostatic force of attraction between ions of opposite charges* is called ***electrovalent*** or ***ionic bond***. The *heat liberated* during the process is called ***lattice energy***; it is an *exothermic* process.

In order to form a *neutral ionic compound* the two opposite ions combine in the *inverse ratio* of their charges, so *that the number of electrons lost by the metal atom equals the number of electrons gained by the non-metal atom*. For instance:

**1. Combination of atoms of sodium and chlorine**

**I.** Sodium atom, Na: $1s^2 2s^2 2p^6 3s^1$ (2,8,1), a metal, loses its only valence electron to form a sodium cation, $Na^+$, which has a stable neon structure:

$$\underset{1s^2 2s^2 2p^6 3s^1 \\ (2,8,1)}{Na} - e^- \rightarrow \underset{1s^2 2s^2 2p^6 \\ (2,8)}{Na^+} \quad (oxidation)$$

**II.** Chlorine atom, Cl, $1s^2 2s^2 2p^6 3s^2 3p^5$ (2,8,7), with seven valence electrons, accepts the only electron lost by sodium atom, to complete its valence shell and form a chlorine anion, $Cl^-$, that has argon structure:

$$\underset{1s^2 2s^2 2p^6 3s^2 3p^5 \\ (2,8,7)}{Cl} + e^- \rightarrow \underset{1s^2 2s^2 2p^6 3s^2 3p^6 \\ (2,8,8)}{Cl^-} \quad (reduction)$$

**III.** The opposite ions now combine:

$$Na^+ + Cl^- \rightarrow Na^+Cl^- \text{ or } NaCl$$

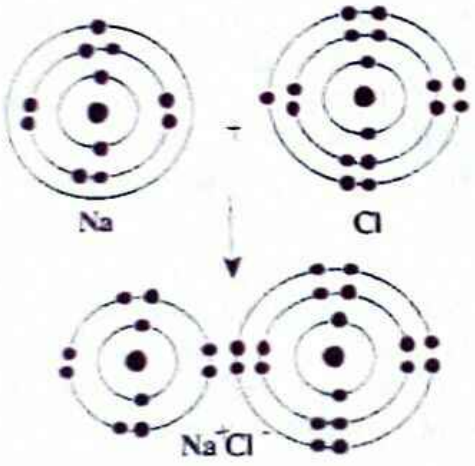



Fig 6.1 *Formation of sodium chloride*

Since sodium atom must ***lose*** **one** electron in order to form a stable $Na^+$, and a chlorine atom must *gain* **one** electron, in order to complete its valence shell and form $Cl^-$, the opposite ions combine in the ratio **1:1**.

***Structure of Sodium chloride***

Sodium chloride exists *as face-centred cubic crystals*, composed of cations, $Na^+$ and anions, $Cl^-$ regularly arranged as shown in figure 6.2.

A close look at the figure shows that the *number of anions* ($Cl^-$) surrounding a *cation* ($Na^+$) is six. So also, the *number of cations* surrounding a single *anion* is six, i.e. the ***coordination number*** of each of $Na^+$ or $Cl^-$ is six. Hence, the opposite ions exist in the crystal in ratio **6:6**, or in a simple ratio **1:1**.

*Coordination number of a* ***cation*** *is the number of anions surrounding a cation in a crystal (and vice versa).*

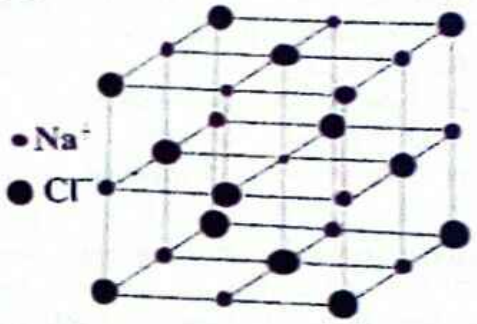



Fig 6.2 *Crystal structure of Sodium chloride*

The chemical formula that represents the *simplest ratio* in which opposite ions combine in an ionic compound is called ***empirical formula***. It is used in representing the composition of an ionic compound. The chemical formula is written such that the symbol of the cation is written first, then, that of the anion, e.g. $Na^+Cl^-$.

For simplicity, the formula is written without the charges, i.e. as **NaCl**. However, it should be noted that *an ionic compound in solid state exists as clusters of ions* (***crystals***), *and not as discrete or separate particles.*

**2. Combination of calcium and fluorine atoms**

**I.** Calcium atom, ${}_{20}Ca$, $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ (2,8,8,2), a metal in Group II, loses its two valence electrons to form $Ca^{2+}$ that has argon structure:

$$\underset{1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 \\ (2,8,8,2)}{Ca} - 2e^- \rightarrow \underset{1s^2 2s^2 2p^6 3s^2 3p^6 \\ (2,8,8)}{Ca^{2+}} \quad (oxidation)$$

**II.** Fluorine atom, ${}_9F$, $1s^2 2s^2 2p^5$ (2,7), a halogen in group VII accepts only one electron to complete its valence shell, and form $F^-$ that has neon structure.

$$\underset{1s^2 2s^2 2p^5 \\ (2,7)}{F} + e^- \rightarrow \underset{1s^2 2s^2 2p^6 \\ (2,8)}{F^-} \quad (reduction)$$

**III.** To form a neutral compound, **one** calcium ion $Ca^{2+}$ (*loss of two electrons*) combines with **two** fluorine ions, $2F^-$ (*gain of two electrons*).

$Ca^{2+} + 2F^- \rightarrow Ca^{2+}(F^-)_2$ *simply* $CaF_2$

The formula $CaF_2$ shows that ions of calcium and fluorine exist in the ratio 1:2 in the crystal formed.

**3. Combination of aluminium and oxygen**

*I.* Aluminium atom, ${}_{13}Al$, $1s^2 2s^2 2p^6 3s^2 3p^1$ (2,8,3), a group III metal, loses its three valence electrons in the outer 3s- and 3p-orbitals (in the third shell) to form $Al^{3+}$ ($1s^2 2s^2 2p^6$) that has neon structure.

$$\underset{1s^2 2s^2 2p^6 3s^2 3p^1}{\underset{(2,8,3)}{Al}} - 3e^- \rightarrow \underset{1s^2 2s^2 2p^6}{\underset{(2,8)}{Al^{3+}}} \quad (oxidation)$$

*II.* Oxygen atom, ${}_8O$, $1s^2 2s^2 2p^4$ (2,6), a non-metal in group VI, gains two electrons to complete an octet and form oxygen ion, called oxide, $O^{2-}$ ($1s^2 2s^2 2p^6$) that also has neon structure:

$$\underset{1s^2 2s^2 2p^4}{\underset{(2,6)}{O}} + 2e^- \rightarrow \underset{1s^2 2s^2 2p^6}{\underset{(2,8)}{O^{2-}}} \quad (reduction)$$

*III.* To form a neutral ionic compound, two aluminium ions ($2\times3$ = *loss of 6 electrons*) combine with three oxygen ions ($3\times2$ = *gain of six electrons*)

$$2Al^{3+} + 3O^{2-} \rightarrow (Al^{3+})_2(O^{2-})_3 \text{ or } Al_2O_3$$

$Al^{3+}$ and $O^{2-}$ have the same electron configuration of neon $1s^2 2s^2 2p^6$ (2,8); they are *isoelectronic ions.*

**Revision Exercises**

11 State two factors that favour the formation of ionic bonds.

12 If an element with high electron affinity combines with another element with low ionization energy, what type of chemical bond will be formed?

13 The ions $X^-$ and $Y^+$ are isoelectronic, each containing a total of 10 electrons. How many protons are in the nuclei of the neutral atoms of X and Y respectively?

A. 10 and 10. B. 9 and 9
C. 11 and 9 D. 9 and 11. [JAMB]

14 Describe briefly, the structure of sodium chloride in solid state. [WAEC]

15 Explain the term *coordination number* with respect to sodium chloride.

16 Illustrate the change in the electronic structure of ${}_9F$ when it reacts with ${}_{20}Ca$. [WAEC]

## How to derive and write the chemical formulae of ionic compounds

*1. Write* the chemical symbol and charge of the *cation*, then, that of the *anion*.

*2. Combine* the opposite ions in the inverse ratio of their charges. For instance: A metal ion, $M^{m+}$ and a non-metal ion, $X^{x-}$ will form a neutral ionic compound with the chemical formula $M_xX_m$ i.e.

$$xM^{m+} + mX^{x-} \rightarrow M_xX_m$$

The table below indicates the chemical formulae of the most stable compound formed when a cation in the vertical column combines with an anion in the horizontal column:

| | $X^-$ | $X^{2-}$ | $X^{3-}$ |
|---|---|---|---|
| $M^+$ | $MX$ | $M_2X$ | $M_3X$ |
| $M^{2+}$ | $MX_2$ | $MX$ | $M_3X_2$ |
| $M^{3+}$ | $MX_3$ | $M_2X_3$ | $MX$ |

**Solved Problems**

**4.** Write the chemical formula of the ionic compound formed between the atoms of the following elements:

a. Calcium and oxygen;
b. Potassium and sulphur;
c. Magnesium and nitrogen.

a. *Calcium Ca atom forms $Ca^{2+}$, while oxygen atom forms $O^{2-}$. The formula of the compound formed will be:*

$$Ca^{2+} + O^{2-} \rightarrow CaO$$

b. *Potassium forms $K^+$ while sulphur forms $S^{2-}$.*

$$2K^+ + S^{2-} \rightarrow (K^+)_2S^{2-} \text{ or } K_2S$$

c. *Magnesium forms $Mg^{2+}$, while nitrogen forms $N^{3-}$.*

$$3Mg^{2+} + 2N^{3-} \rightarrow (Mg^{2+})_3(N^{3-})_2 \text{ or } Mg_3N_2$$

**5.** An element **R** with atomic number 3 reacts with an element **Q** with atomic number 8. The formula of the compound formed is

A. $R_3Q_8$ B. $R_2Q_3$ C. $R_2Q$ D. $RQ_2$ [WAEC]

**Solution:** *C*

*${}_3R$ is $1s^2 2s^1$. It is in group I; it forms $R^+$;*
*${}_8Q$ is $1s^2 2s^2 2p^4$. It is in group VI; it forms $Q^{2-}$;*
*Hence, $R^+$ and $Q^{2-}$ form $R_2Q$. Answer is C.*

## Formulae of Ionic Compounds of Hydrogen

When hydrogen atom, ${}_1H$, ($1s^1$) a non-metal, combines with a metal in group I, II or III in the periodic table, it gains one electron and forms an anion, $H^-$, that has helium structure ($1s^2$):

$$\underset{1s^1}{H} + e^- \rightarrow \underset{1s^2}{H^-} \quad (reduction)$$

Hence, the ionic compounds of hydrogen are similar to those of the halogens (in group VII):

**Group I** ($M^+$ and $H^-$): NaH, LiH and KH.
**Group II** ($M^{2+}$ and $H^-$): $BeH_2$, $MgH_2$ and $CaH_2$.
**Group III** ($M^{3+}$ and $H^-$): $BH_3$ and $AlH_3$.

## Formulae of Ionic Compounds of Some Elements in the Periodic Table

Elements in the same group in the periodic table form similar ions and have similar chemical properties, since their atoms have the same number of valence electrons. As a result, the chemical formulae of their compounds are similar as shown in the following table:

| | Group V $N^{3-}$, $P^{3-}$ | Group VI $O^{2-}$, $S^{2-}$ | Group VII $F^-$, $Cl^-$, $Br^-$, $I^-$ |
|---|---|---|---|
| Group I $Li^+$, $Na^+$, $K^+$ | $Li_3N$, $Na_3P$, $K_3N$ | $Li_2O$, $Li_2S$ $Na_2O$, $Na_2S$ $K_2O$, $K_2S$ | LiF, LiBr, NaF, NaCl KBr, KI |
| Group II $Be^{2+}$, $Mg^{2+}$, $Ca^{2+}$ | $Be_3N_2$ $Mg_3N_2$ $Ca_3P_2$ | BeO, MgO, CaO, CaS, MgS, BeS | $BeF_2$, $BeCl_2$ $MgF_2$, $CaI_2$ $CaBr_2$ |
| Group III $B^{3+}$, $Al^{3+}$ | BN, BP AlN, AlP | $B_2O_3$, $B_2S_3$ $Al_2O_3$, $Al_2S_3$ | $BF_3$, $BBr_3$ $AlCl_3$, $AlI_3$ |

**How to represent ionic bonds**

Ionic bonds are represented by the electron-dot formula originated by Lewis. Here, a dot (• or o) or, a small letter 'x' is used to represent a valence electron. For instance:

1. In the formation of NaCl, the valence electron of Na atom, is transferred to the valence shell of Cl atom.

$$\dot{N}a + \cdot\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}}: \longrightarrow Na^+ \; :\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}}:^-$$

2. When one calcium atom, Ca, combines with two fluorine atoms, 2F, the *two valence electrons* of Ca are transferred to the valence shells of the *two fluorine atoms, such that each F atom gains one electron to complete the valence shell*:

$$\dot{\dot{C}}a + \cdot\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{F}}}: + \cdot\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{F}}}: \longrightarrow Ca^{2+}\left[:\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{F}}}:^-\right]_2$$

**Revision Exercises**

17 An element X in group II forms an ionic compound with an element N in group V in the periodic table. What is the formula of the compound?
A. $X_2N_5$ B. $X_2N_3$ C. $X_5N_2$ D. $X_3N_2$ [WAEC]

18 An element X with the electronic configuration $1s^22s^22p^63s^2$ combines with another element Y with the configuration $1s^22s^22p^63s^23p^5$. What is the formula of the compound formed?
A. $X_2Y_5$ B. $X_2Y_3$ C. $XY_3$ D. $XY_2$ [WAEC]

19 Two elements X and Y combine to form a compound with the formula $X_2Y_3$. Which of the following representations would fit the electronic configuration of X and Y ?

| | X | Y | | X | Y |
|---|---|---|---|---|---|
| A. | 2, 2 | 2, 3 | B. | 2, 6 | 2, 5 |
| C. | 2, 8, 2 | 2, 8, 3 | D. | 2, 8, 3 | 2, 6 [WAEC] |

## General Characteristic Properties of Ionic or Electrovalent Compounds

1. Ionic compounds exist as aggregate of ions of opposite charges, which are held together by strong *electrostatic forces*, leading to the formation of giant crystalline solids at room temperature.

2. They have high melting and boiling points due to the strong electrostatic forces, which hold the ions together. For instance, the melting point of sodium chloride is 801 °C and it boils at 1467 °C.

3. In *solid state*, their crystals are electrically neutral and brittle; hence, they do not conduct electricity in solid state.

4. In *fused* or *molten state*, they form *mobile ions* that transfer charges, and enable them to conduct electricity.

5. They dissolve in water to give aqueous solutions that contain *hydrated ions*, which make them to be *electrolytes*, and hence, conduct electricity. *An electrolyte is a compound, that conducts electricity when in molten state or in aqueous solution.*

6. They are insoluble in organic solvents; hence, do not form ions or conduct electricity in organic solvents, such as ethanol, kerosene, and propanone.

**Revision Exercises**

20 List three general properties of electrovalent compounds. [NECO]

21 What is responsible for the high melting point of electrovalent compounds?

22 Which of the following statements is correct about sodium chloride in the solid state?
A. It exists as aggregates of ions.
B. It conducts electricity.
C. Its melting point is below 100°C.
D. It exists as discrete molecules. [WAEC]

## 6.5 Covalent Combination

In ***covalent bonding***, *electrons are shared* between atoms of the same or different elements, such that each atom contributes to the shared electrons so as to attain noble gas configurations. During the process, *discrete* or *separate* ***molecules*** are formed with ***covalent bonds*** between the *atoms*.

A *covalent bond* is a chemical bond between two atoms, such that each atom contributes the same number of electrons to the shared pair of electrons.

### General features of Covalent bonding

1. *Covalent bonding* involves *sharing of electrons* contributed by the combining atoms from their respective valence shells.

2. *Covalent molecules* are usually formed among atoms of hydrogen, and non-metals of groups IV, V, VI and VII. In fact, group IV elements usually participate in *covalent* rather than *ionic* bonding.

3. An atom contributes for sharing, the number of electrons it requires to complete an octet or a duplet. The number of electrons contributed equals the *covalency* of the atom, and determines the

*maximum number of covalent bonds* the atom can form in a molecule, e.g.

• Hydrogen atom, H, ($1s^1$) requires *one* electron to complete a *duplet*; it contributes its only electron for sharing during covalent bonding. Its *covalency* is *one*. Hydrogen forms only one covalent bond

• The *covalency* of an atom of a group IV element is 4, that of a group V element is 3, group VI element is 2, while that of a group VII element is 1.

4. When two atoms combine covalently, the shared electrons are now in-between two atomic nuclei. *The electrostatic force of attraction in a covalent bond is due to the fact that the shared electrons are simultaneously attracted to two positive atomic nuclei.* Such attractions lead to the formation of ***discrete molecules***, since *covalent bonds are rigid and highly directional.*

• When *one pair of electrons* is shared between two atoms, a *single* covalent bond (–) is formed.

• When *two pairs of electrons* are shared between two atoms, a *double* covalent bond (=) is formed.

• When *three pairs of electrons* are shared between two atoms, a *triple* covalent bond (≡) is formed.

5. The shared pairs of electrons in a covalent bond do not belong to a particular atom; they belong to both atoms, so that the *octet or duplet rule* can be obeyed.

6. Covalent molecules formed between atoms of the same elements are said to be ***homonuclear***, while those formed between atoms of different elements are ***heteronuclear***.

7. The *ratio* in which atoms of two elements combine is in the *inverse ratio* of their *covalencies*, so that the different atoms contribute the same number of electrons for sharing, and produce a stable molecule.

### Factors favoring formation of Covalent bonds

A *covalent bond* is usually formed between atoms of the same or different nonmetals with ***high ionization energies*** and, or ***high electron affinities***.

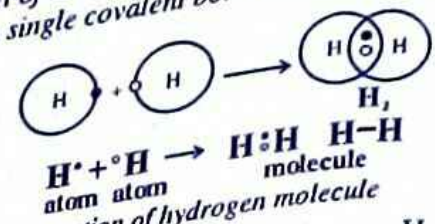
In terms of ***electronegativity***: A *covalent bond will be formed between atoms of nonmetals with the same or slightly different electronegativities.*

### Examples of homonuclear molecules

#### 1. *Formation of hydrogen molecule*

Hydrogen atom, H, ($1s^1$) has a *covalency of one*. When two hydrogen atoms combine, each atom contributes one electron for sharing, so that a pair of electrons is now shared between the two atomic nuclei in the molecule formed (see fig 6.3).

The *electron-dot formula* shows that there are two atoms in the molecule with each atom having a *duplet of electrons* corresponding to that of helium, and a *single covalent bond* between them.


H
H
H

ing to that of neon. The *octet of electrons* is made up of *two lone pairs* and *two bonding pairs*.

Like $H_2$ or $Cl_2$, oxygen molecule, $O_2$, is *diatomic*. The double covalent bond is *pure* and *non-polar*.

**4. *Formation of Nitrogen molecule***

Nitrogen atom, N, $1s^2 2s^2 2p^3$ (2,5) has a covalency of three. When two nitrogen atoms combine, each atom contributes three valence electrons, so that three pairs of electrons (i.e. six electrons) are now located between the two nuclei (see fig 6.6).

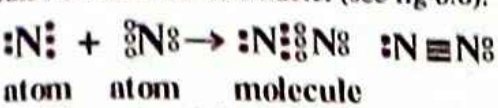



Fig 6.6 *Formation of nitrogen molecule*

The electron-dot formula of nitrogen molecule shows that there is a *triple covalent bond* between the two atoms, so that each atom now has an *octet of electrons*, which corresponds to that of neon. The *octet of electrons* is made up of *one lone-pair* and *three bonding-pairs*.

Nitrogen molecule, $N_2$, is *diatomic*, and the *triple covalent bond* is *pure* and *non-polar*.

**Examples of Heteronuclear Molecules**

**1. *Combination of hydrogen and fluorine***

Like the hydrogen atom, the covalency of an atom of a halogen is one. When an atom of hydrogen, H, ($1s^1$) combines with that of fluorine, F, $1s^2 2s^2 2p^5$ (2,7) each atom contributes one valence electron for sharing, so that a pair of electrons is now located between the two nuclei in the molecule.

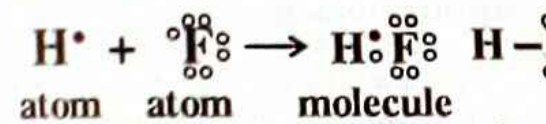



Fig 6.7 *Formation of hydrogen fluoride*

The electron-dot formula of the molecule shows that hydrogen atom acquires a *duplet*, while that of *fluorine* is an *octet*. The octet of electrons on fluorine is composed of *one* bonding-pair and *three* lone-pairs.

*When electrons are shared between the nuclei of atoms of different elements, the distribution of electron density around the nuclei will not be uniform, due to difference in electronegativity.* It makes the covalent bond formed to be *polar*. Hence, the single covalent bond in the molecule of HF is *polar*. The atom of fluorine is more electronegative than that of hydrogen.

The modes of formation of and the electron-pair distributions in HCl, HBr and HI are similar to that of HF molecule. Their single covalent bonds are *polar*.

All *diatomic molecules* are *linear in shape*.

**2. *Formation of Water molecule***

Hydrogen atom, H, $1s^1$, has a covalency of one, while oxygen atom, O, $1s^2 2s^2 2p^4$, has a covalency of two.

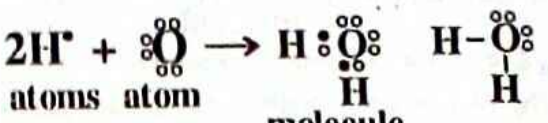



Fig 6.8 *Formation of water molecule*

In the formation of a water molecule, one oxygen atom contributes two of its valence electrons for sharing, while two hydrogen atoms provide one electron each.

The *electron-dot formula* shows that the central oxygen atom shares a pair of electrons with each hydrogen atom, so that each atom in the molecule is able to attain a noble gas structure. The *octet of electrons* on oxygen is composed of *two bonding-pairs* and *two lone-pairs* (*or non-bonding pairs*).

In a water molecule, oxygen is the central atom with two single O–H covalent bonds. Its molecular formula is written as $H_2O$; showing that a molecule of water contains two hydrogen atoms and one oxygen atom.

The two single O–H covalent bonds *within* the water molecule are *polar*; oxygen atom being more electronegative than hydrogen atom. The molecule is *polar*, and has a V-shape (or bent).

The mode of formation of $H_2S$ is similar to that of $H_2O$.

**3. *Formation of Hydrogen peroxide***

Hydrogen peroxide, $H_2O_2$, is a stable compound of hydrogen and oxygen, like water, $H_2O$.

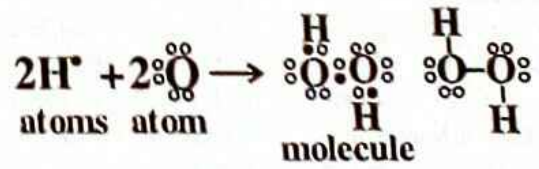



Fig 6.9 *Formation of hydrogen peroxide molecule*

*Electron-dot formula* shows that each oxygen atom contributes two valence electrons, while each hydrogen atom contributes one electron. A pair of electrons is shared between any two atoms, leading to the formation of three single covalent bonds as shown in the structure. The molecule is *polar with a doubly bent shape*.

**4. *Formation of Ammonia molecule, $NH_3$***

In the formation of ammonia, nitrogen atom, N, $1s^2 2s^2 2p^3$ (2,5) contributes its three unpaired valen-

ce electrons for sharing, while three hydrogen atoms contribute one electron each.

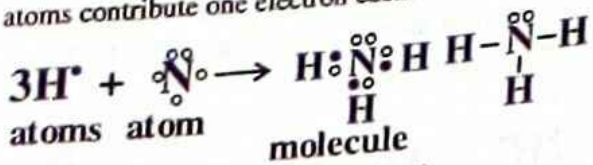



Fig 6.10 *Formation of ammonia molecule*

The electron-dot formula of the molecule shows that the central nitrogen atom shares a pair of electrons with each of the hydrogen atoms, so that each atom attains a noble gas structure. The *octet of electrons* on nitrogen is composed of *three bonding-pairs* and *one lone-pair of electrons*.

Since nitrogen atom is more electronegative than hydrogen atom, the three single N–H *single covalent bonds are polar*. The molecule is also polar. The molecular formula is usually written as $NH_3$. It has a pyramidal shape.

The modes of formation of $PH_3$, $PCl_3$, and $NCl_3$ are similar to that of $NH_3$.

### 5. *Formation of Methane*

In the formation of a molecule of methane, the carbon atom, C, $1s^2 2s^2 2p^2$ (2,4) contributes its four valence electrons for sharing, while four hydrogen atoms contribute one electron each.

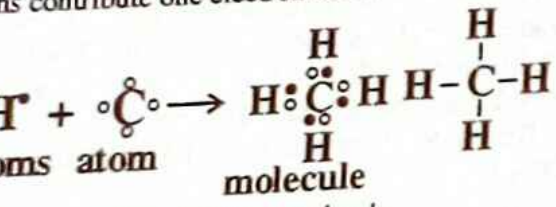



Fig 6.11 *Formation of methane molecule*

The electron-dot formula of methane shows that the central carbon atom shares a pair of electrons with each of the four hydrogen atoms, so that each atom in the molecule is able to attain a stable noble gas structure. This leads to the formation of four single C–H covalent bonds. The octet of electrons on the carbon atom is composed of *four bonding-pairs (no lone-pair of electrons)*.

Since the atoms of carbon and hydrogen have nearly the same electronegativity, the C–H bonds are non-polar. The $CH_4$ molecule is also non-polar, and has a *tetrahedral shape*.

The mode of formation and the shape of $CCl_4$ are similar to that of $CH_4$.

### 6. *Formation of Carbon dioxide*

In the formation of a stable compound of carbon and oxygen, carbon atom, C, $1s^2 2s^2 2p^2$ (2,4) contributes its four valence electrons for sharing, while two oxygen atoms, O, $1s^2 2s^2 2p^4$, (2,6) contribute two electrons each.




6.12 *Formation of carbon dioxide molecule*

Electron-dot formula shows that the central carbon atom shares *two pairs of electrons* (a *double covalent bond*) with each of the oxygen atoms. The *octet of electrons* on carbon is composed of *four bonding-pairs, no lone-pairs*.

Each C=O bond is polar, since oxygen is more electronegative than carbon; but the entire molecule is non-polar, because $CO_2$ is linear in shape.

**Revision Exercises**

28 Define *covalent bond*. [WAEC]

29 State with examples, the difference between a *homonuclear* and *heteronuclear* diatomic molecules.

30 Which of the following molecules has a linear structure: $NH_3$; $CH_4$; $CO_2$; $H_2O$?

31 How many lone pairs of electrons are there on the central atom of the $H_2O$ molecule?

32 When nitrogen combines with hydrogen to form ammonia each atom [WAEC]

A. exists independently. B. becomes highly charged.
C. has a large mass. D. attains a noble gas structure.

## General Physical properties of Covalent compounds

1. Covalent compounds are formed by the sharing of electrons between atoms; it leads to the formation of discrete independent molecules.
2. The compounds exist as gases – such as nitrogen and oxygen; as liquids with low boiling points – such as propanone and ethanol; and as solids with low melting points – such as camphor and iodine.
3. They are non-conductors of heat and electricity.
4. They are non-electrolyte in fused (molten) state; since they do not produce ions, which are responsible for the transfer of charges during electrolysis.
5. They are insoluble in water, being non-polar.
6. They are soluble in non-polar solvents, such as ethanol and benzene; but they are non-electrolytes.

**Revision Exercises**

33 List three characteristics of a covalent compound.

34 State three differences between electrovalent and covalent compounds. [NECO]

## 6.6 Dative (or Coordinate Covalent) Combination

*Dative* or *Coordinate covalent bonding* involves sharing of electrons, as in *covalent bonding*. However, in *dative bonding*, the shared pair of electrons is contributed by one of the participating atoms.

*Dative bonding* occurs between an atom that has a *lone-pair* (*unshared pair*) of electrons in the outer-shell and another atom that has an *empty valence orbital*, hence, requires one pair of electrons to complete an *octet* or a *duplet*.

The atom that contributes the pair of electrons to be shared is called ***donor atom***, while the other is *acceptor atom*. An arrow is used to represent the ***dative bond*** formed; from the *donor* → to the *acceptor*. However, once a dative bond is formed, its nature is the same as that of a covalent bond.

**Examples of donor molecules and ions**

Covalent compounds of nitrogen and oxygen, such as ammonia and water, form dative bonds. This is because the *central atoms* possess lone pairs of electrons in their valence shell; hence, electron-rich. For instance:

•In $NH_3$, the central atom, nitrogen, has a lone pair of electrons. Similarly, phosphorus atom in $PCl_3$ has an available lone-pair of electrons.

• In $H_2O$, the central atom, oxygen, has two lone-pairs of electrons that can be contributed during dative bonding.

•When hydrogen atom $_1H$, $1s^1$, gains an electron, it forms a *hydride ion* $H^-$: $1s^2$, which can act as an electron-pair donor during dative bond formation.

**Examples of acceptor species**

• When hydrogen atom, $_1H$, $1s^1$, loses its electron, it forms hydrogen ion, $H^+$, usually called ***proton***.

$$\underset{1s^1}{H} - e^- \rightarrow \underset{1s^0}{H^+} \quad (oxidation)$$

$H^+$ has an empty 1s-orbital, that requires a pair of electrons to complete a duplet. It is electron-poor, and will take part in dative bonding.

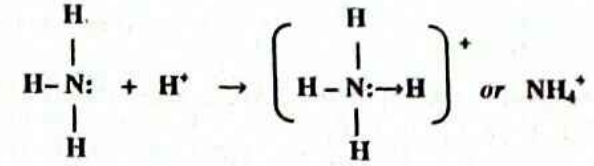
• An oxygen atom, O: $1s^2 2s^2 2p^4$ (2,6) needs a pair of electrons to complete its valence shell and form a stable *octet*. It acts as an acceptor atom during dative bond formation.

• Binary compounds of boron $_5B$, $1s^2 2s^2 2p^1$ (2,3), such as $BH_3$ and $BF_3$ are not purely ionic; they have covalent character, due to *diagonal relationship* with group IV elements. Boron atoms in these compounds behave as if it requires a pair of electrons to complete an *octet*; hence, it acts as an electron acceptor during dative bond formation.

**Examples of dative species**

1. ***Formation of ammonium ion, $NH_4^+$***

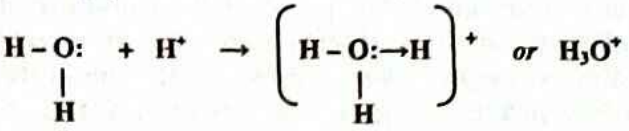
In the formation of $NH_4^+$, the lone-pair of electrons in the valence shell of nitrogen atom in $NH_3$ is contributed for sharing with the empty 1s-orbital of a proton, $H^+$.



$$H^+ + NH_3 \rightarrow NH_4^+$$

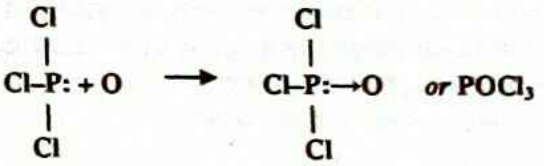
2. ***Formation of hydroxonium ion, $H_3O^+$***

In the formation of *hydroxonium ion*, $H_3O^+$, one of the lone-pairs of electrons in the valence shell of oxygen atom in $H_2O$ is contributed for sharing with the empty 1s-orbital of $H^+$.



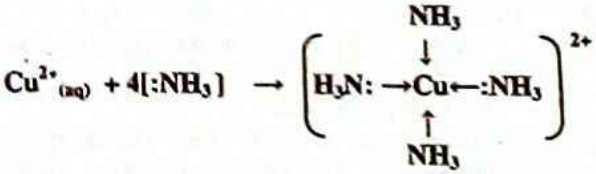
3. ***Formation of $POCl_3$***

Phosphorus atom, P, in $PCl_3$ contributes its lone-pair of electrons for sharing with an oxygen atom, O: (2,6), to form $POCl_3$.



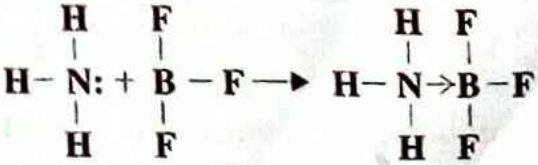
4. ***Formation of complex ion, $Cu(NH_3)_4^{2+}$***

The complex ion, $Cu(NH_3)_4^{2+}$ is formed when four molecules of $NH_3$ contribute their lone-pairs of electrons on nitrogen atoms for sharing with the empty valence orbitals of $Cu^{2+}$.



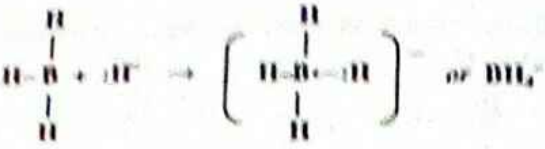
5. ***Formation of $NH_3$-$BF_3$ complex***

In the formation of *$NH_3$-$BF_3$ complex*, the lone-pair of electrons on nitrogen in $NH_3$ is contributed for sharing with the empty valence orbital in B of $BF_3$.



6. ***Formation of $BH_4^-$ complex***

The lone-pair of electrons in $H^-$ is donated for sharing with the empty valence orbital of boron atom in $BH_3$ molecule.



The mode of formation of $AlCl_4^-$ from $AlCl_3$ and $Cl^-$ is similar to that of $BH_4^-$:

$$AlCl_3 + Cl^- \rightarrow AlCl_4^-$$

7. ***Aluminium chloride dimer, $Al_2Cl_6$***



In a molecule of $AlCl_3$, one of the lone-pairs of electrons on one Cl atom is contributed for sharing with the empty valence orbital of Al atom in the other $AlCl_3$ molecule, to form a *dimmer*, $Al_2Cl_6$.

**Note:** Compounds of boron and aluminium have covalent character, due to *diagonal relationship* with group IV elements.

### Physical Properties of Dative Compounds

Coordinate covalent (dative) compounds have the same physical properties as those of covalent compounds. This is because, once formed, *dative bonds* and *covalent bonds* are the same.

### Revision Exercises

35 State with illustrations, the difference between covalent and coordinate covalent (dative) bonds.

36 Name two compounds that will form coordinate covalent (dative) bonds with $H^+$.

37 The bond formed between $H_2O$ and $H^+$ to form hydroxonium ion $H_3O^+$ is [WAEC]
A covalent. B dative. C electrovalent. D ionic.

38 Which of the following statement about dative bonding is **not** correct?
A. There is sharing of electrons.
B. One atom must possess a lone pair of electrons.
C. Each participating atom contributes one electron.
D. It can be formed between molecules. [WAEC]

39 Which of the following pairs of substances will form coordinate covalent bonds?
a. $NH_3$ and $BF_3$; b. $NH_3$ and $CH_4$; c. HCl and $H_2O$;
d. $CH_4$ and $H_2O$; e. HF and HCl [WAEC]

40 Illustrate with a diagram the formation of ammonium ion. [$_1$H, $_7$N] [WAEC]

## 6.7 Uniqueness of ammonium chloride

Ammonium chloride, $NH_4Cl$, is an example of a compound that possesses *covalent*, *dative* and *ionic bonds* within its crystals. Reasons:

- In a molecule of ammonia, $NH_3$, there are pure single N–H *covalent bonds* between the atoms.
- The combination of $NH_3$ and $H^+$ to form $NH_4^+$ is by the formation of a *dative bond*:

$$NH_3 + H^+ \rightarrow NH_4^+$$

- The electrostatic force of attraction between $NH_4^+$ and $Cl^-$ is *ionic*:

$$NH_4^+ + Cl^- \rightarrow NH_4^+Cl^-$$

Ammonium chloride, $NH_4Cl$, exists as white crystals, which *sublimes*, when heated.

### Revision Exercises

41a. List the types of chemical bonds in
i. ammonium chloride; ii. ammonium ion.
b. Which of these bonds is responsible for the solubility of $NH_4Cl$ in a polar solvent?

## 6.8 Metallic Bonding

A metal can be regarded as a collection of atoms in which the valence electrons move freely and continuously in-between positively charged nuclei. This is because atoms of metals have very few valence electrons; hence, possess vacant valence orbitals. Therefore, it is possible for the valence electrons of a metal atom to move freely to the vacant valence orbitals of the neighbouring atoms. In essence, the *valence electrons in metal atoms are delocalized; hence, they are mobile.*

***Metallic bonding*** is the process whereby the positively charged nuclei of metal atoms are simultaneously attracted to the *sea (or cloud) of mobile electrons*. The *electrostatic force of attraction between the positive nuclei and the sea of mobile electrons is called* ***metallic bond***.



*Metallic bonding* is responsible for the typical properties of metals. The difference in their melting points is due to the difference in the number of valence electrons; hence, there is a regular increase in melting points from sodium to magnesium, then, to aluminium across period 3 in the Periodic Table.

### General Physical Properties of Metals

1. Metals possess high electrical and thermal conductivities.
2. They are ductile, malleable, elastic and soft
3. They have high melting points.
4. They possess high tensile strength.
5. They exhibit bright metallic lustre.
6. They form cations with ease.

***Explanation of metallic properties in terms of electronic structure of metals***

The general properties of metals can be explained in terms of their electronic structures:

1. The electrical and thermal conductivities are due to the mobility of the valence electrons in metal atoms; hence, they are able to carry electric current and heat from one part of the metal to the other.
2. Ductility, malleability and elasticity are due to the ability of the mobile electrons in metal atoms to move from one point to another within the metal lattice.
3. High tensile strength and high melting points are due to the strong electrostatic force of attraction between the positive nuclei and the sea of mobile electrons in metal atoms.
4. The bright lustre is due to the emission of light by the valence electrons in metal atoms.
5. Metals form cations with ease, because their valence electrons are mobile, and hence, weakly attracted to the nuclei of the atoms. Therefore, they are readily removed by a relatively low amount of energy (i.e. metals have low ionization energies).

**Solved Problem**

6. Explain the following observations: [WAEC]

a. The chemical reactivity of alkaline metals increases down the group

*Ionization energy decreases down the group. Reactivity depends on the ease of loss of electrons.*

b. Mg has a higher melting point than Na.

*Mg has more valence electrons involved in metallic bonding than Na.*

c. K is a better reducing agent than Na.

*K (potassium) atom loses its valence electron more readily than Na (sodium). Reducing ability depends on the ease of loss of electron.*

**Revision Exercises**

42a. Explain the term *metallic bonding*.

b. What is a metallic bond?

c. State the type of chemical bond between aluminium atoms in a sheet of aluminium.

43 Mention **three** physical properties of metals [WAEC]

44 If the difference between the electronegativities of two elements is large, the type of bond that can be formed between them is

**A** covalent **B** dative **C** ionic **D** metallic [WAEC]

## 6.9 Intermolecular Forces

*Intermolecular forces* are the attractive forces that hold atoms of noble gases and covalent molecules together in liquids and solids. They are relatively *weak attractive forces* when compared with *ionic* and *covalent* bonds.

The most common *intermolecular forces* are:

1. van der Waals forces.
2. Dipole–dipole (dipolar) forces.
3. Hydrogen bonds.

**1. *van der Waals' forces***

*van der Waals' forces* are weak short-range attractive forces operating between covalent molecules. They are the weakest of the inter-molecular forces. *They operate only when the particles are in close contact with one another as in liquids and solids.* They are the only attractive forces between the *atoms of the noble gases* and *non-polar covalent molecules*, and are responsible for the low melting and boiling points of covalent compounds.

Generally, there is an increase in *van der Waals' forces* with increase in atomic or molecular size. Hence, the boiling points of *noble gases* increase down the group in the periodic table. Due to increase in *van der Waals' forces*, there is gradation in the physical properties of the *halogens*: Fluorine and chlorine are gases, bromine is a reddish-brown liquid, while iodine is a black solid that sublimes, when heated.

**2. Dipole-Dipole (Dipolar) Forces**

When electrons are shared between atoms of different elements, the distribution of electron density around the atoms will be such that the more electronegative atom becomes *electron-rich* (δ–), and the other becomes *electron-poor* (δ+). *The partial separation of charges in a polar covalent bond is called* ***dipole***.

*Dipole-dipole (dipolar) forces* operate between *polar covalent molecules* as a result of the weak electrostatic force of attraction between the *positive end of one dipole and the negative end of a neighbouring dipole in polar molecules* such as HCl, HF, $H_2O$, $NH_3$ and $H_2S$ at low temperatures:

$$\overset{\delta+\ \delta-}{H{-}Cl}\cdots\overset{\delta+\ \delta-}{H{-}Cl}\cdots\overset{\delta+\ \delta-}{H{-}Cl}\cdots\overset{\delta+\ \delta-}{H{-}Cl}$$

*Dipolar forces* are stronger than *van der Waals' forces*, but are only about one percent as strong as *covalent bonds*.

**3. Hydrogen bonding**

***Hydrogen bonding*** occurs in polar covalent molecules in which *hydrogen atoms are covalently bonded to small and highly electronegative atoms, such as fluorine, oxygen and nitrogen, as in HF, $H_2O$ and $NH_3$ respectively*. Such atoms possess lone-pairs of electrons.

*The attractive force between the hydrogen atom, which is covalently bonded to an atom of fluorine,*

oxygen or nitrogen and the lone pair of electrons on fluorine, oxygen or nitrogen in a neighbouring molecule is called **hydrogen bond** (**H-bond**).

In the following examples, hydrogen bonds are represented with dotted lines.

**a. Hydrogen bonds between *HF* molecules**



**b. Hydrogen bonds between $H_2O$ molecules**



**c. Hydrogen bonds between $NH_3$ molecules**



*H-bond* is an unusually strong intermolecular attractive force. It is about ten times stronger than the *dipole-dipole force*, but only about ten percent as strong as a *covalent bond*.

The presence of hydrogen bonds between water molecules is responsible for $H_2O$ being a liquid with a high boiling point; if not, it would have being a gas, like $H_2S$. For the same reason, HF is a liquid at room temperature, while HCl is a gas.

## Solved Problem

7. Consider the compounds with the following structures: S–H - - -N and O–H - - -N

In which of the compounds is the hydrogen bond stronger? Give reason for your answer. [WAEC]

*Hydrogen bond is stronger in O–H- - -N because oxygen atom is smaller in size and more electronegative than sulphur atom.*

## Revision Exercises

45 List two *forces of attraction* that can exist *between covalent molecules*. [WAEC]

46 Name the type of intermolecular force of attraction in iodine crystals.

47 State the type of intermolecular forces present in: **a.** hydrogen fluoride; **b.** argon. [WAEC]

48 van der Waals' forces are the dominant intermolecular forces in

A. ammonium chloride. B. chlorine.
C. sodium chloride. D. water [WAEC]

49 Name the types of bonds *within* a water molecule and *between* water molecules.

50 Which of the following compounds has hydrogen bonds between its molecules?

A. HF B. HBr C. HCl D. HI [WAEC]

51 Give the reason why hydrogen fluoride is a liquid at room temperature, unlike hydrogen chloride.

## General Revision Exercises

52 Elements X and Y are represented as $^{40}_{20}X$ and $^{16}_{8}Y$ respectively.

**a.** For each element write the:
- i. electronic configuration using s, p, d notation;
- ii. number of unpaired electrons in the atom;
- iii. orbitals in which the valence electrons are found;
- iv. group and period to which each element belong.

**b.** Write the formula of the compound formed between X and Y.

**c.** State the type of bond that would be formed between X and Y. Explain your answer.

53 Use the form of the periodic table given below to answer the questions that follow:

| | I | II | III | IV | V | VI | VII | 0 |
|---|---|---|---|---|---|---|---|---|
| 1 | C | | | | | | | |
| 2 | | | | B | | | | A |
| 3 | | D | | | | | E | |

**a.** Give the letter representing:
- i. a strong reducing agent;
- ii. a noble gas;
- iii. an element which forms a 2+ ion;
- iv. a strong oxidizing agent;

**b.** Write the formula of the compound formed between:
- i. B and C; ii. B and E; iii. C and E
- iv. D and C; v. D and E.

**c.** Which of the compounds in **b** above are ionic?

54 Which of the following substances does not have the electronic configuration as the sodium ion, $Na^+$? [$_{13}Al$, $_{10}Ne$, $_{11}Na$, $_{8}O$, $_{12}Mg$] [WAEC]

A. $Al^{3+}$ B. Mg C. Ne D. $O^{2-}$

55 Which of the following does not have the electronic structure of $_{18}Ar$? [NECO]

A. $Al^{3+}$ B. $Ca^{2+}$ C. $Cl^-$ D. $K^+$ E. $S^{2-}$

## Answers to Revision Exercises

| | | | | | |
|---|---|---|---|---|---|
| 4. B | 6. D | 8. 12 | 9. 16 | 10. D | 13. D |
| 20. D | 21. D | 24. D | 27. A | 32. D | 37. B |
| 38. C | 44. C | 48. B | 50. A | 54. A | 55. A |

# 7

# •CHEMICAL FORMULAE•
# •IUPAC NOMENCLATURE•

## 7.1 Introduction

A *chemical formula* represents the composition of an element or a compound by the use of chemical symbols and numerals as subscript.

**Revision Exercise**

1. What is a chemical formula?

## 7.2 Chemical Formulae of Elements: Atomicity

A *molecule* is composed of two or more atoms of the same or different elements, except that of a metal or a noble gas. *The number of atoms in a molecule of an element is called* ***atomicity***.

The chemical formula of an element indicates the form in which it exists when on its own, or in a free, and uncombined state.

In writing the chemical formula of an element, its symbol is written first; then, the numeral that indicates its atomicity as a subscript. For example:

1. A **monatomic element** contains *one* atom in a molecule. Such an element exists as discrete atoms e.g. metals, such as Na, Mg and Fe; noble gases, such as He. Hence, the atomicity of sodium is one.

For a *monatomic* elements, the subscript, $_1$, as in $Na_1$, is usually omitted, since a chemical symbol represents *one* atom of the element.

2. A **diatomic element** contains *two* atoms in a molecule, e.g. $H_2$, $O_2$, $N_2$, $F_2$, $Cl_2$, $Br_2$ and $I_2$ . Such an element exists as discrete *diatomic molecules*. Hence, the atomicity of oxygen is 2.

3. A **triatomic element** contains *three* atoms in a molecule, e.g. ozone, $O_3$. Ozone is another form of oxygen gas. Its atomicity is 3.

4. A **polyatomic element** contains *four* or *more* atoms in a molecule, e.g. $P_4$ and $S_8$. Hence, the atomicity of phosphorus is 4.

The chemical formula $\mathbf{H_2}$ indicates *one* molecule of hydrogen and contains *two* atoms; $\mathbf{O_3}$ represents *one* molecule of ozone with *three* oxygen atoms.

When writing the chemical formula representing more than one molecule of an element, the numeral indicating the number of molecules is written first, followed by the chemical formula of the element:

- $3H_2$ represents **three** molecules of hydrogen; it contains **six** ($3 \times 2$) hydrogen atoms.
- $7O_3$ represents **seven** molecules of ozone, and contains **twenty one** ($7 \times 3$) oxygen atoms.
- 2Na represents **two** ($2 \times 1$) atoms of sodium – since it is monatomic.

**Revision Exercises**

2 a. Define the term *atomicity*.

b. State the atomicity of each of the following elements: Iron; iodine; ozone; oxygen; sulphur.

3. The following elements are diatomic **except**

A. chlorine. B. hydrogen.
C. nitrogen. D. phosphorus. [WAEC]

4. Write the chemical formula of each of the following elements: neon; ozone; chlorine; phosphorus.

5. How many atoms are in each of the following?

a. $2S_8$; b. $6P_4$; c. 9 molecules of nitrogen;

## 7.3 Formulae of Binary Compounds

### Simple Chemical Formulae

A ***binary*** compound contains only ***two*** elements. In an ionic compound, the ***electrovalency*** of each of the combining metal and non-metal determine the chemical formula of the compound formed:

- $Na^+ + Cl^-$ give NaCl; • $Ca^{2+} + 2Cl^-$ give $CaCl_2$;
- $2Al^{3+} + 3O^{2-}$ give $Al_2O_3$.

In a covalent molecule, non-metal atoms combine depending on the number of electrons contributed for sharing by each of the elements:

- H + Cl give HCl; • 2H + O give $H_2O$;
- 3H + N give $NH_3$; • 4H + C give $CH_4$.

The chemical formula of a covalent compound is called ***molecular formula***, while that of an ionic compound is called ***empirical formula***. For uniformity, the *empirical formula* of an ionic compound is also called *molecular formula*:

1. The chemical formula $\mathbf{H_2O}$ represents one molecule of water. It contains two hydrogen atoms and

one oxygen atom. The total number of atoms in the formula is **three**.

2. The chemical formula $Al_2O_3$ represents a molecule of an ionic compound, which contains **two** atoms of aluminium and **three** atoms of oxygen. The total number of atoms in the formula is **five**.

**Revision Exercises**

6. Name the elements present in
   a. HCl b. $K_2O_2$ c. $CoCl_2$ d. NaOH
7. Give the number of atoms of each element present, and the total number of atoms in:
   a. $NH_3$ b. $Mg_3N_2$ c. $NH_4Cl$ d. $CH_3COOH$
8. How many oxygen atoms are in each of the following formulae? a. $3Cu_2O$ b. $17H_2O_2$ c. $5I_2O_7$

## 7.4 Formulae Containing Radicals

A ***radical*** is a group of atoms of two or more elements carrying a positive or negative charge, e.g. $NH_4^+$, $OH^-$, $NO_3^-$, $CO_3^{2-}$, $SO_4^{2-}$ and $HCO_3^-$. For each radical, the ***electrovalency*** corresponds to the ***charge*** on the group of atoms.

In order to write the correct chemical formulae containing radicals, a thorough knowledge of the chemical formulae of common radicals is essential. A list is provided in Table 7.1.

The steps for writing a chemical formula are:

1. Write the **cation** first, then, the **anion** – with their correct symbols and charges.
2. Combine the opposite ions in the *inverse ratio of their charges*, using the simplest ratio.
3. When the same radical occurs more than once in a formula, it is enclosed in brackets; the appropriate coefficient is then written as the subscript.

***Examples***

a. In a compound of $Ca^{2+}$ and $OH^-$, one of $Ca^{2+}$ combines with **two** of $OH^-$ in order to neutralize the charges. The formula is written as $Ca(OH)_2$ in order to preserve the identity of $OH^-$. It should not be written as $CaOH_2$ as this indicates **one** calcium atom, **one** oxygen atom and **two** hydrogen atoms. Also, it should not be written as $CaO_2H_2$; in doing so, the identity of $OH^-$ is not preserved.

b. In a compound of $NH_4^+$ and $SO_4^{2-}$, two of $NH_4^+$ combine with **one** of $SO_4^{2-}$ to give $(NH_4)_2SO_4$.

c. In a compound of $Mg^{2+}$ and $HCO_3^-$, one of $Mg^{2+}$ combines with **two** of $HCO_3^-$ to give $Mg(HCO_3)_2$.

d. A compound of $NH_4^+$ and $NO_3^-$ has the formula $NH_4NO_3$. Brackets are not required when a radical occurs only once in a formula.

**Table 7.1** *Common Ions and their Charges*

| Cation | | Anion | |
|---|---|---|---|
| **+1 ion** | | **–1 ion** | |
| **(Monovalent)** | $M^{n+}$ | **(Monovalent)** | $X^{n-}$ |
| Ammonium | $NH_4^+$ | Bromide | $Br^-$ |
| Copper (I) | $Cu^+$ | Chloride | $Cl^-$ |
| Hydrogen | $H^+$ | Cyanide | $CN^-$ |
| Lithium | $Li^+$ | Fluoride | $F^-$ |
| Mercury (I) | $Hg^+$ | Hydride | $H^-$ |
| Potassium | $K^+$ | Hydroxide | $OH^-$ |
| Sodium | $Na^+$ | Iodide | $I^-$ |
| | | Nitrite | $NO_2^-$ |
| | | Nitrate | $NO_3^-$ |
| | | Hydrogencarbonate | $HCO_3^-$ |
| | | Hydrogensulphite | $HSO_3^-$ |
| | | Hydrogensulphate | $HSO_4^-$ |
| | | Permanganate | $MnO_4^-$ |
| | | Chlorate | $ClO_3^-$ |
| | | Ethanoate (Acetate) | $CH_3CO_2^-$ |
| **+2 ion** | | **–2 ion** | |
| **(Divalent)** | $M^{2+}$ | **(Divalent)** | $X^{2-}$ |
| Barium | $Ba^{2+}$ | Oxide | $O^{2-}$ |
| Calcium | $Ca^{2+}$ | Sulphide | $S^{2-}$ |
| Cobalt | $Co^{2+}$ | Peroxide | $O_2^{2-}$ |
| Copper(II) | $Cu^{2+}$ | Carbonate | $CO_3^{2-}$ |
| Iron(II) | $Fe^{2+}$ | Sulphite | $SO_3^{2-}$ |
| Lead(II) | $Pb^{2+}$ | Sulphate | $SO_4^{2-}$ |
| Magnesium | $Mg^{2+}$ | Dichromate | $Cr_2O_7^{2-}$ |
| Mercury(II) | $Hg^{2+}$ | Chromate | $CrO_4^{2-}$ |
| Manganese(II) | $Mn^{2+}$ | Thiosulphate | $S_2O_3^{2-}$ |
| Nickel | $Ni^{2+}$ | Dicarbide | $C_2^{2-}$ |
| Tin(II) | $Sn^{2+}$ | Ethanedioate(Oxalate) | $C_2O_4^{2-}$ |
| Zinc | $Zn^{2+}$ | | |
| **+3 ion** | | **–3 ion** | |
| **(Trivalent)** | $M^{3+}$ | **(Trivalent)** | $X^{3-}$ |
| Aluminium | $Al^{3+}$ | Phosphite | $PO_3^{3-}$ |
| Chromium | $Cr^{3+}$ | Phosphate | $PO_4^{3-}$ |
| Iron(III) | $Fe^{3+}$ | Nitride | $N^{3-}$ |
| **+4 ion** | | | |
| **(Tetravalent)** | $M^{4+}$ | | |
| Manganese(IV) | $Mn^{4+}$ | | |
| Lead (IV) | $Pb^{4+}$ | | |
| Tin (IV) | $Sn^{4+}$ | | |

**Table 7.2** *Formulae of some compounds with radicals*

| *Radicals/Ions* | $H^+$ | $NH_4^+$ |
|---|---|---|
| Oxide, $O^{2-}$ | $H_2O$ | - |
| Hydroxide, $OH^-$ | H·OH ($H_2O$) | $NH_4OH$ |
| Chloride, $Cl^-$ | HCl | $NH_4Cl$ |
| Nitrate, $NO_3^-$ | $HNO_3$ | $NH_4NO_3$ |
| Carbonate, $CO_3^{2-}$ | $H_2CO_3$ | $(NH_4)_2CO_3$ |
| Sulphate, $SO_4^{2-}$ | $H_2SO_4$ | $(NH_4)_2SO_4$ |
| Hydrogencarbonate, $HCO_3^-$ | H·$HCO_3$ ($H_2CO_3$) | $NH_4HCO_3$ |

**Worked Examples**

1. State the number of atoms of each element in $(NH_4)_2C_2O_4$

**Solution**

$(NH_4)_2C_2O_4$ contains two $NH_4$ radicals; hence $(NH_4)_2C_2O_4$ gives $N_2H_8C_2O_4$. There are two atoms of nitrogen, eight atoms of hydrogen, two atoms of carbon, and four atoms of oxygen.

**Revision Exercises**

9 State the number of atoms of each element in
a. $NH_4NO_3$ b. $K_4Fe(CN)_6$ c. $Al_2(SO_4)_3$

10 Copy and complete the table below by writing the chemical formula of the stable compound formed when a cation in the vertical column combines with an anion in the horizontal column:

| | $HCO_3^-$ | $NO_3^-$ | $SO_4^{2-}$ | $PO_4^{3-}$ |
|---|---|---|---|---|
| $H^+$ | | | | |
| $Ca^{2+}$ | | | | |
| $Al^{3+}$ | | | | |
| $NH_4^+$ | | | | |

11 a. Which of the following formulae is **NOT** correct?
$Al_2(SO_4)_3$; $Ca(OH)_2$; $Fe_2O_3$; $Mg(NO_3)_2$
b. Write the correct formula in a above.

12 If a metal R forms a compound with the formula $R(NO_3)_2$, the formula of its sulphate is
A. $R(SO_4)_2$ B. $RSO_4$ C. $R_2SO_4$ D. $R_2(SO_4)_3$

## 7.5 Calculations Involving Chemical Formulae

### To Calculate Relative Molecular Mass

In order to calculate the *relative molecular mass* of *an element* or a *compound*, knowledge of the *relative atomic mass of each element* is required.

The *relative molecular mass of an element or compound* is the sum total of the relative atomic masses of all the atoms present in the *molecular formula*. *Relative molecular mass has no unit.*

**Worked Examples**

Note: Relative atomic masses are in brackets.

2. Calculate the relative molecular mass of:
a. $H_2$ b. $O_2$ c. HCl d. $H_2O$
[H = 1.0; O = 16.0; Cl = 35.5]

a. *To calculate relative molecular mass, $M_r$ of $H_2$:*
*$H_2$ contains two hydrogen atoms. Each H atom has a relative atomic mass of 1.0.*
$\therefore M_r[H_2] = 2 \times 1.0 = 2.00$ *[No unit]*

b. *To calculate relative molecular mass of $O_2$*
$M_r[O_2] = 16.0 \times 2 = 32.0$

c. *To calculate relative molecular mass of HCl*
$M_r[HCl] = 1.0 + 35.5 = 36.5$

d. *To calculate relative molecular mass of $H_2O$*
*A molecule of $H_2O$ contains two hydrogen atoms and one oxygen atom.*
$\therefore M_r[H_2O] = (2 \times 1.0) + (1 \times 16.0)$
$= 2.0 + 16.0 = 18.0$

3. Calculate the relative molecular mass of:
a. $CaCO_3$ b. $Mg(NO_3)_2$ c. $Na_2CO_3 \cdot 10H_2O$
[H = 1, C = 12, N = 14, O = 16, Mg = 24, Ca = 40]

a. *To calculate the molecular mass of $CaCO_3$*
*In $CaCO_3$, there are one atom of calcium, one atom of carbon and three atoms of oxygen.*
i.e. $M_r[CaCO_3] = (40 \times 1) + (12 \times 1) + (16 \times 3)$
$= 40 + 12 + 48 = 100$
$\therefore M_r[CaCO_3] = 100$

b. *To calculate the molecular mass of $Mg(NO_3)_2$*
*In $Mg(NO_3)_2$, there are two $NO_3$ radicals. To ease the calculation, the brackets are opened thus:*
$Mg(NO_3)_2$ is $Mg \quad N_2 \quad O_6$
$= (24 \times 1) + (14 \times 2) + (16 \times 6)$
$= 24 + 28 + 96 = 148$
$\therefore M_r[Mg(NO_3)_2] = 148$

c. *To calculate the molecular mass of $Na_2CO_3 \cdot 10H_2O$*
$M_r[Na_2CO_3] = (23 \times 2) + (12 \times 1) + (16 \times 3)$
$= 46 + 12 + 48 = 106$
$M_r[10H_2O] = 10[(2 \times 1) + 16]$
$= 10[2 + 16] = 10[18] = 180$
$\therefore M_r[Na_2CO_3 \cdot 10H_2O] = 106 + 180 = 286.$

4. A metallic oxide $M_2O_3$ has a relative molecular mass of 160. Calculate the relative atomic mass of M. [O = 16]

*Data provided: $M_r[M_2O_3] = 160$; O = 16*
*To find the atomic mass of M.*
$M_2O_3 = 160$
i.e. $(M \times 2) + (16 \times 3) = 160$
$2M + 48 = 16; \quad 2M = 160 - 48 = 112$
$2M = 112$
$\therefore M = 112/2 = 56$
*Hence, the relative atomic mass of M is 56.0 [No unit]*

**Revision Exercises**

13 Calculate the relative molecular mass of
a. $Cl_2$ b. $SO_3$ c. $Al_2(SO_4)_3$ d. $CuCl_2 \cdot 2H_2O$
[H = 1; O = 16, Al = 27; S = 32; Cl = 35.5; Cu = 63.5]

14 A compound $M(HCO_3)_2$ has a relative molecular mass of 162. Calculate the relative atomic mass of M.
[H = 1; C = 12; O = 16]

### Percentage Composition by Mass

The percentage composition by mass of a compound indicates the percentage by mass of each element present in the compound.

Once the relative molecular mass of a compound is known, the percentage by mass of each element can be calculated as shown in the following:

**Worked Examples**

5. Calculate the percentage composition by mass of
(a) CuO; (b) $H_2SO_4$; (c) $Na_2CO_3 \cdot 10H_2O$

(a) *To calculate percentage by mass of CaO*
*First, calculate its relative molecular mass:*
*$M_r$ [CaO] = 40.0 + 16.0 = 56.0*
*This means: Out of 56 parts, calcium is 40 parts by mass, while oxygen is 16 parts by mass*

$\%\ Ca = 40/56 \times 100/1 = 71.4$

$\%\ O = 16/56 \times 100/1 = 28.6$

**Note:** In a compound contains two elements, if the percentage by mass of one of them is $x$%, the other element will be $(100 - x)$%

Check: In CaO, %Ca = 71.4%

$\therefore\ \%\ O = 100 - \%Ca = (100 - 71.4) = 28.6$

(b) *To calculate percentage by mass of $H_2SO_4$*

$M_r [H_2SO_4] = (1 \times 2) + (32 \times 1) + (16 \times 4)$

$= 2 + 32 + 64 = 98.0$

*$H_2SO_4$ contains 3 elements with symbols H, S and O. That is: Out of 98 parts, total parts by mass of H = 2, parts by mass of S = 32, and parts by mass of O = 64.*

*Hence, % H = 2/98 × 100/1 = 2.0*

*% S = 32/98 × 100/1 = 32.7*

*% O = 64/98 × 100/1 = 65.3*

*Note: % O = 100 − (%H + %S)*

*= 100 − (2.0 + 32.7) = 65.3*

(c) *To calculate percentage by mass of $Na_2CO_3 \cdot 10H_2O$*

**Note:** *In the determination of the percentage composition of hydrated salts, water of crystallization (molecules of water) is treated as an entity.*

*$M_r [Na_2CO_3 \cdot 10H_2O]$*

$= (23 \times 2) + (12 \times 1) + (16 \times 3) + (10 \times 18.0)$

$= 46 + 12 + 48 + 180 = 286$

*$Na_2CO_3 \cdot 10H_2O$ contains Na, C, O and $H_2O$. That is: Out of 286 parts, total parts by mass of Na is 46, parts by mass of C is 12, parts by mass of O is 48, and parts by mass of $H_2O$ is 180.*

*Hence, % Na = 46/286 × 100/1 = 16.1*

*% C = 12/286 × 100/1 = 4.2*

*% O = 48/286 × 100/1 = 16.8*

*% $H_2O$ = 180/286 × 100/1 = 62.9*

6. Calculate the percentage by mass of oxygen in glucose, $C_6H_{12}O_6$? [H = 1; C = 12; O = 16.0]

**Note:** *% by mass of oxygen alone in glucose is required.*

*To calculate percentage by mass of oxygen only*

*$M_r [C_6H_{12}O_6] = (12 \times 6) + (1 \times 12) + (16 \times 6)$*

*$= 72 + 12 + 96 = 180$*

Out of 180 parts by mass, 96 parts are oxygen.

$\therefore\ \%\ O = 96/180 \times 100/1 = 53.3$

7. In $Mg(HXO_3)_2$ the percentage of magnesium by mass is 16.4%. Calculate the
a. relative molecular mass of the compound.
b. relative atomic mass of X.
[H = 1; O = 16; Mg = 24]

a. *To calculate the relative molecular mass*
*Given: % Mg by mass is 16.4%.*
*Let M be the relative molecular mass of the compound.*
*Since there is only one atom of Mg per molecule, then, out of M parts by mass, Mg is 24 parts.*
*Hence, % Mg = 24/M × 100/1 = 16.4*
*Making M the subject of the formula,*
*M = (24 × 100)/16.4 = 146*

*∴ Relative molecular mass is 146 (no unit).*

b. *To find the relative atomic mass of X*
*From a above: $M_r [Mg(HXO_3)_2] = 146$*
*i.e. $(24 \times 1) + (2 \times 1) + (X \times 2) + (16 \times 6) = 146$*
*$24 + 2 + 2X + 96 = 146$*
*$2X = 146 - 122 = 24$*
*$2X = 24$*
*$X = 24/2 = 12$*

*∴ Relative atomic mass of X is 12.0 (no unit)*

**Revision Exercises**

15 Calculate the percentage by mass of potassium hydrogensulphide, KHS. [H = 1, S = 32, K = 39]

16 Calculate the percentage composition by mass of Plaster of Paris, $CaSO_4 \cdot H_2O$.
[H = 1, O = 16, S = 32, Ca = 40]

17 What is the percentage by mass of sulphur in $Al_2(SO_4)_3$? [$Al_2(SO_4)_3$ = 342 , S = 32] (WAEC)
A. 9.36% B. 14.71% C. 21.33% D. 28.07%

18 *Glycine*, an amino acid, has one nitrogen atom per molecule. If the percentage by mass of nitrogen in glycine is 18.7% calculate the relative molecular mass of the amino acid. [N = 14]

19 Which of the following compounds has the highest percentage by mass of carbon?
CO ; $CO_2$ ; $CS_2$ ; $CH_4$ [C = 12; O = 16; S = 32]

## 7.6 Molecular-Empirical Formulae

### Empirical Formula

The ***molecular formula*** of a compound indicates the *actual number* of atoms of each element in it, while the ***empirical formula*** indicates the *simplest ratio* in which the various atoms combine.

In some ionic and covalent compounds, the *empirical* and *molecular formulae* are the same:
- In $Na_2CO_3$, the atoms of the elements combine in the ratio 2 : 1 : 3.
- In methane, $CH_4$, the atoms of the elements combine in the ratio 1: 4.

In many organic compounds, the *empirical* and *molecular formulae* are not the same. For example:

| Compound | Molecular formula | Empirical formula |
|---|---|---|
| *Ethane* | $C_2H_6$ (2 : 6) | $CH_3$ (1 : 3) |
| *Benzene* | $C_6H_6$ ( 6 : 6) | CH (1 : 1) |
| *Glucose* | $C_6H_{12}O_6$ (6:12:6) | $CH_2O$ (1:2:1) |

The *empirical formula* of a compound can be obtained from its *percentage composition by mass*.
The *steps* to follow are:

1. Write down the *percentage by mass of each element*. Each percentage represents the mass of the element in 100 *g* of the compound.
2. Divide the percentage by mass of each element by its relative atomic mass, to obtain the *amount* of atoms of each element.
3. Divide each *amount* of atoms by the smallest of the amounts obtained, to obtain the simplest whole number ratio.

**Note:** *The following precautions should to be taken during the calculations:*

- In the *amounts* of atoms, express the answer to at least three significant figures.
- In order obtain the simplest whole number ratio, do not round up *proper fractions* arbitrarily.

Take note of ratios such as:

**1 : 1.50** is the same as **2(1 : 1.50)** i.e. **2 : 3**
**1 : 1.33** is the same as **3(1 : 1.33)** i.e. **3 : 4**

### Worked Examples

**8.** Calculate the empirical formula of a compound containing 43.4% sodium, 11.3% carbon and 45.3% oxygen. [Na = 23.0; O = 16.0; C = 12.0]

**Solution**

| *Elements present* | Na | C | O |
|---|---|---|---|
| i. Percentage by mass: | 43.4 | 11.3 | 45.3 |
| ii. Divide each by its atomic mass | $\frac{43.4}{23}$ | $\frac{11.3}{12}$ | $\frac{45.3}{16}$ |
| ∴ Amount = | 1.89 | 0.94 | 2.83 |
| iii. Divide each by the smallest | $\frac{1.89}{0.94}$ | $\frac{0.94}{0.94}$ | $\frac{2.83}{0.94}$ |
| ∴ Ratio of amounts = | 2.01 | 1.00 | 3.04 |

Simplest whole number ratio = **2 : 1 : 3**
∴ The empirical formula = $Na_2CO_3$

**9.** Find the empirical formula of an oxide of iron containing 70.0% iron. [Fe = 56; O = 16]

*The elements in the oxide are iron and oxygen. Since it contains 70.0% iron, percentage oxygen will be*
*(100 – 70.0)% = 30.0%.*

| *Elements contained* | Fe | O |
|---|---|---|
| i. Percentage by mass | 70.0 | 30.0 |
| ii. Divide each by its atomic mass | $\frac{70.0}{56}$ | $\frac{30.0}{16}$ |
| ∴ Amount = | 1.25 | 1.88 |
| iii. Divide each by the smaller | $\frac{1.25}{1.25}$ | $\frac{1.88}{1.25}$ |
| = | 1.00 | 1.50 |

The ratio **1.00 : 1.50** is the same as
**2(1.00 : 1.50) = 2 : 3**
∴ The empirical formula = $Fe_2O_3$

**Note:** If ratio **1.0 : 1.5** is approximated to **1 : 2**, the empirical formula becomes $FeO_2$. There is no oxide of iron with such a chemical formula!

**Example 10:** A compound contains 37.1% copper, 41.7% chlorine, and the rest is water of crystallization. Determine its empirical formula.
[Cu = 63.5; Cl = 35.5; $H_2O$ = 18]

**Note:** *In compounds containing water of crystallization, the water molecules are treated as an entity.*

*First, calculate % water of crystallization, i.e.*
$\%H_2O = 100 - (37.1 + 41.7) = 100 - 78.8 = 21.2$

| *Elements contained* | Cu | Cl | $H_2O$ |
|---|---|---|---|
| i % by mass | 37.1 | 41.7 | 21.2 |
| ii Divide each by its its atomic mass | $\frac{37.1}{63.5}$ | $\frac{41.7}{35.5}$ | $\frac{21.2}{18}$ |
| Amount = | 0.58 | 1.17 | 1.18 |
| iii Divide by the smallest | $\frac{0.58}{0.58}$ | $\frac{1.17}{0.58}$ | $\frac{1.18}{0.58}$ |
| = | 1.00 | 2.02 | 2.03 |
| ≈ | 1 | 2 | 2 |

∴ The empirical formula is $CuCl_2{\cdot}2H_2O$.

### Revision Exercises

**20** Write the empirical formulae of the following:
a. $Na_2O_2$ b. $N_2O_4$ c. $CH_3COOH$ d. $(NH_4)_2C_2O_4$

**21** Calculate the empirical formula:
a. 15.8% Al; 28.1% S; 56.1% O.
b. 9.8% Mg; 13.0% S; 26.0% O; 51.2% $H_2O$.

**22** Determine the empirical formula of a compound W, which has 34.2% of iron and 65.8% of chlorine.
[Cl = 35.5, Fe = 56] [WAEC]

**23** An industrial raw material has the following composition by mass: Iron = 28.1%
Chlorine = 35.7%
Water of crystallization = 36.2%
Calculate the formula of the material.
[H = 1, O = 16, Cl = 35.5, Fe = 56] [WAEC]

**24** A hydrated compound contains 25.9% calcium, 20.8% sulphur, 41.6% oxygen, and the rest is water of crystallization. Determine the empirical formula.

## Molecular Formulae

When the *molecular* and *empirical formulae* of a compound are not the same, the *molecular formula* will be a simple *multiple* of the *empirical formula*.

The mathematical relationship is:

***Molecular formula* = *n* × (*Empirical formula*)**

*Or* $\frac{\text{Molecular formula}}{\text{Empirical formula}} = n$

where ***n*** is a whole number (*n* = 1, 2, 3, 4, etc).

When ***n*** = 1, the empirical and molecular formulae are the same, as in methane, $CH_4$.

In ethane, the molecular formula is $C_2H_6$ while the empirical formula is $CH_3$; therefore, ***n*** is 2, i.e.

$C_2H_6 = 2(CH_3)$

**11** A certain *hydrocarbon* contains 80.0% carbon by mass. If its relative molecular mass is 30.0, determine its molecular formula.

[C = 12.0; H = 1.0]

*(Hydrocarbon contains carbon and hydrogen only.)*

Given: Percentage carbon = 80.0%

Hence, % Hydrogen = (100 − 80.0) = 20.0

*First, find the empirical formula.*

| *Elements contained* | | C | H |
|---|---|---|---|
| i Percentage by mass | | 80.0 | 20.0 |
| ii Divide each by its atomic mass | | 80.0/12 | 20.0/1 |
| ∴ Amount | = | 6.67 | 20 |
| iii Divide each by the smaller | | 6.67/6.67 | 20.0/6.67 |
| | = | 1.00 | 3.00 |

The simplest whole number ratio is **1 : 3**

∴ The empirical formula is $CH_3$

*To find the molecular formula;*

Using the expression:

$n \times$ (empirical formula mass) = molecular mass

$n \times (CH_3) = 30$ [Given]

$n[12 + (1 \times 3)] = 30$

$15n = 30$; $n = 30/15 = 2$

∴ Molecular formula = $2(CH_3) = C_2H_6$

**12** A compound contains 4.0 g of hydrogen and 64.0 g of oxygen. If its relative molecular mass is 34.0, find its molecular formula. [H = 1.0; O = 16].

*Note: In this example, the actual mass of each element in the compound has been given; there is no need to calculate the percentage composition by mass. The steps to follow remain the same.*

| *Elements contained* | | H | O |
|---|---|---|---|
| a. Mass (g) | | 4.0 | 64.0 |
| b. Divide each by its atomic mass | | 4.0/1.0 | 64.0/16.0 |
| Amount | = | 4.0 | 4.0 |
| c. Divide each by the smaller | | 4.0/4.0 | 4.0/4.0 |
| Simplest ratio | = | 1 | 1 |

∴ The empirical formula = **HO**.

Using the relationship:

$n \times$ (empirical formula mass) = molecular mass

$n(HO) = 34$

$n(1 + 16) = 34$

$17n = 34$

$n = 34/17 = 2$

∴ Molecular formula = $2(HO) = H_2O_2$.

### Revision Exercises

**25** Which of the following is the relative molecular mass of a compound which has empirical formula $CH_2O$ ? [ H = 1; C = 12; O = 16 ]

**A.** 42 **B.** 45 **C.** 126 **D.** 145 **E.** 180 [WAEC]

**26** An uncommon oxide of nitrogen contains 63.2% of oxygen by mass.

a. Determine its empirical formula.

b. If its relative molecular mass is 76, determine its molecular formula. [N = 14; O = 16]

**27** A compound contains 7.2 g of nitrogen and 1.0 g of hydrogen. If the relative molecular mass of the compound is 32, determine its molecular formula.

[H = 1; N = 14]

**28** A gaseous metallic chloride $MCl_4$ consists of 20.22% of M by mass. The formula of the chloride is

**A.** MCl **B.** $MCl_2$ **C.** $MCl_3$ **D.** $M_2Cl_6$

[M = 27; Cl = 35.5] [JAMB]

## 7.7 IUPAC Nomenclature of Inorganic Compounds

### Concept of Oxidation Number

International Union of Pure and Applied Chemistry (**IUPAC**) rules are being used in naming inorganic compounds.

In order to understand the basic principles underlying the **IUPAC** system, a good knowledge of the concept of oxidation number, and the ability to assign oxidation numbers to the atoms of the elements in a molecule or ion are very essential.

***Definitions of Oxidation Number (O.N.)***

*Oxidation number* can be defined as the:

- apparent charge of an atom in a molecule or ion
- charge of an atom, if the pair of electrons in a covalent bond was assigned to the atom of the *more* electronegative element.

*Oxidation number* is sometimes called *oxidation state*.

***Importance of Oxidation number***

The concept of oxidation number is used in:

- Naming inorganic compounds.
- Determining the number of chemical bonds that can be formed by an atom.
- Identifying *oxidizing* and *reducing agents* in redox reactions.
- Balancing *redox reactions*.

### Rules for assigning Oxidation Number (O.N.)

**1.** *The O.N. of an atom in an uncombined free element, whether monatomic or polyatomic is* **zero**; e.g. Noble gases (He, Ne, Ar, etc), metals (Na, Cu, Zn, etc), and molecules ($H_2$, $O_2$, $N_2$, $P_4$, $S_8$, $I_2$, etc).

**2.** *The ON of one oxygen atom is -2 in its binary compounds* (except in peroxides ($H_2O_2$, $Na_2O_2$ or $O_2^{2-}$ ) where it is **-1**, and in its binary compound with fluorine, $OF_2$ where it is **+2**).



3. *The oxidation number of one hydrogen atom is +1 in its compounds* [except in hydrides of metals (e.g. NaH), where it is -1].

4. *In their compounds group I alkaline metals (Li, Na, K, etc) have ON of +1, group II alkaline-earth metals (Mg, Ca, etc.) have O.N. of +2, while group III metals (B, Al, etc) have O.N. of +3.*

5. *The halogen atom (F, Cl, Br, I, etc.) in group VII have ON of -1 in their binary compounds only.*

6. *ON of the atom in a monatomic ion is equal to the charge on it*; e.g. *ON* of sodium atom in $Na^+$ is +1; that of Al in $Al^{3+}$ is +3; that of S in $S^{2-}$ is -2.

7. *In any radical, the sum of the O.N. of all the atoms equals the charge on its ion.*

8. *In any molecule, the sum of the ON's of all the atoms adds to zero.*

The above rules are used to determine the oxidation number of an atom whose oxidation number cannot be obtained from the rules.

**Worked Examples**

Note: *Oxidation number is either zero, positive, or negative, and is usually with respect to only one atom.*

13 Find the oxidation number of copper in $Cu_2O$.

*To find the O.N. of Cu*

O.N. of one oxygen atom, O is –2. ***(Rule 2)***

In a neutral molecule, sum of all O.N. is zero ***(Rule 8)***

∴ In $Cu_2O$: $Cu_2O$

$2Cu + (-2) = 0$ (rule 8)

$2Cu = +2$

$Cu = +2/2 = +1$

∴ O.N. of a copper atom, Cu in $Cu_2O$ = **+1**.

14 What is the oxidation number of phosphorus in phosphine, $PH_3$?

*In $PH_3$, P is more electronegative than H.*

Hence, each H atom has O.N. of +1. (Rule 3)

∴ In $PH_3$

$P + 3(+1) = 0$ (Rule 8)

$P + 3 = 0$; $P = -3$

∴ O.N. of phosphorus atom, P in $PH_3$ is **–3**

15 Find the oxidation number of nitrogen in $HNO_3$.

*In $HNO_3$, the oxidation number of H atom is +1, while that of O is -2 per atom.*

In $HNO_3$

$+1 + N + 3(-2) = 0$.

$+1 + N - 6 = 0$; $N = 6 - 1 = 5$.

O.N. of nitrogen atom, N in $HNO_3$ is **+5**.

16 Calculate the oxidation number of **X** in $X_2O_7^{2-}$.

*O.N. of each O atom = –2* ***(Rule 2)***

*Net charge on the ion = –2* ***(Rule 7)***

∴ In $X_2O_7^{2-}$

$2X + 7(-2) = -2$ (Rule 7)

$2X - 14 = -2$

$2X = -2 + 14 = +12$

$X = +12/2 = +6$

∴ O.N. of one atom of **X** in $X_2O_7^{2-}$ is **+6**.

**Revision Exercises**

29 Determine the oxidation number of

a. sulphur in $S_8$; $SO_2$; $H_2S$; $H_2S_2O_7$; $SO_4^{2-}$

b. phosphorus in $P_4$; $P_2O_5$; $HPO_3$; $POCl_3$; $HPO_3^{2-}$

30 The oxidation number of iodine in $IO_3^-$ is

A. –5 B. –1 C. +1 D. +5 [WAEC]

31 Which of the following terms indicates the number of bonds that can be formed by an atom? [JAMB]

A. Oxidation number. B. Valence.

C. Atomic number. D. Electronegativity.

## 7.8 Naming Inorganic Compounds

### 1. Binary Compounds

Binary compounds contain *two* elements, and their names end with ***-ide***.

a. The *cation* (*electropositive* element) is named first, followed by that of the *anion* (*electronegative* element) with its name modified to end with ***-ide***, e.g. **CaO** is calcium ***oxide***, and $H_2S$ is hydrogen ***sulphide***.

The systematic ending ***-ide*** is not applicable to binary compounds such as $H_2O$ (water), $NH_3$ (ammonia) and $PH_3$ (phosphine). So also, some radicals are treated like single elements when naming their compounds, e.g.: Ammonium, $NH_4^+$; hydroxide, $OH^-$; and cyanide, $CN^-$. Hence, **HCN** is hydrogen cyanide, while $NH_4OH$ is ammonium hydroxide.

b. The O.N. of an element with more than one O.N.'s is designated by Roman numeral in brackets, e.g. $Cu_2O$ is copper(I) oxide – since the oxidation number of each copper atom is +1; **CuO** is copper(II) oxide. If an element has a fixed O.N., the Roman numeral is omitted, e.g. **NaCl** is sodium chloride; not sodium(I) chloride.

***Examples***

| Formula | IUPAC name |
|---|---|
| $Na_2O$ | Sodium oxide |
| $H_2S$ | Hydrogen sulphide |
| KI | Potassium iodide |
| $Mg_3N_2$ | Magnesium nitride |
| $Fe_2O_3$ | Iron(III) oxide |

c. Stoichiometric names are used for binary compounds of nonmetals:

***Examples***

| Formula | IUPAC name | Conventional name |
|---|---|---|
| CO | Carbon(II) oxide | Carbon monooxide |
| $CO_2$ | Carbon(IV) oxide | Carbon dioxide |
| NO | Nitrogen(II) oxide | Nitric oxide |
| $N_2O$ | Nitrogen(I) oxide | Nitrous oxide |
| $NO_2$ | Nitrogen(IV) oxide | Nitrogen dioxide |

| | | |
|---|---|---|
| $N_2O_5$ | Dinitrogen(V) oxide | Dinitrogen pentoxide |
| $PCl_3$ | Phosphorus(III) chloride | Phosphorus trichloride |

**Note:** Transition elements such as Fe, Cu, Cr, Co, Mn and Ni (except Zn and Sc) and non-metals of groups IV, V, VI and VII (except F and Si) exist in more than one oxidation state.

## 2. Tertiary and Quaternary Compounds

These are compounds containing three and four elements respectively.

### a. Oxoacids

These are acids that contain oxygen atoms.

i. Oxygen is named first as *oxo*, with the number of atoms indicated by the Greek prefix *mono* (1), *di* (2), *tri* (3), *tetra* (4), *penta* (5), etc.

ii. The central atom is then named with the ending *-ate*, and its oxidation number designated by Roman numeral in brackets.

iii. The word *acid* is finally added to the name.

*Examples*

| Oxoacid | IUPAC name | Conventional |
|---|---|---|
| $HNO_2$ | Dioxonitrate(III) acid | Nitrous acid |
| $HNO_3$ | Trioxonitrate(V) acid | Nitric acid |
| $H_2CO_3$ | Trioxocarbonate(IV) acid | Carbonic acid |
| $H_2SO_3$ | Trioxosulphate(IV) acid | Sulphurous acid |
| $H_2SO_4$ | Tetraoxosulphate(VI) acid | Sulphuric acid |
| $H_3PO_4$ | Tetraoxophosphate(V) acid | Phosphoric acid |

### b. Acid radicals

Acid radicals are from *oxoacids*. In naming, the word *acid* in the corresponding name of the *oxoacid* is replaced with *ate*.

*Examples*

| Radical | IUPAC name |
|---|---|
| $NO_2^-$ | Dioxonitrate(III) ion (nitrite) |
| $NO_3^-$ | Trioxonitrate(V) ion (nitrate) |
| $SO_3^{2-}$ | Trioxosulphate(IV) ion (sulphite) |
| $SO_4^{2-}$ | Tetraoxosulphate(VI) ion (sulphate) |
| $CO_3^{2-}$ | Trioxocarbonate(IV) ion (carbonate) |
| $HCO_3^-$ | Hydrogentrioxocarbonate(IV) ion |

### c. Normal and acid salts (anhydrous)

A *salt* is formed when the replaceable hydrogen atoms in an acid are *partially* or *completely* replaced by a metal or ammonium ion to give an *acid salt* or *normal salt* respectively.

The *cation* is named first with its oxidation number indicated by a Roman numeral in brackets (if need be); then, the acid radical (*anion*).

*Examples*

| Salt | IUPAC name |
|---|---|
| $KNO_3$ | Potassium trioxonitrate(V) |
| $CuSO_4$ | Copper(II) tetraoxosulphate(VI) |
| $NH_4Cl$ | Ammonium chloride/trioxonitrate(V) |
| $NaHCO_3$ | Sodium hydrogentrioxocarbonate(IV) |
| $Ca(HSO_3)_2$ | Calcium hydrogentrioxosulphate(IV) |
| $K_2Cr_2O_7$ | Potassium heptaoxodichromate(VI) |

### d. Hydrate salts

These are salts with molecules of water in their crystals. In naming, the corresponding *anhydrous* salt, i.e. without molecules of water, is first named, followed by a *hyd-* stem, then the number of water molecules is written in Latin words.

*Examples*

| Hydrate salt | IUPAC name |
|---|---|
| $Na_2CO_3.10H_2O$ | Sodium trioxocarbonate(IV) decahydrate |
| $FeSO_4.7H_2O$ | Iron(II) tetraoxosulphate(VI) heptahydrate |
| $CoCl_2.6H_2O$ | Cobalt(II) chloride hexahydrate |

### e. Basic salts

A *basic salt* contains hydroxide group. It is named like a double salt, e.g.

$Zn(OH)Cl$ Zinc hydroxide chloride.

### f. Complex salts and Complex ions

A *complex salt* is an ionic compound with a *complex ion*. A *complex ion* contains a metal ion surrounded by neutral molecules or ions called *ligands*. Examples of ligands are $H_2O$, $NH_3$ and $CN^-$.

*Rules for naming Complexes*

i. In a complex salt, the *cation* is named first, then the *anion* – just as in a simple salt.

ii. A complex ion is named as follows:

- State the number of ligands attached to the central cation using the Greek prefixes: mono-, di-, tri-.
- Name the anion ligands using the names ending with the suffix *-o*, e.g. $Br^-$ -bromo, $F^-$ -fluoro, $Cl^-$ -chloro, $I^-$ -iodo, $CN^-$ -cyano, $OH^-$ -hydroxo, $H^-$ -hydrido, while neutral ligands such as $H_2O$ -aqua and $NH_3$ -amine.
- Name the cation in a complex cation using the English name. In a complex anion, the name of the central metal is modified and ends with *-ate*.

*Examples*

| Complex cation | IUPAC name |
|---|---|
| $Cu(NH_3)_4^{2+}$ | Tetraamine copper(II) ion |
| $Fe(H_2O)_6^{2+}$ | Hexaaqua iron(II) ion |

| Complex anion | IUPAC name |
|---|---|
| $Fe(CN)_6^{3-}$ | Hexacyanoferrate(III) ion |
| $Fe(CN)_6^{4-}$ | Hexacyanoferrate(II) ion |

| | |
|---|---|
| $AlH_4^-$ | Tetrahydridoaluminate(III) ion |

| Complex salt | IUPAC name |
|---|---|
| $[Cu(NH_3)_4][NO_3]$ | Tetraammine copper(II) tetraoxosulphate(VI) |
| $K_4[Fe(CN)_6]$ | Potassium hexacyanoferrate(II) |
| $K_3[Fe(CN)_6]$ | Potassium hexacyanoferrate(III) |
| $LiAlH_4$ | Lithium tetrahydridoaluminate(III) |

**Worked Examples**

**17** Write the formula of each of the following:

**a.** Nitrogen(I) oxide

*It is a binary compound of nitrogen (+1) and oxygen (−2). Hence, two atoms of N (+1) combine with one atom of O (−2) to give $N_2O$.*

$$+2 - 2 = 0$$

**b.** Trioxophosphate(III) acid.

*An oxoacid with three O atoms (−2), one P atom (+3). Hence, there are three H atoms (+1), so that*

$+3 + 3 - 6 = 0$, *i.e.* $H_3PO_3$

$$+3+3-6=0$$

**c.** Calcium hydrogentrioxocarbonate(IV)

*It is a salt of $Ca^{2+}$. The anion is an oxoacid radical of H atom (+1), three O atoms (−2) and one C atom (+4). The charge on the radical is $+1 + 4 - 6 = -1$, i.e. $HCO_3^-$.*

*To obtain a neutral compound, one $Ca^{2+}$ (+2) combines with two $HCO_3^-$ (−1) to give $Ca(HCO_3)_2$.*

$$+2 + 2 + 8 - 12 = 0$$

**d.** Chromium(III) tetraoxosulphate(VI)

*It is a salt of $Cr^{3+}$. Anion is an oxoacid radical with four O atoms (−2) and a sulphur atom (+6); the charge on the radical is −2. It is $SO_4^{2-}$.*

*To obtain a neutral compound, two $Cr^{3+}$ (+3) combine with three $SO_4^{2-}$ (−2) to give $Cr_2(SO_4)_3$.*

**e.** Monoxochlorate (I) ion

*It is an oxoacid radical with one O atom (−2) and a Cl atom (+1). Hence, the charge on the radical is $-2 + 1 = -1$, i.e. $ClO^-$*

$$+1 - 2 = -1$$

**18** Give the IUPAC names of the following:

**a.** $PbI_2$ **b.** $HClO_3$ **c.** $Al(NO_3)_3$

**d.** $FeSO_4.7H_2O$ **e.** $Cr_2O_7^{2-}$

Notes: You should be able to do the following:

i. Write the correct chemical formulae and charges of the common oxoacid radicals.

ii. Insert the oxidation numbers of elements with variable oxidation numbers at the appropriate positions in the IUPAC names, if not, such names will be incomplete.

**a.** $PbI_2$

It is a binary compound of a halogen with O.N. −1; hence, the O.N. of Pb is +2. $PbI_2$ is lead(II) iodide

$$(+2 - 2 = 0).$$

**b.** $HClO_3$

It is an oxoacid. O.N of H is +1, three O atoms is 3(−2), hence, that of Cl is +5, so that $+1 + 5 - 6 = 0$.

$HClO_3$ is trioxochlorate(V) acid.

**c.** $Al(NO_3)_3$

The cation is in group III; $Al^{3+}$; hence, the acid radical is $NO_3^-$, in which O.N. of N is +5. $Al(NO_3)_3$ is aluminium trioxonitrate (V).

**d.** $FeSO_4.7H_2O$

The acid radical is $SO_4^{2-}$, hence, the cation is $Fe^{2+}$. S in $SO_4^{2-}$ is +6, and there are seven water molecules. The hydrate is iron(II) tetraoxosulphate(VI) heptahydrate.

**e.** In $Cr_2O_7^{2-}$

The seven O atoms have O.N.'s of $7 \times -2$ while the charge on the ion is $-2$. Hence, the two Cr atoms must be $+12$, so that each Cr atom is +6.

$Cr_2O_7^{2-}$ is heptaoxodichromate(VI) ion

$+12 - 14 = -2$

**19** What is the oxidation number of boron in $Na[B(NO_3)_4]$?

A. +4 B. +3 C. +2 D. +1 (JAMB)

In $Na[B(NO_3)_4]$, the radical is $NO_3^-$, the cation is $Na^+$

i.e. $+1 + B + 4(-2) = 0$, $+1 + B - 8 = 0$

$$B = +8 - 1 = +7$$

i.e. O.N. of boron in $Na[B(NO_3)_4]$ is +7. **Ans: B**

**Revision Exercises**

**32** Give the IUPAC names of the following:

**a.** $MnO_2$ **b.** $H_2CO_3$ **c.** $(VO)^{2+}$, $VO_4^{3-}$ **d.** $CrO_3$

**33** Write the formulae of the following:

**a.** Copper(I) oxide **b.** Calcium dicarbide

**c.** Monoxosulphate (I) acid

**d.** Chromium (III) trioxonitrate (V)

**e.** Ammonium hydrogentrioxocarbonate(IV)

**34** What is the correct IUPAC name for $NO_3^-$? (JAMB)

A. Trioxonitrate (IV) ion B. Dioxonitrate (III) ion

C. Dioxonitrate (IV) ion D. Trioxonitrate (III) ion

**Answers to Revision Exercises**

**3.** D **12.** B **13a.** $PI_3$ **b.** $CaI_2$ **c.** $SrI_2$ **d.** $BaI_2$

**15** K = 34.2%, H = 1.6%, S = 44.4%

**16** Ca = 20.0%, S = 20.0%, O = 32.0%, $H_2O$ = 11.7%

**17.** D **18.** $PbO$ **19.** $CH_4$

**21a.** $Al_2(SO_4)_3$ **b.** $MgSO_4.7H_2O$ **22.** $FeCl_3$

**23.** $FeCl_2.4H_2O$ **24.** $CaSO_4.H_2O$ **25.** E

**26a** $N_2O_5$ **b.** $N_2O_4$ **27.** $N_2H_4$ **28.** C

**30.** D **31.** A **34.** B

# 8

# •THE MOLE CONCEPT•

## 8.1 Introduction - The Mole Concept

Matter is made up of *elementary chemical units* such as *atoms, molecules, ions, electrons, protons, or neutrons*, which are too small to be seen or weighed. Hence, in order to estimate quantities of chemical substances, chemists adopted a concept that involves weighing, *rather than counting*. This is the *mole concept*.

A *mole* of a chemical substance is like a *bag of rice*. A bag of rice is a collection of *grains of rice*; or also, a *mole of a chemical substance* is a collection of its *elementary units*. Like a *dozen* that contains *twelve units*, a *mole* of a chemical substance also consists of a *definite number of elementary units*.

**Definition**

*A mole is the amount of a chemical substance that contains as many elementary units as there are atoms in 12.0 g of carbon-12.*

From this definition, it means that a *mole* of an element is a collection of its *atoms*, such that the total mass, in *grams*, is numerically equal to its relative atomic mass.

That is:

If 1 mole of carbon atoms weighs 12.0 g, then,
1 mole of oxygen atoms will weigh 16.0 g;
1 mole of sodium atoms will weigh 23.0 g, etc.
(Mole is abbreviated, mol.)

**Revision Exercises**

1. What is a mole of a chemical substance?
2. Which of the following is not an elementary unit of a chemical substance?
   A. Atom  B. Electron  C. Mole
   D. Molecule  E. Ion
3. What will be the mass of one mole of hydrogen atoms? (C = 12.0; H = 1.00)

## 8.2 Using Grains to Introduce the Mole Concept

Consider a collection of *grains of rice* of the same variety, and *grains of beans* of the same variety. Suppose the average mass of a grain of rice is **0.020 g**, and that of bean is **0.300 g**. The following deductions can be made from these data:

1. The grains of *rice* and *bean* are in the ratio of **0.020** to **0.300**, or **2:30**, or simply **1:15**. That is, *one grain of rice is 15 times lighter than one grain of bean*, or *one grain of bean is 15 times heavier than a grain of rice*.

2. By analogy, a *grain* represents an *atom* of rice or bean. Hence, if the relative *atomic* mass of rice is taken to be **1.00**, that of a bean will be **15.0**.

3. If a quantity of grains (atoms) of rice weighing **1.00 g** is placed in a pile, and another quantity of grains (atoms) of beans weighing **15.0 g** is placed in another pile, the number of grains (atoms) in each pile will be the same:

| | Rice | Bean |
|---|---|---|
| a. Mass taken | 1.00 g | 15.0 g |
| b. Mass taken / Mass of a grain | 1.00 / 0.02 | 15.0 / 0.30 |
| Number of grains = | 50 | 50 |

4. If a known mass, say, **3.00 g** of rice is placed in a pile, and the same mass (**3.00 g**) of beans is placed in another pile, the number of grains in the piles will be in the *inverse proportion* of their relative *atomic masses*, i.e.

| | Rice | Bean |
|---|---|---|
| a. Mass taken: | 3.00 g | 3.00 g |
| b. Mass taken / Mass of a grain | 3.00 / 0.02 | 3.00 / 0.30 |
| Number of grains = | 150 | 10 |

c. Ratio of rice : bean = 150 : 10 = 15 : 1

**Note:** The ratio of grains of rice to bean of 15:1 is the *inverse* of their relative grain mass of 1:15. This is because a grain of rice is lighter; hence, there are more grains of rice than grains of bean.

The following deductions can be made from the above observations:

1. If known quantities of two elements are taken, such that they are equal to their respective atomic masses, in *grams*, the various quantities will contain the same number of atoms (or elementary units). For example: The relative atomic mass of carbon is 12.0, while that of sulphur is 32.0. Then, the *num-*

*ber of atoms* in **12.0 g** of *carbon* will be equal to the *number of atoms* in **32.0 g** of *sulphur*.

**Inference:** Equal amount, in *moles*, of two or more chemical substances contains the *same number of elementary units* or *particles*.

2. If the same mass of two or more elements is taken separately, the element with the *smallest relative atomic mass* will contain the *highest number of atoms*. That is:

There will be *more* carbon atoms in **1.00 g** of carbon, than the number of sulphur atoms in **1.00 g** of sulphur because *an atom of carbon is lighter than an atom of sulphur*, and vice versa.

**Revision Exercises**

4. Which element contains more atoms: 1.00 g of lead, or 1.00 g of iron? [Fe = 56.0; Pb = 206]
5. Consider 1.0 *mole* of atoms of iron and 1.0 *mole* of atoms of lead. Which element is heavier, and why? [Fe = 56.0; Pb = 206]

## 8.3 Applications of the Mole Concept

### Atoms and Moles of Elements

1. A *mole* is a collection of *atoms* of an element.

2. The *mass of one mole* of a chemical substance is called *molar mass*, $M$, i.e.

*Molar mass = Mass of one mole.*

Its S.I. unit is *grams per mole* (*g/mol* or *gmol*$^{-1}$)

The *mass of one mole* of carbon is 12.0 *g*; i.e.

- molar mass of carbon is 12.0 *g/mol*;
- molar mass of sulphur is 32.0 *g/mol*.

3. The *number of particles* in *one mole* of a chemical substance is called ***Avogadro number***, $N_A$. It is numerically equal to $6.02 \times 10^{23}$. Hence:

- 1 *mole* of carbon weighs 12.0 *g* and contains $6.02 \times 10^{23}$ atoms.

Hence, *a mole is the amount of a chemical substance that contains* $6.02 \times 10^{23}$ *particles of the substance*. It is called ***Avogadro constant***, $L$, which is equal to $6.02 \times 10^{23}$ *mol*$^{-1}$.

4. *Mole* is **not** a *number*; it is the S.I. *unit* of the *amount of a chemical substance*. Hence, *amounts* of carbon in 12.0 *g* of carbon atoms is 1.0 *mole*.

5. *Any unit of mass* can be used in expressing the *molar mass*; i.e.

- 12.0 *kilograms* of carbon will contain the same number of atoms as in 32.0 *kilograms* of sulphur.
- 12.0 *tonnes* of carbon contain the same number of atoms as in 32.0 *tonnes* of sulphur.

Figure 8.1 shows the relationship between the *relative atomic mass* of an element, in *grams*; its *amount*, in *moles*; and the *Avogadro constant*, $L$.

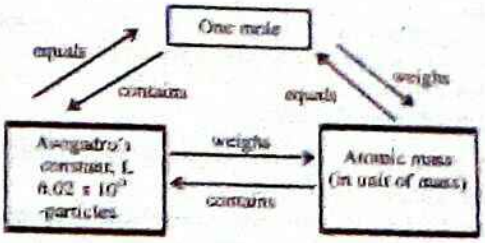



**Fig 8.1** *Inter-relationships between mass-mole-Avogadro constant*

**Revision Exercises**

6a. Define the term *mole*. [WAEC]
b. State the S.I. unit of i. amount; ii. molar mass.
7. Give its numerical value of Avogadro constant.
8. What term is used to describe the number of elementary units present in one mole of a substance?
9. How many *atoms* are in 65.0 *g* of zinc? [Zn = 65.0]
10. What is the mass of $6.02 \times 10^{23}$ atoms of iron? [Fe = 56.0]

### Molecules and Moles

A *molecule* is composed of *two* or *more atoms* that are chemically bonded to form a *unit*. For instance:

- $H_2$ represents *one* molecule of hydrogen containing *two* hydrogen atoms chemically bonded.

***In terms of moles***: $H_2$ represents *one mole* of molecules of hydrogen. It contains *two moles* of atoms of hydrogen, weighs 2.0 *g*, and contains $6.02 \times 10^{23}$ molecules.

- $H_2O$ represents *one* molecule of water containing *two* atoms of hydrogen and *one* atom of oxygen.

***In terms of moles***: $H_2O$ represents *one mole* of molecules of water. It contains *two moles* of hydrogen *atoms* and *one mole* of oxygen *atoms*. It weighs 18.0 *g* and contains $6.02 \times 10^{23}$ molecules.

**Worked Examples**

1. Write the chemical formula, and calculate the molar mass of:

a. Ozone; b. Potassium hydroxide;
c. Calcium hydrogentrioxocarbonate(IV).
[H = 1; C = 12; O = 16; P = 39; Ca = 40]

**Solution**

a. The chemical formula of ozone is $O_3$. Its molar mass:
$O_3 = 16.0 \times 3 = 48.0$ *g/mol*.

b. Potassium hydroxide is KOH. Its molar mass:
KOH = 39.0 + 16.0 + 1.0 = 56.0 *g/mol*.

c. Calcium hydrogentrioxocarbonate(IV) is: $Ca(HCO_3)_2$.
$Ca(HCO_3)_2 = CaH_2C_2O_6$
$= 40 + (1\times2) + (12\times2) + (16\times 6)$
$= 40 + 2 + 24 + 96 = 162$ *g/mol*

2. How many *grams* are in *one mole* of each of the following? a. NaCl b. $NH_3$ c. $Fe_2O_3$

**Answers**

a. $NaCl = 23.0 + 35.5 = 58.5$ g.

b. $NH_3 = 14.0 + (1 \times 3) = 14.0 + 3.0 = 17.0$ g.

c. $Fe_2O_3 = (56.0 \times 2) + (16.0 \times 3)$
$= 112 + 48.0 = 160$ g.

**3.** How many molecules are in one mole of carbon (II) oxide? What will be its mass?

*There are $6.02 \times 10^{23}$ molecules in one mole of carbon (II) oxide. Its chemical formula is CO.*
*One mole of CO weighs $12.0 + 16.0 = 28.0$ g.*

**4.** How many moles of hydrogen atoms are in one mole of ethanoic acid molecules?

*Ethanoic acid is $CH_3COOH$. Hence, one mole of the acid contains four moles of hydrogen atoms.*

**5.** How many atoms are present in one mole of each of the following? **a.** NaOH; **b.** $H_2SO_4$

*a. In NaOH, there are three atoms per molecule; hence, there are $3 \times 6.02 \times 10^{23}$ atoms per mole.*
$= 18.1 \times 10^{23}$ *atoms*

*c. In $H_2SO_4$, there are seven atoms per molecule; hence, there are $7 \times 6.02 \times 10^{23}$ atoms per mole.*
$= 42.1 \times 10^{23}$ *atoms*

**Revision Exercises**

**11** Calculate the molar mass of $Zn(NO_3)_2$.

**12** Which of the following compounds have the same molar mass? {H = 1, C = 12, N = 14, O = 16, S = 32, K = 39, Ca = 40, Cu = 63}

I. $CaCO_3$ II. $KHCO_3$ III. $(NH_4)_2SO_4$ IV. $CuSO_4$

A. I and II only B. II and III only.
C. I, II and III only. D. I, II, III and IV. [WAEC]

**13** How many atoms are in one mole of $Ca(OH)_2$?

## 8.4 Calculations Using Mole Concept

### Proportion Methods

Many chemical calculations are based on *direct* and *inverse proportions*.

**1. *Direct proportion:***

Consider *two* variables: *A*, beakers of the same size, and *B*, mass of beakers. An *increase* in the number of beakers leads to an *increase* in the mass of beakers; i.e.

*A* is *directly* proportional to *B*.

Mathematically: $A \propto B$

**2. *Inverse proportion:***

Consider two variables: Length *l*, of a burning candle at a particular time *t*. An *increase* in time *t*, *decreases* the length *l*, of the burning candle; i.e.

*l* is *inversely* proportional to *t*.

Mathematically: $l \propto 1/t$

### *Calculations from the First Principle*

When a chemical calculation is solved using the *proportion method*, it is said to be from the ***first principle*** or from the ***definition***. It involves identification of a statement of fact.

The following example gives the steps to follow when solving problems involving *direct proportion*.

**Worked Example 6**

A *dozen of beakers* of the same size *weighs* 180 g.

a. What will be the *mass* of 30 beakers?

b. How *many beakers* will weigh 600 g?

{1 dozen = 12}

*From the First Principle Method 1*

a. *To find the mass of 30 beakers*

The *statement of fact* is: 12 beakers weigh 180 g.

The *two variables* involved are: *number of beakers* and the *mass, in grams*. What is *given* in the question is the *number of beakers*, and what is *required* is the *mass*.

The *four* basic steps to follow are:

**Step I:** *State* or *restate* the *statement of fact* such that the given variable comes before the *required* variable; i.e. *number of beakers* before the *mass*:

12 beakers weigh 180 g.

**Step II:** Find the *mass* of 1 beaker by *dividing* the *mass of 12 beakers* by 12. (Mass of one beaker will be less) i.e. 1 beaker weighs 180/12 g.

**Step III:** Find the mass of 30 beakers *required*. *Multiply* the *cost* of 1 beaker by 30. (Mass of 30 beakers will be *more*) i.e. $30 \times 180/12$ g.

**Step IV:** Evaluate the expression and attach the correct unit, i.e. $(30 \times 180)/12 = 450$ g.

**Note:** With adequate practice, it is possible to omit **step II**, so that **step III** is obtained from **step I** by *multiplying* 30 by 180/12.

b. *To find the number of beakers weighing 600 g.*

The two variables involved are: *number* of beakers and *mass*. The *statement of fact* remains

12 beakers weigh 180 g.

**Step I:** The statement of fact is *restated* such that the given variable comes before the *required* variable, i.e.

180 g is the mass of 12 beakers.

**Step II:** Find the number of beakers, which weighs 1 g by dividing the number of beakers by 180, i.e.

1 g is the mass of 12/180 beakers.

**Step III:** Find the number of beakers weighing 600 g by multiplying the mass of 1 beaker by 600, i.e.

600 g is the mass of $600 \times 12/180$ beakers

**Step IV:** Solve the expression and attach the correct unit, i.e. $(600 \times 12)/180 = 40$ beakers

*Method 2* (Alternative Proportion Method)

This proportion method involves *six* steps.

a. *To find the mass of 30 beakers*

The *statement of fact* is: 12 beakers weigh 180 g.

**Step I:** The variables in the statement of fact are stated as being equivalent to one another, i.e.

12 beakers = 180 g

**Step II:** Let *x* be the *required* mass of 30 beakers.

These two variables are stated as being equivalent, and in the same order as in **step I**, i.e.



30 beakers ≡ $x$ g (Not $x$ g ≡ 30 beakers)

**Step III:** Divide like-terms in **steps I and II**, i.e.

$$\frac{12 \text{ beakers}}{30 \text{ beakers}} = \frac{180 \text{ g}}{x \text{ g}} \quad \text{or} \quad \frac{12}{30} = \frac{180}{x}$$

**Step IV:** Cross-multiply, such that the unknown $x$ is on the left-hand-side of the expression, i.e.

$$12 \times x = 180 \times 30$$

**Step V:** Make $x$ the subject of the formula.

$$x = (180 \times 30)/12$$

**Step VI:** Evaluate the final expression, and attach the correct unit of $x$, i.e. $x = 450$ g.

b. *To find the number of beakers weighing 600 g.*

Let $x$ be the number of beakers.

**Step I:** 12 beakers ≡ 180 g (given)
**Step II:** $x$ beakers ≡ 600 g (required)
**Step III:** $12/x = 180/600$
**Step IV:** $180 \times x = 12 \times 600$
**Step V:** $x = (12 \times 600)/180$
**Step VI:** $x = 40$ beakers.

## Use of Mathematical Formulae

A faster method of solving many mathematical problems in chemistry is by the use of the appropriate *mathematical formulae*, which connect *more than three variables*. The *unknown variable* is made the subject of the formula, followed by correct substitution, then, evaluation.

A *mathematical formula* can be obtained from *a statement of fact*, or from the S. I. units of *related variables*. For instance: the S. I. unit of *mass*, $m$ is *grams* (*g*), that of *amount*, $n$ is *moles* (*mol.*), while that of *molar mass*, $M$ is *grams per mole* (*g/mol*). From the three variables, it can be shown that:

$$M = m/n$$

i.e. $\dfrac{\text{Mass, } m \text{ (g)}}{\text{Amount, } n \text{ (mol)}} = \text{Molar mass, } M \text{ (g mol}^{-1}\text{)}$

Or $\text{Amount, } n \text{ (mol)} = \dfrac{\text{Mass, } m \text{ (g)}}{\text{Molar mass, } M \text{ (gmol}^{-1}\text{)}}$

Or Mass, $m$ = Amount, $n$ × Molar mass, $M$

In solving a mathematical problem in chemistry, the following steps are recommended:

1. List the *given* and the *required variables*.
2. Provide a mathematical formula or formulae, that connect(s) the variables.
3. Do the correct substitution; then, make the *unknown* variable the subject of the formula.
4. Evaluate to *three significant figures*, and insert the correct unit – when necessary. (See page 74 for significant figures.)

## Mass-Mole Relationships in Elements and Compounds

### Worked Examples

7. How many moles are in 15.0 *g* of carbon atoms?

[C = 12]

**Answer**

The *unknown* variable is amount of carbon, $n$ = ? *mol*.
The *given* variable is mass of carbon, $m$ = 15.0 *g*.
The *constant* is molar mass of carbon, $M$ = 12 $gmol^{-1}$

*From the First Principle: Method 1*

**Note:** In the statement of fact, the *known* or *given* variable (mass of carbon) is stated first, then, the *unknown (required)* variable (amount).

12 g of carbon atoms equal 1 mole
1 g of carbon atoms equals 1/12 mol
∴ 15 g of carbon atoms equal (15 × 1)/12
= 1.25 mol (3 sig. fig)

*Method 2*

Let $x$ be the amount, in moles.

1 mol of carbon ≡ 12 g (Statement of fact)
$x$ mol of carbon ≡ 15 g (Required)

Cross-multiply such that the unknown is on the left:

$12 \times x = 1 \times 15$
$x = 15/12 = 1.25$ *mol*

*Formula method*

The mathematical formula that connects the mass $m$, amount $n$, and molar mass $M$ of an element is:

$$\text{Amount, } n \text{ (mol)} = \frac{\text{Mass of substance, } m \text{ (g)}}{\text{Molar mass, } M \text{ (g mol}^{-1}\text{)}}$$

i.e. $n = m/M$

Given: mass, $m$ = 15.0 g
Molar mass, $M$ = 12.0 $gmol^{-1}$ (constant, given)
Substituting:
Amount, $n$ = 15.0/12.0 = 1.25 *mol*.

8. Calculate the mass of iron present in 0.025 *mol* of iron filings. [Fe = 56.0]

**Answer**

The required variable is mass, $m$ = ? g
The given variable is amount, $n$ = 0.025 *mol*
The constant is the molar mass, $M$ = 56 g/mol

*From the First Principle: Method 1*

1 *mol* of iron weighs 56 g
∴ 0.025 *mol* weighs 56 × 0.025 = 1.40 g

*Method 2*

Let $x$ be the mass of iron filings.

1 mol of iron ≡ 56 g
0.025 mol of iron ≡ $x$ g

Cross-multiplying: $1 \times x = 56 \times 0.025$
$x = 56 \times 0.025 = 1.40$ g

*Mathematical Formula method*

The mathematical formula that connects the *mass*, *amount* and *molar mass* of a chemical substance is:

Mass, $m$ = Amount, $n$ × Molar mass, $M$
$m = M \times n$

Substituting:
Mass, $m$ = 56 × 0.025 = 1.40 *g*

9. If 0.123 *mole* of an element **X** weighs 8.0 *g*. What is the relative atomic mass of **X**?

*Given*: amount, $n$ = 0.123 *mol*; mass, $m$ = 8.0 *g*.
*Unknown*: molar mass, $M$ in g/mol (mass of one mole).

*From the First Principle*

0.125 *mol* of X weighs 8.0 *g*

$\therefore$ 1 *mol* of X weighs $\frac{8.00}{0.125}$ = 65.0 *g*

Hence, relative atomic mass of X = 65.0 (no unit)

*Formula method*

The appropriate formula is:

*Molar mass* = (*Mass*)/(*Amount*)

Substituting: *Molar mass* = 8.00/0.125 = 65.0 *g/mol*

Hence, relative atomic mass of X = 65.0 (No unit)

**10** Calculate the amount of sodium chloride in 20.0 *g* of the pure salt. (Na = 23.0, Cl = 35.5)

*The given variable: mass* = 20.0 *g*

*Molar mass of NaCl* = 23.0 + 35.5 = 58.5 *g/mol*

*Required: amount of NaCl* = *x mol*

*From the First Principle Method I*

58.5 *g* NaCl = 1 *mol*

20.0 *g* NaCl = *x mol*

Cross-multiplying: 58.5 × *x* = 20 × 1

*x* = 20/58.5 = 0.342 *mol*

*Formula method*

The appropriate formula is:

Amount = (Mass)/(Molar mass)

Substituting: Amount = 20.0/58.5 = 0.342 *mol*.

**11** Given that 0.101 mole of an oxide $X_2O$ weighs 14.4 *g*. Calculate the:

**a.** molar mass of $X_2O$,

**b.** relative atomic mass of X (O = 16.0)

**a.** *To calculate the molar mass of* $X_2O$

Given: amount = 0.101 *mol*; mass = 14.4 *g*.

*From the First Principle*

Let *x* be the mass of 1 mole of $X_2O$.

0.101 *mol* = 14.4 *g*

1 *mol* = *x g*

i.e. 0.101 × *x* = 14.4 × 1

*x* = 14.40/0.101 = 143 *g*

Hence, the molar mass of $X_2O$ = 143 *g/mol*

*Formula method*

Molar mass = Mass/Amount = 14.40/0.101 = 143 $gmol^{-1}$

**b.** *To calculate the atomic mass of* X (O = 16)

From **a** above, *M*.*M*.($X_2O$) = 143, then,

$X_2O$ = 143

i.e. 2X + 16 = 143

2X = 143 − 16 = 127

X = 127/2 = 63.5

Hence, the relative atomic mass of X is 63.5 (no unit)

**12** Calculate the amount of sodium in 13.3 *g* of pure anhydrous sodium trioxocarbonate(IV).

[Na = 23.0; C = 12.0; O = 16.0]

*To calculate the amount the amount of Na in* $Na_2CO_3$

Molar mass of $Na_2CO_3$ = (23 × 2) + (12 × 1) + (16 × 3)

= 46 + 12 + 48 = 106 $gmol^{-1}$

106 *g* (1 *mol*) of $Na_2CO_3$ contain 2 *mol* (2 × 23 *g*) of Na. i.e. 106 *g* of $Na_2CO_3$ contain 2 *mol* of Na.

$\therefore$ 13.3 *g* of $Na_2CO_3$ contain (2 × 13.3)/106 *mol* of Na

= 0.500 *mol*

**Revision Exercises**

**13** What is the molar mass of a substance, if 0.4 mole of the substance has a mass of 25.0 *g*?

A. 6.5 *g* B. 40.0 *g* C. 62.5 *g* D. 2.5 *g* [JAMB]

**14** What is the amount of gold present in 15.5 *g* of a pure gold wedding ring? (Au = 197). [WAEC]

**15** Calculate the mass of 0.005 *mol* of $Na_2CO_3.10H_2O$

[H = 1; C = 12; O = 16; Na = 23]

## Atom–Mass–Mole relationships

### Avogadro constant

*The number of atoms in one mole of a monatomic element is the Avogadro constant, L. It is numerically equal to* $6.02 \times 10^{23}$ *atoms.*

Mathematically:

$$L = \frac{\text{Number of atom, } N}{\text{amount, } n}$$

When the mass of one mole (molar mass, *M*) of an element is divided by the Avogadro constant, *L*, the *mass of an atom* is obtained, i.e.

Mass of an atom =

(Molar mass)/(Avogadro constant)

### Worked Examples

**13** How many atoms are in 2.0 *g* of calcium?

[Ca = 40; Avogadro constant = $6.02 \times 10^{23}$ $mol^{-1}$]

*From the First Principle Method II*

Let *x* be the number of atoms in 2.0 *g* of Ca.

40 *g* of calcium = $6.02 \times 10^{23}$ atoms (From definition)

2 *g* of calcium = *x* atoms

Cross-multiplying: 40*x* = 2 × $6.02 \times 10^{23}$ atoms

*x* = (2 × $6.02 \times 10^{23}$)/40

= $3.01 \times 10^{22}$ atoms

**14** Calculate the mass of one atom of carbon.

[C = 12.0; Avogadro's constant, L = $6.02 \times 10^{23}$]

*From the First Principle*

Let *x* be the mass of one atom of carbon.

$6.02 \times 10^{23}$ carbon atoms = 12 *g* (From definition)

1 atom of carbon = *x g*

i.e. $x(6.02 \times 10^{23}) = (12 \times 1)$

$\therefore$ $x = (12 \times 1)/(6.02 \times 10^{23})$ *g*

= $2.00 \times 10^{-23}$ *g*

(i.e. 0.00000000000000000002 *g*)

*Formula method*

Mass of one atom = (Molar mass)/(Avogadro constant)

Substituting:

Mass of one carbon atom = $12/(6.02 \times 10^{23})$

= $2.00 \times 10^{-23}$ *g*

**15** What is the mass of $6.02 \times 10^{23}$ atoms of magnesium? [Mg = 24, Avogadro constant = $6.02 \times 10^{23}$]

A. 240 *g* B. 24 *g* C. 2.4 *g* D. 0.24 *g* [WAEC]

Let *x* be the mass.

$6.02 \times 10^{23}$ Mg atoms = 24 *g* (From definition)

$6.02 \times 10^{23}$ Mg atoms = *x g*

i.e. $x = (24 \times 6.02 \times 10^{23})/(6.02 \times 10^{23})$ *g* = 240 *g*

**16** How many moles are in $9.03 \times 10^{23}$ atoms of sodium?
[Na = 23; Avogadro number = $6.02 \times 10^{23}$ $mol^{-1}$]

*From the First Principle: Method I*
Let $x$ be the amount of sodium
$6.02 \times 10^{23}$ atoms = 1 mole
$9.03 \times 10^{23}$ atoms = $x$ mole
i.e. $x = (9.03 \times 10^{23})/(6.02 \times 10^{23}) = 1.50$ mol.

*Formula method*
Amount of atoms, n = (No. of atoms)/Avogadro no.)
i.e. $x = (9.03 \times 10^{23})/(6.02 \times 10^{23}) = 1.50$ mol.

**17** A cuboid piece of sodium metal measures 3 cm × 4 cm × 10 cm. If the density of sodium is 0.971 $gcm^{-3}$, calculate the number of atoms in the sodium metal.
[Na = 23; Avogadro number = $6.02 \times 10^{23}$ $mol^{-1}$]
*Given: Density of Na = 0.971 $gcm^{-3}$;*
*Volume of Na = 3 cm × 4 cm × 10 cm = 120 $cm^3$*
*Firstly, mass of Na = density × volume*
*= 0.971 × 120 = 116.52 g*
*From the first principle:*
*23 g (1 mol) of Na = $6.02 \times 10^{23}$ atoms*
*∴ 116.52 g of Na = $(6.02 \times 10^{23} \times 116.52)/23$ atoms*
*= $3.05 \times 10^{24}$ atoms.*

**18** Calculate the mass of calcium that contains the same number of atoms as 9.0 g of carbon.
[C = 12.0; Ca = 40.0]
*Since equal amount, in moles, of two or more elements contain the same number of atoms, then:*
*1 mole (12.0 g) of carbon contains the same number of atoms as 1 mole (40.0 g) of calcium.*
*i.e. 12 g of carbon = 40 g of calcium.*
*∴ 9.0 g of carbon = (40 × 9)/12 g of calcium*
*= 30.0 g of calcium.*

### Revision Exercises

**17** Calculate the number of silver atoms in pure silver bracelet that has a mass of 35.0 g.
[Ag = 108; Avogadro constant = $6.02 \times 10^{23}$]
A $1.95 \times 10^{23}$ B $5.57 \times 10^{23}$
C $3.24 \times 10^{22}$ D $1.95 \times 10^{25}$ [WAEC]

**18** A chip used in a microcomputer contains $5.74 \times 10^{-3}$ g of silicon. Calculate the number of silicon atoms in the chip.
(Si = 28; Avogadro constant = $6.02 \times 10^{23}$)
A $2.04 \times 10^{-4}$ B $2.15 \times 10^{23}$
C $1.23 \times 10^{20}$ D $1.23 \times 10^{2}$ [WAEC]

## Molecule–Mass–Mole Relationship

When the *relative molecular mass* of an element or compound is expressed in grams, it equals the *mass of one mole of molecules*, i.e. the *molar mass*. For instance:

- The molecular formula of diatomic oxygen is $O_2$. Its relative molecular mass is 16 × 2 = 32.0 amu.

*In terms of mole:*
- *1 mole of oxygen molecules contains two moles of oxygen atoms. It weighs 32.0 g and contains $6.02 \times 10^{23}$ molecules.*
- The molecular formula $H_2O$ indicates one molecule of water. It contains *two* hydrogen atoms and *one* oxygen atom. Its relative molecular mass is *18.0 amu.*

*In terms of mole:*
- *1 mole of water molecules contains two moles of hydrogen atoms and one mole of oxygen atoms. It weighs 18.0 g and contains $6.02 \times 10^{23}$ molecules.*

However, care must be taken when dealing with ionic compounds, because they are composed of ions.

### Worked Examples

**19** How many atoms are in 24.0 g of oxygen gas?
[O = 16.0; Avogadro constant = $6.02 \times 10^{23}$ $mol^{-1}$]
*Recall that oxygen gas is diatomic. First, calculate the number of oxygen molecules in 24.0 g of the gas:*
*32.0 g (1 mole) of oxygen gas contain $6.02 \times 10^{23}$ molecules, i.e.*
*32.0 g of oxygen gas = $6.02 \times 10^{23}$ molecules*
*∴ 24 g of oxygen gas = $(6.02 \times 10^{23} \times 24)/32$*
*= $4.52 \times 10^{23}$ molecules.*
*But one molecule of oxygen, $O_2$, contains 2 atoms.*
*∴ Number of atoms = $2 \times 4.52 \times 10^{23}$*
*= $9.04 \times 10^{23}$ atoms.*

**20** How many molecules are in 25.5 g of ammonia?
[$NH_3$ = 17; Avogadro constant is $6.02 \times 10^{23}$ $mol^{-1}$]
**Answer**
*From the data provided:*
*17 g (1 mol) of $NH_3$ contain $6.02 \times 10^{23}$ molecules.*
*∴25.5 g of $NH_3$ contain $(25.5 \times 6.02 \times 10^{23})/17$*
*= $9.03 \times 10^{23}$ molecules.*

**21** How many atoms are in 2.50 moles of a triatomic gas, ozone?
[Avogadro constant is $6.0 \times 10^{23}$ $mol^{-1}$]
**Answer**
*First, calculate the number of molecules in 2.5 moles of the gas:*
*1 mole of gas = $6.0 \times 10^{23}$ molecules*
*∴ 2.50 mole of gas = $6.0 \times 10^{23} \times 2.5$ molecules*
*= $15.0 \times 10^{23}$ molecules.*
*Since 1 molecule of the gas contains 3 atoms,*
*∴ $15.0 \times 10^{23}$ molecules contain $3 \times 15.0 \times 10^{23}$ atoms*
*= $4.50 \times 10^{24}$ atoms*

### Revision Exercises

**19** Calculate the mass of $3.01 \times 10^{23}$ molecules of water.
[H = 1; O = 16; Avogadro constant = $6.02 \times 10^{23}$ $mol^{-1}$]

**20** Calculate the number of molecules in:
a. 6.4 g of sulphur (IV) oxide
b. 1.5 moles of hydrogen chloride.
[H = 1; O = 16; S = 32; Cl = 35.5;
Avogadro constant = $6.02 \times 10^{23}$ $mol^{-1}$]

**21** A vessel contains $18.06 \times 10^{23}$ molecules of ammonia gas at 25 °C. Calculate the number of hydrogen atoms present in the ammonia gas. [Avogadro constant = $6.02 \times 10^{23}$ $mol^{-1}$]

## 8.5 Significant Figures

The term significant figure is used to describe the importance attached to a particular numeral in a number.

It is very important to have a sound knowledge of significant figures, since the final answers in most chemical calculations should be expressed to *three significant figures*.

In a *decimal fraction*:

- The *first significant figure* is the *first non-zero numeral* when counted from the left-hand-side, e.g. in the number 0.0234, the first significant figure is 2, the second is 3, while the third is 4;
- *Zeros* that are between non-zero significant figures are significant, e.g. 0.03005 is to 4 significant figures;
- *Zeros* after a *non-zero* unit are significant, e.g. 0.0900 is to 3 significant figures;
- When *rounding off* a number to a specific significant figure, the numeral 0, 1, 2, 3 or 4 directly following the last digit of the required significant figure is ignored, while numeral 5, 6, 7, 8 or 9 is rounded up to a whole number, and added to the last digit, e.g. when 0.07654 is expressed to 3 significant figures, it becomes 0.0765, while 0.08765 expressed to 3 significant figures is 0.0877.

**Examples:**

**One Significant figure:**
1; 9; 0.1; 0.002; 0.0003; $1 \times 10^3$; $9 \times 10^{23}$

**Two Significant figures:**
10; 99; 1.0; 9.9; 0.10; 0.020; 0.073; 0.0099; $1.0 \times 10^6$; $8.6 \times 10^{-3}$

**Three Significant figures:**
100; 999; 1.00; 2.34; 23.4; 0.234; 0.00234; 0.953; 0.0806; 0.0860; $6.02 \times 10^{23}$; $10.0 \times 10^2$

**Four Significant figures:**
1000; 100.0; 10.00; 0.1000; 0.01000; 0.09876;

### Revision Exercises

**22** How many significant figures are in:
**a** 63.5; **b.** 108; **c.** 0.0033; **d.** 96500.

**23** Express the following to three significant figures:
**a.** 12; **b.** 2; **c.** 0.001; **d.** 0.09363;
**e.** 0.1999; **f.** 2020.

### Answers to Revision Exercises

**2.** C **3.** 1.00 *g* **4.** Fe **7** $6.02 \times 10^{23}$ **9** $6.02 \times 10^{23}$
**10** 56.0 *g* **11** 189 $gmol^{-1}$ **12.** A
**13.** $3.01 \times 10^{24}$ (i.e. $5 \times 6.02 \times 10^{23}$) **14.** C
**15** 0.0787 *mol* **16** 30.0 *g* **17.** D **18.** C
**19** 0.900 *g* **20a** $6.02 \times 10^{23}$; **b** $6.02 \times 10^{23}$ molecules
**21** $6.02 \times 10^{23}$ atoms **22a** 3; **b** 3; **c** 2; **d** 5
**23a** 12.0; **b** 2.00; **c** 0.00100; **d** 0.0936;
**e** 0.200; **f** $2.02 \times 10^3$

# 9

# •CHEMICAL EQUATIONS•
# •TYPES OF CHEMICAL REACTIONS•

## 9.1 Introduction

A *chemical equation* is a *shorthand* method of using chemical formulae to present a chemical or physical change. In presenting such a change, *substances combining* or *disappearing* are called ***reactants***, while those that are *newly formed* or *appearing* are called ***products***.

In a *chemical equation*, the ***reactants*** are written first, on the left, followed by an arrow pointing to the ***products*** written on the right-hand-side of the arrow:

**REACTANTS** ⟶ **PRODUCTS**
***(Left-Hand-Side)*** ***arrow*** ***(Right-Hand-Side)***

### Revision Exercises

1 In a chemical reaction, which substances are called
a. reactants? b. products ?
2 State the function of the arrow in a chemical equation.

## 9.2 Balanced Chemical Equations

### Basic Requirements

1. The chemical equation *must* be a statement of experimental fact, and not a guess.
2. The chemical formulae of *reactants* and *products* must be written as they occur naturally, e.g. diatomic gases, such as hydrogen, nitrogen, oxygen, chlorine and iodine, are written as $H_2$, $N_2$, $O_2$, $Cl_2$ and $I_2$ respectively, when they are reactants or products. Their atoms do not exist separately.
3. The physical states of all chemical substances must be indicated. For example:
   - A *solid* is denoted by *(s)*;
   - A pure *liquid* is denoted by *(l)*;
   - A *gas* is denoted by *(g)*;
   - An *aqueous solution* is a *water solution* of a substance; it is denoted by *(aq)* or *(soln)*.

### How to obtain a balanced equation

The steps to follow are:

1. State the experimental fact.
2. Write the reactants and products, in words, to conform to experimental fact (***Word Equation***).
   In the *word equation:*
   - The plus (+) *sign* between the reactants may be: *reacts with, combines with, burns in, mixes with;*
   - The *arrow* may mean: *to give, to form, to yield, to produce, to liberate, etc.*
   - The plus (+) *sign* between the products may mean: *and, together with, etc.*
3. Write the formulae of the reactants and products from the word equation, as they occur in nature (***Formula equation***). Once a chemical formula is written correctly, the coefficients, written as subscripts, should not be altered.
4. The equation is then ***balanced*** by making sure that the *number of atoms of each element on the left is equal to its number on the right.* This is achieved by *inspection*, and by *writing the appropriate numeral as a coefficient before the chemical formula affected. A chemical equation* ***must*** *conserve atoms.*

Once a chemical equation is balanced, the *law of conservation of matter (or atom)* is obeyed. The law states: *Matter (or atom) cannot be created or destroyed during the course of a chemical change.*

### Examples

1. *Hydrogen gas burns in oxygen gas to produce water.* This is a statement of experimental fact.
   - *Word equation:*

**Hydrogen + Oxygen → Water**

   - *Formula equation:*

$H_{2(g)} + O_{2(g)} \rightarrow H_2O_{(l)}$ *(Not balanced)*

By inspection, there are *two* hydrogen atoms on the left of the arrow and *two* on the right; the equation is balanced with respect to hydrogen. However, there are *two* oxygen atoms on the left and *one* on the right. To balance it on the right, 2 is written *before* $H_2O$ to give:

$H_2 + O_2 \rightarrow 2H_2O$ *(Not balanced)*

*Four* hydrogen atoms are now on the right, while *two* are on the left. To balance it on the left, *2* is written *before* $H_2$:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)} \quad \textit{(Balanced)}$$

The balanced equation means:

*Two molecules* of hydrogen gas combine with *one molecule* of oxygen gas to produce *two molecules* of water.

***Applying the mole concept:***

*2 moles* of hydrogen gas combine with *1 mole* of oxygen gas to give *2 moles* of water molecules.

**Note:** The equation above is balanced, if $H_2O_2$ is written as the product, instead of $H_2O$, i.e.

$$H_2 + O_2 \rightarrow H_2O_2 \textit{ (Balanced)}$$

However, the equation does not conform to experimental fact; hence, it is wrong!

2. When hydrogen gas is passed over heated copper(II) oxide, steam is given off and *brown* copper metal is deposited.

• *Word equation:*

$$\text{Copper(II) oxide} + \text{Hydrogen} \xrightarrow{\textit{heat}} \text{Copper} + \text{Steam}$$

• *Formula equation:*

$$CuO_{(s)} + H_{2(g)} \rightarrow Cu_{(s)} + H_2O_{(g)} \quad \textit{(Balanced)}$$

By inspection, the equation is balanced with respect to copper, hydrogen and oxygen; hence, there is no need to make use of any coefficient.

***Applying the mole concept:***

*One mole* of copper(II) oxide reacts with *one mole* of hydrogen gas to give *one mole* of copper metal and *one mole* of steam.

3. When powdered calcium trioxocarbonate(IV) is heated strongly, it decomposes to give carbon(IV) oxide gas and a white residue of calcium oxide.

• *Word equation:*

**Calcium trioxocarbonate (IV) → Calcium oxide + Carbon(IV) oxide**

• *Formula equation:*

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \quad \textit{(Balanced)}$$

***In terms of moles:*** *one mole* of $CaCO_3$ decomposes to give *one mole* of $CaO$ and *one mole* of $CO_2$.

## Use of Arrows

Sometimes, when a gas is a product of a chemical reaction, an arrow is drawn pointing upward, ↑, and when a solid is deposited or precipitated from aqueous solutions of reactants, the arrow points downward, ↓ e.g.

4. When potassium trioxochlorate (V) is heated gently, the crystals melt and then decompose to liberate oxygen gas and form a white residue of potassium chloride.

• *Word equation:*

**Potassium trioxochlorate (V) → Potassium chloride + Oxygen**

• *Formula equation:*

$$KClO_3 \rightarrow KCl + O_2\uparrow \textit{ (Unbalanced, as } O_{(g)})$$

By inspection, the equation is balanced with respect to potassium and chlorine; but there are *3* oxygen atoms on the left and *2* on the right.

In order to balance the oxygen atoms, the *LCM* of *2* and *3* is *6*; hence, there is the need to make sure that there are *6* oxygen atoms on each side of the arrow. This is achieved by writing *2* as the coefficient of $KClO_3$ and *3* as that of $O_2$ to obtain:

$$2KClO_3 \rightarrow KCl + 3O_2 \textit{ (Unbalanced)}$$

By so doing, the equation is no longer balanced with respect to potassium and chlorine; but by writing *2* as the coefficient of $KCl$ on the right, the equation becomes balanced, i.e.

$$2KClO_{3(s)} \rightarrow 2KCl_{(s)} + 3O_2\uparrow \textit{ (Balanced)}$$

***In terms of moles:*** *Two moles* of $KClO_3$ decompose to give *two moles* of $KCl$, as the residue, and *three moles* of oxygen gas.

## Use of Fractions

To start with, the use of fractions should be avoided when balancing chemical equations, e.g.

5. Lithium metal burns in chlorine gas to give lithium chloride, i.e.

$$Li_{(s)} + Cl_{2(g)} \rightarrow LiCl_{(s)} \quad \textit{(Unbalanced)}$$

The equation is balanced with respect to lithium. To balance Cl atom, write ½ as the coefficient of $Cl_2$ to obtain:

$$Li + \tfrac{1}{2}Cl_2 \rightarrow LiCl \quad \textit{(Balanced)}$$

Although the equation is balanced in terms of *moles*, it is not possible to obtain one-half molecule of chlorine. Hence, there is the need to multiply the reactants and products by a factor of 2, in order to get rid of ½, and obtain:

$$2Li + Cl_2 \rightarrow 2LiCl \quad \textit{(Balanced)}$$

6. Ethane gas burns in oxygen to produce carbon (IV) oxide and water.

$$\underset{\text{(Reactants)}}{C_2H_6 + O_2} \rightarrow \underset{\text{(Products)}}{CO_2 + H_2O}$$

Since oxygen atoms are in the two products, balance carbon atoms first; then, hydrogen atoms, and finally, oxygen atoms.

• Balance carbon atoms:

$$C_2H_6 + O_2 \rightarrow 2CO_2 + H_2O$$

• Balance hydrogen atoms:

$$C_2H_6 + O_2 \rightarrow 2CO_2 + 3H_2O$$

• To balance oxygen atoms:

7 oxygen atoms are in the products. In order to provide 7 oxygen atoms for the reactants, 7/2 (or 3½) molecules of $O_2$ are needed:

$$C_2H_4 + 7/2O_2 \rightarrow 2CO_2 + 3H_2O$$

In order to get rid of the fraction, multiply the reactants and products by a factor of 2 to obtain:

$$2C_2H_4 + 7O_2 \rightarrow 4CO_2 + 6H_2O \quad (Balanced)$$

**Worked Example**

1. Aluminium burns in oxygen to form the corresponding oxide, according to the equation:

$$xAl + yO_2 \rightarrow zAl_2O_3$$

Determine the values of $x$, $y$ and $z$.

**Answer**

In the equation: $Al + O_2 \rightarrow Al_2O_3$

• Balance Al atoms on the left by writing 2 as the coefficient:

$$2Al + O_2 \rightarrow Al_2O_3$$

• Balance O atoms on the left by writing 3/2 as the coefficient of $O_2$:

$$2Al + 3/2O_2 \rightarrow Al_2O_3$$

In order to get rid of the fraction, multiply the reactants and products by a factor of 2 to obtain:

$$4Al + 3O_2 \rightarrow 2Al_2O_3 \quad (Balanced)$$

Since the equation is now balanced, the values of

$$x = 4;\ y = 3 \text{ and } z = 2.$$

## Use of Simultaneous Equations

Equations of chemical reactions can be balanced by the use of simultaneous equations. Such simultaneous equations are obtained from the correct chemical formulae of the reactants and products.

The following examples illustrate the steps involved in the use of simultaneous equations in balancing chemical equations.

**Worked examples**

1. Determine the values of $x$, $y$ and $z$ in the following equation:

$$xH_2 + yO_2 \rightarrow zH_2O$$

*Answer*

• Construct a simultaneous equation with respect to each of the elements hydrogen, H, and oxygen, O, remembering that the *number of atoms of each element on the left must equal to its number on the right of the equation.*

With respect to H: $2x = 2z$ ..... Eqn (1)
With respect to O: $2y = z$ ..... Eqn (2)
From equation (1), $x = z$
From equation (2), $z = 2y$
$\therefore x = z = 2y$

• Make an intelligent assumption; remembering that the values of $x$, $y$, and $z$ must be whole numbers, and in the simplest ratio.

Assume $x = 1$; then, $z = 1$, and $y = ½$.
Assume $x = 2$; then, $z = 2$, and $y = 1$. (Simplest ratio)

• Check, if the equation is balanced using $x = 2$; $z = 2$, and $y = 1$

$$2H_2 + 1O_2 \rightarrow 2H_2O$$

By inspection, the equation is balanced.

2. Determine the values of $x$, $y$ and $z$ in the following equation:

$$xKClO_3 \rightarrow yKCl + zO_2$$

*Answer*

• With respect to potassium, K: $x = y$ ..... Eqn (1)
With respect to chlorine, Cl: $x = y$ ..... Eqn (2)
With respect to oxygen, O: $3x = 2z$ ..... Eqn (3)
From equation (3), $x = 2z/3$ ..... Eqn (4)

• Assume $z = 3$; then, $x = 2$, and $y = 2$. (Simplest ratio)

• Check, if the equation is balanced using $x = 2$; $y = 2$, and $z = 3$.

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

By inspection, the equation is balanced.

3. Determine the values of $w$, $x$, $y$ and $z$ in the following equation:

$$wC_4H_8 + xO_2 \rightarrow yCO_2 + zH_2O$$

*Answer*

• With respect to carbon, C: $4w = y$ ..... Eqn (1)
With respect to hydrogen, H: $8w = 2z$ ..... Eqn (2)
With respect to oxygen, O: $2x = 2y + z$ ..... Eqn (3)
From equation (2), $z = 4w$ ..... Eqn (4)

In equation (3), substituting $y = 4w$, and $z = 4w$, we obtain: $2x = 8w + 4w$
i.e. $2x = 12w$, or $x = 6w$.

• Assume $w = 1$; then, $x = 6$, $y = 4$, and $z = 4$. (Simplest ratio)

• Check, if the equation is balanced using $w = 1$, $x = 6$, $y = 4$, and $z = 4$.

$$1C_4H_8 + 6O_2 \rightarrow 4CO_2 + 4H_2O$$

By inspection, the equation is balanced.

**Revision Exercises**

3. Write *word* and *balanced* chemical equations for each of the following experimental facts:
   a. Sodium metal burns in oxygen gas to give sodium oxide, a white solid.
   b. When ammonia gas is passed over heated black copper(II) oxide, the products are copper, nitrogen and water.
4. Construct *balanced* equations for the following *word* equations:
   a. Hydrogen + chlorine → hydrogen chloride.
   b. Copper(II) trioxonitrate(V) → Copper(II) oxide + nitrogen(IV) oxide + oxygen.
5. Balance the following equations:
   a. $NCl_3 \rightarrow N_2 + Cl_2$
   b. $Fe + O_2 \rightarrow Fe_2O_3$
   c. $CuO + NH_3 \rightarrow Cu + H_2O + N_2$

d. $HCl + Na_2CO_3 \rightarrow NaCl + H_2O + CO_2$

e. $P_4 + S_8 \rightarrow P_4S_3$

6. What are the values of x, y and z respectively in the following equation? [WAEC]

$$MnO_2 + xHCl \rightarrow MnCl_2 + yH_2O + zCl_2$$

A. 4, 1, 2 B. 1, 2, 1 C. 2, 1, 2 D. 4, 2, 1

7. Determine the values of w, x, y and z in the following equation:

$$wC_2H_6 + xO_2 \rightarrow yCO_2 + zH_2O$$

## 9.3 Types of Chemical Reactions

There are various types of *inorganic reactions*; each type with its own distinguishing features:

### 1. Combination or Addition Reaction

Combination or *addition reaction* occurs when *two* or more elements or compounds combine to form a new *single compound*, i.e.

$$A + B \rightarrow C$$

**Examples**

a. When a mixture of iron filings and powdered sulphur is heated, a grey solid, iron(II) sulphide, is produced:

$$Fe_{(s)} + S_{(s)} \rightarrow FeS_{(s)}$$

b. A mixture of gaseous hydrogen and chlorine, in the presence of sunlight, explodes to give hydrogen chloride gas:

$$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$$

### 2. Thermal Decomposition Reaction

It occurs when a *single solid compound*, is heated, and splits into *two* or *more* substances. Usually, at least one of the products is a gas, while the other is a liquid or solid called *residue*. It is the opposite of combination reaction:

$$C \rightarrow A + B$$

**Examples**

a. When red powdered mercury(II) oxide is heated, it produces liquid mercury and oxygen gas:

$$2HgO_{(s)} \rightarrow 2Hg_{(l)} + O_{2(g)}$$

b. Crystals of lead(II) trioxonitrate(V) decompose with *crackling sound*, when heated, to give gaseous nitrogen(IV) oxide and oxygen, and lead (II) oxide as *residue*:

$$2Pb(NO_3)_{2(s)} \rightarrow 2PbO_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

### 3. Displacement or Replacement Reaction

Displacement occurs when an element **A** displaces or replaces another element **B** from a compound of **B**.

$$A + BC \rightarrow AC + B$$

A *displacement reaction* occurs between an *element* and a *compound*. This *reaction type* has been used to arrange *metals* and the *halogens* in order of *reactivity*. This order is referred to as the ***activity series***.

#### *Activity Series in Metals*

The *activity series* in metals shows that a metal *A* higher up in the *series* will displace the *ions of another metal B* below it from a solution of a compound of *B*.

Table 9.1 is the *activity series* in metals together with hydrogen. The *pneumonic* is to enable learners to master the *series* quickly.

The *activity series* can be used to predict whether a reaction will occur, or not; especially, when a *metal* is placed in an *aqueous solution of a salt of another metal*.

**Examples**

1. *Zinc metal* will displace the *ions of copper* from a *solution of copper(II) salt*, thereby depositing *copper metal*. This is because, zinc metal is more reactive, and hence, higher up in the *activity series* than copper metal.

$$Zn_{(s)} + CuSO_{4(aq)} \rightarrow ZnSO_{4(aq)} + Cu_{(s)}$$

**Table 9.1:** *Activity series in metals*

| | | |
|---|---|---|
| **K** | **Potassium (*Most reactive*)** | **Popular** |
| **Na** | **Sodium** | **Scientists** |
| **Ca** | **Calcium** | **Can** |
| **Mg** | **Magnesium** | **Make** |
| **Al** | **Aluminium** | **A** |
| **Zn** | **Zinc** | **Zoo** |
| **Fe** | **Iron** | **In** |
| **Sn** | **Tin** | **The** |
| **Pb** | **Lead** | **Low** |
| **H** | **Hydrogen** | **Humid** |
| **Cu** | **Copper** | **Country** |
| **Hg** | **Mercury** | **More** |
| **Ag** | **Silver** | **Satisfactorily** |
| **Au** | **Gold (*Least reactive*)** | **Good** |

2. An iron nail dissolves, chemically, when used in stirring a solution of a salt of copper or silver:

$$Fe_{(s)} + 2AgNO_{3(aq)} \rightarrow Fe(NO_3)_{2(aq)} + 2Ag_{(s)}$$

3. A metal above hydrogen in the *activity series* will liberate hydrogen gas from a dilute solution of an acid or from water, e.g.

a. When magnesium ribbon is dropped into a moderately concentrated solution of hydrochloric acid, the metal *dissolves* with *effervescence*, to liberate hydrogen gas:

$$Fe_{(s)} + 2HCl_{(aq)} \rightarrow FeCl_{2(aq)} + H_{2(g)}$$

b. Calcium metal reacts vigorously with water to liberate hydrogen gas.

$$Ca_{(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)} + H_{2(g)}$$

4. Hydrogen gas displaces copper from its oxide.

$$H_{2(g)} + CuO_{(s)} \rightarrow Cu_{(s)} + H_2O_{(g)}$$

5. Lead metal is obtained by the action of a metal such as Zn, Al or Mg on a solution of lead(II) salt:

$$Zn_{(s)} + Pb(NO_3)_{2(aq)} \rightarrow Zn(NO_3)_{2(aq)} + Pb_{(s)}$$

It should be noted that displacement reactions are *not reversible* (i.e. *irreversible*). For instance: It is not possible for copper metal to displace ions of zinc from a solution of a zinc salt, or for silver metal to dissolve when used in stirring a solution of a lead salt.

### *Activity Series in the Halogens*

When the halogens in group VII of the Periodic Table are arranged in order of *reactivity*, fluorine gas, being the most reactive, will displace the ions of the other halogens ($Cl_2$, $Br_2$ and $I_2$) from the solutions of their salts; $Cl_2$ will displace those of $Br_2$ or $I_2$; while $Br_2$ will displace only the ions of $I_2$:

$$F_2 > Cl_2 > Br_2 > I_2$$

**Examples**

1. When fluorine gas is passed into a solution of potassium chloride, chlorine gas is liberated.

$$F_{2(g)} + KCl_{(aq)} \rightarrow 2KF_{(aq)} + Cl_2\uparrow$$

2. When chlorine gas is bubbled through a solution of potassium bromide, the solution turns reddish brown, due to the liberation of bromine gas:

$$Cl_{2(g)} + KBr_{(aq)} \rightarrow 2KCl_{(aq)} + Br_2\uparrow$$

3. Bromine gas will liberate iodine gas from a solution of a salt of iodine.

$$Br_{2(g)} + KI_{(aq)} \rightarrow 2KBr_{(aq)} + I_2\uparrow$$

Table 9.2: *Activity series in the halogens*

| | |
|---|---|
| $F_2$ | Fluorine *(most reactive)* |
| $Cl_2$ | Chlorine |
| $Br_2$ | Bromine |
| $I_2$ | Iodine *(least reactive)* |

## 4. Double Decomposition Reactions

*Double decomposition* reaction occurs when *two* compounds react to produce *two* new compounds by exchange of ions:

$$\underline{A}B + \underline{C}D \rightarrow \underline{A}D + \underline{C}B$$

***Four types of double decomposition reactions:***

**a. *Precipitation reaction***

In a *precipitation reaction*, aqueous solutions of *two reactants* combine to produce *two products* in which one is an *insoluble* compound; hence, it is *precipitated*, e.g.

When $HCl_{(aq)}$ is added into $AgNO_{3(aq)}$, a white precipitate of AgCl is one of the products:

$$HCl_{(aq)} + AgNO_{3(aq)} \rightarrow HNO_{3(aq)} + AgCl\downarrow$$

**b. *Neutralization Reaction***

It is a reaction in which an *acid* reacts with a *base* to produce *salt* and *water* only; e.g.

| | Acid | Base | Salt | Water |
|---|---|---|---|---|
| • | $HCl_{(aq)}$ + | $NaOH_{(aq)}$ → | $NaCl_{(aq)}$ + | $H_2O_{(l)}$ |
| • | $H_2SO_{4(aq)}$ + | $CuO_{(s)}$ → | $CuSO_{4(aq)}$ + | $H_2O_{(l)}$ |

**c. *Formation of Volatile Acids***

When a mixture of a *less volatile acid* and *a salt of a more volatile acid* is heated, the *more volatile acid* is liberated.

**Common Acids in Order of Volatility:**

| |
|---|
| $H_2SO_4$ (b.pt. 333 °C) *(least volatile)* |
| $CH_3COOH$ (b.pt. 118 °C) |
| $HCl$ (b.pt. 110 °C) |
| $HNO_3$ (b.pt. 84 °C) |
| $H_2SO_3$ *(very volatile)* |
| $H_2CO_3$ *(most volatile; unstable)* |

Concentrated $H_2SO_4$ is the *least* and *non-volatile*; it displaces other acids when heated with a salt of any of the other acids, e.g.

i. When a mixture of NaCl crystals and conc $H_2SO_4$ is heated, HCl gas is given off:

$$2NaCl_{(s)} + H_2SO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + 2HCl\uparrow$$

Similarly;

• $2KNO_{3(s)} + H_2SO_{4(aq)} \rightarrow K_2SO_{4(aq)} + 2HNO_3\uparrow$

**Note:** Concentrated HCl or $HNO_3$ will not react with a salt of $CH_3COOH$; because $CH_3COOH$ is *less volatile*.

ii. When a bench solution of an acid, such as HCl, $H_2SO_4$, $HNO_3$, or $CH_3COOH$ is added to a trioxocarbonate(IV) salt, there is *effervescence*; carbon (IV) oxide gas is given off:

$$Na_2CO_{3(s)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + H_2O_{(aq)} + CO_2\uparrow$$

**d. *Liberation of Ammonia gas***

When a mixture of an *ammonium salt* and an *alkali* (a *water-soluble base*) is heated, ammonia gas is given off:

$$NH_4Cl_{(s)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)} + NH_3\uparrow$$

## 5. Reversible Reaction

A chemical or physical process that can be made to proceed either forward or backward, under different conditions of temperature and pressure is said to be *reversible*. Consider the reaction:

$$A + B \rightarrow C + D$$

If the reaction is performed in a closed vessel, as soon as C and D are produced, they re-combine, to produce A and B again, i.e.

$$C + D \rightarrow A + B$$

*Opposing arrows* represent *reversible reactions*:

$$A + B \rightleftharpoons C + D$$

A *state of equilibrium* occurs when the rates of forward and backward reactions are the same in a reversible reaction.

At equilibrium, all the reactants and products are in the system, e.g.

a. *Action of steam on red-hot iron:*

$$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4\,(s)} + 4H_{2\,(g)}$$

b. Water and steam exist at equilibrium at boiling point:

$$\underset{\text{(water)}}{H_2O_{(l)}} \rightleftharpoons \underset{\text{(steam)}}{H_2O_{(g)}}$$

A reaction in which the products cannot readily recombine to give the reactants is said to be *irreversible*. In such a reaction, a single arrow is used pointing to the products, e.g. combustion reactions:

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$

## 6. Thermal Dissociation

It is a type of *reversible* reaction in which only a change in temperature determines the direction of the reaction:

a. When ammonium chloride is heated in a *closed container*, it decomposes to give a mixture of gaseous ammonia and hydrogen chloride (forward reaction). On cooling, the gases combine to produce ammonium chloride again (backward reaction).

$$NH_4Cl_{(s)} \rightleftharpoons NH_3\uparrow + HCl\uparrow$$

These changes are by *sublimation*.

b. Other examples are:

- $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
- $CaCO_{3\,(s)} \rightleftharpoons CaO_{(s)} + CO_{2\,(g)}$

## 7. Catalysis (Catalysed Reactions)

***Catalysis*** is a chemical process whereby the rate of a reaction is changed or altered by a ***catalyst***.

A ***catalyst*** is a substance, which alters the rate of a reaction without being used-up itself.

### *General Characteristics of Catalysis*

a. A catalyst remains unchanged in quantity and in physical state after a reaction.

b. A small quantity of a catalyst *catalyses* a large quantity of reactants.

c. Catalytic action is specific; a substance that catalyses one reaction may not catalyse another.

### *Types of Catalysts*

There are two types: *natural* and *artificial*.

*Natural catalysts* are *sunlight* and *enzymes*.

*Artificial catalysts* are usually *transition metals* and *their oxides*.

### Examples of catalysed reactions

When employed in a reaction, the *catalyst* is usually written on the arrow in the equation of reaction.

a. Powdered $MnO_2$ catalyses thermal decomposition of $KClO_3$:

$$2KClO_{3\,(s)} \xrightarrow{MnO_{2(s)}} 2KCl_{(s)} + 3O_{2\,(g)}$$

b. Iron filings catalyses the formation of ammonia from its elements:

$$N_{2\,(g)} + 3H_{2\,(g)} \xrightarrow{Fe_{(s)}} 2NH_{3\,(g)}$$

A reaction as in a above in which the reactant and the catalyst are in the same physical state (solid) is said to be *homogeneous catalysis*, while a reaction as in b in which the reactants (gaseous) and the catalyst (solid) are in different physical states is said to be *heterogeneous catalysis*.

## 8. Oxidation-Reduction *(Redox)* Reactions

The term ***redox*** is coined from the words ***reduction*** and ***oxidation***; *the two processes occur simultaneously in the same reaction.*

### Old Definitions:

***In terms of Oxygen*** *(electronegative element)* ***and Hydrogen*** *(electropositive element)*

- ***Oxidation*** is the *addition of oxygen to*, or *removal of hydrogen from* a substance, e.g.

a. *Burning of magnesium metal in oxygen:*

$$2Mg_{(s)} + O_{2\,(g)} \rightarrow 2MgO_{(s)}$$

In this reaction, magnesium metal is *oxidized* by *addition of oxygen* to form magnesium oxide.

b. *Decomposition of ammonia:*

$$2NH_{3\,(g)} \rightarrow N_{2\,(g)} + 3H_{2\,(g)}$$

In this reaction, ammonia is *oxidized* to nitrogen by the *removal of hydrogen*.

- ***Reduction*** is the *removal of oxygen from*, or *addition of hydrogen to* a substance, e.g.

a. *Pass hydrogen gas over heated copper(II) oxide:*

$$H_{2\,(g)} + CuO_{(s)} \rightarrow Cu_{(s)} + H_2O_{(g)}$$

In this reaction, copper(II) oxide is *reduced* to copper metal by the *removal of oxygen atom*.

b. *Formation of ammonia:*

$$N_{2\,(g)} + 3H_{2\,(g)} \rightarrow 2NH_{3\,(g)}$$

**Revision Exercises**

8. Balance and state the type of reaction in the following equation:

$$FeCl_3 + H_2S \rightarrow FeCl_2 + HCl + S$$

9. Consider the following equation of a reaction:

$$H_2S + O_2 \rightarrow H_2O + S$$

a. Balance the equation.
b. State the oxidizing and reducing agents.
c. Mention the reactant that has been oxidized, and state the product of oxidation.
d. Identify the reactant that has been reduced, and state the product of reduction.

10 Which of the following **cannot** displace copper from an aqueous solution of copper (II) salt? [WAEC]
A. Magnesium B. Zinc C. Aluminium D. Silver

11 List **two** metals that can displace iron(II) ions from solution.

12 Which of the following represents correctly the rearrangement of particles during double decomposition reaction ? [WAEC]
A. PQ + RS → PS + QR B. PQ + RS → PR + SQ
C. PQ + RS → PR + QS D. PQ + RS → PS + RQ

## 9.4 Laws of Chemical Combinations

The Dalton's atomic theory provided a satisfactory basis for the *gravimetric laws* of chemical combinations by mass.

His postulates gave rise to *three gravimetric laws*:

- Law of conservation of mass (indestructibility of matter).
- Law of definite proportion or constant composition.
- Law of multiple proportion.

### 1. Law of Conservation of Mass (or Matter)

The law was suggested by ***Lavoisier*** (1774).

It states:

*During the course of a chemical reaction, matter is neither created nor destroyed.*

**Verification of the Law**

a. Measure 50.0 $cm^3$ of bench solution of dilute hydrochloric acid, and transfer into a clean conical flask.

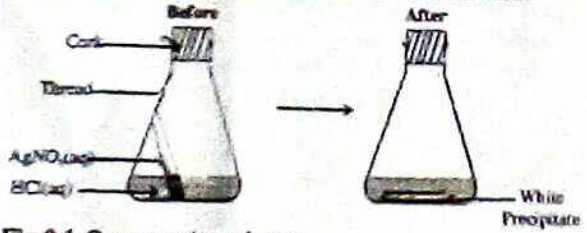



**Fig 9.1** *Conservation of mass*

b. Half-fill a clean test tube with a bench solution of silver trioxonitrate (V). Lower it, with care, by the use of a thread into the conical flask; then, cork the conical flask (see figure 9.1). *Do not mix the solutions yet.*

c. Weigh the entire set-up on a chemical balance, and record the mass ($x$ g).

d. *Mix* the two solutions. There is immediate formation of a *white precipitate*. Wait for a while.

e. Re-weigh the entire set-up as before and record the mass ($y$ g).

**Expected result:** Total mass *before mixing* (*mass of reactants*) and *after mixing* (*mass of products*) will be equal.

The same set-up can be used to illustrate the law by the use of any precipitation reactions, such as solutions of potassium iodide and lead(II) trioxonitrate (V).

Note: *Reactions in which a solid or a gas is a reactant cannot be used to demonstrate this law. This is because it is difficult to weigh gaseous reactants; while reactions involving solid reactants are relatively slow.*

**Explanation of the law of conservation of mass by the Dalton's atomic theory**

*When a reaction occurs in a **closed vessel**, all the atoms present **before** the reaction are still present **after** the reaction. Hence, the **total mass** of the **reactants** will be **equal** to the total mass of the **products**.*

Consequently, equations of chemical reactions ***must be balanced***, in order to conform to the *law of conservation of mass*.

### 2. Law Definite Proportions or Constant Composition

The law was suggested by ***Proust*** (1799). It states:

*All pure samples of the same compound contain the same elements combined in the same proportion by mass.* **Or**

*All pure samples of the same compound have the same percentage composition by mass.*

**Verification of the Law**

Pure samples of black copper(II) oxide, CuO, can be obtained by *three* different methods:

a. ***Action of heat on copper(II) trioxonitrate(V)*** **[*Sample* A]**

$$\underset{(green)}{2Cu(NO_3)_{2(s)}} \rightarrow \underset{(black)}{2CuO_{(s)}} + 4NO_{2(g)} + O_{2(g)}$$

b. ***Action of heat on copper(II) trioxocarbonate (IV)*** **[*Sample* B]**

$$\underset{(green)}{CuCO_{3(s)}} \rightarrow \underset{(black)}{CuO_{(s)}} + CO_{2(g)}$$

c. ***Action of heat on copper(II) hydroxide*** **[*Sample* C]**

$$\underset{(blue)}{Cu(OH)_{2(s)}} \rightarrow \underset{(black)}{CuO_{(s)}} + H_2O_{(g)}$$

**Gravimetric Analyses of Samples A, B and C**

*Gravimetric analysis is an aspect of quantitative analysis, which involves weighing of the masses of reactants and products of chemical reactions.*

Each of the pure samples of copper(II) oxide is weighed separately into a *porcelain boat*, placed in a *combustion tube*, and then, reduced in a stream of hydrogen, to produce a reddish-brown residue of copper metal (see fig 9.2). Allow to cool, and re-weigh.

$$CuO_{(s)} + H_{2\,(g)} \rightarrow Cu_{(s)} + H_2O_{(g)}$$
(black) (brown)

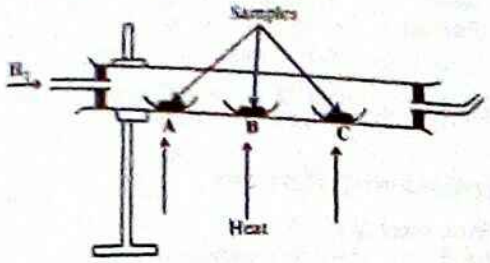



Fig 9.2 *Analysis of samples of copper(II) oxide*

Experimentally, the combustion tube should slope forward, and the stream of hydrogen gas should be allowed to flow over the residue, until it is cold; so as to prevent re-oxidation of the residue, by water vapour.

**Experimental Data and Calculations**

| | Sample A | Sample B | Sample C |
|---|---|---|---|
| Mass of CuO, a | 0.95g | 1.15g | 2.11g |
| Mass of Cu, b | 0.76g | 0.92g | 1.69g |
| Mass of oxygen (a – b) | 0.19g | 0.23g | 0.42g |
| % copper | $\frac{0.76}{0.95} \times \frac{100}{1}$ | $\frac{0.92}{1.15} \times \frac{100}{1}$ | $\frac{1.69}{2.11} \times \frac{100}{1}$ |
| | = 80.0% | = 80.0% | = 80.1% |
| ∴ % oxygen | = 20.0% | = 20.0% | = 19.9% |
| Amount of copper | $\frac{0.76}{63.5}$ = 0.0120 | $\frac{0.92}{63.5}$ = 0.0145 | $\frac{1.69}{63.5}$ = 0.0266 |
| Amount of oxygen | $\frac{0.19}{16}$ = 0.0119 | $\frac{0.23}{16}$ = 0.0144 | $\frac{0.42}{16}$ = 0.0263 |
| Mole ratio of Cu : O | 0.012: 0.012 = 1:1 | 0.015:0.014 = 1:1 | 0.027:0.026 = 1:1 |

**Observations**

1 The percentage by mass of copper, **80.0%**, and oxygen, **20.0%**, are the same in each sample.

2 Copper and oxygen atoms combined in the ratio 1:1 in each sample.

These data show that the law of *constant composition* or *definite proportion* is obeyed.

***Explanation of the law by the Dalton's atomic theory***

*All the atoms of an element are alike in size, shape and mass, but are different from atoms of other elements.*

***Application***: A *chemical* substance is *pure*, if its *experimental* percentage composition by mass *equals* its *theoretical* percentage composition by mass.

**Worked Example 2**

If 1.80 *g* of a metal oxide on analysis contained 1.40 *g* of the metal, and 4.50 *g* of another sample of the oxide, on reduction, gave 3.50 *g* of the metal. Show that these figures agree with the law of constant composition.

**Answer**

| | Sample 1 | Sample 2 |
|---|---|---|
| Mass of oxide | 1.80g | 4.50g |
| Mass of metal | 1.40g | 3.50g |
| Mass of oxygen | 0.40g | 1.00g |
| % metal | $\frac{1.40}{1.80} \times \frac{100}{1}$ = 77.7% | $\frac{3.50}{4.50} \times \frac{100}{1}$ = 77.7% |

The percentage by mass of the metal is the same in the two samples; the law of *constant composition* is obeyed.

## 3. Law of Multiple Proportions

The law states:

*When two elements A and B combine to form two or more compounds, the various masses of one element A, which combine with a fixed mass of the other element B, are in the ratio of small whole numbers.*

**Illustration**

Carbon and oxygen form two oxides: **CO** and **$CO_2$**. In **CO**, *12 g* of carbon atoms combine with *16 g* of oxygen atoms, while in **$CO_2$**, *12 g* of carbon atoms combine with *32 g* of oxygen atoms.

**Observation:** The two masses of oxygen atoms, that combined with a fixed mass of carbon (12 *g*) are in a simple ratio of **16 : 32**, or **1 : 2**.

**Verification of the Law**

Copper forms two oxides: copper(I) oxide, **$Cu_2O$**, and copper(II) oxide, **CuO**. When known masses of the two oxides of copper were reduced in a stream of dry hydrogen gas, the following results were obtained:

| | Sample 1 $Cu_2O$ (red) | Sample 2 CuO (black) |
|---|---|---|
| Mass of oxide | 1.44 g | 2.00 g |
| Mass of copper | 1.28 g | 1.60 g |
| Mass of oxygen | 0.16 g | 0.40 g |

*In order to show that these figures conform to the law of multiple proportions, calculate the mass of one element that combines with 1.0 g (or 100 g) of the other element in each sample. For instance:*

**In Sample 1:**

0.16 g of oxygen combined with 1.28 g of copper;
∴ 1 g of oxygen will combine with
(1.28 × 1)/0.16 = 8.00 g of Cu.

**In Sample 2:**

0.40 g of oxygen combined with 1.60 g of copper;
∴ 1 g of oxygen will combine with
(1.60 × 1)/0.40 = 4.00 g of Cu.

The masses of copper that have combined with a fixed mass (1.0 g) of oxygen in samples 1 and 2 are in the ratio 8.00: 4.00 or 2 : 1.

Hence, the law of multiple proportion is obeyed.

**Worked Examples**

3. The two oxides of sulphur contained 50.0% and 40.0% of sulphur by mass respectively. Do these figures agree with the law of multiple proportions?

| Sample | % Sulphur | % Oxygen |
|---|---|---|
| *Oxide 1* | 50.0 | 50.0 |
| *Oxide 2* | 40.0 | 60.0 |

*In sample 1:*

50 g of sulphur combined with 50 g of oxygen
∴ 100 g of sulphur combined with
(50 × 100)/50 = 100 g of oxygen.

*In sample 2:*

40 g of sulphur combined with 60 g of oxygen
∴ 100 g of sulphur combined with
(60 × 100)/40 = 150 g of oxygen.

*The various masses of oxygen that have combined with 100 g of sulphur are in the ratio 100 : 150 or 2 : 3.*
*Hence, the law of multiple proportions is obeyed.*

4. A metal M forms two oxides A and B. On reduction, 0.828 g of A gave 0.523 g of the metal, while 1.598 g of B gave 1.238 g of the metal.

a. Show that the law of multiple proportions is obeyed.

b. If the relative atomic mass of M is 55, determine the chemical formulae of A and B. [O = 16]

*a. To show that law of multiple proportion is obeyed:*
*First, calculate the mass of the metal, which combines with 1.0 g of oxygen in each oxide:*

***In oxide A:***

(0.828 - 0.523) g of oxygen reacts with 0.523 g of metal
i.e. 0.305 g of oxygen combine with 0.523 g of metal.
∴ 1 g of oxygen combines with (0.523 × 1)/0.305 g
= 1.715 g of the metal.

***In oxide B:***

(1.598 - 1.238) g of oxygen reacts with 1.238 g of metal
i.e. 0.360 g of oxygen combine with 1.238 g of metal.
∴ 1 g of oxygen combines with (1.238 × 1)/0.360 g
= 3.439 g of the metal.

The ratio by mass of the metal in the two oxides that combined with a fixed mass of oxygen is 1.715 : 3.439,
i.e. 1.715/1.715 : 3.439/1.715 = 1 : 2.

*b. To determine the chemical formulae of the oxides:*

In oxide A:

| | M | O |
|---|---|---|
| Mass = | 0.523 g | 0.305 g |
| Amount = | 0.523/55 | 0.305/16 |
| = | 0.00951 mol | 0.0191 mol |
| Mole ratio = | 0.00951 / 0.00951 | 0.0191 / 0.0191 |
| = | 1 | 2 |

∴ Chemical formula of A = $MO_2$

In oxide B:

| | M | O |
|---|---|---|
| Mass = | 1.238 g | 0.360 g |
| Amount = | 1.238/55 | 0.360/16 |
| = | 0.0225 mol | 0.0225 mol |
| Mole ratio = | 0.0225 / 0.0225 | 0.0225 / 0.0225 |
| = | 1 | 1 |

∴ Chemical formula of B = MO.

**Revision Exercises**

13 State the law of multiple proportion.

14 2.85 g of an oxide of copper gave 2.52 g of copper on reduction, and 1.90 g of another oxide gave 1.52 g of copper on reduction. The data above illustrate the law of
A. constant composition B. conservation of mass
C. reciprocal proportions D. multiple proportion [J]

15 Copper reacts with oxygen to form two oxides A and B. On analysis, 1.535 g of A yielded 1.365 g of copper, while 1.452 g of B yielded 1.161 g of copper.
a. Determine the chemical formulae of A and B.
b. Calculate the mass of copper which can react with 0.500 g of oxygen to give: i. A; ii. B.
c. Which law of chemical combination is illustrated by the result in a above. [O = 16; Cu = 63.5]

16 A metal forms two oxides X and Y, which contain 28.9% and 21.0% of oxygen respectively:
a. Calculate the ratio by mass of the metal in the two oxides.
b. What chemical law does this illustrate? [NECO]

17 If 1.00 g of the oxide of metal M gave 0.80 g of the metal when reduced with hydrogen. What is the formula of the oxide? [M = 64, O = 16] [NECO]

## 9.5 Calculations from Equations

### Mass – Mole Relationships

A *balanced chemical equation* describes quantitatively, the amounts, in moles, of the reactants used-up and the products obtained from a reaction. Such an equation is said to be *stoichiometric*, since the *mole ratio* of the reactants, and, or, products that can be obtained from it.

*In order to show that these figures conform to the law of multiple proportions, calculate the mass of one element that combines with 1.0 g (or 100 g) of the other element in each sample. For instance:*

**In Sample 1:**

0.16 g of oxygen combined with 1.28 g of copper;

∴ 1 g of oxygen will combine with

$(1.28 \times 1)/0.16 = 8.00$ g of Cu.

**In Sample 2:**

0.40 g of oxygen combined with 1.60 g of copper;

∴ 1 g of oxygen will combine with

$(1.60 \times 1)/0.40 = 4.00$ g of Cu.

The masses of copper that have combined with a fixed mass (1.0 g) of oxygen in **samples 1** and **2** are in the ratio **8.00: 4.00** or **2 : 1**.

Hence, the law of multiple proportion is obeyed.

**Worked Examples**

**3.** The two oxides of sulphur contained 50.0% and 40.0% of sulphur by mass respectively. Do these figures agree with the law of multiple proportions?

| Sample | % Sulphur | % Oxygen |
|---|---|---|
| *Oxide 1* | 50.0 | 50.0 |
| *Oxide 2* | 40.0 | 60.0 |

*In sample 1:*

50 g of sulphur combined with 50 g of oxygen

∴ 100 g of sulphur combined with

$(50 \times 100)/50 = 100$ g of oxygen.

*In sample 2:*

40 g of sulphur combined with 60 g of oxygen

∴ 100 g of sulphur combined with

$(60 \times 100)/40 = 150$ g of oxygen.

*The various masses of oxygen that have combined with 100 g of sulphur are in the ratio* ***100 : 150*** *or* ***2 : 3****.*

*Hence, the law of multiple proportions is obeyed.*

**4.** A metal **M** forms two oxides **A** and **B**. On reduction, 0.828 g of **A** gave 0.523 g of the metal, while 1.598 g of **B** gave 1.238 g of the metal.

**a.** Show that the law of multiple proportions is obeyed.

**b.** If the relative atomic mass of **M** is 55, determine the chemical formulae of A and B. [O = 16]

***a.*** *To show that law of multiple proportion is obeyed:*

*First, calculate the mass of the metal, which combines with 1.0 g of oxygen in each oxide:*

***In oxide A:***

(0.828 - 0.523) g of oxygen reacts with 0.523 g of metal

i.e. 0.305 g of oxygen combine with 0.523 g of metal.

∴ 1 g of oxygen combines with $(0.523 \times 1)/0.305$ g

= 1.715 g of the metal.

***In oxide B:***

(1.598 - 1.238) g of oxygen reacts with 1.238 g of metal

i.e. 0.360 g of oxygen combine with 1 238 g of metal.

∴ 1 g of oxygen combines with $(1.238 \times 1)/0.360$ g

= 3.439 g of the metal.

The ratio by mass of the metal in the two oxides that combined with a fixed mass of oxygen is 1.715 : 3.439

i.e. **1.715/1.715 : 3.439/1.715 = 1 : 2**

***b.*** *To determine the chemical formulae of the oxides*

In oxide **A**:

| | | M | O |
|---|---|---|---|
| Mass | = | 0.523 g | 0.305 g |
| Amount | = | 0.523/55 | 0.305/16 |
| | = | 0.00951 mol | 0.0191 mol |

$$\text{Mole ratio} = \frac{0.00951}{0.00951} : \frac{0.0191}{0.00951}$$

$$= 1 : 2$$

∴ Chemical formula of **A** = $MO_2$

In oxide **B**:

| | | M | O |
|---|---|---|---|
| Mass | = | 1.238 g | 0.360 g |
| Amount | = | 1.238/55 | 0.360/16 |
| | = | 0.0225 mol | 0.0225 mol |

$$\text{Mole ratio} = \frac{0.0225}{0.0225} : \frac{0.0225}{0.0225}$$

$$= 1 : 1$$

∴ Chemical formula of **B** = **MO**.

**Revision Exercises**

**13** State the law of multiple proportion.

**14** 2.85 g of an oxide of copper gave 2.52 g of copper on reduction; and 1.90 g of another oxide gave 1.52 g of copper on reduction. The data above illustrate the law of

**A.** constant composition **B.** conservation of mass

**C.** reciprocal proportions **D.** multiple proportion [1]

**15** Copper reacts with oxygen to form two oxides **A** and **B**. On analysis, 1.535 g of **A** yielded 1.365 g of copper, while 1.452 g of **B** yielded 1.161 g of copper.

**a.** Determine the chemical formulae of **A** and **B**.

**b.** Calculate the mass of copper which can react with 0.500 g of oxygen to give: **i. A** : **ii. B**.

**c.** Which law of chemical combination is illustrated by the result in **a** above. [O = 16; Cu = 63.5]

**16** A metal forms two oxides **X** and **Y**, which contain 28.9% and 21.0% of oxygen respectively:

**a.** Calculate the ratio by mass of the metal in the two oxides.

**b.** What chemical law does this illustrate? [NECO]

**17** If 1.00 g of the oxide of metal **M** gave 0.80 g of the metal when reduced with hydrogen. What is the formula of the oxide? [M = 64, O = 16] [NECO]

## 9.5 Calculations from Equations

### Mass – Mole Relationships

A *balanced chemical equation* describes quantitatively, the amounts, in moles, of the reactants used-up and the products obtained from a reaction. Such an equation is said to be *stoichiometric*, since the *mole ratio* of the reactants, and, or, products that can be obtained from it.

*Stoichiometric equations* can be used to estimate the *quantities* of *reactants required* for, and, or the *yields* of *products expected* from a reaction.

The steps to follow are:

1. Write a *balanced equation* for the reaction.
2. Write the amounts, in *moles*, under each of the *relevant reactants and products.*
3. Convert the amounts (in *moles*) to mass (in *grams, kilograms* or *tonnes*) as required.
4. Find the quantity required by *direct proportion.* The *statement of fact* with at least *two variables* is obtained from the balanced equation. Remember: the *variable* to be found comes at the end of the statement.
5. Express *final answer* to *three significant figures.*
6. Finally, insert the *appropriate unit.*

**Examples**

**a. *Formation of Iron(II) sulphide***

Iron(II) sulphide is obtained by heating a mixture of iron filings and powdered sulphur:

| | $Fe_{(s)}$ | + $S_{(s)}$ | → $FeS_{(s)}$ |
|---|---|---|---|
| *Unit:* | 1 atom | 1 atom | 1 molecule |
| *Amount:* | 1 mole | 1 mole | 1 mole |
| *Mass:* | 56.0 g | 32.0 g | 88.0 g |

***Mass-mole relationships:***

1 mole (56.0 g) of **Fe** reacts with **1 mole** (32.0 g) of **S** to produce **1 mole** (88.0 g) of **FeS**.

**b. *Decomposition of Ammonia gas*:**

| $2NH_{3\,(g)}$ | → $N_{2\,(g)}$ | + $3H_{2\,(g)}$ |
|---|---|---|
| 2 molecules | 1 molecule | 3 molecules |
| 2 moles | 1 mole | 3 moles |
| (2 × 17) g | (14 × 2) g | (3 × 2) g |
| 34.0 g | 28.0 g | 6.0 g |

***Mass-mole relationships:***

2 moles (34.0 g) of $NH_3$ decompose to give **1 mole** (28.0 g) of $N_2$ and **3 moles** (6.0 g) of $H_2$.

**Worked Examples**

5. Consider the following reaction:

$$2H_{2\,(g)} + O_{2\,(g)} \rightarrow 2H_2O_{(l)}$$

a. How many molecules of hydrogen will combine with five molecules of oxygen ?

b. How many molecules of water will be formed?

Answer

a. *To calculate the number of $H_2$ molecules*

Given: 5 molecules of $O_2$;

Required: Number of $H_2$ molecules.

This is *molecule-molecule* relationship between $H_2$ and $O_2$. From the equation of reaction:

$$2H_{2\,(g)} + O_{2\,(g)} \rightarrow 2H_2O_{(l)}$$

2 molecules 1 molecule 2 molecules

1 molecule of $O_2$ requires 2 molecules of $H_2$

∴ 5 molecules of $O_2$ require (2 × 5) molecules of $H_2$

= 10.0 molecules.

b. *To calculate the number of water molecules formed.*

Given: 5 molecules of $O_2$. From the equation:

1 molecule of $O_2$ produces 2 molecules of $H_2O$,

∴ 5 molecules of $O_2$ require (2×5) molecules of $H_2O$

= 10.0 molecules.

*Or*; Since 10 $H_2$ molecules have been used, then, from the equation of reaction:

2 molecules of $H_2$ will produce 2 molecules of $H_2O$

∴ 10 molecules of $H_2$ will produce (2×10)/2 molecules

= 10.0 molecules of $H_2O$.

6. In the reaction: $3H_2 + N_2 \rightarrow 2NH_3$

a. How many moles of hydrogen gas will react with 2.0 moles of nitrogen gas?

b. How many moles of nitrogen will produce 3.0 moles of ammonia?

c. How many moles of ammonia will be obtained from 4.5 moles of hydrogen?

Answer

a. *To calculate the amount of $H_2$ molecules*

Given: 2.0 moles of $N_2$.

This is *mole-mole relationship* between $N_2$ and $H_2$. From the equation of reaction:

$$3H_2 + N_2 \rightarrow 2NH_3$$

3 mol 1 mol 2 mol

1 mole of $N_2$ requires 3 moles of $H_2$,

∴ 2.0 moles of $N_2$ will require (3 × 2.0) moles of $H_2$

= 6.00 moles.

b. *To calculate the amount of $N_2$*

Given: 3.0 moles of $NH_3$.

This is *mole-mole* relationship between $NH_3$ and $N_2$. From the equation of reaction:

2 moles of $NH_3$ are obtained from 1 mole of $N_2$

∴ 3.0 moles of $NH_3$ are obtained from (1 × 3.0)/2 moles

= 1.50 moles of $N_2$.

c. *To calculate the amount of $NH_3$*

Given: 4.5 moles of $H_2$.

This is *mole-mole* relationship between $H_2$ and $NH_3$. From the equation of reaction:

3 moles of $H_2$ produce 2 moles of $NH_3$

∴ 4.5 moles of $H_2$ produce (2 × 4.5)/3 moles

= 3.00 moles of $NH_3$.

7. What mass of calcium oxide will be obtained by heating 20.0 g of calcium trioxocarbonate(IV) to constant mass? [Ca = 40; C = 12; O = 16]

Answer

| $CaCO_3(s)$ | → $CaO(s)$ | + $CO_2(g)$ | *(Balanced)* |
|---|---|---|---|
| 1 mol | 1 mol | | |
| (40 + 12 + 48) | (40 + 16) | | |
| 100 g | 56 g | | |

*To calculate the mass of CaO formed from 20 g $CaCO_3$*

Given: 20.0 g of $CaCO_3$; Required: Mass of CaO.

This is a *mass–mass relationship* between $CaCO_3$ and CaO; hence, there is no need to insert the amount or mass of $CO_2$ in the balanced equation of reaction.

*Let x be the mass of CaO.*
*From the balanced equation of reaction:*
100 g $CaCO_3$ ≡ 56 g CaO
20 g $CaCO_3$ ≡ x g CaO
i.e. $100x = 56 \times 20$
$\therefore \quad x = (56 \times 20)/100 = 11.2$ g CaO.

**8.** Zinc reacts with copper(II) tetraoxosulphate(VI) according to the following equation:

$$Zn_{(s)} + CuSO_{4\,(aq)} \rightarrow ZnSO_{4\,(aq)} + Cu_{(s)}$$

**a.** State the type of reaction involved.
**b.** Determine the amount of zinc that would react completely with 48.0 *g* of copper(II) tetraoxosulphate(VI). [$CuSO_4$ = 160; Zn = 65]

**a.** It is a *displacement* or *redox* reaction.
**b.** *To determine the amount of zinc, in moles*
Given: 48.0 g of $CuSO_4$; Required: Amount of Zn.
This is mass-mole relationship between $CuSO_4$ (in grams) and Zn (in moles).
From the balanced equation of reaction:

$$Zn_{(s)} + CuSO_{4\,(aq)} \rightarrow ZnSO_{4\,(aq)} + Cu_{(s)}$$
1 mole 1 mole (160 g)

**Note:** The value given as the molar mass of $CuSO_4$, i.e. 160 g/mol, must be used in the calculations.
***160 g*** (1 mole) of $CuSO_4$ require ***1 mole*** of Zn.
$\therefore$ 48.0 g of $CuSO_4$ require $(1 \times 48.0)/160$ mol.
= 0.300 mol. of Zn

**9.** Calcium trioxocarbonate(IV) reacts with trioxonitrate(V) acid according to the equation below:

$$CaCO_{3(s)} + 2HNO_{3(aq)} \rightarrow Ca(NO_3)_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$$

If 20 *g* of the trioxocarbonate(IV) reacted completely with the acid, calculate the amount, in moles, of the trioxonitrate(V) that reacted.
[Ca = 40, O = 16, C = 12] [WAEC]

**Answer**
*To calculate the amount of acid used*
Given: 20 *g* of $CaCO_3$. Required: Amount of $HNO_3$.
It is mass-mole relationship between $CaCO_3$ in grams, and $HNO_3$ in moles.
Let the amount of $HNO_3$ used be *x* mol.
From the equation of reaction:

$$CaCO_{3(s)} + 2HNO_{3(aq)} \rightarrow Ca(NO_3)_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$$
1 *mol* 2 *mol*

$M_r[CaCO_3] = [40 + 12 + 3(16)] = [40 + 12 + 48]$
= 100
i.e. 100 g of $CaCO_3$ ≡ 2 mol of $HNO_3$
20 g of $CaCO_3$ ≡ *x* mol of $HNO_3$
Thus: $100x = (2 \times 20)$
$x = (2 \times 20)/100 = 0.400$ mol.
$\therefore$ Amount of $HNO_3$ used = 0.400 mol.

**10** Calculate the amount of sulphur(IV) oxide required to deposit 12.0 *g* of sulphur on reacting with excess hydrogen sulphide.
[S = 32.0; O = 16.0; H = 1.0] [WAEC]

**Note:** *When one of the reactants in a reaction is in excess, it enables the other reactants to be completely used up. There is no need to insert the amount or mass of reactant in excess in the balanced equation.*

$$SO_{2\,(g)} + 2H_2S_{(g)} \rightarrow 3S_{(s)} + 2H_2O_{(l)}$$
1 mol 3 mol
$(3 \times 32) = 96$ g

*To calculate the amount of $SO_2$ required for 12 g S*
This is mass-mole relationship between *mass* of S and *amount* of $SO_2$.
*Given*: 12.0 g of sulphur; *Required*: Amount of $SO_2$.
From the balanced equation of reaction:
96 g of sulphur require 1 mol of $SO_2$
$\therefore$ 12 g of sulphur require $(1 \times 12)/96$ mol of $SO_2$
= 0.125 mol of $SO_2$

## Application of the Avogadro Constant

**11** How many *molecules* of hydrogen gas will be produced when 0.2 mole of aluminium reacts completely according to the following equation?

$$2Al_{(s)} + 6HCl_{(aq)} \rightarrow 2AlCl_{3(aq)} + 3H_{2(g)}$$

[Avogadro constant = $6.0 \times 10^{23}$ $mol^{-1}$] [WAEC]

*To calculate the number of $H_2$ molecules produced by 0.2 mole of Al*
This is *mole-molecule* relationship.

$$2Al_{(s)} + 6HCl_{(aq)} \rightarrow 2AlCl_{3(aq)} + 3H_{2(g)}$$
2 moles 3 moles
$3\,(6.0 \times 10^{23})$

From the balanced equation of reaction:
2 moles of Al ≡ $3(6.0 \times 10^{23})$ $H_2$ molecules
$\therefore$ 0.2 mol of Al ≡ $(3 \times 6.0 \times 10^{23} \times 0.2)/2$
= $1.80 \times 10^{23}$ molecules of $H_2$

**Note:** The value of the Avogadro constant given above is not $6.02 \times 10^{23}$. In any calculation, it is the value of the constant given that ***must*** be used. Usually, it is to make the calculations easier.

## Revision Exercises

**18** What amount of oxygen will be required for the complete combustion of 3 moles of methane according to the following equation?

$$CH_{4\,(g)} + 2O_{2\,(g)} \rightarrow CO_{2\,(g)} + 2H_2O_{(g)}$$ [WAEC]

**A** 2 mol **B** 3 mol **C** 4 mol **D** 5 mol **E** 6 mol.

**19** Hydrogen chloride gas reacted with oxygen gas to yield water and chlorine gas. What is the mole ratio of the hydrogen chloride gas to oxygen? [WAEC]

**20** Aluminium burns in oxygen to form a white solid:

$$4Al + 3O_2 \rightarrow 2Al_2O_3$$

**a.** Interpret the reaction in terms of moles.
**b.** How many moles of oxygen are needed to burn
i. two moles of aluminium?
ii. 0.5 mole of the metal?
**c.** How many moles of aluminium will produce
i. one mole of aluminium oxide?
ii. 12.8 g of the oxide?
**d.** How many grams of the oxide are formed from 0.25 mole of the metal? [$Al_2O_3$ = 102]

21 $2Na_{(s)} + 2H_2O_{(l)} \rightarrow 2NaOH_{(aq)} + H_{2(g)}$

From the equation above, calculate the mass of sodium hydroxide produced by 2.3 g of sodium.

**A.** 0.40 g **B.** 0.80 g **C.** 4.00 g **D.** 8.00 g

[H = 1, O = 16, Na = 16] [JAMB]

22 How many moles of limestone, $CaCO_3$ will be required to produce 5.6 g of CaO?

**A.** 0.10 **B.** 0.20 **C.** 0.56 **D.** 1.12 [JAMB]

23 Determine the mass of sulphur(IV) oxide obtained when 91.0 g of oxygen reacts completely with sulphur according to the following equation.

$S(s) + O_2(g) \rightarrow SO_2(g)$ [S = 32; O = 16]

**A.** 123 g **B.** 139 g **C.** 155 g **D.** 182 g [WAEC]

24 Calculate the mass of ammonia required to produce $3.01 \times 10^{23}$ molecules of nitrogen according to the equation

$4NH_{3(g)} + 3O_{2(g)} \rightarrow 2N_{2(g)} + 6H_2O_{(l)}$

[H = 1; N = 14; Avogadro constant = $6.0 \times 10^{23}$]

**A.** 51 g **B.** 43 g **C.** 17 g **D.** 8.5 g [WAEC]

## Limiting Reactant – A Reactant in Excess

When one of the reactants in a chemical reaction is in excess, it enables the other reactant to be used-up completely.

It is the *quantity of reactant completely used-up that determines the quantity of the product*. The reactant is called **limiting reactant.**

### Worked Example

12 In the following reaction:

$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

Suppose 20.0 moles of hydrogen are allowed to react with 20.0 moles of oxygen.

a. Which reactant is in excess, and by how much?

b. Determine the amount of water produced.

*a. To determine the reactant in excess*

Given: 20.0 mol of $H_2$ and 20.0 mol of $O_2$

*Possibility 1*: Suppose $H_2$ was completely used-up

From the equation of reaction:

$2H_2 + O_2 \rightarrow 2H_2O$

2 mol 1 mol 2 mol

2 moles of $H_2$ require 1 mole of $O_2$

∴ 20 moles of $H_2$ require $(1 \times 20)/2$ moles of $O_2$
= 10.0 moles of $O_2$

Since the amount of $O_2$ available (20 moles) is more than the amount required (10 moles) then, $O_2$ is in excess by (20.0 – 10.0) moles = 10.0 moles.

*Possibility 2*: Suppose $O_2$ was completely used up.

From the equation of reaction:

1 mole of $O_2$ requires 2 moles of $H_2$

∴ 20 moles of $O_2$ require $(2 \times 20)/1$ moles of $H_2$
= 40.0 moles of $H_2$.

Since the amount of $H_2$ available (20 moles) is less than the amount required (40 moles) then, $H_2$ is less than required, or $O_2$ is present in excess.

Hence, *possibility 1* is to be followed.

*b. To determine the amount of water produced*

Since $H_2$ is the limiting reactant, from the equation,

2 moles of $H_2$ will produce 2 moles of water

∴ 20 moles of $H_2$ will produce $(2 \times 20)/2$ moles
= 20.0 moles of water

Or, with respect to $O_2$ used, from the equation,

1 mole of $O_2$ will produce 2 moles of water

∴ 10 moles of $O_2$ will produce $(2 \times 10)/1$ moles
= 20.0 moles of water

13 When 21.0 g of iron filings and 15.0 g of powdered sulphur were heated, F g of iron(II) sulphide was obtained.

a. Which reactant is in excess, and by how much?

b. What will be the value of F?

[Fe = 56, S = 32] [WAEC]

*Equation of reaction*

$Fe_{(s)} + S_{(s)} \rightarrow FeS_{(s)}$

1 mole 1 mole 1 mole

56.0 g 32.0 g 88.0 g

*a. To calculate the mass of reactant in excess*

Mass of Fe available is 21.0 g; mass of S available is 15.0 g. This is mass-mass relationship.

From the equation of reaction:

With respect to Fe:

56 g of Fe = 32 g of S

∴ 21 g of Fe = $(32 \times 21)/56$ = 12.0 g of S

With respect to S:

32 g of S = 56 g of Fe

∴ 21 g of S = $(56 \times 21)/32$ = 36.5 g of Fe

With respect to Fe: For 21.0 g of Fe to be completely used up, 12.0 g of S will be required. Since 15.0 g of S is available, then, this quantity is more than required. Fe is the *limiting* reactant.

∴ Mass of S in excess = (15.0 – 12.0) g = 3.00 g

*b. To find the value of F.*

The value of F corresponds to the mass of FeS obtained from 21.0 g of Fe (the limiting reactant).

This is mass-mass relationship.

From the equation of reaction:

56 g of Fe = 88 g of FeS

∴ 21 g of Fe = $(88 \times 21)/56$ = 33.0 g of FeS.

Since 33.0 g of FeS is produced, the value of F is 33.0.

### Revision Exercises

25 In the reaction:

$4Al + 3O_2 \rightarrow 2Al_2O_3$

Suppose two moles of aluminium and two moles of oxygen gas react completely.

a. Which reactant remains, and how many moles?

b. How many moles of the oxide are produced?

26 a. 20 g of copper(II) oxide was warmed with 0.05 mole of tetraoxosulphate(VI) acid. Calculate the mass of copper(II) oxide that was in excess.

The equation of reaction is:

$CuO_{(s)} + H_2SO_{4(aq)} \rightarrow CuSO_{4(aq)} + H_2O_{(l)}$

[O = 16, Cu = 64]

b. What type of reaction was involved in a above?

**27** A mixture of 10.0 *g* of iron filings and 10.0 *g* of powdered sulphur was heated strongly in a crucible to produce iron(II) sulphide. [S = 32; Fe = 56]
**a.** Write an equation for the reaction.
**b.** Which reactant is in excess, and by how much?
**c.** How many grams of iron(II) sulphide are formed?

## Purity of a Reactant

A balanced chemical equation gives the amounts of the *pure reactants consumed* and the amounts of the *pure products formed*.

If an *impure* reactant is used in a chemical reaction, the product obtained will be *pure*. This is because only the *pure* portion of an *impure* reactant undergoes chemical reaction. The amount of pure product is then used to determine the extent of *purity* of, or, the quantity of *impurity*.

### Worked Example

**14** When 10.0 g of razor blade completely reacted with an excess solution of hydrochloric acid, 0.110 mole of $FeCl_2$ was obtained. Calculate the mass of iron in the razor blade. [Fe = 56] [WAEC]

*Equation of reaction*

$$Fe_{(s)} + 2HCl_{(aq)} \rightarrow FeCl_{2\,(aq)} + H_{2\,(g)}$$
1 mol (56 g) 1 mol

*To calculate the mass of iron that will produce 0.110 mol of $FeCl_2$*

This is a *mass-mole* relationship.

From the balanced equation of reaction:

1 mole of $FeCl_2 \equiv 56$ g of Fe

$\therefore$ 0.110 mole of $FeCl_2 \equiv (56 \times 0.110)$ g of Fe
$= 6.16$ g

i.e. 6.16 g of pure iron is in 10.0 g of the razor blade.

### Revision Exercises

**28** Calculate the mass of *impurity* in a sample of $CaCO_3$ if 0.050 mole of $CO_2$ was formed when 7.0 g of the sample reacted with excess dilute HCl.

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

[C = 12; O = 16; Ca = 40] [WAEC]

**29** In order to determine the percentage of $NaHCO_3$ in a brand of *baking powder*, 10.0 g of the sample was heated to constant mass to produce 1.65 g of $CO_2$ according to the equation:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

Calculate the
**a.** mass of $NaHCO_3$ in 10.0 g of the sample.
**b.** percentage of $NaHCO_3$ in the sample.

**30** When 30.0 g of *rusted* iron nails reacted with excess of $CuSO_4$ solution, 0.50 mole of copper was deposited according to the equation:

$$Fe(s) + CuSO_4(aq) \rightarrow Cu(s) + FeSO_4(aq)$$

Calculate the mass of iron in the rusted iron nails.
[Fe = 56]

## Percentage Yield

A balanced equation of a reaction gives, in theory, the *maximum* yield of 100% expected from the reaction. Experimentally, it is impossible to obtain a yield of 100% from most chemical reactions.

### Worked Example

**15** In the industrial production of ammonia by *Haber process*, 700 *tonnes* of liquid nitrogen were used. How many *tonnes* of ammonia would be produced, if the yield of ammonia were 6.0%?
[N = 14; H = 1]

*Equation of reaction*

$$N_{2\,(g)} + 3H_{2\,(g)} \rightarrow 2NH_{3\,(g)}$$
1 mol 2 mol
$(2 \times 14) = 28$ *g* $(2 \times 17) = 34$ *g*
28 *tonnes* 34 *tonnes*

*To find the mass of $NH_3$ that can be obtained from 700 tonnes of $N_2$. It is a mass-mass relationship.*

*First, calculate the maximum yield (100%) from the balanced equation of reaction.*

*From the equation:*

*14 tonnes of $N_2$ produce 34 tonnes of $NH_3$*

$\therefore$ 700 tonnes $N_2$ produced $(34 \times 700)/14$ tonnes
$= 1700$ tonnes of $NH_3$.

*Since the yield is 6.0%; then, the quantity of $NH_3$ produced will be 6% of 1700 tonnes, i.e.*

*$1700 \times 6/100 = 102$ tonnes*

### Revision Exercises

**31** Coke burns in air according to the equation:

$$C_{(s)} + O_{2\,(g)} \rightarrow CO_{2\,(g)}$$

How many kilograms of carbon (IV) oxide would be produced from the combustion of 1.0 kg of coke if it is 90.0% carbon?

**32** Butane, $C_4H_{10}$ burns in oxygen thus:

$$2C_4H_{10\,(g)} + 13O_{2\,(g)} \rightarrow 8CO_{2\,(g)}\ 10H_2O_{(l)}$$

**a.** How many kilograms of liquid oxygen would be required to burn one kilogram of butane?
**b.** What would be the mass of carbon (IV) oxide produced, if the yield is 70.0%?

**33** Iron is produced from its ore according to the equation:

$$2Fe_2O_3(s) + 3CO(g) \rightarrow 4Fe(s) + 3CO_2(g)$$

Calculate the percentage yield, if 500 tonnes of the ore produced 145 tonnes of iron. [O = 16; Fe = 56]

## Answers to Revision Exercises

**6.** D **7.** $w = 2$; $x = 13$; $y = 8$; $z = 10$ **10.** D **12.** D **14.** D **15a** A = $Cu_2O$ ; B = CuO; **b i** 4.01 *g* ; **ii** 1.99 *g*. **16a** 2 : 3. **17.** MO **18.** E **19** 4 : 1 **20 bi** 1.50; **20bii** 0.375 mol. ; **c i** 2.00; **ii** 0.251 mol; **d** 63.8*g* **21.** C **22.** A **23.** D **24.** C **25a** $O_2$; 0.500 mol.; **25b** 1.00 mol. **26a** 16.0 *g*. **27b** S; 6.00 g; **c** 22.0 g **28** 2.00 g **29a** 6.3 g; **b** 63.0% **30** 28.0 g **31** 0.900 *kg* **32a** 3.59 *kg*; **b** 2.12 *kg* **33** 41.4%

# 10

# •BEHAVIOUR OF GASES•
# •GAS LAWS•

## 10.1 Introduction

Matter exists in *three physical states – solid, liquid and gas*. Gaseous state is the simplest. A substance is a gas, if under normal atmospheric pressure, its boiling point is *below room temperature*.

Since it is difficult to study the behaviour of individual particles of matter, large collections of particles are usually studied.

**Revision Exercise**

1. In which physical state is a substance that boils at 0 °C? [Room temperature = 25 °C]

## 10.2 Kinetic Theory of Gases

The *kinetic theory* has been proposed to account for, and explain the general behaviours of solids, liquids, and gases in terms of the cohesive forces between their particles, and their energies.

The following postulates (or assumptions) have been made, in order to explain the properties and behaviours of an ***ideal*** gas.

### Basic Postulates of an Ideal Gas

1. A gas consists of a large number of tiny molecules moving at random and in straight lines without resting.
2. The molecules collide with each other and with the walls of the container.
3. The actual volume of the gas molecules is very small and negligible, compared to the volume of the container.
4. During collisions, there are no attractive forces between the molecules; that is, the molecules are completely independent of one another.
5. Collisions between gas molecules are perfectly elastic, i.e. there is no loss of kinetic energy.
6. The *average* kinetic energy of the molecules is *directly* proportional to the absolute temperature.

**Revision Exercise**

2. State three postulates of the kinetic theory. [WAEC]

## 10.3 General Properties of Gases

The following are the general properties of a gas; each property can be explained in terms of the kinetic theory:

1. A gas can *expand* and *fill* any available space; because gas molecules are in continuous motion and never at rest. Hence, a gas has neither definite shape nor volume.
2. A gas has a low density, because intermolecular distance is large, i.e. molecules are far apart; hence, the molecules can be easily compressed.
3. Gas molecules can perform the *three types of motion*: *vibratory*, *rotatory* and *translatory* (random *zigzag* motion); because the molecules are far apart, and completely independent of one another.
4. Gas molecules exert pressure. Gas pressure is a function of the frequency of collision between the gas molecules and with the walls of the container.
5. Gas molecules undergo ***diffusion***. This is the process whereby gas molecules move from region of *high concentration* to a region of *low concentration*. It is *a natural phenomenon*. It is because gas molecules are independent of one another, and can move to occupy any available space.
6. Gases mix in any proportion, because they move about independently.
7. Under conditions of *high pressure* and *low temperature*, gases turn to liquids; the process is called *condensation* or *liquefaction*. When gas molecules are in close contact, cohesive forces, such as *van der Waals forces* and *dipolar forces* become strong and significant.

In terms of entropy, the gaseous state is the most *disordered* state.

**Revision Exercises**

3. Mention three general physical properties of gases.
4. In terms of the kinetic theory explain
   a. expansion of a gas; b. pressure of a gas.
5. List two cohesive forces that may operate between gas molecules.

## 10.4 Definition of Terms

The following terms are generally used to describe the behaviour of gases:

### 1. Gas Volume

The volume of a gas is the space it occupies. It is the same as the volume of the container.

The S.I. unit of volume is cubic metre, $m^3$. However, cubic decimetre $dm^3$, and cubic centimetre, $cm^3$, are commonly used.

For conversion purpose: $1.0\ dm^3 = 1000\ cm^3$

**Note:** $1.0\ dm^3$ is approximately 1.0 *litre (l)*, while $1.0\ cm^3$ is approximately 1.0 *milliliter (ml)*. They are not S.I. units.

### 2. Temperature

Temperature is a measure of the degree of hotness or coldness of a body. It is measured by the use of a *thermometer*.

The unit of temperature is degree *absolute* or *Kelvin*, **K**; it measures *absolute temperatures*.

The *Kelvin temperature scale* has the same interval as the *Celsius or centigrade scale*, measured in Celsius degree, °C. However, Kelvin temperatures are 273 degrees *higher* than the corresponding Celsius temperatures. Thus, 0 °C on the Celsius or centigrade scale is 273 **K** on the absolute or Kelvin temperature scale:

| | Celsius Scale, °C | Kelvin Scale, K |
|---|---|---|
| *Boiling point of water* | 100 | 373 |
| *Melting point of ice* | 0 | 273 |
| *Absolute zero* | –273 | 0 |

In order to convert t °C to Kelvin scale, T K, just add 273 to its value.

i.e. $t\,°C = (273 + t)\,K = T\,K$.

(where t is the temperature on the Celsius scale and T is the temperature on the Kelvin scale).

**Worked Examples**

1. Convert the following temperatures to Kelvin scale: **a.** 27°C; **b.** –10°C.

**Answer**

**a.** $27\,°C = (27 + 273)\,K = 300\,K$

**b.** $-10\,°C = (-10 + 273)\,K = 263\,K$

In order to convert absolute temperature, T **K** to degree Celsius, t°C, subtract 273 from the value.

i.e. $T\,K = (T - 273)\,°C = t\,°C$

**Worked Examples**

2. Convert the following temperatures to Celsius scale: **a.** 290 *K*; **b.** 200 *K*.

**Answers**

**a.** $290\,K = (290 - 273)\,°C = 17\,°C$

**b.** $200\,K = (200 - 273)\,°C = -73\,°C$

Generally, heat flows from a region of *high* concentration to a region of *low* concentration.

### 3. Pressure

*Pressure* is defined as *force per unit area*. It determines the direction of flow of matter; usually, from a region of high concentration to a region of low concentration.

A ***barometer*** is used in measuring the *atmospheric pressure*, while a ***manometer*** is used for the *pressure of gases*.

The S.I. unit of pressure is *Newton per square metre*, $Nm^{-2}$. For large pressures, $kNm^{-2}$ is used.

$1000\ Nm^{-2} = 1.0\ kNm^{-2}$

Gas pressures are also expressed in *atmospheres, atm*. The *atmospheric pressure is one atmosphere*.

For conversion purposes:

1 *atmosphere* = 760 *mmHg*;

$= 1.01 \times 10^5\ Nm^{-2}$.

### 4. Standard Temperature and Pressure, s.t.p.

Temperature and pressure are the two variables that affect gas volumes. In order to compare volumes of various gases, the standard experimental conditions are 273 *K* (0 °C) and one *atmosphere*, i.e. 760 *mmHg* or $1.01 \times 10^5\ Nm^{-2}$. These conditions are called ***standard temperature and pressure***, *s.t.p.* or S.T.P.

**Revision Exercises**

6 State the S.I. unit of:
**a.** volume; **b.** temperature; **c.** pressure.

7 What is s.t.p ? State the conditions.

8 Convert the following temperatures to Kelvin scale:
**a.** 25 °C; **b.** 95 °C; **c.** –13 °C; **d.** –208 °C.

9 Convert the following temperatures to Celsius scale:
**a.** 300 K; **b.** 504 K; **c.** 173 K; **d.** 85 K.

10 What is the value of -14 °C on the Kelvin temperature scale? [WAEC]
**A.** 259 K **B.** 259 °K **C.** 287 K **D.** 287 °K

## 10.5 Variation of Gas Volume with Pressure: Boyle's Law

The two variables that determine the volume of a fixed mass of gas are temperature and pressure. Robert Boyle (1627 – 1691), an English physicist, studied the effect of *pressure change* on *gas volume*. His observations led to the ***Boyle's law***, which describes the physical behaviour of gases. It states that:

*The volume of a given mass of gas is* ***inversely*** *proportional to the pressure, if temperature is constant.*

This statement means that at constant temperature, an *increase* in the pressure exerted on a fixed mass of gas leads to a *decrease* in the gas volume, and vice versa.

Mathematically: $V \propto 1/P$ ..... 10.1

or $V = k/P$

i.e. $PV$ = a constant $k$ .....10.2

(where $k$ = constant of proportionality).

The expression in equation 10.1 can be written in the form:

$[PV = k]_{m,T}$ ..... 10.3

(where mass, **m**, and temperature, **T**, are constant). Usually, the *number of molecules in a given mass of gas remains the same.*

From equation 10.3, Boyle's law can be stated as: *The product of pressure and volume is a constant for a fixed mass of gas at a constant temperature.*

**Experimental Illustration**

Consider a fixed mass of gas confined in a cylinder of volume **V**. If the pressure **P** exerted is *doubled* to 2P, the new volume becomes *half* of the initial volume, i.e. ½V; so that **PV** remains constant (see figure 10.1).

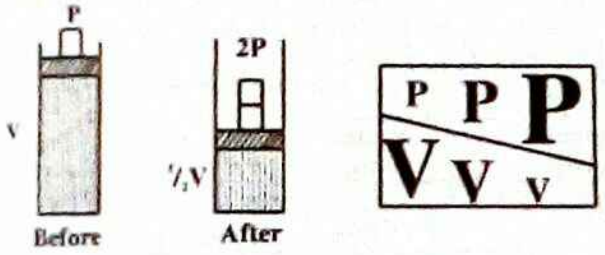



Fig 10.1 *To Illustrate Boyle's law*

Hence, if the initial pressure $P_1$ of a gas of initial volume $V_1$ is changed to a new or final pressure $P_2$, its new or final volume $V_2$ at constant temperature T is obtained from the expression:

$P_1V_1 = P_2V_2$ (m and T constant) ... 10.4

Rearranging:

$P_2/P_1 = V_1/V_2$ ... 10.5

Equation 10.5 shows that if the pressure *increases* by a factor $x$ ($P_2 > P_1$), then, the volume *decreases* by the same factor $x$ ($V_1 > V_2$), and vice versa.

Equation 10.4 is the mathematical expression for the Boyle's law. It is used when a fixed mass of gas is subjected to a *change in pressure or volume* at constant temperature.

The data in Table 10.1 can be used to explain the Boyle's law at constant temperature. The following trends can be obtained from the data:

1. An *increase* in pressure **P** leads to a *decrease* in volume **V**, and vice versa.
2. The *product of pressure* **P** *and volume* **V** (**PV**) is a constant.
3. **P** is *directly proportional to* **1/V**, or **V** is *directly proportional to* **1/P**.

**Table 10.1** *Data to illustrate the Boyle's law*

| P (atm) | V ($dm^3$) | PV | 1/P | 1/V |
|---|---|---|---|---|
| 1.0 | 10.00 | 10.0 | 1.000 | 0.100 |
| 2.0 | 5.00 | 10.0 | 0.500 | 0.200 |
| 2.5 | 4.00 | 10.0 | 0.400 | 0.250 |
| 4.0 | 2.50 | 10.0 | 0.250 | 0.400 |
| 7.5 | 1.33 | 10.0 | 0.133 | 0.752 |
| 10.0 | 1.00 | 10.0 | 0.100 | 1.000 |

The following information can be obtained from the graphical illustrations of Boyle's law.

1. A plot of pressure **P** against **1/V** (or **V** against **1/P**) gives a straight line passing through the origin (figure 10.2a).
2. A plot of **PV** against pressure **P** (or volume **V**) is a straight horizontal line graph (figure 9.2b).
3. A plot of **P** against **V** is a curve, which is asymptotic with the x- and y-axes.

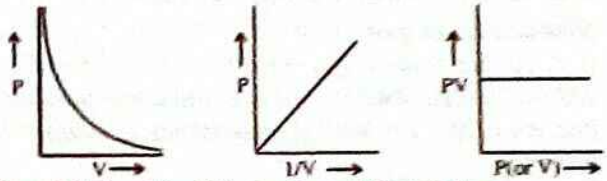



Fig 10.2 *Graphical illustrations of Boyle's law*

Any gas that conforms to any of these graphs at all temperatures and pressures is called a ***perfect*** or an ***ideal*** gas.

**Kinetic Theory Explanation of Boyle's Law**

The pressure of a gas is due to the continuous bombardment of the molecules with the walls of the container. At constant temperature, the average kinetic energy (or velocity) of the gas molecules is constant. If the size of the container is ***reduced to a half***, the frequency of collision of the molecules with the walls of the container will be ***doubled***. This is because the distance to the walls has been ***reduced to a half***. Therefore, the gas pressures will ***double*** the initial value.

Conversely, if the container is ***doubled*** in size, the frequency of collision of the molecules with the walls becomes ***reduced by a half***, since the distance the molecules will move before colliding with the walls has been ***doubled***. Hence, the gas pressure will be ***half*** of the initial value.

Generally, an *increase* in the volume of container at constant temperature, *decreases* the pressure of gas, and vice versa (PV = constant). However, the pressure of a gas in a closed container remains

constant, if the volume of the container and the temperature remain constant.

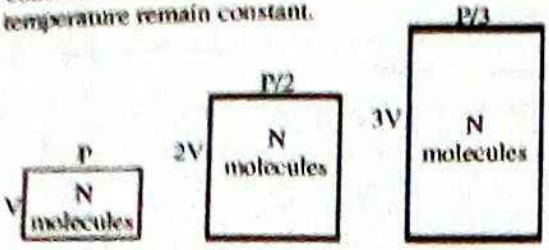



**Fig 10.3** *To Explain the Boyle' law*

Figure 10.3 shows that when N molecules of a gas is confined in a box of volume V, its pressure P becomes ½P when the volume is doubled to 2V, and becomes ⅓P when the volume is tripled to 3V, in order for PV to remain constant at constant temperature.

## Calculations based on Inverse Proportion

Chemical calculations on Boyle's law are based on *inverse* proportions. Here, an *increase* in pressure leads to a *decrease* in volume in the same proportion, and vice versa, at constant temperature.

### Worked Examples

3. A certain mass of gas occupies 200 $cm^3$ at 1.0 × $10^5$ $Nm^{-2}$. Calculate its volume when the pressure becomes 2.0 × $10^5$ $Nm^{-2}$ at constant temperature.

**Answer**

Data provided:
Initial pressure, $P_1 = 1.0 \times 10^5\ Nm^{-2}$;
Initial volume, $V_1 = 200\ cm^3$;
Final pressure, $P_2 = 2.0 \times 10^5\ Nm^{-2}$;
Final volume, $V_2 = ?\ cm^3$
Temperature is constant; Boyle's law is applicable.

***Formula Method***

According to Boyle's law: $P_1V_1 = P_2V_2$
Substituting: $1.0 \times 10^5 \times 200 = 2.0 \times 10^5 \times V_2$
Making the unknown $V_2$ the subject of the formula,

$$V_2 = \frac{1.0 \times 10^5 \times 200}{2.0 \times 10^5} = 100\ cm^3$$

**Note:** $V_1$ and $V_2$, and $P_1$ and $P_2$, must be expressed in the same units of volume and pressure respectively.

***Inverse proportion: Method I***

At 1.0 × $10^5$ $Nm^{-2}$ pressure, gas volume is 200 $cm^3$
At 2.0 × $10^5$ $Nm^{-2}$ (*increase* in P) volume V *decreases* to 200 × (1.0 × $10^5$)/(2.0 × $10^5$) $cm^3$ = 100 $cm^3$
Hence, the final volume $V_2$ = 100 $cm^3$

4. A sample of nitrogen occupies a volume of 0.60 $dm^3$ at 400 K and atmospheric pressure. What will be its volume at 400 K and 507 *mmHg*?

[1 atmosphere = 760 mm Hg]

Data provided:
Initial pressure, $P_1$ = 1 atmosphere = 760 mmHg
Initial volume, $V_1 = 0.60\ dm^3$
Final pressure, $P_2$ = 507 mmHg
Final volume, $V_2 = ?\ dm^3$

Since the temperature of 400 K is constant, then, it is Boyle's law.

***Formula Method***

According to Boyle's law: $P_1V_1 = P_2V_2$
Substituting: $760 \times 0.60 = 507 \times V_2$
Making $V_2$ the subject of the formula
$\therefore V_2 = (760 \times 0.60)/507 = 0.900\ dm^3$

***Inverse proportion method***

Pressure *decreased* from $P_1$ to $P_2$ by a factor of
$P_1/P_2 = 760/507 = 1.499$
∴ Volume will *increase* by a factor of 1.499;
i.e. $V_2 = 1.499 \times V_1 = 1.499 \times 0.60 = 0.900\ dm^3$.

5. The ratio of the initial to the final pressure of a given mass of gas is 1:1.5. Calculate the final volume, if the initial volume was 300 $cm^3$. [JAMB]

**Answer**

Data provided: $P_1$ = 1.0 unit; $P_2$ = 1.5 units;
$V_1 = 300\ cm^3$; $V_2 = ?\ cm^3$ (required)
According to Boyle's law: $P_1V_1 = P_2V_2$
Substituting: $1.0 \times 300 = 1.5 \times V_2$
$\therefore V_2 = (1.0 \times 300)/(1.5) = 200\ cm^3$

## Revision Exercises

11a State the Boyle's law
i. in words; ii. mathematically.
b Explain Boyle's law in terms of the kinetic theory.
c Draw a sketch to illustrate the Boyle's law.

12 Fill the following gaps:
(Measurements at constant temperatures)

| Initial Pressure | Initial Volume | Final Pressure | Final Volume |
|---|---|---|---|
| 1.0 × $10^5$ $Nm^{-2}$ | 300 $cm^3$ | 1.5 × $10^5$ $Nm^{-2}$ | a |
| b | 3.50 $dm^3$ | 760 mm Hg | 700 $cm^3$ |
| 0.42 atm | – | 1.26 atm | y $dm^3$ |
| 840 mmHg | V $cm^3$ | – | 3V $cm^3$ |

13 The following results were obtained at room temperature in an experiment to verify one of the gas laws using a glass syringe:

| Pressure, P, of air in syringe (atm) | Volume, V, of air in syringe ($cm^3$) | 1/V |
|---|---|---|
| 0.100 | 10.00 | ? |
| 0.125 | 8.00 | ? |
| 0.150 | 6.60 | ? |
| 0.175 | 5.60 | ? |
| 0.200 | 4.80 | ? |
| 0.225 | 4.40 | ? |

a. Determine the reciprocal of the volume, 1/V for each value of V.
b. Plot a graph of P against 1/V using any convenient scales. Comment on the curve.
c. Which of the gas laws is in agreement with these results?

14 A given quantity of gas occupies a volume of 228 $cm^3$ at a pressure of 750 mmHg. What will be its volume at atmospheric pressure? [JAMB]
A. 200 $cm^3$ B. 225 $cm^3$ C. 230 $cm^3$ D. 235 $cm^3$

## 10.6 Variation of Gas Volume with Temperature

### Introduction

Jacques Charles (1787), a French physicist, studied the effect of temperature change on gas volume. He made the following observations on the physical behaviour of gases:

- All gases expand or contract in volume **V** by the same quantity as temperature changes provided the mass ***m*** and pressure **P** remain the same.
- The change in volume **V** is about 1/273 of the gas volume at 0 °C (273 K) for every degree rise or fall in temperature.

A close observation shows that if a given mass of gas is cooled to -273 °C, its volume becomes zero; since it would have turned to a solid!

### The Absolute Zero

Lord Kelvin invented the *absolute temperature scale*. On this scale, *the temperature at which the volume of a fixed mass of gas would be zero is 0 K (-273.15 °C)*. This temperature is called ***absolute zero***. *At* ***absolute zero****, there is no motion of any form; kinetic energy is zero.*

The advantage of Kelvin scale is that it eliminates the use of *zero* or *negative* temperature values when solving problems involving gases. This is because, on the ***absolute scale***, -273°C = 0 ***K***, while 0 °C = 273 ***K***.

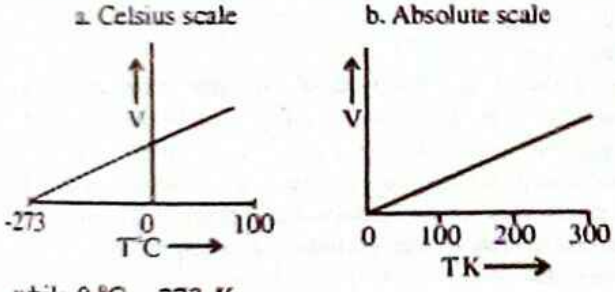



Figure 10.4 shows the variation of gas volume with temperature at constant pressure:

**Fig 10.4** *Variation of gas Volume with Temperature*

### Charles' Law

Charles' law states that:

*The volume of a fixed mass of gas is* ***directly*** *proportional to the absolute temperature at constant pressure.*

It means: an *increase* in the temperature of a fixed mass of gas leads to an *increase* in the gas volume in the same proportion, and vice versa, provided the *pressure* remains the same.

Mathematically, $[\ V \propto T\ ]_{m,P}$ ....10.6

$[\ V = kT\ ]_{m,P}$ ....10.7

i.e. $[V/T = \text{constant } k\ ]_{m,P}$ .....10.8

(***k*** = constant of proportionality).

Thus, for a fixed mass of gas, **V/T** is constant, provided that mass **m** and pressure **P** are constant.

Hence, if the initial temperature $T_1$ of a gas of initial volume $V_1$ is changed to a new temperature $T_2$, its new volume $V_2$, at constant pressure, can be obtained from the following mathematical expression:

$$\left(\frac{V_1}{T_1} = \frac{V_2}{T_2}\right)_{m,P} \quad \text{..... 10.9}$$

Equation 10.9 can be re-arranged to give:

$$V_1/V_2 = T_1/T_2 \quad \text{.....10.10}$$

Equation 9.10 shows that in ratio form:

$$V_1 : V_2 = T_1 : T_2 \quad \text{.....10.11}$$

Equations 10.9 and 10.10 are the mathematical expressions for the Charles' law. They are used when a fixed mass of gas is subjected to a *change in temperature or volume, at constant pressure.*

### Evidence to support Charles' law

- *Air-filled balloon* expands when the temperature increases at constant atmospheric pressure, until it bursts.
- Air enclosed in a flask expands as it is being heated, until it blows off the stopper (fig 10.5).

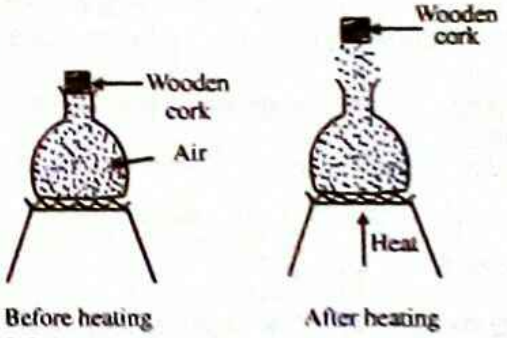



**Fig 10.5** *Temperature effect on gas Volume*

Figure10.6 illustrates graphical representations of the Charles' law.

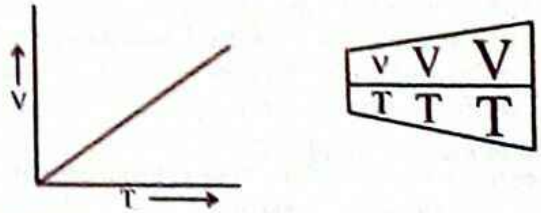



**Fig 10.6** *Graphical illustrations of Charles' law*

### Kinetic theory explanation of Charles' law

An *increase* in temperature *raises* the average kinetic energy, and hence, the average velocity of gas molecules. The molecules move more rapidly and collide with the walls more frequently. For gas pressure to remain constant, the volume of the con-

tainer must *increase* with an *increase* in temperature.

Conversely, a *decrease* in the temperature *lowers* the average kinetic energy of the molecules; it *lowers* their average velocity, and hence, *lowers* the frequency of collision of gas molecules with the walls. For gas pressure to remain constant, the volume of the container must be ***reduced*** as the temperature is ***lowered***.

**Worked Examples**

Chemical calculations based on Charles' law are solved by *direct* proportion. The gas law is used to calculate the volume V or the temperature T when a fixed mass of gas is subjected to a *change* in temperature or volume, at constant pressure P.

In all the calculations involving Charles' law, the temperatures must be in degree Kelvin, K; since gas volume varies *directly* with degree Kelvin (and not with degree Celsius, °C).

**6.** The volume of a fixed mass of gas measured at atmospheric pressure and 27 °C is 3.0 $dm^3$. Calculate the volume at 127 °C and at the same pressure.

**Answer**

Data provided:

Initial volume, $V_1 = 3.0\ dm^3$

Initial temperature $T_1 = 27°C = (27 + 273)\ K = 300\ K$

Final temperature, $T_2 = 127°C = (127 + 273) = 400\ K$

Final volume, $V_2 = ?\ dm^3$ (required)

Pressure is constant; Charles' law is to be applied.

***Formula Method***

According to Charles' law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \qquad \text{(P constant)}$$

Substituting: $\frac{3}{300} = \frac{V_2}{400}$

Making the unknown $V_2$ the subject of the formula

$$V_2 = \frac{3 \times 400}{300} = 4.00\ dm^3$$

***Direct proportion: Method 1***

At 300 K volume is 3.0 $dm^3$ (given)

At 400 K (an *increase T*), volume *V increases* to

$3.0 \times 400/300 = 4.0\ dm^3$

i.e. Final volume = 4.00 $dm^3$

***Direct proportion: Method 2***

Temperature *increased* from $T_1$ to $T_2$ by a factor of

$T_2/T_1 = 400/300 = 1.5$.

Hence, the volume will also *increase* from $V_1$ to $V_2$ by a factor of 400/300.

i.e. $V_2 = 3.0 \times 400/300 = 4.0\ dm^3$

∴ Final volume = 4.00 $dm^3$.

**7.** A given mass of gas occupies 500 $cm^3$ at 25 °C. Calculate the temperature, in degree Celsius, at which its volume becomes doubled, at constant pressure.

*Data provided:*

$V_1 = 500\ cm^3$; $T_1 = 25\ °C = 25 + 273 = 298\ K$

$V_2 = 2 \times 500\ cm^3 = 1000\ cm^3$; $T_2 = ?\ K$

***Formula method***

According to Charles' law : $V_1/T_1 = V_2/T_2$

Substituting: $500/298 = 1000/T_2$

i.e. $T_2 = (298 \times 1000/500 = 596\ K$

∴ Final temperature in °C = (596 − 273) °C = 323 °C.

***Direct proportion:***

Gas volume is 500 $cm^3$ at 298 K (given)

When gas volume is *doubled* to 1000 $cm^3$, temperature will also be *doubled*; $298 \times 1000/500 = 298 \times 2 = 596\ K$

∴ Final temperature in °C = 596 − 273 = 323 °C.

**8.** A gas sample with initial volume of 3.25 $dm^3$ is heated and allowed to expand to 9.75 $dm^3$ at constant pressure. What is the ratio of the final absolute temperature to the initial absolute temperature? [JAMB]

Data provided: $V_1 = 3.25\ dm^3$; $V_2 = 9.75\ dm^3$

Required: To find the ratio $T_2 : T_1$.

Since pressure is constant, Charles' law is to be applied,

i.e. $V_1/T_1 = V_2/T_2$

Rearranging the formula: $V_1/V_2 = T_1/T_2$

i.e. $V_1 : V_2 = T_1 : T_2$

Substituting: $3.25 : 9.75 = T_1 : T_2$

i.e. $T_2 : T_1 = 9.75 : 3.25 = 3 : 1$

∴ $T_2 : T_1 = 3 : 1$

**9.** Explain why an inflated balloon expands in warm water. [WAEC]

**Solution**

*An inflated balloon is filled with air made up of gas molecules. In warm water, there is an increase in temperature, which increases the kinetic energy of the gas molecules. Hence, the molecules move faster and collide with the wall of the balloon more frequently, leading to an expansion of the balloon, at constant atmospheric pressure.*

## Revision Exercises

**15a** State the Charles' law

i. in words; ii. mathematically.

**b** Explain Charles' law in terms of the kinetic theory.

**c** Draw a sketch to illustrate the Charles' law.

**16** What is absolute zero of temperature? State its value in: **a.** Celsius temperature; **b.** Kelvin temperature.

**17** Fill in the following gaps:

(Measurements at constant pressures)

| Initial Volume | Initial Temp. | Final Volume | Final Temp. |
|---|---|---|---|
| 200 $cm^3$ | 30 °C | – | − 30 °C |
| 35.0 $cm^3$ | 15 °C | 105 $cm^3$ | – |
| – | 330 K | 7.50 $dm^3$ | 66.0 K |
| 2*V* $cm^3$ | – | 5*V* $cm^3$ | *T* K |

18 A fixed mass of gas has a volume of 92 $cm^3$ at 3 °C. What will be its volume at 18 °C, if the pressure remains constant ?

19 A gas sample initially at 35 °C is cooled to – 42 °C. Calculate the ratio of the *initial volume* to the *final volume* at constant pressure. [JAMB]

A. 1: 2 B. 2 : 3 C. 3 : 4 D. 5 : 6

20 Explain why an inflated balloon bursts in the hot sun.

## 10.7 The General Gas Equation

The *general gas equation* is the combination of Boyle's and Charles' laws:

*From Boyle's law:* $V \propto 1/P$ (m and T constant)

*From Charles' law:* $V \propto T$ (m and P constant)

For a fixed mass of gas, it can be shown that:

$$V \propto T \times 1/P$$

or $$V = kT/P$$

Rearranging the variable, we obtain:

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

When the initial volume $V_1$ of a gas at temperature $T_1$ and pressure $P_1$ is subjected to changes in temperature to $T_2$ and pressure to $P_2$, its new volume $V_2$ is obtained from the equation:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{.... 10.13}$$

Equation 10.13 is the ***general gas equation***, made up of *six* variables. It can be used to calculate the volume, pressure, or temperature of a fixed mass of gas once the other *five* variables are known.

It should be noted that when the temperature T is constant, then, $T_1 = T_2$; the gas equation becomes:

$$P_1V_1 = P_2V_2 \text{ (Boyle's law).}$$

When the pressure P is constant, then $P_1 = P_2$; the gas equation becomes:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{(Charles' law)}$$

When the volume V is constant, $V_1 = V_2$; the gas equation becomes:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad \text{(Pressure-temperature law)}$$

**Worked Examples**

10 A certain mass of gas occupies 330 $cm^3$ at 27 °C and $9.0 \times 10^4$ $Nm^{-2}$ pressure. Calculate its volume at s.t.p. (Standard pressure $= 1.0 \times 10^5$ $Nm^{-2}$)

*Data provided:* $V_1 = 330\ cm^3$; $P_1 = 9.0 \times 10^4\ Nm^{-2}$

$T_1 = (27 + 273)\ K = 300\ K$

*Standard temperature,* $T_2 = 273\ K$

*Standard pressure,* $P_2 = 1.0 \times 10^5\ Nm^{-2}$

*Required: To find* $V_2 = ?\ cm^3$

*Using the gas equation:* $(P_1V_1)/T_1 = (P_2V_2)/T_2$

Substituting: $\frac{9.0 \times 10^4 \times 330}{300} = \frac{1.0 \times 10^5 \times V_2}{273}$

Making $V_2$ the subject of the formula:

$$V_2 = \frac{9.0 \times 10^4 \times 330 \times 273}{1.0 \times 10^5 \times 300} = 270.3\ cm^3$$

$\therefore V_2 = 270\ cm^3$ (to 3 significant figures).

11 The temperature of a gas is 57 °C. At what temperature would its original volume be halved while the pressure is tripled? [WAEC]

*Given:* $T_1 = 57 + 273 = 330\ K$; $V_1 = V$; $V_2 = \frac{1}{2}V$; $P_1 = P$; $P_2 = 3P$.

*Required:* $T_2 = ?\ K$

*Using the gas equation:* $(P_1V_1)/T_1 = (P_2V_2)/T_2$

*Substituting:* $(P \times V)/300 = (3P \times \frac{1}{2}V)/T_2$

Making $T_2$ the subject of the formula:

$$T_2 = \frac{3P \times V \times 330}{2 \times P \times V} = \frac{3 \times 330}{2} = 495\ K$$

In degree Celsius: 495 K = (495 – 273) °C = 222 °C

**Revision Exercises**

21 Show that for a given mass of gas PV/T = a constant, and define all the variables in the expression.

22 If 190 $cm^3$ of hydrogen gas is collected at 26 °C and 736 mmHg, calculate its volume at s.t.p. (Standard pressure = 760 mmHg) [NECO]

23 To what temperature must a gas at 273 K be heated in order to double its volume and pressure? [JAMB]

A. 298 K B. 546 K C. 819 K D. 1092 K

24 A given mass of gas occupies 500 $cm^3$ at 30 °C and $6.5 \times 10^4$ $Nm^{-2}$. Calculate the volume of the gas at stp. [Standard pressure = $1.01 \times 10^5$ $Nm^{-2}$] [WAEC]

## 10.8 Pressure –Temperature Changes

Consider the gas equation:

**PV/T = a constant**

The equation shows that if the volume **V** of a fixed mass of gas is kept constant, the pressure **P** exerted will be *directly* proportional to the absolute temperature **T**, i.e.

$$[P \propto T]_{m,V}$$

Table 10.3 gives the variation of pressure of water vapour with temperature. It is evident that an *increase* in temperature leads to an *increase* in the vapour pressure, at constant volume (figure 10.7).

**Table 10.3** ***Pressure of Water Vapour***

| Temp [°C] | Pressure [$Nm^{-2}$] |
|---|---|
| 0 | $6.0 \times 10^2$ |
| 10 | $1.2 \times 10^3$ |
| 17 | $1.9 \times 10^3$ |
| 20 | $2.3 \times 10^3$ |
| 25 | $3.1 \times 10^3$ |
| 30 | $4.2 \times 10^3$ |
| 50 | $1.2 \times 10^4$ |
| 100 | $1.0 \times 10^5$ |

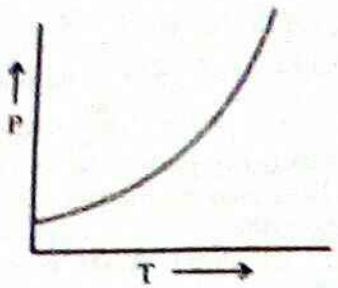



**Fig 10.7** *Variation of Pressure with temperature*

### Kinetic Theory Explanation

Gas pressure is due to the continuous bombardment of the walls of the container by the gas molecules. An *increase* in temperature *increases* the frequency of collision with the walls; leading to an *increase* in pressure, at constant gas volume .

Conversely, a *decrease* in temperature leads to a *decrease* in the frequency of collision of the gas molecules with the walls of the container. It leads to a *decrease* in pressure, if the volume of the container remains constant.

### Solved Problems

**12** Explain why an increase in the temperature of a gas of fixed volume results in an increase in pressure. [WAEC]

**Solution**

*An increase in temperature increases the kinetic energy of gas molecules. The molecules move faster and collide with the walls of the container more frequently, leading to an increase in pressure at constant volume.*

**13** Consider a cylinder filled with a gas to which a piston is attached. What will happen to the:

a. gas molecules, if the temperature is increased ?
*The gas molecules move faster.*

b. piston, if the temperature is raised?
*The piston moves up.*

c. pressure, if the piston is fixed in place and the temperature is raised?
*The pressure will increase.*

**14** Explain in terms of kinetic theory why a tyre should not be over-inflated.

**Answer**

*An over-inflated tyre contains a large number of air molecules in the inner tube. This leads to frequent collisions of the air molecules with the walls of the tyre, and hence, an increase in pressure in the tyre.*

*As the tyre moves on the road, the temperature of the air molecules increases, due to friction, and the kinetic energy increases. Since the volume of the tyre remains constant, the air molecules move faster and collide with the walls of the tyre more frequently. This leads to a steady increase in pressure, and the tyre may eventually burst.*

### Revision Exercises

**25** Explain in terms of kinetic theory why there is an increase in pressure in a motor tyre on a sunny day.

**26** What is the temperature of a given mass of gas initially at 0 °C and 9 atmospheres, if the pressure is reduced to 3 atmospheres at constant volume ?
A. 91K B. 182 K C. 273 K D. 819 K [JAMB]

**27** A gas measures 1.0 $dm^3$ at a temperature of 27 °C and 300 mmHg. To what Celsius temperature must the gas be heated, when its pressure rises to 480 mmHg and for its volume to remain unchanged ?
[JAMB]

## 10.9 Dalton's Law of Partial Pressure

### Mixture of Gases

John Dalton, the originator of the atomic theory, also studied the physical behaviour of mixtures of gases that do not react. His observations led to the Dalton's law of *partial* pressure, which states that:

*The pressure exerted by a mixture of gases is equal to the sum of their partial pressures, provided that the gases do not react at that temperature.*

*The **partial pressure** of a gas is the pressure it exerts when it is alone in a container at a given temperature.*

### Experimental Illustration

Suppose a fixed mass of hydrogen gas exerts a pressure $pH_2$ when alone in a container of volume V, and a given mass of nitrogen gas exerts a pressure $pN_2$ when alone in another container of the same volume V, at the same temperature.

If the two gases now occupy the same container of volume V at the same temperature, it would be found that the mixture of gases exerts a total pressure $P_{Total}$ that equals the sum of their partial pressures (figure 10.8c). That is:

$$P_{Total} = pH_2 + pN_2$$




**Fig 10.8** *To illustrate Dalton's law of partial pressure*

Generally, for a mixture of *n* gases:

$$P_{Total} = p_1 + p_2 + p_3 + \ldots + p_n \qquad \ldots 10.14$$

where $p_1$, $p_2$, $p_3$ ... and $p_n$ are the *partial pressures* of *n* gases.

### Gases Collected Over Water

When a gas is collected over water, it becomes wet by water vapour. Since water vapour is a gas, it exerts its own pressure, and a mixture of gases is obtained.

The pressure exerted is, therefore, the sum of the *partial pressures* of the gas and that of the water vapour at that temperature, i.e.

$$P_{Total} = P_{gas} + P_{water\ vapour}$$

In order to obtain the *partial pressure of the dry gas* (without water vapour), the partial pressure of water vapour at that temperature is subtracted from the pressure of the gas collected over water. Hence,

$$P_{gas} = P_{Total} - P_{water\ vapour}$$

**Kinetic theory explanation of Dalton's law**

At a given temperature, the average kinetic energy of a fixed mass of gas is constant. Since in a mixture of gases molecular collisions are perfectly elastic (no loss of energy), the frequency of collision of each gas molecule with the walls of the container (its partial pressure) will be the same as when it is alone in the container at the same temperature. Hence, the total pressure exerted will be equal to the sum of the partial pressures of the various gases in the mixture.

**Worked Examples**

15 20.0 $dm^3$ of hydrogen were collected over water at 17 °C and 79.7 $kNm^{-2}$ pressure. Calculate the

a. pressure of dry hydrogen at this temperature.

b. volume of dry hydrogen at s.t.p.

(Vapour pressure of water is 1.90 $kNm^{-2}$ at 17 °C; 1 atmosphere = 101.3 $kNm^{-2}$)

Answer

a. *To find the pressure of dry hydrogen.*

Since the gas is collected over water, then, Dalton's law is to be applied.

Given: $P_{Total}$ = 79.7 $kNm^{-2}$ at 17 °C

$P_{water\ vapour}$ = 1.90 $kNm^{-2}$ at 17 °C

Required: $p_{gas}$ at 17 °C

According to Dalton's law:

$$p_{gas} = P_{Total} - P_{water\ vapour}$$

Substituting:

$$p(H_2) = (79.7 - 1.90)\ kNm^{-2} = 77.8\ kNm^{-2}$$

b. *To find the volume of dry hydrogen at s.t.p.*

Data provided:

$P_1 = (79.7 - 1.90)\ kNm^{-2} = 77.8\ kNm^{-2}$

$V_1 = 20.0\ dm^3$; $T_1 = 17°C = (273 + 17)\ K = 290\ K$

$P_2$ = standard pressure = 101.3 $kNm^{-2}$

$T_2$ = standard temperature = 273 K.

Required: *To find the final volume, $V_2$.*

Using the gas equation, and substituting:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2};\ \frac{77.9 \times 20}{290} = \frac{101.3 \times V_2}{273}$$

Making the unknown $V_2$ the subject of the formula:

$$\therefore\ V_2 = \frac{77.8 \times 20 \times 273}{101.3 \times 290} = 14.5\ dm^3.$$

16 Two flasks were connected by a narrow tube with a closed tap. One flask contains 300 $cm^3$ of oxygen at $1.0 \times 10^5\ Nm^{-2}$, while the other contains 200 $cm^3$ of nitrogen at $2.0 \times 10^5\ Nm^{-2}$. fig 10.9




**Fig 10.9**

After opening the tap, calculate the

a. partial pressure of each gas;

b. total pressure of the mixture, at constant temperature.

*In solving this problem, a combination of Boyle's law and Dalton's law of partial pressure will be used.*

a. *To find the partial pressure of each gas.*

The size of the container determines the volume of a gas. With the tap closed, the initial volume of oxygen is 300 $cm^3$, while that of nitrogen is 200 $cm^3$.

When the tap is opened, both gases now occupy a total volume of (300 + 200) $cm^3$ = 500 $cm^3$.

i. *To calculate the partial pressure of $O_2$.*

At constant temperature, the Boyle's is used; i.e.

$$P_1V_1 = P_2V_2$$

$P_1 = 1.0 \times 10^5\ Nm^{-2}$; $V_1 = 300\ cm^3$

$P_2 = ?\ Nm^{-2}$; $V_2 = 500\ cm^3$

Making $P_2$ the subject of the formula, and substituting:

$$P_2 = P_1V_1/V_2$$

$$= (1.0 \times 10^5 \times 300)/500 = 0.6 \times 10^5\ Nm^{-2}.$$

Hence, $p(O_2) = 0.6 \times 10^5\ Nm^{-2}$

ii. *To calculate the partial pressure of $N_2$.*

$$P_1V_1 = P_2V_2$$

$P_1 = 2.0 \times 10^5\ Nm^{-2}$; $V_1 = 200\ cm^3$

$P_2 = ?\ N\ m^{-2}$; $V_2 = 500\ cm^3$

Making $P_2$ the subject of the formula, and substituting:

$$P_2 = P_1V_1/V_2$$

$$= (2.0 \times 10^5 \times 200)/500 = 0.8 \times 10^5\ Nm^{-2}.$$

Hence, $p(N_2) = 0.8 \times 10^5\ Nm^{-2}$

b. *To find the pressure of the mixture of gases.*

According to Dalton's law:

$$P_{Total} = p(O_2) + p(N_2)$$

$$= [(0.6 \times 10^5) + (0.8 \times 10^5)]\ Nm^{-2}$$

$$= 1.40 \times 10^5\ Nm^{-2}$$

**Revision Exercises**

28 a. State Dalton's law of partial pressure.

b. What is the *partial pressure* of a gas?

29 In a mixture of gases which do not react chemically together, the pressure exerted by the individual gases is called

A. atmospheric pressure. B. partial pressure.

C. total pressure. D. vapour pressure. [WAEC]

30 Two containers of the same volume contain respectively a sample of oxygen at $1.52 \times 10^5\ Nm^{-2}$ and a sample of nitrogen at $1.01 \times 10^5\ Nm^{-2}$. What will be the pressure, if both gases are held in the same container at the same temperature?

31 A gas was collected over water at s.t.p. What would be its pressure, if the saturated vapour pressure of water at s.t.p. is 13 mmHg?
[Standard pressure = 760 mmHg] [WAEC]

32 A container is partitioned into two compartments. One contains 5.0 $dm^3$ of helium at 4.0 atmospheres, while the other contains 3.0 $dm^3$ of air at 6.0 atmospheres (fig 10.10).

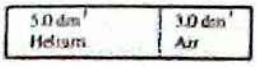



**Fig 10.10**

After the partition is removed at constant temperature, calculate the:
a. partial pressure of: i. helium; ii. air.
b. pressure of the mixture.

## 10.10 Law of Combining Volumes of Gases

### Gay-Lussac's Law

Whereas Boyle's, Charles' and Dalton's laws describe the *physical* behaviour of gases, Gay-Lussac's law describes the *chemical* behaviour of gases.

Gay-Lussac studied mixtures of gases that would react under suitable conditions. The results of the study led to the ***Gay-Lussac's law*** of combining volumes of gases which states:
*When gases react, they do so in volumes, which bear a simple ratio to one another and to the volumes of gaseous products, provided all gaseous volumes are measured at the same temperature and pressure.*

The results of some of the reactions are:
- ***One*** volume of hydrogen reacts with ***one*** volume of chlorine to produce ***two*** volumes of hydrogen chloride.
- ***One*** volume of nitrogen combines with ***three*** volumes of hydrogen to produce ***two*** volumes of ammonia.
- Carbon burns in ***one*** volume of oxygen to produce ***one*** volume of carbon(IV) oxide.

Although Gay-Lussac's law is of great importance, it failed to relate gaseous reactions to the atomic theory of Dalton. Hence, the kinetic theory cannot be used to explain the law.

### Avogadro's Principle

It was after the death of Gay-Lussac that Amadeo Avogadro, who also studied the behaviour of gases when they react, recognized the significance of the Gay-Lussac's law. His hypothesis, which later became ***Avogadro's principle or law***, states that:
*Equal volume of all gases, under the same conditions of temperature and pressure contain the same number of molecules.*

Mathematically:

$$V \propto N \quad \text{[at constant T and P]}$$

(where **V** is the gas volume and **N** is the number of molecules).

The law shows that the *volume* occupied by a gas depends on the *number of molecules* it contains, at a given temperature and pressure. An *increase in the number of gas molecules* leads to an *increase in gas volume*, and vice versa.

From the Avogadro's principle, we expect the *ratio of number of molecules of all the gases* in a balanced chemical equation, to be the same as the *ratio of volumes of all the gases* in the reaction. In other words, Avogadro's principle could be used to explain Gay-Lussac's law – as illustrated with the following examples:

1. *Formation of hydrogen chloride*
***One*** *volume* of hydrogen gas combines with *one volume* of chlorine gas to produce *two volumes* of hydrogen chloride gas (Gay-Lussac's law).
***Applying Avogadro's law:*** *One molecule* of hydrogen gas combines with *one molecule* of chlorine gas to produce *two molecules* of hydrogen chloride gas.

From the above information, each molecule of hydrogen and chlorine is *diatomic*.

$$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$$
1 volume 1 volume 2 volumes (Gay-Lussac's)
1 molecule 1 molecule 2 molecules (Avogadro's)

2. *Formation of ammonia*

$$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$$
1 volume 3 volume 2 volumes (Gay-Lussac's)
1 molecule 3 molecules 2 molecules (Avogadro's)

Hence, each molecule of nitrogen contains at least two atoms.

3. Formation of carbon(IV) oxide:

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$
1 vol 1 vol (Gay-Lussac's)
1 molecule 1 molecule (Avogadro's)

Hence, carbon(IV) oxide contains two atoms (or one molecule) of oxygen.

**Notes:**
- The Gay-Lussac's and Avogadro's laws are applied to *gaseous reactants and products* only.
- Most gaseous elements are diatomic, while those of noble gases are monatomic.
- The atomic theory of Dalton did not take into consideration the fact that atomicities of some elements are greater than one.

## Chemical Calculations based on the Laws of Combining Volumes of Gases

Chemical calculations based on Gay-Lussac's law involve *gas volume-gas volume relationships* in a chemical reaction. Such calculations are by *direct* proportion, since *gas volume* is *directly* proportional to the *number of gas molecules*, as indicated by the coefficients in the balanced equation of reaction (Avogadro's principle).

### Worked Examples

**17** Water vapour is produced according to the following equation:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$$

What volume of oxygen will combine with 10.0 $cm^3$ of hydrogen, and how many $cm^3$ of water vapour will be produced under the same conditions of temperature and pressure?

**Answer**

Given: 10.0 $cm^3$ of $H_2$

*To find the volume of $O_2$ required to combine with $H_2$*

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$$
2 volumes 1 volume 2 volumes

Applying Gay-Lussac's law:

2 unit volumes of $H_2$ require 1 unit volume of $O_2$

i.e. 2 $cm^3$ of $H_2 \equiv$ 1 $cm^3$ of $O_2$

$\therefore$ 10 $cm^3$ of $H_2 \equiv (1 \times 10)/2$ $cm^3$ of $O_2$

$= 5.0$ $cm^3$

*To calculate the volume of steam produced*

From the equation of reaction:

2 $cm^3$ of $H_2 \equiv$ 2 $cm^3$ of $H_2O$

$\therefore$ 10 $cm^3$ of $H_2 \equiv (2 \times 10)/2$ $cm^3$ of $O_2$

$= 10.0$ $cm^3$ of $H_2O$

Or, from the equation of reaction:

1 $cm^3$ of $O_2 \equiv$ 2 $cm^3$ of $H_2O$

$\therefore$ 5 $cm^3$ of $H_2 \equiv (2 \times 5)/1$ $cm^3$ of $O_2$

$= 10.0$ $cm^3$ of $H_2O$

**18** Ammonia is produced by *Haber process* accord-ing to the equation:

$$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$$

If 20 $cm^3$ of nitrogen were mixed with 90 $cm^3$ of hydrogen under suitable conditions:

a. Which gas is in excess, and by how much?

b. What will be the volume of ammonia produced?

c. What is the total volume of the gas mixture at the end of the reaction?

**Answer**

Applying Gay-Lussac's law:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$
1 volume 3 volumes 2 volumes

a. *To establish the gas in excess.*

Volume of nitrogen available = 20 $cm^3$

Volume of hydrogen available = 90 $cm^3$

i. Suppose hydrogen gas is completely used up:

From the equation of reaction, 3 unit volumes of hydrogen require 1 unit volume of nitrogen,

i.e. 3 $cm^3$ of $H_2$ require 1 $cm^3$ of $N_2$

$\therefore$ 90 $cm^3$ of $H_2$ require $(1 \times 90)/30$ $cm^3$ = 30 $cm^3$

Since only 20 $cm^3$ of $N_2$ is available, it means this volume is not enough; it will be completely used up. Hence, it is the volume of nitrogen that will determine the volume of the product (limiting reactant).

ii. Suppose nitrogen gas is completely used up:

From the equation of reaction, 1 unit volume of nitrogen requires 3 unit volumes of hydrogen

i.e. 1 $cm^3$ of $N_2$ requires 3 $cm^3$ of $H_2$

$\therefore$ 20 $cm^3$ of $N_2$ require $(3 \times 20)$ $cm^3$ of $H_2 = 60$ $cm^3$

Since 90 $cm^3$ of hydrogen is available; it is in excess by $(90 - 60)$ $cm^3 = 30.0$ $cm^3$

b. *To calculate the volume of $NH_3$ produced.*

Volume of $NH_3$ produced depends on the volume of $N_2$ (20 $cm^3$) or $H_2$ (60 $cm^3$) consumed.

From the equation of reaction:

1 $cm^3$ of $N_2$ produces 2 $cm^3$ of $NH_3$

$\therefore$ 20 $cm^3$ of $N_2$ will produce $(2 \times 20)$ $cm^3$ of $NH_3$

$= 40.0$ $cm^3$.

Or, 3 $cm^3$ of $H_2$ produce 2 $cm^3$ of $NH_3$

$\therefore$ 60 $cm^3$ of $H_2$ will produce $(2 \times 60)/3$ $cm^3$

$= 40$ $cm^3$ of $NH_3$

c. *To find the total volume of gas mixture.*

At the end of the reaction, 40 $cm^3$ of $NH_3$ is produced, while 30 $cm^3$ of $H_2$ is left unused.

$\therefore$ Total volume of gas after reaction will be

$(40 + 30)$ $cm^3 = 70.0$ $cm^3$ of mixture.

The *mixture of gases at the end of the reaction* is called ***residual gas.***

**19** The following reaction occurred when 100 $cm^3$ of carbon(II) oxide was burnt in 70 $cm^3$ of oxygen:

$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$$

Calculate the total volume of gas mixture (residual gas) in the reaction vessel at the end of the reaction, assuming the temperature and pressure were adjusted to the initial values. [WAEC]

*Data provided*: 100 $cm^3$ of CO and 70 $cm^3$ of $O_2$

*To find the volume of gas mixture after reaction*

Gay-Lussac's law is to be applied.

$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$$
2 vol. 1 vol. 2 vol.

First, *find out which of the reactants is in excess.*

i.e. Suppose oxygen is completely used up:

From the equation, 1 vol. of oxygen requires 2 volumes of carbon(II) oxide.

i.e. 1 $cm^3$ of $O_2$ require 2 $cm^3$ of CO.

$\therefore$ 70 $cm^3$ of $O_2$ require $2 \times 70$ $cm^3 = 140$ $cm^3$.

Since only 100 $cm^3$ of CO is available, it is the limiting reactant; it will be completely used up.

From the equation:

2 vol. of CO $\equiv$ 1 vol. of $O_2$

i.e. 2 $cm^3$ of CO $\equiv$ 1 $cm^3$ of $O_2$

$\therefore$ 100 $cm^3$ of CO $\equiv (1 \times 100)/20 = 50.0$ $cm^3$ of $O_2$

Since 70 $cm^3$ of $O_2$ is available, the volume of $O_2$ in excess = (70 – 50) $cm^3$ = 20.0 $cm^3$.

*To find the volume of $CO_2$ produced.*

From the equation:

2 $cm^3$ of CO ≡ 2 $cm^3$ of $CO_2$

∴ 100 $cm^3$ of CO ≡ (2 × 100)/2 = 100 $cm^3$ of $CO_2$

Hence, the total volume of gas mixture after the reaction will be 20.0 $cm^3$ of excess $O_2$ and 100 $cm^3$ of $CO_2$ produced = 120 $cm^3$ of residual gas.

**20** What volume of hydrogen would be left over when 300 $cm^3$ of oxygen and 1000 $cm^3$ of hydrogen are exploded in a sealed tube? [WAEC]

$$2H_{2\,(g)} + O_{2\,(g)} \rightarrow 2H_2O_{(g)}$$

*Data provided:* 300 $cm^3$ of $O_2$ and 1000 $cm^3$ of $H_2$.

Required: *To find the volume of hydrogen in excess.*

Gay-Lussac's law is to be applied.

$$2H_{2\,(g)} + O_{2\,(g)} \rightarrow 2H_2O_{(g)}$$

2 vol. 1 vol.

Since hydrogen is in excess, it means that the 300 $cm^3$ of $O_2$ will be completely used up.

From the equation:

1 $cm^3$ of $O_2$ ≡ 2 $cm^3$ of $H_2$

∴ 300 $cm^3$ of $O_2$ ≡ (2 × 300) $cm^3$ = 600 $cm^3$ of $H_2$

Hence, the volume of hydrogen left over (in excess) will be (1000 – 600) $cm^3$ = 400 $cm^3$.

### Revision Exercises

**33** State the **a.** Gay-Lussac's law of combining volume.
**b.** Avogadro's law.

**34** Which of the following cannot be explained by the use of the kinetic theory?

A. Dalton's atomic theory. B. Boyle's law.
C. Gay-Lussac's law. D. Expansion of gases.

**35** In the reaction:

$$2SO_{2\,(g)} + O_{2\,(g)} \rightarrow 2SO_{3\,(g)}$$

**a.** What volume of sulphur(IV) oxide, $SO_2$, will combine with 50.0 $cm^3$ of oxygen gas ?

**b.** Calculate the volume of sulphur(VI) oxide, $SO_3$, produced.

**36** What volume of hydrogen will be produced if 100 $cm^3$ of ammonia is completely decomposed at constant temperature and pressure?

The equation for the reaction is :

$$2NH_{3\,(g)} \rightarrow N_{2\,(g)} + 3H_{2\,(g)}$$ [WAEC]

A. 50 $cm^3$ B. 150 $cm^3$ C. 200 $cm^3$ D. 300 $cm^3$

**37** If 50 $cm^3$ of carbon(II) oxide were burnt in 40 $cm^3$ of oxygen, determine the gas that would be in excess, and calculate the volume of gas that would be unused.

The equation for the reaction is:

$$2CO_{(g)} + O_{2\,(g)} \rightarrow 2CO_{2\,(g)}$$ [WAEC]

**38** 30 $cm^3$ of hydrogen at s.t.p. combine with 20 $cm^3$ of oxygen to form steam according to the following equation:

$$2H_{2\,(g)} + O_{2\,(g)} \rightarrow 2H_2O_{(g)}$$

Calculate the total volume of the gaseous mixture at the end of the reaction. [WAEC]

A. 50 $cm^3$ B. 35 $cm^3$ C. 30 $cm^3$ D. 25 $cm^3$

## 10.11 Molar Volume of a Gas

### Molar Volume and Avogadro's Constant

When the *mole concept* is applied to gases, *one mole* of a gas contains $6.02 \times 10^{23}$ molecules. *The volume occupied by one mole of a gas under any conditions of temperature and pressure is called the* ***molar volume, $V_m$.***

The *molar volume* of an ideal gas depends on the conditions of *temperature and pressure.* At s.t.p., it is 22.4 $dm^3$ (or 22,400 $cm^3$), while at 25 °C and one atmosphere, it is 24.5 $dm^3$. Its value is quite *low* at *high* pressure. However, under any conditions of temperature and pressure, *molar volume contains $6.02 \times 10^{23}$ molecules.* Hence, at s.t.p:

- One mole of $H_2$ gas occupies 22.4 $dm^3$, contains $6.02 \times 10^{23}$ molecules, and weighs 2.0 g.
- One mole of $O_2$ gas occupies 22.4 $dm^3$, contains $6.02 \times 10^{23}$ molecules, and weighs 32.0 g.
- One mole of $CO_2$ gas occupies 22.4 $dm^3$, contains $6.02 \times 10^{23}$ molecules, and weighs 44.0 g, etc.

### Worked Examples

**21** How many molecules are in a molar volume of a gas at: **a.** s.t.p.? **b.** 20 °C?

**a.** *$6.02 \times 10^{23}$ molecules.* **b.** *$6.02 \times 10^{23}$ molecules.*
*(One molar volume of any gas contains $6.02 \times 10^{23}$ molecules at any temperature and pressure).*

**22** In an experiment, 112 $cm^3$ of carbon(IV) oxide gas were collected s.t.p. How many molecules of the gas are present? (Avogadro constant, L, is $6.02 \times 10^{23}$ $mol^{-1}$; molar volume at s.t.p is 22.4 $dm^3$)

*Data provided:* Volume of $CO_2$ at s.t.p. = 112 $cm^3$;

*To calculate number of molecules of gas at s.t.p.*

One mole of a gas contains $6.02 \times 10^{23}$ molecules and occupies 22.4 $dm^3$ (or 22400 $cm^3$) at s.t.p.

i.e 22400 $cm^3$ of $CO_2$ contain $6.02 \times 10^{23}$ molecules

∴ 112 $cm^3$ of $CO_2$ contain $(6.02 \times 10^{23} \times 112)/22400$
$= 3.01 \times 10^{23}$ molecules.

### Determination of Molecular Mass

The concept of *molar volume* at s.t.p. can be used to determine the relative molecular mass of a gaseous substance.

**Procedure:**

1. A known volume of the gaseous substance is weighed accurately, under suitable temperature and pressure.
2. The volume is then corrected to s.t.p.
3. The mass of the substance that occupies 22.4 $dm^3$ is then calculated.

When the ***molar mass*** of a gas is divided by its ***molar volume*** at a given temperature and pressure, the ***gas density*** under these conditions is obtained.



i.e. *Density of gas*, $\delta$ ($gdm^{-3}$) under any conditions of temperature and pressure is:

$$\delta = \frac{\text{Molar mass, M } (gmol^{-1})}{\text{Molar volume, } V_m\ (dm^3mol^{-1})}$$

**Worked Examples**

**23** Calculate the relative molecular mass of a gas, if its density at s.t.p. is 1.43 $gdm^{-3}$.
(Molar volume at s.t.p. is 22.4 $dm^3mol^{-1}$)

*Data provided*: Density of gas = 1.43 $gdm^{-3}$
Molar volume at s.t.p. = 22.4 $dm^3mol^{-1}$

*Method 1: Formula method*

Density at s.t.p. = (Molar mass)/(Molar volume)
i.e. Molar mass = density × molar volume
= 1.43 × 22.4 = 32.0 $gmol^{-1}$
∴ Molecular mass of gas = 32.0 (no unit)

*Method 2: (Direct proportion method)*

At s.t.p. 1 $dm^3$ of gas weighs 1.43 g (density, given).
∴ 22.4 $dm^3$ of gas weigh (1.43 × 22.4) g = 32.0 g
i.e. one mole of the gas weighs 32.0 g.
Hence, molecular mass of gas = 32.0 (no unit).

**24** Calculate the volume of 0.10 *g* of hydrogen gas at s.t.p. [H = 1; Molar volume at s.t.p. is 22.4 $dm^3$]

*To find the volume of 0.10 g of $H_2$ at s.t.p*
Molar mass of hydrogen gas, $H_2$ = 2(1.0) = 2.0 $gmol^{-1}$
Molar volume of a gas at s.t.p. is 22.4 $dm^3\ mol^{-1}$
i.e. 2.0 g (1 mole) of $H_2$ occupy 22.4 $dm^3$ at s.t.p.
∴ 0.10 g of $H_2$ occupies (22.4 × 0.10)/2 = 1.12 $dm^3$.

## Vapour Density, d

*The vapour density **d**, of a gas is the number of times a given volume of the gas is as heavy as an equal volume of hydrogen, at the same temperature and pressure.*

Since *vapour density* is a ratio of gas volumes; it has no unit. It is related to the relative molecular mass (no unit) by the formula:

***Relative molecular mass = 2 × Vapour density; or Vapour density = ½ × Relative molecular mass.***

i.e. *Relative molecular mass of a gas is twice its vapour density, or vapour density of a gas is a half of its relative molecular mass.*

**Worked Examples**

**25** What is the vapour density of sulphur(IV) oxide gas? (O = 16; S = 32)

Answer
Data provided: *Relevant atomic masses*
Required: *To find the vapour density of $SO_2$*
First, calculate the molecular mass of $SO_2$
i.e. $M_r[SO_2] = 32 + 2(16)$
$= 32 + 32 = 64$
But vapour density = ½ (molecular mass)
$= ½ \times 64 = 32$
∴ Vapour density of $SO_2$ = 32.0

**26** If 400 $cm^3$ of a certain gas weighs 0.5 g at s.t.p Calculate its **a.** molar mass; **b.** vapour density.
[1.0 mole of a gas at s.t.p. occupies 22.4 $dm^3$].

**a.** *To calculate the molar mass*
At s.t.p. 400 $cm^3$ of gas weigh 0.5 g
∴ 22400 $cm^3$ of gas weigh (0.5 × 22400)/400 g
= 28.0 g
∴ Molar mass of gas = 28.0 $gmol^{-1}$

**b.** *To calculate the vapour density*
Vapour density = ½ molecular mass
= ½ × 28 = 14.0 (no unit)

**Revision Exercises**

**Notes:** ***1 mole of a gas occupies 22.4 $dm^3$ at s.t.p.;***
***Avogadro constant = $6.02 \times 10^{23}$ $mol^{-1}$***

**39** How many molecules are there in a molar volume of a gas at **a.** 0 °C? **b.** 100 °C?

**40** How many molecules of oxygen gas are present in 1.0 $dm^3$ of the gas at s.t.p. ?

**41** Given that 44.0 g of $CO_2$ contains $6.023 \times 10^{23}$ molecules, calculate the number of molecules in 5.6 $dm^3$ of the gas at s.t.p.

**42** Calculate the volume occupied at s.t.p. by 6.8 g of ammonia gas. (H = 1.0, N = 14)

**43** Calculate the mass of chlorine gas which occupies a volume of 1.12 $dm^3$ at s.t.p.(Cl = 35.5)
**A** 1.80 g **B** 3.55 g **C** 7.10 g **D** 15.50 g [WAEC]

**44** Calculate the amount (in moles) of a gas which occupies 250 $cm^3$ at s.t.p.

**45** The density of a certain gas is 1.98 $gdm^{-3}$ at s.t.p. What is the molecular mass of the gas?
**A.** 54.0 **B.** 44.0 **C.** 31.0 **D.** 26.0 [JAMB]

**46** Which of the following gases has a vapour density of 14? [H =1, C = 12, N =14, O =16, S = 32, Cl = 35.5]
**A.** $Cl_2$ **B.** $H_2S$ **C.** $NH_3$ **D.** CO [WAEC]

**47** A certain volume of gas was found to weigh 1.76 g and when corrected to s.t.p. occupied 896 $cm^3$. Calculate the vapour density of the gas.
**A.** 11.0 **B.** 22.0 **C.** 44.0 **D.** 88.0

## 10.12 Ideal Gas Equation

The ***ideal gas equation*** *is the combination of Boyle's, Charles' and Avogadro's laws.* It gives the relationship between volume *V*, pressure *P*, *absolute* temperature *T*, and the amount *n*, of a gas.

From the Boyle's law: $[V \propto 1/P]_{n,T}$
From Charles' law: $[V \propto T]_{n,P}$
From Avogadro's law: $[V \propto N]_{n,P}$
From Avogadro's constant: $N \propto n$
Combining the laws:

$$V \propto n \times 1/P \times T$$

i.e. $$V = \frac{nRT}{P}$$

*R* is called ***universal gas constant.*** *It is independent of the quantity of gas.*

Rearranging:

$$PV = nRT \quad \text{.....10.15}$$

Equation 10.15 is called ***ideal gas equation.*** *Any gas that obeys the equation at all temperatures and pressures is said to be ideal or perfect.*

**Values and Units of the Gas Constant, *R***

The value of **R** is determined in respect of the fact that one mole of an ideal gas at s.t.p. occupies 22.4 $dm^3$. It is the same for all gases; hence, it is called ***universal gas constant***.

For 1 mole of an ideal gas, $n = 1$; hence,

$$PV = RT$$

i.e. $$PV/T = R$$

The unit of *molar gas constant*, **R**, depends on the units of pressure **P**, and volume **V**:

- If pressure **P** is expressed in *atmosphere*, volume **V** must be in $dm^3$. Substituting:

$P = 1$ atm; $V = 22.4$ $dm^3$; $T = 273$ K; $n = 1$

$$R = \frac{PV}{T} = \frac{1 \times 22.4}{273} = 0.082 \text{ atmdm}^3\text{K}^{-1}\text{mol}^{-1}$$

i.e. $$R = 0.082\ atmdm^3K^{-1}mol^{-1}$$

**In S.I. units:**

- If pressure **P** is in $Nm^{-2}$, volume **V** is in $m^3$.
- If pressure **P** is in $kNm^{-2}$, volume **V** is in $dm^3$.

Hence, substituting in the ideal gas equation:

$P = 101.3\ kNm^{-2}$; $V = 22.4\ dm^3$; $T = 273\ K$; $n = 1$.

$$PV = RT$$

$$R = \frac{PV}{T} = \frac{101.3 \times 22.4}{273} = 8.31 \text{ JK}^{-1}\text{mol}^{-1}$$

i.e. $$R = 8.31\ JK^{-1}mol^{-1}$$

**Importance of the Ideal Gas Equation**

The *ideal gas equation*: **PV = nRT**, is for ***n*** moles of an ideal gas. It is used in solving problems involving a *fixed amount of gas under one set of non-standard conditions.*

Its use saves time; there is no need of correcting the gas volume to s.t.p. before calculating the volume a given *amount* of gas will occupy under non-standard conditions of temperature and pressure. However, care must be taken with the units of volume and pressure.

From the *ideal gas equation*, the following relationships can be obtained:

- The pressure **P** exerted by a gas, is directly proportional to the amount ***n*** of the gas, if the volume and temperature are constant; i.e.

$$P \ \alpha \ n \qquad \textbf{(V, T constant)}$$

An *increase* in the amount **n** of gas leads to an *increase* in gas pressure **P**, and vice versa, at constant temperature and volume.

Mathematically: $P_1/P_2 = n_1/n_2$

- The volume **V** occupied by a gas is directly proportional to the amount ***n*** of the gas, if temperature and pressure are constant, i.e.

$$V \ \alpha \ n \qquad \textbf{(T, P constant)}$$

An *increase* in the amount **n** of gas leads to an *increase* in the volume **V**, and vice versa, if the temperature and pressure are constant.

Mathematically: $V_1/V_2 = n_1/n_2$

- For a *given amount of gas*, the temperature **T** is directly proportional to both the pressure **P** and volume **V**; i.e.

$$T \ \alpha \ (P \times V) \qquad \textbf{(n constant)}$$

An *increase* in temperature leads to an *increase* in the *gas pressure* as well as its *volume*, and vice versa, if the amount of the gas remains constant.

From the ideal gas equation: **PV = nRT**, and the amount of a gas: **n = m/M** (where ***n*** is the amount in moles, ***m*** is the mass in grams and ***M*** is the molar mass in grams per mole), the gas equation becomes:

$$PV = \frac{m}{M}RT \quad \text{..... 10.16}$$

Equation 10.16 shows that the molar mass of a volatile liquid can be determined once the mass of the vapour of the liquid is known.

Since density, **δ**, is mass per unit volume, **m/V**, equation 10.16 can be written as:

$$P = \frac{\delta}{M}RT \quad \text{..... 10.17}$$

Equation 10.17 shows that the molar mass of a gaseous substance can be determined once its density, at a given temperature and pressure, is known.

**Worked Examples**

**27** The amount of air in a motor tyre is doubled. What will be the relative change in the pressure of air in the tyre, if the temperature and volume of tyre are constant?

*The pressure of air in the tyre becomes doubled; since gas pressure is directly proportional to the temperature at constant volume.*

**28** Calculate the volume occupied by 2.5 moles of an ideal gas at -23 °C and 4.0 atmospheres.

[$R = 0.082$ atmdm$^3$K$^{-1}$mol$^{-1}$]

*Data provided:*

$P = 4.0$ atm; $T = -23 + 273 = 250$ K;

$n = 2.5$ mol; $R = 0.082$ atm dm$^3$ K$^{-1}$ mol$^{-1}$

Required: *To calculate the volume*, $V = ?$ dm$^3$

The appropriate equation is: $PV = nRT$

Making V the subject, and substituting:

$$V = \frac{nRT}{P} = \frac{2.5 \times 0.082 \times 250}{4} = 12.8 \text{ dm}^3$$

29 Calculate the volume occupied by 3.2 g of dry oxygen gas at 300 K and 100 $kNm^{-2}$
(Gas constant, R = 8.31 $Jmol^{-1}K^{-1}$; O = 16.0)
*Data provided*: Mass of $O_2$ = 3.2 g;
P = 100 $kNm^{-2}$; T = 300 K; R = 8.31 $Jmol^{-1}K^{-1}$
Required: *To calculate the volume V of oxygen.*
First, calculate the amount of $O_2$, *n*:

$$n = \frac{\text{mass of } O_2}{\text{molar mass}} = \frac{3.2}{2(16)} = \frac{3.2}{32} = 0.1 \text{ mole}$$

Using the gas equation: PV = nRT.
Making V the subject, and substituting:

$$V = \frac{nRT}{P} = \frac{0.1 \times 8.31 \times 300}{100} = 2.50 \text{ dm}^3$$

Note: Since P is in $kNm^{-2}$; V will be in $dm^3$.

30 Calculate the volume occupied by 0.125 mole of oxygen at 27 °C and $2.02 \times 10^3$ $Nm^{-2}$ pressure.
[1 mole of gas occupies 22.4 $dm^3$ at s.t.p.;
standard pressure = $1.01 \times 10^5$ $Nm^{-2}$] [WAEC]

*Data provided:*
P = $2.02 \times 10^3$ $Nm^{-2}$; T = 27 + 273 = 300 K
n = 0.125 mole; molar volume at s.t.p. = 22.4 $dm^3$;
Standard pressure = $1.01 \times 10^5$ $Nm^{-2}$
*Required: To find the volume, V.*
In this problem, the value of the gas constant R, is not given. This is because pressure P, is in $Nm^{-2}$.
To solve this problem, the volume V, must be corrected to s.t.p.
First, calculate the volume 0.125 mole of oxygen will occupy at s.t.p. i.e.
1.0 mole of oxygen occupies 22.4 $dm^3$ at s.t.p.
∴0.125 mole of oxygen occupies $(22.4 \times 0.125)$ $dm^3$
= 2.80 $dm^3$ at s.t.p.
Then, determine the volume the gas will occupy under the given conditions, using the gas equation:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$P_1 = 1.01 \times 10^5$ $Nm^{-2}$; $T_1 = 273$ K; $V_1 = 2.8$ $dm^3$
$P_2 = 2.02 \times 10^5$ $Nm^{-2}$; $T_2 = 300$ K; $V_2 = ?$ $dm^3$
Substituting: $\frac{1.01 \times 10^5 \times 2.8}{273} = \frac{2.02 \times 10^5 \times V_2}{300}$
Making the unknown, $V_2$, the subject:

$$V_2 = \frac{1.01 \times 10^5 \times 2.8 \times 300}{2.02 \times 10^5 \times 273} = 1.54 \text{ dm}^3$$

*Alternative method*
If gas constant, R, is given as 8.31 $JK^{-1}mol^{-1}$, then, pressure, P, must be converted to $kNm^{-2}$; i.e.
$2.02 \times 10^5$ $Nm^{-2}$ = 202 $kNm^{-2}$
Using the gas equation: PV = nRT.
Making V the subject, and substituting:

$$V = \frac{nRT}{P} = \frac{0.125 \times 8.31 \times 300}{202} = 1.54 \text{ dm}^3$$

**Revision Exercises**

48 Show that for an ideal gas PV = nRT, and define all the terms in the expression.

49 Which of the following expressions correctly represents Charles' law? [WAEC]
A. PV = K B. R $\alpha 1/\sqrt{P}$ C. PV = RT D. V = KT

50 A gas occupies 10 $dm^3$ of space at 4 atmospheres and 20 °C. Calculate the amount, in moles, of the gas present. (R = 0.082 $atmdm^3K^{-1}$) [NECO]

51 Oxygen gas occupies a volume of 2 $dm^3$ at a pressure of 0.5 atm. and a temperature of 27 °C. Calculate the mass of oxygen.(R = 0.082 $atmdm^3K^{-1}$; O = 16)[N]

52 A sample of a gas exerts a pressure of 8.2 atm when confined in a 2.93 $dm^3$ at 20 °C. The amount, in moles, of gas in the sample is
A. 1.00 B. 2.00 C. 3.00 D. 4.00
(R = 0.082 $atmdm^{-3}K^{-1}$) [JAMB]

53 If the quantity of oxygen occupying a 2.76 $dm^3$ container at a pressure of 0.825 atm and 300 K is reduced by a half, what is the pressure exerted by the remaining gas ? [JAMB]
A 1.65 atm B 0.825 atm C 0.413 atm D 0.275 atm

54 In terms of kinetic theory, explain the following observations:
An increase in the amount of air in a motor tyre leads to an increase in pressure, if the temperature and volume of the tyre remain constant.

55 A container of fixed volume contains 2.0 moles of a gas at room temperature. The pressure in the container is 3.0 atmospheres. Suppose the amount of gas in the container is increased by 3.0 moles at the same temperature. The new pressure, in atmosphere, is
A. 2.0 B. 3.0 C. 5.0 D. 8.0 E. 10.0

## 10.13 Mixture of Ideal Gases

### Mole Fractions

Consider a mixture of 2 ideal gases in the amounts, $n_1$ and $n_2$ moles with partial pressures, $p_1$ and $p_2$. The total pressure, $P_T$, of the mixture equals to the sum of their partial pressures at temperature T.
i.e. $P_{Total} = p_1 + p_2$ (Dalton's law)
From the ideal gas equation, PV = nRT; the partial pressure of each gas will be:

$$p_1 = \frac{n_1RT}{V} \quad ; \quad p_2 = \frac{n_2RT}{V}$$

$$P_T = p_1 + p_2 = \frac{n_1RT}{V} + \frac{n_2RT}{V} = (n_1+n_2)\frac{RT}{V}$$

The partial pressure of each gas in the mixture can be expressed as a *mole fraction* of the total amount of gases in the mixture. That is:
For the first ideal gas: $\frac{p_1}{P_T} = \frac{n_1}{(n_1+n_2)}$

$$\therefore p_1 = \frac{n_1}{(n_1+n_2)} P_T$$

For the second gas: $\frac{p_2}{P_T} = \frac{n_2}{(n_1+n_2)}$

$$\therefore p_2 = \frac{n_2}{(n_1+n_2)} P_T$$

The fractions: $n_1/(n_1 + n_2)$ and $n_2/(n_1 + n_2)$ are the *mole fractions* for the two gases respectively. *The fraction of the amount (in moles) of a gas in a mixture of gases is called mole fraction.*

Hence, the partial pressure, $p_1$, of a gas in a mixture of *two* gases, is equal to its *mole fraction* multiplied by the total pressure, $P_T$ of the gas mixture:

$$p_1 = (\text{mole fraction})P_T \quad \text{..... 10.18}$$

Rearranging equation 10.18 gives:

$$\text{Mole fraction} = p_1/P_T \quad \text{.....10.19}$$

Equation 10.19 shows that the *mole fraction* of a gas can be obtained from its partial pressure, $p_1$, and the total pressure, $P_T$, of the mixture of gases.

**Worked Examples**

**31** A 2.0 $dm^3$ bulb contains 1.20 g of hydrogen and 6.40 g of oxygen at 27 °C. Calculate the

a i. mole fraction of hydrogen;
ii. mole fraction of oxygen.
b. pressure of the mixture
c. partial pressure of each gas

[Gas constant, R = 8.31 $Jmol^{-1}K^{-1}$; H = 1; O = 16]

*Data provided:* V = 2.0 $dm^3$; T = 27 + 273 = 300 K;
Mass of hydrogen = 1.20 g; mass of oxygen = 6.40 g;

a. *To calculate the mole fractions*
First, calculate the amounts of the gases:
Amount of $H_2$, $n_1$ = (mass)/(molar mass)
= 1.20/2 = 0.60 mol.
Amount of $O_2$, $n_2$ = 6.40/32 = 0.20 mol.
Total amount of gas mixture = $(n_1 + n_2)$
= (0.60 + 0.2) = 0.80 mol.

i. *Mole fraction of hydrogen:* 0.60/0.80 = 0.75
ii. *Mole fraction of oxygen:* 0.20/0.80 = 0.25

b *To calculate the pressure of the mixture.*
The appropriate formula is the Dalton's law in the form of equation: $P_{Total} = (n_1 + n_2)RT/V$. Substituting:

$$P_{Total} = 0.80 \times 8.31 \times 300/2 = 997 \text{ kNm}^{-2}$$

[Note: From the unit of R, the unit of P is as stated.]

c. *To find the partial pressure of each gas*

$p(H_2)$ = (mole fraction)$P_T$
= 0.75 × 997 = 748 $kNm^{-2}$

$p(O_2)$ = (mole fraction)$P_T$
= 0.25 × 997 = 249 $kNm^{-2}$

**32** If 30.0 $cm^3$ of nitrogen and 20.0 $cm^3$ of hydrogen were mixed at atmospheric pressure, calculate the partial pressure of each gas.

*Given:* 30.0 $cm^3$ of nitrogen and 20.0 $cm^3$ of oxygen.
Pressure, $P_T$ = 1.0 atmosphere.
*To calculate the partial pressure of each gas*
Consider the ideal gas equation: PV = nRT

$$V = nRT/P$$

i.e. gas volume V is directly proportional to its amount, n:

$$V \propto n \quad \text{(at constant P and T)}$$

Consider the expression involving partial pressure, $p_1$, of a gas:

$$p_1 = \frac{n_1}{(n_1 + n_2)} P_{Total}$$

It becomes $p_1 = \frac{V_1}{(V_1 + V_2)} P_{Total}$

Total volume of the mixture:
$V(N_2) + V(O_2) = (30.0 + 20.0)\ cm^3 = 50.0\ cm^3$.

*To calculate the partial pressures:*
$p(N_2) = 30/50 \times 1 = 0.60$ *atm.*
$p(O_2) = 20/50 \times 1 = 0.40$ *atm.*
[Note: $p(N_2) + p(O_2) = 0.60 + 0.40 = 1.0$ *atm.*]

**33** If 0.75 mole of cyclopropane and 0.66 mole of oxygen are mixed in a vessel with a total pressure of 0.70 atmospheres, what is the partial pressure of oxygen in the mixture? [JAMB]
**A.** 0.22 atm **B.** 0.33 atm **C.** 0.44 atm **D.** 0.55 atm.
**Solution: *B***
Data given: Amount of cyclopropane = 0.75 mol
Amount of oxygen = 0.66 mol
Total pressure, $P_T$ = 0.70 atm
*To find the partial pressure of oxygen, $p_1$*
The appropriate formula connects Dalton's law and mole fraction; i.e. $p_1 = (\text{mole fraction})\ P_{Total}$
Mole fraction of oxygen = 0.66/(0.66 + 0.70)
= 0.66/1.41 = 0.468
∴ Partial pressure of oxygen,
$p_1$ = (0.468 × 0.70) atm = 0.328 atm (Ans = *B*)

**Revision Exercises**

**56** A mixture of 0.20 mole of argon, 0.20 mole of oxygen and 0.30 mole of helium exerts a total pressure of 2.1 atmospheres. Calculate the partial pressure of each gas in the mixture. [NECO]

**57** The partial pressure of oxygen in a sample of air is 452 mmHg and the total pressure is 780 mmHg. What is the mole fraction of oxygen? [JAMB]
(Hint: See equation 10.19)
**A.** 0.203 **B.** 0.579 **C.** 2.03 **D.** 5.79

## 10.14 Diffusion of Gases

### Graham's Law of Diffusion

Gases are capable of spreading in all directions, in order to occupy any available space. For instance: when the vapour of perfume is allowed into a room, the smell spreads quickly and fills the entire room. Similarly, the exhaust fumes discharged from a smoky vehicle, gradually become *invisible*. This natural phenomenon is called ***diffusion***.

The process of *diffusion* is due to the *zig-zag* (*translational*) motion of gas molecules. The term



*effusion* is used to describe the movement of gas molecules through a small opening under pressure.

Generally, *diffusion* (or *effusion*) is like pressure; it is usually from a region of *high* concentration to a region of *low* concentration.

**To Demonstrate the Process of Diffusion**

1. Invert a gas jar A full of iodine vapour (dark-brown) over another gas jar B full of colourless air (fig 10.11a).
2. Remove the partition, and leave the set-up for about five minutes (fig 10.11b).

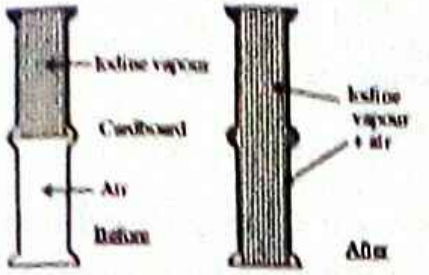



Fig 10.11 *Diffusion process*

**Observation:** The vapour of iodine spreads to occupy the lower jar **B**, so that both jars are now filled with the dark-brown vapour (fig 10.11b).

*Graham* studied the diffusion of gases. His observation that *gases diffuse at different rates*, led to the Graham's law of diffusion, which states:

*The rate, r, of diffusion of a gas is inversely proportional to the square root of its vapour density, d, at constant temperature and pressure.*

Mathematically: $[\ r \propto 1/\sqrt{d}\ ]_{T,P}$

**Corollary:** An *increase* in the vapour density of a gas *decreases* the rate of diffusion, and vice versa.

Gay-Lussac's law is employed when the rates of diffusion of two gases are being compared. Consider two gases with rates of diffusion $r_1$ and $r_2$ and of densities $d_1$ and $d_2$ under the same conditions of temperature and pressure:

$$r_1 \propto \sqrt{d_1} \quad \ldots 10.20$$

$$r_2 \propto \sqrt{d_2} \quad \ldots 10.21$$

Dividing equation 10.20 by equation 10.21, we obtain:

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} \quad \text{(T and P constant)} \quad \ldots 10.22$$

[Note the inverse proportion of the expression.]

Since *the vapour density d, of a gas is a half of its relative molecular mass* M, then, vapour density is directly proportional to relative molecular mass; equation 10.22 can therefore be written as:

$$\frac{r_1}{r_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}} \quad \text{(T and P constant)} \quad \ldots 10.23$$

Equation 10.22 or 10.23 is used when comparing the rates of diffusion of two gases, or when three out of the four variables are known.

Generally, a gas with a *low* molecular mass, like $H_2$ [$M_r(H_2) = 2$] will diffuse faster than another gas with a relatively *high* molecular mass, like $CO_2$ [$M_r(CO_2) = 44$] *under the same conditions*.

**Worked Examples**

**34** Compare the rates of diffusion of hydrogen gas and oxygen gas under the same conditions of temperature and pressure [H = 1.0; O = 16.0]

**Answer**

$M_r(H_2) = 2(1) = 2$; $M_r(O_2) = 2(16) = 32$

Using Graham's law expression, and substituting:

$$\frac{r(H_2)}{r(O_2)} = \frac{\sqrt{M(O_2)}}{\sqrt{M(H_2)}} = \sqrt{(32/2)} = \sqrt{16} = 4$$

i.e. $\frac{r(H_2)}{r(O_2)} = \frac{4}{1}$ *or* $r(H_2) = 4 \times r(O_2)$

That is: the rate of diffusion of hydrogen gas is *four times faster* than that of oxygen gas, under the same set of conditions. The ratio of the rates of diffusion is:

$$r(H_2) : r(O_2) = 4 : 1$$

**35** A gas X diffused through a porous partition at the rate of 3 $cm^3$ per second. Under the same conditions, hydrogen diffused at the rate of 15 $cm^3$ per second. The relative molecular mass of X is

[H = 1]

**A.** 5 **B.** 12 **C.** 18 **D.** 45 **E.** 50 [NECO]

**Answer**

Data provided: $r(X) = 3\ cm^3s^{-1}$; $r(H_2) = 15\ cm^3s^{-1}$

$M_r(H_2) = 2(1) = 2$; $M_r(X) = ?$

Using Graham's law: $\frac{r(X)}{r(H_2)} = \frac{\sqrt{M(H_2)}}{\sqrt{M(X)}}$

Substituting: $\frac{3}{15} = \frac{\sqrt{2}}{\sqrt{M(X)}}$

Squaring both sides: $\frac{(3)^2}{(15)^2} = \frac{(\sqrt{2})^2}{[\sqrt{M(X)}]^2}$

$$\frac{9}{225} = \frac{2}{M(X)}$$

Cross-multiplying, and making M(X) the subject of the formula:

$$M(X) = (225 \times 2)/9 = 50.0$$

i.e. the relative molecular mass of X is 50.0 (no unit)

**36** If 100 $cm^3$ of oxygen diffused in 4 seconds and 50 $cm^3$ of gas Y diffused in 3 seconds, calculate the relative molecular mass of gas Y. [O = 16]

[WAEC]

*Given:* $r(O_2) = \frac{\text{Volume}}{\text{Time}} = \frac{100\ cm^3}{4\ s} = 25\ cm^3s^{-1}$

$r(Y) = 50/3\ cm^3s^{-1}$

$M_r(O_2) = 2(16) = 32$

*Required: To find $M_r(Y)$*

Using Graham's law: $\frac{r(O_2)}{r(Y)} = \frac{\sqrt{M(Y)}}{\sqrt{M(O_2)}}$

Substituting: $\frac{25}{50/3} = \frac{\sqrt{M(Y)}}{\sqrt{32}}$

$\frac{25 \times 3}{50} = \frac{\sqrt{M(Y)}}{\sqrt{32}}$

Simplifying, and squaring both sides:

$\frac{3^1}{2^1} = \frac{M(Y)}{32}$

Simplifying, and making M(Y) the subject:

$M(Y) = (9 \times 32)/4 = 72$

Hence, the relative molecular mass of gas Y is 72.0

## Other Mathematical Expressions from Graham's Law

The *rate* of diffusion of a gas can be expressed in terms of gas volume, V per unit time, t, or distance covered, l per unit time, t.

i.e. $r = V/t$ *or* $r = l/t$

### 1. In Terms of Time, t

If for two gases, the gas volume, *V*, or the distance covered, *l* is the same; then, the rate of diffusion is *inversely* proportional to the time t taken:

i.e. $r \propto 1/t$

i.e. the *shorter* the time taken, the *faster* the rate, and vice versa. Under this condition, Graham's law can be stated as:

*The time taken for a given volume of gas to diffuse (or to cover a given distance) is directly proportional to the square root of its vapour density at constant temperature and pressure.*

i.e. $t \propto \sqrt{d}$

(Distance l, or volume V, T and P constant)

If for two gases of the same volume and with vapour densities $d_1$ and $d_2$, the time taken for diffusion, $t_1$ and $t_2$ are compared under the same conditions, we obtain:

$$\frac{t_1}{t_2} = \frac{\sqrt{d_1}}{\sqrt{d_2}} \quad \ldots\ldots 10.24$$

In terms of relative molecular mass, equation 10.24 becomes:

$$\frac{t_1}{t_2} = \frac{\sqrt{M_1}}{\sqrt{M_2}} \quad \ldots\ldots 10.25$$

(Distance, l, or volume, V, T and P constant)

Equation 10.24 or equation 10.25 shows that:

- It will take $O_2$ gas $[M_r(O_2) = 32]$ a longer time to cover the same distance as He gas $[M_r(He) = 4]$ under the same conditions;
- The time taken to deflate a balloon filled with one $dm^3$ of He gas will be shorter than the time taken to deflate another balloon filled with one $dm^3$ of $O_2$ gas under the same conditions.

**Worked Example 37**

If 100 $cm^3$ of methane, $CH_4$ diffused through a porous pot in 1.0 second, how long will it take the same volume of sulphur(IV) oxide, $SO_2$ to diffuse through the same pot under the same conditions? [H = 1.0; C = 12.0; O = 16.0; S = 32.0]

*To find the time taken for 100 $cm^3$ of $SO_2$ to diffuse*

Given: 100 $cm^3$ of $CH_4$; Time taken for diffusion: 1.0 s;

100 $cm^3$ of $SO_2$

Since gas volume is the same for the two gases, equation 10.24 or 10.25 can be used, i.e.

$$\frac{t(SO_2)}{t(CH_4)} = \frac{\sqrt{M(SO_2)}}{\sqrt{M(CH_4)}}$$

$M(CH_4) = 12 + 4 = 16$; $t(CH_4) = 1.0$ s;

$M(SO_2) = 32 + 32 = 64$

$$\frac{t(SO_2)}{1} = \frac{\sqrt{64}}{\sqrt{16}} = \frac{8}{4} = \frac{2}{1}$$

$\therefore\ t(SO_2) = 2.0$ s

That is: 100 $cm^3$ of $SO_2$ diffused through in 2.0 seconds.

### 2. In Terms of Volume V, or Distance l

If for *two* gases, the time t, taken for diffusion is the same, then, their rates will be *directly* proportional to their distances or their volumes:

$r \propto l$ or $r \propto V$

That is: the *longer* the distance covered (or the *larger* the gas volume), the *faster* the rate, and vice versa. Under this condition, Graham's law can be stated as:

*The volume of gas that diffuses out within a given time is inversely proportional to the square root of its vapour density at constant temperature and pressure.*

Mathematically: $V \propto 1/\sqrt{d}$

(Time t, T and P constant)

Similarly, when the distance *l*, is considered:

$l \propto 1/\sqrt{d}$

(Time t, T and P constant)

When the volumes of two gases, $V_1$ and $V_2$ that diffuse out of porous pots are compared under the same conditions, it can be shown that:

$$\frac{V_1}{V_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} \quad \text{(t, T and P constant)} \ldots\ldots 10.26$$

Similarly, when the distance, *l*, is considered:

$$\frac{l_1}{l_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} \quad \text{(t, T and P constant)} \ldots\ldots 10.27$$

Equations 10.26 and 10.27 show that:

- Within the same time, a larger volume of $H_2$ gas $[H_2 = 2]$ will diffuse out of a container than that of $O_2$ gas $[O_2 = 32]$ under the same conditions;
- Within the same time, $H_2$ gas $[H_2 = 2]$ will cover a longer distance than $O_2$ gas $[O_2 = 32]$ under the same conditions.

**Worked Example**

**57** Suppose hydrogen diffuses at the rate of y $cm^3$ per second from a certain apparatus. Calculate in term of y, the volume of oxygen, which diffuses in 10 seconds under the same conditions.

(H = 1.0; O = 16.0] [JAMB]

**Answer**

Let volume of oxygen = V $cm^3$

$r(H_2)$ = y $cm^3$ per second (given)

$r(O_2)$ = vol/time = V/10 $cm^3$ per second.

$M(H_2) = 2 \times 1 = 2$; $M(O_2) = 16 \times 2 = 32$.

Using Graham's law:

$$\frac{r(H_2)}{r(O_2)} = \frac{\sqrt{M(O_2)}}{\sqrt{M(H_2)}}$$

Substituting: $\frac{y}{V/10} = \sqrt{\frac{32}{2}} = \sqrt{16} = 4$,

i.e. $y \times \frac{10}{V} = 4$

$4V = 10y$

$V = 10y/4 = 2.50y\ cm^3$.

∴ Volume of oxygen = $2.50y\ cm^3$.

## Kinetic Theory Explanation of Graham's Law of Diffusion

According to the kinetic theory, the average kinetic energy of gas molecules is *directly* proportional to the absolute temperature.

At constant temperature, the average kinetic energy of gas molecules is constant. Hence, a gas with *low* relative molecular mass (like hydrogen) will *diffuse faster*, being lighter, than another gas with a *higher* relative molecular mass (like oxygen, carbon(IV) oxide or sulphur(IV) oxide).

### Revision Exercises

**58** State Graham's law of diffusion.

**59** What property of gases does Graham's law deal with? [WAEC]

A. Volume B. Pressure C. Mass D. Solubility

**60** Arrange the following gases, He, $CH_4$ and $N_2$ in order of increasing rates of diffusion. Give a reason for the order. [H = 1, He = 4, C = 12, N = 14] [WAEC]

**61** What is the ratio of the rate of diffusion of carbon (IV) oxide to that of propane ($C_3H_8$), under the same conditions ? (H = 1; C = 12; O = 16)

A. 1:1 B. 1:2 C. 2:1 D. 2:3 E. 3:1 [NECO]

**62** If d represents the density of a gas and k is a constant. State the relationship between the rate of diffusion r, and d. [JAMB]

A $r = k/\sqrt{d}$ B $r = kd$ C $r = k/d$ D $r = k\sqrt{d}$

**63** if 100 $cm^3$ of oxygen diffused in 4 seconds and 50 $cm^3$ of gas Y diffused in 3 seconds, calculate the relative molecular mass of gas Y. [O = 16]

**64** A given volume of oxygen diffuses through a porous plug in 8.0 seconds. How long will it take the same volume of sulphur(IV) oxide to diffuse through under the same conditions ? (O = 16; $SO_2$ = 64)

A. 5.7 s B. 8.0 s C. 11.3 s D. 16.0 s [WAEC]

**65** A gas X diffuses twice as fast as gas Y under the same conditions. If the relative molecular mass of X is 28, calculate the relative molecular mass of Y.

A. 14 B. 56 C. 112 D. 120 [WAEC]

## Experiments to Illustrate Graham's Law of Diffusion

**1. *Hydrogen diffuses faster than air***

When hydrogen gas is inverted over a porous pot full of air to which a manometer is attached, hydrogen diffuses *into* the pot more rapidly than air diffuses *out*.

This leads to an *increase* in gas pressure on the water in the U-tube, and forces the water level *up* on the right hand side, fig 10.12a. However, the levels become the same after air has been replaced completely by hydrogen.

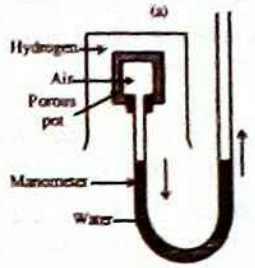



**Fig 10.12a** *Diffusion of gases*

**2. *Air diffuses faster than carbon(IV) oxide***

When a porous pot full of air is placed in a beaker full of carbon(IV) oxide, air molecules diffuse *out* of the porous pot faster than carbon(IV) oxide diffuses *in*.

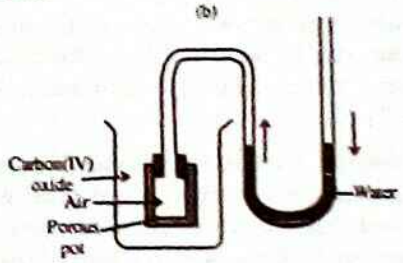



**Fig 10.12a** *Diffusion of gases*

There is a *decrease* in the gas pressure inside the pot; hence, the atmospheric pressure forces the water level in the U-tube *up* on the left hand side, fig 10.13b. The levels become the same after carbon(IV) oxide has been replaced completely by air.

**3. *Ammonia diffuses faster than hydrogen chloride***

When ammonia gas comes in contact with hydrogen chloride gas, a dense white fume of ammonium chloride is formed.

$$NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)}$$

**Procedure**

a. Two reagent bottles containing, say, 100 $cm^3$ of concentrated ammonia solution **A**, and 100 $cm^3$ of concentrated hydrochloric acid **B**, are connected by a long glass delivery tube to which two locked taps **C** and **D** are attached. A distance of 100 cm, **CD** separates both.

b. When the taps at **C** and **D** are opened simultaneously, ammonia gas from bottle **A** diffuses *faster* than the hydrogen chloride gas from bottle **B**. Hence, the *white* deposit formed inside the tube is *nearer* to the tap at **D** (i.e. nearer to the reagent bottle containing concentrated hydrochloric acid).




**Fig 10.13** *Ammonia gas diffuses faster than hydrogen chloride gas*

c. Within the limit of experimental errors, the ratio of the distances covered by ammonia gas, $l_1$, to that of hydrogen chloride gas, $l_2$, will be **3 : 2** i.e.

$$\frac{\text{distance covered by ammonia, } l_1}{\text{distance covered by HCl gas, } l_2} = \frac{3}{2}$$

That is: ammonia gas diffuses 1.5 times faster than hydrogen chloride gas.

### Applications of the Principles of Diffusion

**1. Separation of Gases**

The principle of diffusion is employed as a separation technique:

- A mixture of gases with widely different molecular masses can be separated by diffusion, e.g. a mixture of hydrogen [$M_r(H_2) = 2.0$] and chlorine [$M_r(Cl_2) = 71.0$].

**2. Collection of Gases by Displacement of Air**

- Gases that are lighter than air, i.e. with vapour density lower than 14, are collected by downward displacement of air. Examples are: $H_2$ and $NH_3$.
- Gases that are heavier than air, i.e. with vapour density higher than 14, are collected by upward displacement of air. Examples are: $Cl_2$ and $CO_2$.

**Solved Problem**

**39** Equal volumes of gases Y and Z are maintained at the same temperature and pressure. If the mass of a molecule of Y is twice that of Z, state and explain, which of the molecules has the greater average velocity.

**Answer**

*Molecules of Z have the greater average velocity than Y. Since both gases are at the same temperature, their average kinetic energies will be the same. However, since the molecules of Z are lighter than those of Y, they will move much faster than those of Y.*

**Revision Exercises**

**66** Name the process involved in the spread of the smell of perfume across a room.

**67** Which of the following pairs of gases diffuses faster under the same conditions? [WAEC]

a. Air and ammonia ($M_r$ of air = 29);

b. Hydrogen sulphide and carbon(IV) oxide.

**68** Which of the following gases has the highest rate of diffusion under similar conditions ?

(H = 1; O = 16; S = 32; Cl = 35.5)

A. $O_2$ B. $Cl_2$ C. HCl D. $SO_2$ [WAEC]

**69** Explain why a balloon filled with hydrogen becomes *deflated* faster than a balloon filled with air under the same conditions. [WAEC]

**70** Which of the following gases is lighter than air?

A. HCl B. $CO_2$ C. $SO_2$ D. $NH_3$ [WAEC]

**71** A vessel of volume 20.0 $dm^3$ contains equal numbers of hydrogen and oxygen molecules. If the pressure is 900 mmHg, which of the following statements is wrong ?

A. The average kinetic energies of both gases are the same.

B. The average velocity of hydrogen molecules is greater than that of oxygen molecules.

C. The frequency of collision of hydrogen molecules with the walls is more than that of oxygen molecules.

D. If oxygen molecules are removed from the vessel, the pressure will drop to 125 mm Hg.

E. Equal amounts of both gases are present in the vessel.

## 10.14 The Brownian Motion in Gases

When a microscope is focused on cigarette smoke enclosed in a container, it will be observed that the smoke particles move continuously in a zig-zag fashion, and in all directions without coming to rest. Robert Brown (1827), a botanist, made a similar observation while studying pollen grains that were suspended in water. The movement is called the ***Brownian motion***. It is a natural phenomenon.

The smaller the suspended particle, the more rapid and erratic the motion; and the higher the temperature, the more vigorous the motion of the suspended particles – whether in a gas or in a liquid.

*Brownian motion* can be accounted for by the kinetic theory of gases: A finely divided particle suspended in air or in a liquid will be kept in random motion, due to the continuous bombardment of the particle by the gas or liquid molecules.

As temperature increases, the average kinetic energy of the particles increases; this leads to a more vigorous motion. Hence, the lighter the suspended particles, the more vigorous and erratic the random motion.

**Revision Exercises**

72 What is *Brownian motion*?

73 What name is given to the phenomenon observed when dust particles collide randomly in a beam of sunlight?

## 10.15 Maxwell Distribution of Molecular Velocity of Gases

Experiments have shown that in any given mass of gas, all the molecules do not move with the same velocity because, the kinetic energies of the individual molecules are never the same.

The general form of distribution of molecular velocities is obtained from a plot of number (or fraction) of molecules with a particular velocity against the velocity.

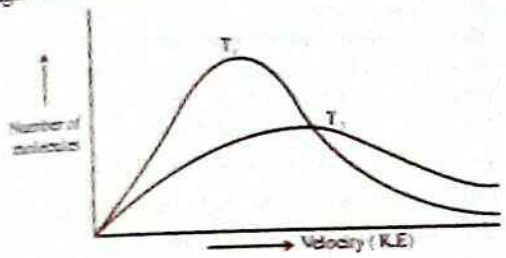



Fig 10.14 *Effect of temperature on velocity*

The curve $T_1$ shows that at this temperature, a few molecules have either very low or very high velocities, while most of the molecules have medium velocities. The curve $T_2$ shows that at a higher temperature, more molecules acquire higher velocities and hence, become more energetic as shown by the flattened shape of the curve at $T_2$ in fig 10.14.

**Revision Exercises**

74 With the aid of a diagram show that an increase in temperature leads to an increase in the average molecular velocity of a given mass of gas.

75 Explain in terms of the kinetic theory, why an increase in temperature leads to an increase in the average molecular velocity.

## 10.16 Ideal and Real Gases

### Differences between Ideal and Real Gases

1. An **ideal** gas obeys gas laws at *all* temperatures and pressure, while a **real** gas obeys the laws at *high* temperature and *low* pressure.

2. The *actual volume* of the molecules of an **ideal** gas is negligible compared with the volume of the container, while the *actual volume* of the molecules of a **real** gas is not negligible, i.e. *molecules of a real gas occupy space.*

3. In an **ideal** gas there are no intermolecular attactions at all temperatures and pressures, while intermolecular attraction is strong and appreciable in a **real** gas at *high* pressure and *low* temperature.

4. There is no **ideal** gas; all common gases are **real.**

### Deviation from Ideal Behaviour

Any gas that obeys the gas laws at all temperatures and pressure is called an ***ideal*** or ***perfect*** gas. Hence, the gas equation: **PV = nRT** is applicable to *ideal* gases only.

A plot of **PV** against **P** for an ideal gas at constant temperature gives a straight horizontal line (see fig 10.6). However, real or common gases deviate from this ideal behaviour as shown in fig 10.15.

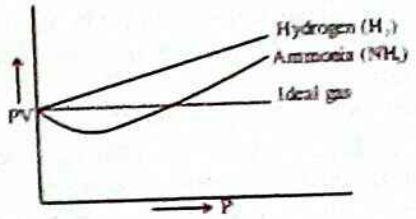



**Fig 10.15** *Comparing ideal and real gases*

#### *Deviation from Boyle's Law*

At *low* pressures, *real* gases obey Boyle's law. Under these conditions, the molecules move independently, since intermolecular distances are quite large.

However, at *high* pressure, the molecules become compressed and in close contact. Under these conditions, the volume occupied by the gas molecules is no longer negligible.

#### *Deviation from Charles' Law*

At *high* temperature *real* gases obey Charles' law. Under this condition, the molecules are energetic and move independently; since there will be no intermolecular attractions. However, at *low* temperature and *high* pressure intermolecular attractions become very strong and appreciable.

Generally, *polar* gas molecules, like $H_2O$, $NH_3$ and HCl deviate more from *ideality* than *non-polar* molecules, like hydrogen, oxygen, and noble gases.

**Solved Problems**

**40** Under what condition does the behaviour of a gas becomes: **a.** ideal? **b.** non-ideal?

**Answer**

**a.** *The behaviour of a gas becomes ideal at high temperature, and low pressure.*

b. *The behaviour of a gas becomes non-ideal at low temperature and high pressure.*

**41** Why do gases deviate from *ideality*?

**Answer**

*Gases deviate from ideality because of intermolecular attractions at low temperatures and high pressures.*

**Revision Exercises**

**76** Give **three** differences between an *ideal gas* and a *real gas*.

**77** State **one** condition under which a gas behaves ideally. [WAEC]

## 10.17 Calculations from Equations

### Mass-Mole-Gas Volume Relationships

The coefficients in the balanced equation of a chemical reaction indicate the amounts, in moles, of reactants and products. If Avogadro's principle is applied, *two or more gases of the same volume, under the same conditions of temperature and pressure, will be of the same amount, in moles.*

Hence, the ***mole ratio*** of all the gases in a balanced equation of a reaction is the same as their ***volume ratio***.

Consider the following reactions:

- $H_{2\,(g)} + Cl_{2\,(g)} \rightarrow 2HCl_{(g)}$

| | | | |
|---|---|---|---|
| *Mole ratio:* | 1 mole | 1 mole | 2 moles |
| *Vol. ratio:* | 1 vol. | 1 vol. | 2 vol. |

- $2H_2S_{(g)} + SO_{2(g)} \rightarrow 2H_2O_{(l)} + 3S(s)$

| | | | |
|---|---|---|---|
| 2 moles | 1 mole | 2 moles | 3 moles |
| 2 vol. | 1 vol. | *(liquid)* | *(solid)* |

Calculations based on *mass-mole-volume* involve the use of *molar volumes*. Any information on gas volumes obtained from a balanced equation of a reaction is taken to be at s.t.p. Under these conditions, molar volume is a constant and equals 22.4 $dm^3$ per mole, e.g.

In the formation of hydrogen chloride at s.t.p:

$$H_{2\,(g)} + Cl_{2\,(g)} \rightarrow 2HCl_{(g)}$$

| | | | |
|---|---|---|---|
| *Mole ratio:* | 1 mole | 1 mole | 2 moles |
| *Vol. ratio:* | 1 vol. | 1 vol. | 2 vol. |
| *At s.t.p.:* | 22.4 $dm^3$ | 22.4 $dm^3$ | 2 × 22.4 $dm^3$ |

The steps to follow are:

1. Write a balanced equation for the reaction.
2. Write the amounts, in moles, under the relevant reactants and/or products.
3. Convert the amount, in moles, to mass, in grams.
4. Write for each gaseous reactant or product the molar volume at s.t.p.
5. Calculate the quantity required by *direct* proportion.
6. When the conditions are not at s.t.p., the volume at s.t.p is first determined from the balanced equation of reaction; this volume is then corrected to the conditions provided.

**Worked Examples**

**42** Consider the reaction:

$$C_{(s)} + O_{2\,(g)} \rightarrow CO_{2\,(g)}$$

a. How many moles of pure carbon will burn in 2.8 $dm^3$ of oxygen completely at s.t.p?

b. What will be the volume of carbon(IV) oxide produced under the same conditions?

[Molar volume of a gas is 22.4 $dm^3$ at s.t.p.]

**Answer**

a. *To find the amount of carbon*

Given: 2.8 $dm^3$ of $O_2$; molar volume at s.t.p.

This is mole-gas volume relationship.

Applying Avogadro's hypothesis to the equation of reaction:

$$C_{(s)} + O_{2\,(g)} \rightarrow CO_{2\,(g)}$$

1 mol 1 mol

22.4 $dm^3$ 22.4 $dm^3$

At s.t.p. 22.4 $dm^3$ of $O_2$ require 1 mole of carbon.

∴ 2.8 $dm^3$ of $O_2$ require $(1 \times 2.8)/22.4$ mol.

= 0.125 mol. of carbon.

b. *To find the volume of $CO_2$ evolved at s.t.p.*

This is volume-volume relationship:

At s.t.p. 1 mol of $O_2$ will produce 1 mol of $CO_2$;

Applying Avogadro's hypothesis:

2.8 $dm^3$ of $O_2$ will produce 2.8 $dm^3$ of $CO_2$

∴ Volume of $CO_2$ evolved at s.t.p. = 2.80 $dm^3$

**43** Calculate the amount of $H_2S$ required to react completely with 11.2 $dm^3$ of $SO_2$ at s.t.p.

The equation for the reaction is:

$$2H_2S_{(g)} + SO_{2(g)} \rightarrow 2H_2O_{(l)} + 3S_{(s)}$$

[One mole of a gas occupies 22.4 $dm^3$ at s.t.p.]

**A.** 1.0 mole **B.** 1.5 mole **C.** 2.0 mole **D.** 4.0 mole [WAEC]

*Given:* 11.2 $dm^3$ of $SO_2$ at s.t.p; Molar volume at s.t.p.

*Required: To find the amount of $H_2S$*

This is mole-gas volume relationship:

Equation of reaction at s.t.p.:

$$2H_2S_{(g)} + SO_{2(g)} \rightarrow 2H_2O_{(l)} + 3S_{(s)}$$

2 moles 1 mole

22.4 $dm^3$

From the equation of reaction:

22.4 $dm^3$ of $SO_2$ require 2 moles of $H_2S$ at s.t.p

∴ 11.2 $dm^3$ of $SO_2$ = $(2 \times 11.2)/22.4$ of $H_2S$

= 1.0 mole of $H_2S$ at s.t.p.

**44** Magnesium of mass 1.2 *g* reacts completely with chlorine.

a. Write a balanced equation for the reaction.

$$Mg_{(s)} + Cl_{2(g)} \rightarrow MgCl_{2(s)}$$

b. Calculate the volume of chlorine used at s.t.p.

[Molar volume of gas at s.t.p. = 22.4 $dm^3$; Mg = 24.0; Cl = 35.5] [WAEC]

*Given: 1.2 g of Mg. Required: Volume of $Cl_2$ consumed.*
*This is mass – gas volume relationship.*

$Mg_{(s)} + Cl_{2(g)} \rightarrow MgCl_{2(s)}$
1 mol 1 mol.
24 g 22.4 $dm^3$

*From the equation of reaction:*
1 mol of Mg ≡ 1 mol of $Cl_2$
i.e. 24 g of Mg ≡ 22.4 $dm^3$ of $Cl_2$
∴ 1.2 g of Mg ≡ (22.4 × 1.2)/24 $dm^3$ of $Cl_2$
= 1.12 $dm^3$ of $Cl_2$

**45** Calculate the volume of carbon(IV) oxide produced at s.t.p. when 1 kg of potassium hydrogentrioxocarbonate(IV) is totally decomposed by heat. [Molar volume at s.t.p is 22.4 $dm^3$; $KHCO_3$ = 100]
**A.** 28 $dm^3$ **B.** 56 $dm^3$ **C.** 112 $dm^3$ **D.** 196 $dm^3$ [JAMB]

*Given: 1 kg (1000 g) of $KHCO_3$; $M(KHCO_3)$ = 100.*
*To calculate the volume of $CO_2$ liberated at s.t.p.*
This is mass-gas volume relationship.
Equation of reaction at s.t.p:

$2KHCO_{3(s)} \rightarrow K_2CO_{3(s)} + H_2O_{(l)} + CO_{2(g)}$
2 moles 1 mole
2(100 g) = 200 g 22.4 $dm^3$

From the balanced equation of reaction:
200 g of $KHCO_3$ ≡ 22.4 $dm^3$ of $CO_2$
∴ 1000 g (1 kg) ≡ (22.4 × 1000)/200 $dm^3$ of $CO_2$
= 112 $dm^3$ of $CO_2$ at s.t.p.

**46** Bleaching powder reacts with dilute HCl according to the following equation:

$CaOCl_{2(s)} + 2HCl_{(aq)} \rightarrow CaCl_2 + H_2O + Cl_{2(g)}$

Calculate the mass of bleaching powder that will produce 400 $cm^3$ of chlorine at 25 °C and a pressure of $1.20 \times 10^5$ $Nm^{-2}$. [O = 16.0, Cl = 35.5, Ca = 40.0; 1 mole of gas occupies 22.4 $dm^3$ at s.t.p., standard pressure = $1.01 \times 10^5$ $Nm^{-2}$] [WAEC]

*Required: To calculate the mass of $CaOCl_2$ that will produce 400 $cm^3$ of $Cl_2$ under non-standard conditions.*
This is mass-gas volume relationship. First, calculate the volume occupied by 400 $cm^3$ $Cl_2$ at s.t.p.
$P_1 = 1.20 \times 10^5$ $Nm^{-2}$; $T_1 = 25 + 273 = 298$ K;
$V_1 = 400$ $cm^3$
$P_2 = 1.01 \times 10^5$ $Nm^{-2}$; $T_2 = 273$ K; $V_2 = ?$ $cm^3$.
Using the gas equation: $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

Substituting: $\frac{1.20 \times 10^5 \times 400}{298} = \frac{1.01 \times 10^5 \times V_2}{273}$

Making the unknown $V_2$ the subject:

$$V_2 = \frac{1.20 \times 10^5 \times 400 \times 273}{1.01 \times 10^5 \times 298} = 435 \text{ cm}^3$$

i.e. the volume of $Cl_2$ at s.t.p. is 435 $cm^3$.

Now, from the equation of reaction at s.t.p:

$CaOCl_{2(s)} + 2HCl_{(aq)} \rightarrow CaCl_2 + H_2O + Cl_{2(g)}$
1 mole 1 mole
127 g 22.4 $dm^3$

22400 $cm^3$ of $Cl_2$ ≡ 127 g of $CaOCl_2$
∴ 435 $cm^3$ of $Cl_2$ ≡ (127 × 435)/22400 g.
= 2.47 g (3 sig. figures)

## Revision Exercises

[1 mole of a gas occupies 22.4 $dm^3$ at s.t.p.]

**78** Calculate the volume of oxygen at s.t.p. that will be required to burn completely 1 mole of ethene, $C_2H_4$, according to the following equation

$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$

**79** What volume of hydrogen is produced at s.t.p. when 2.60 g of zinc reacts with excess HCl according to the following equation ?

$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2 + H_2(g)$
[Zn = 65] [WAEC]

**80** Consider the following equation:

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

Calculate the mass of sodium required to produce 500 $cm^3$ of hydrogen at s.t.p. [Na = 23]

**81** Calculate the volume of oxygen produced by decomposing 24.5 g of potassium trioxochlorate (V) at stp.

$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$
[K = 39.0; Cl = 35.5, O = 16.0]

**82** 0.0075 mole of calcium trioxocarbonate(IV) is added to 0.015 mole of a solution of hydrochloric acid. The volume of gas evolved at s.t.p. is [JAMB]
**A.** 224 $cm^3$ **B.** 168 $cm^3$ **C.** 112 $cm^3$ **D.** 100 $cm^3$

**83** Calculate the volume of hydrogen that would be liberated by dissolving 2.40 g of calcium in water at 27 °C and 100.0 kN $m^{-2}$

$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$
[Ca = 40.0; O = 16.0; H = 1.0]

## Answer to Revision Exercises

**8a.** 298 K. **b.** 368 K. **c.** 260 K. **d.** 65 K **9a.** 27 °C **9b.** 231 °C **c.** -106 °C **d.** -188 °C **10.** A **12a.** 200 $cm^3$ **12b.** 152 mmHg. **c.** 3y $dm^3$. **d.** 280 mmHg **14.** B **17a.** 160 $cm^3$, **b.** 591 °C **c.** 37.5 $dm^3$ **d.** 0.47 K **18.** 97.0 $cm^3$ **19.** C **22.** 168 $cm^3$ **23.** D **24.** 290 $cm^3$ **26.** A **27.** 207 °C **28.** B **30.** $1.20 \times 10^5$ **31.** 747 mmHg **32a i.** 2.50 atm. **ii.** 2.25 atm, **32b.** 4.75 atm. **34.** C **35a** 100 $cm^3$ **b** 100 $cm^3$ **36.** B **37.** $O_2$; 15.0 $cm^3$ **38.** B **39a** $6.02 \times 10^{23}$ **39b** $6.02 \times 10^{23}$ **40.** $2.69 \times 10^{23}$ **41.** $1.51 \times 10^{23}$ **42.** 8.96 $dm^3$ **43.** B **44.** 0.112 mol. **45.** B **46.** D **47.** B **50.** 1.66 mol. **51.** 1.30 g. **52.** A **53.** C **55.** D **56.** Argon: 0.60 atm; Oxygen: 0.60 atm. **56.** Helium: 0.90 atm. **57.** B **60.** $N_2 < CH_4 < He$ **61.** A **62.** C **63.** 72.0 **64.** C **65.** C **68.** A **70.** D **71.** D **78.** 67.2 $dm^3$ **80.** 1.03 g. **81.** 6.72 $dm^3$ **82.** B **83.** 1.49 $dm^3$

# •BEHAVIOUR OF LIQUIDS AND SOLIDS•

## 11.1 Introduction

When a gas is compressed, then, cooled to a low temperature, it forms a liquid by a process called *liquefaction*; and when the liquid is further cooled, it turns a solid. When a solid is heated to a high temperature, it melts to form a liquid, which boils to form a gas. Therefore, the liquid state is intermediate between the gaseous and solid states.

A substance is a liquid, if its melting point is far below the room temperature of about 25 °C and its boiling point is above 25 °C; while a substance is a solid, if its melting point is well above 25 °C.

**Revision Exercises**

1. Which state of matter is regarded as the intermediate state and why ?
2. A substance X melts at 17 °C. Is it a solid or a liquid at room temperature? Explain.

## 11.2 General Properties of Liquids

The following physical properties of a liquid illustrate its intermediate nature. Each property can be explained by the *kinetic theory*:

1. A liquid, like a solid, but unlike a gas, maintains its volume.

The kinetic theory explains that the cohesive forces between liquid molecules are so strong that there are no spaces between them.

2. A liquid, like a gas, but unlike a solid, has no definite shape; it flows, and takes the shape of the container.

*Kinetic theory explanation*: Although the attractive forces between the particles are strong, the average kinetic energy of the particles is enough to make them mobile; i.e. the particles have no fixed positions, and can regroup together. Hence, a liquid flows, and can be poured from one container into another.

3. Liquids, like solids, are incompressible.

Kinetic theory explains that liquid particles are always in close contact, with virtually no space between them; hence, they have high density, and cannot be compressed – unlike gases that are easily compressed.

4. As in gases, liquid particles are in motion, but slowly. They can *rotate* and *vibrate*, but cannot *translate*.

When finely divided particles of a solid, such as pollen grains, that are suspended in a liquid are viewed under a microscope, they move about randomly and continuously, due to the continuous collisions with the particles of the liquid. This is the ***Brownian motion*** in a liquid.

5. Like gases, liquid particles diffuse, but slowly.

This is because the average kinetic energy of the particles is enough to keep them in a slow motion. Hence, it is possible for two liquids, such as water and alcohol, to mix in any proportion.

6. Liquid molecules undergo ***evaporation***; a process in which liquid particles *change into vapour before it boils*. It is a *surface* phenomenon.

*Evaporation* is possible in a liquid, since the particles at the surface can easily acquire enough kinetic energy to overcome the intermolecular attractive forces, and hence, change into vapour.

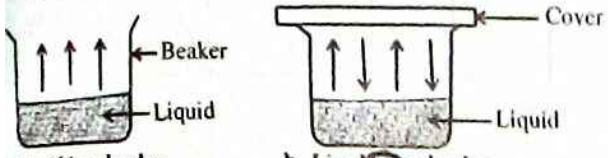
Compared with the gaseous state, there is more orderliness among the liquid particles.

**Revision Exercises**

3. State **three** physical properties of a liquid.
4. List **two** properties of liquids that are
   a. different from those of gases.
   b. similar to those of gases.
5. Explain why the entropy of a liquid is less than that of a gas.

## 1.3 Evaporation of a Liquid

vaporation in a liquid occurs when the particles at e surface change into vapour, once they have ough kinetic energy to do so.




a. *Liquid in a beaker without a cover*

b. *Liquid in a beaker with a cover*

Fig 11.1

This phenomenon can be demonstrated by observing the level of a liquid, such as methylated spirit, placed in a beaker at room temperature (fig 11.1a). With time, the liquid level continues to fall, until the beaker becomes empty.

***Kinetic Theory Explanation***:

In liquids, as in gases, the particles at a given temperature $T_1$ have different kinetic energies – ranging from very low to very high values (fig. 11.2). The particles at the surface with enough kinetic energy to overcome the intermolecular attractive forces escape as vapour.

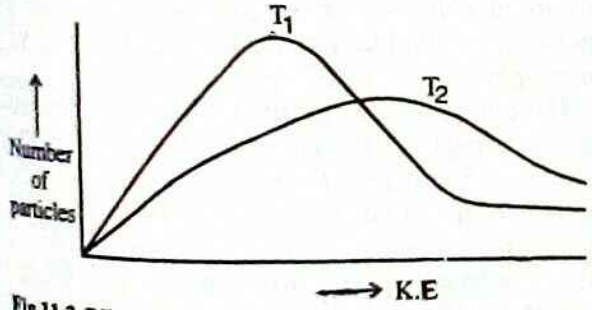



Fig 11.2 *Effect of temperature on the kinetic ecergy of gases*

As the highly energetic particles leave the liquid, there is a decrease in the average kinetic energy of the rest; leading to a fall in the temperature of the remaining liquid. Hence, cooling accompanies evaporation.

The process of evaporation continues steadily at a particular temperature, until no liquid remains.

Evaporation process can be represented by word equation:

**LIQUID + HEAT → VAPOUR**

That is: when liquid particles *absorb* enough heat, they vapourize. It is an endothermic physical change

**Solved Problems**

1. Evaporation causes cooling. Explain.

*When liquid particles evaporate, they escape with some heat energy, thereby, lowering the average kinetic energy of the remaining particles. Under this situation, the temperature falls, and cooling takes place.*

2 Which of the following properties of a liquid increases when vapourized?

A. Randomness. B. Density. C. Boiling point. D. Intermolecular forces. [WAEC]

Solution: A

**Revision Exercises**

6. Give two characteristic features of evaporation.
7. By the use of word equation, illustrate the process of evaporation.
8. In terms of kinetic energy, explain the process of evaporation.

## 11.4 Equilibrium Vapour Pressure

### Dynamic Equilibrium

When a glass cover is placed on a beaker half-filled with a liquid and kept at a constant temperature $T_1$, the liquid level falls for a while, then, becomes constant (see fig. 11.1b).

***Explanation:*** At a constant temperature $T_1$, evaporation takes place at the surface at a constant rate; hence, the liquid level falls. This process can be represented thus:

**LIQUID + HEAT → VAPOUR**

Since the beaker is covered, there is no chance for the vapour particles to escape. As expected, the vapour particles continuously collide with each other, and those particles with low kinetic energies start to condense and form liquid during collisions. Their number increases as collision rate increases. The process of condensation can be represented thus:

**VAPOUR → LIQUID + HEAT**

With time, a situation is reached in which the rates of evaporation and condensation become the same. Under this condition, there is equilibrium between the liquid and its vapour; the liquid level becomes constant.

At equilibrium, the two opposing processes continue at the same rate. The system at this point is at a ***physical dynamic equilibrium***.

The state of dynamic equilibrium is represented as:

**LIQUID + HEAT ⇌ VAPOUR**

**Saturated Vapour Pressure**

Vapour particles in a closed container exert pressure, being gaseous. *The pressure exerted by the vapour when in equilibrium with its liquid is called* ***saturated vapour pressure.***

The magnitude of the vapour pressure is independent of the quantity of liquid in the container. It depends only on its *nature* and its *temperature.*

1. ***Nature of liquid***: Every liquid has its characteristic intermolecular forces. For instance:

- In *non-polar covalent liquids*, such as petrol, the only intermolecular forces between the particles are the *weak van der Waals forces;*
- Those between the *polar covalent molecules*, such as water and alcohols are the combined *van der Waal's forces, dipolar forces, and hydrogen bonds*, which make them stronger;
- *Interionic forces between ionic liquids*, such as molten sodium chloride are *the strong ionic bonds.*

Liquid particles with *weak cohesive forces* evaporate readily; it results in a ***high*** *vapour pressure*, e.g. the vapour pressure of *ether* at 20 °C is 60.0 $kNm^{-2}$. Such liquids are said to be *volatile.*

Liquid particles with *strong cohesive forces* evaporate slowly or are *non-volatile*, e.g. the vapour pressure of water at 20 °C is 2.30 $kNm^{-2}$.

Generally, the magnitude of the vapour pressure of a liquid at a particular temperature is a measure of the cohesive forces between the particles.

2. ***Temperature***: A temperature change means a change in the average kinetic energy of the liquid.

Generally, a *rise* in the temperature of a liquid *increases* the average kinetic energy of the particles and *increases* the number of particles capable of escaping (see figure 11.2). Consequently, there is an increase in the *saturated vapour pressure.*

**Revision Exercises**

**9** Explain the term *saturated vapour pressure.*

**10** Mention *two* factors that affect the vapour pressure of a liquid.

**11** In terms of kinetic theory, explain the effect of an increase in temperature on saturated vapour pressure.

**12** Explain why petrol is more volatile than water.

## 11.5 Boiling Points of Liquids

### Variation of Vapour Pressure with Temperature

The variation of *vapour pressures* of a liquid with *temperatures* shows that *rise* in temperature leads to an *increase* in the vapour pressure, first slowly, then, steeply (see fig 11.3).

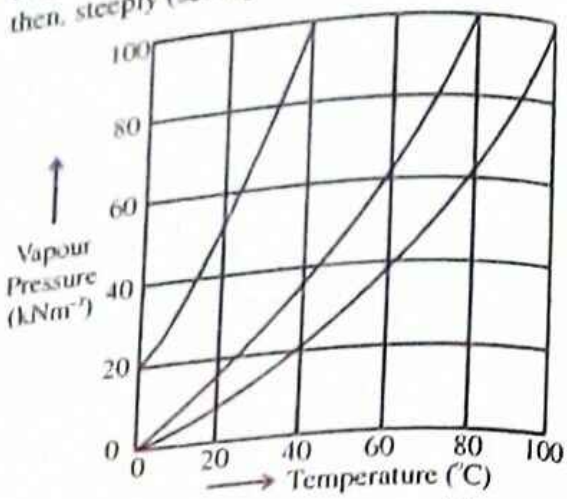



**Fig 11.3** *Variation of vapour pressure with temperature*

When a liquid is heated in a container, there is a gradual increase in the average kinetic energy of the particles; with time, the liquid starts to evaporate. *When the vapour pressure of the liquid is the same as the atmospheric pressure, the liquid boils.*

**Normal Boiling Point**

The *normal boiling point of a liquid* is *the temperature at which the vapour pressure of the liquid is equal to the standard atmospheric pressure of one atmosphere,* $1.01 \times 10^5 Nm^{-2}$.

The *normal boiling point of a liquid* is a measure of the strength of the cohesive forces between the particles. The *higher the normal boiling point, the stronger the cohesive forces between the particles.* For instance: the *normal* boiling of water is 100 °C, that of ethanol is 78 °C, while that of ethoxyethane (*ether*) is 35 °C.

**Boiling Points at Non-Standard Pressures**

A liquid can boil at any temperature, by altering the *external* pressure. *At a pressure lower than the atmospheric pressure, a liquid boils at a lower temperature, and vice versa.*

At atmospheric pressure, water boils at 100 °C. When the external pressure is *lower* than one atmosphere (on top of Mount Everest, where the pressure is 0.5 atmosphere, or on the moon), water boils at a *lower* temperature. In fact, a liquid can be made to boil at room temperature, without heating, by drastically reducing the external pressure.

Organic liquids that will decompose before their *normal* boiling points are usually purified in the laboratory by *distillation under reduced pressures.*

The operation of a '*pressure cooker*' in the kitchen is based on the principle that at a *high pressures*, water boils at a temperature *higher* than 100 °C, in order to quicken the cooking process. When water is *superheated* (at a high pressure), it boils at about180 °C.

**Differences between a gas and a vapour**

1. A *gas* is single in composition, while a *vapour* is a mixture of a gas and a liquid.
2. A *vapour condenses more readily than a gas.*

**Solved Problem**

3. Water cannot cook beans on the moon. Explain

*The boiling point of water depends on the external pressure. On the moon, the external pressure is quite low; hence, water boils at a lower temperature than its normal boiling point of 100 °C at atmospheric pressure.*

*Since beans require prolonged cooking in boiling water, it cannot cook beans on the moon, where it starts to boil when it is just warm.*

**Revision Exercises**

13 Define the term *normal boiling point.*

14 Give one difference between *a gas* and *a vapour.*

[WAEC]

## 11.6 Evaporating and Boiling

*Evaporation* and *boiling* are similar physical processes: both involve a change from *liquid to gaseous state*. They differ in the following respects:

1. *Evaporation* occurs only at the surface of a liquid, while *boiling* occurs in the entire body, accompanied by bubbles.
2. *Evaporation* occurs at all temperatures, while *boiling* occurs only at a temperature in which the vapour pressure of the liquid equals the atmospheric pressure.
3. *Evaporation* causes cooling and a *decrease* in the entropy of the system, while *boiling* causes heating and an *increase* in the entropy of the system.

**Revision Exercises**

15 List *two* characteristic features of boiling.

16 State ***one*** similarity and ***one*** difference between boiling and evaporation.

## 11.7 Critical Temperature and Pressure

The ***critical temperature*** of a liquid is the highest temperature at which it can exist as a liquid, or at which a gas can be liquefied. Above the critical temperature, a liquid does not exist, or a gas cannot be liquefied readily.

The *pressure* required to liquefy a gas at the *critical temperature* is called the **critical pressure**, while the *volume occupied by one mole of a gas at critical temperature and pressure is the* **critical volume**. Water has a critical temperature of about 370 °C.

**Revision Exercises**

17 Define: a. *Critical* temperature. b. *Critical* volume c. *Critical* pressure.

## 11.8 General Properties of Solids

The following are the characteristic properties of solids; they can be explained by the kinetic theory:

1. Solids, like liquids, but unlike gases maintain their volumes; hence, has definite mass.
2. Solids, unlike liquids and gases, have definite shapes. They do not flow.
3. Solids are practically incompressible.

***Explanations:*** The definite shape and volume, and the incompressibility of solids indicate that solid particles are in close contact with one another and in fixed positions, due to the *strong cohesive forces between the particles.*

4. Solid particles can only *vibrate* about their fixed positions. This vibratory motion depends on the kinetic energy, and hence, on the temperature of the solid. At high temperature, the kinetic energy is high and the vibratory motion is very strong, and vice versa.
5. Solid particles can diffuse, but rather slowly, due to the weak vibratory motions of the particles.

In solid state, the particles are in the *most ordered state*; hence, *the entropy is the lowest.*

**Revision Exercises**

18 List three physical properties of a solid.

19 State two properties of solids that are
   a. different from those of liquids.
   b. similar to those of liquids.

20 All the following properties are true of solids **EXCEPT** that it
   A. cannot be compressed. B. does not evaporate.
   C. has a definite weight. D. has a definite shape.
   E. has definite volume. [NECO]

## 11.9 Types of Solids

### Crystalline and Amorphous solids

There two types of solids: *crystalline* and *non-crystalline* (*amorphous*).

1. ***Crystalline solids*** are made up of particles that are *orderly* arranged to give a regular geometry. The crystals have sharp and definite melting points. Sodium chloride and most ionic compounds are *crystalline* solids.

2. ***Amorphous solids*** are made up of particles that are not orderly arranged; hence, shapeless and with non-definite melting and boiling points. Examples are paraffin wax and glass.

### Attractive Forces in Crystals

The five types of attractive forces that hold matter in solid state are: *ionic, covalent, metallic, van der Waals, and hydrogen bonds*. These attractive forces give rise to four classes of solid crystals: *ionic, covalent, metallic and molecular*.

1. ***Ionic crystals*** are made up of positive and negative ions, that are bonded together by the strong electrostatic forces of attraction called *ionic* bonds. Examples are sodium chloride and calcium oxide.

2. ***Covalent crystals*** are made up of atoms that are chemically bonded by the strong highly directional covalent bonds that lead to the formation of *macromolecules*. Examples: diamond, graphite and silica (sand, $SiO_2$).

3. ***Metallic crystals*** are composed of positively charged atomic nuclei bonded together by a sea of mobile electrons (*electron cloud*). Examples are: sodium, iron, silver and aluminium.

4. ***Molecular crystals*** are composed of molecules that are held together by the *extremely weak van der Waals forces* – as in *non-polar* molecules, such as liquid air, oxygen and hydrogen; solid iodine, sulphur and carbon(IV) oxide; and the *hydrogen bonds* – as in *polar* molecules, such as water, alcohols, and ammonia.

### Revision Exercises

21 List three types of cohesive forces that exist in solids

22 Which of the following exists as a molecular solid?

A. Silica B. Sodium C. Iodine D. Diamond

## 11.10 Changes of State: Entropy Change

### Definition

*Entropy* describes the *disorderliness* in a system. At absolute zero temperature (0 K) a solid has zero entropy; that is, no disorder, and no motion. A rise in temperature from absolute zero increases the average kinetic energy of the particles, and at the same time, increases the entropy.

By way of comparison, a solid has lower entropy than a liquid, while a gas has the highest entropy. When a solid, which is composed of particles that are ordered, is heated, it melts to form a liquid composed of particles that are more disordered. On further heating, a liquid becomes a gas, which is composed of completely disordered particles. These conversions represent *changes of states*.

### Heating Curves

A *heating curve* describes the variation of temperature with time as heat is uniformly added to a solid. When a solid X at 0 °C and time $t_o$ is heated, there is a gradual increase in the average kinetic energy of the particles; the heat absorbed increases the *vibratory motion* of the particles as the temperature rises from time $t_o$ to $t_1$.

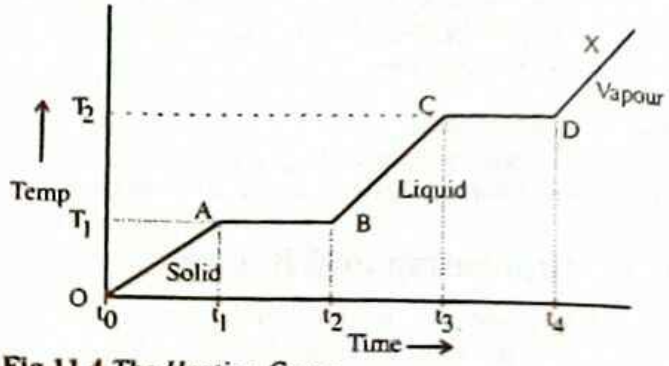



**Fig 11.4** *The Heating Curve*

At time $t_1$, the heat absorbed increases the potential energy of the particles, in order to overcome the attractive forces and change the solid into a liquid. The average kinetic energy does not change during this period; hence, the temperature $T_1$ remains constant from time $t_1$ to $t_2$ represented by the horizontal line **AB**. The temperature $T_1$ at which the solid and liquid *co-exist* is called ***melting point***. Hence, melting occurs at a constant temperature; the process is endothermic, and represented as:

$$\text{SOLID} + \text{HEAT} \rightleftharpoons \text{LIQUID}$$

The *heat that must be absorbed in order to convert one mole of a solid into a liquid, at its melting point*, is called the ***molar (latent) heat of fusion***.

At time $t_2$ all the solid particles have been converted into liquid. The heat absorbed by the liquid increases the average kinetic energy of the particles; hence, the temperature rises from time $t_2$ to $t_3$. At time $t_3$ the heat absorbed increases the potential energy of the particles, in order to overcome the intermolecular attractive forces and change the liquid to gas. The average kinetic energy re-

mains constant; hence, the temperature at $T_2$ does not change from time $t_3$ to $t_4$ represented by the horizontal line CD. The temperature $T_2$ at which the liquid and gas *co-exist* is called the ***boiling point***. Hence, at boiling point, the temperature is constant; the process is endothermic, and can be represented thus:

$$\text{LIQUID} + \text{HEAT} \rightleftharpoons \text{GAS}$$

*The heat that must be absorbed in order to convert one mole of a liquid into a gas at its boiling point* is called ***molar (latent) heat of vaporization.***

At time $t_4$ the conversion of the liquid into gas is complete. The heat absorbed increases the average kinetic energy of the particles; hence temperature rises.

### Cooling Curve

A *cooling curve*, like the *heating curve*, describes the variation of temperature with time, but in an exactly opposite manner.

When heat is uniformly removed from a gaseous substance **X**, the average kinetic energy of the particles decreases and the temperature falls from time $t_0$ to $t_1$.

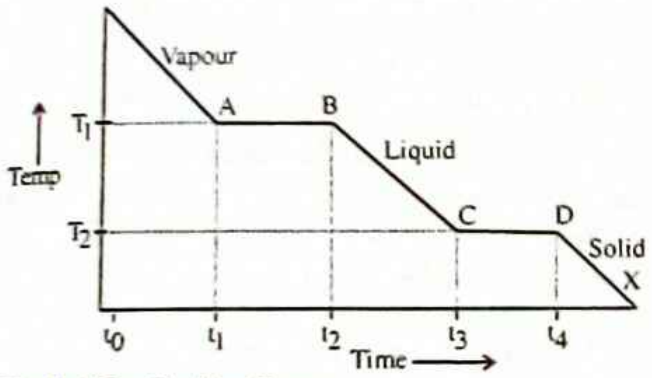



**Fig 11.5** *The Cooling Curve*

At time $t_1$ the heat lost by the gas molecules is used to lower the potential energy of the particles, in order for the attractive forces to act on them and convert the gas to liquid. Since the average kinetic energy does not change, the temperature at $T_1$ remains constant from time $t_1$ to $t_2$ ( line **AB**). This temperature is called ***condensation or liquefaction point***. The process is exothermic, and the opposite of *vaporization*.

$$\text{GAS} \rightleftharpoons \text{LIQUID} + \text{HEAT}$$

At time $t_2$, the gas particles have changed completely into liquid. Further cooling only decreases the average kinetic energy of the particle; hence, the temperature falls between time $t_2$ and $t_3$.

At time $t_3$, the energy released to the surrounding is due to a decrease in the potential energy of the particles, in order to allow the liquid particles to arrange themselves into a regular geometry and form crystals. During this conversion, the average kinetic energy remains constant; hence, the temperature at $T_2$ is also constant from time $t_3$ to $t_4$, represented by the line **CD**.

The temperature $T_2$ at which the liquid and solid *co-exist* is called the ***freezing point***. The process is exothermic. It is the opposite of *melting or fusion*.

$$\text{LIQUID} \rightleftharpoons \text{SOLID} + \text{HEAT}$$

At time $t_4$, only the solid exists. Further cooling decreases the average kinetic energy; hence, the temperature falls.

### Solved Problem

**4.** Explain why the human body experiences a cooling sensation when methylated spirit touches the skin.

*When methylated spirit, a highly volatile liquid, touches the skin, its molecules draw the heat of vaporization from the body to cause evaporation. Hence, as the molecules evaporate, the body temperature falls, thereby, causing the cooling of the body.*

### Revision Exercises

**23** In terms of equilibrium state, define the following:
a. Melting point; b. Boiling point; c. Freezing point.

**24** At which point does a liquid and solid exist at equilibrium?
**A.** Boiling **B.** Evaporation **C.** Melting
**D.** Sublimation. **E.** Evaporation [NECO]

**25** Use the heating curve of a solid **X** in figure 11.4 to answer the following questions.
a. What is the melting point of **X**?
b. If the vapour of **X** is cooled, at what temperature will it start to condense?
c. As **X** is heated, state what happens to the:
i. frequency of collision of the particles of **X**.
ii. value of entropy of the system.

**26** What is *latent heat of vaporization*?

## 11.11 Comparing Forces of Attraction in Solids

### Melting and Boiling points of Solids

Physical properties, such as volatility, melting and boiling points of a solid depend on the strength of the forces of attraction between the atoms, molecules, or ions that make up the solid.

In an ionic solid, such as sodium chloride, NaCl,

forces of attraction between the opposite ions are so strong that a large amount of heat must be absorbed before the ions can vibrate vigorously, overcome the *inter-ionic* forces, and form a liquid.

In the molten ionic liquid, the strong *inter-ionic* forces still persist between the opposite ions. Hence, ionic solids are hard, non-volatile, have high melting and boiling points, and high molar heats of fusion. They are good conductors of heat and electricity in molten state. *The large difference between the melting point and the boiling point is due to the stronger cohesive forces between the liquid particles than between the solid particles.*

In molecular solids, such as iodine, sulphur, camphor and naphthalene, the *intermolecular forces are the weak van der Waals forces*, which are so weak that relatively small amount of heat makes the molecules to vibrate vigorously for the solid to sublime. Hence, molecular solids are soft, volatile, with low melting points, and low molar heats of vaporization. They are non-conductors of heat and electricity in solid or in molten state, since they are composed of molecules.

## Solubility of Solids in Liquid Solvents

The solubility of a solid in a liquid depends on the *nature (polarity) of the solid* and the *polarity of the liquid*.

- An ionic solid, being polar, will dissolve in a polar liquid. *Like dissolves like*. For instance: NaCl, an *ionic* solid, dissolves in water, a *polar* solvent, to produce hydrated ions. Hence, the resulting solution is an electrolyte:

$$NaCl_{(s)} + H_2O_{(l)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$

- A non-polar solid will dissolve in a non-polar liquid. *Like dissolves like*. For instance: iodine, a molecular solid, is soluble in non-polar solvents such as benzene and alcohol; but the resulting solution is a non-electrolyte.
- An ionic solid will not dissolve in a non-polar liquid. For instance: sodium chloride will not dissolve in petrol, kerosene, or benzene.
- A molecular solid will not dissolve in a polar liquid. For instance: iodine will not dissolve in water.

### Revision Exercises

**37** Explain the following observations.

a. Calcium oxide has a higher melting point than sulphur.
b. Iodine crystals are soluble in benzene but insoluble in water.
c. Electrovalent liquids have higher boiling points than covalent liquids.
d. Benzene is miscible with ethanol but immiscible with water.

## Answers to Revision Exercises

**20.** A **22.** C **24.** C

# 12

# •AIR AND AIR POLLUTION•

## 12.1 Composition of Air

The earth is completely enveloped in a blanket of air, which is referred to as the *atmosphere*. The chief natural gaseous constituents of air and their percentage compositions by volume are as follow:

| Constituent | % by Volume |
|---|---|
| Nitrogen | 78.1 |
| Oxygen | 20.9 |
| Noble (or rare) gases | 1.0 |
| Carbon(IV) oxide | 0.03 |
| Water vapour | *Variable* (0 – 1.2) |

Generally speaking, nitrogen accounts for about 4/5 of the atmosphere by volume, while oxygen occupies the remaining 1/5.

**Revision Exercises**

1. Which of the following gases makes up the largest percentage of the atmospheric air?
   A. Carbon (IV) oxide. B. Hydrogen. C. Nitrogen. D. Noble gases E. Oxygen. [NECO]
2. Which of the following is not a natural component of the atmosphere?
   A. Water vapour B. Carbon(II) oxide C. Nitrogen D. Carbon(IV) oxide [WAEC]

### Oxygen in the Atmosphere

Oxygen constitutes about 21% by volume of air, and is the most active component of air. It supports *life*. It is responsible for the ***rusting*** *of iron* and *burning* (***combustion***) of a substance in air.

**Determination of proportion of Oxygen in Air**

The following experiments can be used to determine the proportion of oxygen in air, and to show that oxygen supports combustion.

#### 1. *Burning of Phosphorus in Air*

Phosphorus is a very reactive solid non-metal. It burns readily in oxygen to give an oxide.

$$4P_{(s)} + 5O_{2(g)} \rightarrow 2P_2O_{5(s)}$$

**Procedure**

a. Fill a graduated glass tube with pure water, and invert into a trough of water. Adjust the water level in the glass tube, so as to be the same as the water level in the trough. Allow the air inside the tube to be saturated with water vapour, then, note the *volume of air* enclosed above the water level in the tube ($x$ cm$^3$).

b. Carefully introduce into the tube, a piece of yellow phosphorus on a wire (see fig. 12.1).

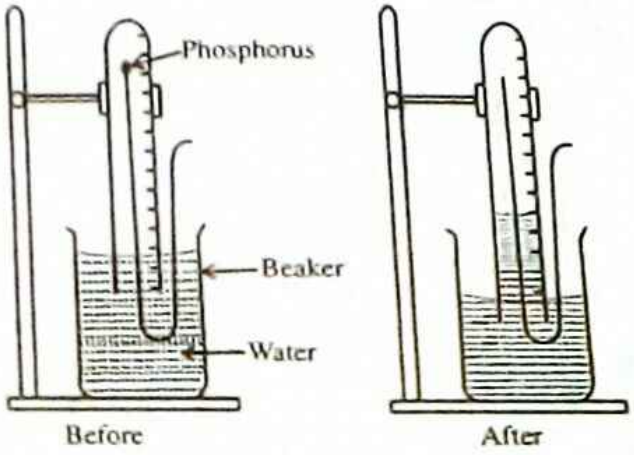



Fig 12.1 *Burning of Phosphorus in Air*

As the phosphorus smolders, the water level in the glass tube rises, until oxygen in the enclosed air has been used up, leaving nitrogen, carbon(IV) oxide, and the noble gases.

c. When the phosphorus ceases to smolder, remove it. Then, carefully adjust the water levels in and outside the glass tube until they are the same. Read the *volume of mixture gases* left ($y$ cm$^3$).

d. The volume of oxygen used up is $(x - y)$ cm$^3$

e. The percentage of oxygen in air will be:

$$\frac{(x-y)}{x} \times \frac{100}{1}\%$$

f. Within the limit of experimental error, the percentage of oxygen by volume will be about 20.0%.

#### 2. *Use of Alkaline Pyrogallol Solution*

*Alkaline pyrogallol* is a solution of *pyrogallol* in sodium hydroxide solution. It absorbs oxygen readily.

**Procedure**

a. Put a few drops of alkaline pyrogallol solution in a graduated glass tube, and cover it with an airtight glass. Then, shake the set-up for a while.

b. With care, invert it over the water in a trough; then, remove the glass cover.

**Observation:** *The water-level rises in the glass tube as the alkaline pyrogallol absorbs the oxygen enclosed.*

The volume of water inside the tube corresponds to the volume of oxygen absorbed. It will be about 20% by volume of the air enclosed initially.

### 3. *Burning of Candle in Air*

a. Invert a gas jar over a burning candlestick placed in a trough of water. Note the level of water in the jar (see fig. 12.2).

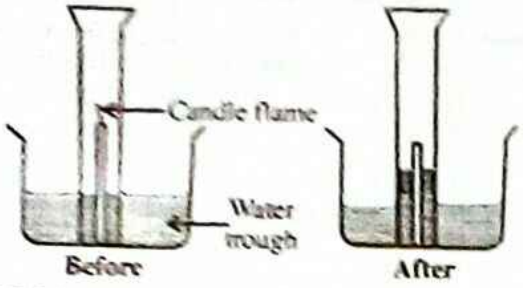



**Fig 12.2** *Burning of Candle in Air*

**Observation:** *The water level falls initially, due to the expansion of air in the jar, then, starts to rise. When all the oxygen has been used up, the candle goes out.*

b. Note the rise in the level of water. This is the volume of oxygen in the volume of air enclosed. It will be about 20.0% by volume of the total air enclosed initially (see figure 12.2).

These experiments show that oxygen is the only reactive component of the atmospheric air.

### Worked Example 1

What volume of air would be required for the complete combustion of 15.5 *g* of phosphorus to phosphorus(V) oxide at s.t.p?

[O = 16; P = 31; Air is 20% oxygen by volume; Molar volume of gas at s.t.p. is 22.4 $dm^3$]

**Solution**

Given: 15.5 *g* of phosphorus.

*To find the volume of pure oxygen required for the complete combustion of 15.5 g of phosphorus*

This is mass-gas volume relationship.

Equation of reaction at s.t.p.:

$$4P_{(s)} + 5O_{2(g)} \rightarrow 2P_2O_{5(s)}$$
$$(4 \times 31)\ g \quad (5 \times 22.4)\ dm^3$$
$$124\ g \quad 112\ dm^3$$

From the equation: At s.t.p.

124 g of phosphorus require 112 $dm^3$ of oxygen

∴ 15.5 g of phosphorus will require

$(15.5 \times 112)/124\ dm^3 = 14.0\ dm^3$ of $O_2$

*To find volume of air that will contain 14.0 $dm^3$ of $O_2$*

20 $dm^3$ of oxygen is in 100 $dm^3$ of air;

∴ 14 $dm^3$ of oxygen will be in $(14 \times 100)/20\ dm^3$
$= 70.0\ dm^3$ of air

Hence, volume of air required = 70.0 $dm^3$

### Revision Exercises

3. Name a solution that can be used to detect the presence of oxygen in the atmosphere.

4. A quantity of air was passed through a weighed amount of alkaline pyrogallol. An increase in the weight of the pyrogallol would result from the absorption of

A. nitrogen B. neon C. argon D. oxygen

5. Calculate the volume of air required to produce 35.0 *g* of phosphorus(V) oxide during the combustion of an excess of phosphorus.

[O = 16; P = 31. All gas volumes measured at the same temperature and pressure. Air is about 20% oxygen by volume.]

## Carbon(IV) oxide in the Atmosphere

1. Carbon(IV) oxide is about 0.03% by volume of atmospheric air.

2. The presence of carbon(IV) oxide in air is due to its *production* by the following processes:

a. Combustion of fuels containing carbon – such as wood, coke, coal, coal gas, kerosene, and petrol.

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$

b. *Respiration* processes in plants and animals. Carbon(IV) oxide is breathed out by animals.

c. All decaying processes.

d. Fermentation process.

3. Carbon(IV) oxide is being *removed* from the atmosphere continuously by the process of *photosynthesis*. During this process, green plants absorb carbon(IV) oxide from air to synthesize sugars.

4. These two opposing processes of *production* and *consumption* of carbon(IV) oxide keep its percentage approximately constant in the atmosphere.

5. The presence of $CO_2$ in the atmosphere can be detected by passing air into ***lime-water*** [solution of calcium hydroxide, $Ca(OH)_2$] (see fig. 12.3).

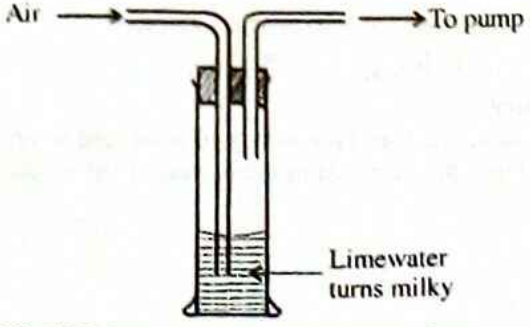



**Fig 12.3** *Testing for $CO_2$ in the atmosphere*

*The limewater turns milky, due to the formation of insoluble calcium trioxocarbonate (IV), $CaCO_3$.*

$Ca(OH)_{2(aq)} + CO_{2(g)} \rightarrow CaCO_{3(s)} + H_2O$
(colourless) (white)

**Note:** *Caustic potash*, a concentrated water-solution of KOH, will also remove $CO_2$ from air.

**Worked Example 2**

Calculate the volume of air required to produce 200 $cm^3$ of carbon(IV) oxide during the combustion of an excess of coke. [All gas volumes measured at the same temperature and pressure. Air is about 20% oxygen by volume]

*To find the volume of pure oxygen required to produce 200 $cm^3$ of $CO_2$*

This is gas volume-gas volume relationship.

Equation of reaction: $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$
Mole ratio: 1 mole 1 mole
Avogadro's law: 1 volume 1 volume

From the equation:
1 $cm^3$ of $CO_2$ requires 1 $cm^3$ of pure $O_2$
∴ 200 $cm^3$ of $CO_2$ require 200 $cm^3$ of pure $O_2$
But 20 $cm^3$ of pure oxygen is in 100 $cm^3$ of air
∴ 200 $cm^3$ of oxygen is in $(100 \times 200)/20 = 1000$ $cm^3$
Hence, volume of air required = 1000 $cm^3$

**Revision Exercises**

6. What is the percentage by volume of carbon(IV) oxide in the atmosphere?
7. When air is passed through alkaline pyrogallol and then potash, the major gases left are
   A. nitrogen and carbon (IV) oxide.
   B. nitrogen and oxygen. C. the noble gases.
   D. nitrogen and the noble gases. [WAEC]
8. Mention **one** process, apart from respiration, which increases the amount of carbon(IV) oxide in the atmosphere.
9. List **two** substances that can be used to remove carbon(IV) oxide from a sample of air.
10. Calculate the volume of carbon(IV) oxide released when 30 $dm^3$ of air was passed over an excess of red hot coke.
    [All gas volumes measured at the same temperature and pressure. Air is about 20% oxygen by volume].

## Water Vapour in Air

1. The quantity of water vapour in the atmosphere varies; depending on the season and geographical location.
2. The presence of water vapour or moisture in the atmosphere is due to the *evaporation* of water from the oceans, rivers, lakes, seas, and water reservoirs.
2. Its presence can be detected by exposing a substance that absorbs moisture from the atmosphere, e.g. fused $CaCl_2$, or pellets of NaOH (or KOH).

**Revision Exercise**

11 When air is passed through a tube containing fused calcium chloride, the component that is absorbed is
   A. carbon (IV) oxide B. nitrogen C. oxygen
   D. water vapour E. noble gases

## Noble (Rare) Gases

1. The atmospheric air is about 1.0% by volume of noble gases; although they are chemical inactive.
2. *Argon* is the most abundant noble gas in air; then, neon.
3. *Helium* is used in filling balloons; being very light, and does not support combustion. A mixture of helium and oxygen is used by sea divers.
4. Helium, neon and argon lights are used in advertising electrical signs; they produce beautiful colours. Neon light is used in aerodrome beacons, because of its high fog penetration.
5. Argon is used in gas-filled electric bulbs, since it retards vapourisation and prevents oxidation of bulb filament.
6. A mixture of krypton and xenon is used in photographer's flash tube, for high-speed pictures.
7. Radon is radioactive; its radiation is used in the treatment of cancer.

**Worked Example 3**

25 $cm^3$ of a mixture of noble gases was obtained from air after the removal of other constituents. What was the original volume of air? [JAMB]

*To find the volume of air that would contain 25 $cm^3$ of noble gases*

100 units volume of air contain 1 unit volume of noble gases.
i.e. 1 $cm^3$ of noble gases is in 100 $cm^3$ of air.
25 $cm^3$ of noble gases will be in $(100 \times 25)/1$ $cm^3$
= 2500 $cm^3$

**Revision Exercises**

12 Calculate the volume of oxygen that would be present in 1.25 $dm^3$ of atmospheric air.
13 Mention **one** use of: **a.** argon **b.** krypton.
14 Which property of helium makes it suitable for filling balloons?
15 The mixture of gases used in a photographer's flash tube is
   A. argon and krypton B. krypton and xenon
   C. helium and argon D. argon and xenon
   [JAMB]

## Impurities in Air

1. The chief gaseous impurities in air are:
   - Hydrogen sulphide, $H_2S$;
   - Sulphur(IV) oxide, $SO_2$;
   - Carbon (II) oxide, CO.

2. Soot (fine carbon particles) and dust particles are the main solid impurities in air.

Dust particles in the atmosphere cause the condensation of water vapour; for the cloud to give up its water as rain.

**Revision Exercises**

16 Mention two gaseous and one solid impurity in the atmosphere.

17 Which of the following is an impurity in air?
A. $H_2O$ B. $CO_2$ C. CO D. $O_2$ E. $N_2$

## 12.2 Air as a Mixture

The following observations could be used to conclude that air is a mixture, and not a compound.

1. The composition of air varies from one place to another, depending on the humidity. It is only approximately constant; it does not obey the law of constant (or definite) composition.

2. If nitrogen, oxygen and carbon(IV) oxide are mixed together, there is no volume change, no explosion, and no sign of any chemical reaction.

3. Air can be separated into its main constituents by fractional distillation of liquid air.

4. There is no chemical formula to express the composition of air.

### Air dissolved in water

1. The presence of dissolved air in all sources of water explains why water is regarded as a mixture. That dissolved gases are in water can be demonstrated by heating a beaker containing tap water or well water. Bubbles of gas can be seen being formed on the sides of the beaker before boiling occurs.

2. The percentage composition by volume of dissolved air in water is as follows.

| Constituent | % by Volume |
|---|---|
| Nitrogen | 63.9 |
| Oxygen | 33.2 |
| Carbon(IV) oxide | 2.9 |

- The higher percentage of oxygen in water than in air shows that oxygen is more soluble in water than in air.
- Air boiled out of water as steam is richer in oxygen and carbon(IV) oxide than atmospheric air.

3. In stagnant water bodies, such as ponds, lakes, and reservoirs, the percentage of dissolved oxygen may be more than 35%, due to photosynthesis in aquatic plants.

4. The presence of dissolved air in water provides gases that sustain the lives of aquatic plants and animals, e.g. algae, fishes, and crabs.

**Revision Exercises**

18 List three reasons why air is regarded as a mixture.

19 Which gas is responsible for the survival of living things in water?

20 Air boiled out of water as steam is richer in
A. nitrogen and oxygen
B. carbon(IV) oxide and oxygen
C. noble gases and carbon (IV) oxide
D. oxygen and noble gases. [JAMB]

## 12.3 Exposure of Certain Substances to Ordinary Air

When certain substances are *exposed* to the atmosphere, they either ***gain*** or ***lose*** weight. The three categories of substances are:

### 1. Deliquescent Substances

These are compounds that usually absorb moisture from the atmosphere and form a saturated solution. Such a compound is said to be ***deliquescent***.

Deliquescent compounds ***gain weight***, when exposed to the atmosphere, e.g. fused $CaCl_{2(s)}$, $FeCl_{3(s)}$; pellets of $NaOH_{(s)}$ or $KOH_{(s)}$, and $P_2O_{5(s)}$.

### 2. Hygroscopic Substances

These are substances that usually absorb moisture from the atmosphere without forming a solution. Such a substance is said to be ***hygroscopic***.

Hygroscopic solids *gain* weight when exposed to the atmosphere, e.g. NaCl, CaO, CuO, fresh iron nails, and $CuSO_4$ (anhydrous).

*Concentrated* $H_2SO_4$ is a hygroscopic liquid. It absorbs moisture from the atmosphere to form a *dilute* solution.

### 3. Efflorescent Substances

These are crystalline compounds, which, on being exposed usually *lose* their water of crystallization to the atmosphere. They are said to be *efflorescent*.

The commonest *hydrated* compound, which is efflorescent is $Na_2CO_3 \cdot 10H_2O$. On exposure, the crystals lose their water molecules to the atmosphere to form powdered *anhydrous* compound, $Na_2CO_3 \cdot H_2O$.

$$Na_2CO_3 \cdot 10H_2O_{(s)} \xrightarrow{\text{Exposure to air}} Na_2CO_3 \cdot H_2O_{(s)} + 9H_2O_{(g)}$$

**Drying agents**

*Deliquescent* and *hygroscopic* compounds are used as *drying agents* for gases, liquids and solids, since they are capable of absorbing moisture.

***Drying of Gases***

- Concentrated $H_2SO_4$ placed in a Woulf's bottle is used in drying neutral and acidic gases (fig 12.4a).
- Fused $CaCl_{2(s)}$ is placed in a U-tube (fig 12.4b).
- Lime, $CaO_{(s)}$ placed in a drying tower, is used in drying ammonia gas, $NH_3$ (fig 12.4c).

***Drying of Liquids***

- Lumps of fused calcium chloride are placed in *organic* liquids to be dried.

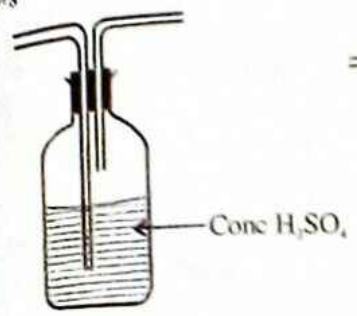



Fig 12.4a *A Woulf 's bottle*




**Fig 12.4b** *A U-tube*

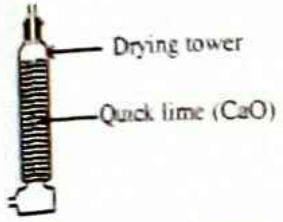



Fig 12.4c *A Drying Tower*

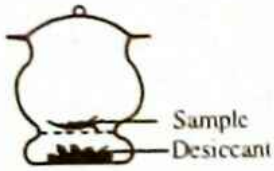



**Fig 12.4d** *A Desiccator*

***Drying of Solids***

- When drying a solid, fused $CaCl_2$, conc $H_2SO_4$, or *silica gel* can be used as the *drying agent*, called *desiccant*, in a *desiccator*, (see fig 12.4d).

**Revision Exercises**

21 What term is used to describe a substance that, on exposure to air
a. decreases in mass? b. increases in mass?
22 State why fused calcium chloride is often used as a drying agent.
23 Mention the term used to describe the drying agent in a desiccator.

## 12.4 Fractional Distillation of Liquid Air

When atmospheric air is compressed to about 200 atmospheres, heated, and then cooled, and finally allowed to expand, it turns to liquid at –200 °C.

The major constituents of *liquefied air*, which are nitrogen and oxygen, can be obtained by fractional distillation. Nitrogen boils first at –196 °C, being more volatile than oxygen, which boils at –183 °C.

**Revision Exercises**

24 Which separation technique can be used to obtain oxygen from air?
25 In terms of the kinetic theory, explain how air becomes liquefied.

## 12.5 Air Pollution

### What is Pollution?

*Pollution* is a phenomenon in which certain substances that are harmful to living things are present, in large excess, in the *environment*. Such contaminants are called ***pollutants***.

### Air Pollution

Many oxides of *p*-block elements are associated with *air pollution*. They are: oxides of carbon, nitrogen, and sulphur. Others are soot (carbon particles), hydrogen sulphide, lead compounds, gaseous hydrocarbons, and chlorofluorocarbons.

### Types of Air Pollution

There are two forms of air pollution: *natural and environmental (artificial or man-made).*

***Natural pollution*** of air is caused by the combustion of fuels (such as coal, petrol, kerosene, and gases), volcanic eruptions, forest fires, and biological activities. The substances involved contain carbon, nitrogen and sulphur. Fog or harmattan, which is due to the suspension of sand and dust particles in air, is a natural source of air pollution.

***Environmental pollution*** of air is due to high human population, agricultural activities, industrialization and chemical warfare.

### Air Pollutants

1. The main air pollutants are *soot* and *carbon(II) oxide*, CO. They get into the atmosphere due to the incomplete combustion of fuels (such as firewood, kerosene, petrol, or diesel oil) in the exhaust fumes from smoky motor vehicles, and from industries.

*Soot*, a pure form of carbon, is the black deposits in the exhaust-pipes of vehicles. If inhaled, can dam-age the respiratory system.

*Carbon(II) oxide* is the most dangerous air pollutant; being colourless and poisonous. If inhaled, it can cause blood-poisoning.

**2.** Pollutants from lead compounds are due to the addition of tetraethyl lead, $Pb(C_2H_5)_4$ to petrol, in order to increase its octane number, and prevent knocking in engines. Inhaling lead in the atmosphere can lead to poisoning of the nervous tissue.

**3.** Pollutants, such as ammonia, $NH_3$ are released into the atmosphere during waste treatment in the industries, while oxides of nitrogen, such as nitrogen(II) oxide, NO, and nitrogen(IV) oxide, $NO_2$ are released during combustion of fuels and fertilizer production. Nitrogen(IV) oxide, $NO_2$ is acidic. It dissolves in rainwater to produce *acid rain*. It fades coloured materials, and causes lung cancer and pneumonia.

**4.** Hydrogen sulphide, $H_2S$ comes from chemical plants and sewage; sulphur(IV) oxide, $SO_2$ comes from the combustion of fuels, and electric power stations. Both $H_2S$ and $SO_2$ are acidic; they dissolve in rainwater to produce *acid rain* – just like $NO_2$. $H_2S$ causes blackening of painted walls of buildings, and corrosion of out-door marble statutes, due to the reactions with lead compounds in paints.

**5.** Due to industrialization, large human population and agricultural activities, the amount of carbon (IV) oxide in the atmosphere is more than required. Atmospheric $CO_2$ is responsible for the *retention* of the *long-wave* (*infrared*) radiations being emitted by the earth. The large excess of $CO_2$ in the atmosphere is responsible for the *global warming* being experienced presently. The effect of this is that there will be flooding, and high temperature related diseases such as cancer, sunburn, and cerebral spinal meningitis (CSM) will be on the increase. *A climatic condition associated with the retention of radiation in the atmosphere* is known as the ***green house effect***.

**6.** Pollutants from gaseous hydrocarbons, such as natural gas (methane) get into the atmosphere as a result of chemical processes and crude oil explorations.

*Chlorofluorocarbons* [CFCs], such as $CCl_3F_2$ and $CCl_3F$ (*Freons*) are *non-toxic* compounds that are used as coolants (in refrigerators and air-conditioners), and aerosol propellants for perfumes and insecticides, and in paints. Large quantities of *Freons* have been confirmed to be in the atmosphere, and now known that in the upper atmosphere (*stratosphere*) they interact chemically with ozone, leading to the *depletion* of the *ozone layer*, and the formation of the ***ozone hole***.

The *ozone layer sieves* and *shields* the earth from the intense *short-wave* (*ultraviolet*) solar radiations. The bad effect of this is that the earth is being exposed to *ultraviolet* radiations, which are dangerous to human health – causing sun-burns, cataracts of the eyes, skin cancer, and damaging the body immune system..

### How to Control Air Pollution

*Air pollution* can be controlled by

- Use of devices in vehicles that provide complete combustion of fuels.

### Revision Exercises

26 a. What is pollution?
   b. Explain the term air pollution.
   c. Mention **two** sources of air pollution.

27 a. Name **three** air pollutants and explain why they are pollutants.
   b. Suggest **one** way of reducing air pollution in our cities.

28 State **one** air pollutant that causes
   a. blood poisoning;
   b. blackening of the walls of building.

29 Mention **one** air pollutant associated with the
   a. depletion of ozone layer in the atmosphere
   b. corrosion of outdoor marble statutes.

30 Give **two** examples of air pollutants, which cause acid rain.

31 The uncovered raw food that is sold along major roads is likely to contain some amounts of
   A. Pb. B. Cu. C. Ag. D. Na. [JAMB]

32 *Global warming* arises from atmospheric pollution by
   A. radioactive fallout B. carbon(IV) oxide
   C. agrochemicals. D. sulphur(IV) oxide. [W]

33 Which of the following substances causes the depletion of the ozone layer in the atmosphere?
   A. Carbon(IV) oxide. B. Chlorofluorocarbon.
   C. Sulphur(IV) oxide. D. Hydrocarbons. [WAEC]

34 The gas that is most useful in protecting humans against solar radiation is
   A. chlorine. B. ozone.
   C. carbon(IV) oxide. D. hydrogen sulphide. [JAMB]

## Answers to Revision Exercises

| | | | | | |
|---|---|---|---|---|---|
| 1. C | 2. B | 4. D | 5. 69.0 $dm^3$ | | 7. D |
| 10 6.00 $dm^3$ | | 11. D | 12. 250 $cm^3$ | | 15. B |
| 17. C | 20. B | 31. A | 32. B | 33. B | 34. B |

# 13

# •WATER•HARDNESS•POLLUTION•

## 13.1 Sources of Water

1. The natural sources of water are: rain, spring, well, river, lake, ocean and sea.
2. Pure water does not occur naturally; however, the degree of purity varies from rainwater (contains about 0.001% dissolved impurities) to sea-water (contains about 3.6% dissolved impurities).
3. Impurities in *natural water* are gases, such as nitrogen, oxygen and carbon(IV) oxide, and dissolved salts of iron, sodium, potassium, calcium and magnesium.
4. When equal volumes of samples of water from *rain*, *well* and *sea* in separate evaporating dishes are evaporated to dryness, the quantity of dissolved salts left as *residues* will be least in rain-water, followed by that of well-water; while sea-water will have the largest quantity of residue.

**Revision Exercises**

1. List *three* natural sources of water.
2. Mention *two* gaseous impurities in water.

## 13.2 Gases Dissolved in Water

1. The gases in air are also present in all sources of water. This explains why water is regarded as a mixture.
2. The percentage composition of gases in water by volume is as follows:

| Constituent | % by Volume |
|---|---|
| Nitrogen | 63.9 |
| Oxygen | 33.2 |
| Carbon(IV) oxide | 2.9 |

The higher percentage of dissolved oxygen in water (33.2% by volume) than in air (20.9% by volume) shows that oxygen is more soluble in water than in air.

3. The presence of gases in water sustains the lives of aquatic plants and animals, e.g. algae, fishes and crabs.

**Revision Exercises**

3. Mention two dissolved gases in water.
4. Explain why the sample of air collected through the process of boiling natural water is richer in oxygen than atmospheric air.
5. Natural water collected from rivers and ponds contain oxygen, carbon(IV) oxide and

A. hydrogen B. sulphur(IV) oxide
C. nitrogen D. chlorine. [WAEC]

## 13.3 Pure Water

*Pure water* is obtained by *simple distillation* of water sample that has been contaminated by *dissolved impurities*, e.g. well water, sea water, or water collected from a pond.

The water sample is placed in a *distillation flask* and the pieces of apparatus are set up as shown in fig 13.1. The mixture is heated, until it boils.

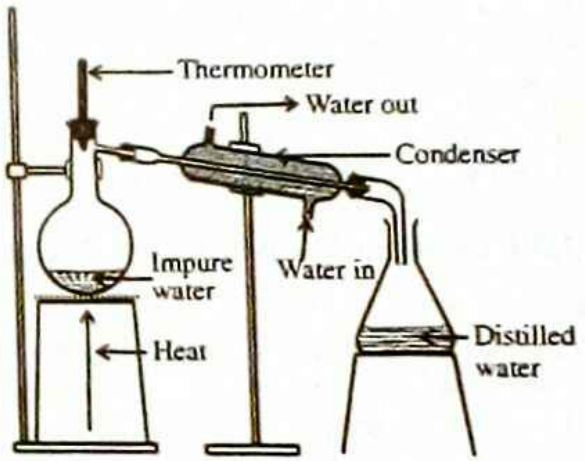



**Fig 13.1** *Purification of water by simple distillation*

As water boils, it changes into ***steam***, which condenses on passing through *water-cooled Liebig condenser*, into pure water, called ***distillate***. The dissolved impurities are left in the distillation flask as the *residue*.

Water obtained by distillation is called ***distilled water***. It is the *purest form of water*.

**Revision Exercises**

6. Describe briefly how a sample of pure water can be obtained from water collected from a pond.
7. Name the laboratory method employed in obtaining pure water from sea water.

## 13.4 Physical Properties of *Pure* Water

1. Pure water is a colourless and odourless liquid.
2. It has a characteristic *insipid* taste.
3. It has no effect on litmus paper.
4. It boils at 100 °C under atmospheric pressure.
5. It freezes at 0 °C.
6. It has a maximum density of 1.00 $gcm^{-3}$ at 4 °C.
7. It turns *white* anhydrous $CuSO_4$ powder *blue*, or *blue* anhydrous $CoCl_2$ powder *pink*. [This is not a laboratory test for *pure* water].

A liquid that boils at 100 °C at atmospheric pressure, freezes at 0 °C, and has a density of 1.0 $gcm^{-3}$ is *pure water*. These are the criteria for purity of water.

**Revision Exercises**

8 State three physical properties of pure water.
9 List two criteria for purity of water.
10 What is observed when water is added to anhydrous $CuSO_4$?
11 When a few drops of water is added to a blue anhydrous cobalt(II) chloride, the colour changes to
A. white. B. pink. C. red. D. blue. [JAMB]

## 13.5 Chemical Properties of Water

### Reaction with Metals

Metals can be divided into three categories based on their reactivity with water: *active*, *semi-active* and *non-reactive* metals.

#### 1. *Active Metals*

Metals, such as potassium, sodium and calcium react vigorously with *cold* water, giving off colourless and odourless hydrogen gas, and forming an alkaline solution. The reaction is exothermic.

- $Ca_{(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2\,(aq)} + H_{2\,(g)}$

**Note:** Care should be taken when using sodium and potassium. They react violently with water.

#### 2. *Semi-active metals*

Metals, such as Mg, Al, Zn and Fe do not react with *cold* or *hot* water. However, they react readily with *steam* at red heat, to liberate hydrogen gas, and produce the corresponding oxide of the metal; e.g.

- $Mg_{(s)} + H_2O_{(g)} \rightarrow MgO_{(s)} + H_{2\,(g)}$
- $3Fe_{(s)} + 4H_2O_{(g)} \rightarrow Fe_3O_{4\,(s)} + 4H_{2\,(g)}$

The reaction of iron with steam is reversible.

#### 3. *Inactive (passive) metals*

Metals, such as Pb, Cu, Hg, Ag and Au do not react with *water* or *steam*.

| | |
|---|---|
| K<br>Na<br>Ca | They react vigorously with *cold water* with decreasing reactivity, to liberate hydrogen.<br>$Ca_{(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)} + H_2\uparrow$ |
| Mg<br>Al<br>Zn<br>Fe | They react with *steam* to liberate hydrogen gas.<br>$Zn_{(s)} + H_2O_{(g)} \rightarrow 2ZnO_{(s)} + H_2\uparrow$ |
| Pb<br>Cu<br>Hg<br>Ag<br>Pt<br>Au | They do not react with *water* or *steam*; hence, they do not displace hydrogen from *water* or *steam*. |

### Reactions with Non-metals

1. Pass *steam* over *white-hot* carbon; a mixture of carbon(II) oxide and hydrogen gas is produced.
   - $C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2\,(g)}$
2. Chlorine gas dissolves in water to produce a mixture of hydrochloric acid and monooxochlorate (I) acid, HClO.
   - $Cl_{2(g)} + H_2O_{(l)} \rightarrow HCl_{(aq)} + HClO_{(aq)}$

### Reactions with Oxides of Metals

Oxides of metals are ***basic***. *Basic oxides that are soluble in water to give the corresponding hydroxides are called* ***alkalis***; e.g. $Na_2O$, $K_2O$ and CaO.

- $Na_2O_{(s)} + H_2O_{(l)} \rightarrow 2NaOH_{(aq)}$
  (Sodium oxide) (Sodium hydroxide)
- $CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2\,(aq)}$
  (Calcium oxide) (Calcium hydroxide)

The reactions are exothermic.

### Reaction with Oxides of Non-metals

Oxides of non-metals are either ***acidic*** or ***neutral***. Those that are ***acidic*** dissolve in, and react with water, to give the corresponding acids. *Acidic oxides are called* ***acid anhydrides***.

An *acid anhydride* is an *acidic oxide* that dissolves in, and react with water to produce an acid; e.g. $SO_2$, $SO_3$, $NO_2$, $CO_2$, $P_2O_3$ and $P_2O_5$

- $CO_{2\,(g)} + H_2O_{(l)} \rightarrow H_2CO_{3\,(aq)}$
- $SO_{2\,(g)} + H_2O_{(l)} \rightarrow H_2SO_{3\,(aq)}$
- $SO_{3\,(g)} + H_2O_{(l)} \rightarrow H_2SO_{4\,(aq)}$

$NO_2$ is a *mixed anhydride*, because it produces two acids when it reacts with water.

- $2NO_{2\,(g)} + H_2O_{(l)} \rightarrow HNO_{2\,(aq)} + HNO_{3\,(aq)}$
- $P_2O_{3\,(s)} + 3H_2O_{(l)} \rightarrow 2H_3PO_{3\,(aq)}$
- $P_2O_{5\,(s)} + 3H_2O_{(l)} \rightarrow 2H_3PO_{4\,(aq)}$

### Action of Water on Metallic Carbides

When *cold* water is added to a metallic carbide, there is effervescence; a gaseous hydrocarbon and the corresponding hydroxide are produced:

- $CaC_{2(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)} + C_2H_{2(g)}$
  (Calcium dicarbide) (ethyne)
- $Al_4C_{3(s)} + 12H_2O_{(l)} \rightarrow 4Al(OH)_{3(aq)} + 3CH_{4(g)}$
  (Aluminium carbide) (methane)

**Revision Exercises**

12 Mention two elements that will react with *cold* water producing hydrogen and an alkaline solution.

13 List two elements that will react with *steam* at red heat to produce hydrogen.

14 Give one example of a metal, which at red heat react reversibly with steam.

15 Steam reacts with X on heating strongly as indicated:

$$X_{(s)} + H_2O_{(g)} \rightarrow XO_{(s)} + H_{2(g)}$$

X is: A. Cu B. Fe C. Zn D. Pb [WAEC]

16a. Mention two acidic oxides.

b. What term is used to descried an acidic oxide that dissolves in water to produce an acid?

## 13.6 Water as a Universal Solvent

1. Water is the commonest and a universal solvent, because being polar, it dissolves more substances than any other liquid solvent. It can dissolve both ionic and covalent compounds.

2. When a substance dissolves in water, an aqueous solution of the substance is obtained,. e.g.

$$NaOH_{(s)} + H_2O_{(l)} \rightarrow NaOH_{(aq)}$$

3. Aqueous solutions of ionic compounds contain the corresponding hydrated cations and anions, e.g.

- $NaCl_{(aq)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$
- $Ca(NO_3)_{2(aq)} \rightarrow Ca^{2+}_{(aq)} + 2NO_3^-{}_{(aq)}$

Note: In aqueous solutions, radicals, such as $ClO_3^-$, $NO_3^-$ and $SO_4^-$ retain their identities.

4. Without the formation of ions, many chemical reactions will not occur. For example:

When crystals of sodium chloride and silver trioxonitrate(V) are mixed together, there will be no visible reaction:

$$AgNO_{3(s)} + NaCl_{(s)} \rightarrow \text{No visible reaction}$$

However, a mixture of their aqueous solutions produce white precipitate of silver chloride:

$$AgNO_{3(aq)} + NaCl_{(aq)} \rightarrow NaNO_{3(aq)} + AgCl_{(s)}$$
(colourless) (colourless) (colourless) (white)

**Revision Exercises**

17 Explain why water is referred to as a universal solvent. [WAEC]

18 Write an equation to indicate the ions produced in aqueous solution by each of $Ca(HCO_3)_2$.

## 13.7 Formation of Water

Water is formed during the following processes:

1. *Combustion of hydrocarbons*

Hydrocarbons are compounds containing carbon and hydrogen as the only elements. They burn in oxygen to produce steam and carbon(IV) oxide.

***Combustion of Candle***

Set up the apparatus as shown in fig 13.2.

Place a burning candle under the inverted funnel; then, connect the bent tube to the pump, so that the products of combustion are drawn into the test tube. Wait for about thirty minutes.

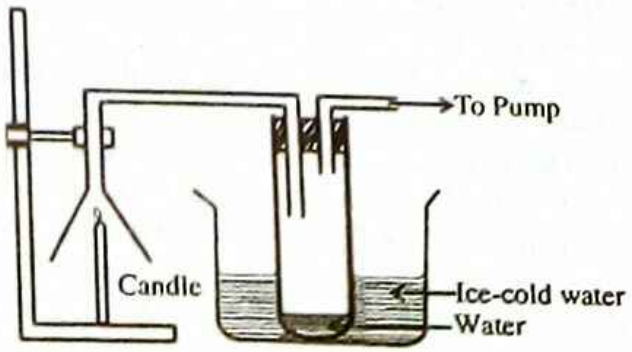



Fig 13.2 *Formation of Water*

It will be observed that the ice-cold water in the beaker has caused a liquid to condense in the test tube. The boiling point of the liquid will show it is water.

2. *Synthesis of Water*

Water is formed when dry hydrogen gas burns in oxygen at a jet, and the flame is directed to the bottom of a water-cooled beaker (see fig 28.5 in Section 28.3).

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$$

This experiment illustrates that water is an oxide of hydrogen.

**Revision Exercises**

19 List two chemical processes that produce water.

20 How many grams of water would be formed by burning 14.0 $dm^3$ of dry hydrogen gas in an excess of pure oxygen?
[Molar volume at s.t.p. is 22.4 $dm^3\ mol^{-1}$; $H_2O = 18$]

## 13.8 Composition of Water

The following experiments can be used to illustrate that water is made up of hydrogen and oxygen.

### 1. Gravimetric Composition of Water

This is the *composition of water by mass.*

**Procedure**

a. Dry hydrogen gas is passed over a ***known mass*** of heated black copper(II) oxide. Hydrogen gas is

oxidized to steam, while the black copper(II) oxide is reduced to a brown mass of copper metal:

$$CuO_{(s)} + H_{2(g)} \rightarrow Cu_{(s)} + H_2O_{(g)}$$

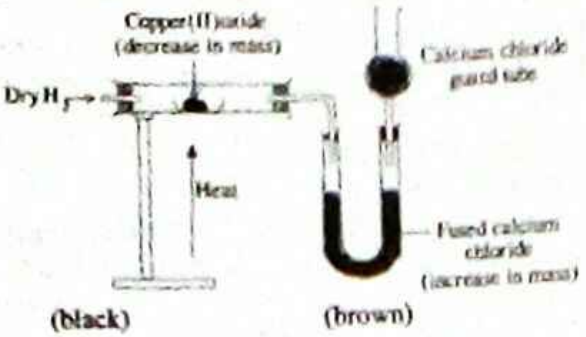



**Fig 13.3** *Gravimetric composition of water*

The *decrease* in mass of copper(II) oxide gives the mass of oxygen that has been used to form the steam.

**b.** The steam produced is absorbed by a *known mass* of fused calcium chloride, a drying agent.

$$CaCl_{2(s)} + 2H_2O_{(g)} \rightarrow CaCl_2{\cdot}2H_2O_{(s)}$$

The *increase* in mass of the fused calcium chloride gives the mass of water produced.

**c.** The *mass of water produced minus the mass of oxygen consumed*, gives the *mass of hydrogen* that has combined with oxygen.

**d.** Within the limit of experimental error, 1.00 *g* of hydrogen combines with 8.00 *g* of oxygen.

**f.** The percentages by mass of hydrogen and oxygen in water are 11.0% and 89.0% respectively.

### 2. Composition of Water by Volume

In the decomposition of water by *electrolysis* (see chapter 22), *two* volumes of hydrogen gas and *one* volume of oxygen are produced under the same conditions:

$$2H_2O_{(l)} \rightarrow \underset{2\text{ vol.}}{2H_{2(g)}} + \underset{1\text{ vol.}}{O_{2(g)}}$$

**Revision Exercises**

**21** Describe an experiment to show that water contains hydrogen and oxygen only.

**22** What would be the mass of water produced when 4.0 g of copper(II) oxide is treated with an excess of hydrogen gas? ( H = 1.0; O = 16.0;CuO = 80)

**23** Calculate the volume of oxygen gas evolved by the electrolytic decomposition of 3.0 g of water. (Molar volume at s.t.p. is 22.4 $dm^3\ mol^{-1}$).

## 13.9 Bonding in water

A water molecule, $H_2O$, is formed by the covalent combination of two atoms of hydrogen and one atom of oxygen. It leads to the formation of two single covalent bonds *within* the molecule. There are two lone-pairs of electrons on the central oxygen atom that are not used in bonding; they repel each other, causing the molecule to acquire a V-shape (figure 13.4a).

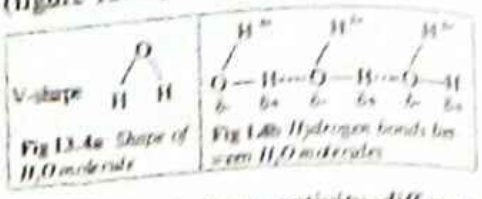



**Fig 13.4a** *Shape of $H_2O$ molecule*

**Fig 13.4b** *Hydrogen bonds between $H_2O$ molecules*

*Due to the large electronegativity difference between atoms of hydrogen and oxygen, the covalent bonds within the water molecule are polar, and the entire molecule is also polar.*

Again, there are hydrogen bonds between water molecules (fig. 13.4b). The attractive forces due to hydrogen bonds are fairly strong, and are responsible for the existence of water as a liquid at room temperature, and its high boiling point.

**Revision Exercises**

**24** State the type of bond **a.** *within* a water molecule;
**b.** *between* water molecules.

**25** What is the shape of a water molecule?

## 13.10 Unique Properties of Water

**1.** Water has a density of 1.00 $gcm^{-3}$ at 4 °C.

**2.** Below 4 °C, water expands and forms a solid ice. In ice, there are more hydrogen bonds than in liquid water. The extra hydrogen bonds are responsible for the expansion and the *low density* of *ice*.

**3.** As ice is being warmed, the heat absorbed is used in breaking the extra hydrogen bonds between the molecules in ice, making them to come in close contact and fill the empty spaces. This leads to contraction from 0 °C to 4 °C. Above 4 °C, normal expansion of water follows.

**4.** At atmospheric pressure, water boils at 100 °C, and changes to steam.

**5.** The *relatively high boiling point of water* is due to *hydrogen bonds between the molecules of water.*

**Revision Exercises**

**26** List two unique properties of water.

**27** What is responsible for the relatively high boiling point of pure water?

**28** State the effect of hydrogen bonding in water.

## 13.11 Importance of Water

### 1. Biological

Dissolved gases in water are of importance to plants and animals living in water. For example:

**a.** Dissolved oxygen is used for respiration.

a. Carbon(IV) oxide dissolves calcium salts in water, which are used by animals with shells in the formation of their shells.
b. Nitrogen dissolved in water is converted into trioxonitrate(V) acid, $HNO_3$, which is used in the formation of proteins in plants.

2. **Economic**
a. *Domestic uses*: Water sustains life. It is used for drinking, washing, cooking, and in construction work.
b. *Industrial uses*: Water is used as a solvent in the chemical industry; in running steam engines to generate electricity.
Distilled water is used in the preparation of laboratory reagents, in batteries, in bleaching, in dyeing and in other manufacturing processes, such as brewing and food processing.
c. *Agricultural use*: Water is used for irrigation, and dry season farming.

**Revision Exercises**
3 State two usefulness of dissolved air in water.
4 List two industrial and two biological importance of water.

## 13.12 Treatment of Water for Town Supply

The treatment of water in water treatment plant, usually passes through the following stages:

**1. Aeration and Sedimentation**
Water is stored in the dam for many days, for mud particles to settle down by sedimentation, remove smell and gases such as $CO_2$ and $H_2S$, and to kill the bacteria by exposure to air and sunlight.

**2. Coagulation (Flocculation)**
Water is made to pass through large settling tanks in the waterworks, where calculated amount of *potash alum*, $KAl(SO_4)_3$ or *sodium dioxoaluminate (III)*, $NaAlO_2$, is added for the coagulation of clay (or colloidal) particles.

**3. Filtration**
The sediments and the coagulated particles are removed by passing the water through ***sand beds*** composed of layers of coarse gravels, then through layers of fine sands, and finally, through layers of fine charcoal, to remove fine sediments, smell, and un-wanted colouring matter.

**4. Disinfection**
Calculated amounts of the following are added to treat water for town supply:
- Chlorine, to kill bacteria or germs
- Iodine salt (*iodide*), for the prevention of goitre – caused by iodine deficiency in human body.
- Fluorine salt (*fluoride*), is added – for prevention of tooth decay.
- Solution of $CuSO_4$, to prevent growth of algae.

**5. pH measurement**
The water is subjected to quality control by pH adjustment, by adding calculated amount of *quick lime*, CaO, to maintain a pH between 6.0 and 8.0.

**6. Distribution**
The treated water is finally pumped to sealed reservoirs in the town, where it is stored for use.

*Treated water for town supply is called pipe-borne water. It is germ-free, contains dissolved gases and mineral salts; hence, suitable for domestic uses.*

**Solved Problem 1**
State the function of each of the following substances in the purification of water for town supply:
a. Sodium dioxoaluminate(III) ($NaAlO_2$);
*To coagulate the clay particles.*
b. Lime (calcium hydroxide);
*To control the pH of the treated water.*
c. Calculated amount of iodine;
*To remove iodine deficiency.*
d. Sand bed.
*To remove sediments and coagulated particles.*

**Revision Exercises**
31 List four basic processes that are used for purification of water for town supply.
32 State the role of each of the following substances in the treatment of river water for town supply:
a. Sand bed; b. Alum; c. Chlorine.
33 Which of the following processes is not involved in the treatment of water for town supply?
A. Chlorination B. Coagulation C. Dehydration
D. Sedimentation. [WAEC]

## 13.13 The Water Cycle

1. When rain falls, the water flows through the earth's surface into the rivers, and eventually into the seas.
2. Part of the rain water is used up by plants and animals, while a portion drains through the earth, to form springs and into wells.
3. During respiration in plants and animals, water is transpired into the atmosphere. Similarly, water evaporates from rivers, lakes, and seas, to form water vapour in the atmosphere.
4. Condensation of water vapour leads to the formation of clouds, which eventually falls as rain.
5. The process starts again (see figure 13.5).

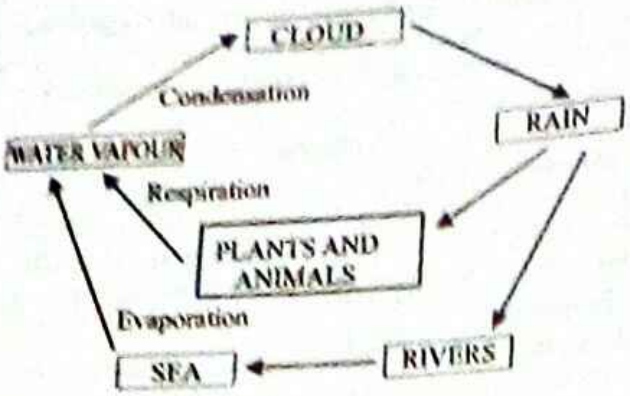



Fig 13.5 *The Water Cycle*

**Revision Exercises**

34 Mention two processes involved in the water cycle.

35 Describe the formation of the cloud.

## 13.14 Hardness of Water

### Introduction

It is a common observation that rain water produces *lather* readily with soap, while it is not so with water sample from the well, river, or sea.

***Hard*** water is a water sample that does not produce lather readily with soap, while *soft* water produces lather readily with soap.

*Hardness of water* is due to the presence of soluble salts of calcium, magnesium and, or, iron in wells, rivers and seas.

**Revision Exercises** [WAEC]

46 Define *hard water*.

47 Distinguish between *hard* and *soft* water.

### Types of Hardness

There are two types of hardness of water:
***Temporary*** hardness and ***permanent*** hardness.

1. ***Temporary hardness*** is caused by the presence of hydrogentrioxocarbonate(IV). $HCO_3^-$, of Ca, $Ca(HCO_3)_2$; Mg, $Mg(HCO_3)_2$; or Fe, $Fe(HCO_3)_2$.

*Temporary hard water* is formed when rainwater that contains dissolved carbon(IV) oxide, $CO_2$ flows through a locality where there are deposits of limestone, marble, or chalk, $CaCO_3$. The *carbonated water* is a weak acid; it dissolves the limestone marble or chalk to form a solution of the hydrogentrioxocarbonate(IV) salt:

$$\underset{\text{(Limestone)}}{CaCO_{3(s)}} + \underset{\text{(in rain water)}}{CO_2 + H_2O} \rightarrow \underset{\text{(soluble salt)}}{Ca(HCO_3)_{2(aq)}}$$

*Temporary hardness* is so-called because it can be removed readily by *boiling*.

2. ***Permanent hardness*** is hardness that cannot be removed by boiling. It is due to the presence of tetraoxosulphate(VI) or chloride of calcium, magnesium or iron, [i.e. $CaSO_4$, $MgSO_4$, $FeSO_4$, $CaCl_2$, $MgCl_2$ or $FeCl_2$] in natural water. Although $CaSO_4$ is only slightly soluble in water, its solubility is high enough to cause permanent hardness.

Generally, samples of natural water from rivers and wells (except rain water) have varying degrees of both temporary and permanent hardness.

**Revision Exercises**

36a. List two types of hardness of water.

b. Name two salts that cause *each* type of hardness.

## 13.15 Detection of Hardness

*Hardness* is *detected* in a water sample by the formation of *insoluble scum with soap*.

*Soap* is the sodium or potassium salt of a fatty (organic) acid; e.g. sodium stearate, or NaSt. (St = stearate) [Chemical formula: $C_{17}H_{35}COO^-Na^+$].

When soap is used in hard water, the corresponding salt of calcium or magnesium of the fatty acid is formed. It is a double decomposition reaction. Since the calcium or magnesium salt is insoluble in water, it is precipitated as ***scum***.

- $\underset{\text{(soap)}}{2NaSt_{(aq)}} + \underset{\text{(in hard water)}}{CaSO_{4(aq)}} \rightarrow \underset{\text{(soluble)}}{Na_2SO_{4(aq)}} + \underset{\text{(scum)}}{CaSt_{2(s)}}$
- $\underset{\text{(soap)}}{2NaSt_{(aq)}} + \underset{\text{(in hard water)}}{Ca(HCO_3)_2} \rightarrow \underset{\text{(soluble)}}{2NaHCO_3} + \underset{\text{(scum)}}{CaSt_{2(s)}}$

**Revision Exercise**

37 Explain how hardness in water can be detected.

## 13.16 Removal of Hardness

The following methods can be used to remove *hardness* of water; hence, obtain *soft* water.

**1. To remove temporary hardness**

a. By ***boiling***: The *hard water is boiled, to decompose the acid salt.* The *soft* water obtained is then filtered, to remove the *residue*.

- $\underset{\text{(in hard water)}}{Ca(HCO_3)_{2(aq)}} \rightarrow \underset{\text{(insoluble)}}{CaCO_{3(s)}} + H_2O_{(l)} + CO_{2(g)}$

However, this method is not economical.

b. ***Addition of slaked lime***: On a large scale, a calculated amount of slaked lime, $Ca(OH)_{2(s)}$ is added to the temporary hard water, to precipitate $CaCO_3$.

$$Ca(OH)_{2(s)} + \underset{\text{(in hard water)}}{Ca(HCO_3)_{2(aq)}} \rightarrow \underset{\text{(insoluble)}}{2CaCO_{3(s)}} + 2H_2O$$

c. ***Addition of washing soda***: On a large scale, crystals of sodium trioxocarbonate(IV), washing soda, are added to the water sample in order to precipitate $CaCO_3$.

$$Na_2CO_{3(s)} + Ca(HCO_3)_{2(aq)} \rightarrow CaCO_{3(s)} + 2NaHCO_{3(aq)}$$

**2. To remove both Temporary and Permanent Hardness [Total Hardness]**

*Temporary* and *permanent* hardness (*total hardness*) in a water sample can be removed, *at the same time*, by the following methods:

**a. *Addition of crystals of sodium trioxocarbonate (IV) [Washing soda]***

$$\underset{\text{(in hard water)}}{Na_2CO_{3(aq)}} + CaSO_{4(aq)} \rightarrow \underset{\text{(insoluble)}}{CaCO_{3(s)}} + Na_2SO_{4(aq)}$$

b. By ***distillation***: The *hard water* is boiled, and the vapour is cooled, to obtain *distilled water*. The residue is left in the distillation flask.

c. By *ion-exchange (Permutit method):*

***Use of cation exchange resin***

***Permutit*** is the trade name of sodium aluminium tetraoxosilicate(IV), $NaAlSiO_4$. It is commercially called *sodium permutit*, $NaR$ (R = *Permutit*). It is a *cation exchange resin*.

When *hard water* passes through *Permutit*, it exchanges its sodium ions with calcium ions present in the hard water. The water that comes out is '*soft*'. It is free of the ions causing hardness.

$$2NaR_{(s)} + CaSO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + CaR_{2(s)}$$

***Permutit*** *water softener* can be *regenerated* by washing the spent resin with *brine* (saturated sodium chloride solution). The sodium ions replace the calcium or magnesium ions present in it.

$$CaR_{2(s)} + 2NaCl_{(aq)} \rightarrow CaCl_{2(aq)} + 2NaR_{(s)}$$

***Ion-exchange resins*** are used in industrially. They are called *'deionizers'* since they remove *ions* present in a water sample. However, they are not capable of removing *harmful bacteria* and *non-ionic organic matter* in a water sample.

**Revision Exercises**

38 State **three** methods that can be used to remove hardness in a sample of water caused by $Ca(HCO_3)_2$.

39 List **three** methods of removing both permanent and temporary (total) hardness at the same time.

40 Write an equation for the reaction involved in the removal of temporary hardness of water by:
a. boiling; b. with slaked lime.

41 A sample of water which has passed through a de-ionizer may still contain
A. temporary hardness. B. organic impurities.
C. permanent hardness. D. heavy metal ions.
[WAEC]

## 13.17 Advantages and Disadvantages of Hardness

### Disadvantages of Hardness

1. Hard water wastes soap. Soap used in hard water produces *scum* first, before further addition of soap starts to produce lather.
2. When hard water is boiled, it deposits *insoluble* $CaCO_3$ in *kettles* and *boilers*. The deposits form *scales* in *boilers* and *fur* in *kettles*. Such deposits block water-pipes, and being a conductor of heat, the deposits of $CaCO_3$ result in more heat being required to boil water in a kettle or in a boiler.
3. Hard water is not suitable for use in the laundry, and in textiles, tanning and paper manufacturing industries, because of *scum*. It damages fabrics, by removing dyestuffs.

### Advantages of Hardness

1. Hard water provides calcium salts used in the manufacturing of food in plants. Calcium salts are also used in the formation of shells by some water animals like fish and crabs.
2. It is suitable for use in the beer brewing industry, because of its characteristic taste.
3. Calcium salts are necessary for the development of strong bones and teeth.
4. The presence of dissolved salts and gases gives natural water its characteristic taste.
5. When calcium hydrogentrioxocarbonate(IV), decomposes, it produces pure $CaCO_3$, which is used in making cement.

### Advantages of Soft Water

1. Soft water does not waste soap; it produces lather readily with soap without forming scum.
2. Soft water does not deposit ***scales*** in *boilers* and *fur* in *kettles*.
3. It is suitable for use in the laundry, and textiles, tanning, and paper manufacturing industries.

### Disadvantages of Soft Water

1. Soft water attacks, slowly, water-pipes made of lead. Hence, water flowing through lead-pipes is made a little bit hard, so as not to attack the pipes.
2. It has no taste; hence, not suitable for brewing.
3. It does not contain calcium salts required for the development of strong bones and teeth.

**Revision Exercises**

42 List **two** disadvantages of hard water

43 State the effect of hard water in laundry.

44 List **two** advantages of hard water.

45 State **one** disadvantage and **one** advantage of soft water.

46 State **two** advantages of soft water over hard water.

## 13.18 Use of Detergents

*Detergents*, with trade names, such as ***Omo***, ***Klin*** and ***Ariel*** are now more commonly used, instead of *soap*. They dissolve in water easily, and are not

affected by hardness. They form lather readily, without forming scum.

**Revision Exercises**

47 State one advantage of detergent over soap in hard water.

48 Which of detergent and soap
- a. does not form scum with hard water?
- b. produce lather readily with hard water?
- c. is affected by hardness of water?

## 13.19 Degree of Hardness in Water

The degree of hardness in a water sample can be determined, approximately, by finding the volume of soap solution required to produce a permanent lather with a known volume of the water sample. This volume is then compared with the volume of soap solution required to produce a permanent lather with distilled water. Distilled water, being free of any forms of hardness, will require only a small volume of soap solution to produce a permanent lather.

The larger the volume of soap solution required to produce a permanent lather, the higher the degree of hardness of the water sample.

A rough *order of increasing degree of hardness of water samples* (depending on the locality) is:

**Distilled water ≤ rainwater < well < seawater**

**Worked Examples**

3 25.0 $cm^3$ of a sample of water produced lather on the addition of 33.0 $cm^3$ of a standard soap solution. Another 25.0 $cm^3$ of the same sample of water that has been boiled required 15.0 $cm^3$ of the soap solution. If 25 $cm^3$ of distilled (or deionised) water required 3.0 $cm^3$ of the soap solution to produce lather, calculate the ratio of temporary hardness to permanent hardness in the water sample.

**Solution**

- *The water sample contained both types of hardness*
- *Volume of soap solution used for 25 $cm^3$ of distilled water represents that of completely soft water (no hardness)*
- *Volume of soap solution required for both types of hardness = (33.0 – 3.0) $cm^3$ = 30.0 $cm^3$*
- *Boiling removes temporary hardness only; hence, volume of soap solution required for permanent hardness = (15.0 – 3.0) $cm^3$ = 12.0$cm^3$*

*∴ Volume of soap solution required to remove temporary hardness = (30.0 – 12.0) $cm^3$ = 18.0 $cm^3$*

*or (33.0 – 15.0) $cm^3$ = 18.0 $cm^3$*

- *The ratio of temporary hardness to permanent hardness is 18.0 :12.0 = 3 : 2.*

**4. The following results were obtained when 25.0 $cm^3$ portions of two different water samples labelled X and Y were separately treated with a standard soap solution.**

| Experiment | Volume of soap solution that produced permanent lather $cm^3$ |
|---|---|
| Sample X initially | 17.4 |
| Sample X after boiling | 2.0 |
| Sample Y initially | 35.5 |
| Sample Y after boiling | 10.5 |
| Sample Y after addition of $Na_2CO_3$ crystals | 2.0 |

From the above information

a. Compare the hardness in samples X and Y.
- *The degree of hardness of X is less than that of Y.*
- *Sample X has only temporary hardness, while Y has both temporary hardness and permanent hardness.*
- *The degree of temporary hardness in X is less than the temporary hardness in Y.*

b. Of what use are the crystals of $Na_2CO_3$ in the experiment?

*Crystals of $Na_2CO_3$ were used in removing total hardness (both temporary and permanent).*

c. What volume of soap solution would be expected to produce permanent lather with 25 $cm^3$ of distilled (or deionised) water, and why? [WAEC]

*2.0 $cm^3$ of soap solution would be required, since distilled (or deionised) water has no hardness.*

**5. Describe briefly a simple experiment to determine the type of hardness in a sample of water.**

- *Place about 50 $cm^3$ of sample of water in a beaker, and boil, using a Bunsen burner flame. Allow to cool.*
- *Add soap solution gradually to the boiled sample of water with swirling.*
- *If a permanent lather is formed easily, the sample contains temporary hardness; if not, it contains permanent hardness.*

**Revision Exercises**

49 State with reason, which of rainwater and seawater has the highest degree of hardness.

50 State with reason, which of pure water and seawater will produce lather readily with soap.

## 13.20 Water and Soil Pollution

### Water Pollution

Like *air pollution*, *water pollution* occurs when certain substances that are harmful to living things are present in high concentrations in the natural sources of water.

*Water pollutants* include atmospheric solid impurities, such as dust and soot, and gaseous impurities such as $CO_2$, $SO_2$, $H_2S$, and oxides of nitrogen (NO and $NO_2$); *sewage* – domestic wastes, such as gar-

bage (refuse), and water wastes (organic wastes); *agricultural waste*, e.g. fertilizers and crop-spraying insecticides; *silt*; *industrial wastes*; *heat (thermal pollutants)*; *crude oil spillage*; and *radioactive wastes*.

When rain falls, the rainwater washes from the atmosphere soot and dust, $CO_2$, $H_2S$, $SO_2$, oxygen and nitrogen. During thunderstorm and lightening, nitrogen and oxygen in air react to form NO and $NO_2$. In fact, rain-water may be regarded as a very dilute solution of $HNO_3$, $H_2CO_3$ and $H_2SO_3$ – due to the presence of $NO_2$, $CO_2$ and $SO_2$ respectively in the atmosphere. However, these impurities are present in minute quantities; hence, rainwater remains the purest natural source of water.

Sewage, refuse, human wastes, and water wastes are usually dumped on open grounds, or directly into rivers. These wastes are organic matter, which can be decomposed by bacteria into harmless materials (***biodegradable***). However, during this process, the bacteria use-up the oxygen dissolved in water. Hence, pollution of rivers or any water supply by organic wastes leads to reduction of dissolved oxygen to levels dangerous to fish and other aquatic organisms. Again, such water supply becomes contaminated by harmful bacteria, and acquires unpleasant odour and taste; making it unfit for domestic use.

When inorganic fertilizers containing $PO_4^{3-}$, that have been applied to crops, are washed by erosion into lakes and ponds, they encourage the growth of weeds and algae on the water surface.

Industrial wastes are made up of metal scraps, plastics and chemicals from various kinds of industry. The wastes contain compounds of lead and mercury, acids, alkalis, dyes, chlorinated solvents, DDT, $NO_3^-$, $PO_4^{3-}$, and so on, which are ***non-biodegradable*** or *slow to degrade* to harmless materials. They are washed by rain-water from the land, and eventually enter into wells and rivers; thereby, polluting the water supply with harmful heavy metal ions, such as $Hg^{2+}$ and $Pb^{2+}$.

*Silts* are finely divided clay particles. They enter into water supply by erosion of soil.

Some industries discharge *warm water effluents* from their power plants into rivers and lakes. This leads to ***thermal pollution***; it raises the temperature of water and lowers the level of dissolved oxygen in rivers and lakes.

***Crude oil spillage*** or dumping of oily waste in a body of water is another major source of water pollution in rivers, lakes, wells, and seas. The resultant effect is the reduction of oxygen level in these water-bodies, thereby, endangering the survival of marine and aquatic lives.

Radioactive wastes from nuclear reactions are usually dumped into the seas. They are difficult to dispose. Such wastes are harmful.

Seawater is the most polluted natural source of water. It contains about 3.6% of dissolved salts, largely sodium chloride (2.8%).

### Soil Pollution

Most *water pollutants* are initially present in the soil before being washed into the rivers, wells, and seas by ***erosion***. They include: *domestic wastes*, such as refuse or garbage, and water wastes (organic wastes); *agricultural wastes*, such as crop-spraying insecticides and pesticides; *industrial wastes*, such as plastics and metal scraps; *crude oil spillage*; and *radioactive wastes*.

When these pollutants are present in soil, they do not allow crops to grow well, or survive.

### Control of Water and Soil Pollution

*Water and Soil pollution* can be controlled by

- *Burying* or *burning* of refuse;
- Treatment of *sewage and industrial effluents*, in order to remove the pollutants before being discharged;
- Conversion of *chemical wastes into biodegradable* matter before being disposed; and
- *Recycling* of solid wastes can control environmental pollution.
- Use of *sanitary land-fills*.
- Proper monitoring of the treatment and disposal of industrial wastes, by environmental agencies.

### Revision Exercises

**51** Mention **three** types of pollution. [WAEC]

**52** List **three** sources of water pollution.

**53** Name **four** water pollutants, and explain why they are pollutants.

**54** Name **two** gases that are associated with acid rain.

**55** Give **two** examples of soil pollutants, and explain why they are pollutants.

**56** Which of the following pollutants is biodegradable?
**A.** Hydrogen sulphide. **B.** Lead compounds
**C.** Metal scraps. **D.** Plastics. **E.** Sewage [NECO]

**57** Give **two** ways by which pollution can be prevented. [WAEC]

### Answers to Revision Exercises

**5.** C **11.** B **15.** C **20.** 11.3 g **22.** 3.60 g
**23.** 1.87 $dm^3$ **33.** C **41.** B **56.** E

# 14

# • ACIDS AND BASES • pH •

## 14.1 Introduction

Traditionally, any substance that has a *sour taste* and is *corrosive* is regarded as an ***acid***, while any substance has a *bitter taste* and *soapy to feel* is a ***base***. These descriptions are based on the *physical properties* of acids and bases.

In this chapter, the terms – *acids* and *bases* – are defined in the modern ways, and their properties, methods of preparation, and uses enumerated.

**Revision Exercise**

1. State **one** physical property of **a.** an acid; **b.** a base.

## 14.2 Acids

### Occurrence

The two types of acids are: ***Organic*** and ***inorganic***.

1. ***Organic acids*** occur naturally in plants and animals. In fact, most of the fruits we eat are acidic. For instance: ethanoic acid is present in vinegar, while citric acid is found in lemon and orange juice. They are responsible for the sour taste of unripe fruits. A list of common organic acids and their sources are in Table 14.1.

2. ***Inorganic acids*** are called *mineral* acids, since they are synthesized from mineral ores. They are *man-made*. Examples are hydrochloric acid, HCl, trioxonitrate(V) acid, $HNO_3$, and tetraoxosulphate (VI) acid, $H_2SO_4$. They are highly corrosive.

**Table 14.1** ***List of common organic acids***

| Organic acid | Source |
|---|---|
| *Ethanoic acid* | Vinegar |
| *Lactic acid* | Sour milk |
| *Tartaric acid* | Grape and sour soup |
| *Citric acid* | Lemon and orange |
| *Palmitic acid* | Palm oil |
| *Amino acid* | Protein |
| *Methanoic acid* | Bees and ants' stings |

### Definitions

**Arrhenius definition of an Acid**

An *acid* produces *hydroxonium ions* in water, e.g.

- $HCl_{(g)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$
- $CH_3COOH_{(l)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$

When an acid dissolves in water, first, it dissociates to produce hydrogen ion $H^+$, a proton, which readily combines with water, to form aqueous hydroxonium ion, $H_3O^+_{(aq)}$ i.e.

- $HNO_3 \rightarrow H^+ + NO_3^-$ (dissociation)
- $H^+ + H_2O \rightarrow H_3O^+_{(aq)}$

Hence, in water, $H^+$ exists as $H_3O^+$.

In water, ions are surrounded by water molecules, i.e. they become *hydrated*, and are denoted by (aq). Water solution of an acid is called *aqueous acid* or *acidified water*.

**Bronsted-Lowry concept of Acids**

An acid is a *proton donor*, e.g.

$$HCl + NH_3 \rightarrow NH_4^+ + Cl^-$$

HCl donates its proton to ammonia to form ammonium ion.

**Lewis concept of Acids**

An acid is an *electron-pair acceptor*. This definition is more generalized than the others.

Lewis acids do not have hydrogen atoms in their molecules, but have empty valence orbitals on their central atoms – as in $BF_3$, $AlCl_3$ and $FeCl_3$:

$$AlCl_3 + Cl^- \rightarrow AlCl_4^-$$

In this reaction, the empty valence orbital on the aluminium atom in $AlCl_3$ accepts a pair of electrons from $Cl^-$.

### Strengths of Acids

*On the basis of their strengths, acids are classified into strong and weak acids.*

1. ***Strong acids*** are completely (100%) ionized or dissociated in water under any set of conditions. They are *strong* electrolytes, e.g. $H_2SO_4$, HCl and $HNO_3$. They are inorganic acids, i.e.

- $HCl_{(g)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$ (100%)
  1 *mol* → 1 *mol* + 1 *mol*

2. ***Weak acids*** are organic acids; they are only slightly ionized (about 0.4%) in water under any set of conditions. They are *weak* electrolytes, e.g. Ethanoic acid, $CH_3COOH$, and ethanedioic acid, $H_2C_2O_4 \cdot 2H_2O$. Others are inorganic acids: $HNO_2$, $H_2CO_3$, $H_2SO_3$ and $H_3PO_4$.

$CH_3COOH_{(l)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$ (0.4%)
(1 mol) (0.004 mol) (0.004 mol)

**Solved Problem**
1. $H_2SO_4$ is described as a strong acid. Why?
*Solution*
*$H_2SO_4$ is a strong acid, because it is completely ionized in water.*

**Revision Exercises**
2. What is an acid? Give one example of an acid.
3. Define
a. an Arrhenius acid and give *one* example.
b. a Bronsted-Lowry acid and give *one* example.
c. a Lewis acid and give one example.
4. State the natural source of
a. ethanoic acid; b. citric acid; c. amino acids
5. Explain what is meant by the strength of an acid.
6. Why is ethanoic acid regarded as a weak acid?

## Physical Properties of Aqueous Acids

1. Acids have *sour taste* e.g. lemon, grapefruits and sour milk.
*[Never perform any taste test in the laboratory!]*
2. They have corrosive action; strong acids cause acid burn.
3. They are strong electrolytes.

## Chemical Properties of Aqueous Acids

1. Their aqueous solutions turn blue litmus paper to red, due to the *formation of $H_3O^+$ in water.*
2. An acid reacts with a base to produce a salt and water only. It is a *neutralization reaction*:
• $HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$
(Acid) (Base) (Salt) (Water)
3. An acid reacts with a metal more reactive than hydrogen in the *activity series*, to liberate hydrogen gas and produce a salt:
• $Zn_{(s)} + H_2SO_{4(aq)} \rightarrow ZnSO_{4(aq)} + H_{2(g)}$
4. An acid reacts with a trioxocarbonate(IV) salt, to liberate carbon(IV) oxide and produce a salt and water, e.g.
• $CaCO_{3(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$
5. An acid reacts with a trioxosulphate(IV) salt, to liberate sulphur(IV) oxide, and produce a salt and water:
• $Na_2SO_{3(s)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + H_2O + CO_{2(g)}$

## Methods of Preparation of Aqueous Acids

**1. *Action of an acid anhydride on water***
An ***acid anhydride*** is an oxide of a non-metal that reacts with water to produce an acid:
a. Carbon(IV) oxide gas reacts with water to form a weak acid, trioxocarbonate(IV) acid, $H_2CO_3$.
• $CO_{2(g)} + H_2O_{(l)} \rightarrow H_2CO_{3(aq)}$
b. Sulphur(IV) oxide gas reacts with water to form a weak acid, trioxosulphate(IV) acid, $H_2SO_3$
$SO_{2(g)} + H_2O_{(l)} \rightarrow H_2SO_{3(aq)}$

**2. *Displacement reaction***
A *stronger* or *less volatile* acid displaces a *weaker* or *more volatile acid from its salt*. The order of *decreasing* strengths of acids:
$H_2SO_{4\,(aq)}$ ***(Non-volatile)***
$CH_3COOH_{(aq)}$
$HCl_{(aq)}$
$HNO_{3\,(aq)}$
$H_2SO_{3\,(aq)}$
$H_2S_{(aq)}$
$H_2CO_{3\,(aq)}$ ***(Most volatile)***

Concentrated $H_2SO_4$ is a *non-volatile acid*; it will displace or liberate other acids from their salts, e.g.
a. When a mixture of concentrated $H_2SO_4$ and crystals of sodium chloride is heated, volatile hydrogen chloride gas is produced:
• $H_2SO_{4(aq)} + 2NaCl_{(s)} \rightarrow Na_2SO_{4(aq)} + 2HCl_{(g)}$
A solution of hydrogen chloride gas in water is called hydrochloric acid.
• $HCl_{(g)} + H_2O_{(l)} \rightarrow HCl_{(aq)}$
b. Addition of concentrated $H_2SO_4$ to crystals of potassium trioxonitrate(V) liberates fumes of trioxonitrate(V) acid, which, on cooling, produce the acid.
• $H_2SO_{4\,(aq)} + 2KNO_{3(s)} \rightarrow K_2SO_{4\,(aq)} + HNO_{3\,(l)}$
Reactions a and b above show that $H_2SO_{4(aq)}$ is a less volatile and a stronger acid than $HCl_{(aq)}$ and $HNO_{3(aq)}$.
c. When dilute hydrochloric acid is added to a trioxocarbonate(IV) salt, there is effervescence; the colourless and odourless gas produced is carbon (IV) oxide.
• $2HCl_{(aq)} + Na_2CO_{3\,(s)} \rightarrow 2NaCl_{(aq)} + H_2O + CO_{2(g)}$
A solution of carbon(IV) oxide in cold water is called *carbonated water*; it is weakly acidic:
• $H_2O_{(l)} + CO_{2(g)} \rightarrow H_2CO_{3(aq)}$
d. When dilute hydrochloric acid is added to crystals of iron(II) sulphide, hydrogen sulphide gas is liberated.
• $FeS_{(s)} + 2HCl_{(aq)} \rightarrow FeCl_{2\,(aq)} + H_2S_{(g)}$
Reactions c and d above show that $HCl_{(aq)}$ is a less volatile and a stronger acid than $H_2CO_{3(aq)}$ and $H_2S_{(aq)}$.

Since ethanoic acid, $CH_3COOH$ is less volatile, $HCl_{(aq)}$ or $HNO_{3(aq)}$ cannot be used to prepare it.

***3. Direct combination of the elements***

This method is suitable for the preparation of hydrochloric acid and other hydrogen halides. For instance: Hydrogen gas burns in chlorine gas to produce hydrogen chloride gas:

- $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$

The gas dissolves readily in water to produce hydrochloric acid.

- $HCl_{(g)} + H_2O_{(l)} \rightarrow HCl_{(aq)}$

**Revision Exercises**

7. Give three physical properties of an acid. [NECO]
8. Write an equation for the reaction between iron filings and dilute tetraoxosulphate (VI) acid.
9. List two general methods of preparing acids.[WAEC]

### Solution of Hydrogen chloride gas in Methylbenzene

*Methylbenzene*, $C_6H_5CH_3$ is called *toluene*. It is a *non-polar* organic solvent.

When dry hydrogen chloride gas dissolves in methylbenzene, it exists as molecules; it does not produce ions, $H_3O^+$. Hence, the resulting solution has no effect on dry blue or red litmus paper; does not conduct electric current; and does not react with trioxocarbonate(IV) salts to liberate $CO_2$.

Similarly, a solution of any organic acid in any organic solvent does not contain ions, $H_3O^+$.

The characteristic property of an acid is its ability to produce hydroxonium ions, $H\text{-}O^+$, in water.

### Uses of mineral acids

The general uses of acids include:

1. In the production of salts.
2. In the dissolution of metals.
3. As electrolytes.
4. As redox reagents.

**Revision Exercises**

10 Solution of hydrogen chloride gas in methylbenzene is not acidic to litmus. Explain.

11 Mention two general uses of mineral acids.

## 14.3 Bases

### Definitions

### General Definition

A ***base*** is either an *oxide* or *hydroxide of a metal*, e.g. sodium oxide, magnesium hydroxide, zinc oxide, and calcium hydroxide (slaked lime). They exist as solids.

Most bases are insoluble in water. *Basic oxides that are soluble in water form the corresponding hydroxides*, e.g.

- $Na_2O_{(s)} + H_2O_{(l)} \rightarrow 2NaOH_{(aq)}$

It is a chemical change. *Soluble bases are called alkalis*.

### Arrhenius Definition of a Base

A *base* is a substance which reacts with $H_3O^+$ or $H^+$ to produce *water*, i.e.

- $OH^- + H^+ \rightarrow H_2O_{(l)}$
- $O^{2-} + 2H^+ \rightarrow H_2O_{(l)}$

An *alkali is a base that dissolves in water to produce hydroxide ions, $OH^-$*:

- $NaOH_{(s)} + H_2O_{(l)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$

The characteristic property of a soluble base is due to the production of $OH^-$ in water.

### Bronsted-Lowry Concept of Bases

A *base* is a proton-acceptor, e.g.

| | *BASE* | *ACID* | | | |
|---|---|---|---|---|---|
| a. | $NH_3$ | + $HCl$ | $\rightarrow$ | $NH_4^+$ | + $Cl^-$ |
| b. | $H_2O$ | + $HCl$ | $\rightarrow$ | $H_3O^+$ | + $Cl^-$ |
| c. | $H_2O$ | + $H_2O$ | $\rightarrow$ | $H_3O^+$ | + $OH^-$ |

In the examples above, $NH_3$ and $H_2O$ molecules are bases; they accept protons from the acids. The reaction in **c** shows that $H_2O$ can act as a *weak acid* as well as a *weak base* – it is amphoteric.

### Lewis Concept of Acids

A *Lewis base* is an *electron-pair donor*. They are species that possess lone-pairs of electrons that a can be shared with an empty valence orbital:

| | *BASE* | *ACID* | | | |
|---|---|---|---|---|---|
| a. | $NH_3$ | + $H_3O^+$ | $\rightarrow$ | $NH_4^+$ | + $H_2O$ |
| b. | $Cl^-$ | + $AlCl_3$ | $\rightarrow$ | $AlCl_4^-$ | |
| c. | $NH_3$ | + $BF_3$ | $\rightarrow$ | $BF_3\text{-}NH_3$ | (a complex) |

In **a**, $NH_3$ donates the lone-pair of electrons on nitrogen atom to the proton in $H_3O^+$; in **b**, $Cl^-$ donates a lone-pair electron to the empty valence orbital on the aluminium atom in $AlCl_3$, while in **c**, $NH_3$ donates the lone-pair of electrons on nitrogen atom to the empty valence orbital on the boron in $BF_3$. The species form dative bonds.

### Physical Properties of Alkalis

1. Alkalis have bitter taste, e.g. lime water.
2. Their water solutions are slippery and soapy to touch e.g. NaOH solution.
3. They are electrolytes.

### Chemical Properties of Bases

1. A base will react with an acid to produce a salt and water only; e.g.

a. Sodium hydroxide neutralizes hydrochloric acid to produce sodium chloride and water.

$$NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$$

b. Copper(II) oxide, a black solid, dissolves in dilute tetraoxosulphate(VI) acid to produce a blue solution of copper(II) tetraoxosulphate(VI).

$$\underset{\text{(black)}}{CuO_{(s)}} + \underset{\text{(colourless)}}{H_2SO_{4\,(aq)}} \rightarrow \underset{\text{(blue)}}{CuSO_{4\,(aq)}} + H_2O_{(l)}$$

2. Aqueous solution of an alkali turns red litmus paper to blue, due to the production of $OH^-$.

3. *When a mixture of an alkali and an ammonium salt is heated, a colourless gas with a pungent smell is given off; the gas is ammonia*, e.g.

$$KOH_{(aq)} + NH_4Cl_{(aq)} \xrightarrow{\text{heat}} KCl_{(aq)} + H_2O_{(l)} + NH_{3(g)}$$

4. An alkali reacts with an *acid anhydride* to form a salt and water only; it is a neutralization reaction, e.g. When carbon(IV) oxide is passed into aqueous sodium hydroxide, a solution of sodium trioxocarbonate(IV) and water are produced.

$$2NaOH_{(aq)} + CO_{2\,(g)} \rightarrow Na_2CO_{3\,(aq)} + H_2O_{(l)}$$

### Strengths of Alkalis

Alkalis are classified into *strong* and *weak bases*:

1. ***Strong alkalis*** are those that are completely ionized in water. They are strong electrolytes, e.g. KOH, NaOH and $Ba(OH)_2$.

$$KOH_{(s)} + H_2O_{(l)} \rightarrow K^+_{(aq)} + OH^-_{(aq)}$$

$$NaOH_{(s)} + H_2O_{(l)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

2. ***Weak alkalis*** are those that are slightly ionized in water, e.g. $Ca(OH)_{2\,(s)}$, $Mg(OH)_{2(l)}$ and $NH_{3(g)}$.

$$Ca(OH)_{2(s)} + H_2O_{(l)} \rightarrow Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$$

Ammonia gas readily dissolves in water to give an alkaline solution. Ammonia solution is sometimes called ammonium hydroxide.

$$NH_{3\,(g)} + H_2O_{(l)} \rightarrow NH_4OH_{(aq)}$$

$$NH_4OH_{(aq)} \rightarrow NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

### Preparation of Bases

1. ***Combustion of a reactive metal in air***

A reactive metal burns in air to give the corresponding oxide, e.g.

a. Sodium burns in oxygen to give sodium oxide:

$$4Na_{(s)} + O_{2(g)} \rightarrow 2Na_2O_{(s)}$$

2. ***Action of a soluble base on water***

Soluble bases react with water to give the corresponding hydroxides, e.g.

$$\underset{\text{(Quicklime)}}{CaO_{(s)}} + 2H_2O_{(l)} \rightarrow \underset{\text{(Limewater)}}{Ca(OH)_{2\,(aq)}}$$

3. ***Action of a reactive metal on cold water***

Soluble bases (alkalis) are prepared by the action of the metal on cold water, e.g.

Sodium metal reacts violently with cold water, to produce a colourless and odourless gas, which is hydrogen, and an alkaline solution.

$$2Na_{(s)} + 2H_2O_{(l)} \rightarrow 2NaOH_{(aq)} + H_{2(g)}$$

4. ***Precipitation Method***

*Insoluble hydroxides* are precipitated by the action of sodium hydroxide solution on the aqueous solutions of their salts, e.g.

When excess sodium hydroxide solution is added to a solution of a copper(II) salt, a blue precipitate of copper(II) hydroxide is obtained.

$$NaOH_{(aq)} + \underset{\text{(blue)}}{CuSO_{4(aq)}} \rightarrow Na_2SO_{4(aq)} + \underset{\text{(blue)}}{Cu(OH)_{2(s)}}$$

5. ***Decomposition reactions***

*Insoluble basic oxides* are obtained by the action of heat on the metallic hydroxides, trioxonitrate(V) and trioxocarbonate(IV) salts, e.g.

a. $2Al(OH)_{3(s)} \rightarrow Al_2O_{3\,(s)} + H_2O_{(g)}$

b. $CaCO_{3\,(s)} \rightarrow CaO_{(s)} + CO_{2\,(g)}$

c. $2Cu(NO_3)_2 \rightarrow 2CuO_{(s)} + 4NO_{2\,(g)} + O_{2(g)}$

### Uses of Alkalis

1. ***Caustic soda, NaOH,*** and ***caustic potash, KOH,*** are used in the production of soaps, papers, and as drying agents – because they are deliquescent.

2. ***Slaked lime, $Ca(OH)_2$,*** is used as fertilizer – in order to neutralize the acidity of the soil (liming of soil), and in removing hairs from skins of animals.

3. ***Milk of magnesia, $Mg(OH)_{2(aq)}$,*** is used as a laxative – to neutralize excess acid in the stomach. It is a suspension of $Mg(OH)_{2(s)}$ in water.

4. ***Ammonia solution, $NH_{3(aq)}$*** is used in laundry – to neutralize the acids in body-sweat on clothes.

### Basicity of an Acid

*The **basicity of an acid** is the number of hydrogen atoms that can be ionized in water by one molecule of the acid.* It also corresponds to the *amount, in moles, of a strong base (NaOH or KOH) required to neutralize completely one mole of the acid.*

***Monobasic acid*** produces ***one*** hydrogen ion (or hydroxonium ion) per molecule in water, e.g. HCl, HBr, HI, HF, $HNO_3$, $HNO_2$ and $CH_3COOH$.

$$HCl_{(g)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

***One mole of a monobasic acid neutralizes one mole of NaOH or KOH.***

*An acid that produces in water, one hydrogen ion, $H^+$, per molecule is* ***monoprotic.***

***Dibasic acid*** produces *two* hydrogen ions per molecule in water, e.g. $H_2SO_4$, $H_2SO_3$, $H_2C_2O_4$ and $H_2CO_3$.

$$H_2SO_{4\,(aq)} \rightarrow 2H^+_{(aq)} + SO_4^{2-}{}_{(aq)}$$

***One mole of a dibasic acid neutralizes two moles of NaOH or KOH.***

*An acid that produces in water, two hydrogen ions per molecule is* ***diprotic.***

***Tribasic acid*** produces *three hydrogen ions* per molecule in water, e.g. $H_3PO_4$.

- $H_3PO_{4\,(aq)} \rightarrow 3H^+_{(aq)} + PO_4^{3-}{}_{(aq)}$

***One mole of a tribasic acid neutralizes three moles of NaOH or KOH.***

*An acid that produces three hydrogen ions per molecule is* ***triprotic.***

**Notes:**

1. In an organic acid, it is the hydrogen atom in the carboxylic group, -COOH, which is ionizable. Hence, ethanoic acid, $CH_3COOH$, and methanoic acid, HCOOH that have four and two hydrogen atoms per molecule respectively are both *monobasic*, while ethanedioic acid, $H_2C_2O_4$ with two hydrogen atoms is *di*basic, i.e.

$$\begin{matrix} COOH \\ | \\ COOH_{(aq)} \\ \text{(ethanedioic acid)} \end{matrix} \rightarrow 2H^+_{(aq)} + \begin{matrix} COO^- \\ | \\ COO^-{}_{(aq)} \\ \text{(ethanedioate ions)} \end{matrix}$$

2. In an *oxoacid*, the ionizable hydrogen atom is in the hydroxyl group (see Section 34.2).

**Solved Problem**

2. Describe a laboratory test to distinguish between aqueous solutions of HCl and $NH_3$.

*$HCl_{(aq)}$ is acidic; turns blue litmus paper to red. $NH_{3(aq)}$ is alkaline; turns red litmus paper to blue.*

**Note:** *Litmus test is a chemical test.* It is the easiest test for detecting an acidic or alkaline solution. A *mnemonic* for remembering the colour of litmus in aqueous solution of an acid and a base is:

*ACID* — *RED*  *BASE* — *BLUE*

**Revision Exercises**

12 Define a base and give one example.

13 a. What is an alkali?

b. Write a chemical equation to show that KOH is an alkali.

14 Define

a. an Arrhenius base and give *one* example.

b. a Bronsted-Lowry base and give *one* example.

c. a Lewis base and give one example.

15 Write chemical equations to illustrate three methods of preparation of bases.

16 Write an equation to show the reaction between calcium and water.

17a. What is basicity of an acid?

b. State the basicity of each of the following acids:

HCOOH; $H_3PO_4$; $HNO_3$; $CH_3CH_2COOH$.

18 Write an equation to show the dissociation of each of the following acids:

a. $CH_3COOH$; b. $H_2CO_3$ [WAEC]

## 14.4 Classes of Oxides

There are *five* classes of oxides:

### 1. Acidic Oxides (Acid Anhydrides)

These are oxides of non-metals that dissolve in, and react with water, to produce acids, e.g. $CO_2$, $SO_2$, $SO_3$, $NO_2$ and $P_2O_5$. [Note: $P_2O_5$ exists as a dimer, $P_4O_{10}$]

a. Sulphur(VI) oxide is the acid anhydride of tetraoxosulphate(VI) acid.

- $SO_{3\,(g)} + H_2O_{(l)} \rightarrow H_2SO_{4\,(aq)}$

b. Nitrogen(IV) oxide is a *mixed anhydride*; it produces two acids when it reacts with water.

- $2NO_{2\,(g)} + H_2O_{(l)} \rightarrow HNO_{2\,(aq)} + HNO_{3\,(aq)}$

Most of the acidic oxides are gases; they turn *moist* blue litmus paper to red, and neutralize alkalis.

### 2. Basic Oxides

These are oxides of metals, e.g. $Na_2O$, $CaO$, $CuO$, $MgO$ and $Fe_2O_3$. They are solids. They react with an acid to produce salt and water only, e.g.

- $CuO_{(s)} + H_2SO_{4\,(aq)} \rightarrow CuSO_{4\,(aq)} + H_2O_{(l)}$
  (black) (colourless) (blue)

Basic oxides that are soluble in water to form basic hydroxides are called *alkalis*, e.g. calcium oxide, CaO reacts with water to form calcium hydroxide solution.

- $CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2\,(aq)}$

Water-solution of an alkali gives an alkaline solution that turns red litmus paper to blue, and neutralizes an acid.

### 3. Amphoteric Oxides

These are oxides of metals that have both acidic and basic properties, e.g. aluminium oxide, $Al_2O_3$, zinc oxide, ZnO, lead(II) oxide, PbO, and tin(IV) oxide, $SnO_2$. For instance:

a. Reactions of zinc oxide;

- $ZnO_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2\,(aq)} + H_2O_{(l)}$
  (base) (acid) (salt) (water)
- $ZnO_{(s)} + 2NaOH_{(aq)} \rightarrow Na_2ZnO_{2\,(aq)} + H_2O_{(l)}$
  (acid) (base) (salt) (water)

b. Reactions of aluminium oxide:

- $Al_2O_{3(s)}$ + $6HNO_{3(aq)}$ → $2Al(NO_3)_{3(aq)}$ + $3H_2O_{(l)}$
  (base) (acid) (salt) (water)
- $Al_2O_{3(s)}$ + $2KOH_{(aq)}$ → $2KAlO_{2(aq)}$ + $H_2O_{(l)}$
  (acid) (base) (salt) (water)

### 4. Neutral Oxides

They are oxides of non-metals that are neither acidic nor basic; i.e. they have no action on litmus papers, e.g. steam, $H_2O$; carbon(II) oxide, CO; nitrogen(I) oxide $N_2O$; and nitrogen(II) oxide NO.

### 5. Peroxides

These are higher oxides of metals. They have *one* oxygen atom more than the normal oxides, e.g. sodium peroxide, $Na_2O_2$; lead(IV) oxide, $PbO_2$; and barium peroxide, $BaO_2$. They react with an acid to produce hydrogen peroxide, e.g.

$Na_2O_{2(s)}$ + $2HCl_{(aq)}$ → $2NaCl_{(aq)}$ + $H_2O_{2(l)}$

Higher oxides or peroxides do not undergo neutralization with acids. For instance, lead(IV) oxide reacts with concentrated HCl to give a salt, water, and chlorine.

$PbO_{2(s)}$ + $4HCl_{(aq)}$ → $PbCl_{2(aq)}$ + $2H_2O_{(l)}$ + $Cl_{2(g)}$

### Revision Exercises

19 List **three** types of oxides and give **one** example of each type.

20 Name **two** a. acidic oxides; b. basic oxides; c. neutral oxides; d. amphoteric oxides.

21 a. What are acidic oxides? [WAEC]
b. Classify each of the following as acidic oxide/basic oxide/neutral oxide:
CO; $Fe_2O_3$; $N_2O$; $SO_3$; CuO; $NO_2$

22 a. What are *acid anhydrides?* [NECO]
b. Give **one** example each of the anhydride of i. a monobasic acid; ii. a dibasic acid.

23 Write **two** equations to show why zinc oxide is classified as an amphoteric oxide.

## 14.5 Mass-Mole Relationship in Acids and Bases

The mathematical relationship between the mass **m**, amount **n**, and molar mass **M** of a chemical substance is:

Amount, **n** (mol.) = (Mass, **m**)/(Molar mass, **M**)

### Worked Examples

**3.** How many moles are present in 10.0 *g* of pure NaOH? [NaOH = 40.0 $gmol^{-1}$]

**Solution**

*To find the amount of NaOH in 10.0 g*

Given: mass = 10 *g*; Molar mass of NaOH = 40 $gmol^{-1}$

Since amount, **n** (mol) = (Mass, **m**)/(Molar mass, **M**)

Substituting: amount = 10/40 = 0.0250 *mol* (3 s. f.)

**4.** What would be the mass of 0.504 *mole* of $NaHSO_4$? [$NaHSO_4$ = 120 $gmol^{-1}$]

**Solution**

*To find the mass of 0.504 mol of $NaHSO_4$*

Given that: amount = 0.504 *mol*;

Molar mass of $NaHSO_4$ = 120 $gmol^{-1}$

Amount, **n** (mol) = (Mass, **m**)/(Molar mass, **M**)

Making mass **m** the subject of the formula, and substituting: mass = 0.504 × 120 *g* = 60.5 *g* (3 sig. fig.)

**5.** Given that 0.101 *mole* of an acid **HX** weighs 12.9 *g*. Calculate the a. molar mass of the acid; b. relative atomic mass of **X**. [H = 1.0]

**Solution**

a. *To find the molar mass of the acid HX.*

Given that 0.101 *mol* weighs 12.9 *g*.

Amount, **n** (mol) = (Mass, **m**)/(Molar mass, **M**)

Making molar mass the subject of the formula, and substituting: Molar mass = 12.9/0.101 $g\ mol^{-1}$
= 128 $g\ mol^{-1}$ (3 sig. fig.)

*Proportion Method*

Molar mass of a substance is the mass of 1 *mole*.

Since 0.101 *mol* of HX weighs 12.9 *g* (given)

∴ 1 *mole* will weigh 12.9/(0.101) *g* = 128 *g*

i.e. molar mass of HX is 128 $g\ mol^{-1}$.

b. *To find the relative atomic mass of X.*

Since HX is 128, and H = 1(given); i.e.

H + X = 128; substituting: 1 + X = 128

X = 128 − 1 = 127 (no unit)

### Revision Exercises

24 Calculate the amount, in moles present in
a. 2.45 *g* of pure $H_2SO_4$;
b. 1.0 *kg* of 98% pure $H_2SO_4$

25 Calculate the mass of the substance present in 0.105 mole of $Ca(OH)_2$;

26 Given that 0.101 mole of an oxide $X_2O$ weighs 14.4 g. Calculate the
a. molar mass of the oxide;
b. relative atomic mass of **X**.

## 14.6 Acid-Base Reactions

### Calculations from Equations

### Mass-Mole Relationships

When an *acid* neutralizes a *base*, the products are salt and water. For example:

- $2HNO_{3(aq)}$ + $CuO_{(s)}$ → $Cu(NO_3)_{2(aq)}$ + $H_2O_{(l)}$
  (acid) (base) (salt) (water)

From the balanced equation of a neutralization reaction, a number of deductions can be made:

a. $NaOH_{(aq)}$ + $HCl_{(aq)}$ → $NaCl_{(aq)}$ + $H_2O_{(l)}$
1 *mol* 1 *mol* 1 *mol* 1 *mol*
40.0 *g* 36.5 *g* 58.5 *g* 18.0 *g*

1 *mol* (40.0 *g*) of NaOH reacts with 1 *mol* (36.5 *g*) of HCl to produce 1 *mol* (58.5 *g*) of NaCl and 1 *mol* (18.0 *g*) of $H_2O$.

The following relationships can be obtained from the above *statement of fact*:

1 mol of NaOH ≡ 1 mol of HCl (mole – mole)
40.0 g of NaOH ≡ 36.5 g of HCl (mass – mass)
1 mol of NaOH ≡ 36.5 g of HCl (mole – mass)

**b.** $2HNO_{3(aq)} + CuO_{(s)} \rightarrow Cu(NO_3)_{2(aq)} + H_2O_{(l)}$

| | | | |
|---|---|---|---|
| 2 mol | 1 mol | 1 mol | 1 mol |
| 2 × 63 g | 79.5 g | 187.5 g | 18.0 g |

The following relationships between the *acid* and *base* can be obtained from the above *fact*:

2 moles of $HNO_3$ ≡ 1 mol of CuO (mole – mole)
126 g of $HNO_3$ ≡ 79.5 g of CuO (mass – mass)
2 moles of $HNO_3$ ≡ 79.5 g of CuO (mole – mass)

Calculations based on relationships from equations of reactions involve *direct* proportions from two variables. Recall that the *statement of fact* from the balanced equation is stated such that the *given variable* is stated before the *required variable*.

**Worked Examples**

**6.** Calculate the

**a.** mass of $HNO_3$ required to neutralize 6.0 *g* of KOH completely.

**b.** amount of NaOH that will neutralize 24.5 g of $H_2SO_4$ completely.

**Note:** Balanced equations are required.

**a.** *To find the mass of $HNO_3$ required.*

Given: mass of KOH = 6.0 g.
This is mass-mass relationship.
Equation of reaction:

$HNO_3 + KOH \rightarrow KNO_3 + H_2O$ (Balanced)

1 mol 1 mol
63 g 56 g

From the balanced equation of reaction:
56 g (1 mol) of KOH ≡ 63 g (1 mol) of $HNO_3$
∴ 6 g of KOH ≡ (63 × 6)/56 g
= 6.75 g of $HNO_3$ (3 sig. fig.)

**b.** *To find the amount of NaOH.*

Given that the mass of $H_2SO_4$ = 24.5 g
This is mass-mole relationship
Equation of reaction:

$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

2 mol 1 mol
2 × 40 g 98 g

From the balanced equation of reaction;
98 g (1 mol) $H_2SO_4$ ≡ 2 mol of NaOH
∴ 24.5 g of $H_2SO_4$ ≡ (2 × 24.5)/98 mol
= 0.500 mol of NaOH (3 s. f.)

**7.** If 3.0 *g* of an acid **X** completely neutralized 1.0 *g* of NaOH; calculate the mole ratio of **X** to NaOH, expressing your answer as a whole number ratio of one. [X = 120; NaOH = 40.0]

**Solution**

*To find the mole ratio of X to NaOH*

Given that: mass of X = 3 g; mass of NaOH = 1 g.

First, find the amount of X in 3 *g* of X.
Amount of X = (mass of X)/(molar mass of X)
= 3.0/120 mol = 0.025 mol of X
Then, find the amount of NaOH in 1.0 g of NaOH
Amount of NaOH = (mass of NaOH)/(molar mass)
= 1/40 mol = 0.025 mol NaOH
∴ Mole ratio of X to NaOH = 0.025 : 0.025
Divide by the smaller $\frac{0.025}{0.025} : \frac{0.025}{0.025} = 1 : 1$
i.e. mole ratio of X to NaOH = 1 : 1

**Revision Exercises**

**27** How many grams of NaOH will neutralize completely 10.0 *g* of HCl.

**28** How many moles of KOH will neutralize completely 0.050 mole of $H_2SO_4$?

**29** What amount, in moles, of $Na_2CO_3$ will neutralize completely 2.4 g of $NaHSO_4$?
Equation of reaction is:

$Na_2CO_3 + 2NaHSO_4 \rightarrow 2Na_2SO_4 + H_2O + CO_2$

**30** In an acid-base reaction, 2.25 g of a dibasic acid neutralize completely 2.80 g of potassium hydroxide. What is the molar mass of the acid? [KOH = 56]

## 14.7 Concentrations of Acids or Bases

### Concentration of a Solution

The term ***concentration*** is analogous to the term ***sweetness*** of a solution. For instance: a solution containing ***one cube*** of sugar dissolved in 100 $cm^3$ of water will be *less* sweet (of *low concentration*), compared with a sugar solution that contains ***ten cubes*** of sugar dissolved in the same volume of water; it will be ***sweeter*** (of ***high concentration***).

An aqueous solution of, say, a *base* is obtained by *dissolving the base in water*. The ***mass, m,*** or ***amount, n*** of the base, in ***moles***, in a given ***volume V*** *of solution*, determines its ***concentration*** C.

**A Standard Solution**

A ***standard solution*** *is a solution of* ***known*** *concentration*. It is prepared, if the substance can be obtained in a *pure state*. For instance: a solution known to contain 1.0 *g* of *pure* sodium hydroxide, NaOH, in say, 250 $cm^3$ of solution, is a ***standard solution***.

A *standard solution* of a *pure* substance is prepared by *weighing* accurately a *known mass* of the substance, *dissolving* it in water, and making up the solution to a *definite* volume in a *volumetric* (or *standard*) *flask*.

**[Recall: Solute + Solvent = Solution.]**

**Units of Concentration**

The *concentration of a solution* can be expressed, *quantitatively*, in *three* standard forms:

1. ***Mass concentration***, ρ is the *mass*, m of the solute in *grams*, present in *1 $dm^3$ of solution*. It is expressed in *grams per $dm^3$ ($g/dm^3$ or $gdm^{-3}$)*.
**Note:** The density, δ of a solution is expressed in *grams per $cm^3$ ($gcm^{-3}$)*. It is a smaller unit of mass concentration.

2. ***Molar concentration***, C is the *amount*, n of the solute, in *moles*, present in *1 $dm^3$ of solution*. It is expressed in *moles per $dm^3$ ($mol/dm^3$ or $moldm^{-3}$)*.
*Molar concentration* is sometimes called *molarity* M. A solution, which contains *one mole* of a substance in 1 *$dm^3$ of solution*, is a *one-molar solution*, 1.00 M. The use of the term *molarity* is obsolete.

3. ***Percentage concentration*** is the *mass* m (or volume V) of a substance in 100 *grams* (or 100 *$cm^3$*) of solution. For instance:
a. 10% (*m/m*) NaOH means a solution that contains *10 g* of pure NaOH in *90 g* of water (or *100 g* of solution).
b. 10% (*m/v*) NaOH means *10 g* of pure NaOH in *100 $cm^3$* of solution.
c. 90% (*v/v*) ethanol means *90 $cm^3$* of pure ethanol in *10 $cm^3$* of water (or *100 $cm^3$* of solution).

### Variable Parameters of a Solution

The *three* variables that are used in describing a *solution* are: its *concentration* C; the *amount*, *n* (or *mass*, m) of *solute in the solution*; and the *volume*, *V of the solution*.

### Mathematical relationships

**1. Molar concentration:** The S. I. unit is ***mole per $dm^3$ ($mol/dm^3$ or $moldm^{-3}$)***

Molar conc C = Amount n*(mol)*/Volume V*($dm^3$)* *($mol/dm^3$)*

i.e. $C = n/V$
*or* $V = n/C$
*or* $n = CV$

**2. Mass concentration:** The S.I. unit is ***grams per $dm^3$ ($g/dm^3$ or $gdm^{-3}$)***.

Mass concentration, ρ *($gdm^{-3}$)* = Mass, m *(g)*/Vol. V *($dm^3$)*

**3. Molar and mass concentrations** are related by the mathematical expression:

**Mass conc = Molar conc × Molar mass**
($g/dm^3$) ($mol/dm^3$) (g/mol)

***Or*** **molar concentration** = $\frac{\text{mass concentration}}{\text{molar mass}}$

***Or*** **molar mass** = $\frac{\text{mass concentration}}{\text{molar concentration}}$

In order to compare the concentrations of two or more solutions of the same or different chemical substances, their concentrations must be expressed in the ***same units***.

**4. Mass of solute** *present in a given volume of a standard solution* can be obtained from the following relationships:

For a given solution: $n = CV$
For a known substance: $n = m/M$
i.e. $m/M = CV$
$\therefore\ m = MCV$ *($V$ in $dm^3$)*

## Calculations involving Aqueous Solutions of Acids and Bases

### Worked Examples

**8.** A solution contains 1.0 *g* of pure NaOH in 250 *$cm^3$* of solution. Calculate its concentration in:
a. *$gdm^{-3}$*; b. *$moldm^{-3}$* [NaOH = 40 *$gmol^{-1}$*]

a. *To find the concentration in $gdm^{-3}$: i.e. mass of NaOH in 1000 $cm^3$ (1 $dm^3$) of solution.*
Given: 1.0 *g* of NaOH dissolved in 250 *$cm^3$* of solution.
Required: Mass of NaOH dissolved in 1 *$dm^3$* (1000 *$cm^3$*)

*Method 1*: *From the first principle*
The statement that connects the two variables: mass, in grams (required) and volume of solution (given) is:
250 $cm^3$ of solution contain 1.0 g of NaOH (given).
$\therefore$ 1000 $cm^3$ of solution contain $(1.0 \times 1000)/250$ g
$(1.0 \times 4)$ g = 4.0 g NaOH.
i.e. mass concentration is 4.00 grams per $dm^3$

*Method 2*: *Formula method*
Mass conc = (Mass in grams)/(Volume in $dm^3$)
Mass = 1.0 g; Volume = 250/1000 = 0.25 *$dm^3$*
Substituting: mass conc = 1.0/0.25 = 4.00 *$gdm^{-3}$*

b. *To find the concentration in $moldm^{-3}$ i.e. amount in 1 $dm^3$ of solution.*
Using the expression:
Molar conc = (Mass conc)/(Molar mass)
Mass concentration = 4.0 g/$dm^3$ (from a above)
Molar mass NaOH = 40 g/mol
$\therefore$ Molar concentration = 4.0/40 = 0.100 mol/$dm^3$.

**9.** What volume of 0.20 *$moldm^{-3}$* HCl solution would contain 7.30 *g* of the acid? [HCl = 36.5]

**Solution**
*First, calculate the amount of acid in 7.3 g HCl*
Amount = (Mass)/(Molar mass) = 7.3/36.5 = 0.20 *mol*
*Then, find the volume of the solution that contains 0.20 mol; using the expression:*
Amount = molar conc *($moldm^{-3}$)* × Volume *($dm^3$)*
i.e. Volume *($dm^3$)* = (Amount)/(Molar conc.)
= 0.20/0.20 = 1.00 *$dm^3$*.

**Alternative method** (*From the First Principle*)
The statement of fact is:
1.0 *$moldm^{-3}$* HCl contains 36.5 *g* of acid in 1000 *$cm^3$*.
Hence, 1.0 *$moldm^{-3}$* HCl contains 7.3 *g* of acid in $(1000 \times 7.3/36.5)$ *$cm^3$*.
$\therefore$ 0.20 *$moldm^{-3}$* HCl contains 7.3 *g* of acid in $(1000 \times 7.3/36.5 \times 1/0.20)$ *$cm^3$*.
= 1000 *$cm^3$* or 1.00 *$dm^3$*

**18** Calculate the mass of anhydrous $Na_2CO_3$ in 25.0 $cm^3$ of 0.100 $moldm^{-3}$ solution.
[$Na_2CO_3$ = 106 $gmol^{-1}$]

*First, calculate the amount of $Na_2CO_3$ in 25 $cm^3$ of 0.100 $moldm^{-3}$ solution, using the expression:*
Amount (mol) = conc (mol $dm^{-3}$) × volume ($dm^3$)
= 0.100 × 25/1000 = 0.0025 mol
*Then, convert 0.0025 mol, to mass, in grams; using the expression:*
Mass (g) = amount (mol) × molar mass ($gmol^{-1}$)
= 0.0025 × 106 = 0.265 g (3 sig. fig.)

**Alternative formula method**
Using $m = MCV/1000$, and substituting:
$m$ = 106 × 0.100 × 25/1000 = 0.265 g

**Alternative method** (*From the First Principle*)
The statement of fact is:
1000 $cm^3$ of 1.0 $moldm^{-3}$ $Na_2CO_3$ contain 106 g.
Hence, 25 $cm^3$ of 1.0 $moldm^{-3}$ $Na_2CO_3$ contain (106 × 25/1000) g.
∴ 25 $cm^3$ of 0.10 $moldm^{-3}$ $Na_2CO_3$ contain (106 × 25/1000 × 0.10/1) g.
= 0.265 g.

### Revision Exercises

**31** What is a standard solution?

**32** State the difference between
a. a *weak acid* and a *dilute* acid; [WAEC]
b. a dilute NaOH and concentrated NaOH solutions.

**33** A solution of sodium hydroxide containing 6.0 g in 250 $cm^3$ of solution has a concentration of
A. 0.04 $moldm^{-3}$ B. 0.60 $moldm^{-3}$
C. 0.96 $mol\ dm^{-3}$ D. 0.15 $moldm^{-3}$
[NaOH = 40 $gmol^{-1}$] [WAEC]

**34** A contains 2.5 g of HCl in 250 $cm^3$ of solution.
B contains 8.5 g of HCl in 1 $dm^3$ of solution.
Which solution is more concentrated and why?

**35** Calculate the
a. amount of acid present in 250 $cm^3$ of a 0.20 $moldm^{-3}$ $H_2SO_4$.
b. mass of KOH present in 250 $cm^3$ of a 0.10 $moldm^{-3}$ solution. [KOH = 56.0]
c. volume of 1.0 $moldm^{-3}$ $HNO_3$ solution that would contain 0.10 mole of the acid.

**36** How many grams of $H_2SO_4$ will be required for the preparation of 0.175 $dm^3$ of 6.0 $moldm^{-3}$ solution?
[$H_2SO_4$ = 98.0 $gmol^{-1}$]
A. 206 g B. 103 g C. 98.1 g D. 51.5 g [WAEC]

## 14.8 Water as a Neutral Solvent

Water is a *polar covalent molecule*. It undergoes self-ionization, to produce $H^+$ and $OH^-$, i.e.

$$H_2O_{(aq)} \rightarrow H^+_{(aq)} + OH^-_{(aq)}$$

$H^+_{(aq)}$ combines with another water molecule to produce hydroxonium ion, $H_3O^+$:

$$H^+_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)}$$

A combination of the two equations gives:

$$H_2O_{(l)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$$

The extent of ionization is quite small. At 25 °C their concentrations are equal: 0.0000001 $moldm^{-3}$
i.e. $[H_3O^+] = [OH^-] = 1.00 \times 10^{-7}$ $moldm^{-3}$
For this reason, water is described as being *neutral and a non-electrolyte*.

**Note:** $[H_3O^+]$ and $[OH^-]$ mean *concentration of ions in* $moldm^{-3}$.

At 25 °C, the product of $[H_3O^+]$ and $[OH^-]$ for *pure water and any dilute solution of an electrolyte is constant*, i.e.

$$[H_3O^+][OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.00 \times 10^{-14}\ mol^2dm^{-6}$$

Or, simply: $[H^+][OH^-] = 10^{-14}$

When an ***acid***, such as HCl, ionizes in water, it increases the concentration of $H_3O^+$ in the solution. Under this condition, $[H_3O^+] > [OH^-]$; hence, the resulting solution becomes ***acidic***.

Similarly, when a ***base***, NaOH, dissociates in water, it increases the concentration of $OH^-$ in the solution. Under this condition, $[OH^-] > [H_3O^+]$; hence, the resulting solution becomes ***alkaline***.

### Revision Exercises

**37** Write an equation to represent the dissociation of a molecule of water.

**38** Water is regarded as a neutral solvent. Explain.

**39** Explain why limewater is alkaline to litmus.

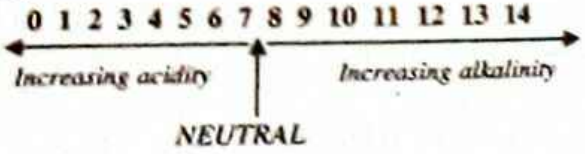
## 14.9 pH of a solution

### pH meter, pH scale and pH value

The **pH** of a solution is a measure of the degree of *acidity* or *alkalinity* of the solution. It is measured by an instrument or a devise called ***pH meter***.

The ***pH scale*** ranges from 0 to 14; the lower and upper limits respectively.

The ***pH value*** is a measure of the hydroxonium ion concentration, $[H_3O^+]$ or $[H^+]$ in a dilute solution.




The pH of pure water or a given solution is independent of its volume. For instance: the pH of 250 $cm^3$ of pure water is the same as that of 100 $cm^3$ of the same sample of water.

- A pH value ***less*** than 7 indicates an ***acidic*** solution: $[H_3O^+] > [OH^-]$
- A pH value of ***exactly*** 7 indicates a ***neutral*** solution: $[H_3O^+] = [OH^-]$

• A pH *greater* than 7 indicates an *alkaline* solution: $[H_3O^+] < [OH^-]$

The acidity of a solution *increases* as the pH *decreases*, i.e. a solution with a pH of 6.8 is *weakly acidic*, when compared with another solution with a pH of 2.5, which will be *strongly acidic*.

Conversely, alkalinity *increases* as the pH value *increases*, i.e. a solution with a pH of 7.3 is *weakly alkaline*, when compared with another solution of pH of 12.5, which will be *strongly alkaline*.

Generally, the *lower* the pH value, the *more acidic* (or the *less alkaline*) the solution; while the *higher* the pH value, the *less acidic* (or the *more alkaline* the solution).

**Revision Exercises**

40 What is meant by the pH of a solution?

41 a. Name the instrument used for determining a pH value.

b. State the lower and upper limits of the pH scale.

42 Solutions X, Y and Z have pH values 3.0, 5.0 and 9.0 respectively. Which of the following statements is correct?

A. All the solutions are acidic.
B. All the solutions are basic.
C. Y and Z are more acidic than water.
D. Y is more acidic than X.
E. Z is the least acidic. [NECO]

43 If solutions X, Y and Z have pH values of 13, 4 and 2 respectively; their order of increasing acidity is:

A. Z < X < Y B. X < Y < Z
C. Y < Z < X D. Z < Y < X [WAEC]

## Definitions and Calculations of pH

The **pH** of a solution can be defined as:

- *The concentration of hydroxonium or hydrogen ions in a solution.*
- *The degree of acidity or alkalinity of a solution.*
- *The negative logarithm to base ten of hydroxonium ion concentration.*
- *The logarithm to base ten of the reciprocal of hydroxonium ion concentration.*

Mathematically:

$\mathbf{pH} = -\log_{10}[H_3O^+]$ *or* $\mathbf{pH} = -\log_{10}[H^+]$

$\mathbf{pH} = \log_{10}\{1/[H_3O^+]\}$ *or* $\mathbf{pH} = \log_{10}\{1/[H^+]\}$

The pH of a solution is a shorthand method of representing the hydrogen or hydroxonium ion concentration, $[H^+]$ or $[H_3O^+]$. For example:

When $[H^+] = 0.1$ or $(10^{-1})$ *moldm*$^{-3}$, pH = 1.

In fact, pH is simply the exponent to which the base 10 in the logarithm is raised with the sign changed.

Mathematically: $\log_{10}10^{\pm x} = \pm x$.

**Worked Examples**

11 Calculate the pH of pure water at 25 °C, if the hydroxonium ion concentration is $1.0 \times 10^{-7}$ mole per dm$^3$

**Solution**

*To find pH when* $[H_3O^+] = 1.0 \times 10^{-7}$

Since $pH = -\log[H_3O^+]$ and $[H_3O^+] = 1.0 \times 10^{-7}$

Then, $pH = -\log(1.0 \times 10^{-7})$

$= -(0 - 7) = 7$

*Or* $pH = \log\{1/[H^+]\} = \log\{1/(1.0 \times 10^{-7})\}$

$= \log(1.0 \times 10^{7})$

$= 0 + 7 = 7$

That is: the pH of pure water at 25 °C is 7. It is neutral.

12 What is the pH of a solution containing:

a. 0.01 mole per dm$^3$ of HCl?

b. 0.01 mole per dm$^3$ of $H_2SO_4$?

**Solution**

a. *To find the pH of 0.01 moldm*$^{-3}$ *HCl.*

$HCl_{(aq)}$ is a strong acid; it is completely ionized in water:

$HCl_{(g)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$

1 mol 1 mol

From the above equation:

1 *mol* of HCl gives 1 *mol* of $H_3O^+$;

∴ 0.01 *mol* of HCl gives 0.01 *mol* $H_3O^+$

Hence, $[H_3O^+] = 0.01$ *moldm*$^{-3}$

$= 1.0 \times 10^{-2}$ or $10^{-2}$ *moldm*$^{-3}$

Since $pH = -\log[H_3O^+]$;

Then, $pH = -\log(10^{-2}) = -(-2) = 2$

b. *To find the pH of 0.01 moldm*$^{-3}$ $H_2SO_4$.

$H_2SO_4$ is a strong acid; it is completely ionized in water:

$H_2SO_{4(l)} + 2H_2O_{(l)} \rightarrow 2H_3O^+_{(aq)} + SO_4^{2-}{}_{(aq)}$

1 mol 2 mol

From the above equation:

1 *mol* of $H_2SO_4$ gives 2 *mol* of $H_3O^+$;

∴ 0.01 mol of $H_2SO_4$ gives $2 \times 0.01$ mol of $H_3O^+$

$= 0.02$ mol.

Hence, $[H_3O^+] = 0.02$ *moldm*$^{-3}$

$= 2.0 \times 10^{-2}$ *moldm*$^{-3}$

Since $pH = -\log[H_3O^+]$; then

$pH = -\log(2.0 \times 10^{-2})$

$= -[0.301 + (-2)] = -[0.301 - 2]$

$= -[-1.699]$

i.e. $pH = 1.699 = 1.70$ (3 sig. fig.)

**Note**: pH of 0.01 *moldm*$^{-3}$ $H_2SO_4$ is lower than that of 0.01 *moldm*$^{-3}$ HCl. This is because $H_2SO_4$ is dibasic, hence, more acidic than HCl, which is monobasic.

13 Calculate the pH of a solution containing 0.001 mole per dm$^3$ of NaOH. [WAEC]

**Solution**

*To find the pH of 0.001 moldm*$^{-3}$ *NaOH.*

NaOH is a strong base; it ionizes in water completely:

$NaOH_{(s)} + H_2O_{(l)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$

1 *mole* 1 *mole*

From the above equation:

1 mole of NaOH produces 1 mole of $OH^-$

∴ 0.001 mol will produce 0.001 mol of $OH^-$

Hence, $[OH^-] = 0.001$ or $1.0 \times 10^{-3}$ *moldm*$^{-3}$

But for a dilute solution:

$$[H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

i.e. $[H_3O^+] \times (1.0 \times 10^{-3}) = 1.0 \times 10^{-14}$

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-3}} = 1.0 \times 10^{-11}$$

Since pH = -log $[H_3O^+]$; then,

pH = -log $(10^{-11})$ = -(-11) = 11

Hence, the pH of 0.001 *moldm*$^{-3}$ NaOH solution is 11; it is strongly alkaline.

**14** A solution has a pH of 4. What is the $[H_3O^+]$?

**Solution**

Since pH = -log $[H_3O^+]$ and pH = 4; rearranging,

-log $[H_3O^+]$ = pH or, log $[H_3O^+]$ = - pH

$[H_3O^+]$ = antilog (-pH) = antilog (- 4) = $10^{-4}$

= $1.00 \times 10^{-4}$ *moldm*$^{-3}$

**15** An orange juice has a pH of 3.80.

**a.** What is the $[H_3O^+]$ in the juice?

**b.** What is the $[OH^-]$ in the same juice?

**Solution**

**a.** *To find $[H_3O^+]$ in a juice with a pH of 3.8*

pH = -log $[H_3O^+]$ and pH = 3.8; then,

log $[H_3O^+]$ = - pH

$[H_3O^+]$ = antilog (- pH)

= antilog (- 3.80)

Since antilog of (-3.80) = antilog of (0.20 – 4.0)

∴ $[H_3O^+]$ = antilog (0.20 – 4.0)

= antilog (0.20) × antilog (- 4.0)

= $1.60 \times 10^{-4}$ mole per dm$^3$

**b.** *To find $[OH^-]$ in the same juice*

In a dilute solution; $[H_3O^+][OH^-] = 10^{-14}$

$[H_3O^+] = 1.60 \times 10^{-4}$

∴ $[OH^-] = (1.00 \times 10^{-14})/(1.60 \times 10^{-4})$

= $6.25 \times 10^{-11}$

**16** The $[H_3O^+]$ of a 1.0 *moldm*$^{-3}$ solution of ethanoic acid is $1.80 \times 10^{-5}$ *moldm*$^{-3}$. What percent of the acid is ionized in the aqueous solution?

**Solution**

*To find percent ionization of ethanoic acid.*

Since $1.8 \times 10^{-5}$ *mole* of $H_3O^+$ is produced from 1 *mole* of ethanoic acid, the percent ionized will be:

$(1.8 \times 10^{-5} \times 100)/1 = 0.00180$ %.

### Revision Exercises

**44** Define pH of a solution.

**45** Calculate the

**a.** pH of 0.01 *moldm*$^{-3}$ $HNO_3$ solution.

**b.** pH of a 0.050 *moldm*$^{-3}$ solution of tetraoxosulphate(IV) acid.

**c.** pH of 0.050 *moldm*$^{-3}$ KOH solution.

**d.** $[H_3O^+]$ and $[OH^-]$ in a solution with a pH of 1.55.

**46** Calculate the pH of 0.20 *moldm*$^{-3}$ of $Ca(OH)_2$, assuming that $Ca(OH)_2$ is a strong electrolyte.

**47** A sample of fruit juice has a pH of 4.2. What is the concentration in mol dm$^{-3}$ of hydroxide ions, $[OH^-]$ in the juice ?

**A.** $1.58 \times 10^{-5}$ **B.** $1.58 \times 10^{-10}$ **C.** $6.31 \times 10^{-5}$
**D.** $6.31 \times 10^{-10}$ **E.** $9.80 \times 10^{-10}$ [NECO]

**48** The concentration of $H_3O^+$ in 1.0 *mol dm*$^{-3}$ solution of $C_6H_5COOH$ (benzoic acid) is $8.0 \times 10^{-3}$ *mole per dm*$^3$. Calculate its percent ionization.

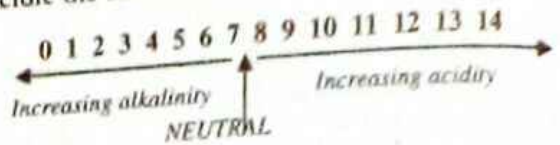
## Concept of pOH

**pOH** is a measure of the concentration of $OH^-$ in a solution; i.e. its alkalinity. The trend in the variation of pOH is exactly opposite to that of pH. For instance:

The alkalinity of a solution *increases* as the pOH value *decreases*. Hence, a solution with a pOH value of 6.8 is *weakly* alkaline, when compared with another solution with a pOH of 2.5, which will be *strongly* alkaline.

Conversely, acidity *increases* as the pOH value *increases*. Hence, a solution with a pOH of 7.3 is *weakly* acidic, when compared with another solution with a pOH of 12.5, which will be *strongly* acidic.

Generally, the *lower* the pOH value, the *more* alkaline or the *less* acidic the solution; while the *higher* the pOH value, the *less* alkaline or the *more* acidic the solution.




Mathematically,

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

For any dilute solution, **pH + pOH = 14**

Hence, **pH = 14 – pOH**

Or **pOH = 14 – pH**

For example: The pH of 0.0010 *moldm*$^{-3}$ of NaOH solution is 11, hence, its pOH = 14 – 11 = 3.

Similarly, since pH of pure water is 7, its pOH is also 7. Hence, for a *neutral* solution,

**pH = pOH = 7.**

Recall that $[H_3O^+][OH^-] = 1.00 \times 10^{-14}$

### Worked Examples

**17a** What is the $[OH^-]$ in a solution of pOH of 5.55?

**b** What is the $[H_3O^+]$ in the same solution in a above?

**Solution**

**a.** *To find $[OH^-]$ when pOH is 5.55*

Since pOH = -log $[OH^-]$ and pOH = 5.55.

Rearranging:

- log $[OH^-]$ = pOH; or, log $[OH^-]$ = - pOH

$[OH^-]$ = antilog (- pOH)

= antilog (- 5.55)

Since antilog of (- 5.55) = antilog of (0.45 – 6.00)

∴ $[OH^-]$ = antilog of (0.45 – 6.00)

= antilog (0.45) × antilog (- 6.00)

= $2.82 \times 10^{-6}$ *moldm*$^{-3}$

**b.** *To find $[H^+]$ in the same solution*

In a dilute solution; $[H_3O^+][OH^-] = 10^{-14}$

$[OH^-] = 2.82 \times 10^{-6}\ moldm^{-3}$

$\therefore [H_3O^+] = (1.00 \times 10^{-14})/(2.82 \times 10^{-6})$

$= 3.55 \times 10^{-9}\ moldm^{-3}$

18 A glass cup of orange juice is found to have a pOH of 11.40. Calculate the concentration of the hydrogen ions in the juice. [NECO]

**Solution**

*To find $[H^+]$, when pOH = 11.4*

In a dilute solution, pH + pOH = 14.

$pH = 14 - pOH$

$= 14 - 11.4 = 2.6$

Since $pH = -\log [H^+]$ and pH = 2.6, then,

$\log [H^+] = -pH$

$[H^+] = \text{antilog}(-pH)$

$= \text{antilog}(-2.6)$

Since antilog of (-2.60) = antilog of (0.4 - 3.0)

$\therefore [H^+] = \text{antilog}(0.4 - 3.0)$

$= \text{antilog}(0.4) \times \text{antilog}(-3.0)$

$= 2.51 \times 10^{-3}$ *mole per dm³*

**Revision Exercises**

49 Solutions A, B and C have pOH values 2.5, 4.0 and 10.0 respectively. Which of the solutions is least alkaline ?

50 If solutions X, Y and Z have pOH values of 1.6, 5.0 and 3.0 respectively; arrange the solutions in order of increasing alkalinity.

51a. What is the $[OH^-]$ in a solution of pOH of 3?

b. What is the $[H_3O^+]$ in the same solution in a above?

52 An orange juice is found to have a pOH of 9.5. What is the $[H^+]$ in the juice?

53 Which of the following conclusions about a solution of pH 4 is correct?

A. It contains more $OH^-$ than $H_3O^+$.

B. Its pOH value will be 10.

C. It is more acidic than a solution of pH 2.

D. Its hydrogen ion concentration is $4.0 \times 10^{-1}$ $moldm^{-3}$.

54 Calculate the

a. concentration of $H_3O^+$ in 0.025 $moldm^{-3}$ aqueous solution of HCl.

b. pH and pOH of the solution in 6a above. [WAEC]

### pH of a weak acid or weak alkali

A *weak* acid is only slightly or partially ionized in water; therefore, the hydroxonium ion concentration of an aqueous solution of a *weak* acid will be *lower* than expected. Consequently, its pH will be *higher* than expected. For instance:

A 0.10 $moldm^{-3}$ $HCl_{(aq)}$, a *strong* acid, has a pH of 1.0; while the pH of 0.10 $moldm^{-3}$ ethanoic acid, a *weak* acid is 3.0.

Similarly, the pH of a 0.10 $moldm^{-3}$ $NaOH_{(aq)}$, a strong base, is 13.0; while that of 0.10 $moldm^{-3}$ $NH_{3\,(aq)}$, a weak base, is 11.0

**Importance of pH values**

The pH values of chemical substances are important scientifically, and industrially:

1. In agriculture, the pH of soil ranges from 4 to 10. It is the pH value of a soil sample that determines the type of crop to be grown on it.

2. In medicine, there is a pH range for each of the body fluids, as shown below. Any large difference leads to health problems.

| Body fluid | pH range |
|---|---|
| Gastric juice | 1.6 – 1.8 |
| Bile | 7.6 – 8.6 |
| Urine | 5.5 – 7.0 |

3. In the industry, the treatments of liquid wastes, called ***effluents***, depend on their pH values.

4. In the treatment of water for public supply, there is the need for the pH of water to be maintained between 6 and 8; so that the water being supplied for public consumption is not too acidic or too alkaline.

**Revision Exercises**

55 Arrange the body fluids listed above in their order of increasing acidity.

56 Arrange the following equimolar solutions in order of increasing pH:

$NH_3(aq)$ ; $HCl(aq)$ ; $CH_3COOH$ ; $NaOH$ ; $Ca(OH)_2$

## 14.10 Acid-Base Indicators

### Common Acid-Base Indicators

*An acid-base indicator* is a *weak* organic acid or base that gives different colours in acidic and alkaline solutions, i.e. depending on the hydroxonium ion concentration, **pH** of the solution.

Acid-base indicators are used to test whether a solution is acidic, alkaline, or neutral, and are employed during acid-base titrations, to detect the end points. They are in the form of solutions or test papers.

Table 14.1 shows the list of the common acid-base indicators, the colours they exhibit in various types of solutions, and the pH ranges where changes in colours take place.

**Table 14.1 *Common Indicators***

| INDICATOR | COLOUR IN | | | pH of transition |
|---|---|---|---|---|
| | Acid | Neutral | Alkali | |
| Litmus | Red | Purple | Blue | 6.0 – 8.0 |
| Methyl orange | Pink | Orange | Yellow | 3.1 – 4.4 |
| Phenolphthalein | Colourless | Colourless | Pink | 8.3 – 10.0 |
| Methyl red | Pink | Red | Yellow | 4.4 – 6.3 |

### Universal Indicator

Common *acid-base indicators* cannot be used to determine the degree of acidity or alkalinity of a coloured solution; a more advanced indicator, the ***universal indicator***, has been developed to indicate the degree of acidity or alkalinity of such solutions.

A *universal indicator* is a mixture of dyes; it is composed of many indicators such as methyl orange, phenolphthalein and methyl red. It has the ability to indicate the pH values between 2 and 13. It is either in the form of a solution or test paper. It exhibits various colours: from red to orange, yellow, green, blue, indigo and finally, violet ***(ROYGBIV)***; depending on the pH of the solution.

Usually, charts that indicate the various colours and their corresponding pH values are commercially available (see Table 14.2).

**Table 14.2:** ***Universal indicator***

| pH | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|---|
| Colour | *RED* | | | *ORANGE* | *YELLOW* | | *GREEN* | | |

| pH | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|
| Colour | *BLUE* | *INDIGO* | | *VIOLET* | | |

### Revision Exercises

**57** What is an acid-base indicator? Why is it employed in an acid-base titration?

**58** Name **three** types of acid-base indicators.

**59** The colour of phenolphthalein indicator in dilute $HNO_{3(aq)}$ is [WAEC]

**A.** colourless **B.** orange **C.** pink **D.** purple

**60** The table below shows some solutions and their pH values.

| *Solution* | A | B | C | D | E |
|---|---|---|---|---|---|
| *pH* | 1.2 | 7 | 12 | 6.5 | 7.7 |

**a.** State which of the solutions would

**I.** react with zinc to liberate hydrogen.

**II.** change the colour of phenolphthalein to pink.

**III.** not change the colour of litmus paper.

**b.** Which of the solutions is

**I.** strongly acidic? **II.** strongly alkaline? [WAEC]

## 14.10 pH titration curves

When a *solution of a base* is gradually added into a *solution of an acid*, there is a general *increase* in the pH of the mixture. However, the overall shape of the *pH curve* depends on the strengths of the acid and base involved in the reaction.

***General Procedure:*** Place 25.0 $cm^3$ of the acid in a 100 $cm^3$ conical flask; then, gradually add the base from a burette into the conical flask with swirling, and measure the pH of the mixture intermittently.

There are **four** different situations.

**1. Titration of a *strong* acid and a *strong* base**

As a solution of 0.100 $moldm^{-3}$ NaOH is gradually added into 25 $cm^3$ of 0.100 $moldm^{-3}$ $HCl_{(aq)}$, the pH increases slowly initially, then, very rapidly and sharply at the end point, and finally, slowly, when the mixture becomes alkaline.

Figure **14.1a** shows that there is a rapid change in pH from 3 to 11, where equi-molar amounts of $H_3O^+$ and $OH^-$ are present in the mixture.

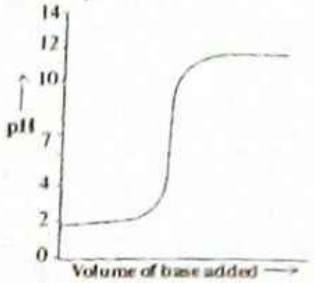



**Fig 14.1a** *Titration of a strong acid and a strong base*

Any indicator that changes its colour within the range between pH of 3 and 11 can be used for the titration of a *strong acid* and a *strong base*; i.e. methyl orange, methyl red, or phenolphthalein.

**2. Titration of a *strong* acid and a *weak* base**

When a $NH_{3(aq)}$, *a weak base*, is gradually added into a solution of 0.100 $moldm^{-3}$ $H_2SO_4$, a strong acid, the pH increases slowly first, then, rapidly at the end-point, and finally, slowly, when excess $NH_{3(aq)}$ must have been added (fig. **14.1b**).

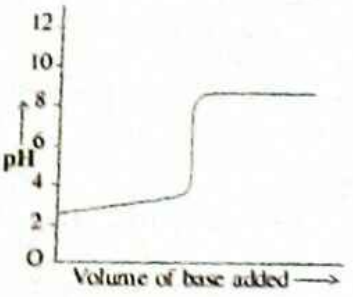



**Fig 14.1b** *Titration of a strong acid and a weak base*

The indicator to be used for the titration of a *strong acid* and a *weak base* is methyl orange; it is the only indicator that changes its colour within the pH of 3 and 8.

**3. Titration of a *weak* acid and a *strong* base**

When a solution of 0.100 $moldm^{-3}$ KOH, a strong base, is gradually added into a solution of a weak acid, ethanedioic acid ($H_2C_2O_4$; 0.100 $moldm^{-3}$), there is a large increase in the pH initially, then, rapidly at the end point, and finally, slowly.

The indicator to be used must change its colour within the pH range of 6 and 11. Hence, phenolph-

thalein is the only suitable indicator for the titration of a weak acid and a strong base (fig. 14.1c).

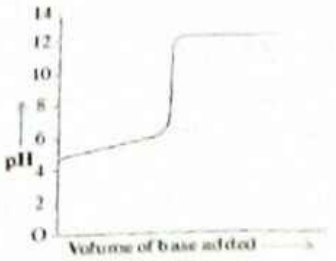



**Fig 14.1c** *Titration of a weak acid and a strong base*

**4. Titration of a weak acid and a weak base**

When aqueous ammonia, a weak base, is gradually added into a solution of 0.100 $moldm^{-3}$ ethanoic acid, a weak acid, there is no point in time when there is a rapid change in pH; that is, no sharp end-point. Hence, there is no suitable indicator (fig. **14.1d**). A pH meter can be used.

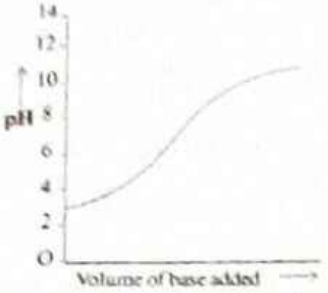



**Fig 14.1d** *Titration of a weak acid and a weak base*

Table 14.1 shows the choice of indicator in acid-base titrations.

**Table 14.1**: *Choice of Indicators*

| Titration of | Example | Suitable Indicator |
|---|---|---|
| Strong acid and strong base | $HCl_{(aq)}$ and $NaOH_{(aq)}$ | Methyl orange, methyl red, or phenolphthalein |
| Strong acid and weak base | $H_2SO_{4(aq)}$ and $Na_2CO_{3(aq)}$ | Methyl orange |
| Weak acid and strong base | $H_2C_7O_{4(aq)}$ and $KOH_{(aq)}$ | Phenolphthalein |
| Weak acid and weak base | $CH_3COOH_{(aq)}$ and $NH_{3(aq)}$ | No suitable indicator. *Use pH meter.* |

***Use of pH meter in acid-base titrations***

A unique advantage of the pH meter over other methods of determining the acidity or alkalinity of a solution is that it can be used in the acid-base titrations of coloured solutions. For instance: None of the common indicators can be used in the acid-base titrations involving *Coca-Cola* – a weakly acidic solution, or to determine the pH of blood, urine, or a fruit juice.

Again, a *pH meter* is used in the titrations involving *weak* acids against *weak* bases.

**19** In a titration experiment, $H_2SO_{4(aq)}$ was titrated against $NaOH_{(aq)}$.

**a.** Name a suitable indicator that could be used in the titration.

**b.** What would be the colour of the named indicator in a above in:

i. $H_2SO_{4(aq)}$? ii. $NaOH_{(aq)}$?

iii. a titration mixture of $H_2SO_{4(aq)}$ and $NaOH_{(aq)}$ at end point?

*a. Any one of the following indicators can be used for the titration between $H_2SO_4$ and NaOH (strong acid versus strong base): Methyl orange, methyl red, phenolphthalein or litmus solution.*

**b.** Colours of the suitable indicators in the solutions:

| Indicator | Colour in $H_2SO_4$ | Colour in NaOH | Colour at end point |
|---|---|---|---|
| Methyl orange | Pink | Yellow | Orange |
| Phenolphthalein | Colourless | Pink | Colourless |
| Methyl red | Pink | Yellow | Red |
| Litmus solution | Red | Blue | Purple |

**20** Explain why methyl orange **cannot** be used as an indicator during the titration of a strong base with a weak acid. [WAEC]

*Methyl orange changes its colour in an acidic medium. Since the titration mixture of a strong base and a weak acid will be alkaline at the endpoint, methyl orange **cannot** be used.*

## Revision Exercises

**61** Describe how the pH value of sodium hydroxide solution varies as dilute hydrochloric acid is added into it, until the acid is in large excess.

**62** Sketch the pH titration curve involving a strong acid and a strong base.

## Answers to Revision Exercises

**24a** 0.0250 *mol.* **b** 1.50 *mol.* **25** 7.77 *g.* **26a** 43.0 $gmol^{-1}$ **26b** 63.5 **27** 11.0 *g* **28** 0.100 *mol.* **29** 0.0100 *mol.* **30** 90.0 *g* **33.** B **34.** A **35a** 0.0500 *mol.* **b** 140 *g.* **35c** 100 $cm^3$ **36.** B **42.** E **43.** B **45a** 2.0; **b** 1.0 *g*; **45c** 12.7; **d** $[H^+] = 1.00 \times 10^{-5}$ $moldm^{-3}$ **46** 10.6 **47.** B **48** 0.888% **49.** C **50** Y < Z < X. **51a** $[OH^-] = 1.00 \times 10^{-5}$ $moldm^{-3}$ **b** $[H_3O^+] = 1.00 \times 10^{-5}$ $moldm^{-11}$ **52** $3.65 \times 10^{-9}$ $moldm^{-3}$ **53.** B **54a** 0.0250 $moldm^{-3}$; **b.** pH = 1.60; pOH = 12.4 **59.** A **60a I.** A; **II.** C and E; **III.** B; **b I.** A **II.** C

# 15

# • SALTS • IONIC REACTIONS •

## 15.1 Occurrence

Salts are found in nature; they occur as mineral ores and rock deposits: Sodium chloride occurs naturally as *rock salt*; calcium trioxocarbonate(IV) occurs *as chalk, limestone and marble*; while zinc sulphide occurs as *zinc blend*.

**Revision Exercises**

1. Name the natural form of
   a. sodium chloride; b. calcium trioxocarbonate(IV).
2. Mention an ore of zinc.

## 15.2 Definitions of a Salt

A *salt* can be defined in the following ways:

1. A salt is formed, when the replaceable hydrogen atoms of an acid have been *completely* or *partially* replaced by a metal or ammonium ion. e.g.

a. When the hydrogen ion, $H^+$ in hydrochloric acid, HCl is replaced by sodium ion, $Na^+$, sodium chloride, NaCl is formed, i.e.

$\underline{H}Cl$ (an acid) becomes $\underline{Na}Cl$ (a salt)

b. When one of the hydrogen ions in $H_2SO_4$ is replaced by potassium ion, $K^+$, a salt is formed.

$\underline{H}_2SO_4$ (an acid) becomes $\underline{K}HSO_4$ (a salt).

2. A *salt* is formed when the *positive ion (cation) of a base* combines with the *negative ion (anion) of an acid*; e.g.

a. Sodium ion in sodium hydroxide combines with the chloride ion in hydrochloric acid to form sodium chloride salt:

$$\underline{Na}OH_{(aq)} + H\underline{Cl}_{(aq)} \rightarrow \underline{NaCl}_{(aq)} + H_2O_{(l)}$$

b. Copper(II) ion in copper(II) oxide, CuO combines with the tetraoxosulphate(VI) ion in $H_2SO_4$, to form $CuSO_4$:

$$\underline{Cu}O_{(s)} + H_2\underline{SO_4}_{(aq)} \rightarrow \underline{CuSO_4}_{(aq)} + H_2O_{(l)}$$

*All salts are solids at room temperatures.*

**Revision Exercises**

3. Define the term salt? Give two examples.
4. Explain why sodium chloride is regarded as a salt.
5. Write the formulae of the acid and the base that produce each of the following salts:
   a. $KNO_3$ b. $Pb(CH_3COO)_2$ c. ZnS d. $(NH_4)_2CO_3$

## 15.3 Types of Salts

There are *six* main types of salts: ***normal*** salts, ***acid*** salts, ***basic*** salts, ***hydrated*** salts, ***double*** salts and ***complex*** salts.

1. A ***normal salt*** is formed when *all* the *replaceable* hydrogen atoms in an acid are completely replaced by metal or ammonium ions, e.g.

- HCl (*monobasic acid*) forms NaCl (*normal salt*).
- $H_2SO_4$ (*dibasic*) produces $K_2SO_4$ (*normal salt*).
- $H_3PO_4$ (tribasic) forms $Ca_3(PO_4)_2$ (*normal salt*).

Generally, *monobasic* acids, such as HCl and $HNO_3$ produce *normal salts only*.

2. An ***acid salt*** is formed when the *replaceable* hydrogen ions in an acid are *partially* replaced by metal or ammonium ions, e.g.

If only *one* of the *two* hydrogen atoms in $H_2SO_3$ is replaced by a sodium atom, an *acid salt*, $NaHSO_3$ is formed (see Table 14.1).

**Table 15.1** ***Some acids and their salts***

| Acid | Acid salt | Normal salt |
|---|---|---|
| HCl | None | NaCl; $CaCl_2$ |
| $HNO_3$ | None | $KNO_3$; $Zn(NO_3)_2$ |
| $HNO_2$ | None | $NaNO_2$ |
| HCN | None | KCN |
| $H_2SO_4$ | $KHSO_4$; $Mg(HSO_4)_2$ | $K_2SO_4$ ; $MgSO_4$ |
| $H_2CO_3$ | $NaHCO_3$; $Ca(HCO_3)_2$ | $CaCO_3$; $Na_2CO_3$ |
| $H_2S$ | KHS ; $NH_4HS$ | $K_2S$ ; $(NH_4)_2S$ |
| COOH<br>\|<br>COOH | COONa<br>\|<br>COOH | COONa<br>\|<br>COONa |
| $H_3PO_4$ | $NaH_2PO_4$ ; $Na_2HPO_4$ | $Na_3PO_4$; $Ca_3(PO_4)_2$ |

Generally, *dibasic* and *tribasic* acids form *both* the *normal* and *acid salts*. This is because such acids ionize in stages, e.g.

a. $H_2SO_4$ ionises in *two* stages:

*Stage 1*: $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$ (acidic ion)

*Stage 2*: $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ (normal ion)

b. $H_3PO_4$ ionises in *three* stages:

*Stage 1*: $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$

*Stage 2*: $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$

*Stage 3*: $HPO_4^- \rightleftharpoons H^+ + PO_4^{3-}$

An acid salt dissolves in water to produce hydrogen (or hydroxonium) ion; it is acidic, e.g.

$KHSO_{4(s)} + H_2O_{(l)} \rightarrow Na^+_{(aq)} + H_3O^+_{(aq)} + SO_4^{2-}{}_{(aq)}$

3. A ***basic salt*** is formed by the *partial* replacement of the hydroxide ions in a metallic hydroxide:

| Base | Basic salt | Normal salt |
|---|---|---|
| $Zn(OH)_2$ | Zn(OH)Cl | $ZnCl_2$ |
| $Mg(OH)_2$ | Mg(OH)Cl | $MgCl_2$ |

Zn(OH)Cl is called zinc hydroxychloride. A water-soluble basic salt produces hydroxide ions in water.

4. An ***hydrate*** is a salt with *water of crystallization*. They are crystalline: $Na_2CO_3 \cdot 10H_2O$ (*white*); $CuSO_4 \cdot 5H_2O$ (*blue*); $FeSO_4 \cdot 7H_2O$ (*light green*).

Salts *without water of crystallization* are said to be *anhydrous*.

5. A ***double salt*** is formed when two simple salts combine, in stoichiometric ratio, to form a single compound.

The general chemical formula for double salts is:

$$X_2SO_4 . Y_2(SO_4)_3$$

where $X = Na^+$, $K^+$ or $NH_4^+$ (monovalent ion)

$Y = Al^{3+}$, $Fe^{3+}$ or $Cr^{3+}$ (trivalent ion)

*Alum* is an example of a *double salt*. The two types of alum are:

a. *Potassium alum*: $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$.

This is the common alum used as a coagulant. It is crystalline and white; its empirical formula is

$$KAl(SO_4)_2 \cdot 12H_2O.$$

b. *Iron(III) alum*: $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$.

It is crystalline and purple in colour. Its empirical formula is $NH_4Fe(SO_4)_2 \cdot 12H_2O$.

Another example of a double salt is obtained when a water solution of stoichiometric proportion of $FeSO_4$ and $(NH_4)_2SO_4$ is recrystallised to give crystals of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$. It is called iron (II) ammonium tetraoxosulphate(VI) hexahydrate.

An aqueous solution of a *double salt* will give the reactions of the constituents' single salts.

6. A ***complex salt*** contains a *complex ion*. An ion in which a metal ion forms dative bonds with anions or neutral molecules are *complex ions*, e.g. $[Cu(NH_4)]^{2+}$, $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$. Hence, $[Cu(NH_4)](OH)_2$ and $K_4[Fe(CN)_6]$ are complex salts. See Section 7.6 for naming of complex salts.

**Revision Exercises**

6 a. List **three** types of salts and give **one** example of each type.

b. Mention **two** salts that cause hardness in water.

7. Classify each of the following as: normal salt/acid salt/basic salt/double salt.

$Na_2HPO_4$; $CH_3COOK$; $Mg(NO_3)_2$; $FeCl_3$; Zn(OH)Cl; $KAl(SO_4)_2 . 12H_2O$; $Ca(HCO_3)_2$.

8. Which of the following compounds is not a double salt? **A.** $Zn(OH)NO_3$ **B.** $KAl(SO_4)_2$. **C.** $KCr(SO_4)_2$ **D.** $(NH_4)Fe(SO_4)_2$. [WAEC]

9. Which of the following is/are complex salts?

**a.** $Na_2S_2O_3 \cdot 5H_2O$; **b.** $Mg(OH)Cl$; **c.** $[Cu(NH_3)_4]Cl_2$; **d.** $KMnO_4$; **e.** $K_4Fe(CN)_6$

10 Which of the following acids forms normal salt only?

**A.** Tetraoxosulphate(VI) acid.
**B.** Tetraoxophosphate(V) acid.
**C.** Trioxonitrate(V) acid.
**D.** Trioxosulphate(IV) acid. [WAEC]

11 Which of the following can produce acid salts?

**a.** $HNO_2$; **b.** $H_2SO_3$; **c.** $CH_3COOH$; **d.** $H_3PO_4$.

12 Why is tetraoxosulphate(VI) acid able to produce two types of salts, unlike trioxonitrate (V) acid? [W]

## 15.4 Solubility of Salts in Water

Salts are ionic compounds that dissolve in water to produce ions; hence, they are electrolytes.

However, some salts are only *slightly* or *partially* soluble in water. Their solubility in water is so small that they are regarded as being *insoluble* – as indicated in the following rules.

**Solubility Rules**

1. All salts of sodium, potassium, and ammonium are *soluble* in water.
2. All *trioxonitrate(V) salts* [*nitrates*, $NO_3^-$] are *soluble* in water.
3. All chlorides are *soluble* in water; except those of *lead*, *mercury* and *silver* that are *insoluble*.
4. All *tetraoxosulphate*(VI) *salts*, [*sulphates*, $SO_4^{2-}$] are soluble in water; except those of lead and barium. Calcium tetraoxosulphate(VI), $CaSO_4$ is only *slightly soluble* in water.
5. All *trioxosulphate*(IV) *salts* [*sulphites*, $SO_3^{2-}$] are *insoluble* in water; except those of *sodium*, *potassium* and *ammonium* that are *soluble*.
6. All *trioxocarbonate*(IV) salts [*carbonates*, $CO_3^{2-}$] are *insoluble* in water; except those of *sodium*, *potassium*, and *ammonium* that are *water-soluble*.
7. All *sulphides*, $S^{2-}$ are *insoluble* in water; except those of *sodium*, *potassium* and *ammonium* that are *soluble*.
8. All *acid salts* are *soluble* in water.

**Solved Problem 1**

Which of the following salts is slightly soluble in water? [JAMB]

**A.** $CaSO_4$ **B.** $PbCl_2$ **C.** $Na_2CO_3$ **D.** AgCl

**Answer: A**

**Revision Exercises**

**13** Mention **two** chlorides that are insoluble in water.

**14** In which of the following groups are all the salts insoluble in water ?

A. $K_2CO_3$; $CaSO_4$; $AgNO_3$ B. $ZnCO_3$; $BaSO_4$; AgCl
C. $NaHCO_3$; $PbSO_4$; $CaSO_4$ D. $PbCl_2$; NaCl; $ZnCl_2$

**15** Which of the following mixtures of salts can be separated by adding water, stirring and filtering?

A. $ZnSO_4$ and $Na_2SO_4$ B. $NaHCO_3$ and $CaCl_2$
C. $K_2SO_4$ and $CaCO_3$ D. $Na_2CO_3$ and $NaNO_3$

## 15.5 Hydrated and Anhydrous Salts

**1.** Salts that contain *water of crystallization* are called ***hydrates*** or ***hydrated salts***.

**2.** ***Water of crystallization*** *is the definite amount of water with which salts are associated on crystallizing from saturated solutions.*

**3.** Common examples of hydrated salts are:

- $Na_2CO_3 \cdot 10H_2O$ (white)
- $CuSO_4 \cdot 5H_2O$ (blue)
- $ZnSO_4 \cdot 7H_2O$ (white)
- $FeSO_4 \cdot 7H_2O$ (green)

**Note:** The dot (·) in the formula of a hydrated salt denotes a loose association.

**4.** ***Hydrates*** are *crystalline*. Salts *without water of crystallization* are called ***anhydrous***; they are *powdery*, e.g.

- $CuSO_4$ (*white*);
- $Na_2CO_3$ (*white*)

**5.** *All hydrated salts form crystals, but not all crystalline salts are hydrated.* For instance: NaCl forms *anhydrous crystals*; it is *not hydrated*. Other examples of salts with *anhydrous crystals* are: $KNO_3$, $KClO_3$, $NH_4NO_3$ and $(NH_4)_2SO_4$.

**6.** *The water of crystallization is usually given off partially or completely, when the crystals are exposed to the atmosphere, or when heated.*

**Revision Exercises**

**16** Explain what is meant by the term *water of crystallization*.

**17** State the difference between an *anhydrous* and *hydrated* salts.

**18** Which hydrated salt is used as water softener?

## 15.6 Physical Properties of Salts

The following phenomena are the characteristic properties of salts:

### 1. Efflorescence

***Efflorescence*** is the *process* whereby a *hydrated salt* ***loses*** its *water of crystallization*, partially or completely, to the atmosphere. Such *hydrated salts are said to be* ***efflorescent***.

Examples are:

$Na_2CO_3 \cdot 10H_2O$; $CuSO_4 \cdot 5H_2O$; $FeSO_4 \cdot 7H_2O$.

*Efflorescent salts lose* weight and their crystalline forms when heated, or when exposed to the atmosphere, to become *anhydrous* and *powdery*.

**Exposure to air**

a. $Na_2CO_3 \cdot 10H_2O_{(s)} \longrightarrow Na_2CO_3 \cdot H_2O_{(s)} + 9H_2O_{(g)}$
(white crystals) (white powder)

**heat**

b. $CuSO_4 \cdot 5H_2O_{(s)} \longrightarrow CuSO_{4(s)} + 5H_2O_{(g)}$
(blue crystals) (white powder)

### 2. Deliquescence

***Deliquescence*** is a phenomenon whereby, a compound absorbs moisture (or water vapour) from the atmosphere to *form a saturated solution*. Such a salt is said to be ***deliquescent***, e.g. fused calcium chloride, $CaCl_2$; magnesium chloride, $MgCl_2$; iron(III) chloride, $FeCl_3$; and calcium trioxonitrate(V), $Ca(NO_3)_2$.

***Deliquescent salts gain weight when exposed to the atmosphere.*** They have great affinity for water.

Sodium hydroxide, NaOH and potassium hydroxide, KOH are deliquescent alkalis, while phosphorus(V) oxide, $P_2O_5$ is a deliquescent oxide.

### 3. Hygroscopy

***Hygroscopy*** is a phenomenon in which a compound absorbs moisture from the atmosphere *without forming a solution*. Such a compound is ***hygroscopic***. Examples are: calcium oxide (quick lime, CaO); copper (II) oxide, CuO; and anhydrous $CuSO_4$. Concentrated $H_2SO_4$ is a hygroscopic liquid.

Hygroscopic compounds have great affinity for water, *they* ***gain*** *weight when exposed to the atmosphere.*

### Drying agents and Desiccants

*Deliquescent* and *hygroscopic* compounds are popularly used in the laboratory as drying agents for gases, liquids and solids, e.g.

a. Concentrated $H_2SO_4$, $CaO_{(s)}$ and fused $CaCl_{2(s)}$ are used as drying agents, for drying gases.

b. Anhydrous $MgSO_4$ and fused $CaCl_2$ are used as drying agents for organic solvents such as alcohols and propanone (acetone).

c. Fused $CaCl_2$, $CaO_{(s)}$, $CuO_{(s)}$ and *silica gel* are used as *desiccants*.

A ***desiccant*** is a *drying agent usually placed in the desiccator – a device used to keep solids dry.*

**Revision Exercises**

**19a** Define the following terms and give an example of a salt which exhibits each of the phenomena:

i. Efflorescence; ii. Deliquescence;
iii. Hygroscopy.

b Which of the salts mentioned in a above can be used as a drying agent?

20 Which of the following decreases in mass on exposure to air?
A. Sodium hydroxide pellets. B. Iron nails
C. Iron(III) chloride
D. Sodium trioxocarbonate(IV) decahydrate.

21 Consider the reaction represented by the following equation:

$$Na_2CO_3{\cdot}10H_2O_{(s)} \xrightarrow{\text{Exposure to air}} Na_2CO_3{\cdot}H_2O_{(s)} + 9H_2O_{(g)}$$

What name is given to this type of reaction? [WAEC]

22 a Define each of the following terms:
i. deliquescent ii. hygroscopic iii. efflorescent

b Which of the following is **not** deliquescent?
$CaCl_2$; CaO; $FeCl_3$; KOH; NaOH

23 What is a desiccant? Give **two** examples.

24 What name is given to the laboratory apparatus used in keeping solids dry?

## 15.7 Gravimetric Analysis of Salts

### Determination the Percentage of Water of Crystallization in a Salt

**Procedure**

1. Weigh a crucible on a balance; record its mass.
2. Place two spatulaful of hydrated sodium trioxocarbonate(IV) crystals in the crucible; reweigh.
3. Heat the crucible and its content for about five minutes on a triangular pipe-clay, placed on a tripod stand, using a Bunsen burner flame.
4. Allow the crucible to cool in a desiccator, then, weigh.
5. Heat the crucible and its content again, cool, and reweigh.
6. Repeat the process of heating, cooling, and weighing – until a constant mass is obtained for two consecutive measurements.
7. Hypothetical data for the calculation:

Mass of crucible = $x$ g
Mass of crucible + crystals = $y$ g
Mass of crucible + anhydrous salt = $z$ g
Mass of crystals of salt = $(y - x)$ g
Mass of anhydrous salt = $(z - x)$ g

∴ Mass of water of crystallization
$= (y - x) - (z - x)$
$= (y - x - z + x) = (y - z)$

$$\% \text{ water of crystallization} = \frac{(y-z)}{(y-x)} \times \frac{100}{1}$$

**Worked Example**

2. On heating 5.0 *g* of a salt Y to constant mass, 1.8 *g* of water of crystallization was given off. Calculate the number of molecules of water of crystallization in one molecule of Y, given that the molar mass of its anhydrous form is 160 $gmol^{-1}$.

**Solution**

*Data provided: Mass of hydrated salt = 5.0 g*
*Mass of water of crystallization = 1.8 g.*
*Molar mass of anhydrous salt = 160 $gmol^{-1}$*
*From the above data, mass of anhydrous salt in 5 g of hydrated salt = (5.0 – 1.8) g = 3.2 g*

Let $x$ be the number of molecules of water of crystallization.

Equation of reaction:

| **Hydrated salt** | → | **Anhydrous salt** | + | **Water of crys.** |
|---|---|---|---|---|
| 1 mol | | 1 mol | | $x$ mol |
| $(160 + 18x)$ g | | 160 g | | $18x$ g |

From the above data, mass of anhydrous salt in 5 g of hydrated salt = (5.0 – 1.8) g = 3.2 g

*Method 1*

From the equation:
160 g of anhydrous salt ≡ $18x$ g water of crys
3.2 g of anhydrous salt ≡ 1.8 g water of crys

That is: $\frac{160}{3.2} = \frac{18x}{1.8}$

Cross-multiplying:
$18x \times 3.2 = 160 \times 1.8$
$x = (160 \times 1.8)/(18 \times 3.2) = 16/3.2 = 5.0$

That is: 1 mole of anhydrous salt Y contains 5 moles of water of crystallization.

∴1 molecule of anhydrous salt Y contains 5 molecules of water of crystallization.

*Method 2*

3.2 g anhydrous salt contain 1.8 g water molecules
∴ 160 g of anhydrous salt will contain

$$\frac{1.8 \times 160}{3.2} \text{ g} = 90.0 \text{ g}$$

$M[H_2O] = (2 \times 1) + 16 = 18\ gmol^{-1}$

Amount of water = (mass)/(molar mass)
= 90/18 = 5.0 moles

i.e. 1 mole of anhydrous salt Y contains 5 moles of water of crystallization.

∴ 1 molecule of Y contains 5 molecules of water of crystallization.

**Worked Example 3**

The following results were obtained when a *hydrated* zinc salt, $ZnSO_4{\cdot}xH_2O$ was heated to a constant mass, to obtain the *anhydrous* salt. What is the value of $x$?

Weight of crucible = 10.00 g
Weight of crucible and crystals = 14.10 g
Weight of crucible and residue = 12.30 g
[Zn = 65; S = 32; O = 16; H = 1]

**Solution**

*From the data provided:*
Mass of hydrated salt = (14.10 – 10.00) g = 4.10 g
Mass of anhydrous salt = (12.30 – 10.00) g = 2.30 g
∴ Loss in mass = mass of water of crystallization
= (4.10 – 2.30) g = 1. 80 g

The problem involves mass-mass relationships, which requires *direct* proportion.

Equation of reaction:

$$ZnSO_4 \cdot xH_2O \xrightarrow{\text{heat}} ZnSO_4 + xH_2O$$

1 mole — 1 mole — $x$ mole

$(161 + 18x)$ g — 161 g — $18x$ g

From the balanced equation of reaction:
1 mole $(161 + 18x)$ g of the hydrated salt will produce 1 mole (161 g) of the anhydrous salt and $x$ mole $(18x)$ g of water of crystallization; i.e.

$(161 + 18x)$ g of $ZnSO_4 \cdot xH_2O \equiv 161$ g of $ZnSO_4$
$\equiv 18x$ g of $xH_2O$ ...15.1

From the experimental results:
4.10 g of the hydrated salt produced 2.30 g of anhydrous salt and 1.80 g of water of crystallization, i.e.

4.10 g of $ZnSO_4 \cdot xH_2O \equiv 2.30$ g of $ZnSO_4$
$\equiv 1.8$ g of $xH_2O$ ... 15.2

Dividing equation 15.1 by equation 15.2, we obtain:

$$\frac{(161 + 18x)\text{ g}}{4.10\text{ g}} = \frac{161\text{ g}}{2.30\text{ g}} = \frac{18x\text{ g}}{1.80\text{ g}}$$

i.e. $$\frac{161}{2.30} = \frac{18x}{1.80}$$

$18x = (161 \times 1.80)/2.30 = 126$

$18x = 126$

$x = 126/18 = 7.0$

Hence, $x = 7$ (a whole number)

Or $$\frac{161 + 18x}{4.10} = \frac{161}{2.30}$$

$161 + 18x = (161 \times 4.10)/2.30 = 287$

i.e. $161 + 18x = 287$

$18x = 287 - 161 = 126$

$x = 126/18 = 7$ (a whole number)

### Revision Exercises

**25** What is water of crystallization? [WAEC]

**26** Name two salts that contain water of crystallization.

**27** When sodium trioxocarbonate(IV) decahydrate loses its water of crystallization to the atmosphere, the process is

A. deliquescence. B. efflorescence
C. hygroscopic. D. effervescence. [JAMB]

**28** The percentage of water of crystallization in $ZnSO_4 \cdot 7H_2O$ is

A. 33% B. 44% C. 55% D. 87%
[Zn = 65, S = 32, O = 16, H = 1] [JAMB]

**29** Hydrated calcium chloride ($CaCl_2 \cdot xH_2O$) contains 49.32% water of crystallization. Calculate the value of $x$. [$CaCl_2 = 111$, $H_2O = 18$] [WAEC]

**30** When $CuSO_4 \cdot xH_2O$ crystals were exposed to the atmosphere for a few days, there was a loss in mass.

a. What name is given to this phenomenon?

b. Give another example of a salt that exhibits this phenomenon?

c. If 0.200 mole of $CuSO_4 \cdot xH_2O$ has a mass of 50.0 g, calculate its molar mass, and hence, the value of $x$.

**31** On heating 13.15 *g* of $NiSO_4 \cdot yH_2O$, 7.75 *g* of the anhydrous salt was obtained. Determine the value of $y$. [H = 1, O = 16, S = 32, Ni = 39] [WAEC]

**32** A 4.3 *g* of hydrated sodium tetraoxosulphate(VI) ($Na_2SO_4 \cdot xH_2O$) was heated to remove the water of crystallization. The remaining anhydrous salt has a mass of 2.12 g. Calculate the value of $x$ in the hydrated salt. [H = 1; O = 16; Na = 23; S = 32] [WAEC]

## 15.8 Preparation of Salts

Salts are classified into two – based on their solubility in water: *soluble and insoluble salts*. All salts that are *soluble in water* are prepared by method of ***crystallization***, while *insoluble* salts are prepared by method of ***precipitation***. Hence, it is essential to be familiar with the *solubility rules* (see section 15.4).

### Preparation of Normal Salts

In a *normal salt*, all the replaceable hydrogen atoms in the acid have been replaced by a metal or ammonium ion.

The following are the types of chemical reactions used in preparing normal salts in the laboratory:

1. Reaction between an *acid* and a *base* (neutralization). It is the most general method.
2. Action of a dilute acid on a trioxocarbonate(IV) salt.
3. Action of a dilute acid on a reactive metal.
4. Precipitation reactions.
5. Direct combination of a metal and a non-metal.

### 1. Preparation of soluble salts by neutralization reactions.

A neutralization reaction involves an acid and a base. There are two procedures: It is either from a *soluble* base (an *alkali*) or an *insoluble* base.

#### a. Preparation of a soluble salt from an alkali

***Preparation of NaCl crystals***

Reagents required:

- Solution of sodium hydroxide (2.0 *moles per dm*$^3$; bench reagent).
- Solution of hydrochloric acid (2.0 *moles per dm*$^3$; bench reagent).

*Equation of reaction*

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$$

This procedure is by *titration*:

i. Pipette 25 $cm^3$ of the sodium hydroxide solution into a conical flask, then add two or three drops of methyl orange.

ii. From a burette, run, gradually, the hydrochloric acid solution into the conical flask with swirling of the conical flask, until the indicator changes colour from *yellow* to *orange*. This is the end point; neutralisation is complete. Let the volume of acid used be $V$ $cm^3$.

iii. Repeat the titration using another 25 $cm^3$ portion of the alkali, and adding the correct volume $V$ $cm^3$ of the acid from the burette, *without using the indicator*. Shake the mixture thoroughly.

iv. Transfer the colourless solution into an evaporating dish, and evaporate the solvent, until the solution is saturated, i.e. crystals start to form on a glass rod dipped into the solution on cooling. This process is called *concentration*.

v. Allow the remaining solution to cool, in order to obtain crystals of sodium chloride.

vi. Filter the crystals, and dry between filter papers.

*Equation of reaction*

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$$

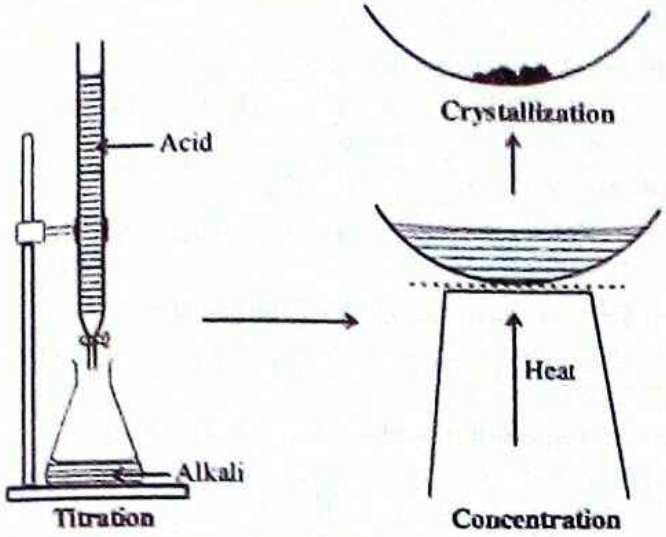



Fig 15.1 *Preparation of salt by neutralization*

Note: All salts of potassium, sodium and ammonium can be obtained by titration method, from the appropriate acids and alkalis; e.g.

i. *To obtain $KNO_3$ crystals*:

$$KOH_{(aq)} + KNO_{3\,(aq)} \rightarrow KNO_{3\,(aq)} + H_2O_{(l)}$$

ii. *To obtain hydrated $Na_2SO_4$ crystals*:

$$2NaOH_{(aq)} + H_2SO_{4\,(aq)} \rightarrow Na_2SO_{4\,(aq)} + 2H_2O_{(l)}$$

iii. *To obtain $NH_4Cl$ crystals*:

$$NH_{3\,(aq)} + HCl_{(aq)} \rightarrow NH_4Cl_{(aq)}$$

*Or* $NH_4OH_{(aq)} + HCl_{(aq)} \rightarrow NH_4Cl_{(aq)} + H_2O_{(l)}$

### b. Preparation of a soluble salt from an insoluble base

***Preparation of $CuSO_4$ crystals***

*Equation of reaction:*

$$CuO_{(s)} + H_2SO_{4\,(aq)} \rightarrow CuSO_{4\,(aq)} + H_2O_{(l)}$$

(black) (blue)

**Procedure:**

i. Place 50 $cm^3$ of bench tetraoxosulphate(VI) acid in a beaker. Add the base, black powdered copper(II) oxide, a little at a time into the acid with stirring and warming, until it can no longer dissolve. A blue solution is obtained. This process is called ***digestion***.

ii. *Filter* the mixture, *concentrate* the filtrate, and allow the saturated solution to crystallize, to obtain blue crystals of $CuSO_4 \cdot 5H_2O$.

iii. Filter the crystals, and dry between filter papers.

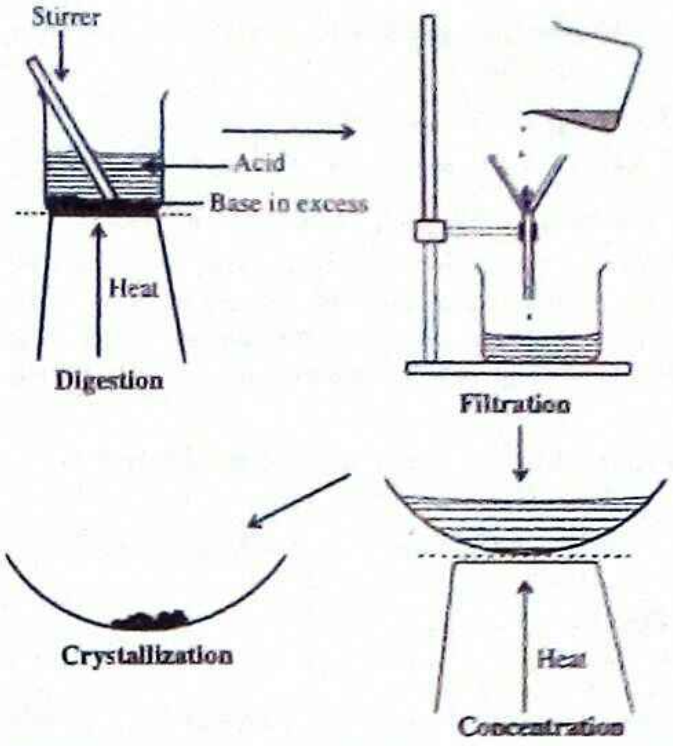



Fig 15.2 *Preparation of a salt from an insoluble base*

Note: All the soluble salts of zinc, magnesium, calcium and lead can be obtained by the use of the oxide of the metal and the appropriate acid, e.g.

• ***To obtain $Pb(NO_3)_2$ crystals***.

$$PbO_{(s)} + 2HNO_{3\,(aq)} \rightarrow Pb(NO_3)_{2\,(aq)} + H_2O_{(l)}$$

(white) (colourless)

• ***To obtain $ZnSO_4$ crystals***:

$$ZnO_{(s)} + H_2SO_{4\,(aq)} \rightarrow ZnSO_{4\,(aq)} + H_2O_{(l)}$$

(white) (colourless)

### 2. Action of acid on a trioxocarbonate(IV)

When a dilute mineral acid (bench reagent) is added to any trioxocarbonate(IV) salt, effervescence occurs, due to the evolution of a colourless and odourless gas, which is carbon(IV) oxide, and the formation of a salt and water. It is *not* a neutralization reaction.

***Preparation of $CuCl_2$ crystals***

Equation of reaction:

$$CuCO_{3\,(s)} + 2HCl_{(aq)} \rightarrow CuCl_{2\,(aq)} + CO_{2\,(g)} + H_2O_{(l)}$$

(dirty green) (light green)

**Procedure**

a. Place 50 $cm^3$ of dilute hydrochloric acid (bench reagent) in a beaker, and add three spatulaful of powdered $CuCO_3$ with warming and stirring. There is immediate effervescence. The gas evolved is colourless and odourless; it is carbon(IV) oxide, $CO_2$.

b. Continue the addition of the $CuCO_3$ with stirring and warming, until it can no longer dissolve or effervescence stops (digestion is complete).

c. Filter the mixture, concentrate the filtrate, and then, crystallize by cooling.

d. Filter the crystals, and dry between filter papers.

This reaction can be conveniently used to prepare *all* soluble salts; e.g.

***To obtain $Pb(NO_3)_2$ crystals***

$$PbCO_{3(s)} + 2HNO_{3(aq)} \rightarrow Pb(NO_3)_{2(aq)} + H_2O + CO_2\uparrow$$

### 3. Action of an acid on a reactive metal

This reaction is used for the preparation of soluble salts of metals that are well above hydrogen in the reactivity series, such as K, Na, Ca, Mg Al, Zn and Fe. Hydrogen gas is usually liberated during the reaction.

**Preparation of iron(II) tetraoxosulphate(VI)**

*Equation of reaction:*

$$\underset{\text{(grey)}}{Fe_{(s)}} + H_2SO_{4(aq)} \rightarrow \underset{\text{(green)}}{FeSO_{4(aq)}} + H_{2(g)}$$

**Procedure**

a. Place 50 $cm^3$ of $H_2SO_4$ solution (2.0 moles per $dm^3$) in a beaker, add some iron filings and warm with stirring. There is effervescence, as the metal dissolves. The gas evolved in colourless and odourless, it is hydrogen.

b. Add more of the metal with stirring, until it can no longer dissolve, or effervescence ceases (*digestion*).

c. Filter the mixture to remove undissolved iron filings.

d. Concentrate the filtrate, and allow the saturated solution to cool, in order to obtain light green crystals of the hydrated salt, $FeSO_4.7H_2O$.

e. Filter the crystals and dry them between filter papers.

This method can be conveniently used to prepare crystals of the following salts.

i. ***To obtain $MgCl_2$ crystals:***

$$\underset{\text{(ribbon)}}{Mg_{(s)}} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$$

ii. ***To obtain $ZnSO_4$ crystals***

$$\underset{\text{(granule)}}{Zn_{(s)}} + H_2SO_{4(aq)} \rightarrow ZnSO_{4(aq)} + H_{2(g)}$$

### 4. Precipitation of an insoluble salt (Double decomposition reaction)

*Precipitation reaction* is the most suitable for the preparation of *insoluble salts*. Aqueous solutions of *two soluble compounds* containing the *metallic* and *acidic radicals* of the desired salt are mixed together to produce its precipitate. Hence, it is very important to be familiar with the *solubility rules*.

***Preparation of lead(II) chloride***

In order to prepare $PbCl_2(s)$, aqueous solutions of a soluble salt of *lead* and a soluble *chloride* are used.

Equation of reaction:

$$\underset{\text{(colourless)}}{Pb(NO_3)_{2(aq)}} + \underset{\text{(colourless)}}{2NaCl_{(aq)}} \rightarrow 2NaNO_{3(aq)} + \underset{\text{(white)}}{PbCl_{2(s)}}$$

**Procedure**

a. Place 25 $cm^3$ of $Pb(NO_3)_2$ solution (0.10 $moldm^{-3}$) in a beaker, add NaCl solution (0.10 $moldm^{-3}$) gradually with stirring. Allow sedimentation to take place. Add more NaCl solution, until there is no more precipitation.

b. Filter the precipitate, wash with cold distilled water, and dry in the oven, or in air.

Note: *Lead(II) chloride, $PbCl_2$ is soluble in hot water but insoluble in cold water.*

Other examples of *insoluble* salts that can be prepared by precipitation reactions are:

i. ***To obtain $AgCl$ crystals***

$$\underset{\text{(colourless)}}{AgNO_{3(aq)}} + \underset{\text{(colourless)}}{NaCl_{(aq)}} \rightarrow NaNO_{3(aq)} + \underset{\text{(white)}}{AgCl_{(s)}}$$

ii. ***To obtain $PbI_2$ crystals***

$$\underset{\text{(colourless)}}{Pb(NO_3)_{2(aq)}} + \underset{\text{(colourless)}}{2KI_{(aq)}} \rightarrow 2KNO_{3(aq)} + \underset{\text{(yellow)}}{PbI_{2(s)}}$$

iii. ***To obtain $BaSO_4$ crystals***

$$\underset{\text{(colourless)}}{BaCl_{2(aq)}} + \underset{\text{(colourless)}}{H_2SO_{4(aq)}} \rightarrow HCl_{(aq)} + \underset{\text{(white)}}{BaSO_{4(s)}}$$

### 5. Direct combination of elements

Anhydrous binary salts are usually prepared by this reaction.

**a. Preparation of *anhydrous* iron(III) chloride**

Dry chlorine gas is passed over heated iron filings held in a glass tube. The wire glows to form sublimates of iron(III) chloride that forms a brown solid on cooling.

$$2Fe_{(s)} + 3Cl_{2(g)} \rightarrow 2FeCl_{3(s)}$$

Note: $FeCl_{2(s)}$ *cannot* be prepared by direct combination.

**b. Preparation of iron(II) sulphide**

A mixture of 0.10 mole (5.6 g) of iron filings and 0.10 mole (3.2 g) of powdered sulphur is heated strongly with stirring in a *crucible dish*, to give a dark-grey solid of iron(II) sulphide.

$$Fe_{(s)} + S_{(s)} \rightarrow FeS_{(s)}$$

Generally, direct combination is used to prepare anhydrous chlorides and sulphides of most metals.

## Preparation of Acid Salts

Acid salts are prepared by the use of oxoacids that have two or more replaceable hydrogen atoms, e.g. $H_2SO_4$, $H_2SO_3$, $H_2CO_3$ and $H_3PO_4$.

Generally, when an alkali reacts with an excess of such oxoacids, acid salts are obtained.

### 1. Preparation of sodium hydrogentetraoxosulphate(VI) salt

In order to prepare the acid salt, $NaHSO_4$, the normal salt, $Na_2SO_4$ is first prepared by titration method as described in 15.8(1a) for the preparation of NaCl.

**Procedure:**

Suppose 25 $cm^3$ portion of 2.0 $moldm^{-3}$ NaOH solution required $V$ $cm^3$ of 2.0 $moldm^{-3}$ $H_2SO_4$ solution for complete neutralization, in order to obtain a solution of normal salt $Na_2SO_4$.

Another $V$ cm$^3$ of the $H_2SO_4$ solution is again added to the solution (making a total of $2V$ cm$^3$). The solution is thoroughly mixed, and then concentrated. The acid salt obtained is then crystallized, filtered, and the crystals dried between filter papers.

*Equations of reactions*

Stage 1: $2NaOH_{(aq)} + H_2SO_{4\,(aq)} \rightarrow Na_2SO_{4\,(aq)} + H_2O$

Stage 2: $Na_2SO_{4\,(aq)} + H_2SO_{4\,(aq)} \rightarrow 2NaHSO_{4\,(aq)}$

Similarly, the acid salt, $KHSO_4$ can be prepared.

### 2. Preparation of sodium hydrogentrioxocarbonate(IV)

a. Pass a *large excess* of carbon(IV) oxide into 50 cm$^3$ sodium hydroxide solution (2.0 moles per dm$^3$) held in a beaker. The acid salt separates out of the solution as white crystals, since it is moderately soluble in water.

b. Filter the acid salt, and dry between filter papers.

*Equations of reactions:*

Stage 1: $CO_{2\,(g)} + 2NaOH_{(aq)} \rightarrow Na_2CO_{3\,(aq)}$

Stage 2: $CO_{2\,(g)} + Na_2CO_{3\,(aq)} + H_2O_{(l)} \rightarrow 2NaHCO_{3\,(s)}$

### 3. Preparation of hydrated sodium trioxocarbonate(IV)

Crystals of $Na_2CO_3$ cannot be obtained by the acid-base titration – being a salt of a strong base and a weak acid. Instead, it is obtained by the action of heat on the acid salt, $NaHCO_3$ to constant.

**Procedure:**

a. Place about 10.0 g of $NaHCO_3$ crystals in a crucible dish and heat strongly; allow to cool in a desiccator, and then weigh.

b. Repeat the process of heating, cooling, and weighing; until a constant mass is obtained.

c. The residue obtained is *anhydrous* $Na_2CO_3$.

*Equation of reaction:*

$$2NaHCO_{3\,(s)} \longrightarrow Na_2CO_{3\,(s)} + H_2O_{(g)} + CO_{2\,(g)}$$

Note: Anhydrous $Na_2CO_3$ or $K_2CO_3$ cannot be decomposed by heat at all.

***To obtain hydrated $Na_2CO_3$ from the anhydrous salt***

a. Place about 50 cm$^3$ of distilled water in a suitable beaker, and heat to boiling point.

b. Add about 5.0 g of powdered anhydrous $Na_2CO_3$, a little at a time, into the boiling water with stirring. The salt dissolves to give a colourless solution. Filter while hot.

c. Concentrate the filtrate, and crystallize, in order to obtain crystals of $Na_2CO_3 \cdot 10H_2O$.

d. Filter the crystals, and dry between filter papers.

### Solved Problems

3. Describe a suitable laboratory procedure for preparing pure sample of zinc tetraoxosulphate(VI) crystals, starting from zinc oxide.

Note: *Since zinc oxide is a base, the appropriate acid to be used to obtain zinc tetraoxosulphate(VI) crystals is dilute tetraoxosulphate(VI) acid*, i. e.

$$ZnO_{(s)} + H_2SO_{4\,(aq)} \rightarrow ZnSO_{4\,(aq)} + H_2O_{(l)}$$

***Procedure***

a. Measure 100 cm$^3$ of bench dilute $H_2SO_4$ with a measuring cylinder, and transfer into a 500 cm$^3$ beaker.

b. Add five spatulaful of powdered zinc oxide into the acid; stir and warm the mixture on a Bunsen burner.

c. Continue to add the ZnO with stirring and warming, until it can no longer dissolve.

d. Filter the mixture into a clean beaker, and concentrate the filtrate by evaporation, until it is saturated.

e. Allow the saturated solution to cool, to obtain the crystals.

f. Filter the crystals, and dry between filter papers.

4. Write an equation to show the preparation of calcium trioxocarbonate(IV) by double decomposition (precipitation reaction).

**Solution**

*$CaCO_3$ is an insoluble salt. A soluble salt of calcium and any soluble trioxocarbonate(IV) salt are used, i.e.*

$$CaCl_{2\,(aq)} + Na_2CO_{3\,(aq)} \rightarrow CaCO_{3\,(s)} + 2NaCl_{(aq)}$$

5. State a method of preparing each of the following salts: a. Lead(II) trioxocarbonate(IV);
b. Iron(II) chloride;

a. *$PbCO_3$ is an insoluble salt, it is prepared by double decomposition (precipitation) method.*

b. *$FeCl_2$ is a soluble salt; prepared by crystallization.*

### Revision Exercises

33 List three types of chemical reactions suitable for the preparation of soluble salts.

34 Name one laboratory technique used for preparing each of soluble and insoluble salts.

35a Outline a suitable procedure for the preparation of $ZnCl_2$ crystals starting from zinc granules. [WAEC]

b Write a balanced equation for the reaction in a.

36 Solutions of $H_2SO_4$ and NaOH of equal concentrations were prepared separately.
Write a balanced equation for the formation of the
a. acid salt; b. normal salt,
from their reactions. [WAEC]

## 15.9 Calculations Involving Salts

### Calculations from Equations

***Mass-Mole Relationships***

### Worked Example

4. Calculate the mass of $CuSO_4$ produced when excess of CuO neutralized completely with 0.100 mole of $H_2SO_4$. The equation for the reaction is:

$$CuO_{(s)} + H_2SO_{4\,(aq)} \rightarrow CuSO_{4\,(aq)} + H_2O$$

[$CuSO_4 = 160$]

**Solution**

*To find the mass of $CuSO_4$ produced.*

Given: Amount of $H_2SO_4$ = 0.100 mol.

Required: Mass of $CuSO_4$ produced.

This is *mass-mole* relationship.

Equation of reaction:

$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$ (Balanced)

*1 mol* *1 mol (160 g)*

From the balanced equation of reaction:

1 mol of $H_2SO_4 \equiv 160$ g of $CuSO_4$

$\therefore$ 0.100 mol $H_2SO_4 \equiv (160 \times 0.100)/1$ g.

$= 16.0$ g $CuSO_4$ (3 sig. fig.)

***Mass-Mole-Volume of solution relationships***

**Worked Example 5**

Calculate the mass of $ZnSO_4$ produced when excess of $ZnCO_3$ is added to 50.0 $cm^3$ of 4.00 *mol* $dm^{-3}$ of $H_2SO_4$. The equation for the reaction is:

$ZnCO_{3(s)} + H_2SO_{4(aq)} \rightarrow ZnSO_{4(aq)} + CO_2 + H_2O$

[$ZnSO_4 = 161$ $gmol^{-1}$]

**A** 0.200 *g* **B** 1.29 *g* **C** 32.2 *g* **D** 39.0 *g* [WAEC]

**Solution**

*To find the mass of $ZnSO_4$ produced.*

Given: 50.0 $cm^3$ of 4.00 $moldm^{-3}$ of $H_2SO_4$.

Required: Mass of $ZnSO_4$ produced.

First, calculate the amount of acid in 50.0 $cm^3$ of 4.00 $moldm^{-3}$ of $H_2SO_4$:

Amount, n = Conc ($moldm^{-3}$) $\times$ volume($dm^3$)

$= 4.00 \times 50/1000 = 0.2$ mol.

Equation of reaction:

$ZnCO_3 + H_2SO_4 \rightarrow ZnSO_4 + CO_2 + H_2O$

*1 mol* *1 mol (161 g)*

From the balanced equation of reaction:

1 mol of $H_2SO_4 \equiv 161$ g of $ZnSO_4$

$\therefore$ 0.200 mol $H_2SO_4 \equiv (161 \times 0.2)/1$ g.

$= 32.2$ g $ZnSO_4$ [Ans = C]

**Revision Exercises**

37 Calculate the mass of $FeCl_2$ produced when 3.50 g of iron filings were treated with an excess of bench hydrochloric acid. [Fe = 56, $FeCl_2$ = 127]

38 Calculate the amount of acid salt formed, when 500 $cm^3$ of 0.200 *mole per* $dm^3$ NaOH were completely neutralized by a solution of $H_2SO_4$.

## 15.10 Hydrolysis of Salts

***Hydrolysis*** is the term used to describe the reactions between water and certain salts. It is the reverse of *neutralization* reaction.

### Classes of Normal Salts

On the basis of hydrolysis, there are *four* classes of *normal* salts:

**1. Salt of a strong acid and a strong base**

Sodium chloride, NaCl, is an example. In aqueous solution, NaCl reacts with water to produce NaOH, a strong base, and HCl, a strong acid.

$$NaCl_{(s)} + H_2O_{(l)} \rightarrow \underset{\text{(strong)}}{NaOH_{(aq)}} + \underset{\text{(strong)}}{HCl_{(aq)}}$$

Since the concentration of $H^+$ balances that of $OH^-$, *there will be no hydrolysis;* the solution will be neutral (pH = 7).

Generally, *a salt of a strong acid* ($Cl^-$, $NO_3^-$ and $SO_4^{2-}$) *and a strong base* ($Na^+$ and $K^+$) *will not undergo hydrolysis in water; the resulting solution will be neutral*, e.g. KCl, $NaNO_3$ and $K_2SO_4$.

**2. Salt of a strong acid and a weak base**

Ammonium chloride is an example. It hydrolyses in water to produce $NH_4OH_{(aq)}$, a weak base, and $HCl_{(aq)}$, a strong acid, which is completely ionized.

$$NH_4Cl_{(s)} + H_2O_{(l)} \rightarrow \underset{\text{(weak)}}{NH_4OH_{(aq)}} + \underset{\text{(strong)}}{HCl_{(aq)}}$$

The resulting solution contains more $H^+$ than $OH^-$ making the solution to be acidic (pH less than 7).

Generally, a salt of a strong acid ($Cl^-$, $NO_3^-$ or $SO_4^{2-}$) and a weak base (except $Na^+$ and $K^+$) undergoes cation hydrolysis in water to produce an acidic solution. Examples are $NH_4NO_3$, $AlCl_3$, $ZnSO_4$, $FeCl_3$, $MgCl_2$, $Ca(NO_3)_2$ and $(NH_4)_2SO_4$.

**3. Salt of a weak acid and a strong base**

Sodium trioxocarbonate(IV), $Na_2CO_3$ is an example. It hydrolyses in water to produce NaOH, a strong base, and $H_2CO_3$, a weak acid.

$$Na_2CO_{3(s)} + H_2O_{(l)} \rightarrow \underset{\text{(strong)}}{2NaOH_{(aq)}} + \underset{\text{(weak)}}{H_2CO_{3(aq)}}$$

The resulting solution contains more $OH^-$ than $H^+$ ions; hence, alkaline (pH higher than 7).

Generally, a salt of a strong base ($Na^+$ or $K^+$) and a weak acid ($CO_3^{2-}$, $HCO_3^-$, $S^{2-}$, $HS^-$, $SO_3^{2-}$, $CH_3COO^-$ and $C_2O_4^{2-}$) will undergo anion hydrolysis in water to produce an alkaline solution.

This explains why aqueous solution of $Na_2CO_3$ or $K_2CO_3$ is used in acid-base titration. Other examples are $NaHCO_3$, $KHCO_3$, $CH_3COONa$, $Na_2S$, $K_2S$, NaCN and KCN.

**4. Salt of a weak acid and a weak base**

Ammonium sulphide, $(NH_4)_2S$, is an example. It hydrolyses in water to give a mixture of a weak acid, $H_2S$, and a weak base, $NH_4OH_{(aq)}$.

$$(NH_4)_2S_{(s)} + H_2O_{(l)} \rightarrow \underset{\text{(weak)}}{NH_4OH_{(aq)}} + \underset{\text{(weak)}}{H_2S_{(aq)}}$$

The resulting solution is either weakly alkaline or weakly acidic. Its exact pH can be determined by the use of a pH meter only.

Other examples are $CH_3COONH_4$ and $(NH_4)_2CO_3$ and ammonium sulphide $(NH_4)_2S$.

**Solved Problem 6**

State with reason whether aqueous solution of each of the following will be acidic, basic, or neutral:

**a.** $Na_2SO_4$ **b.** $CH_3COONa$ **c.** $AlCl_3$

*a. $Na_2SO_4$ is a salt of a strong base, NaOH and a strong acid, $H_2SO_4$; hence, it does not undergo hydrolysis. Its aqueous solution will be neutral, pH = 7.*

*b. $CH_3COONa$ undergoes hydrolysis to give a mixture of a weak acid, $CH_3COOH$, and strong base, NaOH; hence, the resulting solution will be alkaline, pH > 7:*

$$CH_3COONa_{(aq)} + H_2O_{(l)} \rightarrow CH_3COOH_{(aq)} + NaOH_{(aq)}$$

*c. $AlCl_3$ hydrolyses in water to give a mixture of a weak base, $Al(OH)_3$ and a strong acid, HCl. Hence, the resulting solution will be acidic, pH < 7:*

$$AlCl_{3(aq)} + 3H_2O_{(l)} \rightarrow Al(OH)_{3(aq)} + 2HCl_{(aq)}$$

**Revision Exercises**

39 What is hydrolysis?

40 What phenomenon accounts for the acidity of aqueous solutions of some salts?

41 $AlCl_3$ undergoes hydrolysis in aqueous solution. The product gives effervescence with
A. NaOH B. $CH_3COONa$ C. $NaHCO_3$ D. $Na_2SO_4$

42 State the effect of $NH_4NO_{3(aq)}$ on
a. blue litmus paper; b. red litmus paper.

43 Which of the following pairs of salts would give a solution with a pH of exactly 7?
A. $CH_3COOK$ and $C_6H_5COONa$
B. $FeCl_3$ and $NH_4Cl$
C. NaCl and $Na_2SO_4$
D. $Na_2CO_3$ and $NH_4Cl$ [WAEC]

44 The salt formed from a reaction between citric acid and sodium hydroxide in solution will be
A. acidic B. basic C. complex D. neutral [JAMB]

46 Consider the following solutions:
$Na_2SO_{4(aq)}$, $CH_3COOK_{(aq)}$, $Pb(NO_3)_{2(aq)}$, $MgCl_{2(aq)}$.
Which of them has/have a pH a. greater than 7; b. equal to 7; c. less than 7. [WAEC]

## 15.10 Buffer Solutions

A *buffer* is a solution that resists changes in pH on addition of a small amount of an acid or alkali.

There are *two* types of buffer solutions:

### 1. Acid Buffer

It is a *solution of a weak acid and its salt*, e.g. a solution of ethanoic acid ($CH_3COOH$) and sodium ethanoate ($CH_3COONa$). They ionize in thus:

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$
(slightly ionized)

$$CH_3COONa_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + Na^+_{(aq)}$$
(completely ionized)

When a small volume of concentrated HCl is added to the buffer solution, the ions, $H^+$, produced by $HCl_{(aq)}$ are absorbed by the $CH_3COO^-_{(aq)}$ to produce a weak acid, $CH_3COOH_{(aq)}$; thereby, reducing the concentration of $H^+$.

$$CH_3COO^-_{(aq)} + H^+_{(aq)} \rightarrow CH_3COOH_{(aq)}$$

### 2. Alkaline Buffer

It is a *solution of a weak base and its salt*, e.g. aqueous solution of ammonia, $NH_{3(aq)}$, and its chloride, $NH_4Cl$. They are ionized in solution thus:

$$NH_4OH_{(aq)} \rightleftharpoons NH_4^+_{(aq)} + OH^-_{(aq)}$$
(weakly ionized)

$$NH_4Cl_{(s)} \rightleftharpoons NH_4^+_{(aq)} + Cl^-_{(aq)}$$
(strongly ionized)

When a small amount of a strong base, NaOH is added to the buffer solution, the ions, $OH^-$ produced are absorbed by the $NH_4^+{}_{(aq)}$; thereby reducing the concentration of $OH^-$.

### Uses of Buffer solution

- In industrial processing of foods and drinks.
- In many medical, biological, biochemical and chemical processes, buffer solutions are used in order to maintain constant pH's. For example, human blood is composed of many salts of weak acids and weak bases, in order to maintain a constant pH of 7.4.

**Revision Exercises**

47 What is a buffer solution? [WAEC]

48 Using an example, show how a buffer solution functions. [WAEC]

49 a Select from the following pairs of compounds, the one that will act as a buffer in an aqueous solution:
I. $CH_3COOH$ and $CH_3COONa$
II. $CH_3COONa$ and HCl
III. $CH_3COOH$ and NaCl.
b With the aid of equation, explain how the pair of a above behaves when a small amount of **each** of the following substances is added:
I. aqueous NaOH; II. dilute HCl. [WAEC]

50 State TWO uses of a buffer solution. [NECO]

51 What is responsible for the constant pH of human blood?

## 15.11 Ionic Reactions

Ionic compounds are composed of ions in solid state, and produce cations and anions in aqueous solutions. Since many reactions are carried out in solid states and in aqueous solutions, such reactions can be represented by ionic equations.

### Ionic Equations

In writing an ionic equation:

1. Reactants that are *ionic* or *polar covalent* in solid state, or in aqueous solutions are represented by their respective ions.
2. Gases, metals, and non-metals in uncombined states are written as neutral species.
3. Products that are *ionic* or *polar* (strong electrolytes) are represented by their respective ions.

4. Products that are *insoluble in water, weak* or *non-electrolytes* are written as neutral species.

**How to Balance an Ionic Equation**

In order to balance an ionic equation:

1. The number of atoms of each element on both sides of the equation must be equal.
2. The number of positive (or negative) charges on both sides must be the same.
3. The sum total of positive and negative charges on each side of the equation must add to zero.
4. In the *overall* (or *net*) equation, ions that are appearing as reactants and as products (*spectator ions*) are ignored; they cancel out.

**Examples of Ionic Reactions**

**1. Ionization of a strong acid**

Strong acids are strong electrolytes: they ionize in water completely, to produce hydroxonium ions:

a. *Ionization of hydrogen chloride in water:*

$$HCl_{(g)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

b. *Ionization of $H_2SO_4$ in water*

$$H_2SO_{4(l)} + 2H_2O \rightarrow 2H_3O^+_{(aq)} + SO_4^{2-}{}_{(aq)}$$

**2. Neutralisation reactions**

These are reactions in which an *acid* reacts with a *base* to produce *salt* and *water* only e.g.

a. $\underset{\text{(acid)}}{HCl_{(aq)}} + \underset{\text{(base)}}{NaOH_{(aq)}} \rightarrow \underset{\text{(salt)}}{NaCl_{(aq)}} + \underset{\text{(water)}}{H_2O_{(l)}}$

In terms of ions in aqueous solution:

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O$$

Ignoring $Na^+$ and $Cl^-$, the net equation is:

$$\underset{\text{(acid)}}{H^+_{(aq)}} + \underset{\text{(alkali)}}{OH^-_{(aq)}} \rightarrow H_2O_{(l)}$$

The net equation shows that $H^+$ from an acid reacts with the $OH^-$ from an alkali, to form water, $H_2O$

b. $\underset{\text{(acid)}}{H_2SO_{4(aq)}} + \underset{\text{(base)}}{CuO_{(s)}} \rightarrow CuSO_{4(aq)} + H_2O_{(l)}$

Ionically:

$$2H^+_{(aq)} + SO_4^{2-} + Cu^{2+}{}_{(s)} + O^{2-}{}_{(s)} \rightarrow Cu^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)} + H_2O_{(l)}$$

Ignoring $SO_4^{2-}$ and $Cu^{2+}$, the net equation is:

$$2H^+_{(aq)} + O^{2-}{}_{(aq)} \rightarrow H_2O_{(l)}$$

The net equation shows that $H^+$ from an acid reacts with the $O^{2-}$ from a metallic oxide, to form water, $H_2O$.

**3. Liberation of hydrogen gas**

When a metal above hydrogen in the *activity series* reacts with a dilute acid, hydrogen gas is liberated:

Net ionic equation:

$$Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}{}_{(aq)} + H_{2(g)}$$

$$2Na_{(s)} + 2H^+_{(aq)} \rightarrow 2Na^+_{(aq)} + H_{2(g)}$$

It is a displacement/redox reaction.

**4. Liberation of ammonia gas**

When a mixture of an *ammonium salt* and an *alkali* is heated, ammonia gas is liberated:

$$NH_4^+{}_{(s)} + OH^-{}_{(s)} \rightarrow NH_3 + H_2O$$

**5. Displacement reactions**

A metal M above another metal N in the *activity series* will displace the ions of metal N from an aqueous solution of its salt.

Consider the reaction:

$$Zn_{(s)} + CuSO_{4(aq)} \rightarrow ZnSO_{4(aq)} + Cu_{(s)}$$

Ionically: $Zn_{(s)} + Cu^{2+}{}_{(aq)} \rightarrow Zn^{2+}{}_{(aq)} + Cu_{(s)}$

The net reaction shows that zinc is more reactive than copper.

Similarly: $Fe_{(s)} + 2Ag^+{}_{(aq)} \rightarrow Fe^{2+}{}_{(aq)} + 2Ag_{(s)}$

**5. Precipitation reactions**

In a precipitation reaction, a mixture of aqueous solutions of *two* strong electrolytes react to give *two* products in which *one* is *insoluble* in water. It is a *double decomposition* reaction, e.g.

a. A mixture of aqueous solutions of a silver salt and a chloride produces a *white* precipitate of silver chloride, i.e.

$$Cl^-{}_{(aq)} + Ag^+{}_{(aq)} \rightarrow AgCl_{(s)}$$

b. Other examples:

$$Ba^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)} \rightarrow BaSO_{4(s)} \text{ (white ppt.)}$$

$$Pb^{2+}{}_{(aq)} + 2I^-{}_{(aq)} \rightarrow PbI_{2(s)} \text{ (yellow ppt.)}$$

**6. Action of acids on a trioxocarbonate(IV) salt**

When a dilute acid is added to a trioxocarbonate (IV) salt, there is effervescence; the gas evolved is carbon (IV) oxide.

$$CO_3^{2-}{}_{(s)} + 2H^+_{(aq)} \rightarrow H_2O_{(l)} + CO_{2(g)}$$

Similarly: $SO_3^{2-}{}_{(s)} + 2H^+_{(aq)} \rightarrow H_2O_{(l)} + SO_{2(g)}$

**8. Action of an acid on a sulphide salt**

An acid reacts with a sulphide to liberate hydrogen sulphide gas, i.e.

$$S^{2-}{}_{(s)} + 2H^+_{(aq)} \rightarrow H_2S_{(g)}$$

**9. Hydrolysis of salts**

a. *Anion hydrolysis of a salt of a strong base and a weak acid produces an alkaline solution*, i.e.

$$CO_3^{2-}{}_{(s)} + 2H_2O_{(l)} \rightarrow H_2CO_{3(aq)} + 2OH^-{}_{(aq)}$$

b. *Cation hydrolysis of a salt of a strong acid and a weak base produces an acidic solution*, i.e.

$$Al^{3+}{}_{(aq)} + 3H_2O_{(l)} \rightarrow Al(OH)_{3(aq)} + 3H^+{}_{(aq)}$$

**10. Dissociation of ionic compounds**

Ionic compounds dissociate into their respective cations and anions when in molten state or in

aqueous solutions. Under these conditions, the radicals retain their identities:

a. $KCl \rightarrow K^+ + Cl^-$

b. $KClO_3 \rightarrow K^+ + ClO_3^-$

c. $Al_2(SO_4)_3 \rightarrow 2Al^{3+} + 3SO_4^{2-}$

d. $Mg(OH)_2 \rightarrow Mg^{2+} + 2OH^-$

**Solved Problem 7**

X forms a trivalent cation while Y forms a divalent anion. Write the dissociation of a compound of X and Y.

*X forms $X^{3+}$ and Y forms $Y^{2-}$. To form a neutral compound, the ions combine thus:*

$$\underset{(2\times+3)}{2X^{3+}} + \underset{(3\times-2)}{3Y^{2-}} \text{ to give } X_2Y_3.$$

*The dissociation of $X_2Y_3$ is:*

$$X_2Y_3 \rightarrow 2X^{3+} + 3Y^{2-}$$

**Revision Exercises**

52 Write ionic equation to represent the action of heat on a mixture of an alkali and anammonium salt.

53 Write the dissociation of the following compounds:
a. $Cu_2O$ b. $Mg_3P_2$ c. $KMnO_4$ d. $(NH_4)_2Cr_2O_7$

## 15.13 Concentration of Ions in a Solution

### Ion–Mole Relationship

Care must be taken when estimating the concentrations of the cations and anions produced by strong electrolytes in water. This is because the concentrations of the respective ions depend on the number of ions produced by *one* molecule or *one* formula unit of a strong electrolyte in water e.g.

1. *One* mole of $HCl_{(g)}$ produces *two* moles of ions in water.

$$\underset{1\text{ mol}}{HCl_{(g)}} + aq \rightarrow \underset{1\text{ mol}}{H^+_{(aq)}} + \underset{1\text{ mol}}{Cl^-_{(aq)}}$$

2. *One* mole of $H_2SO_4$ ionises in water to produce *three* moles of ions:

$$\underset{1\text{ mol}}{H_2SO_4{}_{(aq)}} + aq \rightarrow \underset{2\text{ mol}}{2H^+_{(aq)}} + \underset{1\text{ mol}}{SO_4^{2-}{}_{(aq)}}$$

3. *One* mole of $FeCl_3$ dissolves in water to produce *four* moles of ions:

$$\underset{1\text{ mol}}{FeCl_{3\,(s)}} + aq \rightarrow \underset{1\text{ mol}}{Fe^{3+}_{(aq)}} + \underset{3\text{ mol.}}{3Cl^-_{(aq)}}$$

4. *One* mole of $Al_2(SO_4)_{3(s)}$ ionizes in water to produce *five* moles of ions.

$$\underset{1\text{ mol}}{Al_2(SO_4)_{3\,(s)}} + aq \rightarrow \underset{2\text{ mol}}{2Al^{3+}_{(aq)}} + \underset{3\text{ mol}}{3SO_4^{2-}{}_{(aq)}}$$

**Solved Problems**

7. Write an equation to show the number of ions produced by tetraoxophosphate(V) acid on dissociation. (Assume it is a strong acid). [WAEC]

*The formula of tetraoxophosphate(V) acid is $H_3PO_4$. It dissociates thus:*

$$\underset{1\text{ mol}}{H_3PO_4} \rightarrow \underset{3\text{ mol}}{3H^+} + \underset{1\text{ mol}}{PO_4^{3-}}$$

*One mole of $H_3PO_4$ dissociates into three moles of $H^+$ ions and one mole of $PO_4^{3-}$ ion (four moles of ions).*

8. Explain the following observation: The concentration of chloride ions in 0.10 $moldm^{-3}$ calcium chloride is not the same as in 0.10 $moldm^{-3}$ sodium chloride solution.

*Ionization of each of the salts is:*

a. $\underset{1\ mol}{CaCl_{2(s)}} + aq \rightarrow Ca^{2+}_{(aq)} + \underset{2\ mol}{2Cl^-_{(aq)}}$

b. $\underset{1\ mol}{NaCl_{(s)}} + aq \rightarrow Na^+_{(aq)} + \underset{1\ mol}{Cl^-_{(aq)}}$

*One mole* of $CaCl_2$ produces *two moles* of chloride ions, while *one mole* of NaCl produces *one mole* of chloride ions. Since both salts are strong electrolytes and of the same concentration, 0.10 $moldm^{-3}$ $CaCl_2$ will produce more chloride ions than 0.10 $moldm^{-3}$ NaCl.

**Revision Exercises**

54 Write an equation to show the number of ions produced by each of the following on dissociation. (Assume each compound is a strong electrolyte).
a. Copper(II) chloride;
b. Potassium trioxochlorate(V);
c. Ethanedioic acid;
d. Ammonium heptaoxodichromate(VI).

55 How many moles of ions will be produced by one mole of each compound in question 54 above?

### Ions and Avogadro Constant

One mole of ions of any specie contains the Avogadro constant L, which is $6.02 \times 10^{23}\ mol^{-1}$.

1. Consider the ionization $HCl_{(g)}$ in water:

$$\underset{1\text{ mol}}{HCl_{(g)}} + aq \rightarrow \underset{1\text{ mol}}{H^+_{(aq)}} + \underset{1\text{ mol}}{Cl^-_{(aq)}}$$

1 mole of $HCl_{(g)}$ produces 1 mole of $H^+$ i.e.
1 mole of $HCl_{(g)}$ produces $6.02 \times 10^{23}$ $H^+$.

2. In the ionization of $H_2SO_4$:

$$\underset{1\text{ mol}}{H_2SO_4{}_{(aq)}} + aq \rightarrow \underset{2\text{ mol}}{2H^+_{(aq)}} + \underset{1\text{ mol}}{SO_4^{2-}{}_{(aq)}}$$

1 mole of $H_2SO_4$ ionizes in water to produce $2 \times (6.02 \times 10^{23})$ $H^+$ in water.

**Worked Examples**

9. Estimate the number of hydrogen ions produced by 0.1 *mole* of $H_2SO_4$ in water.
[Avogadro constant is $6.02 \times 10^{23}\ mol^{-1}$]

*To find the number of $H^+$ ions in 0.1 mol $H_2SO_4$*
The acid ionizes completely in water thus:

$$H_2SO_{4(aq)} + aq \longrightarrow \underset{2\ mol}{2H^+_{(aq)}} + \underset{1\ mol}{SO_4^{2-}{}_{(aq)}}$$
1 mol

1 mole of $H_2SO_4$ produces 2 moles of $H^+$;
i.e. 1 mole of $H_2SO_4 \equiv 2 \times 6.02 \times 10^{23}$ $H^+$;
$\therefore$ 0.1 mol of $H_2SO_4 \equiv 0.1 \times 2 \times 6.02 \times 10^{23}$ $H^+$
$= 1.20 \times 10^{23}$ $H^+$.

**10** Calculate the amount of trioxonitrate (V) ions in 1.25 $dm^3$ of 0.01 *mol* $dm^{-3}$ solution of $Al(NO_3)_3$. [WAEC]

*The salt ionizes completely thus:*

$$\underset{1\ mol}{Al(NO_3)_{3(s)}} \xrightarrow{H_2O_{(l)}} Al^{3+}{}_{(aq)} + \underset{3\ mol}{3NO_3^-{}_{(aq)}}$$

*To calculate the amount of $NO_3^-$ in the solution*
First, calculate the amount of salt in the solution: i.e.
Amount = conc ($moldm^{-3}$) × volume ($dm^3$)
$= 0.01\ mol\ dm^{-3} \times 1.25\ dm^3$
$= 0.0125$ mole.
But 1 mole of $Al(NO_3)_3$ produces 3 moles of $NO_3^-$
$\therefore$ *amount of trioxonitrate (V) ions*
$= 3 \times 0.0125$ mole
$= 0.0375\ mol$ or $3.75 \times 10^{-2}\ mol$ (3 sig. fig)

### Revision Exercises

[Avogadro constant is $6.02 \times 10^{23}$ $mol^{-1}$]

**56** How many hydrogen ions will be produced by one mole of each of the following? (Assume they are strong electrolyte).
a. HCl(aq); b. $H_2S$(aq); c. $NaHSO_4$(aq)

**57** Calculate the amount of hydrogen ions in 500 $cm^3$ of 0.10 $moldm^{-3}$ $H_3PO_4$. (Assume that the acid is a strong electrolyte).

## 15.14 Conductivity of Electrolytes

One characteristic property of a water-solution of an acid, an alkali, or a soluble salt is the ability to conduct electricity; i.e. act as an electrolyte.

Electrical conductivity of a solution is due to the presence of mobile hydrated *ions*. Generally, the larger the number of ions in a solution, the higher the conductivity. Consider the following experimental observations:
The order of increasing electrical conductivity of a set of pure liquids is:

**$H_2O$ < $CH_3COOH$** (1.0 mol/$dm^3$) < **HCl** (1.0 mol/$dm^3$)

***Explanation:***

*•Pure water does not contain ions; it is a non-electrolyte. Hence, it has the lowest conductivity.*

*•Ethanoic acid is a weak monobasic acid; it is only slightly ionized in dilute solution. Hence, its conductivity is higher than that of pure water.*

*•Hydrochloric acid is a strong monobasic acid; it produces more ions in solution than ethanoic acid of equal concentration. Hence, its conductivity is the highest.*

### Revision Exercises

**58** The *molar* conductance of sodium hydroxide solution is higher than that of aqueous ammonia of the same concentration, because sodium hydroxide
A. has a higher molar mass.
B. produces more ions in solution.
C. is a compound of a metal.
D. is highly deliquescent. [WAEC]

**59** What will be the *relative* molar conductivities of sodium chloride and aluminium chloride? (Assume they are strong electrolytes).

### Answers to Revision Exercises

**8.** A **9.** c and e **10.** C **11.** b and d **14.** B
**15.** C **20.** D **30c** 250 *g* $mol^{-1}$; $x = 5$. **27.** B
**28.** B **29.** $x = 6$ **31.** $y = 6$ **32.** $x = 8$
**37** 7.94 *g*. **38** 0.100 *mol* **41.** C
**42.** C **43.** C **44.** B **49a.** I
**55a** 3 *mol*; **b** 2 *mol*; **c** 3 *mol*; **d** 5 *mol*.
**57** 0.150 *mol* **56a** $6.02 \times 10^{23}$ ions;
**56b** $1.20 \times 10^{24}$ ions; **56c** $6.02 \times 10^{23}$ ions
**58.** B **59.** $AlCl_3$(aq) >> NaCl(aq)

# 16

# •VOLUMETRIC ANALYSIS•

## 16.1 Introduction

*Volumetric analyses* involve measuring the volumes of solutions of reactants in chemical reactions. However, weighing is involved, if a solid reactant is involved.

Many types of chemical reactions involve volumetric analyses. However, only those in respect of neutralization, precipitation, displacement and redox reactions are treated in this chapter.

The main objective of volumetric analysis is to quantitatively determine the amounts of the reactants used in a chemical reaction, and hence, establish the stoichiometry (mole ratio), in order to obtain a balanced equation for the reaction.

**Revision Exercise**

1. What is *volumetric analysis*?

## 16.2 Preparation of Solutions

Many chemical reactions are carried out in aqueous solutions; hence, there is the need to be familiar with the various methods of preparing solutions of chemical substances.

### Standard Solutions

A *standard solution* is a solution of *known* concentration. Its concentration can be expressed in grams per $dm^3$ (*mass concentration*) or in moles per $dm^3$ (*molar concentration*).

The mathematical relationship between *mass concentration* and *molar concentration* of a solution of a chemical substance is:

$$\underset{(gdm^{-3})}{\text{Mass conc}} = \underset{(moldm^{-3})}{\text{molar conc}} \times \underset{(gmol^{-1})}{\text{molar mass}}$$

### Primary Standards

A *standard solution* is prepared by the use of a *primary standard*. A *primary standard* is a substance that can be obtained in a high state of purity.

It is anhydrous, non-deliquescent, non-hygroscopic, and soluble in water.

*Examples of primary* standards are:

- Anhydrous sodium trioxocarbonate(IV), $Na_2CO_3$
- Benzenecarboxylic (benzoic) acid, $C_6H_5CO_2H$
- Potassium hydrogenphthalate, $C_6H_5C_2O_4HK$
- Ethanedioic acid dihydrate, $H_2C_2O_4{\cdot}2H_2O$

**Note:** Hydrated ethanedioic acid, $H_2C_2O_4{\cdot}2H_2O$ is a primary standard, because it does not effloresce.

Standard solutions of mineral acids, alkalis and salts cannot be prepared. ***Reasons***:

- Some of them are corrosive and volatile liquids, e.g. $HCl_{(aq)}$, $HNO_{3(aq)}$, and $NH_{3(aq)}$.
- Concentrated $H_2SO_4$ is hygroscopic.
- KOH and NaOH pellets are deliquescent solids; hence, absorb moisture and carbon(IV) oxide from the atmosphere.
- Many salts are hydrated; hence, they are efflorescent, e.g. hydrated $Na_2CO_3$.

When a substance is not available in a pure state, a process of *titration* called *standardization* is used to obtain its standard solution.

### Methods of Preparation

Standard solutions of primary standards can be prepared by *weighing*, and by *dilution* methods.

**1. Weighing method**

Suppose 250 $cm^3$ of a solution of 0.100 $moldm^{-3}$ *anhydrous* $Na_2CO_3$ is to be prepared.

**Procedure:**

**a.** Calculate the mass of $Na_2CO_3$ required:

Mass, m = amount, n × molar mass, M.

Amount, n (mol) = Conc. C ($moldm^{-3}$) × Vol. V ($dm^3$)

= 0.100 × 250/1000 = 0.0250 mol.

$M[Na_2CO_3] = 106\ gmol^{-1}$

∴ Mass, m = 0.025 × 106 = 2.65 g

Recall: m = MCV/1000 [V in $cm^3$]

Substituting: m = 106 × 0.100 × 250/1000 = 2.65 *g*

**b.** *Weigh* roughly, about 5.0 *g* of anhydrous $Na_2CO_3$; purify it by heating for about 10 minutes in an *evaporating dish*, and then, allow to cool in a desiccator.

**c.** *Weigh* accurately a *stoppered weighing bottle*; then, weigh exactly 2.650 *g* of the anhydrous $Na_2CO_3$ into it.

**d.** Transfer the solid into a *beaker*; rinse the weighing bottle with distilled water from a *wash bottle*, in order to transfer the entire solid into the beaker.

e. Dissolve the solid in distilled water by stirring with a *glass rod*, and warm, if necessary, to obtain a homogeneous solution.

f. Transfer the solution into a clean and dry 250 $cm^3$ *standard flask* (fig 16.1a) by pouring it down the glass rod through a *filter funnel*. Then, rinse the beaker several times with distilled water, with intermittent swirling.

g. Make up the solution to the mark on the *standard flask* (fig 16.1b) with distilled water from a *wash bottle*. Insert the stopper and shake well, in order to obtain a homogeneous solution.

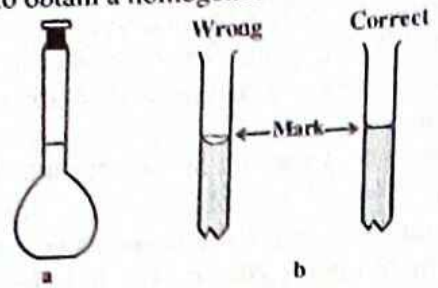



**Fig. 16.1** *Standard (Volumetric) flask*

h. The solution is exactly 0.100 $moldm^{-3}$ of anhydrous $Na_2CO_3$.

**Note:** If the hydrated salt, $Na_2CO_3 \cdot 10H_2O$, is to be used in preparing the 250 $cm^3$ of 0.100 $moldm^{-3}$ solution, the mass of the hydrated salt required will be obtained thus:

$M[Na_2CO_3 \cdot 10H_2O] = (106 + 180) = 286\ gmol^{-1}$.

Amount of *anhydrous* $Na_2CO_3$ required is 0.0250 mol.

$\therefore$ Mass, m $= 0.025 \times 286 = 7.15\ g$.

### Worked Examples

**1.** Calculate the mass of hydrated ethanedioic acid, $H_2C_2O_4 \cdot 2H_2O$ needed to prepare 5.0 $dm^3$ of a 0.105 $moldm^{-3}$ solution. [$H_2C_2O_4 \cdot 2H_2O = 126\ gmol^{-1}$]

*To find the mass of $H_2C_2O_4 \cdot 2H_2O$*

Data provided: Molar conc = 0.105 $moldm^{-3}$

Volume required = 5.0 $dm^3$; Molar mass = 126 $gmol^{-1}$

First, calculate the *amount* of the acid required, i.e.

Amount (mol) = conc ($moldm^{-3}$) × volume ($dm^3$)

$= 0.105 \times 5 = 0.525$ mole.

Then, convert the amount (in *mole*) to mass (in *gram*).

Mass (g) = amount (*mol*) × molar mass ($gmol^{-1}$)

$= (0.525 \times 126)\ g = 66.2\ g$ (3 sig. fig.)

(Alternative method): m = MCV/1000 [V in $cm^3$]

Substituting: $m = 126 \times 0.105 \times 5 = 66.2\ g$

**2.** If 4.16 *g* of barium chloride were dissolved in 200 $cm^3$ of water, calculate the concentration of the resulting solution in $moldm^{-3}$. [$BaCl_2$=208] [WAEC]

*To find molar concentration of $BaCl_2$*

Given: Molar mass of salt = 208 $gmol^{-1}$;

Mass of salt = 4.16 *g*; Volume of solution = 200 $cm^3$

First, find the mass concentration:

Mass conc ($gdm^{-3}$) = mass (*g*)/volume ($dm^3$)

$= 4.16/0.200 = 20.8\ gdm^{-3}$

Then, find the molar concentration:

Molar conc = (Mass conc)/(Molar mass)

$= 20.8/208 = 0.100\ moldm^{-3}$

### Revision Exercises

2. Define a standard solution?

3 a. What is a primary standard?

b. State two characteristic properties and one example of a primary standard.

4. Give the reason why a standard solution of sodium hydroxide is not prepared by weighing accurately a given mass of the solid and making it up to the required volume. [WAEC]

5. If you are provided with anhydrous $Na_2CO_3$, spatula and stirrer, list three other materials you would require to prepare a standard solution of $Na_2CO_3$.

6. If 25.0 *g* of $K_2CrO_4$ were dissolved in 250 $cm^3$ of water, calculate the concentration of the resulting solution in *mol* $dm^{-3}$. [O = 16, K = 39, Cr = 52]

7. Calculate the mass of NaOH present in 25.00 $cm^3$ of a 0.100 mole per $dm^3$ solution. [NaOH = 40]

8. An eyedropper is calibrated such that 20 drops are required to deliver 1.0 $cm^3$. Calculate the

a. volume of one drop;

b. amount of base in one drop of a 0.100 *mole per* $dm^3$ NaOH solution.

### 2. Dilution Method.

*Dilution method* is used in *preparing a solution of low concentration from a solution of high concentration.*

When a known volume $V_1$ *(initial)* of a *standard solution* of concentration $C_1$ *(initial)* is diluted with water, its volume *increases* to $V_2$ *(final)*, while its concentration *decreases* to $C_2$ *(final)*. However, the amount, n of the substance in the diluted solution remains constant. i.e.

*Before dilution*:

Amount, $n_1$ (mol) = $C_1$ ($moldm^{-3}$) × $V_1$ ($dm^3$)

i.e. $n_1 = C_1 \times V_1$

*After dilution*:

Amount, $n_2$ (mol) = $C_2$ (mol $dm^{-3}$) × $V_2$ ($dm^3$)

i.e. $n_2 = C_2 \times V_2$

Logically; $n_1 = n_2$

$\therefore \quad C_1V_1 = C_2V_2$ (n constant) ...16.1

This expression is of importance in all dilutions.

**Note:** $V_1$ and $V_2$ *must* be expressed in the same unit of volume, while $C_1$ and $C_2$ must be expressed in the same unit of concentration.

Generally, in any dilution: $C_1 > C_2$ and $V_2 > V_1$

Rearranging equation 16.1 above, we obtain:

$$C_1/C_2 = V_2/V_1$$

The ratio (or proportion) $C_1/C_2$ or $V_2/V_1$ is called ***dilution factor***, i.e. *the number of times a solution has been diluted.*

The volume of distilled water to be added to the *initial* volume $V_1$ for the dilution is the difference between the *final* volume $V_2$ and the *initial* volume $V_1$ of the solutions; i.e.

*Volume of water for dilution* = $(V_2 - V_1)$ unit vol.

**Worked Examples**

3. If 10.0 $cm^3$ of a solution of a 2.0 $moldm^{-3}$ $HNO_3$ were diluted with water to obtain a solution 0.100 $moldm^{-3}$, calculate the

a. dilution factor; b. final volume of solution; c. volume of distilled water added.

*Given*: Initial conc. $C_1 = 2.00\ moldm^{-3}$;
Initial vol. $V_1 = 10\ cm^3$; Final $C_2 = 0.100\ moldm^{-3}$

a. *To find the dilution factor from $C_1$ and $C_2$*
Dilution factor = $C_1/C_2 = 2.0/0.10 = 20$
i.e. the solution has been diluted 20 times; it is a 20-fold dilution.

b. *To calculate the final volume $V_2$ of solution.*
Method 1: Since initial volume $V_1$ is 10.0 $cm^3$, and the solution has been diluted 20 times, then,
$V_2/V_1 = 20$; But $V_1 = 10\ cm^3$ (given)
$\therefore\ V_2 = (20 \times 10)\ cm^3 = 200\ cm^3$
i.e. final volume $V_2$ of solution is 200 $cm^3$.

Method 2: Using the expression $C_1V_1 = C_2V_2$
and substituting: $2.0 \times 10 = 0.1 \times V_2$
Making $V_2$ the subject of the formula:
$V_2 = (2.0 \times 10)/0.1 = 200\ cm^3$
i.e. final volume of solution = 200 $cm^3$

c. *To calculate the volume of distilled water added.*
Volume of water added = $(V_2 - V_1)\ cm^3$
$= (200 - 10.0)\ cm^3 = 190\ cm^3$

4. The stock solution of concentrated $H_2SO_4$ is 18.0 $moldm^{-3}$. Calculate the volume of the stock solution, in $cm^3$, that should be diluted, in order to obtain 10.0 $dm^3$ of a 0.100 $moldm^{-3}$ solution.

*To find the initial volume $V_1$ of stock solution*
Given: Initial conc $C_1 = 18.0\ moldm^{-3}$;
Final conc $C_2 = 0.10\ moldm^{-3}$; Final vol. $V_2 = 10.0\ dm^3$.
Method 1: Using the expression $C_1V_1 = C_2V_2$
and substituting: $18.0 \times V_1 = 0.1 \times 10.0$
Making $V_1$ the subject of the formula:
$V_1 = (0.10 \times 10.0)/18.0 = 0.0556\ dm^3$
i.e. Final volume $V_1$ in $cm^3$ = 55.6 $cm^3$

Note: Since $V_2$ is in $dm^3$, $V_1$ will also be in $dm^3$; then, converted to $cm^3$.

Method 2: *First, find the dilution factor*
Dilution factor = $C_1/C_2 = 18.0/0.10 = 180$
i.e. $V_2/V_1 = 180$
Since $V_2 = 10000\ cm^3$ (Given: 10.0 $dm^3$)
$\therefore\ V_1 = 10000/180\ cm^3 = 55.6\ cm^3$

**Revision Exercises**

9 If 10 $cm^3$ of distilled water is added to 10 $cm^3$ of an aqueous salt solution, the concentration of the solution
A. increases. B. decreases
C. remains constant D. doubles [WASC]

10 If 25.0 $cm^3$ of distilled water was added to 25.0 $cm^3$ of 0.200 $moldm^{-3}$ solution, what would be the concentration of the resulting solution ?
A. 0.500 $moldm^{-3}$ B. 0.400 $moldm^{-3}$
C. 0.125 $moldm^{-3}$ D. 0.100 $moldm^{-3}$ [WAEC]

11 0.1 $moldm^{-3}$ solution of sodium hydroxide was diluted with distilled water to 0.001 $moldm^{-3}$. What is the dilution factor? [WAEC]
A. 1000.00 B. 100.00 C. 10.00 D. 0.01

## 16.3 Acid – Base Titrations

### Neutralization in aqueous solutions

*Neutralization* is the reaction between an *acid* and a *base* to produce *salt* and *water* only.

It is, essentially, the reaction between the hydrogen ion from the acid, and the hydroxide ion from the base, to form water.

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

***Titration*** is used to determine the *average volume of the acid required to neutralize completely a known volume of the base.*

In an *acid-base titration*, the solution of the acid is gradually added into the solution of a base, *in the presence of a suitable indicator*, until the reaction is complete as signaled by a *sudden change in the colour of the indicator*. This is the ***end point***, *neutralization point*, or *equivalence point* of the reaction.

*At the end point, the amounts, in moles, of the acid used and the base taken, are exactly in the same ratio as that required in the balanced equation of reaction.* This is the fundamental basis of all titrations. That is:

$$\frac{\text{Mole of acid used}}{\text{Mole of base taken}} = \frac{\text{mole of acid } (n_a) \text{ in the equation}}{\text{mole of base } (n_b) \text{ in the equation}}$$

The relevant variables in acid-base titration are:
$C_a$ = Concentration of acid, in $moldm^{-3}$
$V_a$ = Volume of acid used, in $cm^3$ (or $dm^3$)
$C_b$ = Concentration of base, in $moldm^{-3}$
$V_b$ = Volume of base taken, in $cm^3$ (or $dm^3$)
$n_a$ = Amount of the acid: its coefficient in the balanced equation of reaction.
$n_b$ = Amount of the base: its coefficient in the balanced equation of reaction.

The units of $C_a$ and $C_b$ *must be in* $moldm^{-3}$, while that of $V_a$ and $V_b$ *must* be in $cm^3$ (or $dm^3$). The importance of units cannot be over-emphasized in chemical calculations.

At the *end point* of an acid-base titration, the *amount of acid used* is directly proportional to the

coefficient of the acid in the balanced equation of reaction: i.e. $C_aV_a \ \alpha \ n_a$

Similarly, the *amount of base taken* is directly proportional to the coefficient of the base in the balanced equation of reaction: i.e.

$$C_bV_b \ \alpha \ n_b$$

Since both the acid and the base are the reactants in the same reaction, then:

$$\frac{C_aV_a}{C_bV_b} = \frac{n_a}{n_b} \quad or \quad \frac{C_aV_a}{n_a} = \frac{C_bV_b}{n_b}$$

This expression is the ***mole ratio formula***. It consists of *six* variables. It is of importance in all *acid-base titrations*.

The ratio $n_a : n_b$, or $n_b : n_a$ is the ***mole ratio*** of the *acid to base* or *base to acid* respectively. It is obtained from the balanced equation of reaction:

1. In the reaction:

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$$

$n_a = 1 \qquad n_b = 1$

Mole ratio of acid and base, $n_a : n_b = 1 : 1$

***One*** mole of HCl neutralizes ***one*** mole of NaOH; HCl is ***monobasic*** or *basicity* of HCl is one.

2. In the reaction:

$$H_2SO_{4(aq)} + 2KOH_{(aq)} \rightarrow K_2SO_{4(aq)} + 2H_2O_{(l)}$$

$n_a = 1 \qquad n_b = 2$

Mole ratio of acid to base is $n_a : n_b = 1 : 2$, or base to acid is $n_b : n_a = 2 : 1$.

***One*** mole of $H_2SO_4$ neutralizes *two* moles of KOH; $H_2SO_4$ is ***dibasic*** or its *basicity* is *two*.

## Acid-Base Titration Apparatus

The two most important pieces of apparatus in acid-base titrations are the burette and pipette. Others are conical flask, retort stand with clamp, filter funnel and white tile.

***The burette***

The burette is a long glass tube graduated from 0.00 $cm^3$ to 50.00 $cm^3$ (maximum). It can be read to a maximum of two places of decimal.

The second place of decimal is either 0 (zero) or 5 (five), and not 1, 2, 3, 4, 6, 7, 8 and 9; i.e. A burette reading can be 0.05, 0.10, 13.30, 49.95, etc, but not 0.01, 13.34, 49.99, etc. Always read the lower meniscus of the liquid.

***The Pipette***

The commonest type is *bulb* or *transfer pipette*. It is a glass tube with a bulb in the middle and tip at the end (fig 16.2a). It is constructed to deliver a specific volume. The commonest pipettes have capacities of 20.0 $cm^3$ and 25.0 $cm^3$.

## Acid-Base Indicators

***Indicators*** are mixtures of weak organic acids and bases that change colours depending on the hydrogen ion concentrations, pH, of the solutions.

They are used in acid-base titrations to detect the *end points* of the reactions, or to test for the acidity or alkalinity of a solution (see Table 16.2).

**Table 16.2:** ***Common indicators and their colours***

| INDICATOR | COLOUR | | |
|---|---|---|---|
| | In alkali | In acid | At endpoint |
| Litmus solution | Blue | Red | Purple |
| Methyl orange | Yellow | Pink | Orange |
| Methyl red | Yellow | Pink | Red |
| Phenolphthalein | Pink | Colourless | Colourless |

## Choice of Indicators in Acid-Base Titrations

The choice of the indicator for a pair of acid and base depends on the strengths of the acid and base, and the *pH of the mixture at the end point*, which must fall within the pH range in which the indicator changes its colour (see Table 14.1, Section 14.10). A wrong choice of indicator usually leads to a wrong end point.

## Procedure for Acid-Base Titration

1. Wash the pipette, burette and conical flasks with soap solution, rinse with water, and then, allow to drain.
2. Rinse the pipette with about 5 $cm^3$ of the solution of the base to be put in it; then, pipette 25 $cm^3$ of the solution into the conical flask. Do not blow the remaining drops; instead, allow the tip of the pipette to touch the base of the flask, while holding it in a slanting position. (fig 16.2a). Finally, add two or three drops (maximum) of methyl orange.
3. Rinse the burette with about 5 $cm^3$ of the solution of the *acid* to be put in it. Then, clamp it firmly and vertically on a retort stand (fig 16.2c). Fill it with the solution of the acid by the use of a funnel. Remove the funnel; then, run out some of the solution through the jet, to expel air bubbles between the tap (or clip) and the jet (fig 16.2d). Finally, record the *initial* burette reading.
4. Place the conical flask containing the solution of the base under the burette on a white tile (or any white surface). Run in the solution of the acid gradually into the conical flask, and *swirl* intermittently, until the colour of the solution changes from *yellow* to *orange*. This is the *end point*. Record the *final* burette reading, and find the volume of acid used (*final* minus *initial*).

5. Repeat the titration with another 25 $cm^3$ portion of the base, but stop the addition of the acid at about 2.0 $cm^3$ before the previous end point; then, add the acid drop by drop with swirling of the conical flask, until the colour of the indicator just changes. Find the volume of acid used.

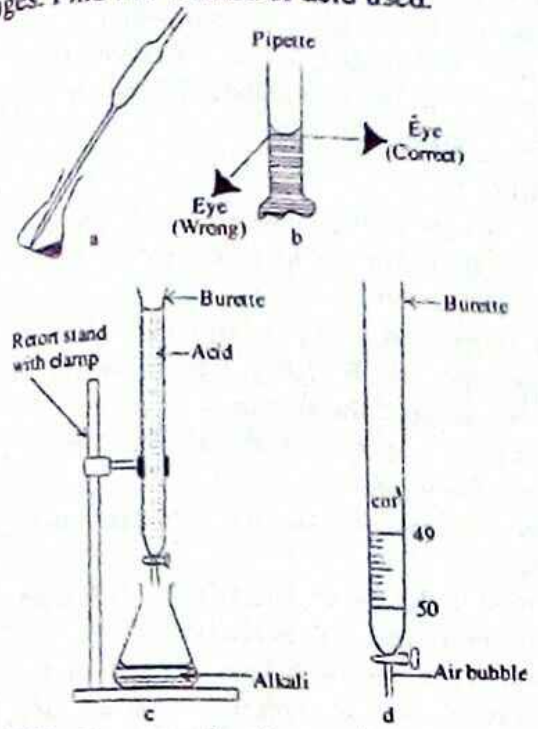



Fig16.3*Titration procedure/precautions*

6. Perform *one* or *more titrations* – until *at least two* titre values (volume of acid used) agree within 0.20 $cm^3$.

7. Find the average volume of acid used from *at least two titre values that agree within* **0.20 $cm^3$**.

Note: Do not put the solution of the base into the burette during titration; an alkali will attack or react with glass or rubber.

## Precautions during Titration:

### Sources of Error

In order to obtain accurate results during titrations, the following precautions should be taken; if not, they are likely sources of error:

1. Rinse the pipette with the solution of the base; to avoid diluting it with the remains of water used in rinsing.
2. Rinse the burette with the solution of the acid; to avoid diluting it with the remains of water used in rinsing.
3. Remove air bubbles from the burette or pipette, to obtain accurate volume of solution.
4. Pipette to the mark (fig 16.3b); to avoid using more or less solution than required.
5. Avoid *parallax error* in reading meniscus level (fig 16.3b); to obtain accurate volume.
6. Avoid spillage of solution from the pipette when transferring; to avoid using less volume of solution than required.
7. Do not blow the last drop at the tip of pipette; to avoid using more solution than the pipette is constructed to deliver.
8. Never rinse the conical flask with the solution of base; to avoid using more solution than required.
9. Clamp the burette in a vertical position; to avoid parallax error while taking the reading.
10. Remove the funnel from the burette before taking the initial reading; to avoid an increase in the volume of solution in the burette.
11. Burette tap/clip must be tight; to avoid leakage.
12. Always use two or three drops (maximum) of the indicator, so as to obtain a sharp end point.
13. Swirl the conical flask during titration; to obtain a homogenous solution.
14. Place the conical flask on a white surface; to avoid over-shooting the end point.
15. Read the burette to two decimal places, for consistency.
16. Obtain at least two sets of burette readings; for consistency or accuracy of titre values.

### Revision Exercises

**12a.** What are indicators?

**b.** Name **two** indicators and state the colour of each of the named indicators in:

**i.** lemon juice; **ii.** lime water ; **iii.** pure water.

**13** List **five** precautions necessary to ensure accurate results during titration.

**14** Explain the following observation:

During an acid-base titration, the distilled water used in flushing drops of acid from the sides of the conical flask does not introduce any error.

**15** A student was instructed to transfer 25.0 $cm^3$ of a given NaOH solution from a beaker into a conical flask without using a funnel.

**a.** Name the apparatus required for the accurate measurement of the 25 $cm^3$ portion.

**b.** State **three** possible sources of error in the measurement.

**c.** What colour would be observed on adding few drops of methyl orange indicator to the portion in the conical flask? [WAEC]

## Recording in Titration

- State the size of the pipette, in $cm^3$.
- Tabulate the burette readings:

| **Burette reading** | **I** ($cm^3$) | **II** ($cm^3$) | **III** ($cm^3$) |
|---|---|---|---|
| *Final* | 21.65 | 43.05 | 22.70 |
| *Initial* | 0.00 | 21.65 | 1.35 |
| **Volume of acid used** | 21.65 | 21.40 | 21.35 |

• Calculate the average volume of acid used from at least two titre values that are within 0.20 $cm^3$.

Notes:

1. The unit of volume should not be omitted.
2. Burette readings must be consistent; it should be to two places of decimal.
3. It should *not* be read to the nearest whole number. A burette reading of 23 $cm^3$ exactly is wrong; 23.00 $cm^3$ is right.
4. Burette reading should not go beyond 50.00 $cm^3$; e.g. 50.05 $cm^3$, or 63.70 $cm^3$ is wrong!
5. Avoid arithmetical errors.
6. Calculate the average volume of acid used from at least two *consistent titres* (titres within 0.20 $cm^3$ of one another). From the data above, only titres **II** and **III** are *consistent*.

Average volume from **II** and **III**

$$= \frac{21.40 + 21.35}{2} \quad = \frac{42.75}{2} \quad = 21.38 \text{ cm}^3$$

7. Average titre should be expressed to *two places of decimal*. For instance: in the example above, 21.375 $cm^3$ is written as 21.38 $cm^3$, and not 21.4 $cm^3$ or 21.40 $cm^3$; if done, the purpose for averaging is defeated!

**Revision Exercises**

16a. What are consistent titres?

b. Select *consistent titres* from the given values: 22.35 $cm^3$, 22.55 $cm^3$ and 22.90 $cm^3$ [WAEC]

17 Consider the following sets of titre values. For each set, identify the *titre values* to be used in averaging; hence, calculate the average titre value for each set.

| | I ($cm^3$) | II ($cm^3$) | III ($cm^3$) |
|---|---|---|---|
| a. | 25.50 | 25.35 | 25.40 |
| b. | 18.70 | 18.55 | 18.85 |

18 In an acid-base titration, a 25.0 $cm^3$ pipette was used and an average titre of 26.50 $cm^3$ was obtained. What does this imply? [WAEC]

## Importance of Acid-Base Titrations

1. To *standardize* a solution of an acid or a base (*Standardization*).
2. To determine the relative molar mass of an acid or a base.
3. To establish the mole ratio of acid to base.
4. To determine the percentage purity/impurity of an acid or a base.
5. To estimate the percentage of water of crystallization in an acid or a base.
6. To determine the solubility of an acid or a base.
7. To determine the degree of temporary hardness of a water sample.
8. To determine the amount of acid or base in excess, after a reaction (*back titration*).
9. To prepare salts.

The following worked examples are to illustrate the importance of standard solutions and how to handle, interpret and treat titration data.

### 1. Standardization of a solution

A solution of an acid of *unknown concentration* can be *standardized*, i.e. its concentration determined, by the use of a standard solution of a base, and vice versa.

**Example 5:**

**A** is a solution of tetraoxosulphate(VI) acid.

**B** is a solution containing 0.050 mole of anhydrous $Na_2CO_3$ per $dm^3$

a. Put solution **A** in the burette and titrate 20 or 25 $cm^3$ portions of **B** using methyl orange as the indicator. Record the size of your pipette. Tabulate the burette readings, and calculate the average volume of acid used.

b. From your results and the data provided, calculate the

i. amount of $Na_2CO_3$ in 25.0 $cm^3$ of **B** used;

ii. concentration of **A** in $moldm^{-3}$;

iii. number of hydrogen ions in 1 $dm^3$ of **A**;

iv. mass of $Na^+$ formed in solution during the titration. [Avogadro number = $6.02 \times 10^{23}$ $mol^{-1}$]

The equation of reaction is:

$$H_2SO_{4(aq)} + Na_2CO_{3(aq)} \longrightarrow Na_2SO_{4(aq)} + H_2O_{(l)} + CO_{2(g)}$$

**Solution**

• Size of pipette: 25 $cm^3$

• Titration results (Hypothetical data)

| Burette reading | I ($cm^3$) | II ($cm^3$) | III ($cm^3$) |
|---|---|---|---|
| *Final* | 24.75 | 49.15 | 25.70 |
| *Initial* | 0.00 | 24.75 | 1.35 |
| Volume of acid used | 24.75 | 24.40 | 24.35 |

Average volume of **A** used from titrations **II** and **III**:

$$= \frac{24.40 + 24.35}{2} \quad = \frac{48.75}{2} \quad = 24.38 \text{ cm}^3$$

**Notes:**

• Only the titre values from the titrations I and II can be used in averaging, since they are within 0.20 $cm^3$.

• Rough or first titre can also be used in averaging, if it is within 0.20 $cm^3$ of any another titre value.

• Do not round up 24.38 $cm^3$ to 24.40 $cm^3$.

b i. *To calculation the amount of $Na_2CO_3$ in 25.0 $cm^3$*

Given: Concentration of **B** = 0.050 $moldm^{-3}$

Amount = Conc ($moldm^{-3}$) × Volume ($dm^3$)

= 0.050 × 25/1000 = 0.00125 *mol.*

ii. *To calculate the molar concentration of A.*

Average volume of **A** (acid) used = 24.38 $cm^3$

Method 1: *From the First Principle*
From the balanced equation of reaction:
1 mol of $Na_2CO_3$ = 1 mol of $H_2SO_4$
∴ 0.00125 mol $Na_2CO_3$ = 0.00125 mol $H_2SO_4$
i.e. 24.38 $cm^3$ of **A** contained 0.00125 mol $H_2SO_4$
∴ 1000 $cm^3$ of **A** contained
$(0.00125 \times 1000)/24.38 = 0.0513$ mol
Hence, concentration of **A** is 0.0513 $moldm^{-3}$.

Method 2: *Formula method*
The various titration variables are:
$C_A = x$ moldm$^{-3}$; $V_A = 24.38$ cm$^3$; $n_A = 1$
$C_B = 0.050$ moldm$^{-3}$; $V_B = 25$ cm$^3$; $n_B = 1$
From the data above, it is safe to use the mole ratio expression, in order to calculate the concentration, $C_A$ of acid in **A**, which is the required variable.
Using the expression: $(C_AV_A)/(C_BV_B) = n_A/n_B$
Substituting: $(C_A \times 24.38)/(0.050 \times 25) = 1/1$
Making $C_A$ the subject of the formula:
∴ $C_A = (1 \times 0.050 \times 25)/(24.38 \times 1)$
$= 0.0513$ $moldm^{-3}$

iii. *Number of hydrogen ions in 1 $dm^3$ of A*
1 $dm^3$ of **A** contained 0.0513 mol of $H_2SO_4$.
$H_2SO_4$ ionizes in water completely:

$$\underset{1\text{ mol}}{H_2SO_4} + aq \rightarrow \underset{2\text{ mol}}{2H^+_{(aq)}} + SO_4^{2-}{}_{(aq)}$$

1 mol of $H_2SO_4$ produces 2 moles of $H^+$
∴ 0.0513 mol produces $2 \times 0.0513$ moles of $H^+$
$= 0.103$ mol of $H^+$
But 1 mole of $H^+$ contains $6.02 \times 10^{23}$ ions;
∴ 0.103 mol of $H^+$ contain $0.103 \times 6.02 \times 10^{23}$ ions
$= 6.20 \times 10^{22}$ ions.

iv. *Mass of $Na^+$ in the solution during titration*:
Amount of $Na_2CO_3$ used = 0.00125 mol.
In solution, 1 mole of $Na_2CO_3$ ≡ 2 moles of $Na^+$
∴ 0.00125 mol $Na_2CO_3$ ≡ $2 \times 0.00125$ moles of $Na^+$
$= 0.00250$ mol of $Na^+$
But 1 mole of $Na^+$ weighs 23.0 *g*,
∴ 0.00250 mol of $Na^+$ weighs $23 \times 0.00250$ *g*
$= 0.0575$ *g*

**Example 6:**

**A** is 0.125 *mol* $dm^{-3}$ $H_2SO_4$
**B** contains *Y* $gdm^{-3}$ of KOH.
In an acid-base titration 25.0 $cm^3$ of **B** required an average of 21.60 $cm^3$ of **A** for complete neutralization.

a. Write a balanced equation of reaction, and state the mole ratio of acid to base.
b. Calculate the
i. amount of $H_2SO_4$ in the average volume of acid used;
ii. concentration of **B** in $moldm^{-3}$;
iii. value of *Y*.
iv. mass of salt formed when 500 $cm^3$ of **B** is completely neutralized by **A**.

a. *To write a balanced equation*

$$H_2SO_{4\,(aq)} + 2KOH \rightarrow K_2SO_{4\,(aq)} + 2H_2O_{(l)}$$

The mole ratio of acid : base = 1 : 2
b i. *To find the amount of $H_2SO_4$ in the average titre.*
Given: Average titre of **A** = 21.26 $cm^3$;
Molar conc of **A** = 0.125 $moldm^{-3}$
Amount = Molar conc × Volume ($dm^3$)
$= 0.125 \times 21.60/1000 = 0.00270$ mol.

ii. *To find the molar concentration of B*
Method 1: *Proportion method*
From the balanced equation of reaction:
1 mol of $H_2SO_4$ ≡ 2 mol of KOH
∴ 0.00270 mol $H_2SO_4$ ≡ $2 \times 0.00270$ mol KOH
$= 0.00540$ mol KOH.
i.e. 25.0 $cm^3$ of **B** contained 0.00540 mol KOH
∴ 1000 $cm^3$ of **B** contained
$(0.00540 \times 1000/25)$ mol = 0.216 mol
Hence, concentration of **B** is 0.216 $moldm^{-3}$.

Method 2: *Formula method*
$C_A = 0.125$ mol dm$^3$; $V_A = 21.60$ cm$^3$; $n_A = 1$
$C_B = x$ mol dm$^3$; $V_B = 25$ cm$^3$; $n_B = 2$
Using the expression: $(C_AV_A)/(C_BV_B) = n_A/n_B$
Substituting: $(0.125 \times 21.60)/(C_B \times 25) = 1/1$
Making $C_B$ the subject of the formula:
∴ $C_B = (0.125 \times 21.60)/(25 \times 1) = 0.216$ $moldm^{-3}$

iii. *To calculate the value of Y.*
First, calculate the concentration of **B** in $gdm^{-3}$
Mass conc = Molar conc × Molar mass
Molar conc = 0.216 $moldm^{-3}$
Molar mass of KOH = 39 + 16 + 1 = 56 $gmol^{-1}$
∴ Mass conc = $0.216 \times 56 = 12.1$ $gdm^{-3}$.
Hence, the value of *Y* = 12.1 (3 sig. fig.)

**Note**: Although 2 *moles* of KOH appeared in the balanced equation of reaction, the molar mass of KOH, i.e. 56.0 $gmol^{-1}$ is used in the formula, in order to obtain the mass concentration, and *not* $56.0 \times 2$ (or 112 $gmol^{-1}$)

iv. *To calculate the mass of salt produced from KOH.*
From the balanced equation of reaction:
2 moles of KOH produce 1 mole of $K_2SO_4$.
*Amount of KOH in 500 $cm^3$ of B:*
Amount = Conc ($moldm^{-3}$) × Volume ($dm^3$)
$= 0.216 \times 500/1000 = 0.108$ *mol.*
Since 2 moles of KOH ≡ 1 mole of $K_2SO_4$
∴ 0.108 *mol* of KOH ≡ ½ × 0.108 mol
i.e. Amount of salt = 0.0540 mol of $K_2SO_4$
Mass of salt = amount (mol) × molar mass of salt
Molar mass of $K_2SO_4 = (39 \times 2) + 32 + (16 \times 4)$
$= 78 + 32 + 64 = 174$ $gmol^{-1}$.
Hence, mass of salt = $(0.0540 \times 174)$ g = 9.40 *g*

## Revision Exercises

**19** $Na_2CO_{3(aq)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + H_2O_{(l)} + CO_{2(g)}$
How many moles per $dm^3$ of sodium trioxocarbonate (IV) are there in a 25 $cm^3$ solution, which required 10 $cm^3$ of 0.05 moldm$^{-3}$ hydrochloric acid solution to neutralize it?

A. 0.100 mole B. 0.001 mole
C. 1.000 mole D. 0.010 mole. [JAMB]

20a Write a balanced chemical equation for the complete reaction between dilute tetraoxosulphate (VI) acid and aqueous sodium hydroxide.

b If 20 $cm^3$ of 0.125 $moldm^{-3}$ of tetraoxosulphate(VI) acid solution reacted with a solution of sodium hydroxide, calculate the amount, in moles of sodium hydroxide required for a complete reaction. [WAEC]

21 What volume in $cm^3$ of 0.1 $moldm^{-3}$ tetraoxosulphate (VI) acid will be required to produce a neutral salt using 50 $cm^3$ of 0.2 $moldm^{-3}$ potassium hydroxide?
A. 25 B. 50 C. 75 D. 100 [JAMB]

22 Calculate the mass of the normal salt formed, when 500 $cm^3$ of 0.500 *mole per* $dm^3$ NaOH were completely neutralized by a solution of $H_2SO_4$.

## 2. Determination of Relative Molar Mass

In order to determine the relative molar mass of an acid or base by titration, the mass concentrations of the acid and base are given, but only one of them can be expressed in mole per $dm^3$. The balanced equation of reaction is provided – so as to establish the mole ratio.

**Example 7:**

A contains 1.60 g of trioxonitrate(V) acid in 250 $cm^3$ of solution.

B contains 9.0 $gdm^{-3}$ of $XHCO_3$.

25.00 $cm^3$ portions of B required an average of 24.90 $cm^3$ of A for complete neutralization.

Calculate the

a. concentration of acid in A in *mol* $dm^{-3}$

b. concentration of $XHCO_3$ in B in *mol* $dm^{-3}$

c. molar mass of $XHCO_3$; d. value of X.

Equation of reaction:

$$HNO_{3(aq)} + XHCO_{3(aq)} \rightarrow XNO_{3(aq)} + CO_{2(g)} + H_2O_{(l)}$$

[H = 1; C = 12; O = 16]

**Solution**

The relevant variables:

$C_A$ = ? mole per $dm^3$; $V_A$ = 24.9 $cm^3$; $n_A$ = 1

$C_B$ = ? mole per $dm^3$; $V_B$ = 25.0 $cm^3$; $n_B$ = 1

*a. To calculate the concentration of A in moldm$^{-3}$*

The given mass concentration of solution A is 1.60 g of $HNO_3$ in 250 $cm^3$.

i.e. 250 $cm^3$ of solution contained 1.60 g of acid

$\therefore$ 1000 $cm^3$ of solution A contained

$(1.60 \times 1000/250)\ g = (1.60 \times 4)\ g = 6.40\ g$.

Mass concentration of solution A = 6.40 $gdm^{-3}$

But molar conc = (Mass conc)/(Molar mass)

Molar mass of $HNO_3 = (1\times1) + (14\times1) + (16 \times 3)$

$= 1+14 + 48 = 63\ gmol^{-1}$

$\therefore$ Molar conc $C_A = 6.40/63 = 0.102\ moldm^{-3}$

*b. To calculate the molar concentration of B.*

Mass conc of $XHCO_3$ in B = 9.0 $gdm^{-3}$.

Since the value of X in the base $XHCO_3$ is not known, the mole ratio expression must be used in order to find its molar concentration, i.e.

$$(C_AV_A)/(C_BV_B) = n_A/n_A$$

Substituting : $(0.102 \times 24.90)/(C_B \times 25) = 1/1$

Making $C_B$ the subject of the formula:

$$C_B = \frac{0.102 \times 24.90}{25} = 0.120\ moldm^{-3}$$

*c. To calculate the molar mass of $XHCO_3$*

Molar conc = (mass conc)/(molar conc.)

$= 10.0/(0.102) = 98.0\ gmol^{-1}$

*d. To find the value of X in $XHCO_3$*

Molar mass of $XHCO_3 = 98.0\ gmol^{-1}$

i.e. $X + 1 + 12 + (16 \times 3) = 98.0$

$X + 1 + 12 + 48 = 98.0$

$X + 61 = 98.0$

$X = 98.0 - 61.0 = 37.0$

Hence, the relative atomic number of X = 37.0

**Revision Exercise**

23 10.0 g of $XHCO_3$ was dissolved in water and made up to 1.0 $dm^3$. If 25.00 $cm^3$ of this solution required 24.90 $cm^3$ of 0.100 $moldm^{-3}$ HCl for neutralization, calculate the molar mass of the acid salt and the atomic mass of X.

## 3. Determination of Mole Ratio

In order to determine the stoichiometry (mole ratio) of acid and base by titration, their aqueous solutions must be standard solutions. However, the balanced equation of reaction will not be provided.

**Example 8:**

25.20 $cm^3$ of a 0.0505 $moldm^{-3}$ solution of a mineral acid neutralized completely 25.09 $cm^3$ of a 0.101 mole per $dm^3$ solution of a hydrogentrioxocarbonate(IV) solution.

Calculate the

a. amount of acid used; b. amount of base used;

c. mole ratio of acid to hydrogentrioxocarbonate (IV) in the reaction, expressing your answer as a whole number ratio of one.

*The relevant variables in the acid-base titration are:*

$C_a$ = 0.0505 moldm$^{-3}$; $V_a$ = 25.2 cm$^3$; $n_a$ = ?

$C_b$ = 0.101 moldm$^{-3}$; $V_b$ = 25.0 cm$^3$; $n_b$ = ?

*a. To calculate the amount of acid used:*

Amount = molar conc × volume (in $dm^3$)

$= (0.0505 \times 25.2)/1000$

$= 0.00127$ mol. *or* $1.27 \times 10^{-3}$ mol.

*b. To calculate the amount of base used*

Amount = molar conc × volume (in $dm^3$)

$= 0.101 \times 25/1000$

$= 0.00253$ mol *or* $2.53 \times 10^{-3}$ mol.

c. *To find the mole ratio.*
Mole ratio of acid to hydrogentrioxocarbonate(IV) is:
0.00127 : 0.00253
Dividing each by the smaller:
$\frac{0.00127}{0.00127} : \frac{0.00253}{0.00127} = 1 : 1.99 \approx 1 : 2$
i.e. $n_a : n_b = 1 : 2$

**Revision Exercise**

24 Consider the equation
$2KOH_{(aq)} + H_2SO_{4\,(aq)} \rightarrow K_2SO_{4\,(aq)} + 2H_2O_{(l)}$
If 20 $cm^3$ of $KOH_{(aq)}$ is neutralized by 20 $cm^3$ of $H_2SO_{4(aq)}$, the molar concentration of the base and the acid are in the ratio
A. 1: 2 B. 2: 1 C. 1: 1 D. 4: 1 [WAEC]

## 4. Determination of the Degree of Purity of a Substance

The degree of purity of an acid or a base can be determined by titration. For instance:
Suppose a sample of hydrochloric acid is contaminated by one of its salts, sodium chloride. A *known* mass of the *impure* acid is dissolved in a *known volume* of solution. The resulting solution of the *impure* acid is then titrated against a standard solution of a pure alkali.

It should be borne in mind that during the course of the titration, only the pure acid in the mixture is neutralized by the standard solution of alkali; the *impurity* remains in the solution. Hence, the molar concentration obtained corresponds to that of the *pure acid* in the mixture.

The *mass concentration of an impure substance in a given solution is always greater than that of the pure portion, due to impurity.* The difference between the mass concentration of impure substance and the mass concentration of pure substance, gives the mass concentration of the impurity.

**Example 8:**
A is 0.100 $moldm^{-3}$ hydrochloric acid.
B contains 6.0 $g$ of a mixture of anhydrous $Na_2CO_3$ and NaCl in 1 $dm^3$ of solution.
25.00 $cm^3$ portions of **B** required an average of 22.65 $cm^3$ of **A** for complete neutralization.
From the above data, calculate the
a. amount, in moles, of $Na_2CO_3$ in 1 $dm^3$ of **B**;
b. mass of $Na_2CO_3$ in 250 $cm^3$ of **B**;
c. percentage by mass of NaCl in the mixture.

Equation of reaction:
$2HCl_{(aq)} + Na_2CO_{3(aq)} \rightarrow 2NaCl_{(aq)} + CO_{2(g)} + H_2O_{(l)}$

a. *To calculate the molar conc of $Na_2CO_3$ in B.*
The molar concentration corresponds to the pure anhydrous $Na_2CO_3$ that has been neutralized by the acid; hence, the mole ratio expression is to be used:
i.e. $(C_AV_A)/(C_BV_B) = n_A/n_A$
The relevant variables are:
$C_A = 0.100\ moldm^{-3}$; $V_A = 22.65\ cm^3$; $n_A = 2$;
$C_B = ?\ moldm^{-3}$; $V_B = 25.0\ cm^3$; $n_B = 1$.
Substituting: $(0.100 \times 22.65)/(C_B \times 25) = 2/1$
Making $C_B$ the subject of the formula:
$$C_B = \frac{0.100 \times 22.65}{2 \times 25} = 0.0453\ moldm^{-3}$$

b. *To calculate the mass of $Na_2CO_3$ in 250 $cm^3$ of B.*
First, calculate the mass concentration of B:
Mass conc = molar conc × molar mass
Molar mass of $Na_2CO_3 = (23\times2) + (12\times1) + (16\times3)$
$= 46 + 12 + 48 = 106\ gmol^{-1}$
Molar conc = $0.0453\ moldm^{-3}$
$\therefore$ Mass conc = $0.0453 \times 106 = 4.80\ gdm^{-3}$
i.e. 1000 $cm^3$ of B contain 4.80 $g$ of $Na_2CO_3$
$\therefore$ 250 $cm^3$ of B contain $4.80 \times 250/1000$ g
$= 1.2$ g of $Na_2CO_3$
i.e. B contains 1.20 $g$ of $Na_2CO_3$ in 250 $cm^3$.

c. *To calculate the % NaCl in the mixture.*
% NaCl in the mixture corresponds to the % Impurity.
Mass conc of impure substance = 6.0 $gdm^{-3}$
Mass conc of pure $Na_2CO_3$ = 4.80 $gdm^{-3}$.
$\therefore$ Mass conc of impurity, NaCl
$= (6.00 - 4.80)\ gdm^{-3} = 1.20\ gdm^{-3}$
% Impurity, NaCl = $1.20/6.00 \times 100/1 = 20.0\%$
Note: % Purity = (100 – 20.0)% = 80.0%
*Or* % Purity = $4.80/6.00 \times 100/1 = 80.0\%$

**Example 9:**
**A** is 0.105 $moldm^{-3}$ hydrochloric acid;
**B** contains 6.00 $g$ of baking powder, $NaHCO_3$ per 100 $cm^3$ of solution.
In a titration, an average of 27.48 $cm^3$ of **A** neutralized completely, 25.00 $cm^3$ of **B**.
a. Write a balanced equation for the reaction;
b. Calculate the
i. concentration of $NaHCO_3$ in $moldm^{-3}$ in **B**;
ii. amount of $NaHCO_3$ in 100 $cm^3$ of **B**;
iii. volume of carbon (IV) oxide produced from 100 $cm^3$ of solution B at s.t.p.;
iv. percentage by mass of $NaHCO_3$ in the sample of baking powder.
[1 mole of a gas = 22.4 $dm^3$ at stp]

a. *Equation of reaction between HCl and $NaHCO_3$.*
$HCl_{(aq)} + NaHCO_{3\,(aq)} \rightarrow NaCl_{(aq)} + H_2O + CO_{2\,(g)}$

b i. *To find the molar conc of $NaHCO_3$ in B.*
Since $NaHCO_3$ is just one of the components of baking powder, its concentration can only be found by the use of the mole ratio expression;
$(C_AV_A)/(C_BV_B) = n_A/n_A$
The relevant variables are:
$C_A = 0.105\ moldm^{-3}$; $V_A = 27.48\ cm^3$; $n_A = 1$
$C_B = ?\ moldm^{-3}$; $V_B = 25.0\ cm^3$; $n_B = 1$
Substituting: $(0.105 \times 27.48)/(C_B \times 25) = 1/1$

**Revision Exercise**

**29** **D** is a solution of hydrochloric acid.
**E** is 0.050 mol $dm^{-3}$ anhydrous $Na_2CO_3$.
**F** contains 7.0 g of MOH per $dm^3$ of solution.
In a double titration experiment, 25.0 $cm^3$ of **E** required an average of 23.15 $cm^3$ of **D** for complete neutralization, while 25.0 $cm^3$ of **F** required an average of 28.70 $cm^3$ of **D** for complete neutralization.

a i. Write a balanced equation of reaction between **D** and **E**.

ii. Calculate the concentration of **D** in *mol* $dm^{-3}$.

b i. Write a balanced equation of reaction between **D** and **F**.

ii. Calculate the

α. concentration of **F** in mol $dm^{-3}$;

β. molar mass of MOH;

γ. relative atomic mass of M.

## 16.4 Precipitation Reactions

### Introduction

*Precipitation reactions* are *double decomposition reactions*. When aqueous solutions of two reactants are mixed together, one of the products is precipitated: being insoluble in water. For instance: When aqueous solutions of sodium chloride and silver trioxonitrate(V) are mixed together, a white precipitate of silver chloride is produced.

$$NaCl_{(aq)} + AgNO_{3(aq)} \rightarrow NaNO_{3(aq)} + AgCl\downarrow$$

For a thorough understanding of precipitation reactions, there is the need to be familiar with the *solubility rules*, in order to know those substances that are *insoluble* in water (see Section ).

### Solved Problem 13

12.0 $cm^3$ of a 1.0 $moldm^{-3}$ solution of silver trioxonitrate(V) were added to 50.0 $cm^3$ of 0.10 $moldm^{-3}$ solution of calcium chloride

a. Write an ionic equation for the reaction.

b. Calculate the amount, in moles, of

i. silver ions in 12.0 $cm^3$ of a 1.0 $moldm^{-3}$ solution of silver trioxonitrate(V);

ii. chloride ions in 50.0 $cm^3$ of 0.10 $moldm^{-3}$ solution of calcium chloride.

c. Which of these ions is in excess, and by how much?

d. Calculate the mass of silver chloride precipitated

a. *To write an ionic equation for the reaction*

$$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$$

b. i. *To find the amount of silver ions in 12 $cm^3$ of 1.00 $moldm^{-3}$ of $AgNO_{3(aq)}$*

First, calculate the amount of salt in the solution:

Amount, $n$ = conc ($moldm^{-3}$) × volume ($dm^3$)
= 1.0 × 12/1000 = 0.012 mole $AgNO_3$

In water, the salt dissociates thus:

$$AgNO_{3(s)} + aq \rightarrow Ag^+_{(aq)} + NO_3^-{}_{(aq)}$$
1 mole 1 mole 1 mole

i.e. 1 mole of $AgNO_{3(aq)}$ gives 1 mole of $Ag^+_{(aq)}$
∴ 0.012 mole of $AgNO_{3(s)}$ gives 0.012 mole $Ag^+_{(aq)}$
i.e. Amount of $Ag^+_{(aq)}$ in solution = 0.0120 mole

ii. *To find the amount of chloride ions in 50 $cm^3$ of 0.10 mol $dm^{-3}$ of $CaCl_2$ solution.*

First, calculate the amount of salt in the solution:

Amount = 0.1 × 50/1000 = 0.005 mole

In water, the salt dissociates thus:

$$CaCl_{2(s)} + aq \rightarrow Ca^{2+}_{(aq)} + 2Cl^-_{(aq)}$$
1 mole 1 mole 2 moles

From the equation:
1 mole of $CaCl_{2(s)}$ in solution gives 2 moles of $Cl^-$
∴ 0.005 mol of $CaCl_{2(s)}$ give 2 × 0.005 mole of $Cl^-$
i.e. Amount of $Cl^-_{(aq)}$ = 2 × 0.005 = 0.0100 mole

c. *To find which of the ions is in excess*

Ionic equation is: $Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$
1 mole 1 mole

i.e. 1 mole of $Ag^+$ requires 1 mole of $Cl^-$
But amount of $Ag^+_{(aq)}$ = 0.012 mole, and
amount of $Cl^-_{(aq)}$ = 0.010 mole.

Since the amount of $Cl^-$ available is 0.010 mole, it means $Ag^+$ is in excess.

Amount of $Ag^+$ in excess = (0.012 - 0.010) mole
= 0.002 mole.

d. *To find the mass of AgCl precipitated*

In the equation:

$$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$$
1 mole 1 mole

1 mole of $Cl^-$ precipitates 1 mole of $AgCl_{(s)}$
∴ 0.010 mole of $Cl^-$ precipitate 0.010 mole of $AgCl_{(s)}$
But 1 mole of AgCl = 108 + 35.5 = 143.5 g
∴ 0.010 mole of AgCl = 0.010 × 143.5 = 1.44 g
i.e. Mass of $AgCl_{(s)}$ precipitated = 1.44 g.

**Revision Exercises**

**30** Calculate the mass of the salt required to prepare 1.0 $dm^3$ of 0.050 $moldm^{-3}$ KI solution. [KI = 166]

**31** Suppose 25.0 $cm^3$ of a 0.500 *mole per* $dm^3$ solution of $BaCl_2$ were added to 100 $cm^3$ of a 0.200 *mole per* $dm^3$ $Na_2SO_4$ solution.

a. Write an ionic equation for the reaction;

b. Calculate the amount, in moles of each of
i. $Ba^{2+}$ and ii. $SO_4^{2-}$ originally present.

c. Which of the ions is in excess?

d. Calculate the quantity of $BaSO_4$ precipitated in
i. moles; ii. grams.

## 16.5 Displacement Reactions

In a displacement reaction, a metal higher up in the *activity series* displaces the ions of another metal lower in the series from an aqueous solution of its salt. For instance: copper is more reactive than

silver; it is higher in the activity series than silver. Hence, copper will displace silver ions from its aqueous solution:

$$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

In volumetric analysis, a *known volume* of a standard solution of a salt is treated with a specified quantity, or *excess* of the metal.

**Example 14:**

In an experiment, 100 $cm^3$ of 2.00 $moldm^{-3}$ $H_2SO_4$ was added to 5.0 g of magnesium wire in a beaker.

a. Write a balanced equation for the reaction.

b. Calculate the

i. amount of $H_2SO_4$ in 100 $cm^3$ of 2.00 $moldm^{-3}$ solution;

ii. mass of magnesium that reacted;

iii. mass of salt produced.

**Solution**

a. *Equation of reaction between $H_2SO_4$ and Mg.*

$$Mg_{(s)} + H_2SO_{4\,(aq)} \rightarrow MgSO_{4\,(aq)} + H_{2\,(g)}$$

b i. *Amount of $H_2SO_4$ in 100 $cm^3$ of 200 $moldm^{-3}$*

Amount (mol) = Conc ($moldm^{-3}$) × Vol ($dm^3$)

= 2.00 × 100/1000 = 0.200 mol.

ii. *To find the mass of Mg that reacted with $H_2SO_4$.*

Amount of $H_2SO_4$ used = 0.200 mol.

This is mass-mole relationship.

From the balanced equation of reaction:

1 mol of $H_2SO_4$ ≡ 1 mol (24.0 g) of Mg

∴ 0.20 mol of $H_2SO_4$ ≡ 24.0 × 0.20 g of Mg

= 4.80 g of Mg.

i.e. 4.80 g of Mg reacted with the acid.

iii. *To find the mass of $MgSO_4$ produced.*

Amount of $H_2SO_4$ used = 0.200 mol.

This is mass-mole relationship.

From the balanced equation of reaction:

1 mol of $H_2SO_4$ ≡ 120 g (1 mol) of $MgSO_4$

∴ 0.20 mol of $H_2SO_4$ ≡ 120 × 0.20 g of $MgSO_4$

= 24.0 g of $MgSO_4$.

Or: Mass of Mg used = 4.80 g.

This is mass-mass relationship.

From the balanced equation of reaction:

24 g (1 mol) of Mg ≡ 120 g (1 mol) of $MgSO_4$

∴ 4.8 g of Mg ≡ (120 × 4.8)/24 g

= 24.0 g of $MgSO_4$.

**Example 15:**

Copper turnings of mass 1.06 g were placed in 250 $cm^3$ of 0.20 $moldm^{-3}$ $AgNO_3$.

a. Calculate the amount of silver ions present;

b. Determine whether all the copper will dissolve in the solution. [Cu = 63.5]

The equation for the reaction is:

$$Cu_{(s)} + 2Ag^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$$ [WAEC]

a. *To calculate the amount of silver ions present in 250 $cm^3$ of 0.20 $moldm^{-3}$ $AgNO_3$*

Amount (mol) = Conc ($moldm^{-3}$) × Vol ($dm^3$)

= 0.20 × 250/1000 = 0.0500 mol.

In aqueous solution:

$$AgNO_{3\,(aq)} \rightarrow Ag^+(aq) + NO_3^-{}_{(aq)}$$

1 mol of $AgNO_3$ produces 1 mol of $Ag^+$ ions

∴ 0.05 mol of $AgNO_3$ produces 0.05 mol of $Ag^+$

Hence, amount of silver ions = 0.0500 mol.

b. *To determine whether all the Cu will dissolve.*

Mass of copper = 1.06 g;

Amount of $Ag^+$ = 0.5 mol.

This is mass-mole relationship.

From the balanced equation of reaction:

2 moles of $Ag^+$ will dissolve 63.5 g (1 mol) of Cu.

∴ 0.05 mol of $Ag^+$ will dissolve 63.5 × 0.05/2 g

= 1.59 g of Cu.

Since the mass of copper turnings placed in the solution is just 1.06 g, all the copper will dissolve.

### Revision Exercises

32 Calculate the mass in grams of $FeSO_4$ that would be produced by 0.5 mole of Fe according to the equation

$$Fe_{(s)} + H_2SO_{4(aq)} \rightarrow FeSO_{4(aq)} + H_{2\,(g)}$$

[Fe = 56, S = 32, O = 16, H = 1]

A. 28 B. 56 C. 76 D. 112 E. 152 [NECO]

33 Suppose 5.0 g of an *impure* iron reacted completely with 75.0 $cm^3$ of a 1.0 mole per $dm^3$ $CuSO_4$ solution.

a. Write a balanced equation for the reaction.

b. Calculate the

i. amount of $CuSO_4$ in 75.0 $cm^3$ of the solution;

ii. mass of iron that reacted;

iii. percentage purity of the sample of iron.

[Fe = 56; $CuSO_4$ = 160]

34 8.0 g of an element X reacted with an excess of copper(II) tetraoxosulphate(VI) solution to deposit 21.3 g of copper. The correct equation for the reaction is

A. $X_{(s)} + CuSO_{4(aq)} \rightarrow Cu_{(s)} + XSO_{4(aq)}$

B. $X_{(s)} + 2CuSO_{4(aq)} \rightarrow 2Cu_{(s)} + X_2(SO_4)_{3(aq)}$

C. $2X_{(s)} + CuSO_{4(aq)} \rightarrow Cu_{(s)} + X_2SO_{4(aq)}$

D. $2X_{(s)} + 3CuSO_{4(aq)} \rightarrow 3Cu_{(s)} + X_2(SO_4)_{3(aq)}$

[X = 24; Cu = 64] [JAMB]

## 16.6 Redox Titrations

### Introduction

*Redox titrations* involve reactions between *oxidizing* and *reducing* agents.

The solutions used as *oxidizing agents* are: acidified $KMnO_4$, acidified $K_2Cr_2O_7$, $KIO_3$ and $I_2$. The *reducing agents* are solutions of: iron(II) salts; ethanedioic acid dihydrate, $H_2C_2O_4 \cdot 2H_2O$; sodium ethanoate, $Na_2C_2O_4$; and sodium trioxosulphursulphate(IV), $Na_2S_2O_3$.

All the basic principles involved in acid-base titrations are applicable to redox titrations. When the

mole concept is applied to redox reagents, the amount of substance present in a given solution can be determined.

**Solved Problem 16**

How many moles of $KMnO_4$ are in 250 $cm^3$ of 0.102 *moles per* $dm^3$ solution?

*To calculate amount in moles.*

Given: Concentration = 0.102 *mole per* $dm^3$

*Formula Method*: Volume in $dm^3$ = 250/1000 = 0.250

Using: Amount = conc ($moldm^{-3}$) × vol ($dm^3$)

= 0.102 × 0.250 = 0.0255 *mol*

*From the First Principle*

1000 $cm^3$ (1$dm^3$) solution contain 0.102 *mole* $KMnO_4$

∴ 250 $cm^3$ solution contain (0.102 × 250)/1000

= 0.0255 *mol* $KMnO_4$

## End-point of a Redox titration

Indicators, such as methyl orange and phenolphthalein are not used in redox titrations:

- In a redox titration involving $KMnO_4$ solution and a colourless reducing agent, an external indicator is *not* required; $KMnO_4$ acts as its own indicator. The end-point is the first *permanent pink colour*.
- In a redox titration involving iodine and a colourless reducing agent, *starch solution* is used. The end-point is signaled by a change from *blue-black to colourless*.

At the *end-point*, the amounts of the *oxidizing agent*, $n_{OA}$ and that of the *reducing agent*, $n_{RA}$ are exactly in the same ratio as that required in the balanced equation of reaction. That is:

$$\frac{\text{Mole of OA used}}{\text{Mole of RA used}} = \frac{\text{mole of OA in the equation}}{\text{mole of RA in the equation}}$$

i.e. $(C_{OA}V_{OA})/(C_{RA}V_{RA}) = n_{OA}/n_{RA}$

**Solved Problem 17**

25.0 $cm^3$ of a hot solution of 0.0302 $moldm^{-3}$ hydrated ethanedioic acid, acidified with dilute $H_2SO_4$ required an average of 28.75 $cm^3$ of $KMnO_4$ solution to complete the reaction.

a. How many moles of the acid are there in 25 $cm^3$ of the solution?

b. How many moles of $KMnO_4$ react with 25 $cm^3$ of the acid?

c. How many moles of $KMnO_4$ are in 1 $dm^3$ of solution?

The equation of the reactions is:

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

a. *To calculate the amount of acid in 25 $cm^3$ of solution*

Given: Concentration = 0.0302 *mole per* $dm^3$

Volume in $dm^3$ = 25/1000 = 0.0250 $dm^3$.

Using: Amount = conc ($moldm^{-3}$) × vol ($dm^3$)

= 0.0302 × 0.0250 = 0.000755 *mol*.

b. *To calculate the amount of $KMnO_4$.*

From the balanced equation of reaction:

5 moles of $C_2O_4^{2-}$ ≡ 2 moles of $MnO_4^-$

∴ 0.000755 mol $C_2O_4^{2-}$ ≡ (0.000755 × 2)/5 mol $MnO_4^-$

= 0.000302 *mol* $KMnO_4$

c. *Amount of $KMnO_4$ in 1 $dm^3$ of solution.*

The volume of $KMnO_4$ solution used is 28.75 $cm^3$

i.e. 28.75 $cm^3$ of solution contain 0.000302 *mol* $KMnO_4$

∴ 1000 $cm^3$ (1 $dm^3$) contain (0.000302 × 1000)/(28.75)

= 0.0105 *mol* $KMnO_4$

## Revision Exercises

35 Calculate the mass of $H_2C_2O_4 \cdot 2H_2O$ required to prepare 500 $cm^3$ of 0.125 mole per $dm^3$ solution. [$H_2C_2O_4 \cdot 2H_2O$ = 126]

36 10.0 *g* of *impure* iron(II) salt were dissolved in water and made up to 250 $cm^3$ of solution. 25.0 $cm^3$ of this solution, acidified with dilute tetraoxosulphate(VI) acid required 20.10 $cm^3$ of 0.050 mole per $dm^3$ of $KMnO_4$ solution before a faint pink colour appeared. The equation for the reaction is:

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

a. How many moles of iron (II) ions react with one mole of $MnO_4^-$ from the equation of reaction?

b. How many moles of $KMnO_4$ are used in the reaction?

c. How many moles of $Fe^{2+}$ react with 20.10 $cm^3$ of $KMnO_4$ solution?

d. How many grams of $Fe^{2+}$ are in the 250 $cm^3$ of original solution?

e. What is the percentage by mass of iron in the impure iron(II) salt? [Fe = 56]

37 Give the reason why an external indicator is not required in a redox titration involving $KMnO_4$(aq).

38 State the colour change observed when $KMnO_4$(aq) is employed in a redox titration.

39 Name the indicator employed and the colour change observed in a redox titration involving aqueous iodine.

## Answers to Revision Exercises

6 0.515 *mol* $dm^{-3}$ 7 0.100 *g*

8a 0.0500 $cm^3$; b $5.00 \times 10^{-6}$ *mol* 9. B 10. D

11. B 16b 22.35 $cm^3$ and 22.22 $cm^3$ 19. D

20b 0.00500 mol 21. B 22 17.8 *g*

23 100 $gmol^{-1}$; X = 39.0 24. B

25a 0.100 $moldm^{-3}$; b 0.0857 $moldm^{-3}$;

25c 10.9 g d 85.8% 26 31.0% 27. D

28. C 29b ii β = 56.5 *g* $mol^{-1}$; γ = 39.5 30 8.30 *g*

31a. $Ba^{2+} + SO_4^{2-} \rightarrow BaSO_{4(s)}$

b i 0.0125 mol; ii 0.0200 mol; c. $SO_4^{2-}$

d i. 0.0125 mol; ii 2.91 *g* 32. C

33b i 0.0750 mol; ii 4.20 g; iii 84.0% 34. A

35 7.88 g 36a 5 *moles*; b 0.00101 *mol*; c 0.00505 *mol*

# 17

# •SOLUBILITY • SOLUBILITY CURVES •

## 17.1 Introduction

### What is Solubility?

In qualitative term: ***Solubility*** *is the property of a* ***solute*** *(solid, liquid, or gaseous substance) to dissolve in a* ***solvent*** *(solid, liquid, or gaseous substance) and form a solution.*

### Dissolution Processes

When a *solute* dissolves in a *solvent*, the mixture obtained is a *solution*, which is *homogeneous*, and exists in a single phase, i.e. as a gas, liquid, or solid. *Air, sweat, and steel are gaseous, liquid and solid solutions respectively. A solution is a homogeneous mixture of two or more substances.*

*Dissolution process can be physical or chemical:*

- The dissolution of common salt in water is a *physical* change; the salt can be recovered from the solution by *crystallization*, or by *evaporation* to dryness, while the solvent, water, can be recovered by *distillation*.
- The dissolution of black powdered copper(II) oxide in dilute tetraoxosulphate(VI) acid is a chemical change. The blue crystals of the hydrated salt can be obtained by crystallization.

### Revision Exercises

1. What is solubility?
2. Name two laboratory techniques that can be used to recover the solute from a liquid solution.

## 17.2 Solubility of Solids in Liquids

### Saturated and Unsaturated Solutions

When a *spatulaful* of common salt, is placed in a beaker containing 50 $cm^3$ of pure water, and the mixture is stirred, the salt dissolves to give a colourless solution. As more of the salt is added to the solution with stirring, it dissolves. However, a stage is reached in which further addition of the salt to the solution does not lead to dissolution at the particular temperature.

This observation shows that there is a limit to the quantity of a solute a given volume of solvent (water) can dissolve at a particular temperature.

*An* ***unsaturated*** *solution is a solution that will dissolve more of the solute at a given temperature.*

*A* ***saturated*** *solution is a solution that will not dissolve more of the solute in the presence of excess solute, at a given temperature.*

### Dynamic Equilibrium in a Solution

In a *saturated solution*, there exist a *dynamic equilibrium* between the *solution* and the *undissolved solute*:

$$\text{Solute + Solvent} \rightleftharpoons \text{Solution}$$

At *saturation point*, the quantity of the excess solute remains constant; hence, the concentration of the solution is constant. Therefore, *a solution is saturated when the solute is in dynamic equilibrium with the solution at a particular temperature.*

### Revision Exercises

3. Define the term *saturated solution*. [WAEC]
4. Distinguish between *saturated* and *unsaturated* solutions.
5. What term is used to describe a solution, which is in equilibrium with its solute?
6. What process is illustrated below?

$$S_{(s)} \overset{H_2O}{\rightleftharpoons} S_{(aq)}$$

   A. Decomposition of a solid.
   B. Melting point of a solid.
   C. Formation of saturated solution of a solid.
   D. Sublimation of a solid. [WAEC]

7. A change in the temperature of a saturated solution disturbs the equilibrium between the
   A. undissolved solute and the solvent.
   B. undissolved solute and the dissolved solute.
   C. dissolved solute and the solution.
   D. dissolved solute and the solvent. [WAEC]

### Factors that Influence Solubility of Solids in Liquids

The following *four* factors influence or affect the solubility of solids in liquids:

#### 1. Nature (Polarity) of the Solute

Generally, ionic compounds are soluble in *polar* solvents, like water, but insoluble in *non-polar* solvents, like petrol; while covalent compounds are

soluble in *non-polar* solvents, like petrol, but insoluble in *polar* solvents, like water. For instance: sodium chloride is soluble in water, but insoluble in petrol. *Like dissolves like.*

**2. Nature (Polarity) of the Solvent**

Generally, a polar solvent will dissolve an ionic compound, while a non-polar solvent will dissolve a covalent compound. *Like dissolves like.*

**3. Temperature Change**

There is no general rule to describe the variation of solubility of solids with a change in temperature. Reason: When a solid dissolves in a liquid, heat may be given out (exothermic) or absorbed (endothermic), or there may be no significant temperature change. Hence, there are three distinct trends:

- For an ionic compound that dissolves in water with *absorption of heat*, solubility *increases* as temperature *increases*, e.g. $KNO_3$ and $KClO_3$.
- For those compounds that dissolve in water with *liberation of heat*, an *increase* in temperature *decreases* the solubility, e.g. $CaSO_4$ and $Ca(OH)_2$.
- When an ionic compound dissolves in water with no noticeable change in temperature, there will be no significant increase in solubility as temperature increases, e.g. NaCl.

For most ionic compounds, an *increase* in temperature leads to an *increase* in solubility. So also, the solubility of a given solute at a particular temperature varies from one solvent to another.

**4. Common ion Effect**

The solubility of an ionic compound in water is not affected by the presence of another compound already in the solution, except if both compounds have the same cations or anions. For instance:

- The solubility of NaCl in water is the same as its solubility in a dilute sugar solution, or in dilute $H_2SO_4$. This is because there is no cation or anion common to NaCl, sugar, and $H_2SO_4$.
- The solubility of NaCl in water is much higher than its solubility in dilute HCl or aqueous $NaNO_3$. This is because in NaCl and HCl, chloride ion is common, while in NaCl and $NaNO_3$, sodium ion is common. The *decrease* in the solubility is due to a phenomenon called *common ion effect.*

## How to increase the rate of dissolution of a solid in a liquid

The *three* common methods of increasing the rate at which a solid dissolves in a liquid are:

**1. *By stirring the mixture***; so that the liquid particles are in contact with as many solid particles as possible.

**2. *By grinding the solid into powder***, in order to *increase the surface area* of the solid particles in contact with the liquid. This explains why *granulated* sugar dissolves in water faster than the same quantity of *cubes* of sugar.

**3. *By heating the mixture***; in order to increase the average kinetic energy of the liquid particles, and hence, increase the solubility of the solid.

## Effect of solute on the physical properties of the solvent in a solution

When a solid dissolves in a liquid to form a solution, the liquid particles become heavier, hence, its density increases, i.e. a *solution is denser than its pure solvent.* For instance: 100 $cm^3$ of a sugar solution is denser than 100 $cm^3$ of pure water

The following physical properties of the pure liquid are affected:

**1. *Lowering of vapour pressure:*** The rate of evaporation of the liquid particles is decreased. Hence, the vapour pressure of a solution is less than that of its pure solvent at a given temperature.

**2. *Elevation of boiling point*:** A solution will boil at a higher temperature than the pure solvent. This is because *more heat energy must be absorbed by a solution in order to overcome the attractive forces between the liquid and the solid particles.*

This explains why a dilute sugar solution, a solution of common salt in water, or a sample of *hard* water boils at a temperature above the normal boiling point of pure water.

**3. *Lowering of freezing point*:** A solution freezes at a lower temperature than the pure solvent. This is because *more heat energy must be released* in order to freeze a solution. This explains why *a saturated solution of NaCl (brine) can be used as a freezing mixture. It freezes at a temperature far below the freezing point of pure water.*

### Revision Exercises

**8** Mention **three** factors that affect the solubility of a solid in a liquid.

**9** Explain the term *common ion effect.*

**10** What term is used to describe the fact that sodium chloride is more soluble in water than in dilute hydrochloric acid at a given temperature?

**11** Mention **two** methods of increasing the rate of dissolution of sodium chloride in water without increasing the volume of the solution.

**12** Explain why a solid dissolves faster in hot water than in cold water.

**13** List **three** physical properties of water, which are affected when it forms a dilute solution with a salt.

**14** For a given solute, the concentrations of its saturated solution in different solvents are

A. the same at the same temperature.
B. different at the same temperature.
C. the same at different temperature.
D. constant. [JAMB]

## 17.3 Solubility of Salts in Water

### Quantitative Definitions of Solubility

*The solubility of a solid in a liquid is the concentration of the saturated solution.* Solubility can be defined quantitatively as follows:

1. *The solubility of a solid in a liquid is the maximum amount (or mass)* of the *solid* that dissolves in 1 $dm^3$ of *solution* at a given temperature. It is expressed in *moles/$dm^3$* (or *grams/$dm^3$*).

2. *The solubility of a solid in a liquid is the maximum amount (or mass)* of the *solid* that dissolves in 100 *g* (or 1000 *g*) of *solvent* at a given temperature. It is expressed in *moles/kg* (or *grams/kg*).

### Determination of solubility of a Salt at 27 °C

**Stage 1:** ***Preparation of Saturated Solution.***

1. Put 100 $cm^3$ of distilled water in a beaker, add the salt little by little into it, and warm on a Bunsen burner with stirring. Continue the addition of the salt with stirring, and keeping the beaker warm at about 50 °C, until the salt can no longer dissolve.
2. Allow the saturated solution to cool to room temperature; this is the saturated solution of the salt at 27 °C. It will be noticed that as the *hot* saturated solution cools, the excess solid in the solution separates out, to give a saturated solution at a *lower* temperature.

**Stage 2:**

***Evaporation of saturated solution to dryness***

1. Weigh accurately a clean dry evaporating dish: $x$ *g*.
2. Rinse a 25 $cm^3$ pipette with the saturated solution, in order to warm it.
3. Pipette 25 $cm^3$ of the saturated solution at 27 °C, as quickly as possible (without pipetting any undissolved solid) into the evaporating dish and re-weigh: $y$ *g*.
4. Place the dish on a steam bath and evaporate to dryness. Allow to cool in a *charged* desiccator, and then re-weigh.
5. Repeat the process of heating and cooling, until a constant mass is obtained: $w$ *g*.

**Stage 3:** ***Calculation of the solubility at 27 °C***

The following hypothetical values will be used to illustrate how to calculate the solubility of a salt.

**Data required:**

- Mass of the evaporating dish: $x = 15.20$ *g*
- Mass of evaporating dish + 25 $cm^3$ of saturated solution: $y = 40.70$ *g*
- Mass of dish + anhydrous salt: $w = 20.70$ *g*

**Solubility in moles per $dm^3$**

Mass of anhydrous salt = $(w - x)$ = (20.70 – 15.20) *g*
= 5.50 *g*

i.e. 25 $cm^3$ of saturated solution contain 5.50 *g* of salt.
∴ 1000 $cm^3$ of saturated solution contain
5.50 ×1000/25 *g* = 220 *g* of salt.

*To convert 220 g to moles*

Amount (*mol*) = (Mass of salt)/(Molar mass)
Molar mass of $KNO_3$ = 39 + 14 + 48 = 101 $gmol^{-1}$
i.e. Amount, in moles = 220/101 = 2.18 moles
∴ Solubility of $KNO_3$ at 30 °C = 2.18 $moldm^{-3}$

*Solubility in grams per 100 g of water*

Mass of water used = $(y - w)$ = (40.70 - 20.70) *g*
= 20.0 *g*
Mass of salt used = $(w - x)$ = (20.70 - 15.20) *g*
= 5.50 *g*

i.e. 20.0 *g* of water at 27 °C saturated 5.50 *g* of salt.
∴ 100 *g* of water will saturate 5.50 × 100/20 *g* of salt
i.e. 5.50 × 5 *g* = 27.5 *g* of salt.
Hence, the solubility of the salt at 27 °C is
27.5 *g* per 100 *g* of water.

### Worked Examples

**1.** What is the solubility of X in $moldm^{-3}$, if 25.0 $cm^3$ of its saturated solution contains 4.0 *g* of X?
[X = 60]

*To calculate the solubility of X in $moldm^{-3}$*

Given: 25.0 $cm^3$ of saturated solution contain 4.0 *g* of X

Method 1: *From the First Principle*

First, calculate the mass concentration:
25 $cm^3$ of saturated solution contain 4.0 *g* of X
∴ 1000 $cm^3$ of saturated solution contain
4.0 × 1000/25 = 160 g of X
i.e. Mass conc of the saturated solution is 160 $gdm^{-3}$
Now, since 60 *g* of X equal 1 *mol*
∴ 160 *g* of X equal 1 × 160/60 = 2 .67 *mol*
Hence, the solubility of X is 2.67 $moldm^{-3}$

Method 2: *Formula method*

$$\text{Molar concentration, C} = \frac{\text{Amount, in mol.}}{\text{Volume, in dm}^3}$$

Amount = (mass of X)/(molar mass of X) = 4/60 *mol*.
= 0.0667 *mol*
Volume of solution in $dm^3$ = 25/1000
= 0.025 $dm^3$

$$\therefore \text{ Molar conc} = \frac{0.0667}{0.025} = 2.67\ moldm^{-3}$$

**2.** If the solubility of $KHCO_3$ is 0.40 $moldm^{-3}$ at room temperature, calculate the mass of $KHCO_3$ in 100 $cm^3$ of the solution at this temperature.
[$KHCO_3$ = 100 $gmol^{-1}$] [WAEC]

*To calculate the mass of $KHCO_3$ in 100 $cm^3$ of solution*

First, calculate the amount of $KHCO_3$ in 100 $cm^3$ of 0.40 $moldm^{-3}$ using the following relationship:
Amount = Conc ($moldm^{-3}$) × Vol ($dm^3$)
= 0.40 × 100/1000 *mol*. = 0.040 *mol*.
Then, convert 0.040 mole to mass, in gram:
Mass = Amount (*mol*) × Molar mass ($g\ mol^{-1}$)
= 0.040 × 100 = 4.00 g.
i.e. Mass of $KHCO_3$ = 4.00 g (3 sig. fig)

3. What volume of 0.20 $moldm^{-3}$ NaOH solution would yield 5.0 g of NaOH on evaporation to dryness? [NaOH = 40 $gmol^{-1}$]

*To find volume of solution that contains 5.0 g NaOH*

*Given: concentration = 0.20 $moldm^{-3}$*

*Molar mass of NaOH = 40.0*

*Method 1: From the first principle*

*First, calculate the mass conc of the solution, using:*

*mass conc = molar conc × molar mass*

*= 0.20 × 40 = 8.0 $gdm^{-3}$*

*Then, calculate the volume of solution that would contain 5.0 g of NaOH.*

*Since 8.0 g of NaOH are in 1000 $cm^3$ of solution;*

*∴ 5.0 g NaOH will be in 1000 × 5/8 = 625 $cm^3$.*

*Method 2: Formula method*

*First, calculate the amount of NaOH in 5.0 g, using:*

*Amount = mass/molar mass. Substituting:*

*Amount = 5/40 = 0.125 mol.*

*Then, calculate the volume occupied by 0.125 mol. of NaOH, using:*

$$\text{Volume, in } dm^3 = \frac{\text{Amount (mol)}}{\text{Conc } (moldm^{-3})}$$

*Substituting: Volume = 0.125/0.20 = 0.625 $dm^3$*

*∴ Volume, in $cm^3$ = 0.625×1000 = 625 $cm^3$.*

4. Water is added to 120 g of a salt $MCl_2$ to produce 60 $cm^3$ of a saturated solution at 298 K. The solubility of the salt at that temperature was 8.00 $moldm^{-3}$. Calculate the mass of the salt which remained undissolved. [M = 24, Cl = 35.5]

**Solution**

*Given: Solubility of $MCl_2$ at 298 = 8.00 $moldm^{-3}$.*

*First, calculate the mass of $MCl_2$ that will be present in 60 $cm^3$ of the saturated solution:*

*i.e. 1000 $cm^3$ of saturated solution contain 8.00 mol.*

*∴ 60 $cm^3$ of saturated solution contain*

*$(8 \times 60)/1000 = 0.480$ mol.*

*Molar mass of $MCl_2$ = 24 + 2(35.5)*

*= 24 + 71 = 95 g/mol.*

*∴ Mass of $MCl_2$ in 60 $cm^3$ of the saturated solution*

*= (0.480 × 95) g = 45.6 g.*

*Since 60 $cm^3$ of the original solution contained 120 g;*

*∴ mass of $MCl_2$ that remained undissolved will be;*

*(120 – 45.6) g = 74.4 g.*

### Revision Exercises

15 What is solubility of a solid in a liquid?

16 Mention three pieces of apparatus required for the determination of the solubility of a salt at a given temperature.

17 Outline a suitable method for determining the solubility of $NaNO_3$ at 30 °C.

18 144 g of KCl dissolved in 1 $dm^3$ of water at 90 °C. Calculate the solubility of KCl at this temperature. [K = 39; Cl = 35.5] [WAEC]

19 14.8 g of a salt (z) dissolved in 250 $cm^3$ of distilled water gives a concentration of 0.80 $moldm^{-3}$. Calculate the molar mass of the salt (z) in $gmol^{-1}$.

A. 13.5 B. 18.5 C. 47.4 D. 74.0 [WAEC]

20 If 50.0 $cm^3$ of a saturated solution of $KNO_3$ at 40 °C contained 5.05 g of the salt. What is the solubility of the salt at 40 °C [$KNO_3$ = 101] [WAEC]

21 Calculate the mass of anhydrous $Na_2CO_3$ in 25.0 $cm^3$ of the saturated solution at 30 °C, if its solubility at this temperature is 1.80 $moldm^{-3}$. [C = 12; O = 16; Na = 23]

22 What volume of a saturated solution of Y at 0 °C would yield 7.0 g of the dry salt, if the solubility of Y at 0°C is 2.0 $moldm^{-3}$? [Y = 140]

23 In an experiment to determine the solubility of a given salt Y, the following data were provided:

Mass of dry empty dish = 7.16 g

Mass of dish + saturated solution of salt Y = 17.85 g

Mass of dish + salt Y = 9.30 g

Temperature of solution = 20 °C

Molar mass of salt Y = 100 $gmol^{-1}$

Density of solution Y = 1.00 $gcm^{-3}$

Calculate the solubility of salt Y in

a. $gdm^{-1}$ b. $moldm^{-3}$ [WAEC]

## 17.4 Solubility Curves

The solubility curve of a salt represents the variation of its *solubility* with *temperature*.

It is obtained by determining the solubility of the salt in a solvent, water, at various temperatures. Then, a graph is plotted with the *solubility* (or *concentration*) of the salt, in moles per $dm^3$ or in grams per 100 g of water along the y-axis (vertical) and the *temperature*, in degree Celsius, on the x-axis (horizontal). The table below shows the solubility of $KClO_3$ in water at various temperatures, using approximated values.

**Table 17.2: *Solubility data of $KClO_3$***

| Temp. °C | 0 | 20 | 40 | 60 | 80 | 100 | x-axis |
|---|---|---|---|---|---|---|---|
| Solubility / mol $dm^{-3}$ | 0.50 | 0.70 | 1.20 | 2.00 | 3.10 | 4.40 | y-axis |

### Importance of Solubility Curves

**Case I:** The following information can be obtained from a particular solubility curve as depicted by the solubility curve of $KClO_3$ in figure 17.1.

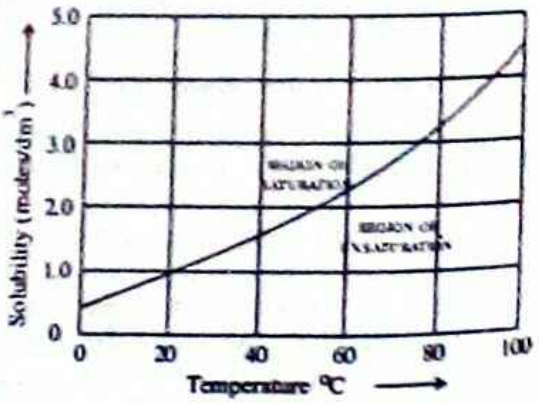



**Fig 17.1** *Solubility curve of $KClO_3$*

1. The solubility curve shows that there is an increase in the solubility of the salt as temperature increases, and vice versa.

2. The area above the curve represents *region of super-saturation*, while the area below represents *region of unsaturation*. Any point along the curve represents the *saturation point, equilibrium point or solubility point.*

3. The solubility of the salt can be found at any other temperature that has not been determined experimentally. For example: the solubility of $KClO_3$ salt at 30 °C is 0.90 $moldm^{-3}$.

4. It is possible to know whether a given solution is saturated or unsaturated. For example:

- If a solution of the salt at 30 °C contains 0.90 $mol/dm^3$, the solution is at the saturation point (point A on the curve); it is just *saturated*.
- If a solution of the salt contains 2.0 $mol\ dm^{-3}$ at 30 °C, it is above the curve (point **B**). It is more than *saturated* (*supersaturated*); i.e. excess salt remains in the solution at point **B**.
- If a solution of the salt contains 0.50 $moldm^{-3}$ at 30 °C, it is below the curve. The solution is *unsaturated* at point C.

5. The temperature at which a *hot unsaturated* solution will start to deposit crystals on cooling can be found; e.g. a solution containing 1.50 $moldm^{-3}$ at 80 °C is *hot* and *unsaturated*. On being cooled to 49 °C, the solution becomes *saturated* (a point on the curve). Hence, the solution will start to crystallize at 49 °C.

6. It is possible to estimate the mass of crystals that would be obtained on cooling a *hot unsaturated* solution to a low temperature; e.g.

*To calculate the mass of crystals that will be obtained when 1000 $cm^3$ (1 $dm^3$) of a solution containing 1.50 moles per $dm^3$ is cooled from 80 °C to 25 °C.*

Amount of salt in 1000 $cm^3$ (1 $dm^3$) of solution (Solubility) at 80 °C = 1.50 moles.
Amount of salt in 1000 $cm^3$ (1 $dm^3$) of solution (Solubility) at 25 °C = 0.80 mole.
∴ Amount of salt crystallized = (1.50 – 0.80) mol
= 0.70 mol.
But molar mass of $KClO_3$ = 122.5 $gmol^{-1}$
∴ Mass of crystals = 0.70 × 122.5 g
= 85.8 g.

**Case II:** The following information can be obtained from two or more solubility curves drawn on the same graph, as shown in figure 17.2, using the approximated data in Table 17.3.

The curves enable comparison to be made on the solubility of two or more salts, e.g.

1. There is a *large increase* in the solubility of $KNO_3$ as temperature increases; that of **KCl** is *moderate*; while that of **NaCl** is *quite small* – it is approximately independent of temperature. However, the solubility of $CaSO_4$ *decreases* with *increasing* temperature, and becomes constant at about 60 °C.

**Table 17.3:** *Solubility data of some salts*

| Temp (°C) | 0 | 20 | 40 | 60 | 80 | 100 |
|---|---|---|---|---|---|---|
| Solubility (mol $dm^{-3}$) NaCl | 6.10 | 6.20 | 6.30 | 6.40 | 6.60 | 6.80 |
| Solubility (mol $dm^{-3}$) KCl | 3.60 | 4.40 | 5.20 | 6.00 | 6.60 | 7.40 |
| Solubility (mol $dm^{-3}$) $KNO_3$ | 1.40 | 3.10 | 5.90 | 10.0 | 16.0 | |
| Solubility (mol $dm^{-3}$) $CaSO_4$ | 3.40 | 1.70 | 0.60 | 0.20 | 0.20 | 0.20 |

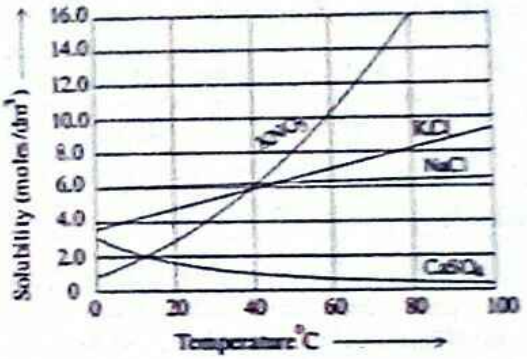



**Fig 17.2** *Solubility curves of some salts*

2. The solubilities of **NaCl** and **KCl** are *directly* proportional to the temperature (straight-line graphs).

3. **KCl** is more soluble than $KNO_3$ at temperatures lower than 30 °C; but above 40°C, $KNO_3$ is more soluble. The two salts have the same solubility at about 35 °C (at the intercept).

4. **NaCl** is more soluble than **KCl** at temperatures below 80 °C, but less soluble than **KCl** at temperatures above 80 °C. They have the same solubility at 80 °C.

## Applications of Solubility Curves

1. To separate and purify mixtures of solids.
2. To identify the most suitable solvents for the extraction of solutes from natural sources.
3. To determine the amounts of solid drugs in a solution of mixture of drugs.

**Worked Example**

5. If the solubility of $KNO_3$ is 3.10 $moldm^{-3}$ at 20 °C, determine whether a solution of $KNO_3$ containing 303 $gdm^{-3}$ at 20 °C is saturated or unsaturated. [$KNO_3$ = 101 $gmol^{-1}$]

*To determine whether a solution of $KNO_3$ containing 303 $gdm^{-3}$ is saturated or unsaturated*

First, convert 303 $gdm^{-3}$ to $moldm^{-3}$, using:

Conc ($moldm^{-3}$) = Conc ($gdm^{-3}$)/Molar mass

Molar mass of $KNO_3$ = 101 $gmol^{-1}$

∴ Conc ($moldm^{-3}$) = 303/101 = 3.00 $moldm^{-3}$

Since the concentration of the given solution of $KNO_3$ at 20 °C (3.0 $moldm^{-3}$) is *less* than its solubility at 20 °C (3.10 $moldm^{-3}$), then, the given solution is *unsaturated*.

**Revision Exercises**

24 State what is observed, generally, on cooling a hot saturated solution.

25 Given that the solubility of $KHCO_3$ is 0.55 $moldm^{-3}$ at room temperature, determine whether a solution containing 50.0 $gdm^{-3}$ at the same temperature is saturated or unsaturated. [$KHCO_3$ = 100] [WAEC]

26 a. What is a solubility curve?

b. The table below gives the solubilities of salts **X** and **Y** at various temperatures:

| Temp (°C) | 0 | 20 | 40 | 60 | 80 | 100 |
|---|---|---|---|---|---|---|
| Solubility of X ($mol\ dm^{-3}$) | 0.30 | 0.38 | 0.58 | 0.85 | 1.30 | 1.95 |
| Solubility of Y ($mol\ dm^{-3}$) | 0.55 | 0.62 | 0.68 | 0.75 | 0.80 | 0.88 |

i. Plot the solubility curves of **X** and **Y** on the same graphs using suitable scales.

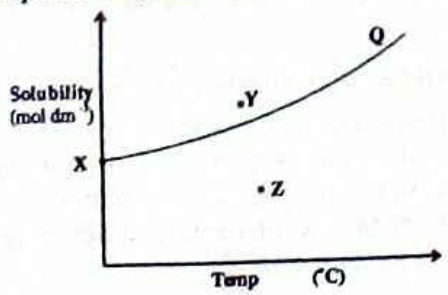
ii. Which salt is less soluble at 80 °C?

iii. At what temperature is the solubility of **X** and **Y** the same, and what is their solubility at this temperature?

iv. Calculate the mass of **X** that would be deposited when 1 $dm^3$ of a solution containing 1.0 *moles per* $dm^3$ is cooled from 80 °C to 30 °C. [X = 120]

27 When 20.0 g of a salt **W** was dissolved in 25.0 g of water at a certain temperature, 90.0% of the salt dissolved to give a saturated solution; determine the solubility of **W** in grams per 100 g of water.

28 The graph below represents the solubility curve of a salt represented by letter **Q**.




At which of the points labeled **X**, **Y** and **Z** is a solution of **Q**

a. unsaturated b. supersaturated c. saturated? [W]

29 The heat of solution of $Ca(OH)_2$ is −16.2 $kJmol^{-1}$. State with reason the effect of increase in temperature on the solubility of $Ca(OH)_2$. [WAEC]

30 Give **TWO** applications of solubility curve. [NECO]

## 17.5 Fractional Crystallization

When aqueous solutions of two or more salts with widely different solubilities at a certain temperature range are mixed together, separation is possible by *fractional crystallization*.

*Fractional crystallization* is the process whereby the crystals of a salt are obtained by cooling a saturated solution containing two or more salts.

When a mixture of salts in a *hot* unsaturated solution is cooled to a low temperature, the salt with the *lowest solubility* separates out first; e.g. On cooling a hot unsaturated solution containing equal amounts (1 mole) of **KCl** and $KNO_3$ to about 10 °C, only the crystals of $KNO_3$ separate out; those of **KCl** remain in the solution (see figure 17.2).

**Worked Examples**

6 1.0 $dm^3$ of an aqueous solution at 90 °C contains 404 g of $KNO_3$ and 245 g of $KClO_3$.

a. Determine which of the two salts will separate out when the solution is cooled to 60 °C.

[$KNO_3$ = 101; $KClO_3$ = 122.5; Solubility of $KNO_3$ in water at 60 °C is 5.15 $moldm^{-3}$; Solubility of $KClO_3$ in water at 60 °C is 1.61 $moldm^{-3}$]

b. Calculate the mass of salt that will separate out at 60 °C. [WAEC]

a. *To determine which of the salts separates out.*

First, calculate the amount of each salt present in 1 $dm^3$ of the solution at 90 °C.

i.e. Amount of $KNO_3$ = (mass)/(molar mass)
= 404/101 = 4.00 *moles*.

Amount of $KClO_3$ = (mass)/(molar mass)
= 245/122.5 = 2.00 *moles*.

At 60 °C, the solubility of $KNO_3$ is 5.15 $moldm^{-3}$ i.e. 5.15 moles are present in 1 $dm^3$ of saturated solution.

Since 4.0 moles are present in the given 1 $dm^3$ of solution, the solution is unsaturated with respect to $KNO_3$. Hence, no crystals of $KNO_3$ will separate out at 60 °C.

At 60 °C, the solubility of $KClO_3$ is 1.61 $moldm^{-3}$ i.e. 1.61 moles are present in 1 $dm^3$ of saturated solution.

Since 2.0 moles are present in the given 1 $dm^3$ solution, the solution is saturated with respect to $KClO_3$. Hence, crystals of $KClO_3$ will separate out at 60 °C.

*b. To calculate the mass of $KClO_3$ that separates.*
Amount of $KClO_3$ in 1 $dm^3$ of solution = 2.0 mol.
Solubility of $KClO_3$ at 60°C = 1.61 moles per $dm^3$
Amount of $KClO_3$ crystallized = (2.00 – 1.6) mol.
= 0.390 mol.
Since 1 mole of $KClO_3$ weighs 122.5 g
∴ 0.390 mol will weigh 0.390 × 122.5 g = 47.8 g.
i.e. Mass of $KClO_3$ that crystallized out is 47.8 g.

7. The solubility of a salt is 75 g in 100 g of water at 100 °C, and 25 g in 100 g of water at 30 °C. What mass of the salt crystallizes, if 50 g of its solution saturated at 100 °C were cooled to 30 °C? [NECO]

*To calculate mass of salt that will crystallize at 100 °C*
First, calculate the mass of salt in 50 g of solution:
Mass of saturated soln = Mass of water + mass of salt
= (100 + 75) g = 175 g. i.e.
175 g of saturated solution contained 75 g of salt
∴ 50 g of saturated solution contained 75 × 50/175
= 21.4 g of salt
Hence, mass of water = (50.0 – 21.4) g = 28.6 g
i.e 28.6 g of water saturate 21.4 g of salt at 100 °C.
Since 100 g of water will saturate 25 g of salt at 30 °C,
∴ 28.6 g of water will saturate 25 × 28.57/100
= 7.14 g of salt at 30 °C
Hence, the mass of salt that will crystallize at 30 °C will be: (21.4 – 7.14) g = 14.26 g = 14.3 g (3 sig. fig.)

### Revision Exercises

31 State the physical method that can be used to separate a mixture of $NaNO_3$, $KNO_3$ and KCl in an aqueous solution.

32 You are provided with an aqueous solution containing $KNO_3$ and KCl (see figure 17.2 for the solubilities of the salts). Describe how pure crystals of the salts can be obtained.

## 16.6 Concentrating a Solution

The two physical methods that can be used to *increase* the concentration of a given solution at a particular temperature are by:

1. *Increasing* the quantity of solute in the solution.
2. *Partial* evaporation of the solvent, such that the solution is still unsaturated at the given temperature.

When the solvent, water, in a given aqueous solution of volume $V_1$ and of concentration $C_1$ is partially evaporated to obtain an unsaturated solution, its volume *decreases* to $V_2$, while its concentration *increases* to $C_2$; the amount n of the solute in the solution remains constant. This is *concentration method*. It is the exact opposite of *dilution method* (see Section 15.3).

Hence: $C_1V_1 = C_2V_2$ ..... 17.1

When concentrating a solution by partial evaporation, the initial concentration $C_1$ is always less than the final concentration $C_2$, while the initial volume $V_1$ is always greater than the new final volume $V_2$

i.e. $C_1 < C_2$ and $V_2 < V_1$

Rearranging, equation 17.1 becomes:

$$V_1/V_2 = C_2/C_1$$

The ratio (or proportion) $V_1/V_2$ *or* $C_2/C_1$ is called the *concentration factor*, I; i.e. the *number of times a solution has been concentrated*.

As in dilution, the volume of solvent, such as water, that has been lost by evaporation is the difference between the initial volume $V_1$ and the final volume $V_2$ of the solutions i.e.

Volume of solvent lost = $(V_1 - V_2)$ unit volume.

### Worked Examples

8. Calculate the concentration of the solution obtained when 500 $cm^3$ of a 0.10 $moldm^{-3}$ solution was evaporated to 125 $cm^3$.

*To find the final concentration $C_2$*
Given: Initial conc $C_1$ = 0.10 *mol* $dm^{-3}$;
Initial vol $V_1$ = 500 $cm^3$; Final vol $V_2$ = 125 $cm^3$
Using the expression: $C_1V_1 = C_2V_2$
Substituting: $0.1 \times 500 = C_2 \times 125$
Making $C_2$ the subject of the formula:

$$C_2 = \frac{0.1 \times 500}{25} \therefore 0.400\ moldm^{-3}$$

i.e. Final concentration $C_2$ = 0.400 $moldm^{-3}$

9 Calculate the volume of water lost when 100 $cm^3$ of 0.25 $moldm^{-3}$ solution was evaporated to a concentration of 0.40 $moldm^{-3}$.

*To find the volume of water lost by evaporation.*
Given: $V_1$ = 100 $cm^3$; $C_1$ = 0.25 $moldm^{-3}$
$V_2$ = ? $cm^3$; $C_2$ = 0.40 $moldm^{-3}$
First, calculate the final volume $V_2$ of the solution on evaporation:
Using $C_1V_1 = C_2V_2$ and substituting:
$0.25 \times 100 = 0.40 \times V_2$

$$V_2 = \frac{0.25 \times 100}{0.40} = 62.5$$

Hence, the volume of water lost by evaporation is:
$V_1 - V_2 = (100 - 62.5)\ cm^3 = 37.5\ cm^3$.

### Revision Exercises

33 What is the concentration of a solution obtained when 1.0 $dm^3$ of a 0.505 $moldm^{-3}$ was concentrated to 505 $cm^3$ ?

34 Calculate the volume of water that should be removed from 500 $cm^3$ of 0.010 *mol per* $dm^3$ solution in order to concentrate it ten times.

35 225 $cm^3$ of a 0.225 $moldm^{-3}$ solution was concentrated until the concentration became tripled. Calculate the
a. final concentration;
b. final volume of solution;
c. volume of water removed by evaporation.

## 17.7 Supersaturated Solutions

### Definition

A solution is *supersaturated* if it contains *more* solute than it can dissolve at a given temperature in the presence of undissolved solute.

Supersaturation is common in salts with water of crystallization, e.g. $Na_2SO_4 \cdot 10H_2O$ and $Na_2S_2O_3 \cdot 5H_2O$. The point A in figure 17.1 represents a situation in which a solution of the salt is supersaturated; i.e. it contains more salt than it can dissolve.

### How to obtain a supersaturated solution

Put some crystals of $Na_2S_2O_3 \cdot 5H_2O$ in a test tube, and warm gently; the crystals melt to form a liquid. The liquid obtained is the solution of the salt in its own water of crystallization; the solution is supersaturated.

### How to crystallize a supersaturated solution

A supersaturated solution will produce crystals under any of the following conditions:

1. ***By seeding***: A *crystal* of the salt is added into the solution; it *grows* in size immediately.
2. ***By swirling*** the test tube, and allowing dust to enter the solution.
3. ***By scratching*** the bottom of the container with a glass rod; in order to provide a rough surface for crystals to form.

### Solubility of $Na_2SO_4 \cdot 10H_2O$ in water

When the solubility of hydrated $Na_2SO_4$ is determined at different temperatures, two distinct curves are obtained, with the *transition temperature point* at 36 °C.

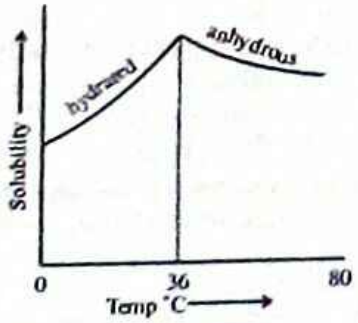



**Fig 17.3** *Solubility curve of $Na_2SO_4$*

Below 36 °C, solubility increases as temperature increases; the curve represents the solubility of the *hydrated* salt. Above 36 °C, solubility decreases as temperature increases; the curve represents the solubility of the *anhydrous* salt (see figure 17.3).

### Solved Problem

**10** Why is the temperature 36 °C referred to as the transition point for sodium tetraoxosulphate(VI) salt? [NECO]

*Below 36 °C, the salt exists as the hydrate, while above 36 °C, it exists as the anhydrous salt. Hence, 36 °C is called the transition point for sodium tetraoxosulphate (VI) salt.*

### Revision Exercises

**36** Distinguish between a *saturated solution* and a *supersaturated solution*.

**37** How would you know that a solution is supersaturated?

**38** When a crystal was added to its solution, it did not dissolve and the solution remained unchanged, showing that the solution is

A. concentrated. B. supersaturated. C. unsaturated
D. colloidal E. saturated. [NECO]

**39** When a crystal was added to its solution, it did not dissolve, but grew in size immediately; showing that the solution is

A. concentrated B. supersaturated
C. unsaturated D. saturated E. dilute [NECO]

## 17.8 Solubility of Gases in Liquids

*The solubility of a gas in a liquid is defined as the volume of gas, in $cm^3$, required to saturate 1 $cm^3$ of the liquid at a given temperature and pressure.*

Most of the common gases are soluble in water. The presence of dissolved atmospheric gases, such as oxygen, enables aquatic plants and animals to survive.

Unlike the solubility of solids in liquids, solubility of gases in water generally *decreases* with an *increase* in temperature (with the exemption of HCl gas). This is evident in the following observations:

- The insipid taste of boiled water, which is as a result of the removal of dissolved air;
- The decrease in the level of dissolved oxygen in lakes or rivers by thermal (heat) pollution.

Unlike in solids, solubility of gases is directly proportional to the partial pressure of the gas at a given temperature; i.e. an increase in gas pressure leads to an increase in solubility, and vice-versa.

Certain aerated drinks, like *Coca-Cola*, *soda water* and *Lucozade* contain carbon (IV) oxide, and bottled under pressure. When the bottle is opened, the gas pressure is reduced. Its solubility, therefore, decreases, and the characteristic '*piss*' sound is accompanied by bubbles of gas (or effervescence).

In terms of their extent of solubility in water, common gases can be categorized as follows:

1. Gases, such as ammonia, $NH_3$ and hydrogen chloride, HCl are *highly* soluble in cold water. In fact, they react with water. Their aqueous solutions are, therefore, used as laboratory reagents.
2. Gases such as $SO_2$, $NO_2$, $Cl_2$, $H_2S$, $N_2O$ and $CO_2$ are *fairly* soluble in water; hence, they are not collected over cold water during their laboratory preparations. $H_2S$ is collected over warm water.
3. Other gases such as $O_2$, $N_2$, $H_2$ and CO are only *slightly* soluble in water, they can be collected over water.

**Solved Problems**

11 State and explain **two** aspects in which the solubility of solids differ from those of gases.

- *Temperature change*: Generally, solubility of solids *increases* with *increasing* temperature, while solubility of gases *decreases* with *increasing* temperature.
- *Pressure change*: Pressure change does not affect the solubility of solids, while an increase in pressure leads to an increase in the solubility of gases, and vice-versa.

12 State the effect of thermal pollution on the level of dissolved oxygen in rivers, giving reason(s).

*The effect of thermal pollution is that it lowers the level (or quantity) of dissolved oxygen in rivers.*

*The reason being that thermal pollution raises the temperature of water. Since the solubility of gases in water decreases as temperature increases, it decreases the quantity of dissolved oxygen in rivers.*

**Revision Exercises**

40 Define the solubility of a gas in a liquid.

41 State **two** factors that affect the solubility of a gas in a liquid solvent.

42 Explain why opening a bottled aerated drink is usually accompanied by gas bubbles.

43 Which of the following statements is **correct**? The solubility of

A. gases increases with increase in temperature.
B. gases decreases with increase in temperature.
C. most solid solutes decreases with increase in temperature.
D. most solid solutes is constant. [WAEC]

44 Name **two** gases that are

a. highly soluble in water;
b. fairly soluble in water;
c. slightly soluble in water.

## 17.9 Determination of Solubility by Titration Method

The solubility of a salt, such as anhydrous $Na_2CO_3$, $K_2CO_3$, $NaHCO_3$ or $KHCO_3$ can be determined by titration. This is achieved by preparing a saturated solution of the salt at room temperature, and then, diluting it to a known volume. Dilution may not be necessary, if the saturated solution is not of high concentration.

The *diluted* solution is then titrated against a standard solution of an acid, if the aqueous solution of the salt is alkaline, and vice versa.

**Determination of the solubility of anhydrous $Na_2CO_3$ by titration**

13 **A** contains 0.101 $moldm^{-3}$ HCl.
**B** is obtained by diluting 25.0 $cm^3$ of a saturated solution of anhydrous $Na_2CO_3$ at 25 °C to 1000 $cm^3$ with distilled water.
25.00 $cm^3$ portions of **B** required an average of 24.35 $cm^3$ of **A** for complete neutralization using methyl orange as the indicator.
From the above data, calculate the

a. concentration of solution **B** in $moldm^{-3}$
b. solubility of $Na_2CO_3$ at 25°C in $moldm^{-3}$
c. mass of $Na_2CO_3$ obtained when 1 $dm^3$ of the saturated solution was evaporated to dryness.

Equation of reaction:

$$2HCl_{(aq)} + Na_2CO_{3\,(aq)} \longrightarrow 2NaCl + H_2O + CO_2$$

[Na = 23; O = 16; C = 12]

a. *To calculate the concentration of solution B.*
Since solution B is of unknown concentration, the mole expression must be used to calculate its concentration.
The required variables are:

$C_A = 0.101\ moldm^{-3}$; $V_A = 24.35\ cm^3$; $n_A = 2$
$C_B = ?\ moldm^{-3}$ $V_B = 25.0\ cm^3$ $n_B = 1$

Using $\frac{C_A V_A}{C_B V_B} = \frac{n_A}{n_B}$ ; and substituting:

$$\frac{0.10 \times 24.35}{C_B \times 25} = \frac{2}{1}$$

Making $C_B$ the subject of the formula:

$$\text{i.e. } C_B = \frac{0.101 \times 24.35}{25 \times 2} = 0.0492\ moldm^{-3}$$

b. *To calculate the solubility of $Na_2CO_3$.*
Method 1: Proportion method[*From 1st Principle*]
Concentration of B is found to be 0.0492 $moldm^{-3}$ of $Na_2CO_3$.
Since B is obtained by diluting 25.0 $cm^3$ of the saturated $Na_2CO_3$ solution to 1000 $cm^3$, then,
25.0 $cm^3$ of saturated solution contained 0.0492 *mol.*
$\therefore$ 1000 $cm^3$ (1$dm^3$) of saturated solution contained
$0.0492 \times 1000/25 = 1.97$ moles.
i.e. The solubility of anhydrous $Na_2CO_3$ at 25 °C
$= 1.97\ moldm^{-3}$.

Method 2: *Formula method (Dilution principle)*
25 $cm^3$ ($V_1$) of the saturated solution of unknown concentration $C_1$, was diluted to 1000 $cm^3$ ($V_2$) to obtain solution **B**, whose concentration $C_2$ was found to be 0.0492 $mol\ dm^{-3}$.

Using: $C_1V_1 = C_2V_2$
Substituting: $C_1 \times 25 = 0.0492 \times 1000$

$$\therefore \quad C_1 = \frac{0.0492 \times 1000}{25} = 1.97\ moldm^{-3}$$

i.e. The solubility of anhydrous $Na_2CO_3$ at 25 °C is $1.97\ moldm^{-3}$.

c. *To calculate the mass of $Na_2CO_3$ present in 1 $dm^3$ of 1.97 $moldm^{-3}$ solution.*

First, find the amount of $Na_2CO_3$ in 1.0 $dm^3$ of $1.97\ moldm^{-3}$ solution:

Amount = Conc (in $moldm^{-3}$) × Vol (in $dm^3$)
= 1.97 × 1.0 = 1.97 moles.

Then, convert the amount (in *mol*) to mass (in *g*):

Mass (g) = Amount (mol) × Molar mass ($gmol^{-1}$)

Molar mass $Na_2CO_3$ = 46 + 12 + 48 = $106 gmol^{-1}$

$\therefore$ Mass of $Na_2CO_3$ = 1.97 × 106 = 208.8 *g*
= 209 *g* (3 sig. fig.)

Hence, the mass of $Na_2CO_3$ obtained on evaporating 1.0 $dm^3$ of the saturated solution is 209 *g*.

## Revision Exercises

**45** **A** is a solution containing 10.6 *g* per $dm^3$ of $H_2SO_4$.
**B** is a saturated solution of $NaHCO_3$ at 25 °C.
In a titration experiment, 25.0 $cm^3$ of **B** required an average of 27.30 $cm^3$ of **A** for complete neutralization using methyl orange as the indicator.

a. Write a balanced equation for the reaction.

b. Calculate the

i. concentration of **A** in $moldm^{-3}$.

ii. solubility of **B** at 25.0 °C

iii. concentration of **B** in $gdm^{-3}$.

**46** **D** contains 1.60 *g* of $HNO_3$ per 250 $cm^3$ solution.
**E** is a solution obtained by diluting 25.0 $cm^3$ of a saturated solution of $NaHCO_3$ at 25 °C to 1.0 $dm^3$ with distilled water.
25.0 $cm^3$ portions of **E** required an average of 30.45 $cm^3$ of **D** for complete neutralization using methyl orange as the indicator.
From the above data, calculate the

a. concentration of solution **D** in $moldm^{-3}$

b. concentration of solution **E** in $moldm^{-3}$

c. solubility of $NaHCO_3$ at 25 °C in $moldm^{-3}$

d. mass of $NaHCO_3$ obtained when 500 $cm^3$ of the saturated solution was evaporated to dryness.

Equation of reaction:

$$HNO_{3(aq)} + NaHCO_{3\,(aq)} \rightarrow NaNO_3 + H_2O + CO_2$$

[Na = 23 ; O = 16 ; N = 14; C = 12; H = 1.0]

## Answers to Revision Exercises

**6.** C **7.** B **14.** B **18** 1.93 $moldm^{-3}$
**19.** D **20** 1.00 $moldm^{-3}$ **21** 0.191 *g* **22** 25.0 $cm^3$
**23a** 250 $g\ dm^{-3}$; **b** 2.50 $moldm^{-3}$
**27** 72.0 *g*/100 *g* of water. **33** 1.00 $moldm^{-3}$
**34** 450 $cm^3$
**35a** 0.678 $mol\ dm^{-3}$; **b** 75.0 $cm^3$; **c** 150 $cm^3$
**38.** E **39.** B **43.** B
**45b** i 0.108 $mol\ dm^{-3}$; ii 0.236 $mol\ dm^{-3}$; iii 19.7 $g\ dm^{-3}$
**46a** 0.102 $mol\ dm^{-3}$; **b** 0.0670 $mol\ dm^{-3}$;
**c** 2.68 $mol\ dm^{-3}$; **d** 112 *g*

# 18

# •ENERGY EFFECTS – ENERGETICS•

## 18.1 Introduction

### Energetics

When about 5 $cm^3$ of concentrated $H_2SO_4$ is added to about 20 $cm^3$ of distilled water in a beaker, the resulting solution becomes very hot, whereas, the dissolution of crystals of $NH_4Cl$ in water makes the resulting solution to become very cold. The aspect of chemistry, which deals with the study of energy changes accompanying physical and chemical processes, is called *thermochemistry* or *energetics*.

Energy is the ability to do work. The various forms of energy include *heat, light, sound, electrical, potential, kinetic, mechanical and nuclear*.

It is possible to convert one form of energy into another. Examples of energy conversions include:

- Conversion of chemical energy into electrical energy – as in battery cells used in radio, torchlight and clock.
- Conversion of electrical energy into heat energy – as in electrical pressing iron.

The SI unit of energy is Joule, J, or kiloJoule, kJ. For conversion purpose, 1000 J = 1.0 kJ.

### Thermodynamic Terms

*Thermodynamic* means the *flow of heat energy*.

1. A ***system*** is the material or collection of materials (or the reactants) under study. It can be in a simple apparatus such as a *test tube*, or as complex as a *refinery*.

2. The ***surrounding*** is that portion of matter, which is not under study, but can exchange materials with the system.

3. An ***isolated system*** *does not* exchange *heat energy* and *matter* with its surrounding. For instance: when a reaction is conducted in a *vacuum flask* or a *lagged* container, it becomes an *isolated system*.

4. An ***open system*** exchanges both *matter* and *heat energy* with its surrounding. For instance: a reaction conducted in a *test tube* or a *beaker* is an *open system*.

5. *A **closed system** exchanges **only heat** with its surrounding*. For instance: a reaction involving the collection of a gas over water is a *closed system*.

### Revision Exercises

1. What is thermochemistry?
2. Mention two forms of energy.
3. Define each of the following thermodynamic terms: a. Surrounding; b. Open system; c. Closed system.
4. What is the difference between an open system and a closed system.

## 18. 2 Energy Effects in Chemical Reactions

### Heat Content or Enthalpy

Every chemical substance has its own *energy* called the *heat content* or *enthalpy* – represented by **H**.

The *heat content* or *enthalpy*, **H** of any substance cannot be determined experimentally; only the *enthalpy change* that accompanies a physical or chemical process, can be determined. *Enthalpy change* is represented by **ΔH** (pronounced *delta* H).

Mathematically, *enthalpy change*, **ΔH** is the difference between the *heat content of products*, ∑H(products) and the *heat content of reactants*, ∑H(reactants), i.e.

$$\Delta H = \sum H_{(products)} - \sum H_{(reactants)}$$

### Enthalpy (or Heat) Change, ΔH

A chemical or physical process is either accompanied by the absorption or evolution of heat. The *enthalpy change*, **ΔH** is the heat absorbed or evolved during the course of a chemical or physical process, at constant temperature and pressure.

The *enthalpy change*, **ΔH** is usually recognized by a rise or fall in the temperature of the system.

### Exothermic and Endothermic Changes

The two types of energy changes that accompany *physical* and *chemical processes* are *exothermic* and *endothermic changes*.

### 1. Exothermic Changes

*In an exothermic change, heat is liberated by the reactants to the surrounding.* It leads to a *rise* in the temperature of the system, and corresponds to a *loss of heat by the reactants to the surrounding.*

Examples of exothermic processes include:

- Addition of a concentrated acid to water;
- Dissolution of pellets of NaOH (or KOH) or CaO in water;
- Displacement reactions;
- Neutralization reactions;
- Passing $SO_3$ gas into water, and
- All combustion reactions.

**Experimental Illustrations**

a i. Put about 5 $cm^3$ of distilled water in a boiling tube and take its initial temperature, $T_1$. Add 4 or 5 pellets of sodium hydroxide into the water, stir the mixture carefully with a thermometer, and then, record the highest temperature, $T_2$ of the mixture.

ii. Repeat the experiment by adding 2 $cm^3$ of concentrated HCl or $H_2SO_4$ (with care!) into the water, and take the temperature, $T_2$ of the mixture.

b. Put about 10 $cm^3$ of 2.0 $moldm^{-3}$ HCl into a boiling tube and take its initial temperature, $T_1$. Add 3 or 4 granules of zinc metal or a spatulaful of iron filings. Stir the mixture carefully with a thermometer and record the highest temperature, $T_2$ of the mixture.

**Observations**

In each of the above experiments, the final temperature $T_2$ is greater than the initial temperature $T_1$ i.e. $T_2 > T_1$. There is a *rise* in temperature of the mixture; hence the mixture becomes warm or hot. The temperature change, $T_2 - T_1$ is positive; hence, the processes are *exothermic*, i.e. heat is *given out* by the reactants to the surrounding.

### 2. Endothermic Processes

In an *endothermic process*, heat is *absorbed by the reactants* from the surrounding. It leads to a *fall* in the temperature of the system and corresponds to a *gain of heat by the reactants from the surrounding.*

Examples of endothermic processes include:

- Dissolution of crystals of $NH_4Cl$, $NH_4NO_3$, $KNO_3$ or $CH_3COONa$ in water;
- Addition of water to a *mixture* of crystals of $NH_4Cl$ and $Ba(OH)_2$.

**Experimental Illustrations**

a. Place about 10 $cm^3$ of distilled water in a boiling tube and take its initial temperature, $T_1$. Add a spatulaful of ammonium chloride crystals into the water. Stir the mixture carefully with a thermometer, and record the lowest temperature, $T_2$ of the mixture.

b. Place 10 $cm^3$ of distilled water in a test tube and take its initial temperature $T_1$. Place a spatulaful each of crystals of barium hydroxide and ammonium chloride in a boiling tube, and quickly add the water from the test tube into it. Stir the mixture with a thermometer, and record the lowest temperature, $T_2$ of the mixture.

**Observations**

In each of the above experiments, the final temperature $T_2$ is *less* than the initial temperature $T_1$. There is a *fall* in the temperature of the mixture; hence, the mixture becomes cold. The temperature change, $T_2 - T_1$ is negative; hence, the processes are *endothermic*, i.e. *heat is absorbed by the reactants from the surrounding.*

**Solved Problem 1**

The droplets of water observed around a bottle of milk taken out of the refrigerator is due to the fact that the

A. temperature of the milk drops as it loses heat into the surrounding.

B. water vapour in the air around the bottle loses some of its energy to the bottle.

C. saturated vapour pressure of the milk is equal to the atmospheric pressure.

D. water vapour in the air around the bottle gains some energy from the bottle. [JAMB]

**Answer:** *B*

**Revision Exercises**

5. Mention two types of energy changes that accompany chemical reactions.
6. Distinguish, in terms of energy changes, between an exothermic and an endothermic process.
7. Some pellets of NaOH were put into a test tube. How does the test tube feel to touch on adding water? What term is used to describe the phenomenon?

## 18.3 Signs of Enthalpy Changes

The sign assigned to the *enthalpy change*, $\Delta H$ of a reaction is based on the *first law of thermodynamics* called *law of conservation of energy*. It states:

*Energy is neither created nor destroyed during a physical or chemical process, but can be converted from one form into another.*

Considering the relationship: *Enthalpy change.*

$$\Delta H = \sum H(\text{products}) - \sum H(\text{reactants})$$

There are two cases:

**Case I:** The *heat content of the products* is *more* than that of the *reactants*, i.e.

$$\sum H(\text{Products}) > \sum H(\text{Reactants})$$

Consider a hypothetical reaction:

$$A \rightarrow B + C$$

Given that $\sum H(\text{reactants}) = 45.0$ kJ

$\sum H(\text{products}) = 70.0$ kJ

Enthalpy change is given as:

$$\Delta H = \sum H(\text{products}) - \sum H(\text{reactants})$$

Substituting:

$$\Delta H = (70.0 - 40.0)\ \text{kJ} = +30.0\ \text{kJ}.$$

The above equation can be written in *two* ways:

a. $\mathbf{A + 30.0\ kJ \rightarrow B + C}$

This equation shows that when reactant **A** *absorbs* 30.0 kJ of heat from the surrounding, it decomposes to produce **B** and **C**.

b. $\mathbf{A \rightarrow B + C;\quad \Delta H = +30.0\ kJ}$ ...1

The equation means: when reactant **A** decomposes to produce **B** and **C**, the heat *absorbed from the surrounding* is 30.0 kJ, i.e. the reaction is *endothermic*.

Any chemical equation that includes the enthalpy change, ΔH as in equation 1 is a *thermochemical equation*.

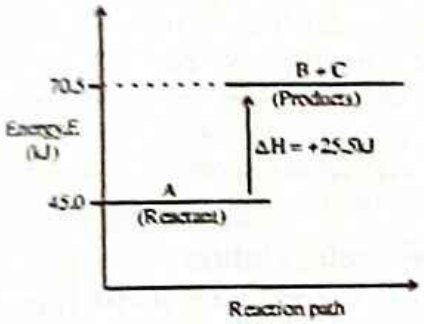



Fig 18.1 *An Endothermic Change*

The above chemical change can be represented by an energy profile diagram, which is a plot of *potential energy*, **E** on the *y-axis* against the *path of the reaction* on the *x-axis*, see figure 18.1.

The upward direction of the arrow from the reactant **A** to products **B** and **C** shows that *heat is absorbed by the reactants from the surrounding*..

Case II: The *heat content of the products* is less than that of the *reactants*, i.e.

$$\sum H(\text{products}) < \sum H(\text{reactants}).$$

Consider a hypothetical reaction:

$$\mathbf{D + E \longrightarrow X + Y}$$

Given that $\sum H(\text{reactants}) = 60.0$ kJ

$$\sum H(\text{products}) = 35.0\ \text{kJ}$$

Enthalpy change, ΔH, is given as:

$$\Delta H = \sum H(\text{products}) - \sum H(\text{reactants})$$

Substituting:

$$\Delta H = (35.0 - 60.0)\ \text{kJ} = -25.0\ \text{kJ}$$

The above equation can be written in *two* ways:

i. $\mathbf{D + E \rightarrow X + Y + 25.0\ kJ}$

This equation shows that when reactants **D** and **E** combine together to produce **X** and **Y**, 25.0 kJ of heat energy is liberated to the surrounding.

ii. $\mathbf{D + E \rightarrow X + Y;\quad \Delta H = -25.0\ kJ}$

The *thermochemical equation* shows that when **D** and **E** react to produce **X** and **Y**, the heat liberated to the surrounding is 25.0 kJ, i.e. the reaction is *exothermic*.

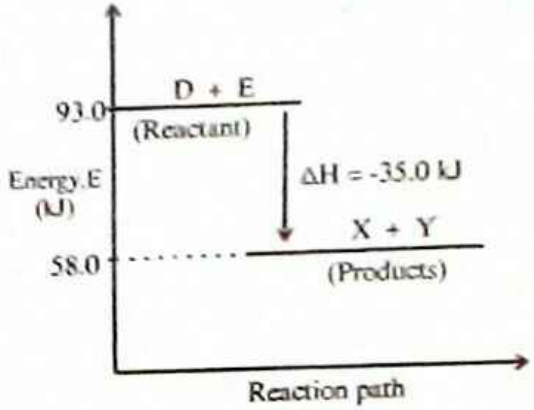



Fig 18.2 *An Exothermic Change*

An energy profile diagram, as in figure 18.2, can be used to represent the above chemical change.

The downward direction of the arrow from the reactants **D** and **E** to the products **X** and **Y** shows that *heat is liberated* to the surrounding.

## Factors Affecting Enthalpy Changes

The following factors determine the value of ΔH of a reaction:

- Physical states of reactants and products.
- Quantity or concentration of reactants.
- Temperature, and
- Pressure (for gaseous reactants and products).

### Revision Exercises

8 State two factors, which determine the value of ΔH in a reaction. [WAEC]

9 Which of the following statements is true of an endothermic reaction?

I. Heat is absorbed from the surrounding.
II. The heat content of the products is more than that of the reactants.
III. The enthalpy change is positive.
IV. The surrounding is at a lower temperature than the system.

A. I only B. I and II only
C. I, II and III only D. I, II, III and IV. [WAEC]

10 In a chemical reaction, ΔH is positive when

A. H(product) > H(reactant)
B. H(product) < H(reactant)
C. H(product) = H(reactant)
D. H(product) = Zero [WAEC]

## 18.4 Types of Enthalpy Changes

There are specific names given to the enthalpy changes accompanying certain types of physical and chemical changes:

### 1. Standard Heat of Formation, $\Delta H^{\theta}_f$

*The standard heat of formation*, $\Delta H^{\theta}_f$ of a *compound* is the *enthalpy change* that accompanies the formation of *one mole* of the compound from its *elements* under standard conditions of temperature and pressure. [Super-script, ($^{\theta}$) means standard conditions].

For standardization, the *enthalpy of formation* of a *compound* is determined under standard conditions of temperature of 25 °C (298 K) and one atmospheric pressure. For an ***element***, its standard state is the most stable state at 298 K and one atmosphere, and ***its standard heat of formation, $\Delta H^{\theta}_f$, is taken to be zero***. For instance:

a. The *standard heat of formation of one mole of carbon*(IV) *oxide* from its element is –393 kJ; the process is *exothermic*.

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H^{\theta}_f = -393 \text{ kJmol}^{-1}$$

b. The *standard heat of formation of one mole of water* from its element is –286 kJ; the process is *exothermic*.

$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} \quad \Delta H^{\theta}_f = -286 \text{ kJmol}^{-1}$$

It should be noted that the heat change of a reaction depends on the temperature of the system and the physical states of the reactants and products. For instance, if the combustion of hydrogen is determined just above 100 °C, less heat will be liberated:

$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)} \quad \Delta H^{\theta}_f = -244 \text{ kJmol}^{-1}$$

Hence, in order to avoid ambiguity, physical state symbols for solids, (s), liquids, (l), gases, (g) and aqueous solutions, (aq) or (soln) are usually included in thermochemical equations.

c. The *standard heat of formation of one mole of hydrogen iodide* from its element is +26.0 kJmol$^{-1}$; the process is *endothermic*.

$$\tfrac{1}{2}H_{2(g)} + \tfrac{1}{2}I_{2(s)} \rightarrow HI_{(g)} \quad \Delta H^{\theta}_f = +26.0 \text{ kJmol}^{-1}$$

Because of the difference in physical state of a reactant or product, it is possible for a reaction to be endothermic at one temperature, and exothermic at another. For instance, the reaction between hydrogen and iodine at a higher temperature is exothermic.

$$\tfrac{1}{2}H_{2(g)} + \tfrac{1}{2}I_{2(g)} \rightarrow HI_{(g)} \quad \Delta H^{\theta}_f = -6.0 \text{ kJmol}^{-1}$$

Generally, the more *exothermic* the standard heat of formation of a compound, the greater is its *energetic stability*. Hence, $CO_{2(g)}$ is energetically more stable with respect to its elements than $H_2O_{(l)}$ with respect to its elements; because more heat is liberated during the formation of one mole of $CO_2$ than during the formation of one mole of water, under the same conditions.

### 2. Standard Heat of Combustion

*The standard heat of combustion*, $\Delta H^{\theta}_c$ of *an element or a compound* is the *enthalpy change* when *one mole of the element or compound completely burned in excess of oxygen under standard conditions*. For example:

a. $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H^{\theta}_c = -393 \text{ kJmol}^{-1}$

b. $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)} \quad \Delta H^{\theta}_c = -981 \text{ kJmol}^{-1}$

It is an exothermic process; heat is always liberated. The *bomb calorimeter* is the equipment used in the accurate determination of the heats of combustion of chemical substances. The equipment is designed such that it can withstand high temperature and high pressure.

Note: The standard heat of formation of $CO_2$ is equal to the standard heat of combustion of carbon.

### 3. Heat of Neutralization

The *heat of neutralization* is the heat liberated when *one mole* of hydroxonium ion $H_3O^+$ reacts with *one mole* of hydroxide ion, $OH^-$ to form *one mole* of water:

$$H_3O^+_{(aq)} + OH^-_{(aq)} \rightarrow 2H_2O_{(l)} \quad \Delta H = -57.3 \text{ kJmol}^{-1}$$

or $$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} \quad \Delta H = -57.3 \text{ kJmol}^{-1}$$

The standard heat of neutralization, $\Delta H$, between a *strong acid* and a *strong base* is -57.3 kJmol$^{-1}$; it is a *constant*. Consider the following reactions:

- $HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)} \quad \Delta H = -57.3 \text{ kJmol}^{-1}$
- $HNO_{3(aq)} + KOH_{(aq)} \rightarrow KNO_{3(aq)} + H_2O_{(l)} \quad \Delta H = -57.3 \text{ kJ mol}^{-1}$
- $\tfrac{1}{2}H_2SO_{4(aq)} + KOH_{(aq)} \rightarrow \tfrac{1}{2}K_2SO_{4(aq)} + H_2O_{(l)} \quad \Delta H = -57.3 \text{ kJ mol}^{-1}$

**Observation**: *The heat change, $\Delta H$ is the same for the three different neutralization reactions.*

**Reason**: In the above reactions, $HCl_{(aq)}$, $HNO_{3(aq)}$ and $H_2SO_{4(aq)}$ are *strong acids*, while $NaOH_{(aq)}$ and $KOH_{(aq)}$ are *strong bases*; they are all completely *ionized* in dilute solutions. In each of the reactions, *one mole* of hydroxonium ions from the acid combines with *one mole* of hydroxide ions from

the base; hence, the heat of neutralization, $\Delta H$, will be the same for each of the reactions:

$H_3O^+_{(aq)} + OH^-_{(aq)} \rightarrow 2H_2O_{(l)}$ ; $\Delta H = -57.3$ kJ mol$^{-1}$

*Weak acids* and *weak bases* are not completely ionized even in dilute solutions. Hence, the heat of neutralization involving a *weak acid* or a *weak base* is less than 57.3 kJ mol$^{-1}$, and is not constant:

a. $NaOH_{(aq)} + HCN_{(aq)} \rightarrow NaCN_{(aq)} + H_2O_{(l)}$

$\Delta H = -34.0$ kJ mol$^{-1}$

b. $NH_{3(aq)} + HNO_{3(aq)} \rightarrow NH_4NO_{3(aq)} + H_2O_{(l)}$

$\Delta H = -38.3$ kJ mol$^{-1}$.

A *lagged simple calorimeter* can be used to obtain an approximate value of heat of neutralization.

## 4. Molar Heat of Vapourization

The *molar heat of vapourization*, $\Delta H^{\theta}_{Vap}$ is the heat *absorbed* when *one mole* of a substance in liquid state is changed to a gas at its boiling point e.g.

$H_2O(l) \rightarrow H_2O(g)$; $\Delta H^{\theta}_{Vap} = +41.0$ kJ mol$^{-1}$

It means that the heat that must be *absorbed* in order to convert *one* mole of water to its vapour at boiling point is 41.0 kJ. It is an endothermic process. It is called *latent heat of vapourization*.

## 5. Molar Heat of Fusion

The *molar heat of fusion*, $\Delta H^{\theta}_{Fus}$, is the heat *absorbed* in order to melt *one mole* of a solid at its melting point. It is an endothermic process. It is sometimes called *latent heat of fusion*.

$H_2O(s) \rightarrow H_2O(l)$; $\Delta H^{\theta}_{Fus} = +25.2$ kJmol$^{-1}$

## 6. Heat of Hydration

The *heat of hydration*, $\Delta H_{Hyd}$ is the heat *liberated* when *one mole* of an *anhydrous* substance *absorbs* a specified amount of water to form a specified *hydrated* substance:

$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4.5H_2O(s)$

(White) (Blue)

$\Delta H = -90.0$ kJmol$^{-1}$

## 7. Molar Heat of Crystallization

The *molar heat of crystallization* is the heat that must be *removed* in order to *freeze one mole* of a liquid. It is an exothermic process; it is the reverse of the heat of fusion.

$H_2O(l) \rightarrow H_2O(s)$ ; $\Delta H^{\theta}_{cry} = -25.2$ kJ mol$^{-1}$

## 8. Molar Heat of Precipitation

The *molar heat of precipitation* is the heat *evolved* or *absorbed* when *one mole* of an insoluble substance is precipitated on mixing solutions of appropriate electrolytes e.g.

$BaCl_{2(aq)} + Na_2SO_{4(aq)} \rightarrow 2NaCl_{(aq)} + BaSO_4 \downarrow$

$\Delta H = -4.80$ kJmol$^{-1}$

Ionically:

$Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \rightarrow BaSO_{4(s)}$; $\Delta H = -4.80$ kJmol$^{-1}$

## 9. Molar Heat of Solution

The *molar heat of solution* $\Delta H(soln)$ is the heat *liberated* or *absorbed* when *one mole* of a substance dissolves in a known amount of a solvent.

The *heat of solution*, $\Delta H(soln)$ varies with the amounts of *solute* and *solvent* in the *solution*, and from one substance to another. For instance:

When 1.0 g of NaOH pellets dissolves in 20 cm$^3$ of water, the heat *liberated* will be less than when 2.0 g of NaOH pellets dissolve in the same 20 cm$^3$ of water.

## 10. Heat of Dilution

The *heat of dilution* is the *enthalpy change* when a *concentrated* solution of a substance is *diluted from one concentration to another.*

*Heat of dilution* usually *decreases* as dilution *increases*, until the solution is at *infinite dilution when there will be no more heat change with further dilution.*

## 11. Heat of Transformation

The *heat of transformation* is the heat *liberated* or *absorbed* when *one mole* of an *allotropic form* of a substance changes to another e.g.

C(graphite) $\rightarrow$ C(diamond) $\Delta H^{\circ} = +2.0$ kJ mol$^{-1}$

This shows that *graphite is energetically more stable than diamond.*

Similarly:

S(rhombic) $\rightarrow$ S(monoclinic) ; $\Delta H$ = +ve.

## 12. Heat of Atomization

The *heat of atomization* of an element, $\Delta H^{\circ}_{Atom}$ is the enthalpy change when *one mole* of the *gaseous atoms* is formed from the *element* under standard conditions e.g.

- $\frac{1}{2} H_2(g) \rightarrow H(g)$ $\Delta H^{\circ}_{atom} = +218$ kJmol$^{-1}$

## 13. Heat of Sublimation

The *heat of sublimation* of an element, $\Delta H^{\circ}_{Sub}$ is the enthalpy change when *one mole* of the *gaseous atoms* is formed from the *element* under standard conditions e.g.

- $C(s) \rightarrow C(g)$ $\Delta H^{\circ}_{Sub} = +718$ kJ mol$^{-1}$
- $I_2(s) \rightarrow I_2(g)$ $\Delta H^{\circ}_{Sub} =$ + ve
- $Na(s) \rightarrow Na(g)$ $\Delta H^{\circ}_{sub} = +108$ kJ mol$^{-1}$

**Note:** $\Delta H^{\circ}_{Atom}$ and $\Delta H^{\circ}_{Sub}$ are the same.

## 14. Enthalpy Change of a Reaction

The *heat of reaction is the enthalpy change (heat absorbed or evolved)* that accompanies a chemical reaction as represented by its *balanced thermochemical equation*. For instance, in the complete combustion of methane:

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}\ ;\ \Delta H = -809\ kJ$$

The *thermochemical equation* shows that *one mole* of gaseous methane burns in *two moles* of oxygen to produce *one mole* of carbon(IV) oxide together with *two moles* of steam, and 809 kJ of heat energy are *released* to the surrounding.

Generally, the *amount of heat released or absorbed in a chemical reaction is directly proportional to the amounts of reactants consumed.*

**Solved Problem**

**2a.** Define *enthalpy of combustion.* [WAEC]

*The heat of combustion, $\Delta H^{\theta}_{c}$ of a substance is the enthalpy change when one mole of the substance completely burned in excess of oxygen.*

**b.** State whether combustion is an exothermic or endothermic process.

*It is an exothermic process.*

**c.** Name the instrument used for the determination of heat of combustion in the laboratory.

*Bomb calorimeter.*

**3.** Consider the following neutralization reactions:

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O \quad \Delta H_1,$$

$$CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O \quad \Delta H_2,$$

$$NaOH + HCl \rightarrow NaCl + H_2O \quad \Delta H_3$$

**a.** Arrange the enthalpy changes for the reactions in order of increasing magnitude.

**Solution:** $\Delta H_2 < \Delta H_1 < \Delta H_3$ .

**b.** Explain briefly your order in 3a above.

*In a neutralization reaction, a certain amount of heat is evolved when $H^+$ combines with $OH^-$. The stronger the acid and the base, the greater the heat evolved. $\Delta H_2$ is the least since a weak acid and a weak base are involved ; followed by $\Delta H_1$ involving a strong base and a weak acid; while $\Delta H_3$ is the highest, since a strong acid and a strong base are involved.*

**Revision Exercises**

**11** What is meant by each of the following terms?
**a.** Standard heat of formation. **b.** Heat of solution.
**c.** Enthalpy change of a reaction.

**12** Name the enthalpy changes involved in each of the following processes:
**a.** dissolution of sodium hydroxide in water;
**b.** burning of carbon in air;
**c.** reaction between sodium hydroxide and dilute hydrochloric acid. [WAEC]

**13** Write equation, including state symbols, for the complete combustion of methane, $CH_4$.

**14** Name the se-up that can be used to determine the **a.** heat of a reaction; **b.** energy value of petrol.

**15** Consider the reaction:

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

The energy change taking place in the reaction above is enthalpy of

A. formation. B. hydration.
C. neutralization. D. solution. [WAEC]

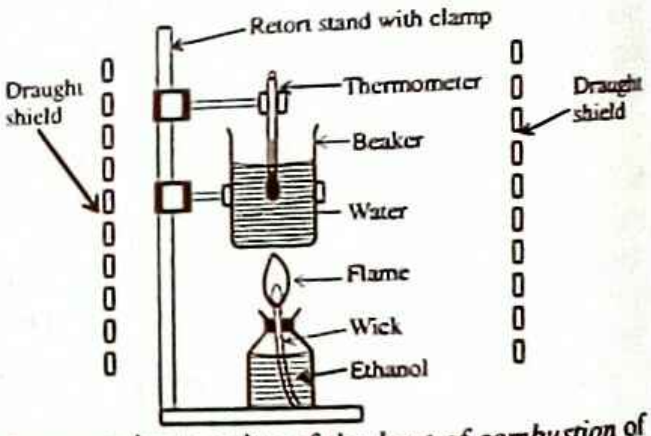
## 18.5 Determination of Heat of Reaction

The heat change, $\Delta H$ that accompanies a physical or chemical process can be determined by the use of a *simple* calorimeter, or a *bomb* calorimeter.

Generally, 4.18 J of heat is required to raise or lower the temperature of 1.0 g of water by 1.0 K (or 1 °C), i.e. the *specific heat capacity* of water is 4.18 $Jg^{-1}K^{-1}$.

Experimentally, heat change, $\Delta H$ is directly proportional to the amount of reactants in the system.

### 1. Determination of the Heat of Combustion




An approximate value of the *heat of combustion* of a liquid fuel, such as ethanol, can be obtained by estimating the *mass of ethanol* required to *raise a known mass of water* by about 20 °C.

**Procedure**

**a.** Transfer about 50 $cm^3$ of ethanol into the bottle of an improvised spirit lamp. Replace the cap to which a wick is attached, and make sure that the wick is immersed in the ethanol. Then, weigh the lamp: $W_1$ g.

**b.** Transfer exactly 100 $cm^3$ of distilled water into a beaker and clamp it as shown below. Measure the initial temperature, $T_1$.

**c.** Light the lamp, and direct the flame to the bottom of the beaker in order to heat up the water in it.

d. Stir the water carefully with a thermometer, until the temperature rise is between 15 °C – 20 °C. Take the final temperature $T_2$ and put off the flame.

e. Reweigh the lamp with the remaining ethanol. $W_2$ g.

### Precautions

a. The set-up should be protected from draught; to minimize heat lost to the surrounding.

b. All measurements: $W_1$, $W_2$, $T_1$ and $T_2$ should be carefully taken and their units correctly recorded.

### Experimental Data

The following data obtained from an experiment will be used to illustrate how to obtain the heat of combustion of a liquid fuel.

Initial temperature of water, $T_1 = 27.0\ ^\circ C = 300.0\ K$

Final temperature of water, $T_2 = 43.5\ ^\circ C = 316.5\ K$

Temperature rise, $T_2 - T_1 = (316.5 - 300.0)\ K$
$= 16.5\ K.$

Mass of 100 $cm^3$ water in the beaker = 100 g.

Initial mass of lamp + ethanol, $W_1 = 28.75$ g

Final mass of lamp + ethanol, $W_2 = 28.39$ g

∴ Mass of ethanol burned =
$W_1 - W_2 = (28.75 - 28.39)$ g
$= 0.36$ g.

### Calculations

*To calculate the heat evolved during the combustion of 0.36 g of ethanol:*

The heat *absorbed* by water corresponds to the heat *evolved* by 0.36 g of ethanol.

Heat evolved =
Mass of water × specific heat capacity × temp. rise
$= 100\ g \times 4.2\ Jg^{-1}K^{-1} \times 16.5\ K$
$= 6930\ J.$

That is: 0.36 g of ethanol liberated 6930J of heat.

*To calculate the heat evolved by one mole of ethanol:*

This is energy-mass-mole relationship.

Molar mass of ethanol, $C_2H_5OH$:
$C_2H_5OH = (12 \times 2) + (1 \times 5) + (16 \times 1) + (1 \times 1)$
$= 24 + 5 + 16 + 1 = 46.0\ gmol^{-1}$

Since 0.36 g of ethanol liberated 6930 J of heat
∴ 46 g (1 mole) of ethanol will liberate
$6930 \times 46/0.36 = 885500\ J$
$= 886\ kJ$ (3 sig fig.)

i.e. The heat of combustion of ethanol is $-886\ kJmol^{-1}$.

### Assumptions:

The following assumptions have been made in the calculations.

a. The mass of 1 $cm^3$ of water is 1.0 g.

b. The heat gained from or lost to the surrounding by the beaker is negligible.

c. The heat lost by the burning lamp to the surrounding is negligible.

d. The specific heat capacity of water is 4.2 $Jg^{-1}K^{-1}$

## 2. Determination of Heat of Neutralization

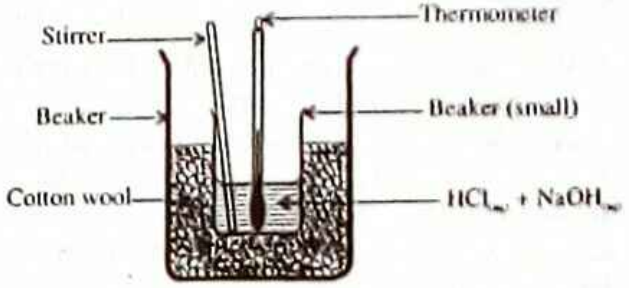
An approximate value for the enthalpy of neutralization, $\Delta H$ of a *strong acid* by a *strong base* can be obtained by estimating the *temperature rise* when equimolar amounts of a *strong acid* and a *strong base* are mixed together.

### Procedure

a. Measure 50.0 $cm^3$ of 1.0 $moldm^{-3}$ sodium hydroxide solution into a plastic cup or a lagged beaker, and record its temperature, $T_1$.

b. Measure 50.0 $cm^3$ of 1.0 $moldm^{-3}$ hydrochloric acid solution into another plastic cup or a beaker, and record its temperature, $T_2$.

c. Pour the hydrochloric acid solution all at once, and as quickly as possible, into the sodium hydroxide solution. Stir the mixture carefully with the thermometer, and record the highest temperature, $T_3$, of the mixture.




A Simple Calorimeter

### Assumptions

a. Mass of 1 $cm^3$ of each solution is 1.0 g.

b. Heat gained or lost by the plastic cup or lagged beaker is negligible

c. Specific heat capacity of the solution is 4.2 $Jg^{-1}K^{-1}$.

### Results

The following data obtained from an actual experiment will be used to calculate the heat of neutralization.

Temperature $T_1$ of NaOH solution = 25.5 °C = 298.5 K

Temperature $T_2$ of HCl solution = 25.7 °C = 298.7 K

The highest temperature $T_3$ of the mixture
$= 32.1\ ^\circ C = 305.1\ K$

Volume of 1.0 $moldm^{-3}$ NaOH = 50.0 $cm^3$ = 50.0 g

Volume of 1.0 $moldm^{-3}$ HCl = 50.0 $cm^3$ = 50.0 g

Equation of reaction:

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$$
1 mol 1 mol

### Calculations

a. *The average temperature of the two solutions:*
$\frac{1}{2}(298.5 + 298.7)\ K = 298.6\ K$

b. *The temperature change* = $(T_3 - 298.6)\ K$
$= (305.1 - 298.6)\ K = 6.50\ K$

c. *To calculate total heat evolved*

Mass of solution = 100 g; Temperature change = 6.5 K

Total heat evolved =
Mass of solution × specific heat capacity × temp change
$= 100\ g \times 4.2\ J\ g^{-1}\ K^{-1} \times 6.5\ K$
$= 2730\ J$

d. *To calculate the heat of neutralization*
From the equation of reaction:
1 mole of acid ($HCl_{(aq)}$) reacts with 1 mole of base ($NaOH_{(aq)}$) to produce 1 mole of water.
*Amount of acid used* = conc ($moldm^{-3}$) × volume ($dm^3$)
$= 1.0\ moldm^{-3} \times 0.050\ dm^3$
$= 0.050\ mol.$
i.e. 0.050 *mol* of acid react with 0.050 *mol* of base to produce 0.050 *mol* of water.
That is: 0.050 mol of water evolved 2730 *J* of heat
∴ 1 mol of water will evolve
$(2730 \times 1)/0.050 = 54600$ J
Hence, heat of neutralization = $-54600\ Jmol^{-1}$
$= -54.6\ kJmol^{-1}$ (3 s. f.)
The negative sign shows that the reaction is *exothermic*.

## 3. Determination of the Enthalpy Change in a Displacement Reaction

**Theory**: *A metal high up in the activity series will displace the ions of another metal below it from a solution of its salt.* For instance:
Zinc metal will displace copper(II) ions from a solution of a copper(II) salt.

$$Zn_{(s)} + CuSO_{4\,(aq)} \rightarrow ZnSO_{4\,(aq)} + Cu_{(s)}$$

The *heat of reaction*, ΔH, of such a reaction can be obtained by measuring the *rise* in temperature of the resulting solution for a *known mass* of the metal.

It should be noted that the *heat of reaction*, ΔH for such a reaction depends on the *mass of the metal*, and the *concentration of solution of the displaced metal used.*

### Procedure

a. Prepare a solution containing 15.0 g of crystals of hydrated $CuSO_4$ in 100 $cm^3$ of solution; allow the solution to cool.

b. Place the solution in a plastic cup (or lagged beaker), and record its temperature $T_1$.

c. Add exactly 1.60 g of zinc *dust* to the solution, and stir carefully with the thermometer for about 10 minutes, to allow time for complete reaction.

d. Record the highest temperature, $T_2$ of the mixture.

### Data

The following results were obtained in an experiment.
Mass of zinc metal = 1.60 g
Volume of $CuSO_4$ solution = 100 $cm^3$ = 100 g
Initial temperature, $T_1$ = 27 °C = 300 K
Final temperature of the mixture, $T_2$ = 38 °C = 311 K
Temperature rise = $T_2 - T_1$ = (311 – 300) K = 11.0 K

### Calculations

*To calculate the heat evolved by 1.6 g of zinc:*
The heat absorbed by the solution corresponds to the heat evolved by 1.6 g of zinc, i.e.
Heat evolved =
Mass of solution × specific heat capacity × temp change
$= 100\ g \times 4.2\ Jg^{-1}K^{-1} \times 11.0\ K = 4620\ J$
That is: 1.60 g of zinc produced 4620 J of heat.

*To calculate the heat evolved by 1 mole (65 g) of zinc:*
Since 1.60 g of zinc produced 4620 J of heat
∴ 65 g (1 mole) of zinc will produce
$4620 \times 65/1.60 = 187688$ J
∴ Heat of reaction, $\Delta H = -188\ kJmol^{-1}$.
The negative sign shows that the reaction is *exothermic.*

## Use of Thermochemical Formula

The expression that connects the *enthalpy change*, ΔH, the *heat content of products*, ∑H(products) and the *heat content of reactants*, ∑H(reactants) can be regarded as the *thermochemical formula*, i.e.

$$\Delta H = \sum H(\text{products}) - \sum H(\text{reactants})$$

The *thermochemical formula* can be used to determine the heat of formation of a compound, if the heat of reaction, and the heats of formation of other compounds in the reaction are known, or, the heat of reaction, if the heats of formation of all the compounds in the reaction are known, e.g.

Consider the reaction represented by the following equation:

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)};\ \Delta H = -891\ kJ$$

Given that the heats of formation of $CO_2$ and $H_2O$ are -393 $kJmol^{-1}$ and -286 $kJmol^{-1}$ respectively, calculate the heat of formation of methane.

**Solution**

Let the heat of formation of $CH_{4(g)} = x$ kJ.
Given: Heat of reaction, ΔH = -981 kJ
Heat of formation of $CO_{2(g)}$ = -393 $kJmol^{-1}$
Heat of formation of $H_2O_{(l)}$ = -286 $kJmol^{-1}$
Heat of formation of $O_{2(g)}$ = 0

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)};\ \Delta H = -981\ kJ$$
$$x \qquad 0 \qquad -393 \qquad 2(-286)$$

Substituting in the thermochemical formula:
$\Delta H = \sum H(\text{products}) - \sum H(\text{reactants})$
$-891 = [-393 + 2(-286)] - [x + 0]$
$-891 = [-393 - 572] - x = -965 - x$
$x = [-965 + 891]\ kJ = -74.0\ kJ$
i.e. the heat of formation of methane = -74.0 $kJmol^{-1}$

### Worked Examples

**4.** Explain why the heat of reaction of the mineral acids with sodium hydroxide is constant in value. [WAEC]

*Mineral acids, such as hydrochloric acid, are strong electrolytes; they are completely ionized in water. Since*

*heat of reaction (neutralization) depends on the concentrations of hydrogen ions and hydroxide ions, its value remains constant as long as the mole ratio of acid to base is 1 : 1.*

5. Calculate the heat of combustion of a compound Z, if 0.06 mole of it on burning, raised the temperature of 400 g of water by 10 Kelvin. [Specific heat capacity of water = 4.2 $Jg^{-1}K^{-1}$] [WAEC]

*To find the heat of combustion of Z*

First, calculate the heat *absorbed* by water; it corresponds to the heat *evolved* by 0.06 mol of Z:

Heat evolved =

Mass of water × specific heat capacity × temp. rise

= 400 × 4.2 × 10 = 16800 J = 16.8 kJ.

i.e. 0.06 mole of Z evolved 16.8 kJ of heat.

Now, *calculate the heat evolved by one mole of Z; it corresponds to the heat of combustion of Z.*

It is energy-mole relationship:

Since 0.06 mole of Z evolved 16.8 kJ of heat,

∴ 1 mole of Z will evolve 16.8/0.06 kJ of heat

= -280 kJ.

Hence, the heat of combustion of Z is -280 $kJmol^{-1}$.

## Revision Exercises

16a Draw a labeled diagram of the set-up used to determine the heat of neutralization.

b State the function of each of the pieces of apparatus labeled in a above.

c What is the name given to the set-up?

17 If 1.10 g of calcium chloride dissolved in 50 $cm^3$ of water caused a rise in temperature of 3.4 °C, calculate the heat of solution in $kJmol^{-1}$. [Ca = 40, Cl = 35.5; specific heat capacity of water = 4.18 $JK^{-1}$]

18 If 5 g of ammonium trioxonitrate(V) on dissolution in water cooled its surrounding water and container by 1.6 kJ. What is the heat of solution?

A. +51.4 $kJmol^{-1}$ B. +25.6 $kJmol^{-1}$

C. +12.9 $kJmol^{-1}$ D. -6.4 $kJmol^{-1}$ [JAMB]

19 Which of the following are required in an experiment to determine the enthalpy of solution of anhydrous $CuSO_4$?

I. Mass of anhydrous $CuSO_4$

II. Volume of water in which the $CuSO_4$ is dissolved

III. Initial temperature of water

IV. Final temperature of the solution

A. I and II only B. III and IV only

C. II, III and IV only. D. I, II, III and IV. [WAEC]

20 If 32.0 g of anhydrous $CuSO_4$ dissolved in 1 $dm^3$ of water generated 13.0 kJ of heat, the heat of solution is A. 26.0 kJ $mol^{-1}$ B. 65.0 kJ $mol^{-1}$

C. 130.0 kJ $mol^{-1}$ D. 260.0 kJ $mol^{-1}$

[Cu = 64, S = 32, O = 16] [JAMB]

21 The heat of combustion of carbon is -393.5 kJ. Calculate the heat change, when 60 g of carbon undergoes complete combustion. [C = 12] [WAEC]

## 18.6 The Laws of Thermochemistry

There are *two* basic *laws of thermochemistry*; both are based on the first law of thermodynamics:

### 1. Lavoisier and Laplace Law (1780)

It states that:

*The heat absorbed is equal to the heat liberated when the reaction is reversed, and vice-versa.*

**Inferences**

a. When a thermochemical equation is reversed, the sign of ΔH changes, i.e. if the forward reaction is exothermic, the reverse will be endothermic, e.g.

i. Combustion of carbon is exothermic:

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta H = -393\ kJmol^{-1}$

If the reaction is reversed, we obtain:

$CO_{2(g)} \rightarrow C_{(s)} + O_{2(g)}$; $\Delta H = +393\ kJmol^{-1}$

ii. Heat of *vapourization* of water is endothermic:

$H_2O_{(l)} \rightarrow H_2O_{(g)}$; $\Delta H = +41.0\ kJmol^{-1}$

The reverse, which corresponds to the heat of *condensation*, will be exothermic:

$H_2O_{(g)} \rightarrow H_2O_{(l)}$; $\Delta H = -41.0\ kJmol^{-1}$

Generally: ΔH(forward) = − [ΔH(backward)]

b. ***Energy-Mass-Mole Relationship:***

The enthalpy change, ΔH, is directly proportional to the amount, in moles, of a reactant or product:

i. Given the molar heat of formation of carbon (IV) oxide, $CO_2$, $\Delta H^\circ_f (CO_2) = -393\ kJmol^{-1}$, i.e.

1 mole of $CO_2$ on being formed from its elements, liberates 393 kJ of heat; then,

2 moles of $CO_2$ on being formed will liberate

2 × 393 kJ of heat.

∴ *n* moles of $CO_2$ on being formed will liberate

*n* × 393 kJ of heat.

ii. Generally, for a given thermochemical equation,

*n* × (Equation of reaction) = *n* × (ΔH).

Consider the formation of *one* mole of hydrogen iodide from its elements:

$\frac{1}{2}H_{2(g)} + \frac{1}{2}I_{2(g)} \rightarrow HI_{(g)}$; $\Delta H^\circ_f = +26\ kJmol^{-1}$

If 2 multiplies the thermochemical equation, then, the enthalpy change must also be doubled, i.e.

$2[\frac{1}{2}H_{2(g)} + \frac{1}{2}I_{2(g)} \rightarrow HI_{(g)}]$; $2[\Delta H^\circ_f = +26\ kJmol^{-1}]$

$H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$; $\Delta H^\circ_f = +56.0\ kJ$

**Worked Examples**

6. Calculate the heat evolved when 0.20 mole of carbon(IV) oxide is formed from its elements. The molar heat of formation of carbon(IV) oxide is given as -393 $kJmol^{-1}$.

*Equation of reaction:*

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H = -393\ kJmol^{-1}$

From the equation of reaction:
1 mole of $CO_2$ liberated 393 kJ of heat;
$\therefore$ 0.20 mol of $CO_2$ will liberate $393 \times 0.20$ kJ.
$= -78.6$ kJ (reaction is exothermic)

7. The heat evolved when 1.0 g of methanol is completely burned in oxygen is 22.8 kJ. Calculate the molar heat of combustion of methanol.
[H = 15; C = 12; O = 16]

*Equation of reaction*:
$CH_3OH(l) + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O(l)$ $\Delta H = ?$
$M[CH_3OH] = 12 + 3 + 16 + 1 = 32.0\ gmol^{-1}$
From the equation of reaction:
1 g of methanol on combustion evolved 22.6 kJ of heat;
$\therefore$ 32 g (1 mole) of methanol will evolve
$22.6 \times 32$ kJ $= 723$ kJ
Hence, molar heat of combustion of methanol,
$\Delta H = -723$ kJ.

8. $2H_2 + O_2 \rightarrow 2H_2O;$ $\Delta H = -571$ kJ
In the equation above, how much heat will be liberated if 12.0 g of hydrogen is burnt in excess oxygen?
A. -571 kJ B. -1142 kJ C. -1713 kJ
D. +1142 kJ [H = 1] [JAMB]

*To calculate the heat liberated by 12.0 g of hydrogen*
It is energy-mass-mole relationship.
From the equation of reaction:
$2H_2 + O_2 \rightarrow 2H_2O;$ $\Delta H = -571$ kJ
2 mol (4.0 g)
4.0 g of $H_2$ liberated 571 kJ of heat,
$\therefore$ 12.0 g of $H_2$ liberated $571 \times 12/4 = -1713$ kJ

## 2. Hess's Law of Constant Heat Summation

The law states:

*The heat of reaction is the same whether the reaction occurs in one, or more steps.*

**Inferences:**

a. *Heat of reaction* depends on the *initial reactants* and the *final products only*; it is independent of the *intermediates*.

b. *Thermochemical equations* or *data* can be *added together* or *subtracted*, as in algebraic equations.

### To Illustrate Hess's Law

The conversion of *ice*, $H_2O(s)$ to steam, $H_2O(g)$ goes through the intermediate *liquid* state $H_2O(l)$.

Given that:

i. $H_2O(s) \rightarrow H_2O(l)$; $\Delta H_1 = +25.2\ kJ\ mol^{-1}$ ...*eqn* 1

ii. $H_2O(l) \rightarrow H_2O(g)$; $\Delta H_2 = +41.0\ kJmol^{-1}$ ...*eqn* 2

Adding the two thermochemical equations gives:

iii. $H_2O(s) + H_2O(l) \rightarrow H_2O(l) + H_2O(g)$ ..... *eqn* 3

Canceling the common term, $H_2O(l)$, it gives:

iv. $H_2O(s) \rightarrow H_2O(g)$ $\Delta H_3 = ?$ ... *eqn* 4

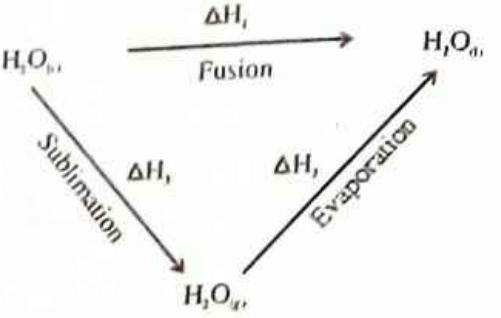
$\Delta H_3$ corresponds to the *enthalpy of sublimation*. It is obvious that the process will be endothermic.

Since equations 1 and 2 were added in order to obtain equation 3, and then, 4, their corresponding enthalpy changes must be added to obtain $\Delta H_3$ i.e.
$\Delta H_1 + \Delta H_2 = \Delta H_3$.

Hence, the heat of sublimation of one mole of ice:
$\Delta H^\circ_{sub} = \Delta H_3 = (+25.2 + 41.0)\ kJmol^{-1}$
$= +66.2\ kJmol^{-1}$

i.e. $H_2O(s) \rightarrow H_2O(g)$; $\Delta H^\circ_{sub} = +66.2\ kJ\ mol^{-1}$

The above thermochemical equations can be represented in the form of an *energy cycle*:




From the energy cycle: $\Delta H_1 + \Delta H_2 = \Delta H_3$

### Applications of Hess's Law – Energy Cycle

When the heat of formation of a compound cannot be determined directly, an *energy cycle* is set up in such a way that the Hess's law can be applied.

For instance: carbon(IV) oxide can be obtained by two methods: by the direct route, and via carbon (II) oxide.

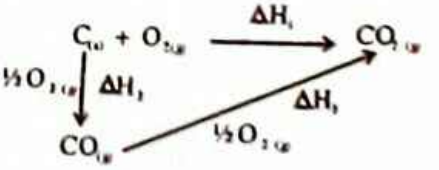
**1. Direct route**: Carbon burns in excess oxygen:
$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H = \Delta H_1$

**2. Indirect route:**

• Carbon burns in limited supply of oxygen to produce carbon(II) oxide:
$C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$ $\Delta H = \Delta H_2$

• The carbon(II) oxide burns further in oxygen, to produce carbon(IV) oxide:
$CO_{(g)} + \frac{1}{2}O_2 \rightarrow CO_{2(g)}$ $\Delta H = \Delta H_3$

The *energy cycle* can be set up as follows:




According to the Hess's law, the heat of formation of $CO_2$ is independent of the route taken.

$\therefore$ $\Delta H_1 = \Delta H_2 + \Delta H_3$

Once the heat of combustion of carbon, $\Delta H_1$ and that of carbon(II) oxide, $\Delta H_3$ are known, the heat

of formation of carbon(II) oxide, $\Delta H_3$ can be determined.

**Worked Example**

9. Calculate the heat of formation of carbon(II) oxide, given that the heats of combustion of carbon and carbon(II) oxide are -393 kJmol$^{-1}$ and -285 kJmol$^{-1}$ respectively.

Method 1: *Construction of Energy Cycle*

Given:

- $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H^{\circ}_c = \Delta H_1 = -393$ kJmol$^{-1}$
- $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H^{\circ}_c = \Delta H_3 = -285$ kJmol$^{-1}$

Required: *To find* $C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$ $\Delta H_2 = ?$

From the energy cycle above, $\Delta H_1 = \Delta H_2 + \Delta H_3$

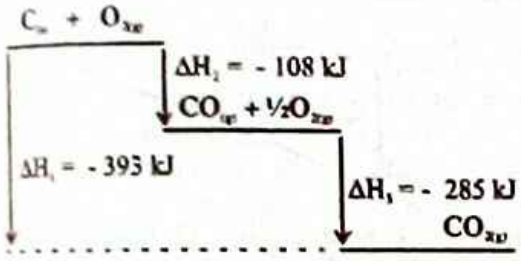
Making $\Delta H_2$ the subject of the formula:

$$\Delta H_2 = \Delta H_1 - \Delta H_3$$

Substituting: $\Delta H_2 = -393 - (-285)$

$= -393 + 285 = -108$ kJmol$^{-1}$

An *energy level* diagram can be used to represent the energy changes:




Method 2: *Combination of Thermochemical Equations*

Given:

- $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H_1 = -393$ kJmol$^{-1}$ ..eqn 1
- $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H_3 = -285$ kJmol$^{-1}$..eqn 2

Required: *To find*

- $C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$ $\Delta H_2 = ?$ ...eqn 3

Since $C_{(s)}$ is a reactant in equation 1 and in the required equation 3, equation 1 is retained as it is. Since $CO_{(g)}$ is a reactant in the given equation 2 and a product in the required equation 3, equation 2 is reversed, to obtain equation 4. Finally, equations 1 and 4 are added, cancelling the common terms, to obtain equation 3, i.e.,

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H_1 = -393$ kJmol$^{-1}$ ..eqn 1

$CO_{2(g)} \rightarrow CO_{(g)} + \frac{1}{2}O_{2(g)}$; $-\Delta H_3 = +285$ kJmol$^{-1}$..eqn 4

$C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$ $\Delta H_2 = ?$ ...eqn 3

Since equation 3 has been obtained by the addition of equations 1 and 4, hence,

$$\Delta H_2 = \Delta H_1 + (-\Delta H_3)$$

$$= -393 + 285 = -108 \text{ kJmol}^{-1}$$

*Method 3: Use of thermochemical formula*

This is the shortest method. The steps to follow are:

a. Write a thermochemical equation that includes $CO_{(g)}$, the compound of which the heat of formation is to be determined;

b. Insert the values of the heats of formation of all the substances in the equation.

c. Finally, use the *thermochemical formula*, i.e.

$$\Delta H(\text{reaction}) = \sum \Delta H(\text{products}) - \sum \Delta H(\text{reactants})$$

Suppose the heat of formation of $CO_{(g)} = x$ kJ

The appropriate thermochemical equation is:

$$C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{1(g)};\ \Delta H = -285 \text{ kJmol}^{-1}$$

$$x \qquad 0 \qquad -393$$

$$\Delta H_r = [\Delta H^{\circ}co_2] - [\Delta H^{\circ}co + \Delta H^{\circ}\tfrac{1}{2}o_2].$$

and substituting;

$$-285 = -393 - [x + 0]$$

$$-285 = -393 - x$$

$$x = -393 + 285 = -108 \text{ kJmol}^{-1}$$

**Revision Exercises**

22 If the heat of combustion of hydrogen is -285.8 kJ, what is the heat of formation of water?

A. – 285.8 kJ B. – 571.6 kJ C. +571.6 kJ
D. +285.8 kJ. [JAMB]

23 How much heat will be liberated if 8.0 g of hydrogen burns in excess oxygen according to the following equation? [H =1]

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ $\Delta H_1 = -571.7$ kJ

A. 142.9 kJ B. 285.9 kJ C. 571.7 kJ
D. 11.43.4 kJ E. 2286.8 kJ [WAEC]

24 In the reaction:

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

The standard heats of formation of $SO_{2(g)}$ and $SO_{3(g)}$ are -297 kJmol$^{-1}$ and -396 kJmol$^{-1}$ respectively. The heat change of the reaction is

A. -99 kJmol$^{-1}$ B. -198 kJmol$^{-1}$ C. +198 kJmol$^{-1}$
D. +683 kJmol$^{-1}$ [JAMB]

25 The heat of combustion of sulphur in excess air to produce sulphur(IV) oxide is -297 kJmol$^{-1}$.

a. Write a thermochemical equation to represent the change.

b. Calculate the heat change, if 6.4 g of sulphur is completely burned in excess air. [S = 32]

26 $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$

What is the energy change in *kJmol$^{-1}$* for the reaction given above? [$\Delta H(CO) = -110.4$ *kJmol$^{-1}$*
$\Delta H(CO_2) = -393$ *kJmol$^{-1}$*]

A. +503.4 B. – 503.4 C. +393.0
D. +282.6 E. – 282.6 [NECO]

27 $SO_{3(g)} + H_2O_{(l)} \rightarrow H_2SO_{4(l)}$

Given the heats of formation for $SO_{3(g)}$, $H_2O_{(l)}$ and $H_2SO_{4(l)}$ as -395 kJmol$^{-1}$, -286 kJmol$^{-1}$ and – 811 kJ mol$^{-1}$ respectively, the enthalpy change accompanying the above equation of reaction is

A. -1032 kJ. B. -130 kJ
C. +130 kJ D. +1032 kJ [JAMB]

## 18.7 Origin of the Enthalpy Changes

### Introduction

The *enthalpy change* in a chemical reaction originates from the fact that during the course of a chemical reaction, as chemical bonds are being broken among the reactants, new bonds are being formed among the products. Such chemical bonds are usually ionic, covalent, and hydrogen bonds.

Generally, *heat is absorbed* when a chemical bond is broken (*endothermic*), while *heat is liberated* when a bond is formed (*exothermic process*).

### Enthalpy Changes in Covalent Compounds

#### Dissociation Energy, D

The *dissociation energy*, D of a covalent bond is the enthalpy change that accompanies the breaking of a particular covalent bond when the reactants and products are in gaseous states. For instance:
The *dissociation energy* of the covalent bonds in one mole of hydrogen molecules is 436 $kJmol^{-1}$:

$$H_{2(g)} \rightarrow 2H_{(g)} \quad \Delta H_{Diss} = +436\ kJmol^{-1}$$

*When there are two or more bonds of the same type in a molecule, the dissociation energy is not usually the same for successive bonds.* For instance: In methane, $CH_4$, the four C–H bonds have different dissociation energies.

#### Bond Energy, E

*Bond energy* is the *average dissociation energy* required to break a particular type of covalent bond from a wide range of molecules. For instance:
The *average dissociation energy* or *bond energy*, of a C-H bond, $E_{C-H}$ is 413 $kJmol^{-1}$. Table 18.1 gives the bond energies of some covalent bonds. It should be noted that *bond energy*, E, is the *energy absorbed* when a covalent bond is broken (*endothermic*) or the *energy evolved* when a covalent bond is formed (*exothermic*).

**Table 18.1** *Bond energies of some covalent bonds (in kJ $mol^{-1}$ at 298 K)*

| | | | |
|---|---|---|---|
| C–H 413 | F – F 158 | C–F 489 | C–O 358 |
| C–C 348 | Cl–Cl 242 | C–Cl 348 | C=O 745 |
| C=C 614 | Br–Br 193 | C–Br 285 | O=O 245 |
| C≡C 839 | I – I 151 | C– I 218 | N≡N 408 |
| H–H 437 | O– H 463 | H–Cl 433 | N–H 391 |

Bond energies are useful when comparing bond strengths, establishing the structures of molecules, calculating the enthalpy changes in chemical reactions, in estimating resonance energy, and in establishing the mechanisms of chemical reactions.

#### Calculation of enthalpy change of a reaction

In any reaction involving covalent molecules in the gaseous phase, the enthalpy change is the *difference between the total energy required for breaking various covalent bonds* and the *total energy liberated when new covalent bonds are formed*. Hess's law is applicable.
Mathematically:

$$\Delta H_{(reaction)} = \sum E_{(bond\ broken)} - \sum E_{(bond\ formed)}$$

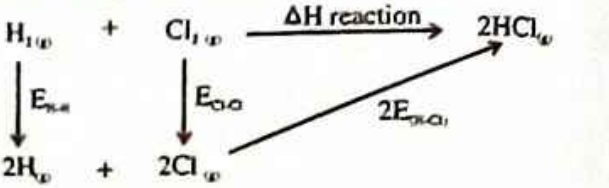
#### Worked Examples

10 Calculate the enthalpy change for the reaction:

$$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$$

(Given: $E_{H-H} = 437\ kJmol^{-1}$; $E_{Cl-Cl} = 242\ kJmol^{-1}$ and $E_{H-Cl} = 433\ kJmol^{-1}$)

*In the above reaction, the enthalpy change is the difference between the total energy required for breaking the covalent bonds in the molecules of hydrogen and chlorine, and the total energy released when covalent bonds are formed in hydrogen chloride molecules. These changes can be represented thus:*




$\Delta H$ (reaction) = $\sum E$ (bonds broken) – $\sum E$ (bonds formed)
= $(E_{H-H} + E_{Cl-Cl}) - (2E_{H-Cl})$ kJ
= (437 + 242) – (2 × 433) kJ
= (679 – 866) kJ
= – 187 kJ.

11 Calculate the enthalpy change for the reaction:

$$H_2C{=}CH_{2(g)} + Cl_{2(g)} \longrightarrow \underset{\displaystyle Cl}{\overset{\displaystyle |}{CH_2}} - \underset{\displaystyle Cl}{\overset{\displaystyle |}{CH_2}}\ (g)$$

[$E_{C-C} = 614\ kJmol^{-1}$; $E_{Cl-Cl} = 242\ kJmol^{-1}$;
$E_{C-C} = 348\ kJmol^{-1}$; $E_{C-Cl} = 348\ kJmol^{-1}$]

**Solution**
In the above reaction:
Bonds broken are: one C=C and one Cl– Cl
Bonds formed are: one C – C and two C – Cl

$\Delta H$ (reaction) = $\sum E$ (bonds broken) – $\sum E$ (bonds formed)
= $[E_{C=C} + E_{Cl-Cl}] - [E_{C-C} + 2E_{C-Cl}]$
= [614 + 242] – [348 + (2 × 348)]
= (856 – 1044) kJ = –188 kJ

### Enthalpy Changes in Ionic Compounds

As *bond energy*, E is to *covalent compounds*, so is *lattice energy*, U to *ionic compounds*

*Lattice energy, U is the heat liberated when one mole of an ionic compound is formed from its free gaseous ions, under standard conditions of temperature and pressure.* It is an *exothermic process*, because oppositely charged ions combine, e.g.

$Na^+_{(g)} + Cl^-_{(g)} \rightarrow Na^+Cl^-_{(s)}$; $\Delta H_{latt} = U = -ve$

Lattice energy, U is also regarded as the energy *absorbed* when an ionic compound is broken or separated into its gaseous ions, i.e.

$NaCl_{(s)} \rightarrow Na^+_{(g)} + Cl^-_{(g)}$; $\Delta H_{latt} = U = +ve$

Lattice energy value is a measure of the *thermodynamic stability* of an ionic compound. Its value depends on the *ionic sizes* and the *charges* on the *ions*. For instance:

- For a given cation, *lattice energy decreases* as the *ionic radius* of the anion *increases*: e.g

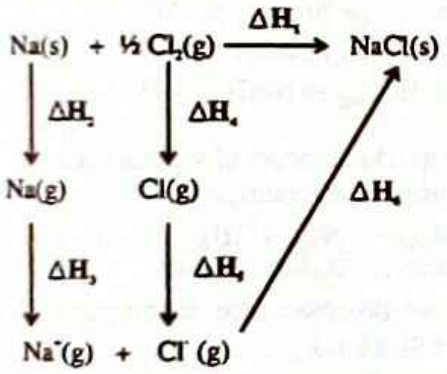
Lattice energy, U of $Na^+F^-$ = 922; $Na^+Cl^-$ = 761; $Na^+Br^-$ = 728, and $Na^+I^-$ = 697 ($kJmol^{-1}$).

- As the *charge on one of the ions increases, lattice energy increases*. e.g. Lattice energy of NaCl = 761; $CaCl_2$ = 2230 ($kJmol^{-1}$).

The *lattice energy* of an ionic compound cannot be determined experimentally; it is obtained *indirectly* by the use of an *energy cycle* called ***Born-Haber Cycle***, which connects various enthalpy changes – as shown below, using the *Born-Haber cycle of sodium chloride*.

**Calculation of Lattice energy: Sodium chloride**

The Born-Haber cycle for NaCl:




The relevant thermochemical data are as follows:

| | ($kJmol^{-1}$) |
|---|---|
| •Enthalpy of formation of NaCl(s), $\Delta H^\circ_f$ | = – 411 ($\Delta H_1$) |
| •Enthalpy of sublimation of Na(s), $S_{Na}$ | = +108 ($\Delta H_2$) |
| •Ionization energy of Na(g), $I_{Na}$ | = +495 ($\Delta H_3$) |
| •Dissociation energy of $Cl_2$(g), $D_{Cl-Cl}$ | = +242 ($\Delta H_4$) |
| •Electron affinity of $Cl_2$(g), $A_{Cl}$ | = -355 ($\Delta H_5$) |
| •Lattice energy, $U_{NaCl(s)}$ | = ? ($\Delta H_6$) |

From the Born-Haber cycle; applying the Hess's law: $\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6$

i.e. $\Delta H^\circ_f = S_{Na} + I_{Na} + \frac{1}{2}D_{Cl-Cl} + A_{Cl} + U_{NaCl}$

Substituting:

$-14 = 108 + 495 + 121 + (-355) + \Delta H_6$

Making unknown $\Delta H_6$, the subject of the formula:

$\Delta H_6 = -411 - 108 - 495 - 121 + 355$

$= -780\ kJmol^{-1}$

## Effect of Lattice Energy on Heat of Solution

When a substance dissolves in a specified amount of water, heat is either absorbed or evolved. The enthalpy change is called heat of solution, $\Delta H_{(soln)}$.

Consider the dissolution of NaCl in *n* moles of water (where *n* is quite large):

$NaCl_{(s)} + nH_2O_{(l)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$

$\Delta H_{(soln)} = +5.0\ kJmol^{-1}$

The process can be imagined to occur in *two* steps:

I The *first step* involves separating the ionic solid into gaseous ions. It is the *lattice energy* of dissociation; it is an *endothermic* process, +U.

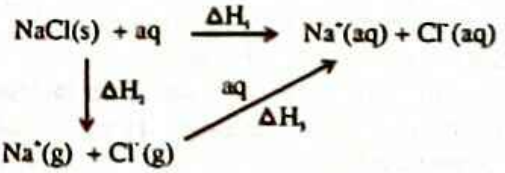
$NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$; $\Delta H_2 = +ve$

ii. The *second step* involves placing the ions in water. It is an *exothermic* process, due to attraction between the ions and the dipolar water molecules. The heat change is called the *hydration energy* $\Delta H_{(hyd)}$.

$Na^+(g) + Cl^-(g) + H_2O(l) \rightarrow Na^+(aq) + Cl^-(aq)$

$\Delta H_3 = -ve$

The various energy changes can be represented by an *energy cycle*:




Applying the Hess's Law: $\Delta H_1 = \Delta H_2 + \Delta H_3$.

$\Delta H_1 = \Delta H_{(soln)}$

$\Delta H_2 = -U = +ve$ (Endothermic)

$\Delta H_3 = \Delta H_{(hyd)} = -ve$ (Exothermic)

i.e. ***Heat of solution***, $\Delta H(soln) = U + \Delta H(hyd)$.

Hence, *heat of solution* depends on whether the *endothermic* or *exothermic* step is greater:

- *If the absolute value of lattice energy is greater than that of hydration energy ($U > \Delta H_{(hyd)}$), the heat of solution is positive; hence, endothermic.*
- *If the absolute value of lattice energy is less than that of hydration energy ($U < \Delta H_{(hyd)}$), the heat of solution is negative; hence exothermic.*

For most ionic solids, lattice energy and hydration energy are large and nearly of the same value:

In sodium chloride, the endothermic step (lattice energy, $U$ = 776 kJmol$^{-1}$) is greater than the exothermic step (hydration energy = -771 kJ).

Since $\Delta H_{(soln)} = -U + \Delta H_{(hyd)}$;

Substituting: $\Delta H(soln) = -(-776) + (-771)$

$= 776 - 771 = +5.0$ kJ

i.e. dissolution of NaCl in water is endothermic.

**Revision Exercises**

28 Sodium oxide, $Na_2O$ is an ionic compound.

a. Draw an energy cycle diagram to illustrate the formation of $Na_2O$ stating what each energy change in the cycle represents.

b. Write an equation relating the energies of the various processes represented in the diagram. [WAEC]

29 State the relationship between heat of solution, lattice energy and hydration energy of a chemical substance.

30 If lattice energy is less than hydration energy, the heat of solution of a reaction will be

A. positive B. negative C. zero D. constant

31 The heat of solution of potassium chloride is given as +24 kJ mol$^{-1}$ while its lattice energy is -710 kJmol$^{-1}$.

a. Calculate the hydration energy of the salt.

b. Draw an energy level diagram relating the three terms in a above.

## 18.8 Entropy and Entropy Changes

### Entropy, S

The *entropy*, S of a system is defined as the *degree of randomness or disorderliness of the system.* Like the enthalpy **H**, *entropy* S, is a state function; it cannot be determined experimentally.

Consider the *three states of matter*:

- The particles that make up a *solid* are in fixed positions; there is complete order. Hence, solids have the lowest entropy.
- In a liquid, there is less order, because the particles are mobile; hence, the entropy of a liquid is higher than that of a solid.
- In a gas, there is complete disorder, since the particles are completely independent of one another. Hence, entropy is greatest in gases.

*Entropy*, S is measured in units of Joules per Kelvin per mole ($JK^{-1}mol^{-1}$). Its value *increases* as *order decreases* or *disorder increases.*

### Entropy Change, ΔS

***The entropy change, ΔS is the state of orderliness or disorderliness that accompanies a physical or chemical process.***

Mathematically:

***Entropy change, ΔS = S(products) – S(reactants)***

- If the entropy of products, S(products) is greater than the entropy of reactants, S(reactants) then, the *entropy change*, ΔS is positive, and vice versa.

According to the *second law of thermodynamics*: *Any process that occurs in nature is accompanied by an increase in entropy.*

In fact, nature prefers conditions of *low enthalpy* (*negative* Δ*H*), and *high entropy* (*positive* Δ*S*).

### Common Processes with Positive Entropy Changes

The following *physical* and *chemical* processes are accompanied by *positive entropy changes* (+ΔS). Invariably, the reverse of each of the processes has a *negative entropy change* (–ΔS).

1. When a *solid* is heated and turns to a liquid (melting), there is an *increase* in entropy at any temperature.
2. When a liquid turns to a gas (evaporation or boiling) there is an *increase* in entropy at any temperature.
3. When a given mass of gas expands with increasing temperature or decreasing pressure, there is an *increase* in entropy.
4. Any reaction in which the reactants are solids or liquids, and one or more of the products are gases is favoured by an *increase* in entropy, e.g.

a. Decomposition reactions have positive entropy changes:

i. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$; $\Delta S$ = +ve

ii. $NH_4Cl(s) \rightarrow NH_3(g) + H_2O(l)$; $\Delta S$ = +ve

b. Reactions in which a gas is evolved:

$$Na_2CO_{3(s)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)} + CO_2\uparrow$$

$\Delta S$ = +ve

5. Reaction in which moles of gaseous products are more than those of reactants, e.g.

$$2NH_{3(g)} \rightarrow N_{2(g)} + 3H_{2(g)} \qquad \Delta S = +ve$$

2 mol. 1 mol. 3 mol.

6. Dissolution processes are accompanied by an increase in entropy e.g.

$$NaCl_{(s)} + H_2O_{(l)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$

7. Evaporation process has a positive entropy change:

$H_2O_{(l)} \rightarrow H_2O_{(g)}$; $\Delta S$ = +ve

8. When two or more gases are mixed together at constant volume, there is an increase in entropy.

**Revision Exercises**

32 Define the term *entropy*.

33 What is meant by the entropy change in a chemical system?

34 State whether entropy increases or decreases during each of the following processes:
a. Condensation of steam. b. Melting of wax.
c. Dissolution of sugar.
d. Adsorption of gas on charcoal.

35 State whether entropy change for each of the following is positive, negative or almost zero:
a. $HCl(g) \rightarrow HCl(l)$ b. $2Cl(g) \rightarrow Cl_2(g)$
c. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$
d. $H_2CO(g) \rightarrow H_2O(g) + C(s)$
e. $2H_2S(g) + SO_2(g) \rightarrow 3S(s) + 2H_2O(l)$
f. $NaCl(s) \xrightarrow{water} Na^+(aq) + Cl^-(aq)$

## 18.9 The Gibb's Free Energy, G

The *heat content* or *enthalpy*, **H** of a chemical substance is composed of two portions. That portion, which is *available for doing work* is called *Gibb's free energy*, **G**. The remaining portion, represented by quantity $q$, *is used in increasing the entropy*, **S** *of the system at an absolute temperature*, **T**.

Mathematically, $q = TS$.

Hence, $H = G + q = G + TS$

Making the *free energy* G the subject, we have:

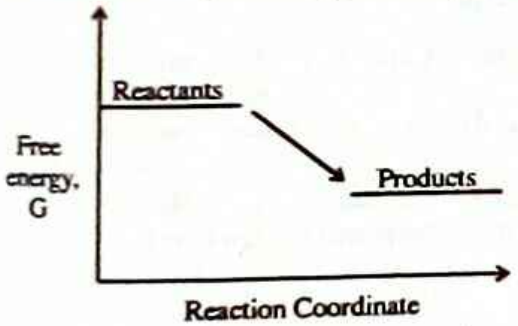
$$G = H - TS$$

When a reaction is carried out at constant temperature and pressure, the *free energy change*, $\Delta G$ is:

$$\Delta G = \Delta H - T\Delta S$$

### Spontaneity of Reactions

For a reaction to be *feasible* or *spontaneous*, the *free energy change*, $\Delta G$ must be negative, i.e. there is a *decrease* in the *free energy* of the system.




Mathematically, $\Delta G = G_{(products)} - G_{(reactants)}$

For a spontaneous reaction:

$G_{(products)} < G_{(reactants)}$; i.e. $\Delta G < O$.

Since *free energy change*, $\Delta G$ depends on *enthalpy change*, $\Delta H$ and *entropy change*, $\Delta S$ of the system, then, for a reaction to be spontaneous $\Delta H - T\Delta S$ *must be negative*, i.e.

$$\Delta H - T\Delta S < 0 \quad or \quad \Delta H < T\Delta S$$

The favourable conditions for the *free energy change*, $\Delta G$ to be negative, so that a reaction is spontaneous are:

1. When a reaction is *exothermic*, ($\Delta H$ is *negative*) and the *entropy change*, $\Delta S$ is *positive*, e.g. combustion reactions.

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$$
$$\Delta H = -ve;\ \Delta S = +ve$$

In such a reaction, $\Delta G$ is *negative at all temperatures*.

2. When a reaction is *exothermic* ($\Delta H$ = -ve) and $\Delta S$ is negative; but $\Delta H$ is far more negative than $T\Delta S$ (at low temperature, T), e.g.

a. $2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)}$; $\Delta H = -ve$; $\Delta S = -ve$

b. $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$; $\Delta H = -ve$; $\Delta S = -ve$.

3. An *endothermic* reaction ($\Delta H$ = +ve) will be spontaneous, if entropy change, $\Delta S$ is large and positive, usually, at a high temperature T, e.g.

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)};\ \Delta H = +ve;\ \Delta S = +ve.$$

$$T\Delta S > \Delta H; \quad \therefore\ \Delta H - T\Delta S < 0.$$

4. When two or more gases are mixed at constant volume, heat is neither liberated nor absorbed, i.e. $\Delta H = 0$. The driving force is due to an increase in entropy at constant volume.

$$\Delta G = 0 - T\Delta S = -ve.$$

### Non-spontaneous Reactions

A reaction will not be spontaneous at all temperatures, if it is *endothermic* (positive $\Delta H$) and the *entropy change*, $\Delta S$ is *negative*. Under these conditions, the *free energy change*, $\Delta G$ is positive.

### Worked Examples

**11** $C_{(s)} + H_2O_{(l)} \rightarrow CO_{(g)} + H_{2(g)}$.

The reaction above was carried out at 27 °C. If the enthalpy change was +4500 J, and the entropy change was +13 $JK^{-1}$, calculate the free energy change, and comment on the value.

**Solution**

Data given: $\Delta H = 4500$ J; $\Delta S = +13\ JK^{-1}$,
$T = 27 + 273 = 300$ K

Free energy change, $\Delta G = \Delta H - T\Delta S$;

Substituting: $\Delta G = 4500\ J - (300 \times 13)\ J$
$= (4500 - 3900)\ J = +600\ J$

*Comment*: Since $\Delta G$ has a positive value, the reaction is not feasible at the stated temperature.

**13** Explain why enthalpy data alone cannot be used to predict whether a reaction can occur spontaneously or not. [WAEC]

*There are many exothermic and endothermic reactions occurring spontaneously. Both the enthalpy and entropy data are used to determine whether a reaction will occur spontaneously or not.*

**14a** State the **THREE** parameters that determine the spontaneity of a reaction.

*The three parameters are: Enthalpy change, Entropy change, and Temperature.*

**b.** Write an expression to show the relationship between the parameters stated above. [NECO]

*The expression is:* $\Delta G = \Delta H - T\Delta S$

## Revision Exercises

**36** Define *free energy*.

**37** Give the formula indicating the relationship between the entropy, free energy and enthalpy changes of a system.

**38** What does each term represent in the following expression: $\Delta G = \Delta H - T\Delta S$?

**39** Which of the following statements is not correct of $\Delta H$, the enthalpy of a reaction? $\Delta H$ is

A. the heat change accompanying a chemical reaction
B. negative for exothermic reactions.
C. positive for endothermic reactions.
D. always positive for spontaneous reactions.
E. zero when gases are mixed at constant volume [W]

**40** $C_{(s)} + H_2O_{(g)} \rightarrow H_{2(g)} + CO_{(g)}$

$\Delta G$ for the reaction above at 1300 K is -43 kJ. At this temperature, the reaction is

A. not feasible. B. at equilibrium.
C. feasible. D. exothermic. [JAMB]

**41** Which of the following is a condition for spontaneous reaction?

A. $\Delta H - T\Delta S$ is zero. B. $\Delta H - T\Delta S$ is positive.
C. $\Delta H - T\Delta S$ is negative. D. $\Delta S$ is zero.

**42** $\frac{1}{2}N_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow NO_{(g)}$; $\Delta H^\circ = 89\ kJmol^{-1}$

If the entropy change for the reaction above at 25 °C is 11.8 $Jmol^{-1}$, calculate the change in the free energy $\Delta G^\circ$, for the reaction at 25 °C.

A. 88.71 kJ. B. 85.45 kJ.
C. -204.0 kJ D. -3427.40 kJ.

**43** The reaction represented by the equation

$C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)}$

was carried out at 27 °C. If the enthalpy change and the entropy change were +4500J and +12 $JK^{-1}$ respectively, What is the free energy change?

A. - 4176 J B. - 900 J C. + 900 J
D. + 476 J E. + 8100 J [NECO]

**44** $H_{2(g)} + Br_{2(g)} \rightarrow 2HBr_{(g)}$

The reaction was carried out at 25 °C. If $\Delta H$ is -72 kJ $mol^{-1}$ and $\Delta S$ is -106 $Jmol^{-1}K^{-1}$, the reaction will

A. proceed spontaneously at lower temperature.
B. not proceed spontaneously at the given temperature.
C. proceed spontaneously at the given temperature.
D. proceed in the reverse direction at the given temperature. [JAMB]

[Hint: First, calculate $\Delta G$ for the reaction.]

**45** Calculate the entropy change in $JK^{-1}mol^{-1}$ for the conversion of one mole of liquid water to vapour at 100 °C. [Heat of vapourisation of water = 2260.87 J] [H = 1, O = 16]

A. 109.10 B. 110.10 C. 110.50
D. 115.20 E. 120.10 [NECO]

## Answers to Revision Exercises

| | | | | |
|---|---|---|---|---|
| 9. D | 10. A | 15. C | 17 720 $kJmol^{-1}$ | 18. B |
| 19. D | 20. B | 21 $1.9 \times 10^3$ kJ | 22. A | |
| 23. D | 24. A | 25b 59.2 kJ | 27. B | 29. E |
| 30. B | 31a - 686 $kJmol^{-1}$ | | 39. D | 40. C |
| 41. C | 42. B | 43. C | 44. C | 45. A |

# 19

# •RATES OF CHEMICAL REACTIONS•

## 19.1 Introduction: Chemical Kinetics

*Chemical Kinetics* deals with the study of the rates of reactions. It provides information on *how long* it takes a reaction to occur; *how fast* a reaction goes; how the rate can be *measured*; and the pathways through which the reactants are converted into products (mechanisms).

Chemical reactions go at different rates:

1. Some reactions are so fast and instantaneous that their rates cannot be measured. These are reactions involving ions in solution, e.g. *precipitation reactions*. For instance: When a solution of a silver salt is mixed with a solution of a chloride, a *white precipitate* of AgCl is produced instantaneously:

$$\underset{\text{(colourless)}}{Ag^+(aq)} + \underset{\text{(colourless)}}{Cl^-(aq)} \rightarrow \underset{\text{(white)}}{AgCl(s)}$$

2. Some reactions proceed at slow rates that their progress can be monitored e.g. catalytic decomposition of hydrogen peroxide at room temperature.

$$2H_2O_2(l) \xrightarrow{MnO_2(s)} 2H_2O(l) + O_2(g)$$

3. Some reactions will not commence unless heat is applied, or the reactants are ignited, e.g.

a. Decomposition of $CaCO_3$ requires heating:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

b. Combustion of petrol or hydrogen is by ignition:

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

At home:

- It takes less time to cook rice than to cook the same quantity of beans;
- A pressure cooker enables raw food to be cooked more rapidly;
- Perishable foods are preserved by refrigeration, in order to slow down the rate at which they deteriorate.

### Revision Exercises

1. What is chemical kinetics?
2. Mention two pieces of information that can be obtained from the kinetics of a reaction.
3. Give one example each of a reaction, which
   a. is fast and immediate; b. is catalyzed;
   c. will not commence unless ignited.

## 19.2 Rates of Chemical Reactions

### Definitions

The rate of a chemical reaction is defined, generally, as the *change in the quantity of a reactant* or *product per unit time.*

It can also be defined with respect to the quantity being measured in the reaction. For instance:

1. For a reaction in solution, the rate is the *change in the concentration of reactant or product per unit time at a given temperature.*

Mathematically:

$$\text{Rate} = \frac{\text{Change in concentration}}{\text{Time taken}}$$

2. For a reaction in which a solid is a reactant or product, the rate is the *change in mass of substance per unit time*, i.e.

$$\text{Rate} = \frac{\text{Change in mass}}{\text{Time taken}}$$

3. For a reaction in which a gas is a reactant or product, the rate is the *change in volume of gas per unit time at a given temperature*, i.e.

$$\text{Rate} = \frac{\text{Change in volume}}{\text{Time taken}}$$

From the above illustrations, it is evident that the unit of reaction rate depends on the quantity being measured. However, reaction rate is *directly* proportional to the *quantity of reactant*, and *inversely* proportional to the *time taken*. A *fast* reaction takes a *shorter time* for completion than a *slow* one.

The variations of concentrations of reactants and products with time are shown in figure 19.1. As a reaction proceeds, the *quantity of reactant decreases* rapidly initially, then, slowly, towards the end of the reaction, until it is completely used up. At the same time, the *quantity of product increases*

*Because the activated complex is unstable, the system readily releases energy to the surrounding, in order to form the products.*

*When the energy absorbed by the reactants to form the activated complex (activation energy), is less* than the energy *released* by the *activated complex* to form the products, then, the *potential energy of products*, $H_P$ will be *lower than that of the reactants*, $H_R$. Under this condition, the *enthalpy change*, $\Delta H$, for the reaction is *negative*, and the reaction is therefore *exothermic*:

$$\Delta H = H_P - H_R = -ve \quad \text{(see fig 19.4)}$$

However, when the *activation energy* is *greater* than the *energy released* to form the *products*, then, the *potential energy of product*, $H_P$ will be *higher* than that of the reactants, $H_R$. Under this condition, the *enthalpy* of reaction, $\Delta H$ is *positive*, and the reaction is *endothermic*:

$$\Delta H = H_P - H_R = +ve \quad \text{(see fig 19.5).}$$

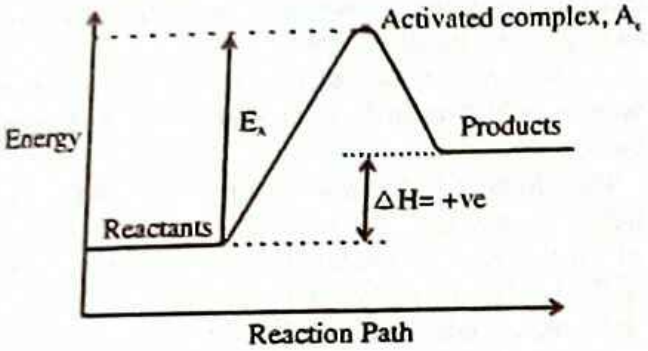



Fig 19.5 *Energy profile diagram for an endothermic reaction*

**Solved Problems**

3. On what principle is collision theory based for a chemical reaction to occur. [NECO]

*Collision theory is based on the principle that reactant particles possess enough activation energy, and that there are effective collisions for a reaction to occur.*

4. State **TWO** conditions that can lead to ineffective collisions during a chemical reaction. [NECO]

- *Inadequate activation energy or low temperature*
- *Poor orientation or non-alignment of particles.*

5. Define the term *activated complex.* [WAEC]

*Activated complex is the unstable species formed by the reactants after absorbing enough energy (activation energy) before forming the products.*

6. Give reason why the rate of reaction between magnesium and dilute hydrochloric acid decreases as the reaction proceeds.

*As the reaction proceeds, there is a decrease in the number of particles of the acid and the metal, leading to a decrease in effective collision; hence, there is a decrease in the rate of reaction.*

**Revision Exercises**

7 The collision theory suggests that for two particles to react, they must collide. What two factors determine whether or not the collision would lead to formation of products? [WAEC]

8 State one reason why a collision may not produce a chemical reaction. [WAEC]

9 Define *activation energy.*

10 Use an energy profile diagram to illustrate what is meant by the *enthalpy change* ($\Delta H$) and the *activation energy* ($E_A$) of a reaction. [WAEC]

11 Consider the reaction:

$$W \longrightarrow X + Y \; ; \; \Delta H = -x \text{ kJ}.$$

Sketch an energy profile diagram for the reaction.

## 19.4 Factors Affecting the Rates of Reactions

The *seven* factors that affect reaction rates are:

- Nature of the reactants;
- Concentration of reactants;
- Effect of temperature;
- Surface areas of reactants;
- Presence of catalyst;
- Pressure changes in gaseous reactants;
- Effect of light or radiation on the reaction.

The *collision theory* can be used in explaining the effects of these factors on the reaction rates.

According to the *collision theory*, any factor that *increases* the rate of collision between the reactant particles will *increase* the rate of reaction, and vice versa.

### 1. The Nature of Reactants

The nature of the particles of reactants can affect the reaction rate. The particles are usually in the form of atoms, molecules, and ions:

a. Reactions involving ions in aqueous solutions – as in inorganic reactions, are usually immediate, due to the electrostatic force of attraction between opposite ions, e.g.

i. **Neutralization reactions:**

Reactions involving an acid and an alkali are fast and instantaneous.

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)}$$

ii. **Precipitation reactions:**

When a solution of a lead(II) salt is mixed with a solution of a tetraoxochromate(VI), a *yellow precipitate* of $PbCrO_4$ is produced instantaneously:

$$\underset{\text{(colourless)}}{Pb^{2+}_{(aq)}} + \underset{\text{(yellow)}}{CrO_4^{2-}_{(aq)}} \rightarrow \underset{\text{(yellow)}}{PbCrO_{4(s)}}$$

b. Reactions that require bond-breaking – as in reactions involving covalent molecules, are very slow at room temperature. Unless heat or a spark is applied, such reactions will not commence e.g. *combustion of fuels:*

Methane does not burn in air, unless it is ignited:

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$$

## 2. Concentration of Reactants

The *concentration* of a solution is a measure of the number of reactant particles in the solution. When a solution is *concentrated*, there are more reactant particles per unit volume than when it is *dilute*.

### Experimental Illustration

*Action of an acid on a metal*

When magnesium wire is dropped into a beaker of dilute hydrochloric acid, the metal dissolves with effervescence; the colourless and odourless gas liberated is hydrogen.

$$Mg_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$$

The data below show the time taken for effervescence to occur when an excess hydrochloric acid of *different concentrations* reacted separately with the *same mass* of magnesium wire (2.0 *g*) at the same temperature:

| Experiment | I | II |
|---|---|---|
| Concentration of acid ($mol\ dm^{-3}$) | 2.00 | 1.00 |
| Volume of acid ($cm^3$) | 20.0 | 20.0 |
| Mass of magnesium (*g*) | 2.0 | 2.0 |
| Time taken (seconds) | 15.0 | 40.0 |

### Observation

A *decrease* in the concentration of the acid *increases* the time taken for effervescence to occur.

### Explanation using the collision theory

In experiment **I**, there are more hydrogen ions in 20.0 $cm^3$ of 2.00 $moldm^{-3}$ HCl than in 20.0 $cm^3$ of 1.00 $moldm^{-3}$ HCl of experiment **II**. The frequency of collisions between hydrogen ions and magnesium atoms is therefore higher in **I** than in **II**. Hence, the period of effervescence in **I** ($t_1$) is less than in **II** ($t_2$).

The *rate of reaction is inversely proportional to the time*; the *shorter the time*, the *faster the rate*. Hence, the rate of reaction is faster in **I** than in **II**, see fig 19.6.

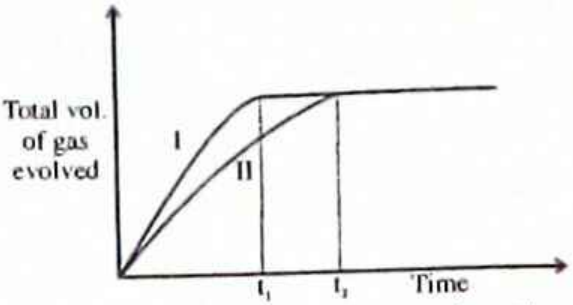



**Fig 19.6** *Effect of concentration on rate of reaction*

Generally, an *increase* in the concentration of reactants makes the particles to be in close contact with one another, thereby *increasing* the frequency of collision, and hence, *increasing* the rate. A *decrease* in the concentration of reactants *decreases* the chances of collisions and hence, *decreases* the rate.

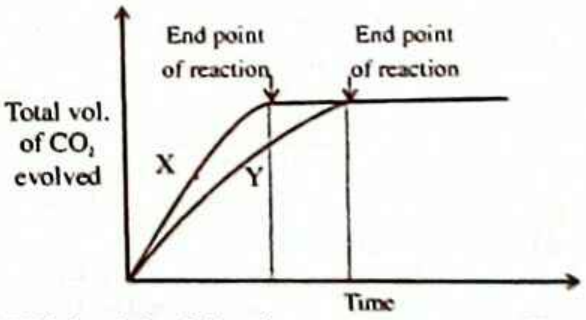
### The law of mass action

The *concentration effect* on reaction rate is based on the *law of mass action*, which states that

*The rate at which a reaction proceeds is directly proportional to the concentrations of the active species in the system at a given temperature.*

### Solved Problems

**7.** The rate curves below represent the reaction between a fixed mass of $Na_2CO_3$ and 0.10 $moldm^{-3}$ solutions of acids **X** and **Y**.




Which of the following statements about **X** and **Y** is false?

**A.** Rate of gas production is the same for **X** and **Y**.
**B.** Total volume of gas evolved is the same for **X** and **Y**.
**C.** **X** is a stronger acid than **Y**.
**D.** **X** ionizes more than **Y** in aqueous solution. [WAEC]
**Solution:** ***A***

**8.** The rate of a reaction usually decreases with a decrease in the concentration of reactants because
**A.** kinetic energy decreases.
**B.** temperature increases. **C.** speed increases.
**D.** reactants collision decreases. [WAEC]
**Solution:** ***D***

**Revision Exercises**

12 Explain in terms of the collision theory, the effect of increase in concentration on reaction rate.

13 The reaction of a fixed mass of iron filings with 0.50 $moldm^{-3}$ HCl(aq) can be made to proceed faster by
- A. adding 0.50 $moldm^{-3}$ NaOH.
- B. using 0.25 $moldm^{-3}$ acid instead.
- C. increasing the volume of acid used.
- D. adding some concentrated HCl.

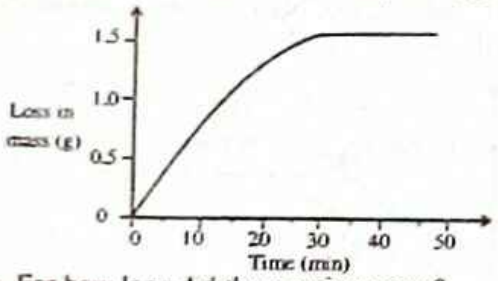
14 The table below shows the results of an experiment performed by reacting 6.0 *g* of a metal M with 10.0 $cm^3$ of 0.50 $moldm^{-3}$ $HCl_{(aq)}$.

| Time (minutes) | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Total vol. of $H_2$ ($cm^3$) | 30 | 45 | 54 | 58 | 60 | 62 | 62 |

- a. Write a balanced ionic equation for the reaction.
- b. State the time at which the concentration of the reactants was highest.
- c. State the volume of hydrogen given off in the second minute.
- d. At what time did the reaction come to completion?
- e. State two effects that would be observed on repeating the experiment using the same mass of M but 1.0 $moldm^{-3}$ $HCl_{(aq)}$. [WAEC]

15 The graph below is the rate curve for the following reaction carried out in an open vessel.

$MgCO_{3(s)} + 2HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$




- a. For how long did the reaction occur?
- b. Why was there a loss in mass?
- c. State whether the reaction rate was fastest at the beginning, the middle or towards the end of the reaction. Give reason for your answer.
- d. List three reaction conditions that can affect the slope of the curve.

16 In four separate experiments, the same quantity of magnesium ribbon was added to an excess of hydrochloric acid. In which of the experiments will hydrogen be given off most rapidly?

| Experiment | Volume of acid ($cm^3$) | Concentration of acid ($moldm^{-3}$) |
|---|---|---|
| W | 10 | 1.0 |
| X | 20 | 0.5 |
| Y | 30 | 2.0 |
| Z | 50 | 1.0 |

A. W B. X C. Y D. Z [WAEC]

## 3. Temperature Effect

For most reactions, rate increases as temperature rises. Studies have shown that the rate of a reaction is approximately doubled, for every 10 °C rise in temperature.

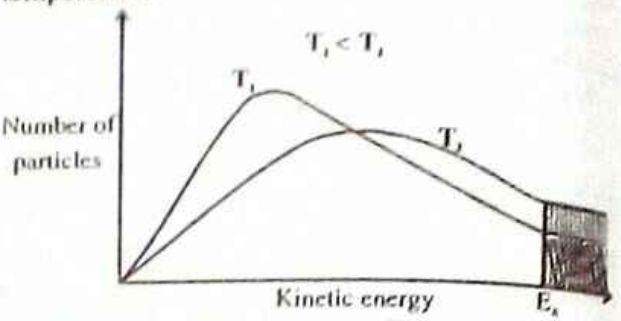



**Fig 19.7** *Effect of Temperature on Kinetic Energy*

The increase in reaction rate is largely due to the increase in the number of reactant particles possessing the *activation energy*. Figure 19.7 illustrates the effect of temperature on kinetic energies of particles. At temperature $T_1$, the dotted area under the curve $T_1$ represents the number of particles that possess the *minimum energy*, $E_A$. As the temperature increases to $T_2$, more reactants acquire more energy greater than the activation energy, $E_A$; hence, reaction rate increases.

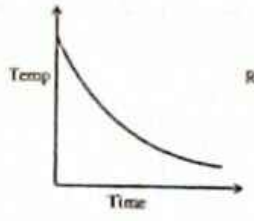



**Fig 19.8**

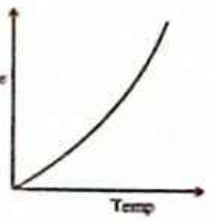



**Fig 19.9**

**Fig 19.8** *Temperature–Time Curve*
**Fig 19.9** *Rate–Temperature Curve*

Figures 19.8 and 19.9 are the exponential curves of variation of temperature with time, and the variation of rate with temperature respectively.

### Experimental Illustration

**Action of a mineral acid on $Na_2S_2O_3$**

**Theory**: When dilute hydrochloric acid is added to a solution of $Na_2S_2O_3$, the reaction taking place is:

$2HCl_{(aq)} + Na_2S_2O_{3(aq)} \longrightarrow 2NaCl_{(aq)} + H_2O_{(l)} + SO_{2(g)} + S\downarrow$

The reaction can be followed by transferring a solution of $Na_2S_2O_3$ into a 100 $cm^3$ beaker placed on a white sheet of paper that has a black **X** mark on it. The acid is then added. The time taken for the **X** mark to disappear on looking down through

the mixture is noted.

| Experiment | I | II |
|---|---|---|
| Volume of bench $HCl_{(aq)}$ | 10 $cm^3$ | 10 $cm^3$ |
| Volume of $Na_2S_2O_3$ | 10 $cm^3$ | 10 $cm^3$ |
| Temperature | 27°C | 37°C |
| Time taken (seconds) | 55 *s* | 28 *s* |

The data above illustrate the effect of temperature on the time taken for sulphur to be deposited when 10.0 $cm^3$ of bench hydrochloric acid is added separately into two beakers, each containing 10.0 $cm^3$ of 0.10 $moldm^{-3}$ $Na_2S_2O_3$ but at different temperatures of 27 °C (room temperature) and 37 °C.

Observation

An *increase* in the temperature of the system *decreases the time* taken to complete the reaction.

### Explanation of Temperature Effect using Collision Theory

The particles of $Na_2S_2O_3$ in experiment **II** are at a higher temperature than those in experiment **I**; this results in an increase in the number of effective collisions. Hence, the reaction rate in **II** is faster than in **I**.

In terms of activation energy: At a higher temperature, more particles in **II** possess the required activation energy than those in **I**, hence, the reaction rate in **II** is faster than in **I**.

### Solved Problem

9. The time taken for sulphur to be deposited in the reaction of $Na_2S_2O_3$ and hydrochloric acid at various temperatures are as follows:

| Temp °C | 25 | 35 | 45 |
|---|---|---|---|
| Time (seconds) | 72 | 36 | 18 |

These results suggest that

A. for a 10° rise in temperature, reaction rate is halved
B. for a 10° rise in temperature, reaction rate is doubled
C. time taken for sulphur to be deposited does not depend on temperature
D. for a 10° rise in temperature, reaction rate is tripled

Solution: *B*

### Revision Exercises

17 Explain in terms of the collision theory, the effect of an increase in temperature on reaction rate.

18 An increase in the rate of a chemical reaction on heating is due to increase in
A. entropy B. enthalpy C. collision rate
D. reactant concentration [WAEC]

## 4. Surface Area of Reactants

The surface area represents the state of *subdivision* of a *solid reactant* in a reaction. It is a measure of the area of the particles exposed, or available for physical or chemical attack.

Consider a *cube of sugar* and *granulated sugar of the same mass*. The surface area of the *granulated* sugar is larger than that of the *cube* of sugar. Similarly, the surface area of *one gram* of magnesium *powder* is larger than that of *one gram* of magnesium *wire* or *ribbon*.

### Experimental Illustration

The data below show the period of effervescence when 2.0 *g* of magnesium *wire* and 2.0 *g* of *powdered* magnesium reacted separately with 20.0 $cm^3$ of bench hydrochloric acid.

| Experiment at 27 °C | I | II |
|---|---|---|
| The form of Magnesium | 2.0 *g* of Mg *wire* | 2.0 *g* of Mg *powder* |
| Volume of bench $HCl_{(aq)}$ | 20 $cm^3$ | 20 $cm^3$ |
| Time taken (seconds) | 22 *s* | 15 *s* |

**Observation:**

The period of effervescence for Mg *powder* (15 *s*) is less than that of Mg *wire* (22 *s*)

### Collision Theory Explanation of Surface Area

In a reaction involving a solid and a liquid, the smaller the particle size of the solid, the larger the area exposed for collisions to occur between the particles and the liquid; hence, the faster the rate.

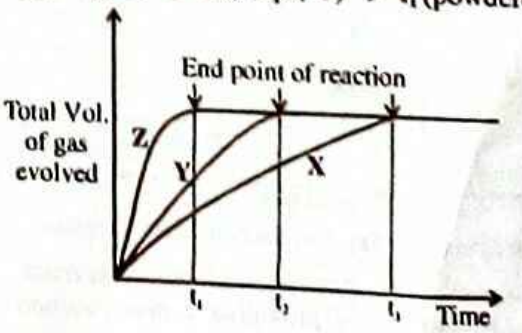
The order of *increasing surface areas of different forms of a solid but of the same mass is*:

- Iron nail < iron wool < iron filings.
- Log of wood < saw dust.
- Zinc rod < granules/pellets < foil < zinc dust.

At home, due to *larger surface area*, charcoal burns more easily when it is *broken into small pieces than when it is in lump form*.

When an excess of bench $HCl_{(aq)}$ is separately added to the same mass of three different forms of marble, $CaCO_3$, the time taken for effervescence to stop will be in the order:

$t_3$ (lump, X) > $t_2$ (chips, Y) > $t_1$ (powdered, Z)



Powdered marble, Z, has the largest surface area; hence, the time taken for effervescence to occur is the shortest.

In terms of surface area:

- Lump < chips < powdered marble ($CaCO_3$).
- Magnesium wire/ribbon < magnesium powder.

**Solved Problems**

**10** A chemical reaction can be made to proceed faster by I. lagging the reaction vessel
II. conducting it in a bigger vessel
III. grinding the reactant(s) if solid
IV. increasing the reaction temperature.
A. IV only B. I and II only C. III and IV only
D. I, II and III only E. I, II, III and IV. [WAEC]
**Solution: C**

**11** Consider the reaction represented by the equation: $Mg_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$
a. Name the type of reaction.
b. Give two ways by which the reaction could be made to proceed faster. [WAEC]

a. *Displacement reaction* or *Redox reaction (Any one)*
b. *(Any two of the following):*
- *By using powdered magnesium;*
- *Increasing the concentration of HCl;*
- *Increasing the temperature of the reaction system.*

## 5. Presence of Catalyst

A *catalyst* is a substance that alters reaction rate, without being used up in the reaction e.g.
The decomposition of $H_2O_2$ is very slow at room temperature, unless it is warmed. The decomposition is instantaneous, if a small quantity of powdered manganese(IV) oxide is added:

$$2H_2O_2(l) \xrightarrow{MnO_2(s)} 2H_2O(l) + O_2(g)$$

**Effect of Catalyst on Activation Energy**

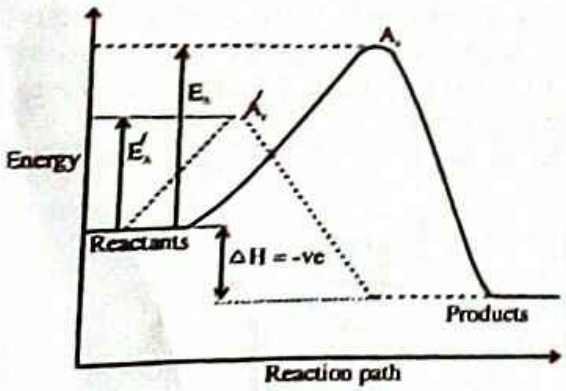



**Fig 19.10** *Effect of catalyst on an exothermic reaction*

When a *catalyst* is employed to *increase* the reaction rate, it does so by providing a *new reaction path with lower activation energy*, $E_{AC}$, at constant temperature T, see figures 19.10 and 19.11. *High activation energy is associated with a slow rate and vice-versa.*

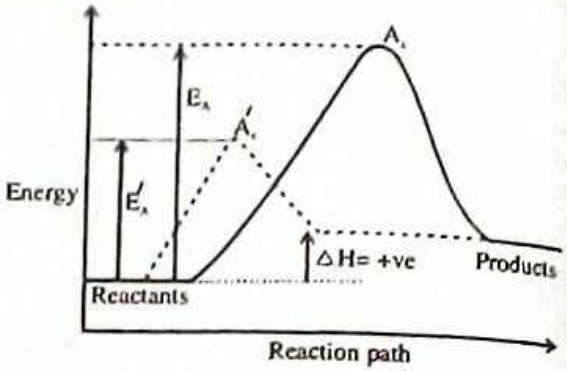



**Fig 19.11** *Effect of catalyst on an endothermic reaction*

It should be noted that the *enthalpy change*, $\Delta H$, for any reaction, whether exothermic or endothermic, is not affected by the presence of a catalyst.

**Effect of Catalyst on Kinetic energy**

*In the presence of a catalyst, more particles possess kinetic energy greater than the activation energy. It leads to an increase in effective collisions, and hence, an increase in reaction rate.*

Figure 19.12 shows the effect of catalyst on the kinetic energy at a particular temperature T.

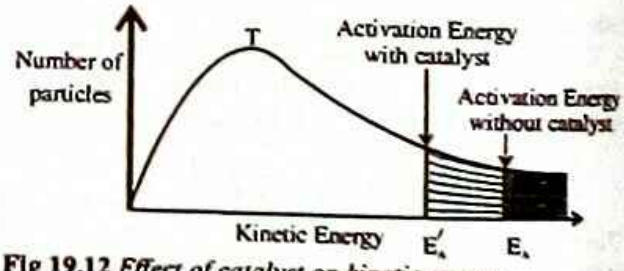
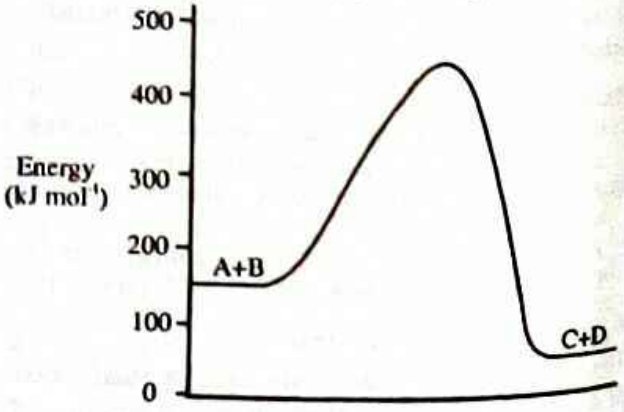



**Fig 19.12** *Effect of catalyst on kinetic energy*

**Solved Problems**

**12** Study the following energy profile diagram.



a. From the diagram, determine the value of the
i. enthalpy of reaction;

*Enthalpy change, $\Delta H$ = $E_{(products)} - E_{(reactants)}$*
*= (50.0 - 150) kJmol$^{-1}$*
*= -100 kJmol$^{-1}$*

ii. activation energy of reaction.

*Activation energy, $E_A$ = $E_{(Acomp)} - E_{(Reactants)}$*
*= (450.0 - 150.0) kJmol$^{-1}$*
*= 300 kJmol$^{-1}$*

b. State whether the diagram is for an exothermic or an endothermic reaction.

*Reaction is exothermic; enthalpy change is negative.*

c. What name is given to a substance, which can provide an alternative pathway for the reaction?

*A catalyst.*

13 State the effect of catalyst on activation energy.

*A catalyst decreases or lowers the activation energy*

## Catalysts as Promoters and Inhibitors

A *catalyst* either *increases the rate of a chemical reaction, if it is a* ***promoter***, or *decreases the rate, if it is an* ***inhibitor***. Commonly used catalysts in chemical reactions are *promoters*.

### Revision Exercises

19 Sketch an energy profile diagram to show the effect of catalyst on the reaction rate, given that the reaction is endothermic.

20 Which of the following is not correct about a catalyst? It

A. has the same mass and composition at the end of the reaction.
B. alters the rate of chemical reaction.
C. is usually specific in action.
D. can start a chemical reaction which will normally not take place. [WAEC]

21 In an experiment, excess of 0.50 *moldm$^{-3}$* HCl was added to 10 *g* of granulated zinc in a beaker. Other conditions remaining constant, state how the reaction rate would be affected in each case, if the experiment was repeated using:

a. 1.0 *moldm$^{-3}$* HCl; b. 10 *g* of zinc dust;
c. a higher volume of 0.50 *moldm$^{-3}$* HCl;

## 6. Effect of Pressure

A change in pressure affects chemical systems in which one or more of the reactants or products are gases. An *increase* in pressure on a given mass of gas at constant temperature leads to a *decrease* in volume (Boyle's law), and hence, an *increase* in *concentration*.

An *increase* in pressure enables gaseous particles to be in close contact and collide more frequently with one another, thereby, increasing the rate of reaction. Conversely, a *decrease* in pressure on a gaseous system *decreases* the rate of reaction.

## 7. Effect of Light or Radiation

Some reactions occur only in the presence of *sunlight*; such reactions will not occur in the *dark*:

a. Hydrogen and chlorine form hydrogen chloride readily on exposure to sunlight, or when irradiated.
b. Photosynthesis in plants does not occur in the dark, except by the absorption of sunlight energy.

In these reactions, sunlight provides the required energy to promote the frequent collisions between the particles, leading to the expected reactions.

A reaction that occurs in the presence of light is called *photochemical* or *photocatalytic* reaction.

### Solved Problem

14 The photocatalytic reaction between hydrogen and chlorine, when carried out in a dimly lit room, is represented by the following equation:

$$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)} \quad \Delta H = -x\ kJmol^{-1}$$

Explain what happens when the reaction is carried out in sunlight.

*In sunlight, molecules of hydrogen and chlorine acquire more energy, move faster, and collide more frequently than when in a dimly lit room. Hence, the reaction rate, increases due to the increased number of reactants with the activation energy required for effe-ctive collisions.*

### Revision Exercises

22 Explain the effect of increase in pressure on the rate of a gaseous reaction. [WAEC]

23 Consider the reaction represented by the following equation: $H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$
The number of effective collisions of molecules of reactants decreases as

A. the temperature is raised.
B. the pressure is increased.
C. the volume of the system is increased.
D. a catalyst is introduced into the system. [WAEC]

24 Which of the following factors does not affect the rate of reaction of non-gaseous reactants?

A. Concentration B. Pressure
C. Surface area. D. Temperature [WAEC]

25 Consider the reaction represented by the equation below:

$Na_2S_2O_{3(aq)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + SO_{2(g)} + S_{(s)}$

a. List two factors that can affect the rate of this reaction.
b. Which of the products can be readily used to measure the rate of reaction. Give a reason for your answer.
c. Name two instruments that can be used to measure the factors in b above. [WAEC]

## 19.5 Reaction Mechanism

The *mechanism of a reaction* is the step-by-step description of how the reactants are converted into products. A *one-step* reaction is simple and fast; but if a reaction involves *two* or *more steps*, it is said to be complex. Such a reaction is usually *slow*.

Every simple step in a complex reaction has its own *energy profile* with one *activated complex*. The *number of activated complex* determines the number of steps in a complex reaction. An *intermediate compound* is formed in the *well* between *two* activated complexes. The *deeper the well*, the more stable the *intermediate*.

For instance: Suppose the formation of water goes through two steps:

I. $H_{2(g)} + O_{2(g)} \xrightarrow{\text{Slow}} H_2O_{2(g)}$; $\Delta H_1 = +85.0$ kJ

II. $H_2O_{2(g)} \xrightarrow{\text{Fast}} H_2O_{(l)} + \frac{1}{2}O_{2(g)}$; $\Delta H_2 = -374.0$ kJ

Step I produces gaseous hydrogen peroxide. The reaction is *slow*, and endothermic.

Step II is the decomposition of $H_2O_2(g)$ into water and oxygen, which is *fast* and *exothermic*.

When the two steps are added together and the common term, $H_2O_2$, cancelled, the net reaction is:

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)};\ \Delta H_3 = -289\ \text{kJ mol}^{-1}$$

The enthalpy change for the net reaction is:

$\Delta H = \Delta H_1 + \Delta H_2 = [85 + (-374)]$ kJ $= -289$ kJ.

The overall reaction is therefore exothermic.

In the above reactions, $H_2O_{2(g)}$ is an *intermediate*; it does not appear in the overall equation, because it is used up completely in step II of the reaction.

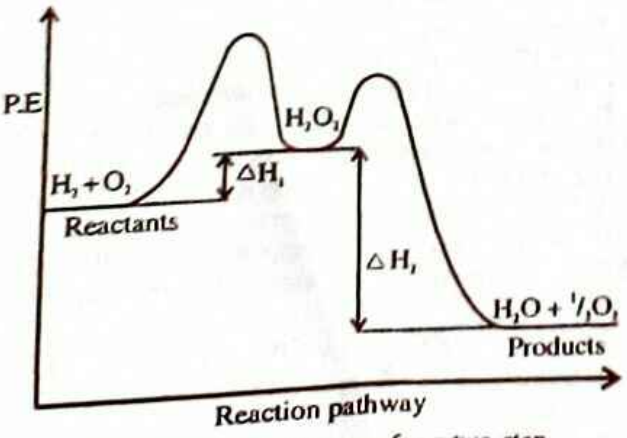



**Fig 19.13** *Energy profile diagram for a two-step reaction*

The energy profile diagram for the overall reaction is shown in fig 19.13. It is a *two-step* reaction in which the *first step* is *endothermic* and has a higher *activation energy*; it is the *slow step*. The *second step* is *exothermic* with a *lower activation energy*; it is the *fast step*. The overall reaction is *exothermic*.

In any reaction involving two or more steps, the *slowest step* is usually the *rate-determining step*.

**Revision Exercises**

26 State the difference between an intermediate and an activated complex in a two-step reaction.

27 The mechanism of a reaction is given as:

$X + X \longrightarrow X_2$ (slow)

$X_2 + Y \longrightarrow YX_2$ (fast)

Draw the energy profile diagram for the reactions, if the first step is exothermic and the overall reaction is also exothermic.

28 Oxidation of $N_2$ to $NO_2$ is a two-step reaction:

$\frac{1}{2}N_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow NO_{(g)}$; $\Delta H_f = +92.0\ kJmol^{-1}$

$NO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow NO_{2(g)}$; $\Delta H_f = -58.0\ kJmol^{-1}$

a Write a balanced equation for the overall reaction;

b Calculate the heat change for the overall reaction;

c Draw the energy profile diagram for the reaction, if the first step is the rate determining step.

## 19.6 Rate Constants and Rate Laws

1. Consider a reaction involving only *one reactant*:

$$\mathbf{A} \longrightarrow \mathbf{Products}$$

The reaction rate, $r$ is *directly proportional to the initial concentration of* A, [A] i.e.

$$\text{Rate}, r \propto [\mathbf{A}]$$

When the *proportionality constant* $k$ is included, the expression becomes: $r = k[\mathbf{A}]$

$k$ is the *rate constant*, while the expression is called the *rate law* or *rate equation*.

2. When a reaction involves *two reactants* having different initial concentrations, the reaction rate will be *directly proportional to their initial concentrations* i.e.

$$\mathbf{A} + \mathbf{B} \longrightarrow \mathbf{Products}$$

$$\text{Rate}, r \propto [\mathbf{A}][\mathbf{B}]$$

When the proportionality constant $k$ is included, the rate law is: $r = k[\mathbf{A}][\mathbf{B}]$

### Order and Molecularity of a Reaction

The *order* of a reaction is the power, $n$, to which the concentration terms in the rate equation must be raised, while the *molecularity* is the number of molecules involved in the reaction. The *order* of a reaction, $n$ is usually determined experimentally; it cannot be deduced from the balanced equation of

reaction, since it may be different from the *molecularity*. For instance:

The decomposition of hydrogen peroxide can be represented by the equation:

$$2H_2O_{2(l)} \longrightarrow 2H_2O_{(l)} + O_{2(g)}$$

The *molecularity is two*. Experimentally, the reaction is *1st order*, $n = 1$, and not *2nd order*, $n = 2$.

i.e. reaction rate, $r = -\frac{d[H_2O_2]}{dt} = k[H_2O_2]$

1. For a reaction involving only *one reactant*:

$$A \longrightarrow \text{Products}$$

The rate equation is: $r = k[A]^n$, where $n$ is the order of the reaction.

In a reaction with a rate equation, $r = k[A]$, the order of the reaction is *one*, i.e. $n = 1$; it is a *first order* reaction with respect to reactant A.

2. For a reaction involving *two reactants*:

$$A + B \longrightarrow \text{Products}$$

In a rate equation, $r = k[A][B]$, the rate depends on the concentrations of A and B. The order with respect to A is *one* and that of B is also *one*. The overall order of the reaction is 2 i.e. $n = 2$; it is a *second order* reaction.

3. Generally, for a *rate equation* $r = k[A]^a[B]^b$, the over-all order of the reaction, $n = a + b$.

## Effect of Concentration on Reaction Rates

1. Consider the rate equation: $r = k[A]^0$

The order of reaction, $n = 0$; it is *zero order*.

Since $[A]^0 = 1$, then, $r = k$.

It means: For a *zero order reaction*, the *rate is independent of the concentration of* A, [A] at any time. If [A] is doubled, tripled, or halved, the rate remains constant. Figure 19.14 shows the variation of rate with concentration for a *zero order* reaction.

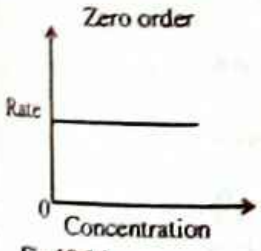



Fig 19.14

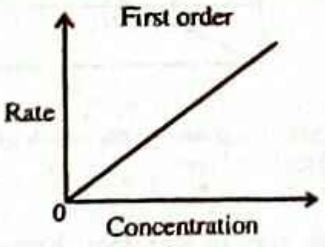



Fig 19.15

**Fig 19.14**: *Variation of rate with concentration for a zero order reaction*

**Fig 19.15**: *Variation of rate with concentration for a first order reaction*

2. Consider the rate equation: $r_1 = k[A]$.

It is a *first order reaction*; $n = 1$.

Consider the following variation of concentration of A, [A] at constant temperature:

a. If [A] is *doubled* to [2A] the new rate, $r_2$ becomes: $r_2 = k[2A] = 2k[A] = 2r_1$.

i.e. the initial rate, $r$ becomes *doubled*.

b. If [A] is *tripled*, the rate, $r$ becomes *tripled*; if [A] is *halved*, the rate, $r$ becomes *halved*, etc.

Hence, for a *first order reaction, rate is directly proportional to the initial concentration of the reactant*. Fig 19.15 shows the variation of *rate* with *concentration* for a *first order* reaction. It is a straight-line graph.

### *Half-life: A first order process*

The *half-life* of a chemical reaction is the time it takes *half* of the quantity of a reactant to be used up or converted into the product.

In a *first order reaction, the time it takes the initial quantity of the reactant to become a half is constant*. This is true of the *radioactive decay processes* (see Section 27.6).

3. Consider the rate equation: $r = k[A]^2$.

It is a *second order reaction*; rate is *directly* proportional to the *square* of concentration of A.

Consider the following variation of concentration of A at constant temperature:

a. If [A] is *doubled* to [2A] the new rate, $r_2$ is:

$$r_2 = k[2A]^2 = 2^2k[A]^2 = 2^2r = (2 \times 2)r = 4r$$

i.e. the initial rate $r$ becomes *doubled twice*, or the rate *increases* by a factor of 4, or it is *quadrupled*.

b. If [A] is tripled, the rate, $r$ becomes *tripled twice* $(3 \times 3)$, i.e rate *increases* by a factor of 9.

c. If [A] is reduced to a half, the rate, $r$ becomes *halved twice* $(\frac{1}{2} \times \frac{1}{2})$, i.e. rate *decreases* to a *quarter*, or *decreases* by a factor of 4.

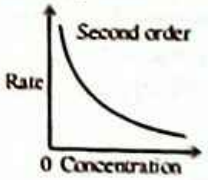



**Fig 19.16** *Variation of rate with concentration for a second order reaction.*

Figure 19.16 shows the variation of *rate* with *concentration* for a *second order* reaction; it is a curve. The variation is exponential.

4. Consider the rate equation, $r = k[A]^2[B]$

It is a *third order reaction*; $n = 2 + 1 = 3$.

Consider the following variations at constant temperatures:

a. If [A] is *doubled*, while [B] is constant, the rate, $r$ becomes *doubled twice*, since the reaction is *second order* with respect to A. i.e. *rate increases by a factor of 4*.

b. If [B] is *doubled* while [A] is held constant, the rate, $r$ becomes *doubled once*, since the reaction is *first order* with respect to B. i.e. rate *increases* by a factor of 2.

**Solved Problem**

15 The following data show the rates of reaction of nitrogen(II) oxide with chlorine at 25 °C.

| Exp. No. | Initial conc. of NO | Initial conc. of $Cl_2$ | Initial reaction rate |
|---|---|---|---|
| 1 | 0.01 | 0.01 | 0.001 |
| 2 | 0.01 | 0.02 | 0.001 |
| 3 | 0.02 | 0.02 | 0.004 |

a. Determine the order with respect to
i. NO and ii. $Cl_2$.

b. Write the rate law expression for the reaction.

a i. *To find the order of the reaction with respect to NO*: In experiments 2 and 3: When $[Cl_2]$ is kept constant and [NO] is doubled, reaction rate increases four-fold [(0.004)/(0.001) = 4], i.e. doubled *twice*.
Hence, the order of reaction with respect to NO is two.
i.e. rate, $r \propto [NO]^2$.

ii. *To find the order of the reaction with respect to $Cl_2$*: In experiments 1 and 2: When [NO] is kept constant and $[Cl_2]$ is doubled, reaction rate remains the same , i.e. constant. Hence, the order of reaction with respect to $Cl_2$ is zero. i.e. rate, $r \propto [Cl_2]^0$.

b. The overall rate equation is:
Rate, $r = k[NO]^2[Cl_2]^0 = k[NO]^2$

## Variation of Rate Constant with Temperature: Measurement of Activation Energy

The *activation energy*, $E_A$ for a reaction can be obtained from the variation of rate constant with temperature. According to the Arrhenius' equation or law:

$$\ln k = -E_A/RT + C$$

where $\ln k = 2.303 \log_{10} k$, $E_A$ = activation energy, $T$ = absolute temperature, $R$ = gas constant, and $C$ = a constant.

A plot of $\ln k$ against $1/T$, gives a straight line that has a slope $-E_A/R$ (see fig. 19.17).

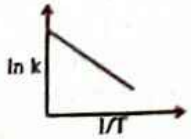



**Fig 19.17** *Variation of rate constant with temperature*

If $k_1$ and $k_2$ are the rate constants at two different Kelvin temperatures $T_1$ and $T_2$ respectively, it can be shown that:

$$\log_{10}\frac{k_2}{k_1} = \frac{E_A}{2.303R} \times \frac{(T_2 - T_1)}{T_1T_2}$$

**Revision Exercises**

29 Distinguish between the *order* and *molecularity* of a reaction.

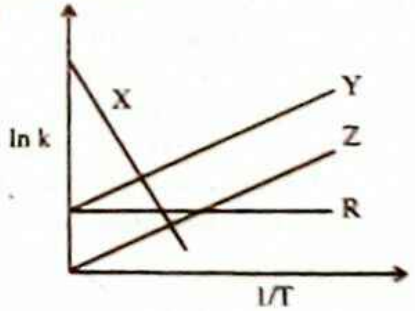
30 If the rate law obtained for a given reaction is rate = $k[X]^n[Y]^m$, what is the order of the reaction?
A. nm B. n/m C. n + m D. n – m [WAEC]

31 $2X_{(g)} + Y_{(g)} \rightarrow Z_{(g)}$
In the equation above, the rate of formation of Z is found to be independent of the concentration of Y and to quadruple when the concentration of X is doubled. The correct rate equation for the reaction is
A. $r = k[X][Y]$ B. $r = [X]^2[Y]$
C. $r = k[X]^0[Y]^0$ D. $r = k[X]^2[Y]^0$ [JAMB]

32 The following data show the rate of reaction of nitrogen (II) oxide with hydrogen at 600 K.

| Exp. | Initial [NO] (*mol dm$^{-3}$*) | Initial $[H_2]$ (*mol dm$^{-3}$*) | Initial rate (*mol dm$^{-3}$ s$^{-1}$*) |
|---|---|---|---|
| 1 | 0.004 | 0.001 | $2.0 \times 10^{-3}$ |
| 2 | 0.004 | 0.002 | $4.0 \times 10^{-3}$ |
| 3 | 0.001 | 0.004 | $0.5 \times 10^{-3}$ |
| 4 | 0.002 | 0.004 | $2.0 \times 10^{-3}$ |

a. What is the order of the reaction with respect to
i. NO; ii. $H_2$.
b. Write a rate equation for the reaction of NO and $H_2$.
c. Using the data from experiment 1, calculate the rate constant $k$.

33



In the diagram above, which of the curves illustrates Arrhenius' law.
A. X B. Y C. Z D. R [JAMB]

## Answers to Revision Exercises

5 $2.00 \times 10^{-5}$ mol dm$^{-3}$ s$^{-1}$ 13. D 16. C 18. C
20. D 23. C 24. B 30. C 31. D
32a i 2; ii 1; b. $r = k[NO]^2[H_2]$; c $1.25 \times 10^5$ 33. A

# 20

# •CHEMICAL EQUILIBRIUM•

## 20.1 Introduction

### Reversible Reactions

Studies have shown that some reactions are such that all the *reactants are never completely converted into products*. In such reactions, the *products, when formed, are converted into reactants*.

A reaction is said to be *reversible*, if it can be made to proceed forward and backward, under a given set of conditions.

Many *natural processes are reversible*:

1. Water *evaporates* from rivers, and seas, to form water vapour in the atmosphere, which on *condensation*, forms cloud, which eventually falls as rain.
2. Atmospheric oxygen is *produced* by *photosynthesis* in plants, while plants and animals *consume* oxygen during *respiration*.
3. In plants, nitrogen from the soil is *converted* into proteins, and when plants die and decay, the proteins are *converted* into nitrogen again.

For reaction involving a gas to be *reversible*, it is carried out in a *closed vessel*, i.e. an *isolated* or *closed* system. In a chemical or physical process, *opposing arrows* represent a reversible reaction:

- $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$

**Revision Exercises**

1. When is a reaction said to be reversible?
2. A reversible reaction is usually carried out
   A. at a high temperature.
   B. at low pressure. C. in a closed vessel.
   D. in the presence of a catalyst.

## 20.2 Reactions at Equilibrium

### Dynamic Equilibrium

Figure 20.1 shows the variation of concentrations of reactants and products with time. *When the rates of forward and backward reactions in a reversible reaction are equal, the reaction is said to be at equilibrium.*

At equilibrium, both the forward and backward reactions are still going on, but because their rates are the same, the concentrations of the reactants and products no longer change with time – as shown by the parallel lines AB and CD in figure 20.1. Hence, chemical equilibrium is *dynamic; not static*. At equilibrium, both the reactants and products are present in the system.

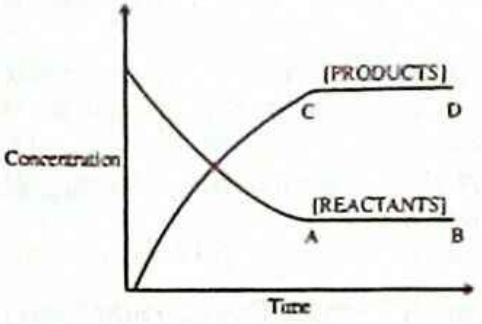



**Fig 20.1** *Variation of concentration with time*

### How to Identify a Reaction at Equilibrium

At equilibrium, certain observable properties become constant depending on the type of reaction. Such properties include:

- Concentrations of the reactants and products;
- Pressure of gases;
- Density or intensity of colour of a solution;
- Temperature of the system.

**Examples:**

1. When water is in equilibrium with its vapour, the *saturated vapour pressure* becomes constant.
2. At *boiling point*, a *liquid* is in equilibrium with its *vapour* at constant temperature:

   Liquid $\rightleftharpoons$ Vapour

3. At *melting point*, a *solid* is in equilibrium with its *liquid*; the temperature remains constant:

   Solid $\rightleftharpoons$ Liquid

4. In a *saturated solution, the undissolved solute is in equilibrium with the solution*:

   Solid + Water $\rightleftharpoons$ Solution

### Properties of systems at equilibrium

1. The equilibrium is dynamic; that is,
• The reactants and products are present at equilibrium, i.e. equilibrium can be achieved from either direction:

• $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

• $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$

2. The concentrations of the reactants and products, pressure, density or intensity of colour, and the temperature of the system are constant – depending on the type of the reaction.
3. The rates of forward and backward reactions are equal.
4. The equilibrium position is not affected by the presence of a catalyst; it only quickens the rate at which equilibrium is achieved.
5. At equilibrium, the *free energy change*, $\Delta G$, of the reaction is *zero*.
6. A system at equilibrium will resist a change.

### Information from an Equilibrium Equation

The following information can be obtained from an equation of a typical reversible reaction:

$$N_{2(g)} + 3H_{2g} \rightleftharpoons 2NH_{3(g)} \quad \Delta H = -92.0 \text{ kJ}$$

1. The two opposing reactions are occurring at the same time – as indicated by the opposing arrows.
2. The two opposing reactions are at equilibrium.
3. The amounts, in moles, of the reactants and products at equilibrium are proportional to the stoichiometry in the balanced equation.
4. The forward reaction is *exothermic* ($\Delta H$ is -ve); hence, the backward (or reverse) reaction will be *endothermic* ($\Delta H$ is +ve), i.e.

$$2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)} \quad \Delta H = +92.0 \text{ kJ}$$

### Limitations of an Equilibrium Equation

An equilibrium equation does not provide the following information in respect of the reaction:
1. The time taken for equilibrium to be achieved.
2. The concentrations of the reactants and products at equilibrium.
3. The mechanism of the reaction.

### Solved Problem

**1. What is meant by an equilibrium system?** [NECO]

*A system in which the rates of forward and backward processes or reactions are equal.*

### Revision Exercises

**3. State whether the following processes are reversible or irreversible:**
a. Burning of sulphur in air.
b. Heating an iron rod to red hot.
c. Sublimation of ammonium chloride.
d. Digestion of starch. e. Evaporation of water.

4. Give three properties of a chemical system in a state of equilibrium. [WAEC]

5. Dynamic equilibrium describes a situation where
A. a reaction gives back the reactants.
B. reactants are converted to products.
C. the concentrations of reactants and products are equal.
D. both the forward and reverse reactions proceed at the same rate. [JAMB]

6. $NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$
The reaction above can only attain equilibrium if
A. it is in an open system
B. it is in a closed system
C. a gaseous reactant is added
D. one of the products is removed. [JAMB]

## 20.3 Equilibrium Constants

### Equilibrium Constant, $K_C$

### Equilibrium Law

Like the *rate law*, the *equilibrium law* is based on the *law of mass action*, which states that:
*The rate at which a reaction proceeds is directly proportional to the concentrations of the active species in the system.*
Consider a reversible reaction:

$$A + B \rightleftharpoons C + D$$

The rate of forward reaction, $r_f$ is:

$$r_f = k_f[A][B] \quad \ldots 1$$

Similarly, the rate of backward reaction, $r_b$ is:

$$r_b = k_b[C][D] \quad \ldots 2$$

where $k_f$ and $k_b$ are the rate constants for the *forward* and *reverse* reactions respectively.
At equilibrium, the rates of forward and backward reactions are equal, i.e. $r_f = r_b$
Hence, $k_f[A][B] = k_b[C][D]$ ...3
On rearranging, equation 3 becomes:

$$\frac{k_f}{k_b} = \frac{[A][B]}{[C][D]} = K_c \quad \ldots 4$$

The ratio $k_f/k_b$ is a constant; it is called *equilibrium constant*, $K_C$, *when concentration terms are used*. Hence, $K_C$ *is the ratio of the forward and reverse rate constants.*
Generally, the equilibrium constant, $K_C$ is the *ratio* of the concentrations of products and reactants at equilibrium, at a given temperature:

$$K_C = \frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]} \quad \ldots 5$$

The expression in 5 is called *equilibrium law*.

**General Equilibrium Equation**

Consider a general reaction in solution:

$$mA_{(aq)} + nB_{(aq)} \rightleftharpoons xC_{(aq)} + yD_{(aq)}$$

where $m$, $n$, $x$ and $y$ are the coefficients in the balanced equation of reaction.

$$K_C = \frac{[C]^x[D]^y}{[A]^m[B]^n}$$

For instance, in the reaction:

$$N_{2(g)} + 3H_{2g} \rightleftharpoons 2NH_{3(g}$$

Applying the equilibrium law:

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

In any equilibrium system in which a solid, or a pure liquid solvent is a reactant or product – as in heterogeneous reactions, the *active mass* of a solid or a pure liquid is assumed to be *unity* and *constant* at a given temperature, e.g.

1. In the decomposition reaction:

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

At equilibrium, the equilibrium law is:

$$K_C = \frac{[CaO_{(s)}][CO_{2(g)}]}{[CaCO_{3(s)}]}$$

Since $CaCO_3$ and CaO are solids, then,

$[CaCO_3(s)] = [CaO(s)] = 1.$

$\therefore \quad K_C = [CO_2(g)]$

2. In an esterification reaction:

$$\text{Acid} + \text{Alcohol} \rightleftharpoons \text{Ester} + \text{Water}$$

Applying the equilibrium law, $[H_2O] = 1$:

$$K_C = \frac{[ESTER]}{[ACID][ALCOHOL]}$$

Hence, it is important to include the physical state symbols of the reactants and products in any equilibrium equation.

**Magnitude of Equilibrium constant, $K_C$**

The following statements are true of the value of $K_C$.

1. The value of $K_C$ is constant at a given temperature.

2. Its value does not depend on the initial concentrations of reactants or products, but depends only on the equilibrium concentrations, which can only be determined experimentally.

3. If $K_C$ is greater than 1 (unity), then, a large amount of products is present in the system at equilibrium, that is, a large amount of reactants has been converted into products before equilibrium is achieved:

$$[\text{Products}] >> [\text{Reactants}]$$

4. If the $K_C$ is less than 1 (unity), it means only a small amount of the reactants has been converted into products before equilibrium is established;

$$[\text{Products}] << [\text{Reactants}]$$

**Equilibrium Constant, $K_P$**

When the *partial pressures, p of gaseous reactants and products are considered at equilibrium*, the equilibrium law for the reaction:

$$\underset{1\text{ vol.}}{N_{2(g)}} + \underset{3\text{ vol.}}{3H_{2g}} \rightleftharpoons \underset{2\text{ vol.}}{2NH_{3g}}$$

$$K_P = \frac{p^2(NH_3)}{p(N_2) \times p^3(H_2)}$$

**Solved Problems**

**2.** Consider the following reaction:

$$A_{2(g)} + 3B_{2(g)} \rightleftharpoons 2AB_{3(g)}$$

Write an expression for the equilibrium constant, $K_C$ for the reaction.

**Solution**

*Applying the equilibrium law:*

$$K_C = \frac{[AB_3]^2}{[A_2][B_2]^3}$$

**3.** Write an expression in terms of partial pressures, for the equilibrium constant for the following:

$$Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_{4(s)} + 4H_2(g)$$

**Solution** $K_P = p(H_2)^4/p(H_2O)^4$

**Equilibrium Constants for the Forward and Backward Reactions**

There is a simple relationship between the equilibrium constants for the forward and backward reactions. Consider a reaction at equilibrium:

$$A \rightleftharpoons B + C$$

The equilibrium expression for the forward reaction is:

$$K_f = \frac{[B][C]}{[A]}$$

If the equilibrium is approached in the reverse direction, the equilibrium expression becomes:

$$K_b = \frac{[A]}{[B][C]}$$

A careful observation shows that $K_b$ is the reciprocal of $K_f$, i.e. $K_b = 1/K_f$. Hence, the product of the to equilibrium constants is unity, i.e.

$$K_f \times K_b = \frac{[B][C]}{[A]} \times \frac{[A]}{[B][C]} = 1$$

**Revision Exercises**

7. Derive a simple expression for the equilibrium constant $K_C$ for the reversible reaction:

$$aA + bB \rightleftharpoons cC + dD$$

8. Write an expression for the equilibrium constant $K_C$ for each of the following reactions:

a. $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ $\quad K_P =$

b. $2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$

9. Write an expression in terms of partial pressures, for the equilibrium constant for each of the following reactions:

a. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

c. $X_{2(g)} + 2Y_{2(g)} \rightleftharpoons 2XY_{2(g)}$

10a State the relationship between the equilibrium constants for the forward and backward reactions.

b When equimolar quantities of hydrogen and iodine were heated together at about 500 °C the system at equilibrium was found to contain 0.20 moldm$^{-3}$ of hydrogen, 0.20 moldm$^{-3}$ iodine and 1.40 moldm$^{-3}$ of hydrogen iodide. Calculate the equilibrium constant, at this temperature for the reaction:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

## Relationship between $K_C$ and $K_P$

Consider a general gaseous equilibrium equation:

$$mA_{(g)} + nB_{(g)} \rightleftharpoons xC_{(g)} + yD_{(g)}$$

where $m$, $n$, $x$ and $y$ are the coefficients in the balanced equation of reaction.

For reactions involving ideal gases, it can be shown that at equilibrium:

$$K_P = K_C\,(RT)^{(x+y)-(m+n)}$$

or, $$K_P = K_C\,(RT)^{\Delta n}$$

where **T** is the absolute temperature, **R** is the gas constant, while

$\Delta n$ = (amount, in moles, of gaseous products) – (amount, in moles, of gaseous reactants)

The value of $\Delta n$ can be positive, negative, or zero:

1. $\Delta n$ is *positive* when the amount of gaseous products is more than the amount of gaseous reactants:

a. $\underset{2\text{ mol}}{2NH_{3(g)}} \rightleftharpoons \underset{1\text{ mol}}{N_{2(g)}} + \underset{3\text{ mol}}{3H_{2(g)}}$

$\Delta n = (1 + 3) - 2 = 4 - 2 = 2$

$\therefore K_P = K_C(RT)^2$

b. $\underset{0\text{ mol}}{CaCO_{3(s)}} \rightleftharpoons \underset{0\text{ mol}}{CaO_{(s)}} + \underset{1\text{ mol}}{CO_{2(g)}}$

$\Delta n = (0 + 1) - 0 = 1 - 0 = 1.$

$\therefore K_P = K_C\,(RT)^1 = K_CRT$

2. $\Delta n$ is *negative* when the amount of gaseous products is less than the amount of gaseous reactants:

a. $\underset{2\text{ mol}}{2SO_{2(g)}} + \underset{1\text{ mol}}{O_{2(g)}} \rightleftharpoons \underset{2\text{ mol}}{2SO_{3(g)}}$

$\Delta n = 2 - (2 + 1) = 2 - 3 = -1$

$\therefore K_P = K_C\,(RT)^{-1} = K_C/(RT)$

b. $\underset{1\text{ mol}}{N_{2(g)}} + \underset{3\text{ mol}}{3H_{2(g)}} \rightleftharpoons \underset{2\text{ mol}}{2NH_{3(g)}}$

$\Delta n = 2 - (1 + 3) = 2 - 4 = -2$

$K_P = K_C(RT)^{-2} = K_C/(RT)^2$

3. $\Delta n$ is *zero* when the amounts of gaseous products and gaseous reactants are equal, e.g.:

a. $\underset{1\text{ mol}}{H_{2(g)}} + \underset{1\text{ mol}}{I_{2(g)}} \rightleftharpoons \underset{2\text{ mol}}{2HI(g)}$

$\Delta n = (1 + 1) - 2 = 2 - 2 = 0.$

b. $\underset{1\text{ mol}}{CO_{(g)}} + \underset{1\text{ mol}}{H_2O_{(g)}} \rightleftharpoons \underset{1\text{ mol}}{CO_{2(g)}} + \underset{1\text{ mol}}{H_{2(g)}}$

$\Delta n = (1 + 1) - (1 - 1) = 2 - 2 = 0$

$\therefore K_P = K_C(RT)^\circ = K_C$

Hence, when $\Delta n = 0$, $K_P = K_C$.

### Units of $K_C$ and $K_P$

$K_C$ or $K_P$ has no unit when the amounts of gaseous products and gaseous reactants are equal.

i.e. $\Delta n = 0$.

But when $\Delta n$ is not zero, the units of $K_C$ and $K_P$ will be $[moldm^{-3}]^{\Delta n}$ and $[kNm^{-2}]^{\Delta n}$ respectively.

### Solved Problem

4. Deduce the relationship between $K_P$ and $K_C$ for the gaseous equilibrium reaction

$$A_{2(g)} + 3B_{2(g)} \rightleftharpoons 2AB_{3(g)}$$

*From the equation of reaction:*

$\underset{1\text{ mol}}{A_{2(g)}} + \underset{3\text{ mol}}{3B_{2(g)}} \rightleftharpoons \underset{2\text{ mol}}{2AB_{3(g)}}$

$\Delta n = 2 - (1 + 3) = 2 - 4 = -2$

*But* $K_P = K_C\,(RT)^{\Delta n}$

$\therefore K_P = K_C(RT)^{-2}$ *or* $K_C = K_P(RT)^2$

**b.** What is the unit of $K_C$ for the reaction?

*The unit of* $K_C = (moldm^{-3})^{\Delta n}$ *Since* $\Delta n = -2$

$\therefore$ *Unit of* $K_C = (moldm^{-3})^{-2}$ $= mol^{-2}dm^6$.

## Equilibrium Constant and Free Energy

For a reaction to be spontaneous, the Gibb's free energy change, $\Delta G$, must be negative: $\Delta G < 0$. However, when a reaction is at equilibrium, the *free energy change*, $\Delta G$ is *zero*; i.e. $\Delta G = 0$. Under this condition, $\Delta H = T\Delta S$.

The quantitative relationship between the free energy change at any temperature, $\Delta G$, the free energy change at standard states, $\Delta G^\circ$, and the

equilibrium constant, K, at a given temperature T is given by the expression:

$$\Delta G = \Delta G^\circ + 2.303RT\log_{10}K$$

where R is the universal gas constant.

At equilibrium, $\Delta G = 0$.

Hence, $\Delta G^\circ = -2.303RT\log_{10}K$.

The value of K under this condition is called the *thermodynamic equilibrium constant.*

**Revision Exercises**

11 State the equilibrium position of a reaction when change in free energy is zero. [NECO]

12 A reaction is said to be at equilibrium if

A. $\Delta G$ is equal to $\Delta H$. **B.** $\Delta G$ is greater than $\Delta H$.
C. $\Delta G$ is less than $\Delta H$. **D.** $\Delta H$ is equal to $T\Delta S$.
E. $\Delta H$ is less than $T\Delta S$. [NECO]

13 The equilibrium constant for a certain system is 50 at 25 °C. Calculate the free energy change for the system.

## 20.4 Changes Affecting the States of Equilibrium

The *three* major changes or factors that affect the position or state of equilibrium of a system are:

1. Changes in concentrations of reactants or products.
2. Changes in pressure on the system
3. Changes in temperature of the system.

### Alteration of Equilibrium Position: *Le Chatelier's Principle*

A French chemist, Henry Le Chartelier, studied how changes in concentration, pressure, temperature, presence of catalyst, and addition of a noble gas into a reaction at equilibrium affect the equilibrium positions.

The results of his studies gave rise to a generalization known as *Le Chatelier's Principle*. It states:

*When a system in equilibrium is subjected to a change in concentration, pressure or temperature, the equilibrium position shifts or adjusts itself, in order to oppose the change.*

It can be stated in another way:

*If a system at equilibrium is disturbed, the system adjusts itself, in order to restore the equilibrium.*

### *Applications of Le Chatelier's Principle to Systems at Equilibrium*

### 1. Effect of Change in Concentration

Consider a chemical reaction at equilibrium:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Hydrogen gas reacts with iodine gas to produce hydrogen iodide gas. At the same time, hydrogen iodide decomposes to produce gaseous hydrogen and iodine.

Addition of one of the reactants, say, hydrogen, to the system will disturb the equilibrium position. According to Le Chatelier's Principle, the system will adjust itself, in order to restore the equilibrium. To restore the equilibrium, *iodine reacts with part of the hydrogen added, to produce more hydrogen iodide*. The overall effect is to shift the equilibrium position to the right, i.e. in favour of the product.

If the product, i.e. hydrogen iodide, is added at equilibrium, part of it must decompose to produce more hydrogen and iodine, in order to restore the equilibrium position, i.e. in favour of the reactants.

***Mathematical consideration:***

Consider an equilibrium system such as:

$$A \rightleftharpoons B + C$$

The equilibrium constant $K_C$ is:

$$K_C = \frac{[B][C]}{[A]}$$

If [A] is increased at equilibrium, $K_C$ decreases at the given temperature. For $K_C$ to remain constant, [B] or [C] must increase, i.e. the forward reaction is favoured by increasing [A]. The opposite effect occurs, if either [B] or [C] is added at equilibrium.

Generally, in an equilibrium system, an *increase* in the concentration of a reactant (by adding more) or, a *decrease* in the concentration of a product (by removal as it is being formed) *shifts the equilibrium position in favour of the formation of more products.*

Conversely, in an equilibrium system, a *decrease* in the concentration of a reactant (by removal) or the *addition* of more products, *shifts the equilibrium in favour of the formation of more reactants.*

**Industrial Application**

In the industry, a large excess of the reactants is used, and the products are removal as they are being formed, in order to favour the forward reaction, and obtain a high yield of the products.

**Solved Problems**

**5.** The reaction of a compound *HIn* in water is represented by the following equation:

$$\underset{\text{(colourless)}}{HIn_{(aq)}} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \underset{\text{(red)}}{In^-_{(aq)}}$$

Explain why the compound is colourless in acid solution.

*In an acid solution, the increase in the concentration of $H_3O^+$ favours the backward reaction. Hence, the compound is colourless in acid solution.*

6. When few drops of aqueous KSCN are added to a solution of iron(III) salt, the following equilibrium is set up:

$$\underset{\text{(yellow)}}{Fe^{3+}_{(aq)}} + \underset{\text{(colourless)}}{3SCN^-_{(aq)}} \rightleftharpoons \underset{\text{(deep red)}}{Fe(SCN)_{3(aq)}}$$

a. Explain what happen if more $KSCN_{(aq)}$ were added to the equilibrium mixture.

*Addition of $KSCN_{(aq)}$ at equilibrium increases the concentration of $SCN^-_{(aq)}$, which favours the forward reaction, and hence, intensify the deep red colour.*

b. Which of the ions in the equilibrium mixture forms an insoluble hydroxide with NaOH(aq)?

*Iron(III) ions ($Fe^{3+}$).*

c. State two changes observed on adding $NaOH_{(aq)}$ to the equilibrium mixture. [WAEC]

- *A yellow solution is formed.*
- *A brown precipitate is deposited.*

7. When $K_2Cr_2O_7$ dissolves in water, the following equilibrium is established:

$$\underset{\text{(Orange)}}{Cr_2O_7^{2-}_{(aq)}} + H_2O \rightleftharpoons \underset{\text{(Yellow)}}{2CrO_4^{2-}_{(aq)}} + 2H^+_{(aq)}$$

a. State the colour observed on adding a few drops of dilute $H_2SO_4$ to the system. *Orange*

b. Explain your answer in a above.

*Addition of dilute $H_2SO_4$ to the system at equilibrium increases the hydrogen ion concentration, which shifts the equilibrium position to the left, and intensifies the orange colour of $Cr_2O_7^{2-}$.*

## 2. Effect of Pressure Change

Pressure change affects only *gaseous reactants and products*; it has *no effect on a solid or a liquid* in an equilibrium system.

There are two cases:

**Case I:** ***Amount (or volume) of gaseous reactants is not equal to the amount (or volume) of gaseous products, i.e. there is a change in volume***

Consider the production of ammonia by Haber process. It is a reversible reaction:

$$\underset{\text{(1 vol.)}}{N_2(g)} + \underset{\text{(3 vol.)}}{3H_2(g)} \rightleftharpoons \underset{\text{(2 vol.)}}{2NH_3(g)}$$

Volume of gaseous reactants = (1 + 3) = 4 volumes
Volume of gaseous products = 2 volumes.

In the above reaction, a *decrease in volume* accompanies the forward reaction, which leads to the formation of ammonia, while an *increase in volume* accompanies the backward reaction, which is the decomposition of ammonia.

According to the Boyle's law, an *increase in pressure* on a gas at constant temperature, leads to a *decrease in volume*, and vice versa. An *increase in pressure* on the above system disturbs the equilibrium. Applying the Le Chatelier's principle, the system will adjust itself by opposing the increase in pressure. To achieve this, the equilibrium position moves in the direction accompanied by a *decrease in volume*.

Generally, an *increase in pressure* on a system in equilibrium shifts the equilibrium position in favour of the side with *smaller volume (or amount) of gas*. Conversely, a *decrease in pressure* shifts the equilibrium position in favour of the side with *larger volume of gas*.

**Case II:** ***Amount (or volume) of gaseous reactants equals amount (or volume) of gaseous products, i.e. no change in volume***

Consider the following reversible reactions:

a. $$\underset{\text{1 vol.}}{H_2(g)} + \underset{\text{1 vol.}}{I_2(g)} \rightleftharpoons \underset{\text{2 vol.}}{2HI(g)}$$

b. $$Fe(s) + \underset{\text{4 vol.}}{4H_2O(g)} \rightleftharpoons Fe_3O_4(s) + \underset{\text{4 vol.}}{4H_2(g)}$$

In any equilibrium system in which the *volume of gaseous reactants is the same as the volume of gaseous products, change in pressure has no effect on the equilibrium position.* However, the *rate at which equilibrium is achieved is faster at higher pressures.*

### Solved Problems

8. Explain how the equilibrium position is affected by a change in pressure in the following reaction:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

**Solution**

$$\underset{\text{1 vol.}}{N_2O_4(g)} \rightleftharpoons \underset{\text{2 vol.}}{2NO_2(g)}$$

*An increase in pressure shifts the equilibrium position to the left, since the volume of gaseous reactants is less than that of the products, while a decrease in pressure shifts the equilibrium position to the right, since the volume of gaseous products is more than that of the reactants.*

9. State the effect of increase in pressure on the equilibrium position of each of the following reactions:

a. $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$

b. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

c. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

a. The equilibrium position shifts to the right.
b. The equilibrium position is not affected.
c. The equilibrium position shifts to the left.

(g) The equilibrium of an endothermic reaction, which proceeds with an increase in volume can be shifted in the reverse direction by

A. increasing the temperature and decreasing the pressure.
B. increasing the pressure and increasing the temperature.
C. decreasing the temperature and increasing the pressure.
D. decreasing the pressure and decreasing the temperature.

Solution: C. [$X(g) \rightleftharpoons C(g) + D(g)$ ; $\Delta H$ = +ve] *[backward reaction is exothermic and accompanied by increase in volume.]*

## 3. Effect of Temperature Change

In any reversible reaction in which the forward reaction is exothermic ($\Delta H$ is -ve), the backward reaction will be endothermic ($\Delta H$ is +ve). However, the magnitude of $\Delta H$ will be equal, e.g.

a. Consider an equilibrium system such as:

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)} ; \quad \Delta H = -774 \text{ kJ}.$$

The forward reaction, which leads to the formation of hydrogen chloride is *exothermic*, while the backward reaction, which leads to the decomposition of hydrogen chloride is *endothermic*.

If at equilibrium, the temperature of the system is raised, the system adjusts itself by *absorbing the heat*. Under this situation, the backward reaction that *absorbs heat* is favoured. Conversely, if at equilibrium, the temperature of the system is *lowered*, the system adjusts itself by *releasing heat*. Under this situation, the forward reaction that releases heat is favoured.

b. Consider a gaseous equilibrium system in a sealed glass tube:

$$\underset{\text{(pale yellow)}}{N_2O_4(g)} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} \underset{\text{(dark brown)}}{2NO_2(g)}$$

At room temperature, the colour of the mixture at equilibrium is *light brown*.

At *high* temperature (*on warming*), the colour turns *dark brown*, because the equilibrium *position favours the formation of product, $NO_2$ (endothermic direction)*.

*At low temperature (on cooling), the colour turns pale yellow, since the equilibrium position is now displaced towards the reactant, $N_2O_4$ (exothermic direction).*

Generally, an *increase* in temperature on a system at equilibrium causes the equilibrium to shift in favour of an *endothermic reaction*, which *absorbs heat*, while a *decrease* in temperature favours an *exothermic reaction*, which *liberates heat*, in order to restore equilibrium.

### Industrial Application

In the industry, an *endothermic* process is carried out at a *high* temperature, in order to obtain a high yield of the products. For an *exothermic* process, a *low* temperature favours a high yield of product. But because *working at a low temperature leads to a low rate of production, an optimum temperature in the presence of a catalyst is usually employed.*

## Effect of temperature change on equilibrium constants

At a constant temperature, the equilibrium constant, $K_c$ or $K_p$ remains constant and is not affected by changes in concentration or pressure. However, *for an endothermic process, an increase in temperature increases the equilibrium constant*, and vice versa, while *for an exothermic reaction, an increase in temperature decreases the equilibrium constant*, and vice versa.

### Solved Problems

**11** In the equilibrium reaction, $A \rightleftharpoons C + D$, more of C and D are produced when temperature is increased. Which of the following statements is a correct deduction? The reaction

A. is exothermic in the forward direction.
B. is endothermic in the forward direction.
C. does not require catalyst.
D. has low activation energy. [WAEC]

**Solution: *B***

**12** Which of the following conditions favours the *reverse reaction* in a system represented by the equation below?

$X_2(g) + 2Y_2(g) \rightleftharpoons 2XY_2(g)$ ; $\Delta H = -x$ kJmol$^{-1}$

A. Low temperature. B. High pressure.
C. Removal of $XY_2$ D. Removal of $X_2$ [WAEC]

**Solution: *D***

**13** State the effect of each of the following on the equilibrium position of the system indicated:

$A(s) + B(g) \rightleftharpoons C(g)$ ; $\Delta H = -x$ kJmol$^{-1}$

a. Cooling the system.

*At low temperature, the equilibrium position shifts forward, in favour of the formation of C.*

b. Removing C as soon as it is formed.
*The equilibrium position shifts forward, in favour of the formation of C.*

**14** Which of the following changes will have **no effect** on the equilibrium position of the reaction below?

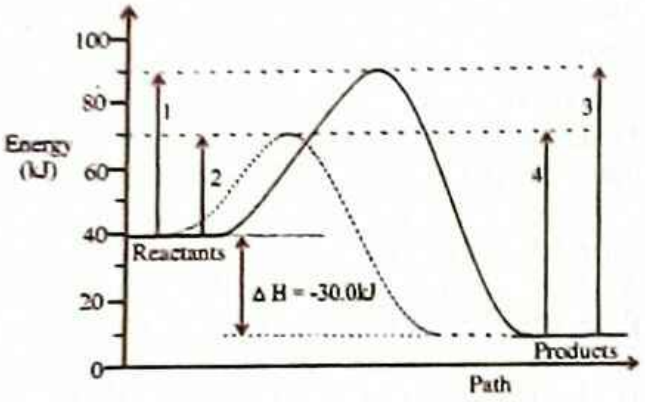
$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$; $\Delta H = -41$ kJ

A. Increase in temperature.
B. Increase in the concentration of CO
C. Removal of $CO_2$ from the mixture.
D. Decrease in pressure. [WAEC]

**Solution:** *D*

### 4. Addition of a Catalyst

The presence of a catalyst in a reversible reaction has *no effect* on the equilibrium position (or equilibrium constant). This is because the rates of forward and backward reactions are increased equally and simultaneously, that is, the activation energies of the forward and backward reactions are lowered by the same amount (see figure 20.2). The *catalyst only shortens the time for attainment of equilibrium.*




1 = Activation energy for the non-catalyzed forward reaction.
2 = Activation energy for the catalyzed forward reaction.
3 = Activation energy for the non-catalyzed backward reaction
4 = Activation energy for the catalyzed backward reaction.

**Fig 20.2** *Effect of catalyst in an equilibrium system*

**Solved Problems**

**15** Consider the following equation:

$H_2S_{(g)} + M^{2+}_{(aq)} \rightleftharpoons MS_{(s)} + 2H^+_{(aq)}$; $\Delta H = -x$ kJ

State and explain the effect of each of the following on the equilibrium position:

a. Increase in temperature;
*An increase in temperature shifts the equilibrium position to the left, because the reverse reaction is endothermic.*

b. Addition of solution of $M(NO_3)_2$;
*The equilibrium position shifts to the right, because there is an increase in the concentration of $M^{2+}$ ions, which favours the formation of more products.*

c. Addition of acidified $KMnO_{4(aq)}$.
*The equilibrium position shifts to the left, because $KMnO_{4(aq)}$ reacts with $H_2S$, thereby decreasing its concentration, which favours the backward reaction.*

**16** Which of the following statements about catalysts in reversible reactions is correct? They
A. have no effect on the activation energy.
B. alter equilibrium position.
C. lower the value of heat energy.
D. affect the forward and reverse reaction rates equally. [WAEC]

**Solution:** *D*

**17** Which of the following is **false** about an equilibrium reaction represented as shown below?

$P + Q \rightleftharpoons R + S$; $\Delta H = -x$ kJmol$^{-1}$

A. Increase in temperature favours the reverse reaction.
B. Addition of a catalyst favours only the forward reaction
C. The reactants and products are present in the equilibrium mixture.
D. The forward and reverse reactions proceed at the same rate.

**Solution:** *B*

### 5. Addition of a Noble Gas

When a noble or an inert gas is introduced into a system at equilibrium, only the total pressure of the system is increased. The addition does not affect the equilibrium position, since the partial pressures or the concentrations of the gases in the system are not affected.

**Solved Problems**

**18** Consider the reaction represented by the equation:

$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$; $\Delta H = +57.2$ kJ mol$^{-1}$

a. When is the reaction said to be at equilibrium?
*The reaction is at equilibrium when the rates of forward and backward reactions are equal.*

b. Mention two conditions that can favour the forward reaction. *(Any two of the following)*
- *High temperature;*
- *Low pressure;*
- *Large excess of $N_2O_{4(g)}$.*
- *Removal of $NO_{2(g)}$ as it is being formed.*

c. Name the principle involved in b above.
*Le Chatelier's principle*

19 Consider the following reaction at 900 K:

$2AB_{3(g)} + B_{2(g)} \rightleftharpoons 2AB_{3(g)}$ ; $\Delta H = -198$ kJ

a. Write an expression for the equilibrium constant, $K_p$ for the reaction.

$$K_p = \frac{[AB_3]^2}{[AB_2]^2[B_2]}$$

b. Will $K_p$ at 300 K be greater than, less than, or equal to $K_p$ at 900 K? Explain.

*$K_p$ at 300 K will be greater than $K_p$ at 900 K. The reaction above is exothermic; a decrease in temperature favours the forward reaction.*

c. How will the equilibrium be affected if the volume of the vessel containing $AB_2$, $B_2$ and $AB_3$ is reduced, keeping the temperature constant?

*Reduction in volume of the vessel at constant temperature means an increase in pressure on the system. Therefore, the equilibrium position moves in favour of the formation of more products, $AB_3$, since it has a smaller volume.*

d. What is the effect of adding one mole of helium gas to the vessel containing $AB_2$, $B_2$ and $AB_3$ at equilibrium at constant temperature?

*Addition of helium gas at equilibrium will not affect the equilibrium position, since the partial pressures of $AB_2$, $B_2$ and $AB_3$ will not be affected.*

### Revision Exercises

14 List three factors that affect chemical equilibrium.

15 State Le Chatelier's principle. [NECO]

16 Consider the equilibrium system represented by the following equation:

$Cu^{2+}_{(aq)}$ (light blue) $+ 4NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)}$ (deep blue)

The deep blue colour will fade on adding

A. $Cu^{2+}_{(aq)}$ B. $H_2SO_{4(aq)}$

C. $NH_{3(aq)}$ D. $NaCl_{(aq)}$ [WAEC]

17 State the effect of the addition of few drops of dilute tetraoxosulphate(VI) acid on the equilibrium position of the following systems:

a i. $Cr_2O_7^{2-}{}_{(aq)} + H_2O \rightleftharpoons 2CrO_4^{2-}{}_{(aq)} + 2H^+_{(aq)}$

ii. $Cu^{2+}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)}$

b Give the reason for your answer in **a i** or **a ii** above.

18 A white precipitate of BiOCl was formed during the following reaction:

$BiCl_{3(aq)} + H_2O_{(l)} \rightleftharpoons BiOCl_{(s)} + 2HCl_{(aq)}$

The $BiOCl_{(s)}$ precipitate will disappear on adding drops of A. $H_2O_{(l)}$ B. $HCl_{(aq)}$

C. $NH_{3(aq)}$ D. $NaOH_{(aq)}$ [WAEC]

19 Consider the following equilibrium reaction:

$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

Which of the following conditions will affect the equilibrium position as well as the value of the equilibrium constant? [JAMB]

A. Decrease in concentration B. Increase in pressure

C. Increase in temperature D. Addition of a catalyst

20 In which of the following reactions would you expect the product(s) to be more stable at high pressures?

A. $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

B. $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

C. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

D. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

21 State the effect of catalyst on the position of equilibrium. [WAEC]

22 Consider the following equilibrium reaction:

$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ ; $\Delta H = +x\ kJmol^{-1}$

a Write an expression for the equilibrium constant $K_c$.

b What would happen to the equilibrium position when the

i. pressure of the system is reduced;

ii. temperature of the system is increased;

iii. concentration of the reactant is increased. [WAEC]

## 20.5 Industrial Applications of Le Chatelier's Principle

In the industry, all the factors affecting equilibrium positions are taken into consideration, in order to obtain a high yield of the product within a short time.

### 1. Manufacture of ammonia

In the Haber process:

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $\Delta H = -92.0$ kJ

1 vol. 3 vol. 2 vol.

The following factors and conditions are considered in order to obtain a high yield of ammonia:

**a.** The reactants (nitrogen and hydrogen) are used in large excess, and the ammonia produced is removed as it is being formed, in order to favour the production of more ammonia.

**b.** The reaction is gaseous. The forward reaction is accompanied by a decrease in volume of gas in the system. Hence, a *high* pressure is employed, to ensure a high yield of ammonia.

**c.** The forward reaction is exothermic; hence, a *low* temperature favours a high yield of ammonia. However, at low temperature, the rate of production of ammonia will be slow; hence, conditions of optimum temperature of about 450 °C, and finely divided iron as catalyst are employed.

## 2. Manufacture of Nitrogen(II) oxide

The reaction at equilibrium is:

$$\underset{1\text{ mol}}{N_{2(g)}} + \underset{1\text{ mol}}{O_{2(g)}} \rightleftharpoons \underset{2\text{ mol}}{2NO_{(g)}} \; ; \; \Delta H = +180\text{ kJ}$$

The following conditions favour the production of nitrogen(II) oxide:

**a.** A large excess of nitrogen or oxygen is used.

**b.** The forward reaction is exothermic; a high temperature is required.

**c.** There is no difference in the amount (or volume) of gaseous reactants and products; hence, pressure has no effect. However, an optimum pressure is required, in order to quicken the production of NO.

### Solved Problem

**20** Consider the reaction represented by the equation:

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \; ; \; \Delta H = +58.2\text{ kJ}$$

**a.** State what happens to the vapour density of $N_2O_4$ as the temperature of the system is increased.

*An increase in temperature at equilibrium decomposes $N_2O_4$ (V.D. = 46) to $NO_2$ (V.D. = 23); hence, its vapour density decreases.*

**b.** If the system were cooled in ice, would the mixture become lighter or darker in colour? Explain.

*The mixture becomes lighter in colour. On cooling in ice, the equilibrium shifts in favour of $N_2O_4$ since the reverse reaction is exothermic. Since $N_2O_4$ is lighter than $NO_2$, the mixture becomes lighter on cooling.*

### Revision Exercises

**23** Consider the following reaction:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H = -90\text{ kJ}$$

a Draw an energy profile diagram for the reaction.

b What is the effect of increase in temperature on the equilibrium system?

c Write an equation to show this effect.

**24** Explain why a high pressure is required for the manufacture of ammonia by the Haber process. [WAEC]

**25** $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H = -90\text{ kJ}$

In the equation above, the yield of ammonia can be decreased by

A. increasing the temperature.
B. increasing the pressure.
C. adding a catalyst.
D. removing ammonia as it is formed. [JAMB]

## Answers to Revision Exercises

2. C 5. D 6. B 10b 49.0 12. D 13b 17. B 19. C 25. A

# 21

# IONIC AND SOLUBILITY EQUILIBRIA

## 21.1 Introduction

When a substance is only slightly ionized in water, there exists a dynamic equilibrium between the *ionized* and *un-ionized* species in aqueous solution.

In an aqueous solution, *equilibrium* exists between the *ionized* and *un-ionized* species. Such species are *weak* acids, *weak* bases, and slightly soluble ionic compounds. This chapter deals with *acid-base* and *solubility equilibria*.

**Revision Exercise**

1. Which of the following gases does not produce ions in water?

A. $NH_3$ B. HCl C. $CH_4$ D. $CO_2$

## 21.2 Acid-Base Equilibria

### Conjugate Acid-Base pairs

Acids and bases oppose one another:

- An acid produces *hydroxonium ions* in water, while a base consumes them. (*Arrhenius* definitions)
- An acid is a *proton-donor*, while a base is an *acceptor* (*Bronsted-Lowry* definitions).
- An acid is an *electron-pair acceptor*, while a base is a *donor* (*Lewis* definitions).

Consider the following reactions:

a. $\underset{\text{(acid)}}{HCl_{(g)}} + \underset{\text{(base)}}{H_2O_{(l)}} \rightleftharpoons \underset{\text{(new acid)}}{H_3O^+_{(aq)}} + \underset{\text{(new base)}}{Cl^-_{(aq)}}$ ...1

b. $\underset{\text{(acid)}}{H_3O^+_{(aq)}} + \underset{\text{(base)}}{NH_{3(g)}} \rightarrow \underset{\text{(new acid)}}{NH_4^+{}_{(aq)}} + \underset{\text{(new base)}}{H_2O_{(l)}}$ ... 2

c. $\underset{\text{(acid)}}{H^+} + \underset{\text{(base)}}{H_2O} \rightarrow H_3O^+$

Consider a reaction represented by the equation:

$$\underset{\text{(acid)}}{\textbf{Acid 1}} + \underset{\text{(base)}}{\textbf{Base 2}} \rightleftharpoons \underset{\text{(new acid)}}{\textbf{Acid 2}} + \underset{\text{(new base)}}{\textbf{Base 1}}$$

When **acid 1** donates its proton, it forms **base 1**; the **base 1** obtained from **acid 1** is the ***conjugate base*** of **acid 1**. Similarly, when **base 2** accepts a proton, it forms **acid 2**; the **acid 2** obtained from **base 2** is the ***conjugate acid*** of **base 2**. For instance:

a. In equation 1 above, $Cl^-$ is the *conjugate base* of HCl, while $H_3O^+$ is the *conjugate acid* of $H_2O$, a base.

b. In equation 2, $H_2O$ is the *conjugate base* of the acid $H_3O^+$, while $NH_4^+$ is the *conjugate acid* of the base $NH_3$.

c. In equation 3, $H_2O$ is the *conjugate base* of $H_3O^+$ while HCl is the *conjugate acid* of the base $Cl^-$.

Generally, a *strong acid* produces a *weak conjugate base*, and vice versa, while a *strong base* produces a *weak conjugate acid*, and vice versa. Table 21.1 gives some reactions to show examples of conjugate acid-base pairs in aqueous solutions. It is evident from reaction a that $H_2O$ is amphoteric.

**Table 21.1** *Some examples of conjugate acid-base pairs*

| | Acid 1 | + | Base 2 | $\rightleftharpoons$ | Acid 2 | + | Base 1 |
|---|---|---|---|---|---|---|---|
| a. | $H_2O$ | + | $H_2O$ | $\rightleftharpoons$ | $H_3O^+$ | + | $OH^-$ |
| b. | HCl | + | $NH_3$ | $\rightleftharpoons$ | $NH_4^+$ | + | $Cl^-$ |
| c. | $H_2SO_4$ | + | $H_2O$ | $\rightleftharpoons$ | $H_3O^+$ | + | $HSO_4^-$ |

**Revision Exercises**

2 a. What is a *Bronsted-Lowry* acid?
b. What is a *Bronsted-Lowry* base? [WAEC]

3. Mention the conjugate base of the following acids:
a. HF b. $NH_4^+$ c. $H_2O$ d. $H_2S$.

4. In each of the following reactions, identify the Bronsted-Lowry acid and base in both the forward and reverse reactions:

a. $H_2O_{(l)} + H_2S_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + HS^-_{(aq)}$

b. $NH_{3(aq)} + H_3PO_{4(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + H_2PO_4^-{}_{(aq)}$

### Dissociation Constant of Weak Acids

The characteristic reaction of a weak acid, HA with water is:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

When a weak acid dissolves in water, a dynamic equilibrium exists between the dissociated and undissociated molecules. The equilibrium constant $K_C$ is written as:

$$K_C = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

As mentioned in Section 20.3, for pure liquids, such as water, $[H_2O] = 1$, we obtain:

$$K_c[H_2O] = \frac{[H_3O^+][A^-]}{[HA]} = K_a \quad \ldots 1$$

The new equilibrium constant, $K_a$ is called the *acid dissociation constant*. Its value is not affected by concentration changes; it is only affected by changes in temperature.

The numerical value of $K_a$ is a measure of the strength of the acid; the larger the $K_a$ value, the greater the extent of dissociation, and hence, the stronger the acid.

The $K_a$ values of some acids at 25 °C are given in Table 21.2. The $K_a$ of HF is larger than that of ethanoic acid; hence, a stronger acid than ethanoic acid.

The value of $K_a$ for a weak acid can be calculated using equation 1 above, once the concentration of the acid, and its pH are known.

**Table 21.2** *Dissociation constants, $K_a$ of some acids at 298 K*

| Acid | $K_a$ | Acid | $K_a$ |
|---|---|---|---|
| $H_2SO_4$ | Very large | HCOOH | $1.60 \times 10^{-4}$ |
| $HNO_3$ | 40.0 | $CH_3COOH$ | $1.80 \times 10^{-5}$ |
| $HNO_2$ | $4.70 \times 10^{-4}$ | $C_6H_5COOH$ | $6.40 \times 10^{-5}$ |
| HF | $6.70 \times 10^{-4}$ | $H_2O$ | $1.00 \times 10^{-14}$ |

## Dissociation Constant of Weak Bases

Since $A^-$ is the conjugate base of the acid HA, the reaction of a weak base with water is written as:

$$A^-_{(aq)} + H_2O \rightleftharpoons HA_{(aq)} + OH^-_{(aq)}$$

Hence, the base dissociation constant, $K_b$ is:

$$K_b = \frac{[HA][OH^-]}{[A^-]} \quad \ldots 2$$

This shows that for a given conjugate acid-base pair, $K_a$ and $K_b$ can be written.

## Dissociation Constant of Water

A water molecule can be regarded as a weak acid as well as a weak base; it is amphoteric. The reaction between two water molecules can be represented by the equation:

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

The equilibrium constant, $K_w$ can be written as:

$$K_w = [H_3O^+][OH^-] \quad \ldots 3$$

$K_w$ is the *dissociation constant* or *ionic product of water.*

From the dissociation constants $K_a$ and $K_b$ of a given conjugate acid-base pair, it can be shown that:

$$K_a \times K_b = [H_3O^+][OH^-] = K_w$$

Experimentally, $K_w = 1.00 \times 10^{-14}$ at 298 K.

In pure (distilled) water:

$[H_3O^+] = [OH^-] = 1.00 \times 10^{-7}$ at 298 K.

i.e. $K_w = [H_3O^+][OH^-] = (1.00 \times 10^{-7})^2$

$= 1.00 \times 10^{-14}$

- In a *neutral solution* $[H_3O^+] = [OH^-] = 1.00 \times 10^{-7}$
- When an acid is added to a neutral solution or pure water, $[H_3O^+] > [OH^-]$, the solution becomes acidic.
- When a base is added, $[OH^-] > [H_3O^+]$; the solution becomes alkaline.

However, for a conjugate acid-base pair:

$$K_aK_b = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$$

For a strong acid, $K_a$ is large; its conjugate base has a small $K_b$. Similarly, for a strong base, $K_b$ is large; its conjugate acid has a small $K_a$.

## pH, pOH, $pK_a$, $pK_b$, and $pK_w$

*Quantities* that are less than one and with extremely wide variations are usually represented by their negative logarithm to base 10, i.e. $-\log_{10}$.

For instance: $-\log_{10}[H^+]$ is **pH**. The prefix **p** stands for $-\log_{10}$. i.e. $-\log_{10}[H_3O^+] = \mathbf{pH}$

Similarly:

$$-\log_{10}[OH^-] = \mathbf{pOH}$$
$$-\log_{10} K_a = \mathbf{pK_a}$$
$$-\log_{10} K_b = \mathbf{pK_b}$$
$$-\log_{10} K_w = \mathbf{pK_w}$$

In pure water and in neutral solutions,

$$[H_3O^+] = [OH^-] = 1.00 \times 10^{-7}$$

Taking the negative $\log_{10}$ of each quantity:

$-\log_{10}[H_3O^+] = -\log_{10}[OH^-] = -\log_{10}(1.00 \times 10^{-7})$

i.e. $pH = pOH = 7$

Hence, for a neutral solution, $pH = pOH = 7.0$.

For any aqueous system:

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$$

Taking the negative $\log_{10}$ of each side.

$$-\log_{10} K_w = -\log_{10}[H_3O^+] - \log_{10}[OH^-]$$
$$= \log_{10}(1.00 \times 10^{-14})$$

i.e. $pK_w = pH + pOH = 14$.

Similarly, since $K_w = K_aK_b = 1.00 \times 10^{-14}$

Then, $pK_a + pK_b = 14$.

- Substances that dissolve in water to give acidic solutions have $pK_a < 7$; while those that give alkaline solutions have $pK_a > 7$.
- A substance that has a $pK_a$ value of 7.0 has acid and base strengths equal to those of water.

The smaller the $pK_a$ value, the stronger the acid.

The $pK_a$ values of some acids at 25 °C are:

HCOOH: $pK_a = 3.74$ $H_2CO_3$ : $pK_a = 6.38$

$CH_3COOH$: $pK_a = 4.76$ $NH_4^+$ : $pK_a = 9.24$

i.e. methanoic acid is stronger than ethanoic acid.

Note that the $pK_a$ or $K_a$ value of a substance is not affected by concentration changes, whereas the pH of a solution changes with concentration.

From equation 1 above: $[H_3O^+] = K_a[HA]/[A^-]$

This can be expressed in the form:

$$pH = pK_a - \log_{10}\frac{[HA]}{[A^-]} \quad \ldots 4$$

Once the *concentration* and the *dissociation constant* of a *weak acid* are known, the pH of the solution can be estimated.

**Worked Example**

1 a. Calculate the pH of the following solutions:
   i. 0.100 $moldm^{-3}$ HCl
   ii. 0.100 $moldm^{-3}$ ethanoic acid at 25 °C ($K_a = 1.80 \times 10^{-5}$)

b. Comment on the pH values in a above.

c. Calculate the $[OH^-]$, and hence, the pOH in each of the solutions in a above.

Solution

1 a i. *To calculate the pH of 0.100 $moldm^{-3}$ HCl*

HCl is a strong acid; it is completely ionized:

$HCl_{(aq)} + H_2O \rightarrow H_3O^+_{(aq)} + Cl^-$

0.1 mol 0.1 mol.

Hence, $[H_3O^+] = 0.1 = 10^{-1}$

$pH = -\log [H_3O^+]$

$= -\log 10^{-1} = -(-1) = 1.0$

ii. *Ethanoic acid is a weak acid; it is slightly ionized. Let x be the amount of the acid, which is ionized in solution. At equilibrium:*

$CH_3COOH_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$

$(0.1 - x)$ $x$ $x$

*If x $moldm^{-3}$ of $CH_3COOH$ dissociates, x $moldm^{-3}$ of $H_3O^+$ and x $moldm^{-3}$ of $CH_3COO^-$ will be produced.*

*The amount of $CH_3COOH$ left undissociated at equilibrium will be $(0.1 - x)$ $moldm^{-3}$.*

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH_{(aq)}]} = \frac{x \times x}{(0.1 - x)}$$

$$K_a = \frac{x^2}{(0.1 - x)} = 1.80 \times 10^{-5}$$

Since $x$ is very small, then, $(0.1 - x) \approx 0.1$

Hence, $x^2/0.1 = 1.80 \times 10^{-5}$

$x^2 = 1.80 \times 10^{-5} \times 0.1 = 1.80 \times 10^{-6}$

$\therefore \quad x = \sqrt{1.80 \times 10^{-6}} = 1.34 \times 10^{-3}$

i.e. $[H_3O^+] = 1.34 \times 10^{-3}$

$pH = -\log [H_3O^+] = -\log (1.34 \times 10^{-3})$

$= -(0.127 - 3) = -(-2.87)$

$\therefore \quad pH = 2.87$

b. *0.1 $moldm^{-3}$ HCl has a lower pH (pH = 1.0); hence, it is more acidic than 0.1 $moldm^{-3}$ ethanoic acid (pH = 2.87). This is because HCl is a strong acid, it is completely ionized in solution; whereas ethanoic acid is weak, it is only slightly ionized in solution.*

c. *To calculate the $[OH^-]$ and pOH of each solution*

$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$

or $pH + pOH = 14$.

i. For 0.1 $moldm^{-3}$ HCl; $[H_3O^+] = 0.1$; $pH = 1$

$\therefore pOH = 14 - pH = 14 - 1 = 13.0$

ii. For 0.1 $moldm^{-3}$ $CH_3COOH$;

$[H_3O^+] = 1.34 \times 10^{-3}$; $pH = 2.87$

$\therefore pOH = 14 - pH = 14 - 2.87 = 11.1$

**Revision Exercises**

5. Write the acid dissociation constant of ethanoic acid.
6. Write an equation to show that a water molecule is amphoteric. Hence, write the ionic product of water.
7. Calculate the pH of 0.001 $moldm^{-3}$ propanoic acid ($K_a = 1.45 \times 10^{-5}$)
8. The $K_a$ value of 0.001 $moldm^{-3}$ solution of a weak acid is $1.6 \times 10^{-6}$. Calculate the
   a. pH; b. $pK_a$. [WAEC]
9. The pH of 0.2 $moldm^{-3}$ solution of a weak acid HA was found to be 2.5 at 298 K. Assuming that the equilibrium concentration of HA is equal to its initial concentration, calculate the acid dissociation constant $K_a$. [WAEC]

## 21.3 Solubility Equilibria: Solubility Products

When the equilibrium law is applied to a saturated solution, it can be stated that *a solution is saturated when undissolved solid particles are in equilibrium with the solution.*

$$Solid \rightleftharpoons Solution$$

Solubility equilibria are limited to ionic compounds whose solubility in water are so small that they can be described as being insoluble or sparingly soluble. Examples include: AgCl, $PbCl_2$, $PbSO_4$, $BaSO_4$, AgBr, ZnS, PbS, and CuS.

Like any equilibrium system, the equilibrium constant $K$ for a sparingly soluble salt is obtained from the equilibrium concentrations. For instance: Consider the solubility of silver chloride in water:

$$AgCl(s) + H_2O(l) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

At equilibrium, the equilibrium constant, $K_C$, is:

$$K_C = \frac{[Ag^+][Cl^-]}{[AgCl][H_2O]}$$

By convention, $[AgCl(s)] = [H_2O(l)] = 1$.

$$\therefore \quad K_C[AgCl] = [Ag^+][Cl^-] = K_{sp}$$

The new equilibrium constant, $K_{sp}$ is known as the *solubility product.*

The solubility product of a slightly soluble compound is the product of the concentration of the ions in a saturated solution. The solubility product expressions for some sparingly soluble salts are:

a. $Cu(IO_3)_2(s) + aq \rightleftharpoons Cu^{2+}(aq) + 2IO_3^-(aq)$
$K_{sp} = [Cu^{2+}][IO_3^-]^2$

c. $A_2B_3(s) + aq \rightleftharpoons 2A^{3+}(aq) + 3B^{2-}(aq)$
$K_{sp} = [A^{3+}]^2[B^{2-}]^3$

The *solubility of a compound* can be calculated once its *solubility product* is known, and vice versa. Table 21.3 gives the *solubility products* of some salts at 25 °C. Like other equilibrium constants, $K_{sp}$ is not affected by concentration changes; it changes with temperature only

**Table 21.3** *Solubility product, $K_{sp}$ of some salts at 25 °C*

| Salt | $K_{sp}$ | Salt | $K_{sp}$ |
|---|---|---|---|
| AgCl | $1.70 \times 10^{-10}$ | ZnS | $1.60 \times 10^{-24}$ |
| AgBr | $1.70 \times 10^{-13}$ | PbS | $1.30 \times 10^{-28}$ |
| $PbSO_4$ | $1.60 \times 10^{-8}$ | CuS | $6.30 \times 10^{-36}$ |
| $PbCl_2$ | $2.00 \times 10^{-5}$ | $BaSO_4$ | $1.00 \times 10^{-10}$ |

### Worked Examples

**2.** The solubility product of silver chloride, AgCl is $1.70 \times 10^{-10}$ at 298 K. Calculate its solubility.

**Solution**

$$AgCl(s) + aq \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
1 mol. 1 mol. 1 mol.

Let $x$ be the solubility in moles per $dm^3$.

At equilibrium, $[Ag^+] = x$; $[Cl^-] = x$

$$K_{sp} = [Ag^+][Cl^-] = 1.70 \times 10^{-10}$$
$$= x \times x = 1.70 \times 10^{-10}$$

i.e. $x^2 = 1.70 \times 10^{-10}$

$x = \sqrt{1.70 \times 10^{-10}} = 1.30 \times 10^{-5}$.

i.e., solubility of AgCl at 25 °C is $1.30 \times 10^{-5}$.

**3.** Saturated solution of $PbCl_2$ contains 4.73 $gdm^{-3}$ at 25 °C. Calculate the solubility product of $PbCl_2$ at this temperature. (Pb = 207; Cl = 35.5)

*Solubility of $PbCl_2$ at 25 °C = 4.73 $gdm^{-3}$ (given)*

*$M[PbCl_2] = 207 + 2(35.5) = 207 + 71 = 278\ gmol^{-1}$*

*∴ Solubility of $PbCl_2$ in mole per $dm^3$*

$$= \frac{4.73\ gdm^{-3}}{278\ gmol^{-1}} = 0.0170\ moldm^{-3}$$

Equation of reaction:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$
1 mol. 1 mol. 2 mol.

At equilibrium: $[Pb^{2+}] = 0.0170\ moldm^{-3}$.

$[Cl^-] = 2(0.0170) = 0.0340\ moldm^{-3}$.

$K_{sp} = [Pb^{2+}][Cl^-]^2 = 0.017 \times (0.0340)^2$
$= 1.96 \times 10^{-5}\ mol^3\ dm^{-9}$

For simplicity, the units of the solubility products are usually omitted. Hence, the solubility product of $PbCl_2$ at 25 °C is simply $1.96 \times 10^{-5}$.

### Uses of Solubility Products

**1. Precipitation of salt**

A salt will be precipitated from an aqueous solution when the product of its ionic concentrations is greater than its solubility product. For instance: AgCl is precipitated in aqueous solution when $[Ag^+][Cl^-] >> K_{sp}$ ($1.70 \times 10^{-10}$).

**2. Qualitative separation of metal ions**

The large difference in the solubility products of ZnS and CuS is used in the separation of $Zn^{2+}$ and $Cu^{2+}$ by adjusting the pH of the aqueous solution.

When $H_2S$ gas is passed into a solution containing $Zn^{2+}$ and $Cu^{2+}$, CuS is precipitated in acid medium first, followed by ZnS in alkaline medium.

**3. Common Ion Effect**

The solubility of a sparingly soluble salt is greater in water than in a solution containing any of its ions, e.g. The solubility of AgCl in water is greater than its solubility in aqueous $HCl_{(aq)}$ or $AgNO_{3(aq)}$. This phenomenon is called *common ion effect*. It is because solubility product is not affected by concentration changes.

### Revision Exercises

**10** What is meant by the term *solubility product*?

**11** The solubilities of lead iodide and silver trioxocarbonate(IV) at 15 °C are as follows:
**a** $PbI_2 = 0.600\ gdm^{-3}$; **b** $Ag_2CO_3 = 0.030\ gdm^{-3}$.
Calculate their solubility products.

**12** The solubility product of silver bromide at 25 °C is $3.82 \times 10^{-13}$. Calculate its solubility.

**13** The solubility products of $Cu(IO_3)_2$ is $1.08 \times 10^{-7}$. Assuming that neither ions react appreciably with water to form $H^+$ and $OH^-$, what is the solubility of this salt? [JAMB]
**A.** $2.7 \times 10^{-8}\ moldm^{-3}$ **B.** $9.0 \times 10^{-8}\ moldm^{-3}$
**C.** $3.0 \times 10^{-3}\ moldm^{-3}$ **D.** $9.0 \times 10^{-3}\ moldm^{-3}$

**14 a.** Explain the following observation:
The solubility of $BaSO_4$ in water is more than in dilute $H_2SO_4$.
**b.** What name is given to the phenomenon in **16a**?

**15** Explain the term *common ion effect*.

### Answers to Revision Exercises

**1.** C **7** 3.92 **8a** 4.40; **b** 4.80
**12** $6.18 \times 10^{-3}$ **13.** C

# 22

# • IONIC THEORY • ELECTROLYSIS •

## 22.1 Introduction

Chemical reactions involve the interaction between electrons and atomic nuclei, during which electrons are transferred from one atom to another, or shared between atoms. Reactions involving *electron-transfer* are called *oxidation-reduction* (*redox*) reactions.

*Redox* reactions involving electron-transfer through a path outside the chemical system are called *electrochemistry* or *electrochemical reactions*.

There are two types of *electrochemical reactions*. The first type occurs during a process called *electrolysis*, while the other type occurs in a set-up called *electrochemical cell*. This chapter deals with *electrolysis*.

### Revision Exercises

1. What name is given to a reaction involving transfer of electrons?
2. Mention two types of electrochemical reactions.
3. State the characteristic feature of electrochemical reactions.

## 22.2 Effect of Electricity on Matter

The observations that certain substances allow electric current to pass through them, while others do not, have been used to classify *elements* into *conductors* and *non-conductors* (*insulators*), and *compounds* into *electrolytes* and *non-electrolytes*.

### Conductors and Non-conductors

*Conductors* are *elements* that allow electricity to pass through them. They are metals, such as iron nail, magnesium wire, zinc rod and copper plate, and *graphite* (an allotrope of carbon).

*Metals* and *graphite* are good conductors of electricity, because their *atoms possess mobile electrons* that move freely from one atom to another, and hence, able to carry electric current along.

*Non-conductors* are *elements* that do not allow electricity to pass through them. They are non-metals, such as sulphur, phosphorus and diamond.

*Non-metals* are poor conductors of electricity, since their *atoms do not possess mobile electrons*; hence, no flow of electrons within the atoms.

*Non-metals that have intermediate properties between conductors and non-conductors* are *semi-conductors*. Examples are silicon and germanium.

### Experiment

***Test for Conductors and Non-conductors***

**Procedure**: Set up the electrical circuit as shown in fig 22.1 and connect the given piece of material between points A and B. Complete the circuit at the switch.

**Observation and Inference**: If the bulb *glows*, then, the material is a *conductor*; if not, it is a *non-conductor*.

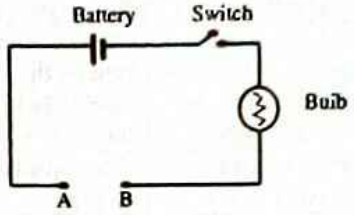



**Fig 22.1** *Test for Conductors*

### Electrolytes and Non-electrolytes

***Electrolytes*** are compounds in molten (or in fused) state, and in aqueous solution conduct electricity, and are decomposed during the process.

Generally, dilute mineral acids such as HCl, $HNO_3$ and $H_2SO_4$; alkalis – NaOH and KOH; and ionic salts – NaCl and $CuSO_4$ are electrolytes.

***Non-electrolytes*** are compounds in molten state or in solution do not allow the passage of electricity.

Generally, covalent solids such as sugars (sucrose and glucose) and paraffin wax; and liquids such as kerosene, petrol and alcohols are non-electrolytes.

### Experiment

***Test for Electrolytes and Non-electrolytes***

**Procedure**: Set up the electric circuit as shown in figure 22.2, and pour the liquid or solution into the beaker. Complete the circuit at the switch.

**Observation and Inference**: If there is a *deflection* in the ammeter (or the bulb *glows*), then, the liquid is an electrolyte. If not, it is a non-electrolyte.

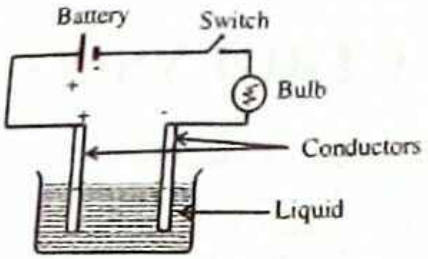



*Fig 22.2 Test for Electrolytes and Non-electrolytes*

### Conductors and Electrolytes: Differences

The differences between a *conductor* and an *electrolyte* are as follows:

| | Conductor | Electrolyte |
|---|---|---|
| 1 | A metal or graphite | An ionic or polar compound |
| 2 | Conducts electricity in solid state | Conducts when molten or in solution. |
| 3 | Electric current is carried by the flow of electrons (electronic conduction) | Electric current is carried by the flow of ions (electrolytic conduction) |
| 4 | Transmits heat by conduction | Transmits heat by convention |
| 5 | Not decomposed by electricity | Decomposed by electric current. |

### Revision Exercises

4 a. What is a conductor? Give two examples.
b. Classify the following as conductor/non-conductor: Iron rod; candle wax; tin can; rubber tube; diamond.
5 a. What is an electrolyte? Give two examples.
b. What is a non-electrolyte? Give two examples.
6. Give two differences between a conductor and an electrolyte. [WAEC]
7. Describe an experiment to determine whether a given solution or liquid is an electrolyte or not. (A diagram for the set-up is essential.) [NECO]

## 22. 3 The Arrhenius Ionic Theory

A Swedish chemist, Swante Arrhenius (1889) proposed the first ionic theory. In the course of time, his theory was modified, in order to conform to new facts.

The postulates of the modern ionic theory are:

- *An electrolyte exists as ions, in molten state, and as hydrated ions, when dissolved in water.*
- *An ion is an atom or a group of atoms, which carries either a positive or a negative charge.*

*An ion differs from the neutral atom from where it is formed.* For example:

a. When a copper atom loses its valence electrons it forms copper(II) ion, $Cu^{2+}$:

$$Cu(s) \rightarrow Cu^{2+}(g) + 2e^-$$

Copper is a shiny brown metal, which is insoluble in water, while copper(II) ion, in water, is blue.

b. Chlorine, $Cl_2$ is a greenish-yellow gas with pungent smell, while chloride ion, $Cl^-$ in water, is colourless and odourless.

$$\underset{\text{(greenish yellow)}}{Cl_2(g)} + 2e^- \rightarrow \underset{\text{(colourless)}}{2Cl^-(aq)}$$

### Strong and Weak Electrolytes

*Strong electrolytes* are compounds that are completely (100%) dissociated into ions in water, e.g.

- *Strong mineral acids*: HCl, $HNO_3$ and $H_2SO_4$.
- *Strong alkalis*: NaOH and KOH;
- *Soluble ionic salts*, such as NaCl and $CuSO_4$.

*Weak electrolytes* are compounds that are only slightly dissociated into ions in water, e.g.

- *Weak acids*: $CH_3COOH$, $H_2CO_3$ and $H_2SO_3$.
- *Weak bases*: aqueous ammonia and lime water.

### Conductance (Conductivity) of Electrolytes

#### Experiment

***To compare the conductivities of 1.0 moldm$^{-3}$ aqueous solutions of different electrolytes***

**Electrolytes**: 1.0 *moldm*$^{-3}$ $H_2SO_4$; 1.0 *moldm*$^{-3}$ $HNO_3$ and 1.0 *moldm*$^{-3}$ $CH_3COOH$.

#### Procedure

1. Set up the electrical circuit as shown in figure 22.2.
2. Place 200 cm$^3$ of the 1.0 *moldm*$^{-3}$ $H_2SO_4$ in the beaker, and then complete the circuit at the switch. Adjust the rheostat, in order to obtain the maximum reading on the ammeter. Record the reading.
3. Repeat the procedure above, using the same volume of 1.0 *moldm*$^{-3}$ $HNO_3$ as the electrolyte, and record the ammeter reading.
4. Again, repeat the procedure, using 200 cm$^3$ solution of 1.0 *moldm*$^{-3}$ $CH_3COOH$ as the electrolyte, and record the ammeter reading.

#### Observations

The highest ammeter reading will be when $H_2SO_4$ is the electrolyte, followed by that of $HNO_3$; while the least ammeter reading will be when $CH_3COOH$ is the electrolyte, i.e. the order of increasing conductance of the solution is:

$$CH_3COOH << HNO_3 < H_2SO_4$$

*Increasing conductivity* $\rightarrow$

#### Explanation

The ionization processes of the acids can be represented by the following equations:

a. $$\underset{\text{1 mole}}{H_2SO_{4(aq)}} \rightarrow \underset{\text{2 moles}}{2H^+_{(aq)}} + \underset{\text{1 mole}}{SO_4^{2-}{}_{(aq)}}$$

b. $HNO_{3(aq)} \rightarrow H^+_{(aq)} + NO_3^-{}_{(aq)}$
1 mole 1 mole 1 mole

c. $CH_3COOH_{(aq)} \rightarrow H^+_{(aq)} + CH_3COO^-{}_{(aq)}$
1 mol < 1 mol < 1 mol

• *$CH_3COOH$ is a weak electrolyte*; it is not completely ionized in water. Its conductance is therefore the least.
• *Both $HNO_3$ and $H_2SO_4$ are strong electrolytes*; hence, they are completely ionized in water. However, the conductance of $H_2SO_4$ is higher than that of $HNO_3$ because in aqueous solution, 1 mole of $H_2SO_4$ produces more ions (3 moles of ions) than $HNO_3$ that produces only 2 moles of ions.

*The conductance of a solution depends on the nature of the dissolved substance, and is directly proportional to the number of hydrated ions in the solution.*

### Solved Problem

1. Explain why NaCl(s) does not conduct electricity, but NaCl(aq) does. [NECO]

*NaCl(aq) contains mobile ions, while NaCl(s) has none.*

### Revision Exercises

8 Distinguish between a strong electrolyte and a weak electrolyte.

9 Classify each of the following as strong electrolyte/weak electrolyte/non-electrolyte:
Potassium chloride; sodium ethanoate; petrol; aqueous ammonia; cane sugar.

10 Which of the following methods cannot be used to distinguish between a strong acid and a weak acid?
A. Conductivity measurement.
B. Measurement of pH.
C. Measurement of heat of reaction.
D. Action on starch iodide paper. [WAEC]

11 The solution that will conduct the highest amount of electricity is
A. 2.0 $moldm^{-3}$ ethanoic acid.
B. 0.5 $moldm^{-3}$ of ethanoic acid.
C. 2.0 $moldm^{-3}$ of hydrochloric acid.
D. 0.5 $moldm^{-3}$ of hydrochloric acid. [JAMB]

12 A solid sample of a potassium salt **P** does not conduct electric current.
a. Give the reason for this observation.
b. Suggest two ways by which **P** can be made to conduct.

13 In the conductance of aqueous potassium tetraoxosulphate(VI) solution, the current carriers are the
A. ions B. electrons C. hydrated ions
D. hydrated electrons [JAMB]

## 22.4 Electrochemical Reactions

### Electrolysis

Certain chemical reactions are *non-spontaneous*, i.e. the *free energy changes*, $\Delta G$ for such reactions are *positive*. Such reactions can be *forced* to occur by the use of electric current. The process is called *electrolysis*.

**Definition:** ***Electrolysis*** *is the process whereby chemical decomposition occurs when an electric current is passed through an electrolyte.*

### Electrolytic Cell

*Electrolysis* occurs in an *electrolytic cell*, which is made up of a pair of electrodes dipping into an *electrolyte* held in a suitable container (figure 22.3).

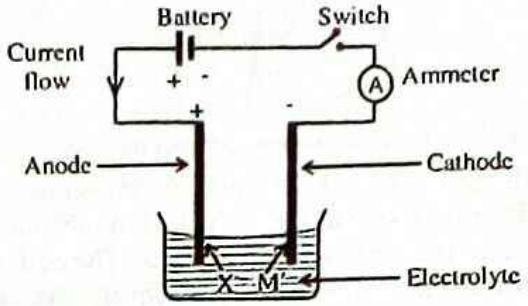



**Fig 22.3** *An electrolytic cell*

• ***Electrodes*** are poles or plates through which the current enters and leaves the electrolytes. They can be metals or graphite (a non-metal). Such metals may be active or passive (inactive).
• The ***anode*** is the electrode through which the current enters the electrolyte. It is usually connected by a wire to the *positive pole* of the source of the electric current, the *battery*.
• The ***cathode*** is the electrode through which the current leaves the electrolyte. It is connected to the *negative pole* of the *battery*.

### Revision Exercises

14 Define the term electrolysis.
15 What are electrodes? Name two types of electrodes.
16 Distinguish between the *anode* and the *cathode*.
17 Draw and label a simple electrolytic cell.

### Mechanism of Electrolysis

An electrolyte is composed of positive and negative ions, and conducts electric current in molten (or fused) state, or when dissolved in water.

The mechanism of electrolysis is based on the ionic theory, and depends on whether the *electrolyte is in molten form, or an aqueous solution.*

### 1. Electrolysis of a Molten Compound

#### Electrolysis of Molten Sodium chloride, NaCl

Sodium chloride is a typical ionic compound. In solid state, the ions in the crystals are not mobile, but in molten state, the electrolyte produces mobile $Na^+$ as the only positive ions, and $Cl^-$ as the only negative ions.

$$NaCl(s) + heat \rightarrow Na^+(l) + Cl^-(l)$$

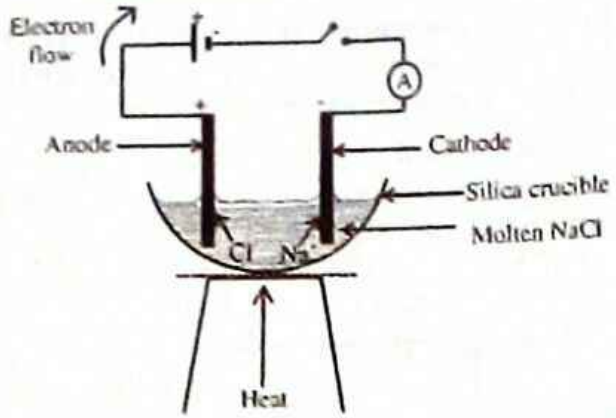



Fig 22.4 *Electrolysis of molten sodium chloride*

When the circuit is completed in the electrolytic cell, electrons move along the wire from the *negative pole* of the battery to the *cathode*. The *cathode* becomes *electron-rich*; hence, *negatively charged*. Consequently, *positive ions*, $Na^+$ migrate to the *cathode*. *Positive ions* are called *cations* (*cathode ions*). The *anode*, which is attached to the *positive pole* of the battery, becomes *electron-deficient*, and hence, *positively charged*. Consequently, *negative ions*, $Cl^-$ migrate to the anode. *Negative ions* are called *anions* (*anode ions*).

***At the Cathode***

Only sodium ions, $Na^+$ are at the cathode. There, they *accept electrons* from the *electron-rich cathode*, and are *discharged as neutral atoms*:

$$Na^+(l) + e^- \rightarrow Na(s)$$

Sodium metal is deposited at the cathode. This is *reduction*, i.e. *reduction occurs at the cathode*.

***At the Anode***

Only chloride ions, $Cl^-$ are at the anode, where they *lose their negative charges* to the *electron-poor anode*, and are *discharged as neutral atoms*.

$$Cl^-(l) \rightarrow Cl(g) + e^-$$

This is *oxidation*, i.e. *oxidation occurs at the anode*. Since chlorine is diatomic, its atoms combine in pairs to form chlorine molecules, i.e.

$$Cl(g) + Cl(g) \rightarrow Cl_2(g)$$

Hence, the overall anode reaction is:

$$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$$

Chlorine gas is evolved at the anode. The *electrons lost by the anions to the anode flow along the wire back to the battery; the cycle is completed.*

**Half-cell reactions and Half-cell equations**

The reaction occurring at each electrode is called *half-cell reaction*; one represents *oxidation* and the other *reduction*. Since both reactions occur at the same time, there must be a balance in the number of *electrons lost to the anode* (*oxidation*) and the number *gained at the cathode* (*reduction*); *oxidation and reduction processes are complementary*.

In the electrolysis of *molten* sodium chloride, 2 moles of electrons are *lost to the anode*, in order to liberate one mole of chlorine; therefore, 2 moles of electrons *must* be *gained at the cathode*, so that 2 moles of sodium atoms are deposited.

The overall reaction in the cell is obtained by the *addition* of the two *half-cell equations*:

*At Anode*: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$ (*Oxidation*)

*At Cathode*: $2Na^+(l) + 2e^- \rightarrow 2Na(s)$ (*Reduction*)

*Net Equation of reaction*:

$$2Na^+(l) + 2Cl^-(l) \rightarrow 2Na(s) + Cl_2(g)$$

Generally, when a *molten compound* is electrolysed, *only one ion-type* migrates to each electrode, and is discharged. Hence, in the electrolysis of *molten* $Al_2O_3$, *aluminium metal* is deposited at the *cathode*, and *oxygen gas* is liberated at the *anode*.

**Solved Problems**

2. Using the Arrhenius theory, explain the process of electricity. [NECO]

*According to Arrhenius theory:*

- *When an electrolyte dissolves in water, it ionizes to give free mobile hydrated positive and negative ions.*
- *When electricity is passed through an electrolyte, the ions migrate to the electrodes.*
- *The positive ions migrate to the cathode, where they gain electrons to form neutral atoms*
- *The negative ions migrate to the anode, where they lose electrons to form neutral atoms.*

3. Explain why oxidation and reduction are complementary. [WAEC]

*Oxidation is the process of electron loss, while reduction is the process of electron gain. Since the two processes occur in order to complete a chemical reaction, they are complementary.*

**Revision Exercises**

18 State the ions present in molten calcium chloride.

19 Oxidation takes place at the anode during electrolysis because the anode
A. is deficient in electrons. B. is rich in protons
C. has excess electrons
D. has attraction for positive ions. [WAEC]

20 Energy conversion in an electrolytic cell is
A. electrical to chemical. B. electrical to light.
C. electrical to mechanical D. chemical to electrical
E. chemical to mechanical. [NECO]

21 Write an equation for the reaction at each electrode when molten calcium chloride is electrolyzed.

## 2. Electrolysis of Aqueous Electrolytes

When an electrolyte dissolves in water, two different cations or anions may be present in the aqueous solution. For instance:

When sodium chloride, NaCl, dissolves in water, the following hydrated ions are produced:

The salt ionizes thus:

$$NaCl(s) + aq \rightarrow Na^+(aq) + Cl^-(aq)$$

Water, although a weak electrolyte, ionizes thus:

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

During the course of the electrolysis, the cations, $Na^+$ and $H^+$ migrate to the cathode, while the anions $Cl^-$ and $OH^-$ migrate to the anode. At the respective electrodes *only one ion-type is discharged.* Which one?

### *Preferential (or Selective) Discharge of Ions*

The three factors that determine the type of ion to be discharged, preferentially or selectively, when different ions migrate to the same electrode are:

- Position of the ion in the *electrochemical series.*
- Relative concentrations of the ions in the electrolyte.
- Nature of the electrodes.

#### a. Position of the ions in the electrochemical series

When metallic ions (*cations*) are arranged according to their ability to *accept electrons*, and hence, act as *oxidizing agents*, an ***electrochemical series*** is obtained.

**DISCHARGE AT THE ELECTRODES**

| *CATHODE (–)* | *ANODE (+)* |
|---|---|
| $K^+$ | $NO_3^-$ |
| $Ca^{2+}$ | $SO_4^{2-}$ |
| $Na^+$ | $Cl^-$ |
| $Mg^{2+}$ | $Br^-$ |
| $Al^{3+}$ | $I^-$ |
| $Zn^{2+}$ | $OH^-$ |
| $Fe^{2+}$ | |
| $Sn^{2+}$ | |
| $Pb^{2+}$ | |
| $H_3O^+$ | |
| $Cu^{2+}$ | |
| $Hg^{2+}$ | |
| $Ag^+$ | |

Similarly, *common anions* form an electrochemical series according to their ability of *lose electrons*, and hence, act as *reducing agents* (see below).

The ***electrochemical series*** is used to identify the ion that will be discharged, preferentially, at a particular electrode. Usually, *the ion lower in the electrochemical series is discharged.* For instance:

i. When $Na^+$ and $H^+$ of the same concentration are at the cathode, $H^+$ is *discharged preferentially*, because $H^+$ has a stronger tendency to accept electron than $Na^+$.

ii. When $OH^-$ and $SO_4^{2-}$ are present at the anode, $OH^-$ is *discharged preferentially*, since it loses electrons more readily to the anode than $SO_4^{2-}$.

***Example***

**Electrolysis of Acidulated Water**

In the *electrolysis of water*, inert platinum electrodes are used, while the *electrolyte* is distilled water to which a few drops of *tetraoxosulphate(VI) acid, $H_2SO_4$* has been added, to provide enough conductivity. This explains why the *electrolysis of water* is sometimes referred to as the *electrolysis of dilute $H_2SO_4$*, and vice versa.

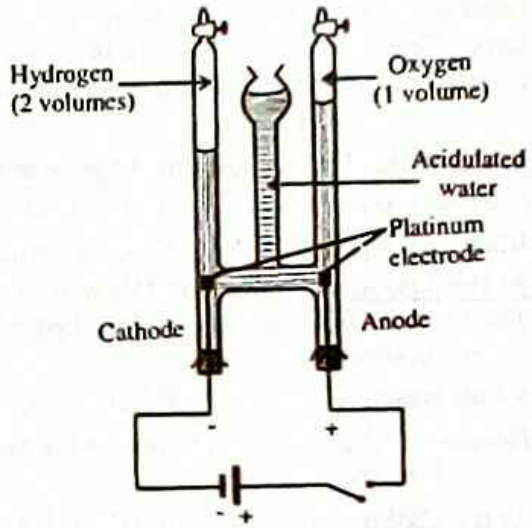



**Fig 22.5** *Electrolysis of water*

The electrolytic cell used for carrying out the electrolysis is called ***Hoffman's voltameter***, fig 22.5.

***Acid ionizes thus:*** $H_2SO_{4(aq)} \rightarrow 2H^+_{(aq)} + SO_4^{2-}{}_{(aq)}$

***Water ionizes thus:*** $H_2O_{(l)} \rightarrow H^+_{(aq)} + OH^-_{(aq)}$

<u>At the Anode</u>

**Ions present:** $OH^-$ and $SO_4^{2-}$

The hydroxide ions are discharged, being lower in the electrochemical series.

***Anode reaction:*** $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

**Results:** a. *One volume of oxygen* is liberated.

b. Acidity of the electrolyte *increases.*

<u>At the Cathode</u>

**Ions present:** $H^+$ (or $H_3O^+$) only.

The hydrogen ion is discharged.

***Cathode reaction***: $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$

Since *four* moles of electrons are lost to the anode, the cathode reaction becomes:

$$4H^+_{(aq)} + 4e^- \rightarrow 2H_{2(g)}$$

**Results:** a. *Two volumes of hydrogen* are liberated.
b. Acidity of the electrolyte *decreases*.

**Overall Effect on the Electrolyte**

The *amount of the acid in the electrolyte remains the same*; but there is an *increase in the concentration of the electrolyte*, because water is being used up during the process electrolysis.

$$2H_2O_{(l)} \rightarrow \underset{2\text{ vol.}}{2H_2\uparrow} + \underset{1\text{ vol.}}{O_2\uparrow}$$

**Note** that the *volume of $H_2$ liberated at the cathode is twice that of $O_2$ evolved at the anode.*

**b. Relative Concentrations of the Ions**

The products of electrolysis of *dilute* and *concentrated* solutions of the same electrolyte are not the same. Consider the electrolysis of *dilute* sodium chloride solution and *concentrated* sodium chloride solution (*brine*).

**Electrolysis of dilute sodium chloride solution**

***Salt ionizes thus***: $NaCl_{(aq)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$

***Water ionizes thus***: $H_2O_{(l)} \rightarrow H^+_{(aq)} + OH^-_{(aq)}$

**At the Anode** **Ions present:** $OH^-$ and $Cl^-$

The hydroxide ions are discharged, being lower in the electrochemical series.

***Anode reaction***: $4OH^-_{(aq)} \rightarrow 2H_2O_{(l)} + O_2\uparrow + 4e^-$

**Results:** • *One volume of oxygen* is liberated.
• *Acidity increases.*

**At the Cathode** **Ions present:** $H^+$ and $Na^+$.

The hydrogen ions are discharged, being lower than $Na^+$ in the electrochemical series.

***Cathode reaction***: $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$

Since *four* moles of electrons are lost to the anode, the cathode reaction becomes:

$$4H^+_{(aq)} + 4e^- \rightarrow 2H_{2(g)}$$

**Results:** • *Two volumes of hydrogen* are liberated.
• *Acidity decreases.*

When a *dilute solution* of an electrolyte is electrolyzed, the products at the electrodes depend on the positions of the ions in the electrochemical series.

**Electrolysis of Concentrated Sodium chloride solution (Brine)**

***Salt ionizes thus***: $NaCl_{(aq)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$

***Water ionizes thus***: $H_2O_{(l)} \rightarrow H^+_{(aq)} + OH^-_{(aq)}$

**At the Anode:** **Ions present:** $OH^-$ and $Cl^-$

$Cl^-$ are discharged in preference to $OH^-$ because of the higher concentration of $Cl^-$ than the $OH^-$ in the electrolyte.

***Anode reaction***: $2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$

**Result:** *One volume of chlorine gas* is liberated.

**At the Cathode:** **Ions present:** $H^+$ and $Na^+$.

$H^+$ is discharged, being lower than $Na^+$ in the electrochemical series.

***Cathode reaction***: $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$

**Result:** *One volume of hydrogen* is liberated.

In the electrolysis of a *concentrated solution* of an electrolyte, *concentration effect* is limited to the *anions of the halogens* ($Cl^-$, $Br^-$ and $I^-$); it does not affect *oxyanions*: $NO_3^-$ and $SO_4^{2-}$.

Again, *concentration effect is not applicable to cations*; it is *limited to anions of the halogens only.*

**c. The Nature of the Electrodes**

The products of electrolysis of an electrolyte are affected by the *nature of the electrode* in ***three*** ways.

**i. Use of inactive (*inert or passive*) electrodes:** When carbon (graphite) and platinum are used as electrodes, they do not take part in the electrode reactions; hence, they do not affect the products at the electrodes. *The ion to be discharged at the respective electrodes depends on its position in the electrochemical series, or its concentration in the electrolyte.*

**ii. Use of active metals as the anode:** When a metal (*excluding platinum*) is used as the anode, and the electrolyte is a salt of the metal, the metal dissolves into the solution. This is because less energy is required to remove electrons from the atoms of a metal in a solution of its salt, than that required to remove electrons from an anion.

**iii. Use of mercury as the cathode:** In the electrolysis of *brine* (concentrated NaCl solution) using an inert cathode (graphite or platinum), both $Na^+$ and $H^+$ migrate to the cathode. $H^+$ is discharged, being lower in the electrochemical series.

However, if a *mercury cathode* is used, it will be difficult for $H^+$ to be discharged, because hydrogen gas creates a high over-voltage; hence, $Na^+$ is discharged preferentially.

**Electrolysis of Copper(II) tetraoxosulphate(VI) solution using Copper Electrodes**

***Salt ionizes***: $CuSO_{4(s)} \rightarrow Cu^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$

***Water ionizes***: $H_2O_{(l)} \rightarrow H^+_{(aq)} + OH^-_{(aq)}$

During the electrolysis, $Cu^{2+}$ and $H^+$ migrate to the *copper cathode*, while $OH^-$ and $SO_4^{2-}$ migrate to the *copper anode*.

**At the Anode: Nature of the anode:** Copper

Ions present: $OH^-$ and $SO_4^{2-}$

*Anode reaction*:

There are *three* possible reactions:

i. Discharge of $SO_4^{2-}$ ; ii. Discharge of $OH^-$.

iii. Copper anode dissolves into ions.

Reaction iii occurs; copper dissolves by electron-loss: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ (oxidation)

Results: a. *Copper anode dissolves to form ions.*

b. *Mass of the anode decreases.*

**At the Cathode: Nature of the cathode:** Copper

Ions present: $Cu^{2+}$ and $H^+$.

*Cathode reaction*:

$Cu^{2+}$ is discharged, being lower than $H^+$ in the electrochemical series: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Results: a. *Copper is deposited* at the cathode as a shiny *brown* metal.

b. *Mass of the cathode increases.*

**Overall Effect on the Electrolyte**

The *intensity* of the *blue colour* of the electrolyte remains the same. Why? The concentration of $Cu^{2+}$ is unchanged; as the copper anode dissolves to form $Cu^{2+}$, the ions migrate to the cathode, and are discharged and deposited as copper metal.

**Solved Problems**

**4.** Which of the following statements is correct about the electrolysis of dil. $H_2SO_4$ using platinum electrodes?

**A.** $SO_4^{2-}$ is preferentially discharged.

**B.** Acidity decreases at the anode.

**C.** Concentration of the acid increases.

**D.** The acid becomes more dilute.

**Solution:** *C*

**5.** If 1 $dm^3$ of gas were evolved at the cathode during the electrolysis of acidified water, what was the volume of gas evolved at the anode?

*500 $cm^3$. The volume of $H_2$ evolved at the cathode is twice the volume of $O_2$ liberated at the anode.*

**Table 22.1** *Products of Electrolysis of Some Common Electrolytes*

| | ELECTROLYTE | CATHODE | | ANODE | | EFFECT ON ELECTROLYSIS |
|---|---|---|---|---|---|---|
| | | Nature | Product | Nature | Product | |
| 1 | Dilute $H_2SO_4$ (acidulated water0 | Pt or C | $H_2$ (2 vol) | Pt or C | $O_2$ (1vol) | Amount of acid remains constant; its concentration increases |
| 2 | Brine concentrated NaCl solution | C | $H_2$ (1vol) | C | $Cl_2$ (1vol) | Electrolyte becomes alkaline. NaOH(aq) formed |
| 3 | Dilute HCl | Pt | $H_2$ (2vol) | Pt | $O_2$ (1vol) | Concentration increases gradually. |
| 4 | Concentrated HCl | Pt or C | $H_2$ (1vol) | C | $Cl_2$ (1vol) | Concentration decreases gradually |
| 5 | NaOH solution | Pt | $H_2$ (2 vol) | Pt | $O_2$ (1 vol) | Concentration increases gradually |
| 6 | Fused NaOH | Pt | Na(s) (4 moles) | Pt | $O_2$ (1mole) | Concentration remains constant. |
| 7 | $CuCl_2$ or $CuSO_4$ Solution | Pt | Cu(s) (2 moles) | Pt | $O_2$ (1 mole) | Concentration decreases; green/ blue colour of solution fades gradually to colourless. Solution becomes acidic. $HCl_{(aq)}$ or $H_2SO_4$ formed. |
| 8 | $CuCl_2$ or $CuSO_4$ Solution | Cu or Pt | Cu(s) | Cu | $Cu^{2+}(aq)$ | Concentration and colour do not change. Mass of cathode increases; mass of anode decreases. |
| 9 | Fused $MgCl_2$ | Pt | Mg(s) | C | $Cl_2$ | Concentration remains constant |
| 10 | Fused $PbBr_2$ | Pt | Pb(s) | C | $Br_2$ | Concentration remains constant |
| 11 | Fused $Na^+H^-$ | Pt | Na(s) | Pt | $H_2$ | Concentration remains constant. |

## 3. Electrolysis of Other Electrolytes

Table 22.1 above gives the products of electrolysis of some electrolytes. Generally, metals and hydrogen are deposited or liberated at the cathode, while gases are usually liberated at the anode.

**Solved Problems**

**6.** State what is meant by the term preferential discharge of ions in electrolysis. [WAEC]

*Preferential discharge means the discharge of a particular type of ion at the electrode, in preference to other types of ions in the electrolyte.*

7. List **three** observable changes that take place when a dilute solution of copper(II) chloride is electrolysed using platinum electrodes. [WAEC]

- *The colour of the solution gradually changes from green to colourless.*
- *A brown deposit at the cathode.*
- *Bubbles of gas at the anode.*

8. State and explain how the pH of the electrolyte changes during the electrolysis of dilute $CuCl_{2(aq)}$ using graphite electrodes? [WAEC]

*The pH of the electrolyte decreases.*
*The discharge of $Cu^{2+}$ at the cathode and $OH^-$ at the anode increases the concentration of $H^+$, thereby, making the electrolyte to become acidic.*

9. Which of the following occurs when a solution containing $CuSO_4$ is electrolysed using copper electrodes?

A. The cathode becomes coated with copper
B. Both electrodes gain electrons.
C. The blue colour of the solution fades gradually.
D. The anode increases in mass.

**Solution**: *A*

10 A concentrated solution of sodium chloride was electrolysed using graphite electrodes.

a. State the ions present in the solution.
*$Na^+$, $Cl^-$, $H^+$ and $OH^-$.*
b. Name the products at the
i. anode. *Chlorine gas.*
ii. cathode. *Hydrogen gas.*
c. Give the by-product of the electrolysis.[WAEC]
*Sodium hydroxide solution, NaOH(aq).*

## Revision Exercises

22 List **three** factors that determine the preferential discharge of ions during electrolysis. [WAEC]

23 a List the ions present in an aqueous solution of iron (II) tetraoxosulphate (VI).
b Name the acid used in the *electrolysis of water*.

24 Mention the ion that will be discharged at each electrode when the following solution is electrolyzed:
a. A concentrated solution of $CuSO_4$ using platinum electrodes.
b. Concentrated hydrochloric acid using platinum electrodes.

25 A concentrated solution containing $H^+$, $Cu^{2+}$, $OH^-$ and $Cl^-$ was electrolyzed using platinum electrodes. The ion that will be discharged at the cathode is
A. $H^+$ B. $Cu^{2+}$ C. $OH^-$ D. $Cl^-$ [JAMB]

26 Write equation for the reaction at each electrode when each of the following is electrolyzed:
a. A dilute solution of sodium chloride using carbon electrodes.
b. A dilute $CuCl_2$ solution using platinum electrodes.

27 An aqueous solution of copper(II) chloride is electrolysed using graphite electrodes. [WAEC]
a. List the ions present in the electrolyte.
b. Which ions would be discharged at the
i. anode; ii. cathode.
c. Write a balanced equation for the reaction at each electrode.
d. What substance would be left after the electrolysis?
e. State the effect of the substance on litmus paper.

## Industrial Applications of Electrolysis

### 1. Refining (Purification) of Metals

Metals, such as silver and copper, are refined or purified by electrolysis. The *impure metal* to be purified is made the *anode*, while the *pure form of the metal* is made the *cathode*; the *electrolyte* is an *aqueous solution of the salt of the metal.*

#### *Purification of impure copper by electrolysis*

**Procedure:**

a. $CuSO_{4(aq)}$ (1.0 $moldm^{-3}$) is placed in a beaker to serve as the electrolyte.
b. The *impure copper* is made the *anode*, while a plate of *pure copper* is made the *cathode*. The circuit is then completed as shown in figure 22.6, and the current is allowed to flow for several hours.

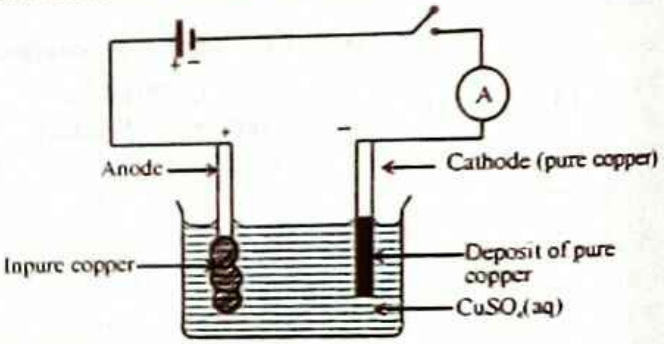



**Fig 22.6** *Refining of copper by electrolysis*

c. During the electrolysis, the *impure* copper anode dissolves in the electrolyte to produce $Cu^{2+}$, which migrates to the cathode, where it is discharged and deposited as *pure* copper metal on the cathode.
d. The impurities, which contain silver and gold, collect at the bottom of the cell as *sludge*.

### 2. Extraction of Metals

Electropositive metals, such as sodium, potassium, calcium, magnesium and aluminium are usually produced by the electrolysis of the appropriate fused salts or oxides. For instance:
a. Sodium metal is produced by the electrolysis of fused sodium chloride
b. Aluminium metal is produced by the electrolysis of *molten alumina* (aluminium oxide, $Al_2O_3$).

### 3. Production of Gases

Gases, such as chlorine, hydrogen and oxygen are the by-products during the electrolytic production

of metals. For instance: chlorine is the by-product at the anode during the production of sodium metal by the electrolysis of fused sodium chloride.

### 4. Electroplating

*Electroplating is the process whereby a thin-layer of a metal is deposited on an object by electrolysis.*

The electrolytic cell holds the solution of the salt of the *plating metal*, the *anode is the plating metal*, while the *cathode is the object to be plated.*

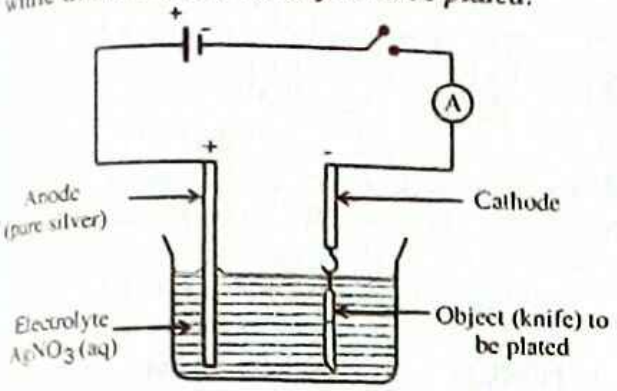



Fig 22.7 *Electroplating by electrolysis*

**Procedure**

In *silver plating*, the electroplating cell consists of a solution of a soluble salt of silver, such as silver trioxonitrate (V), silver metal is connected to the positive pole of the battery, as the anode, while the object to be plated is attached to the negative pole of the battery, the cathode, see figure 22.7.

When the circuit is completed, silver ions in the solution are reduced, and deposited as metallic silver on the object to be plated at the *cathode*.

$$Ag^+(aq) + e^- \longrightarrow Ag(s) \qquad \text{(at } \textit{cathode}\text{)}$$

At the *anode*, the silver anode dissolves to form ions, which migrate to the cathode, in order to maintain the concentration of $Ag^+$ in the electrolyte.

$$Ag(s) \longrightarrow Ag^+(aq) + e^- \qquad \text{(at } \textit{anode}\text{)}$$

### 5. Manufacture of Compounds

Pellets of sodium hydroxide are manufactured by the electrolysis of brine (see Section 34.6).

***Usefulness of Electroplating***

a. Electroplating prevents rusting of iron.
b. It increases the attractiveness of the object plated.
c. It gives thickness to the object plated.

Examples of electroplated objects include: door handles, chromium-plated hospital equipment; silver-plated cutlery; and tin-plated cans.

### Revision Exercises

28 State **three** applications of electrolysis. [WAEC]
29 Describe briefly the purification of copper by electrolysis. [WAEC]
30 Which of the following metals is purified commercially by electrolysis?
A. Zn B. Fe C. Sn D. Cu [JAMB]
31 a Draw and label a simple cell for the electrolytic purification of copper.
b Write an equation for the reaction at **each** electrode in a above. [WAEC]
32 Describe in outline a suitable procedure for electroplating a length of copper wire with silver. [WAEC]
33 Electrolysis CANNOT be used to
A. electroplate metals B. extract elements
C. generate electricity D. manufacture compounds
E. purify metals [NECO]

## 22.5 Faraday's Laws of Electrolysis

There are *two* laws that govern electrolytic processes; they were named after Michael Faraday.

### Faraday's First Law of Electrolysis

Faraday's first law of electrolysis states that:

*The mass of an element liberated or deposited during electrolysis is directly proportional to the quantity of electricity that passes through the electrolyte.*

Mathematically, $\mathbf{m} \propto \mathbf{Q}$

where **m** is mass deposited, in grams, and **Q** is the quantity of electricity passed, in Coulombs.

Quantity of electricity, **Q** = current, **I** × time, **t**

Coulombs = (amperes) × (seconds)

i.e. $\mathbf{Q = It}$

Thus, $\mathbf{m \propto It}$

or $\mathbf{m = kIt}$

where **k** is the constant of proportionality.

When **k** is made the subject of the formula:

$$\mathbf{k = m/It}$$

The reciprocal of k, 1/k, is the charge-to-mass ratio; it is expressed in coulombs per gram, i.e.

$$\frac{1}{k} = \frac{It}{m} = \frac{\text{Quantity of electricity passed}}{\text{Mass deposited}} \quad \ldots 1$$

### Worked Examples

**11** A current of 0.72 amperes was passed through a solution of an electrolyte for 3 hours 20 minutes. Calculate the quantity of electricity passed.

*To calculate the quantity of electricity passed*

Given: Current = 0.72A; time = 3 hours 20 minutes.

Quantity of electricity, Q = current, I × time, t

Coulombs = (amperes) × (seconds)

$Q = ?$ ; $I = 0.72$ A; $t = [(3 \times 60 \times 60) + (20 \times 60)]$ s

$= [10800 + 1200]$ s $= 12000$ s

Substituting, $Q = 0.72 \times 12000$

$= 8640$ C

12 When a current of 0.20 A was passed through an electrolyte, 1200 C of electricity was used. Calculate the time of current flow.

*To find time, t*
Given: Q = 1200 C, and I = 0.20 A.
Quantity of electricity, Q = current, I × time, t = I t.
Making t the subject of the formula, and substituting:
t = Q/I = 1200/0.2 = 6000 s (or 100 minutes)

**Revision Exercises**

34 State Faraday's first law of electrolysis. [WAEC]

35 How many coulombs of electricity would be produced if a current of 0.4 A flows for 1 hour?
A. 96,500 coulombs B. 1,440 coulombs
C. 965 coulombs D. 144 coulombs [WAEC]

36 Calculate the quantity of electricity used during electrolysis when a current of 0.21 ampere flows for 2 hours. [WAEC]

37 Calculate the time it will take 9600 C of electricity to be produced, when a current of 1.60 A is used.
A. 0.5 minute B. 1.0 minutes
C. 10.0 minutes D. 100 minutes

## Faraday and Moles of Electrons

In theory, the quantity of electricity required for the passage of *one mole* of electrons is 96500 C. This quantity of electricity is *one* Faraday, 1 F.
i.e. 1 Faraday, F = 96500 C ≡ 1 mole of electrons.
≡ $6.02 \times 10^{23}$ electrons.
≡ Avogadro constant.

**Worked Example**

13 Determine how many moles of electrons are transferred when 4825 coulombs of electricity are passed through an electrolytic cell.
[1 F = 96500 C] [WAEC]

*To determine amount of electrons transferred by 4825 C*
This is mole-coulomb relationship.
By definition, 1 Faraday ≡ 1 mole of electrons,
i.e. 96500 C ≡ 1 mole of electrons
∴ 4825 C ≡ 4825/96500 mol of electrons
= 0.0500 mol. (3 sig. fig.)

## Faraday – Mass – Mole relationships

1. A *mono*valent metal, such as sodium or silver: *one* mole of electrons or *one* Faraday (96500 C) of electricity deposits 1 mole of the metal. i.e.

$$Ag^{+}_{(aq)} + e^{-} \rightarrow Ag_{(s)}$$
1 mol. 1 mol. 1 mol. (108 g)
1 F (96500 C)

i.e. 1 Faraday (96500 C) of electricity deposits 1 mole of silver, weighing 108 g.

2. For a *divalent* metal, such as copper, magnesium and calcium, *two* Faradays (2 × 96500 C) deposit 1 mole of the metal:

$$Cu^{2+}_{(aq)} + 2e^{-} \rightarrow Cu(s)$$
2 F 1 mol (63.5 g)

For a *diatomic monovalent element*, such as hydrogen and chlorine, *two* Faradays (2 × 96500 C) deposit 1 mole of the element, i.e.

$$2H^{+}_{(aq)} + 2e^{-} \rightarrow H_{2(g)}$$
2 F 1 mol (2.0 g)

$$2Cl^{-}_{(aq)} \rightarrow Cl_{2(g)} + 2e^{-}$$
1 mol 2 F

3. For a *trivalent metal*, 3 Faradays (3 × 96500 C) deposit 1 mole of the metal, e.g.

$$Al^{3+}_{(aq)} + 3e^{-} \rightarrow Al_{(s)}$$
3 F 1 mol (27.0 g)

4. For a *diatomic divalent element*, such as oxygen, *four* Faradays (4 × 96500 C) liberate one mole of molecules of the element, i.e.

$$4OH^{-}_{(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)} + 4e^{-}$$
1 mol 4 F

i.e. 4 Faradays (4 × 96500 C) liberate 1 mole of oxygen gas, weighing 32.0 g.

5. For a metal with charge c, $M^{c+}$, c Faradays (c × 96500 C) deposit 1 mole.

$$M^{c+}(aq) + ce^{-} \rightarrow M(s)$$
c F 1 mol (M g)

*One mole of a chemical substance is the relative molar mass M expressed in grams*, i.e.
Molar mass of a chemical substance = M $gmol^{-1}$
It means: in order to liberate or deposit 1 mole (M g) of an element with charge c, the number of Faradays required is c Faradays.

**Worked Examples**

14 Calculate the amount, in moles, of aluminium that will be deposited by passing 4 Faradays of electricity through a solution of an aluminium salt.

*To calculate amount of Al deposited by 4 Faradays*
This is Faraday-mole relationship.
From the half reaction: $Al^{3+}(aq) + 3e^{-} \rightarrow Al(s)$
3 F 1 mol
3 Faradays deposit 1 mole of aluminium.
∴ 4 F will deposit 4/3 moles
= 1.33 moles of aluminium.

15 What quantity of electricity will liberate 0.125 mole of oxygen gas during the electrolysis of dilute sodium chloride solution? [F = 96500 $Cmol^{-1}$]
A. 24 125 coulombs. B. 48 250 coulombs.
C. 72 375 coulombs. D. 96 500 coulombs.
[JAMB]

*To calculate quantity of electricity*
Given: 0.125 mole of oxygen;

This is Faraday - mole relationship. The required half equation: $4OH^-_{(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)} + 4e^-$

4 mol 1 mol 4 F

i.e. 1 mole of oxygen require $4 \times 96500$ C

∴ 0.125 mole of oxygen require

$0.125 \times 4 \times 96500$ C = 48250 C [Ans = B]

16 How many Faradays of electricity are required to deposit 0.20 mole of nickel, if 0.10 Faraday of electricity deposited 2.98 *g* of nickel during electrolysis of its aqueous solution? [Ni = 59]

A 0.20 B 0.30 C 0.40 D 0.50 [JAMB]

*To calculate number of Faradays required to deposit 0.20 mole of nickel*

Given: 0.10 Faraday deposited 2.98 g of nickel.

First, convert 2.98 g of nickel to amount, in mole.

i.e. amount = 2.98/59 = 0.0505 mole.

Then, 0.0505 mole of nickel required 0.10 Faradays.

∴ 0.20 mole of nickel will require

$(0.20 \times 0.10)/(0.0505)$ F

= 0.396 F = 0.40 F [Ans = C]

17 How many moles of copper will be deposited by 4.0 moles of electrons in the reaction represented by the equation: $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

*To calculate amount of copper deposited*

This is mole-mole relationship.

From the half reaction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

2 mol 1 mol

2 moles of electrons will deposit 1 mole of Cu;

∴ 4 moles of electrons will deposit 4/2 mol of Cu

= 2.00 moles of Cu.

18 Calculate the amount, in moles, of lead that will be deposited by passing 3 Faradays of electricity through a solution of a lead(II) salt.

*To calculate amount of lead deposited by 3 Faradays*

This is Faraday-mole relationship.

From the half reaction: $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$

2 F 1 mol

2 Faradays deposit 1 mole of lead.

∴ 3 F will deposit 3/2 mole

= 1.50 mole of lead.

## Revision Exercises

38 One Faraday of electricity will deposit one mole of

A. lead B. aluminium C. iron D. silver. [W]

39 Consider the reaction represented by the following equation: $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$

How many moles of electrons are required liberate 112 *g* of iron? [Fe = 56]

A. 2 B. 3 C. 4 D. 5 [WAEC]

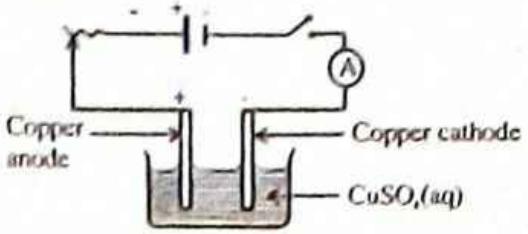
## Verification of Faraday's First Law

**Electrolyte:** $CuSO_4(aq)$

**Nature of Electrodes:** Copper electrodes

**Procedure**

1. Weigh accurately two dry copper plates, and set up the circuit as shown in figure 22.8.
2. Adjust the ammeter to read, say, 0.2 ampere and note the time.




22.8 *Verification of Faraday's First Law*

3. During electrolysis, copper(II) ions in the solution are reduced and get deposited as a brown metal at the cathode, while the copper anode dissolves to form copper (II) ions, which go into solution; so that the concentration of the electrolyte remains constant.
4. Allow the electrolysis to go for exactly 10 minutes (600 seconds), and then, switch off the current.
5. Remove the cathodes, dry and weigh. The difference between the masses of the cathode before and after the electrolytic process gives the *mass of copper deposited at the cathode*. Similarly, the difference between the masses of the anode before and after the electrolytic process gives the *loss in mass of copper at the anode*.
6. Repeat the experiment using another set of electrodes and passing the same current of 0.2 ampere for each of the following periods of time:

a. 1200 seconds, b. 1800 seconds, c. 2400 seconds.

7. The table below shows a hypothetical set of data.

| | Current, A | Time, s | Mass-gain by cathode, g | Mass-loss by anode g |
|---|---|---|---|---|
| 1 | 0.20 | 600 | 0.04 | 0.04 |
| 2 | 0.20 | 1200 | 0.08 | 0.08 |
| 3 | 0.20 | 1800 | 0.12 | 0.12 |
| 4 | 0.20 | 2400 | 0.16 | 0.16 |

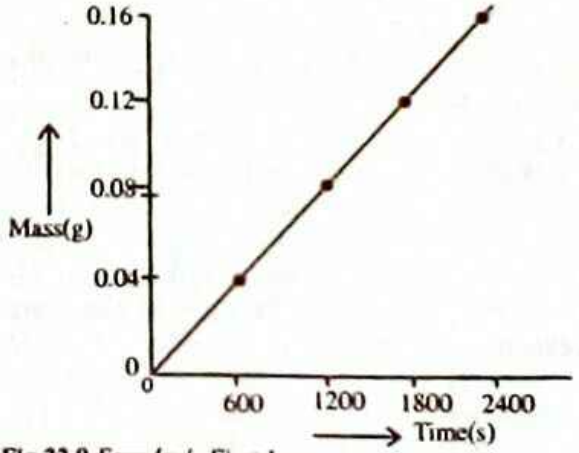



Fig 22.9 *Faraday's First Law*

**Observations from the Table**

a. The mass of copper deposited at the cathode (or lost at the anode) increases as the time of passage of the same electric current increases.

b. The *gain in mass* of the *cathode* is equal to the *loss in mass* of the *anode*, when the same current of 0.20A is passed for any period of time.

c. A plot of graph of *mass of copper deposited* at the cathode against *time* gives a straight line that passes through the origin, see figure 22.9.

**Explanation**

In the electrolysis of $CuSO_4(aq)$:

*Reaction at the cathode* is:

$$\underset{1\text{ mol}}{Cu^{2+}(aq)} + \underset{2\text{ mol}}{2e^-} \rightarrow \underset{1\text{ mol}}{Cu(s)}$$

The equation means:

- 1 mole of $Cu^{2+}$ requires 2 moles of electrons to deposit 1 mole of copper metal, i.e.
- 2 Faradays of electricity (or $2 \times 96500$ C) will be required to deposit 1 mole (63.5 g) of copper.

The straight-line graph shows that the mass of copper deposited at the cathode is directly proportional to the time of passage of electricity through the electrolyte.

**Revision Exercises**

40 Draw a sketch to illustrate Faraday's first law of electrolysis. [WAEC]

41 Describe how you would investigate Faraday's first law of electrolysis, using copper (II) tetraoxosulphate (VI) solution and copper electrodes. [WAEC]

## Faraday, Moles of Ions, and Avogadro's constant

1. For a *mono*valent cation, such as sodium or silver ion, 1 Faraday (or 96500 C) will discharge *one* mole of its ions:

$$\underset{1\text{ mol}}{Ag^+_{(aq)}} + \underset{1\text{ F}}{e^-} \rightarrow Ag_{(s)}$$

*One* mole of ions of silver is discharged by *one* Faraday of electricity.

2. A divalent cation, such as copper(II) ions: 2 F ($2 \times 96500$ C) will discharge 1 mole of its ions:

$$\underset{1\text{ mol}}{Cu^{2+}_{(aq)}} + \underset{2\text{ F}}{2e^-} \rightarrow Cu_{(s)}$$

In order to liberate one mole of hydrogen gas, $H_2$ or chlorine gas, $Cl_2$, two Faradays of electricity discharge two moles of ions.

$$\underset{2\text{ mol}}{2H^+_{(aq)}} + \underset{2\text{ F}}{2e^-} \rightarrow \underset{1\text{ mol}}{H_{2(g)}}$$

$$\underset{2\text{ mol}}{2Cl^-_{(aq)}} \rightarrow \underset{1\text{ mol}}{Cl_{2(g)}} + \underset{2\text{ F}}{2e^-}$$

3. In order to liberate one mole of oxygen gas, four Faradays discharge four moles of ions.

$$\underset{4\text{ mol}}{4OH^-_{(aq)}} \rightarrow 2H_2O_{(l)} + \underset{1\text{ mol}}{O_{2(g)}} + \underset{4\text{ F}}{4e^-}$$

4. For a cation with charge c, $M^{c+}$, c Faradays ($c \times 96500$ C) will discharge 1 mole of its ions:

$$\underset{1\text{ mol}}{M^{c+}_{(aq)}} + \underset{c\text{ F}}{ce^-} \rightarrow \underset{1\text{ mol}}{M_{(s)}}$$

It is therefore correct to say:

*The quantity of electricity required to discharge one mole of ions of an element is directly proportional to the charge on the ion.*

One mole of ions corresponds to the Avogadro constant, $6.02 \times 10^{23}$ mol$^{-1}$.

**Worked Examples**

19 How many Faradays will be required to discharge each of the following ions at the respective electrodes?

a. 3.0 moles of $K^+$

*Since $K^+$ is monovalent, (3 × 1) Faradays will discharge 3 moles of $K^+$ = 3.0 Faradays*

b. 1.5 moles of $Pb^{2+}$

*Since $Pb^{2+}$ is divalent, (1.5 × 2) Faradays will discharge 1.5 moles of $Pb^{2+}$ = 3.0 Faradays*

c. 2.5 moles of $Br^-$.

*Since $Br^-$ is monovalent, (2.5 × 1) Faradays will discharge 2.5 moles of $Br^-$ = 2.5 Faradays*

20 How many aluminium ions will be discharged by 0.33 F?

[Avogadro constant = $6.02 \times 10^{23}$ mol$^{-1}$][WAEC]

*To find the number of ions discharged by 0.33 F*

This is Faraday-ion relationship.

From the half reaction: $\underset{1\text{ mol}}{Al^{3+}(aq)} + \underset{3\text{ F}}{3e^-} \rightarrow Al(s)$

$(6.02 \times 10^{23}$ ions)

3 F will discharge 1 mol of $Al^{3+}$;

i.e. 3 F will discharge $6.02 \times 10^{23}$ $Al^{3+}$;

∴ 0.33 F will discharge $(6.02 \times 10^{23} \times 0.33)/3$ ions.

$= 6.62 \times 10^{22}$ ions

**Revision Exercises**

42 Which of the following ions requires the largest quantity of electricity for discharge at an electrode?

A. 2.0 moles of $Al^{3+}$. B. 2.5 moles of $Cu^{2+}$

C. 3.0 moles of $Na^+$. D. 4.0 moles of $Cl^-$. [JAMB]

43 Calculate the number of copper(II) ions that will be discharged by 0.250 F.

[Avogadro's constant = $6.02 \times 10^{23}$ mol$^{-1}$] [WAEC]

44 Determine the amount of electrons needed to deposit 6.4 g of copper during the electrolysis of copper(II) tetraoxosulphate(VI) solution. [Cu = 64] [WAEC]

A 0.10 mol B 0.20 mol C 1.0 mol D 2.0 mol

## Faraday and Molar mass of an Element

From Faraday's first law:

$It/m$ is a constant ...2

In order to liberate or deposit 1 mole (M g) of an element with charge c, the number of Faradays of electricity required is c, i.e.

$cF/M$ is a constant for an element ...3

When equations 2 and 3 are combined in respect of an element, then:

$$\frac{It}{m} = \frac{cF}{M}$$

Rearranging:

$$\frac{It}{cF} = \frac{m}{M} \quad ...4$$

where

m = mass of element liberated/deposited, in grams.
M = molar mass of the element, in g/mol.
I = current, in amperes
t = time, in second.
c = charge on the element; it corresponds to the number of Faraday, a whole number.
F = Faraday (96500 $Cmol^{-1}$)

Equation 4 is the most general mathematical formula for the 1st law of electrolysis.

- The quantity **m/M** is the amount, **n** in moles, of the element liberated or deposited;
- It is the quantity of electricity, **Q** passed;
- cF corresponds to the quantity of electricity required to liberate **one** mole of the element;
- It/(cF) is the fraction of the quantity of electricity passed; it corresponds to the amount, **n**, in moles.

Hence:

$$\frac{It}{cF} = \frac{m}{M} = n \quad ...5$$

Generally, the mass of an element obtained during electrolysis depends on the:

- time, t of passage of electric current, in seconds;
- magnitude of the current, I in amperes; and
- charge, c on its ion.

### Solved Problems

21 A current of 4.0 amperes was passed through copper(II) tetraoxosulphate(VI) solution for one hour. Calculate the:

a. quantity of electricity passed;
b. amount, in moles, of copper deposited at the cathode. [Cu = 63.5; 1 F = 96500 $Cmol^{-1}$]

a. *To calculate the quantity of electricity passed*
Given: current = 4.0 A; time = 1 hour
Quantity of electricity passed, Q = I (A) × t (s)
Q = ?; I = 4.0 A; t = 1× 60 × 60 = 3600 s
Substituting: Q = 4× 3600 = 14400C

b. *To calculate the amount of copper deposited*
There are two methods:
Method 1: *From the first principle (Proportion method)*
It is Faraday-mole relationship
Reaction at the cathode: $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$
From the cathode reaction:
2 Faradays will deposit 1 mole of copper.
i.e. 2 × 96500C will deposit 1 mole of copper.
∴ 14400C will deposit (1 × 14400) /(2 × 96500)
= 0.0750 mole of copper.

Method 2: *Formula method*
The general formula for the Faraday's first law is:

$$n = \frac{m}{M} = \frac{It}{cF}$$

Given: I = 4.0 A; t = 3600 s; c = 2; F = 96500 C.
Required: Amount, n =? mol.
Using the expression n = (I × t)/(c × F) and substituting:

$$n = \frac{4 \times 3600}{2 \times 96500} = 0.0750 \text{ mol.}$$

22 A current of 0.20 ampere flowed through silver trioxonitrate(V) solution during an electrolytic process that lasted for thirty minutes. Calculate the mass of silver deposited.
(Ag = 108; 1 F = 96500 $Cmol^{-1}$).

*To find the mass deposited*
It is Faraday-mass relationship.
Equation of reaction: $Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$
1 F 1 mol (108 g)
Quantity of electricity passed, Q = I t = 0.20 × 30 × 60
= 360 C
1 Faraday (96500 C) deposits 1 mole (108 g) of silver
i.e. 96500 C deposit 108 g of silver
∴ 360 C deposit (108 × 360)/96500 g
= 0.400 g of silver.
(Note: The formula method can be used.)

23 0.50 *g* of a divalent metal was deposited when a current of 0.45 A was passed through a solution of its salt for thirty minutes, using the appropriate electrodes. Calculate the relative atomic mass of the metal. [Faraday = 96500 $Cmol^{-1}$]

*To calculate the relative atomic mass of the metal*:
Using the formula method: *To find molar mass*, M

$$\frac{m}{M} = \frac{It}{cF}$$

Given: m = 0.50 g; I = 0.45 A; t = (30 × 60) s = 1800 s
c = 2; F = 96500 C
Required: M =? $gmol^{-1}$
Making the unknown M, the subject of the formula and substituting:

$$M = \frac{m \times c \times F}{I \times t} = \frac{0.50 \times 2 \times 96500}{0.45 \times 1800} = 119\ gmol^{-1}$$

∴ Relative atomic mass of the metal is 119 (no unit)

**24** 1400 $cm^3$ of oxygen was liberated at STP during an electrolytic process lasting four hours. Calculate the amount of current that has passed through the electrolyte.
(Molar volume at STP = 22400 $cm^3$).

*To find current, I*

First, find the quantity of electricity to liberate 1400 $cm^3$ of gas. This is Faraday-gas volume relationship.
The anode reaction for the liberation of oxygen is:

*Anode reaction*: $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$
1 mol 4F
(22.4 $dm^3$ at stp)

From the equation:
1 mole of oxygen requires 4 Faradays at STP
i.e. 22400 $cm^3$ of oxygen requires 4 × 96500 C
∴ 1400 $cm^3$ of oxygen requires
$(4 \times 96500 \times 1400)/22400$ C
= 24125 C
i.e. Quantity of electricity passed, Q = 24125C
But $Q = It$
Given: $t = 4 \times 60 \times 60 = 14400$ s.
Making I the subject and substituting:
$I = Q/t = 24125/14400 = 1.68$ amperes
Hence, current passed = 1.68 A.

**25** An element M has a relative atomic mass of 88. When a current of 0.5 amps was passed through the fused chloride of M for 1930 seconds, 0.44 g of M was deposited at the cathode.
**a.** Calculate the number of Faradays needed to liberate 1 mole of M.
**b.** Write the formula for the ion of M
**c.** Write the formula for the chloride of M

**a.** *To find the number of Faradays, c*
Number of Faradays corresponds to the charge, c on M.
Using the formula method: *To find charge, c.*

$$\frac{m}{M} = \frac{It}{cF}$$

Given: m = 0.44 g; M = 88; I = 0.5 A; t = 1930 s;
F = 96500 C Required: c =?
Making the unknown c, the subject of the formula and substituting:

$$c = \frac{I \times t \times M}{m \times F} = \frac{0.5 \times 1930 \times 88}{0.44 \times 96500} = 2$$

∴ 2 Faradays will liberate one mole of M.
Reaction at the cathode: $M^{2+}_{(aq)} + 2e^- \rightarrow M_{(s)}$
**b.** The formula for the ion is $M^{2+}$
**c.** The formula for the chloride is $M^{2+}(Cl^-)_2 = MCl_2$.

## Revision Exercises

**45** The mass of an element liberated at an electrode during electrolysis depends on which of the following? **I.** Nature of the electrode
**II.** Quantity of electricity passed
**III.** Magnitude of electrical charge on its ion
A. II only. B. I and III only. C. II and III only.
D. I, II and III. [WAEC]

**46** Determine the mass of copper deposited by 4.0 moles of electrons in the reaction represented by the equation below. [Cu = 64]
$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$
A. 32 B. 64 C. 128 D. 256 [WAEC]

**47** What mass of magnesium would be obtained by passing a current of 2 amperes for 2 hours 30 minutes through molten magnesium chloride?
A. 1.12 g B. 2.00 g C. 2.24 g D. 4.48 g
[1 Faraday = 96500 C, Mg = 24] [JAMB]

**48** When a current *I* was passed through an electrolyte solution for 40 minutes, a mass X g of a univalent metal was deposited at the cathode. What mass of the metal will be deposited when a current of 2*I* is passed through the solution for 10 minutes?
A. (X/4) g B. (X/2) g C. 2X g D. 4X g [JAMB]

**49** If an atom of aluminium is represented as $^{27}_{13}Al$, what mass of aluminium will be liberated by 0.6 F of electricity? [1F = 96,500 $Cmol^{-1}$]
A 2.7 g B 5.4 g C 8.1 g D 16.2 g [WAEC]

**50** Calculate the quantity of electricity required to deposit 64.0 g of copper from molten copper(II) chloride.
[Cu = 64; F = 96500 C]
A. $6.18 \times 10^6$ C B. $3.09 \times 10^6$ C.
C. $1.93 \times 10^5$ C D. $9.65 \times 10^4$ C [WAEC]

**51** a Calculate the current in amperes required to produce 18.0 g of aluminium in 1.50 hours.
[Al = 27; F = 96500C] [WAEC]
b What current will deposit 3.25g of zinc in 2 hrs?
A 3.25A B 2.00A C 1.34A D 0.67A
[Zn = 65; F = 96500C $mol^{-1}$] [JAMB]

**52** Calculate the time it will take to deposit 1 mole of silver, if a current of 6A is passed through a solution of silver trioxonitrate (V). [F = 96500C] [WAEC]

**53** 0.222 g of a divalent metal is deposited when a current of 0.45 A is passed through a solution of its salt for 25 minutes using platinum electrodes. Calculate the relative atomic mass of the metal.
[1 F = 96,500 C $mol^{-1}$] [WAEC]

**54** 0.50 mole of a cation required 144750 Coulombs of electricity to be completely discharged. Calculate the charge on the cation. [1 F = 96500 C] [WAEC]

**55** Calculate the volume of oxygen evolved at stp when a current of 2.5A is passed through dilute tetraoxosulphate (VI) acid for 2 minutes. [Molar volume of gas at s.t.p. = 22.4 $dm^3$; 1 F = 96500 C]

**56** A solution of $CuSO_4$ was electrolysed between copper electrodes and the following results were obtained:
Mass of copper anode before experiment = 7.20 g
Mass of copper anode after experiment = 4.00 g
Mass of copper cathode before experiment = 5.75 g
From the information provided,
a. calculate the mass of the cathode after the experiment.

b. write an equation for the reaction at the
   i. anode, ii. cathode.
c. state whether the colour of the solution would change during the electrolysis. Give a reason for your answer.
d. if the electrolysis was carried out for 1 hour 20 minutes with a current of 2.0 amperes, determine the value of the Faraday. [Cu = 63.5] [WAEC]

## Faraday's Second Law of Electrolysis

Faraday's second law of electrolysis states that:
*When the same quantity of electricity is passed through different electrolytes arranged in series, the amount, in moles, of each element liberated is inversely proportional to the charge of its ion.*
Mathematically, $n \propto 1/c$

i.e. $nc$ = constant ... 6

where n is the amount, in moles, of the element liberated, and c is the charge on the ion.

Thus, if *the same quantity of electricity*, is passed through *three* different electrolytes in series, the various amounts of elements $n_1$, $n_2$ and $n_3$ liberated or deposited will be related to the charges $c_1$, $c_2$ and $c_3$ of their ions by the expression:

$$n_1c_1 = n_2c_2 = n_3c_3 \quad \ldots 7$$

Since amount $n = m/M$, equation 7 becomes:

$$(m/M)_1c_1 = (m/M)_2c_2 = (m/M)_3c_3 \quad \ldots 8$$

Equation 8 is the *general mathematical formula* for the 2nd law of electrolysis.

## Verification of Faraday's Second Law

### Electrolysis of Different Electrolytes

**Electrolytes:** a. Aqueous $AgNO_3$; b. Aqueous $CuSO_4$

**Nature of Electrodes:** Silver and Copper plates

**Procedure**

1. Weigh accurately dry silver cathode and copper cathode and set up the circuit as shown in figure 22.10.
2. Adjust the ammeter to read, say, 0.20 A.

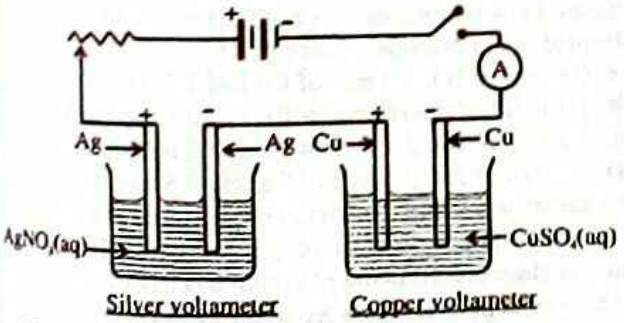



Fig. 22.10 *Faraday's Second Law*

3. *Reactions at the electrodes*
*In the silver voltameter*: Silver ions are reduced and deposited as shiny white metal at the cathode, while the silver anode dissolves to form silver ions, and go into solution.
*In the copper voltameter*: Shiny brown copper metal is deposited at the cathode, while the copper anode dissolves to produce copper (II) ions.
4. Allow the electrolytic process to go for about thirty minutes; then, switch off the current.
5. Remove each cathode, dry and weigh accurately.

**Hypothetical Results and Calculations**

Mass of silver cathode before the experiment = 7.50 g.
Mass of silver cathode after the experiment = 9.70 g.
Mass of copper cathode before the experiment = 6.00 g.
Mass of copper cathode after the experiment = 6.65 g.

*To calculate the amount of silver deposited*
Mass of silver deposited = 9.70 – 7.50 = 2.20 g
Molar mass of silver = 108 g $mol^{-1}$
∴ Amount of silver = 2.20/108 = 0.0204 mole

*To calculate the amount of copper deposited*
Mass of copper deposited = 6.65 – 6.00 = 0.65 g
Molar mass of copper = 63.5 $gmol^{-1}$
∴ Amount of copper = 0.65/63.5 = 0.0102 mole

*To find the mole ratio of Ag : Cu*
Mole ratio of Ag : Cu = (0.0204) : (0.0102)
Dividing each figure by the smaller, and expressing to the nearest whole number, we have:
Mole ratio of Ag : Cu = 2 : 1

**Explanation**

Consider the following electrode reactions:
a. $Ag^+(aq) + e^- \rightarrow Ag(s)$
b. $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

In reaction a, 1 Faraday deposits 1 mole of silver, while in b, 2 Faradays deposit 1 mole of copper.

Now, suppose the same quantity of electricity, say 1 Faraday, (96500 C) is passed through the silver and copper voltameters; then, 1 mole of silver and ½ mole of copper will be obtained at the appropriate electrodes respectively. Under this condition, the mole ratio of Ag: Cu will be 1: ½ = 2:1. This mole ratio is the *inverse* of their charge ratio, i.e $Ag^+$: $Cu^{2+}$ = 1:2.

### Solved Problems

**25** Explain why different quantities of electricity are required to deposit 1 mole of copper and 1 mole of silver respectively during electrolysis. [WAEC]

*Copper and silver ions carry different charges*:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$
$$Ag^+(aq) + e^- \rightarrow Ag(s)$$

i.e. 2 Faradays of electricity will deposit one mole of copper, while 1 Faraday will deposit one mole of silver.

**26** In an electrolytic process, 9650 coulombs of electricity was passed through the appropriate electrolytes in series. Calculate the mass of
a. silver; b. hydrogen obtained.

[H = 1; Ag = 108; Faraday = 96500 $Cmol^{-1}$]

*Since the quantity of electricity in coulombs is given, the proportion method or the general formula for the 1st law of electrolysis can be used to calculate the mass of each of silver and copper separately.*

It is Faraday-mass-mole relationship

a. *To calculate the mass of silver deposited.*

At the silver cathode: $Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$
1 F 1 mol

From the half reaction:

1 F (96500 C) deposit 1 mole (108 g) of silver

i.e. 96500 C deposit 108 g of silver

∴ 9650 C deposit $(108 \times 9650)/96500$ g of silver
10.8 g of silver

b. *To calculate the mass of hydrogen liberated*

At the hydrogen cathode: $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$
2 F 1 mol

From the half reaction:

2 F (or $2 \times 96500$ C) deposit 1 mole (or 2.0 g) of $H_2$

i.e. $2 \times 96500$ C deposit 2.0 g of $H_2$

∴ 9650 C deposit $(2 \times 9650)/(2 \times 96500)$ g of $H_2$
0.100 g of $H_2$

**27** Calculate the mass of lead that would be deposited from a solution of lead(II) trioxonitrate(V) by the same quantity of electricity depositing 1.35 g of copper from a solution of copper(II) salt.
(Cu = 63.5; Pb = 207)

*Since the mass of copper deposited is given, the general formula for the 2nd law of electrolysis can be used.*

i.e. $(m/M)_{Cu}c_{Cu} = (m/M)_{Pb}c_{Pb}$ ... 9

Charge on Cu, $c_{Cu} = 2$; charge on Pb, $c_{Pb} = 2$.

Mole of Cu deposited, $(m/M)_{Cu} = 1.35/63.5 = 0.021$ mol

Mole of Pb deposited, $(m/M)_{Pb} = m/207$; where $m$ is the mass of Pb required.

Substituting in equation 9,

$$\frac{1.35}{63.5} \times 2 = \frac{m}{207} \times 2$$

Making $m_{Pb}$ the subject:

$$m_{Pb} = \frac{1.35 \times 2 \times 207}{63.5 \times 2} = 4.35 \text{ g}$$

i.e. The mass of lead deposited = 4.35 g.

Proportion Method

Since the charge on Pb and Cu are the same, then:

1 mol of Pb ≡ 1 mol of Cu.

i.e. 207 g of Pb ≡ 63.5 g of Cu.

$x$ g of Pb ≡ 1.35 g of Cu.

$x = (207 \times 1.35)/(63.5)$ g

= 4.35 g of Pb.

**28** In an electrolytic process, solutions of $CuSO_4$ and dilute $H_2SO_4$ were electrolysed in series. If 1.27 g of copper was deposited, calculate the volume of oxygen liberated at STP. (Molar volume of gas at STP = 22400 $cm^3$; O = 16; Cu = 63.5)

*To calculate the volume of oxygen gas liberated*

First, calculate the amount, in moles of oxygen evolved. Since the mass of copper deposited is given, the general formula for the 2nd law of electrolysis can be used.

i.e. $n_{Cu}c_{Cu} = n(O_2)\,c(O_2)$ ... 10

Mole of Cu deposited, $(m/M)_{Cu} = 1.27/63.5 = 0.020$ mol

i.e. $n_{Cu} = 0.020$ mol; charge on copper, $c_{Cu} = 2$;

$c(O_2) = 4$ (4 mol of electrons liberate one mol of $O_2$)

$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

Substituting in equation 10:

$0.020 \times 2 = n(O_2) \times 4$

Making $n(O_2)$ the subject of the formula:

$n(O_2) = 0.020 \times 2/4 = 0.010$ mol

i.e. amount of $O_2$ evolved at STP = 0.010 mol.

Now, convert amount of oxygen to volume of gas at stp:

Since 1 mole of $O_2$ at STP occupies 22400 $cm^3$,

∴ 0.010 mole of $O_2$ at STP occupies $22400 \times 0.010$ $cm^3$
= 224 $cm^3$

## Revision Exercises

**57** State Faraday's second law of electrolysis.

**58** A voltameter containing silver trioxonitrate (V) solution was connected in series to another voltameter containing copper (II) tetraoxosulphate (VI) solution. When a current of 0.200 ampere was passed through the solution, 0.780 g of silver was deposited. Calculate the:

a. mass of copper that would be deposited in the copper voltameter;

b. quantity of electricity used and the time of flow.

[Cu = 63.5; Ag = 108; 1 F = 96500 C] [WAEC]

**59** A quantity of electricity liberates 3.6 g of silver from its salt. What mass of aluminium will be liberated from its salt by the same quantity of electricity?
[Al = 27; Ag = 108]

**A** 2.7 g. **B** 1.2 g. **C** 0.9 g. **D** 0.3 g. [UME]

**60** What mass of copper will be deposited by the same quantity of electricity that deposited 9.0 g of aluminium? (Al = 27; Cu = 64)

**A.** 64 g **B.** 32 g **C.** 6.4 g **D.** 3.2 g

**61** If 1.2 Faradays of electricity were passed through electrolytic cells containing $Na^+$, $Cu^{2+}$ and $Al^{3+}$ in series. How many moles of each metal would be formed at the cathode of each cell?

**A** 0.6 mol of Na, 1.2 mol of Cu and 1.2 mol of Al.
**B** 1.2 mol of Na, 0.6 mol of Cu and 0.4 mol of Al.
**C** 1.2 mol of Na, 2.4 mol of Cu and 2.4 mol of Al.
**D** 1.2 mol of Na, 2.4 mol of Cu and 3.6 mol of Al.

**62** Calculate the volume of oxygen (measured at s.t.p.) liberated when copper(II) tetraoxosulphate(VI) solution is electrolysed using platinum electrodes, if 3.65 g of copper is deposited at the cathode.
[Answer to 3 significant figures][ Cu = 64, molar volume at s.t.p. = 22.4 $dm^3$] [NECO]

**63** When brine (sodium chloride solution) was electrolyzed using carbon electrodes, 1. 5 $dm^3$ of chlorine was evolved at s.t.p. Calculate the mass of sodium

hydroxide produced at the same time. (Molar volume of gas at STP = 22.4 $dm^3$; NaOH = 40 $g\ mol^{-1}$)

## Cost of Production by Electrolysis

The following solved problems illustrate the cost of production by electrolysis.

29 If the cost of electricity to produce 1.0 g of silver by electrolysis is $x$ naira. How much will it cost to produce 1.0 g of magnesium?
[Mg = 24; Ag = 108]

*To calculate the cost of producing magnesium by electrolysis*

Given: Production of silver is $x$ naira per gram.
Since the charge on silver is +1 and that of magnesium is +2; in a series arrangement:

1 mole of Ag ≡ ½ mole of Mg
i.e. 2 moles of Ag ≡ 1 mole of Mg
or (2 × 108) g of Ag ≡ 24 g of Mg
i.e. 216 g of Ag ≡ 24 g of Mg

Given that 1 g of Ag costs $x$ naira;
∴ 216 g of Ag will cost ($x$ × 216) naira
= 216$x$ naira.
i.e. cost of producing 24 g of Mg = 216$x$ naira.
∴ 1 g of Mg will cost 216$x$/24 naira
= 9$x$ naira.

30 If the cost of electricity to deposit 1.0 $g$ of magnesium is N5.00, how much would it cost to deposit 10 $g$ of aluminium? [Mg = 24; Al = 27]
[JAMB]

*To calculate the cost of producing aluminium*

Given: Production of magnesium is N5.00 per gram.
Since the charge on magnesium is +2 and that of aluminium is +3; in a series arrangement:

½ mole of Mg ≡ 1/3 mole of Al
i.e. 3 moles of Mg ≡ 2 moles of Al
or (3 × 24) g of Mg ≡ (2× 27) g of Al
i.e. 72 g of Mg ≡ 54 g of Al

Given that 1 g of Mg costs N5.00;
∴ 72 g of Mg will cost (5 × 72) naira = N360.00
Hence, the cost of producing 54 g of Al = N360.00
∴ 10 g of Al will cost (360 × 10)/54 naira
= N66.67

## Revision Exercises

64 If the cost of electricity to produce 1.0 $g$ of magnesium by electrolysis $y$ naira, how much will it cost to produce
a. 1.0 g of silver;
b. 10.0 g of aluminium?
[Mg = 24.0; Al = 27.0; Ag = 108]

## Answers to Revision Exercises

**10.** D **11.** C **13.** C **19.** A **20.** A **25.** B
**30.** D **33.** C **35.** B **36** 1512 C **37.** D
**38.** D **39.** C **42.** A **43** $7.53 \times 10^{22}$ ions
**46.** B **45.** D **46.** C **47.** C **48.** B **49.** B
**50.** C **51a** 35.7 amperes; **b.** C **52** 4.47 hours
**53** 129 **54** 3+ **55** 17.4 $cm^3$
**56a** 8.95 $g$; **d** 95250 C **58a** 0.229$g$ of Cu;
**58b** 697 C; 58.1 min. **59.** D **60.** B **61.** B
**62** 639 $cm^3$ **63** 5.36 $g$.
**64a** 0.11$y$ naira; **b** 1.13$y$ naira.

# 23

# •REDOX PROCESSES•
# •REDOX POTENTIALS•

## 23.1 Introduction

An *oxidation-reduction* (*redox*) reaction involves *transfer of electrons from one reactant to another*. In such a reaction, one reactant is an *oxidant*, while the other is a *reductant*.

This chapter deals with *redox reactions that are used to generate electricity*. Such reactions occur in aqueous solutions. They are spontaneous and are carried out in set-ups called ***electrochemical cells***.

**Revision Exercises**

1. State the characteristic feature of a *redox* reaction.
2. What names are given to the reactants involved in a redox reaction?
3. What name is given to reactions that can be used to generate electricity?

## 23.2 Oxidation and Reduction

### Modern Definitions of Terms

Oxidation and reduction have been defined in terms of *electron-transfer, on one hand, and change in oxidation number*, on the other [see chapter 9, section 2 (8) – redox reactions].

***1. In terms of electron transfer***

***Oxidation** is the process of electron-loss, while **reduction** is the process of electron-gain.*

***2. In terms of oxidation number (O.N.)***

***Oxidation** leads to an increase in oxidation number of an atom, while **reduction** leads to a decrease in the oxidation number of an atom.*

### Redox Reactions

It should be noted that *oxidation* and *reduction* occur simultaneously in the same reaction, e.g.

a. When magnesium wire burns in oxygen, its oxide, a white solid, is formed:

$$\underset{\text{O.N.}}{\overset{\quad Mg_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow MgO_{(s)}}{\overset{0 \quad\quad 0 \quad\quad +2\ -2}{}}} \quad \ldots.1$$

In reaction 1, magnesium atom, Mg is *oxidized* to $Mg^{2+}$ by an *increase* in oxidation number from 0 to +2, while oxygen atom is *reduced* to the oxide, $O^{2-}$ by a *decrease* in oxidation number from 0 to -2.

b. When greenish-yellow chlorine gas is bubbled into a green solution of iron(II) chloride, a yellow solution of iron(III) chloride is obtained:

$$\underset{\text{O.N.}}{\overset{\quad FeCl_{2\,(aq)} + \frac{1}{2}Cl_{2(g)} \rightarrow FeCl_{3(aq)}}{\overset{+2\ -1 \quad\quad 0 \quad\quad +3\ -1}{}}} \quad \ldots.2$$

In the reaction 2, iron(II) in $FeCl_2$ is *oxidized* to iron(III) in $FeCl_3$ by an *increase* in oxidation number from +2 to +3, while chlorine atom in chlorine gas is *reduced* to chloride ion, $Cl^-$ in $FeCl_3$ by a *decrease* in oxidation number from 0 to -1.

### Oxidizing agents and Reducing agents

#### Oxidizing agents

In a *redox reaction*, an ***oxidizing agent*** (***oxidant*** or ***oxidizer***) is *reduced* to a lower oxidation number:

- In reaction 1, oxygen gas is *reduced* to a *lower* oxidation number; hence, it is the an *oxidant*.
- In reaction 2, chlorine gas is *reduced* to a lower oxidation number; hence, the *oxidant*.

Generally, diatomic elements in groups VI and VII in the periodic table are oxidizing agents, e.g. $O_2$, $F_2$ $Cl_2$, $Br_2$ and $I_2$. Others are $H_2O_{2(l)}$, $MnO_{2(s)}$, concentrated $HNO_3$ and $H_2SO_4$, acidified solutions of $KMnO_4$ and $K_2Cr_2O_7$, and solutions of iron(II) salts and iron(II) hydroxide.

#### Reducing agents

In a *redox reaction*, a ***reducing agent*** (***reductant*** or ***reducer***) is *oxidized* to a *higher* oxidation number, e.g.

- In reaction 1 above, magnesium atom is *oxidized* to a *higher* oxidation number; hence, the *reducing agent* in the reaction.
- In reaction 2 above, $Fe^{2+}$ in $FeCl_2$ is oxidized to $Fe^{3+}$, hence, $FeCl_2$ is the *reducing agent*.

Generally, elements in groups I, II and III in the periodic table are reducing agents. Other common reducing agents include concentrated hydrochloric acid, KI(aq), $SnCl_2$(aq), iron(II) salts, and $Fe(OH)_3$. $SO_2$ gas is also a reducing agent. Some non-metals act as oxidizing and reducing agents, e.g. carbon, sulphur and phosphorus.

In a redox reaction, the *reducing agent* is an *electron donor*, while the *oxidizing agent* is an *electron acceptor*.

### *Disproportionation reaction*

Consider the thermal decomposition of potassium trioxochlorate(V):

$$\underset{\text{O.N.}}{\underset{}{2KClO_3(s)}} \rightarrow \underset{+5\ -2}{\underset{}{2KCl(s)}} + \underset{-1}{\underset{}{3O_2(g)}} \quad \underset{0}{\underset{}{}}$$

In this reaction, the O.N. of Cl atom *decreased* from +5 in $KClO_3$ to -1 in KCl, i.e. $KClO_3$ has been *reduced*; hence, it is the *oxidizing agent*. In the same reaction, the O.N. of oxygen atom *increased* from -2 in $KClO_3$ to 0 in $O_2$ gas, i.e. $KClO_3$ has been *oxidized*; hence, it is the *reducing agent*.

In this reaction, $KClO_3$ is acting as a *reducing agent*, and at the same time as *an oxidizing agent*. $KClO_3$ is said to *disproportionate*; the change is a *disproportionation* reaction.

## Laboratory tests for redox reagents

### *Tests for a reducing agent*

An *oxidizing agent* is used to test for a *reducing agent*. Any substance that reacts in one or more of the following reactions is a *reducing agent*:

- Put the solid substance in a test tube, and add a few drops of bench dilute hydrochloric acid.

*There is effervescence; the gas given off is colourless, odourless, has no action on moist red or blue litmus paper, but gives a pop sound with lighted splint.*

*The gas is hydrogen, while the substance is a metal above hydrogen in the activity series.*

- To the solution of the substance, add a few drops of purple acidified $KMnO_4$ solution.

*Purple $KMnO_4$ solution is decolourised.*

- To the solution of the substance, add a few drops of orange acidified $K_2Cr_2O_7$ solution.

*Orange $K_2Cr_2O_7$ solution turns green.*

- To the solution of the substance, add a few drops of brown solution of $FeCl_3$.

*Brown solution turns green.*

### *Tests for an Oxidizing agent*

A *reducing agent* is used to test for an *oxidizing agent*.

Any substance that reacts in one or more of the following reactions is an *oxidizing agent*:

- Allow $H_2S$ gas to come in contact with a solution of the substance on a strip of filter paper.

*There is a yellow deposit of sulphur on the filter paper.*

- To the solution of the substance, add a few drops of colourless acidified potassium iodide solution.

*The solution turns brown, due to the evolution of iodine,* and then, *turns starch solution blue-black.*

- Heat a little of the substance with conc HCl.

*A greenish-yellow gas with pungent smell is evolved. The gas, which bleaches litmus paper is chlorine.*

- Heat the substance strongly in a test tube.

*Gas evolved is colourless, odourless, has no action on litmus paper, but relights a glowing splint. Gas is $O_2$.*

## Solved Problems

**1.** A reducing agent is expected to
- **A.** decolorize acidified $KMnO_4$ solution.
- **B.** decolorize acidified $FeSO_4$ solution.
- **C.** liberate $Cl_2$ from a chloride.
- **D.** liberate $CO_2$ from $NaHCO_3$. [WAEC]

**Answer:** *A*

**2.** Consider the following reaction:

$$\underset{\text{O.N.}}{\underset{}{3Cu}} + \underset{0}{\underset{}{8HNO_3}} \rightarrow \underset{+5}{\underset{}{3Cu(NO_3)_2}} + \underset{+2}{\underset{}{2NO}} + \underset{+5}{\underset{}{4H_2O}} \quad \underset{+2}{\underset{}{}}$$

a. Name the species reduced and the species oxidized. *Trioxonitrate(IV) acid is the species reduced. Copper is the species oxidized.*

b. Give the product of the oxidizing agent and the product of the reducing agent.

*Product of the oxidizing agent($HNO_3$) is NO.*

*Product of reducing agent (Cu) is $Cu(NO_3)_2$.*

## Revision Exercises

**4.** Define *oxidation* and *reduction* in terms of
- **a.** electron transfer.
- **b.** change in oxidation number

**5.** The oxidation number of X in $XO_4^{3-}$ is

**A.** +1 **B.** +2 **C.** +3 **D.** +4 **E.** +5 [NECO]

**6.** In which of the following reactions are the underlined species oxidized?

I. $2\underline{Fe}^{2+}_{(aq)} + Cl_{2(g)} \rightarrow 2Fe^{3+}_{(aq)} + 2Cl^-_{(aq)}$

II. $\underline{S}^{2-}_{(aq)} + Cl_{2(g)} \rightarrow S_{(s)} + 2Cl^-_{(aq)}$

III. $2\underline{Mg}_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)}$

IV. $2Al_{(s)} + 6\underline{H}^+_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3H_{2(g)}$

**A** IV only. **B** I and III only. **C** III and IV only. **D** I, II and III only. **E** I, II, III and IV.

**7.** Name two oxidizing agents and two reducing agents.

**8.** What term is used to describe a redox reaction in which a reactant is simultaneously acting as an oxidizing agent and as a reducing agent?

**9.** Describe a chemical test for each of a named oxidizing agent and a named reducing agent.

### Balancing Simple Redox Equations

In order to obtain the equation of a redox reaction, an *oxidation half reaction* is paired with a *reduction half reaction*. In order to balance such a reaction, the *number of electrons lost* must be equal to the *number of electrons gained*.

Redox equations are balanced by two methods:

1. Ion-electron method.
2. Oxidation number method.

#### 1. Ion-Electron Method

Simple ionic equations contain simple ions, e.g.

When chlorine gas is bubbled into aqueous iron (II) chloride, aqueous iron(III) chloride is obtained:

$$Fe^{2+}_{(aq)} + Cl_{2(g)} \rightarrow Fe^{3+}_{(aq)} + Cl^-_{(aq)}$$

*Ion-electron method involves splitting of the redox reaction into oxidation and reduction halves.*

The steps to be followed are:

a. *Assign oxidation number (O.N.) to each atom of element that has changed in the equation:*

$$Fe^{2+} + Cl_2 \rightarrow Fe^{3+} + Cl^-$$
O. N. +2 0 +3 -1

b. *Separate the reaction into oxidation half and reduction half:*

**Oxidation half:** $Fe^{2+} \rightarrow Fe^{3+}$ [*Increase in O.N.*]

**Reduction half:** $Cl_2 \rightarrow Cl^-$ [*Decrease in O.N.*]

c. *Balance each half reaction as follows:*

i. *Balance the number of atoms on both sides, to conform to the law of conservation of mass:*

**Oxidation half:** $Fe^{2+} \rightarrow Fe^{3+}$ (*Atoms balanced*)

**Reduction half:** $Cl_2 \rightarrow Cl^-$ (*Atoms not balanced*)

A molecule of chlorine, $Cl_2$ produces two chloride ions, i.e. $Cl_2 \rightarrow 2Cl^-$ (Atoms balanced)

ii. *Add appropriate number of electrons to account for the number of electrons lost or gained, i.e. to balance the charges:*

**Oxidation half:** $Fe^{2+} \rightarrow Fe^{3+}$ [*Loss of electrons*]

Change in O.N. of Fe = (+3) – (+2) = +1 corresponds to a *loss* of 1 electron. Add *one electron* to the right-hand-side, i.e.

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$ [*Charges balanced*]
+2 +3 -1

**Reduction half:** $Cl_2 \rightarrow 2Cl^-$ [*Gain of electrons*]

Change in O.N. of each Cl = -1 – 0 = -1 corresponds to a *gain* of 1 electron. $Cl_2$ *gains* $2e^-$. Add $2e^-$ to the left-hand-side, i.e.

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$ [*Charges balanced*]
0 -2 -2

d. *Multiply each half reaction by the appropriate coefficients, to balance electron-loss and electron-gain:*

**Oxidation half:** $Fe^{2+} \rightarrow Fe^{3+} + e^-$

**Reduction half:** $Cl_2 + 2e^- \rightarrow 2Cl^-$

There is a *loss of one electron* in the oxidation half, and a *gain of two electrons* in the reduction half. *Multiply oxidation half by 2.*

**Oxidation half:** $2Fe^{2+} \rightarrow 2Fe^{3+} + 2e^-$

**Reduction half:** $Cl_2 + 2e^- \rightarrow 2Cl^-$

e. *Add the two half reactions, canceling the common terms*, i.e. $2e^-$:

**Net reaction:** $2Fe^{2+} + Cl_2 \rightarrow 2Fe^{3+} + 2Cl^-$

f. *Check on the charges:*

$$2(+2) + 0 = 2(+3) + 2(-1)$$
$$+4 = +6 - 2$$
$$+4 = +4$$

#### 2. Oxidation Number Method

*Oxidation number* method is used without splitting the redox reaction.

- Consider the reaction:

$$Mg + Ag^+ \rightarrow Mg^{2+} + Ag$$

The steps to be followed are:

a. *Assign oxidation number (O.N.) to each atom of element that has changed in the equation:*

$$Mg + Ag^+ \rightarrow Mg^{2+} + Ag$$
O. N. 0 +1 +2 0

Change in O.N. of Mg = +2 – 0 = +2. [*Loss of 2e⁻*]

Change in O.N. of Ag = 0 – (+1) = –1. [*Gain of 1e⁻*]

b. *Equalize changes in oxidation numbers*

For each atom of Mg *oxidized*, two atoms of $Ag^+$ are *reduced*. Multiply Ag atoms by 2:

$$Mg + 2Ag^+ \rightarrow Mg^{2+} + 2Ag$$

c. Check on the charges:

$$0 + 2(+1) = +2 + 2(0)$$
$$+2 = +2$$

- Consider the reaction:

$$Fe^{2+}_{(aq)} + Cl_{2(g)} \rightarrow Fe^{3+}_{(aq)} + Cl^-_{(aq)}$$
O. N. +2 0 +3 -1

First, balance chlorine atoms on the right:

$$Fe^{2+}_{(aq)} + Cl_{2(g)} \rightarrow Fe^{3+}_{(aq)} + 2Cl^-_{(aq)}$$

Change in O.N. of Fe = (+3) – (+2) = +1 [*Loss of 1e⁻*]

Change in O.N. of Cl = -1 – 0 = -1 [*Gain of 1e⁻*]

For each $Fe^{2+}$ oxidized, one Cl atom is reduced. Since there are 2 Cl atoms, multiply Fe atoms by 2.

$$2Fe^{2+}_{(aq)} + Cl_{2(g)} \rightarrow 2Fe^{3+}_{(aq)} + 2Cl^-_{(aq)}$$

Check on the charges:

$$2(+2) + 0 = 2(+3) + 2(-1)$$
$$+4 = +6 - 2$$
$$+4 = +4$$

### Solved Problems

**3.** In the reaction below:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

**a.** Which metal is reduced, and which metal is oxidized?

*Assign oxidation numbers to the species,*

$$\underset{0}{Zn} + \underset{+2}{Cu^{2+}} \rightarrow \underset{+2}{Zn^{2+}} + \underset{0}{Cu}$$

*O.N.*

*$Cu^{2+}$ is reduced to Cu, while Zn is oxidized to $Zn^{2+}$.*

b. Write the half equations for the reaction.

*Oxidation:* $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

*Reduction:* $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

c. State, with reasons, which is the oxidizing agent and which is the reducing agent.

*Oxidizing agent is $Cu^{2+}$, because it is reduced to Cu.*

*Reducing agent is Zn, because it is oxidized to $Zn^{2+}$.*

d. State the change in the oxidation number of the oxidizing agent.

*Change in oxidation number of oxidizing agent is from +2 to 0.*

4. What quantity of electrons (in moles) is lost when one mole of iron(II) ions is oxidized to iron (III) ions. **A.** 4. **B.** 3. **C.** 2. **D.** 1.

Solution: *D* $[Fe^{2+} \rightarrow Fe^{3+} + e^-]$
1 mol 1 mol

5. Consider the reaction:

$$2Al_{(s)} + 6H^+_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3H_{2(g)}$$

What is the total number of moles of electrons transferred from the aluminium atoms to the hydrogen ions?

A. 3 **B.** 4 **C.** 5 **D.** 6 [WAEC]

Solution: *D* [2 moles of Al(s) lost 6 electrons; 6 moles of $H^+$ gained the 6 electrons.]

### Revision Exercises

10 Split each of the following equations into two balanced half cell equations:

a. $Mg + Fe^{2+} \rightarrow Mg^{2+} + Fe$

b. $Al + I_2 \rightarrow Al^{3+} + I^-$

11 a. Write balanced half equations for the following redox reaction:

$$Fe^{3+}_{(aq)} + H_2S_{(g)} \rightarrow Fe^{2+}_{(aq)} + H^+ + S_{(s)}$$

b. Which of the reactants is the reducing agent?

c. State the change in the oxidation number of the reducing agent.

## 23.3 Electrochemical (Voltaic) Cells

When a strip of a metal, such as zinc, is dipped into a solution of its salt, an electrical potential difference is set up between the metal, M(s) and its ions, $M^{n+}(aq)$ at equilibrium:

$$M(s) \rightleftharpoons M^{n+}(aq) + ne^-$$

This is represented as $M(s)/M^{n+}(aq)$. The slanting line, /, represents the boundary or interface between the solid and the liquid. Under this condition, the set-up constitutes a half cell (fig 23.1). *A metal dipped into a solution of its salt is an* ***electrode.***

When two different half cells are separated by a porous partition that allows the diffusion of ions, electron-transfer occurs *externally* through the connecting wire (a conductor) between the two electrodes, as indicated by the glowing of a bulb, or a deflection in the ammeter, A. Such a set-up is called ***galvanic, voltaic,*** or ***electrochemical cell*** (fig 23.2). The flow of electrons through the conductor constitutes an electric current.

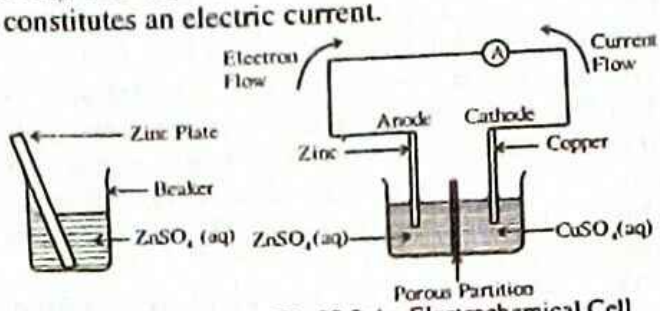



**Fig 23.1** An Electrode **Fig 23.2** An Electrochemical Cell

An *electrochemical cell is a device that uses a spontaneous chemical reaction in aqueous solution to generate electric current,* i.e. *converts chemical energy into electrical energy.*

### Revision Exercises

12 What name is given to

a. a metal strip dipped into a solution of its salt?

b. the arrangement of two different metals in aqueous solutions of their salts to produce an electric current?

13 State the energy conversion in an electrochemical cell.

14 Consider the following representation: $M(s)/M^{n+}(aq)$. What does the slanting line indicate?

## 23.4 Standard Electrode Potentials

When a voltmeter, V is connected between the two electrodes in a *voltaic cell,* the force with which the electrons are being pushed around the cell is called *electromotive force, emf.* It is measured in *volts,* V.

The *emf* value of a cell, $E_{cell}$, is a quantitative measure of the tendency of a redox reaction to occur in the cell. It is equal to the difference between the *electrode potentials,* $E_1$ and $E_2$ of the two electrodes that constitute the cell.

The *electrode potential of an electrode* is a quantitative measure of the ability of an atom or ion to gain electrons at the electrode. Its value depends on the *nature of the metal and its ion (the electrode),* the *concentration of the ions in the solution,* and the *temperature of the cell.*

The *electrode potential* of a *half-cell cannot be measured; except the emf of a cell for a complete circuit with two electrodes*. Instead, the *electrode potential of a half-cell is determined by coupling it with that of hydrogen electrode; the reference standard, assigned zero potential* (0.00 V).

***Standard Hydrogen Electrode***

The *standard hydrogen electrode* consists of a platinised platinum electrode passing through a glass tube, dipping into a *one mole per dm*$^3$ solution of hydrochloric acid (1.0 *moldm*$^{-3}$ $H_3O^+$), with pure hydrogen gas at one atmospheric pressure and 25 °C (298 K) bubbling around the platinised platinum (fig 23.3). The platinised platinum acts as a catalyst, to quicken the rate of attainment of equilibrium between hydrogen gas, $H_2$ and hydrogen ions, $H^+$, in the solution.

The *half reaction for the standard hydrogen electrode*, written in the *reduction form* is:

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \qquad E^\circ = 0.00\ V$$

## Measurement of Standard Electrode Potentials

In order to measure the standard electrode potential of a half cell, its electrode is coupled to the standard hydrogen electrode via a *salt bridge*. A *salt bridge* is an inverted U-tube containing a saturated solution of an electrolyte, such as $Na_2SO_4$, KCl and $KNO_3$. It allows the *migration of ions* between two electrodes (figure 23.3).

In order to compare the electrode potentials of various half-cells, electrode potentials are measured under the following standard conditions:

- Concentration of the electrolyte is 1.0 *moldm*$^{-3}$.
- Gaseous reactant is at one atmospheric pressure.
- Temperature of the cell is 25 °C (298 K).
- Platinum electrode is used when a metal is not involved in the half-cell.

Under these conditions, the *electrode potential* is called the *standard electrode potential*, $E^\circ$. The superscript ($^\circ$) stands for *standard state*.

## Standard electrode potential of Copper half-cell

When a standard copper half cell is coupled to a standard hydrogen half cell, the *emf* of the cell, $E^\circ_{cell}$, is found to be 0.34 V, with the copper electrode forming the *positive* terminal of the cell (fig 23.3).

**Reactions at the Electrodes:**

***At Hydrogen electrode:***

$$H_2(g) \rightarrow 2H^+(aq) + 2e^- \qquad \text{(Oxidation)}$$

***At Copper electrode:***

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad \text{(Reduction)}$$

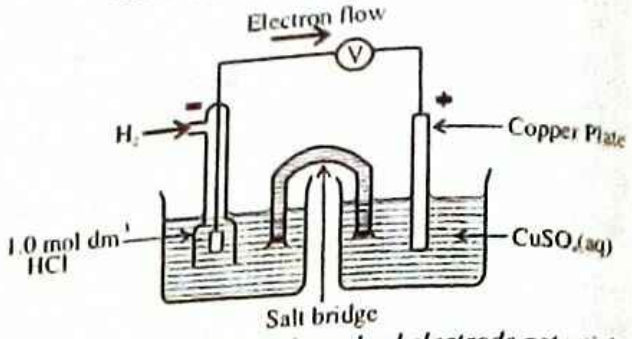



**Fig 23.3** *Determination of standard electrode potential of copper*

Since the standard electrode potential of hydrogen electrode is zero, then, the *emf* of the cell, $E^\circ_{cell}$, is the standard electrode potential of the half-cell attached to the standard hydrogen half-cell. Hence, the half cell reaction for copper is:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad E^\circ = +0.34\ V$$

The *plus sign* shows that in the cell, *the copper electrode is positively charged relative to the standard hydrogen electrode*. It also shows that *$Cu^{2+}$ has a greater attraction for electrons than $H^+$*.

The above half reaction and its standard electrode potential, when written in the *reduction* form is:

$$Cu^{2+}(aq) / Cu(s)\ ;\ E^\circ = +0.34\ V$$

## Standard electrode potential of Zinc half-cell

When a standard zinc half-cell is coupled to the standard hydrogen half-cell, the *emf* of the cell, $E^\circ_{cell}$, is found to be 0.76 V, but with the zinc electrode forming the *negative* terminal relative to the standard hydrogen electrode (fig 23.4).

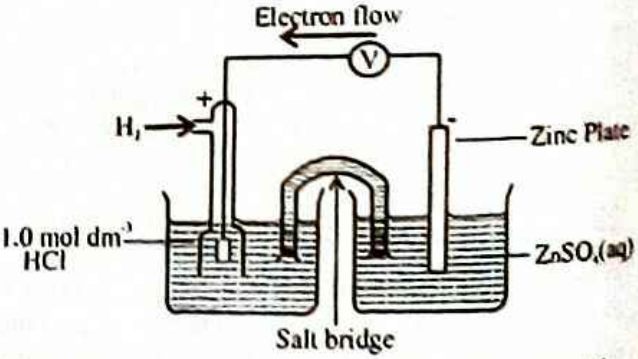



**Fig 23.4** *Determination of standard electrode potential of zinc*

**Reactions of the Electrodes:**

***At the Zinc electrode:***

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad \text{(Oxidation)}$$

***At the Hydrogen electrode:***

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad \text{(Reduction)}$$

The half cell reaction for the zinc electrode is

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $\quad E^\circ = -0.76$ V

Hence, the standard electrode potential for the zinc electrode is:

$Zn^{2+}(aq) / Zn(s)$; $\quad E^\circ = -0.76$ V.

The *negative* sign shows that *the zinc electrode is negatively charged relative to the hydrogen electrode*, i.e. *$H^+$ has a greater attraction for electrons than $Zn^{2+}$.*

**Revision Exercises**

15 Name the electrode to which each half cell should be coupled, if the reduction potentials of the half cells are to be determined.

16 Describe briefly, the standard hydrogen electrode.

17 State *two* conditions under which the standard electrode potentials are determined.

## 23.5 The Electrochemical Series

When common elements and redox reagents are arranged in order of *increasing values of their standard electrode potentials*, the *order* obtained is called ***electrochemical series*** (Table 23.1). *The electrode potential, $E^\circ$ for each electrode is obtained relative to the standard hydrogen electrode.*

The sign convention used in this book is according to the European system adopted by the IUPAC. It is the *reduction potential*; that is, the ability of a species to accept electrons, i.e.

$$M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)}$$

$$X_{(g)} + ne^- \rightarrow X^{n-}_{(aq)}$$

*The value of the standard (reduction) electrode potential is a measure of the tendency of a species to accept electrons, and acts as an oxidizing agent.*

- A *negative* $E^\circ$ value indicates a *weak attraction* to electrons; hence, the species is a *weaker oxidizing agent* than hydrogen ion, $H^+$. The more negative the value, the weaker the attractions for electrons. Lithium ion, $Li^+$ is the weakest oxidizing agent among the species.
- A *positive* $E^\circ$ value indicates a *strong attraction* to electrons; hence, a *stronger oxidizing agent* than hydrogen ion, $H^+$. The more positive the $E^\circ$ value, the stronger the attraction to electrons. The atoms of the halogens have strong attraction to electrons; hence, they form negative ions (halides) readily. Fluorine gas, $F_2$ is the most electronegative, and hence, the strongest oxidizing agent.

**Table 23.1** *Standard Electrode Potential $E^\circ$ of Common Elements and Reagents at 298K*

| Oxidizing $\rightleftharpoons$ Reducing | $E^\circ$, V |
|---|---|
| $Li^+(aq) + e^- \rightleftharpoons Li(s)$ | -3.05 |
| $K^+(aq) + e^- \rightleftharpoons K(s)$ | -2.93 |
| $Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$ | -2.87 |
| $Na^+(aq) + e^- \rightleftharpoons Na(s)$ | -2.71 |
| $Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ | -2.37 |
| $Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$ | -1.66 |
| $Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$ | -1.18 |
| $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ | -0.76 |
| $Cr^{3+}(aq) + 2e^- \rightleftharpoons Cr(s)$ | -0.74 |
| $Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$ | -0.44 |
| $Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$ | -0.40 |
| $Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$ | -0.28 |
| $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ | -0.25 |
| $Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$ | -0.14 |
| $Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$ | -0.13 |
| $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$ | 0.00 |
| $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ | +0.34 |
| $I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$ | +0.54 |
| $Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ | +0.77 |
| $Ag^+(aq) + e^- \rightleftharpoons Ag(s)$ | +0.80 |
| $Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg(l)$ | +0.85 |
| $Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$ | +1.08 |
| $\frac{1}{2} O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O(l)$ | +1.23 |
| $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ | +1.36 |
| $Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$ | +1.36 |
| $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$ | +1.51 |
| $F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$ | +2.87 |

### Activity series versus Electrochemical series

The ***activity series of metals*** and the ***electrochemical series*** are *directly opposite*:

- In the *electrochemical series*, metals are arranged in *increasing order* of the ability of their cations in solutions to accept electrons, and act as *oxidizing agents*. Under this condition, $Cu^{2+}$ in solution is a more powerful oxidizing agent than $Zn^{2+}$.
- The *activity series* arranges the metals in *decreasing order* of ability to react as *reducing agents*. Under this condition, zinc metal, Zn(s) is more *electropositive* and hence, a more reactive *reducing agent* than copper metal, Cu(s).

However, they can be regarded as being similar:

• In the *electrochemical series*, like in the *activity series*, a *metal above* will displace the *ions of a metal below it* from a solution of its salt. For instance: zinc metal, Zn, will displace copper(II) ions, $Cu^{2+}$ from a solution of copper(II) salt.

## Applications of the Electrochemical Series

1. The *values of the standard electrode potentials are used in comparing the relative oxidizing abilities of different species*. For instance:
$Cu^{2+}$ *(with a higher* $E^\circ$ *value) is a stronger oxidizing agent than* $Zn^{2+}$ *(with a lower* $E^\circ$ *value).*

2. The *electrochemical series* can be used to identify the ion to be discharged, preferentially, at the electrodes during electrolysis. For instance: When $Mg^{2+}$ and $Fe^{2+}$ of the same concentration are present at the cathode, $Fe^{2+}$ is discharged in preference to $Mg^{2+}$. This is because $Fe^{2+}$ *(with a higher* $E^\circ$*)*, being lower in the series, will accept electrons more readily than $Mg^{2+}$ *(with a lower* $E^\circ$ *value).*

3. In a *voltaic* (*redox*) cell where two metals compete for electrons, *oxidation (loss of electrons)* occurs at the electrode with the *lower* $E^\circ$ *value*, while *reduction (gain of electrons)* occurs at the electrode with the *higher* $E^\circ$ *value*.

Hence, when two *redox agents* are used in a voltaic cell, electrons flow from the half cell with the *lower* $E^\circ$ value, the *anode*, to the half cell with the *higher* $E^\circ$ value, the *cathode*, e.g.

a. In the following half reactions:

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$; $E^\circ = +0.34$ V (lower)

$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$; $E^\circ = +0.80$ V (higher)

The copper electrode with the lower $E^\circ$ forms the *anode*, and loses its electrons to the silver electrode with the higher $E^\circ$, the *cathode*.

b. In the following half reactions:

$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$; $E^\circ = -0.76$ V (lower)

$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$; $E^\circ = -0.25$ V (higher)

The zinc electrode (lower $E^\circ$) forms the *anode* and loses its two valence electrons to the nickel electrode (higher $E^\circ$ value), the *cathode*.

c. In the following half reactions:

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$; $E^\circ = +0.34$ V (higher)

$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$; $E^\circ = -0.76$ V (lower)

The flow of electrons is from the zinc electrode *(lower* $E^\circ$*)* to the copper electrode *(higher* $E^\circ$*)*.

4. A *reducing agent*, such as zinc, is *oxidized* to $Zn^{2+}$, by an *oxidizing* agent below it in the series, such as $Cu^{2+}$; i.e. zinc metal will displace $Cu^{2+}$ from a solution of copper(II) salt.

Similarly, fluorine, a very strong *oxidizing agent*, will displace $Cl^-$, $Br^-$, or $I^-$ from an aqueous solution of its salt.

## Cathodic Protection

This *device or process is used to protect iron from rusting*. The *pier* or *hull* of a ship is usually made of iron, which quickly rusts in the salty sea-water. To prevent rusting, *bars* of magnesium metal are usually bolted to the *hull*.

By this arrangement, the *bars* of magnesium and the iron *hull* constitute the electrodes, while the seawater, which contains dissolved salts of sodium and magnesium, forms the electrolyte of the voltaic cell. Since magnesium is more electropositive than iron, it forms the anode, and dissolves to form magnesium ions; the iron hull, which forms the cathode is unaffected, and remains intact.

The *bars of magnesium, therefore, functions as a sacrificial anode by protecting the iron hull, the cathode, from rusting* – hence, the term *cathodic protection*.

Generally, any metal above iron in the *activity* or *electrochemical series* can be used instead of magnesium, e.g. aluminium and zinc.

## Zinc-plating and Tin-plating

***Observation***: When an iron sheet that has been *galvanized* with *molten zinc* is scratched, rusting does not occur, even in the presence of water.

***Reason***: Zinc, iron and water (carbonated) constitute a voltaic cell. Zinc, being more electropositive than iron, dissolves and goes into solution as zinc ions. The zinc ions combine with hydroxide ions in water to form insoluble zinc hydroxide, which acts as a protective coating, and thus, prevents iron from rusting.

On the contrary, when a *tin-plated* iron sheet is scratched in the presence of water, iron is oxidized to $Fe^{2+}$ instead of tin. This is because iron is more electropositive than tin. Hence, rusting occurs.

### Solved Problem

**6.** State **three** differences between an electrochemical cell and an electrolytic cell. [WAEC]

**Solution** (*Any three of the following*)

| | Electrochemical Cell | Electrolytic Cell |
|---|---|---|
| 1 | Chemical reaction produces electric current | Electric current produces a chemical reaction |
| 2 | Electrodes are in different electrolytes | Electrodes are in the same electrolyte |

| | | |
|---|---|---|
| 3 | Electrons are produced at the anode | Electrons are produced from a battery. |
| 4 | Anode is the negative electrode | Anode is the positive electrode |
| 5 | Cathode is the positive electrode | Cathode is the negative electrode. |

**Revision Exercises**

18 Consider the following half cell reactions:

$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$; $E^\circ = -0.14$ V

$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$; $E^\circ = -2.37$ V

a. In a voltaic cell, indicate in which half reaction oxidation is taking place, and in which half reaction reduction is taking place.

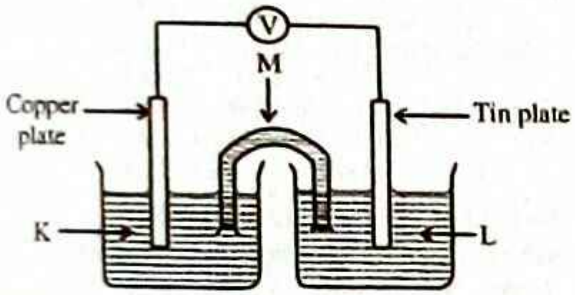
b. State the direction of flow of electrons in the cell.

19 Pure copper metal is obtained when a solution containing $Cu^{2+}$ trickle over scrap iron.

a. Write the equations for the half reactions involved, if the iron becomes $Fe^{2+}$.

b. Indicate in which half reaction oxidation is taking place.

20 In the diagram below:




A. K is $Sn^{2+}_{(aq)}$, L is $Cu^{2+}_{(aq)}$ and M is a salt bridge.
B. K is a salt bridge, L is $Cu^{2+}_{(aq)}$ and M is $Sn^{2+}_{(aq)}$.
C. K is $Cu^{2+}_{(aq)}$, L is a salt bridge and M is $Sn^{2+}_{(aq)}$.
D. K is $Cu^{2+}_{(aq)}$, L is $Sn^{2+}_{(aq)}$ and M is a salt bridge.

21 Explain why zinc forms a more protective coating for iron than tin. [WAEC]

## 23.6 Cell Notation

An *electrochemical* is composed of two half-cells, and can be represented by a *cell notation*. The *cell notation* gives the direction of reaction. By convention, the *anode* reaction of a cell is written first, on the *left*, while the *cathode* reaction is on the *right* of the *double line* in the *cell notation*. For example: the *Daniel cell* is composed of two half-cells: $Zn^{2+}_{(aq)}/Zn_{(s)}$ and $Cu^{2+}_{(aq)}/Cu_{(s)}$. The *cell notation* in Daniel cell is written as:

$$Zn_{(s)} / Zn^{2+}_{(aq)} // Cu^{2+}_{(aq)} / Cu_{(s)}$$

The *single lines* denote the boundaries between a metal and its ions in solution, while the *double line* represents the *porous partition* or the *salt bridge*.

Hence, the half-cell reactions in Daniel cell are:

**At the Anode:** $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

**At the Cathode:** $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

**Cell reaction:** $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

When an inert electrode, such as platinum, is used in a half cell, the reduced form in the half cell is written next to the electrode. Hence, the standard hydrogen electrode is written as:

$$Pt(s) / H_2(g), H^+(aq) \textit{ or } H^+(aq), H_2(g) / Pt(s)$$

and *not*:

$$Pt(s) / H^+(aq), H_2(g) \textit{ or } H_2(g), H^+(aq) / Pt(s).$$

For instance: the cell notation for the hydrogen-zinc couple is:

$$Zn(s) / Zn^{2+}(aq) // H^+(aq), H_2(g) / Pt(s)$$

And for the hydrogen-copper couple, it is:

$$Pt(s) / H_2(g), H^+(aq) // Cu^{2+}(aq) / Cu(s)$$

**Revision Exercises**

22 Consider the cell represented as shown below:

$Zn(s) / Zn^{2+}(aq) // Cu^{2+}(aq) / Cu(s)$

a. What does the vertical double stroke represent?

b. Which of the metals form the cathode? [WAEC]

23 Draw a well-labeled diagram to illustrate the cell

$Mg(s) / Mg^{2+}(aq) // H^+(aq), H_2(g) / Pt(s)$

Indicating which electrodes are the cathodes and anodes as well as the direction of flow of current. Write the equation for each electrode.

24 If the overall reaction in a cell is:

$2Al(s) + 6H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2(g)$

Write the cell notation.

## 23.7 E.M.F. of a Cell and Predicting Reactions

The *standard emf of a cell*, $E^\circ_{cell}$, is used in predicting whether a reaction will occur spontaneously or not. A redox reaction will be spontaneous, if the standard *emf* of the cell, $E^\circ_{cell}$, is *positive*.

The $E^\circ_{cell}$ of a redox reaction is the difference between the *standard electrode potentials* (*potential difference*) of its two half cells. The two half cells must be such that as in the *cell notation*, one represents *oxidation* (the *anode*, on the *left*) and the other is *reduction* (the *cathode*, on the *right*).

The *standard emf (redox potential) of a cell* is:

$$E^\circ_{cell} = E^\circ_{reduced} - E^\circ_{oxidized}$$
$$= E^\circ_{cathode} - E^\circ_{anode}$$
$$= E^\circ_{right} - E^\circ_{left}$$

**Worked Examples**

**7.** Calculate the emf of the Daniel cell represented by the cell notation:

$$Zn_{(s)} / Zn^{2+}_{(aq)} // Cu^{2+}_{(aq)} / Cu_{(s)}$$

Given that: $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$; $E^\circ = -0.76$ V
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$; $E^\circ = +0.34$ V

*To calculate the $E^\circ_{cell}$*

The expression to be used from the cell notation is:

$$E^\circ_{cell} = E^\circ_{right} - E^\circ_{left}$$
$$(\text{or } E^\circ_{cell} = E^\circ_{reduced} - E^\circ_{oxidized})$$
$$E^\circ_{right} = E^\circ_{reduced} = +0.34 \text{ V}$$
$$E^\circ_{left} = E^\circ_{oxidized} = -0.76 \text{ V}$$

On substituting: $E^\circ_{cell} = 0.34 \text{ V} - (-0.76 \text{ V})$
$= 0.34 \text{ V} + 0.76 \text{ V} = 1.10 \text{ V}$

**8 a.** Calculate the emf of the following reaction:

$$2Ag_{(s)} + Fe^{2+}_{(aq)} \rightarrow Fe_{(s)} + 2Ag^{+}_{(aq)}$$

Given that: $Ag^{+}_{(aq)} / Ag_{(s)}$, $E^\circ = +0.80$ V
$Fe^{2+}_{(aq)} / Fe_{(s)}$, $E^\circ = -0.44$ V

**b.** Comment on the value of the emf obtained in a above.

**a.** *To calculate the emf of the cell*

Assign O. N.'s to the species in the reaction:

$$2Ag_{(s)} + Fe^{2+}_{(aq)} \rightarrow Fe_{(s)} + 2Ag^{+}_{(aq)}$$
O. N. 0 +2 0 +1

$Ag_{(s)}$ is *oxidized*, hence the *anode*

$\therefore E^\circ_{anode} = +0.80$ V

$Fe^{2+}$ is *reduced*; hence the *cathode*

$\therefore E^\circ_{cathode} = -0.44$ V.

Using the expression: $E^\circ_{cell} = E^\circ_{reduced} - E^\circ_{oxidized}$
( or $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$)

Substituting: $E^\circ_{cell} = -0.44 \text{ V} - (+0.80 \text{ V})$
$= -0.44 \text{ V} - 0.80 \text{ V}$
$= -1.24$V

**b.** Since the $E^\circ_{cell}$ is negative, the reaction will not occur spontaneously in the forward reaction.

**Notes on the above reaction**

i. A close look at the $E^\circ$ values of the half cells shows that $Ag^+$ has a greater attraction for electrons than $Fe^{2+}$, i.e. $Ag^+$ should be reduced, and Fe(s) oxidized. Hence, the reverse reaction will be spontaneous, i.e.

$$Fe_{(s)} + 2Ag_{(aq)} \rightarrow 2Ag_{(s)} + Fe^{2+}_{(aq)}$$
$E^\circ_{reduced} = 0.80$V; $E^\circ_{oxidized} = -0.44$ V
$E^\circ_{cell} = E^\circ_{reduced} - E^\circ_{oxidized}$
$= 0.80\text{V} - (-0.44\text{V})$
$= 0.80\text{V} + 0.44\text{V} = 1.24\text{V}.$

$$Fe_{(s)} + 2Ag^{+}_{(aq)} \rightarrow Fe^{2+}_{(aq)} + 2Ag_{(s)}$$
$E^\circ_{cell} = +1.24$ V.

ii. The $E^\circ$ value for $Ag^+(aq) / Ag(s)$ [$E^\circ = 0.80$ V] is not affected by the stoichiometry of the balanced equation of reaction, i.e.

$Ag^+(aq) + e^- \rightarrow Ag(s)$ has $E^\circ$ value of +0.80 V;

For the reaction: $2[Ag^+(aq) + e^- \rightarrow Ag(s)]$

$E^\circ$ value is the same +0.44 V, and not 2[+ 0.44 V]!

This is because whether a reaction will occur or not does not depend on the amount of reactants to be used. Again, under standard conditions, $E^\circ$ value is independent of the amount of electrons transferred.

## Free Energy Change

In an electrochemical cell, the relationship between the *standard free energy change*, $\Delta G^\circ$ of the cell reaction and the *emf of the cell*, $E^\circ$ is:

$$\Delta G^\circ = -nFE^\circ$$

where n = moles of electrons transferred in the reaction, and F = value of the Faraday (96500 C).

**Solved Problems**

**9.** A feasible cell was constructed by joining the two half cells below:

$Co^{2+}(aq) + 2e^- \rightarrow Co(s)$ ; $E^\circ = -0.28$
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ ; $E^\circ = +0.34$

What is the standard emf of the cell?

*To calculate the emf of a feasible cell*

To obtain a feasible cell, the cobalt electrode with the lower $E^\circ$ forms the *anode*, while the copper electrode with the higher $E^\circ$ forms the *cathode*, i.e. oxidation occurs at cobalt electrode,

$\therefore E^\circ_{anode} = E^\circ_{oxidized} = -0.28$ V

Reduction occurs at the copper electrode,

$\therefore E^\circ_{cathode} = E^\circ_{reduced} = +0.34$ V

Using the expression: $E^\circ_{cell} = E^\circ_{reduced} - E^\circ_{oxidized}$
( or $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$)

Substituting: $E^\circ_{cell} = +0.34\text{V} - (-0.28\text{V})$
$= +0.34\text{V} + 0.28\text{V}$
$= +0.62$ V

**10** Predict whether nickel metal will dissolve in a one *mole per $dm^3$* solution of a manganese(II) salt.

Given: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$; $E^\circ = -0.25$V
$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$; $E^\circ = -1.18$V

*The expected reaction is:*

$$Ni(s) + Mn^{2+}(aq) \rightarrow Mn(s) + Ni^{2+}(aq)$$
0 +2 0 +2

In the expected reaction, Nickel is oxidized.

$\therefore E^\circ_{oxidized} = -0.25$V.

Reduction occurs at the Mn electrode,

$\therefore E^\circ_{reduced} = -1.18$V

Using the expression: $E^\circ_{cell} = E^\circ_{reduced} - E^\circ_{oxidized}$

Substituting: $E^\circ_{cell} = -1.18\text{V} - (-0.25\text{V})$
$= -1.18\text{V} + 0.25\text{V}$
$= -0.93$ V

Since the net value of $E^\circ$ of the cell is negative, nickel metal will not dissolve in a $Mn^{2+}$ solution.

**11** A half-cell consisting of palladium rod dipping into a one *mole per $dm^3$* solution of a palladium salt is connected to a standard hydrogen half cell. The cell voltage is 0.99 V, and the platinum electrode in the hydrogen half-cell is the anode. Determine the $E^\circ$ for the reaction: $Pd^{2+}_{(aq)} + 2e^- \rightarrow Pd_{(s)}$.

*To determine the $E^\circ$ for the reaction*:

$$Pd^{2+}_{(aq)} + 2e^- \rightarrow Pd_{(s)}$$

Oxidation occurs at the hydrogen electrode, i.e. the anode reaction is: $H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^-$ $E^\circ = 0.00$ V

$\therefore E^\circ_{anode} = 0.00$ V

The electrons released are used at the cathode, by the required reaction: $Pd^{2+}_{(aq)} + 2e^- \rightarrow Pd_{(s)}$ $E^\circ = x$ V

$\therefore E^\circ_{cathode} = x$ V

Since the $E^\circ_{cell}$ is given as 0.99 V

Using the expression: $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

Substituting: $0.99\text{ V} = x\text{ V} - 0.00\text{ V}$

$\therefore x = 0.99$,

i.e. $Pd^{2+}_{(aq)} + 2e^- \rightarrow Pd_{(s)}$ $E^\circ = +0.99$ V

12a Under standard conditions, write the equations to show the relationship between free energy change and i. equilibrium constant;
ii. electrode potential.

Ans: i. $\Delta G^\circ = -2.303RT\log K$; ii. $\Delta G^\circ = -nFE^\circ$

b. From the equations written in **a. i** and **a. ii** above, deduce the formula for the standard electrode potential.

Ans: $-nFE^\circ = -2.303RT\log$

$$E^\circ = \frac{2.303RT\log K}{nF}$$

c. $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+} + Cu_{(s)}$

Given that the equilibrium constant for the reaction above is $1.5 \times 10^{37}$. Calculate its standard electrode potential at 298 K. [1F = 96500 C; molar gas constant = 8.314 $Jmol^{-1}K^{-1}$] [NECO]

Using the *relationship*: $E^\circ = (2.303RT\log K)/nF$

Substituting:

$$E^\circ = \frac{2.303 \times 8.314 \times 298 \times \log(1.5 \times 10^{37})}{2 \times 96500}$$

$$E^\circ = \frac{2.303 \times 8.314 \times 298 \times (0.176 \times 37)}{2 \times 96500}$$

$E^\circ = 0.192$ V

**Revision Exercises**

25

| Half cell | Electrode potential |
|---|---|
| $Zn^{2+}_{(aq)} / Zn_{(s)}$ | – 0.763 V |
| $Ag^+_{(aq)} / Ag_{(s)}$ | + 0.404 V |

From the information above, the emf of the cell represented by $Zn_{(s)} / Zn^{2+}_{(aq)} // Ag^+_{(aq)} / Ag_{(s)}$ is

A. +1.167 V B. – 1.167 V C. – 1.122 V
D. – 0.785 V E. – 0.359 V [WAEC]

26 A feasible cell was constructed by joining the two half cells below:

$Fe^{2+}_{(aq)} + 2e^- \rightarrow Fe_{(s)}$ ; $E^\circ = -0.44$ V

$Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}$ ; $E^\circ = +0.77$ V

Determine the standard emf of the cell.

27 State the relationship between the free energy change $\Delta G^\circ$, of a cell reaction and the emf of the cell, $E^\circ$.

## 23. 8 Operation of Electrochemical Cells

### 1. The Daniell Cell

In a test tube: When a mixture of powdered zinc and blue $CuSO_{4(aq)}$ is stirred, the solution turns colourless as the metal dissolves, with a deposit of brown copper metal. It is a redox reaction:

$$Zn_{(s)} + CuSO_{4(aq)} \rightarrow ZnSO_{4(aq)} + Cu_{(s)}$$

In Daniell cell, the same reaction takes place, but the electron-transfer is through a path outside the chemical system: A zinc plate is placed in a 1.0 $moldm^{-3}$ $ZnSO_4$ solution and a copper plate in a 1.0 $moldm^{-3}$ $CuSO_4$ solution. A porous partition that allows the diffusion of ions separates the two half-cells (see fig 23.2). The two separate half-cells are coupled by a *salt bridge* of saturated $Na_2SO_4$ solution (or an ionic solution) in an inverted U- tube, to allow *migration of ions* (fig 23.5).

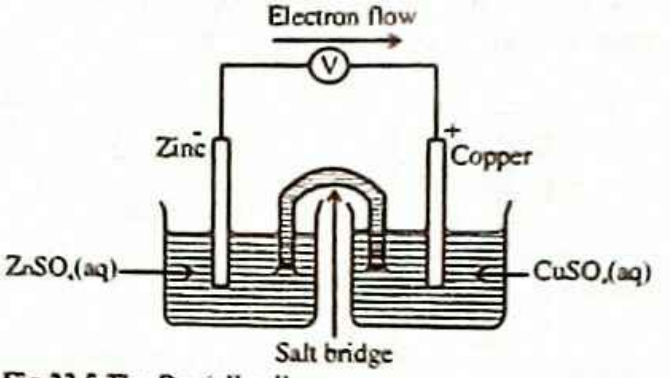



**Fig 23.5** *The Daniell cell*

When a conducting wire connects the two electrodes, electrons are transferred *indirectly* to the copper(II) ions in the form of an electric current as indicated by the voltameter, V.

**At the Zinc electrode (Anode)**

The zinc plate dissolves by loss of electrons to form zinc ions; this is oxidation. Hence, the zinc electrode forms the anode. This is because zinc is a stronger reducing agent than copper.

**Anode reaction:** $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

The anode is electron-rich; hence, negatively charged. The electrons *lost* to the zinc electrode, move through the wire to the copper electrode.

**At the Copper electrode (Cathode)**

The copper(II) ions, $Cu^{2+}$ in the solution *accept* electrons from the electrode to deposit shiny brown copper metal; this is reduction. Hence, the copper electrode forms the cathode. This is because $Cu^{2+}$ has a greater attraction for electrons than $Zn^{2+}$.

**Cathode reaction:** $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

The cathode is electron-poor; hence, positively charged. Addition of the two half reactions give the *cell reaction*, i.e.

**Anode reaction:** $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

**Cathode reaction:** $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

**Net reaction:** $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

*In an electrochemical cell, a redox reaction is used to produce electric current; no external battery.*

## 2. Dry (Leclanché) Cell

The popular batteries being sold under the trade names such as *Berec* and *Tigerhead*, which are used in torches, clocks, and radios, are examples of *dry cells or Leclanché cells*.

In a *dry cell*, the casing is made of zinc metal; it forms the *anode* (–), while the carbon rod, which is dipped in a *paste* of $NH_4Cl$ and $ZnCl_2$ mixture serves as the *cathode* (+). Powdered $MnO_2$ and charcoal surround the carbon rod (fig 23.6).

When the battery is in use or the circuit is completed, oxidation occurs at the zinc anode.

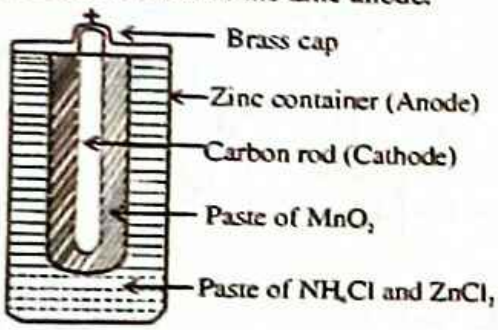



Fig 23.6 *A Dry Cell*

**Anode reaction:** $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

The electrons released to the anode flow through the external wire to the carbon cathode; where reduction of $MnO_2$ occurs.

**Cathode reaction:** $2MnO_{2(l)} + 2e^- \rightarrow Mn_2O_4^{2-}{}_{(l)}$

The function of $MnO_2$ is to act as a *depolarizer*. It prevents hydrogen gas from being liberated by ammonium ion at the cathode. A *paste* of $NH_4Cl$ and $ZnCl_2$ mixture is used, since a dry solid mixture of $NH_4Cl$ and $ZnCl_2$ will not conduct electricity.

When in use, the zinc casing dissolves and forms zinc ions. With time, the casing ruptures and the paste oozes through the water-proof cover.

### *Primary Cells*

The Daniel and dry (Leclanché) cells, are examples of *primary cells*. They *do not supply a steady current*, and the chemical reactions in the cells are *irreversible*, i.e. the *cells cannot be re-charged*.

## 3. Lead Storage Battery (Accumulator)

In a *lead storage battery*, the lead plates form the anode, while lead(IV) oxide forms the cathode; both are dipped into a moderately dilute $H_2SO_{4(aq)}$ as the electrolyte.

When in use as a source of direct current, the accumulator *discharges*; the cell reactions are:

**At the anode:** $Pb_{(s)} \rightarrow Pb^{2+}_{(aq)} + 2e^-$ (Oxidation)

**At the Cathode:**

$PbO_{2(s)} + 4H^+_{(aq)} + 2e^- \rightarrow Pb^{2+}_{(aq)} + 2H_2O_{(l)}$

As the accumulator *discharges* (runs down), the acid is being used up and a white insoluble salt, $PbSO_{4(s)}$ is formed simultaneously.

$$Pb^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \rightarrow PbSO_{4(s)}$$

### *Recharging Process*

In order to restore the accumulator to its original condition, it is *recharged* by passing *direct current* in an opposite direction to the *discharging* process. Under this condition, the reactions at the respective electrodes are reversed:

**Anode reaction:** $Pb^{2+}_{(aq)} + 2e^- \rightarrow Pb_{(s)}$

**Cathode reaction:**

$Pb^{2+}_{(aq)} + 2H_2O_{(l)} \rightarrow PbO_{2(s)} + 4H^+_{(aq)} + 2e^-$

Car batteries, being sold under the trade names such as *Exide*, *Union*, and *Varta* are examples of lead accumulators.

## 4. Fuel Cell

A *fuel cell* is an electrochemical cell in which *heat energy* is converted into *electrical energy*.

In a *fuel cell*, gaseous hydrogen and oxygen are passed into KOH(aq) or NaOH(aq) through porous carbon electrodes. The electrode reactions are:

**At the Anode:**

$2H_{2(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^-$ (Oxidation)

**At the Cathode:**

$2H_2O_{(l)} + O_{2(g)} + 4e^- \rightarrow 4OH^-$ (Reduction)

**Net reaction:** $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$

A *fuel cell* is operated and maintained at high temperatures, in order to vapourize the water produced. It is more efficient than the other processes in which heat of combustion is used to generate electricity. Its efficiency is about 70.0%.

### *Secondary Cells*

Lead-acid accumulator, fuel cell, phone and lamp batteries are *secondary* cells. They deliver *direct current* steadily, because they store or accumulate energy, which are made available when required.

*They can be recharged when it runs down, i.e. the cell reactions are reversible.*

### Arrangement of Electrochemical Cells in Series

It is a common observation that when two torch-light batteries are used instead of one, the torch-light bulb glows brighter.

*Reason:* When two or more electrochemical cells are arranged in series (head-to-tail), there is an increase in the voltage supplied.

### Solved Problems

13 State with reason whether the Daniel cell is an electrolytic cell or an electrochemical cell.

*Daniel cell is an electrochemical cell, because it converts chemical energy into electrical energy.*

14 State two differences between a primary cell and a secondary cell.

Solution (*Any two of the following*)

| Primary cell | Secondary cell |
|---|---|
| 1. Does not supply a steady current | Supplies a steady Current |
| 2. Cannot be recharged, i.e cell reactions are irreversible | Can be recharged, i.e. cell reactions are reversible |
| 3. Does not last long. | Lasts long. |

### Revision Exercises

28 a. What is an electrochemical cell?
b. Give two examples of electrochemical cells.

29 What is the function of $MnO_2$ in the Leclanché cell?

30 In a Leclanché cell, the anode is normally
A. ammonium chloride paste. B. carbon rod.
C. copper vessel. D. manganese(IV) oxide.
E. zinc container. [NECO]

31 Give two examples of primary cells. [WAEC]

32 Name the element used as an electrode in car batteries

33 Give the electrolyte of a named secondary electrochemical cell.

34 Mention one advantage of lead acid battery cell over Leclanché dry cell. [WAEC]

35 The following are reactions that occur in motorcar batteries **EXCEPT**
A. $PbO_{2(s)} + 4H^+_{(aq)} + 2e^- \rightarrow Pb^{2+}_{(aq)} + 2H_2O_{(l)}$
B. $Pb^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \rightarrow PbSO_{4(s)}$
C. $Pb^{2+}_{(aq)} + 2e^- \rightarrow Pb_{(s)}$
D. $Pb^{2+}_{(aq)} + 2H_2O_{(l)} \rightarrow PbO_{2(s)} + 4H^+_{(aq)} + 2e^-$
E. $Pb_{(s)} + H_2SO_{4(aq)} \rightarrow PbSO_{4(s)} + 2H^+_{(aq)}$ [NECO]

36 Write the equation of the reaction at the cathode when recharging a lead-acid accumulator.

## 23.9 Complex Redox Reactions

Redox reactions involving oxy-anions are regarded as complex reactions. Such reactions take place in acidic, alkaline or neutral media.

### Balancing Complex Ionic Equations

As in simple redox equations, complex redox equations can be balanced by two methods:

I. Ion-electron method.
II. Oxidation number method.

### I. Ion-electron Method

The following examples are used to illustrate the proce-dure for balancing half reactions containing *oxyanions* in *acidic medium.*

**Examples**

1. Redox reactions involving tetraoxomanganate (VII) ions in *acidic medium* is written as:

$$MnO_4^- + H^+ \rightarrow Mn^{2+} + H_2O.$$

This is a half equation. The presence of $H^+$ shows that the reaction is in acid medium.

The steps to follow are:

a. *Balance all the atoms except those of H and O.*

$$MnO_4^- \rightarrow Mn^{2+}$$ (Mn atoms balanced)

b. *Assign oxidation numbers to the atoms that have changed:* $MnO_4^- \rightarrow Mn^{2+}$

O.N. +7 +2 [*Reduction: Electron-gain*]

c. *Add appropriate number of electrons to balance electron gain or loss.*

Change in O.N. of Mn = (+2) – (+7) = -5 corresponds to *gain of 5 electrons. Add* $5e^-$ *to the left.*

$$MnO_4^- + 5e^- \rightarrow Mn^{2+}$$

d. *Add appropriate number of* $H_2O$ *molecules to balance oxygen atoms.*

Add $4H_2O$ to the right, to balance O atoms:

$$MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

e. *Add appropriate number of* $H^+$ *to balance hydrogen atoms.*

Add $8H^+$ to the left, to balance H atoms:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

f. *Check on charge:*

$$-1 + 8(+1) + (-5) = +2 + 0$$
$$-1 + 8 - 5 = +2$$
$$+2 = +2$$

2. Balance the following half reaction in acid medium: $Cr_2O_7^{2-} \rightarrow Cr^{3+}$

*To balance in acid medium*

- *Balance Cr atom on the right, to obtain* $2Cr^{3+}$, i.e.

$$Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$$

- *Assign oxidation numbers to atoms of elements that have changed:*

$Cr_2O_7^{2-} \rightarrow Cr^{3+}$

O.N. +6 +3 [*Reduction: Electron-gain*]

- *Add appropriate number of electrons to balance electron gain or loss.*

Change in O.N. of Cr = (+3) – (+6) = -3 corresponds to *gain of 3 electrons per atom.*

Add $6e^-$ to the left to balance *electron-gain*, i.e.

$Cr_2O_7^{2-} + 6e^- \rightarrow 2Cr^{3+}$

- *Add $7H_2O$ to the right to balance O atoms*, i.e.

$Cr_2O_7^{2-} + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

- *Add $14H^+$ to the left balance H atoms*, i.e.

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

- Check on charge: $-2 + 14(+1) + (-6) = +6 + 0$

$-2 + 14 - 6 = +6$

$+6 = +6$

## II. Oxidation Number Method

*Oxidation number method* is used without splitting the redox reaction.

### Examples

1 Consider the following redox reaction in acid solution: $Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$

The steps to follow are:

a. *Balance all the atoms except those of H and O.*

$Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$ (Balanced)

b. *Assign oxidation numbers to atoms of elements that have changed:*

$Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$

O.N. +2 +7 +3 +2

Change in O. N. of Fe is +3 – 2 = +1 [*Loss of $1e^-$*]

Change in O. N. of Mn is +2 – (+7) = -5. [*Gain of $5e^-$*]

c. *Equalize changes in oxidation numbers:*

For each $MnO_4^-$ reduced, five $Fe^{2+}$ must be oxidized.

Thus, multiply Fe by 5 and Mn by 1 (inverse ratio):

$5Fe^{2+} + MnO_4^- \rightarrow 5Fe^{3+} + Mn^{2+}$

d. *Balance oxygen atoms with $H_2O$:*

$5Fe^{2+} + MnO_4^- \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

e. *Balance hydrogen atoms with $H^+$:*

$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

f. *Check on the charges:*

$5(+2) + (-1) + 8(+1) = 5(+3) + 2$

$+10 - 1 + 8 = +15 + 2$

$+17 = +17$

2. Balance the following redox reaction in acid medium: $MnO_4^- + SO_2 \rightarrow Mn^{2+} + SO_4^{2-}$

- *Balance all the atoms except those of H and O.*

$MnO_4^- + SO_2 \rightarrow Mn^{2+} + SO_4^{2-}$ (Balanced)

- *Assign oxidation numbers to atoms of elements that have changed:* $MnO_4^- + SO_2 \rightarrow Mn^{2+} + SO_4^{2-}$

O.N +7 +4 +2 +6

Change in O. N. is +6 – (+4) = +2 [*Loss of $2e^-$*]

Change in O.N. is +2 – (+7) = -5 [*Gain of $5e^-$*]

- *Equalize changes in oxidation numbers:*

Multiply S by 5 (*loss* of 10 electrons) and Mn by 2 (*gain* of 10 electrons)

$2MnO_4^- + 5SO_2 \rightarrow 2Mn^{2+} + 5SO_4^{2-}$

- *Balance oxygen atoms with $H_2O$:*

$2MnO_4^- + 5SO_2 + 2H_2O \rightarrow 2Mn^{2+} + 5SO_4^{2-}$

- *Balance hydrogen atoms with $H^+$:*

$2MnO_4^- + 5SO_2 + 2H_2O \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$

- *Check on the charges:*

$2(-1) = 2(+2) + 5(-2) + 4(+1)$

$-2 = +4 - 10 + 4$

$-2 = -2$

3. Balance the following redox reaction in acid medium: $Cr_2O_7^{2-} + C_2O_4^{2-} \rightarrow Cr^{3+} + CO_2$

- *Balance all the atoms except those of H and O.*

$Cr_2O_7^{2-} + C_2O_4^{2-} \rightarrow 2Cr^{3+} + 2CO_2$

- *Assign oxidation numbers to atoms of elements that have changed:*

$Cr_2O_7^{2-} + C_2O_4^{2-} \rightarrow 2Cr^{3+} + 2CO_2$

O.N. +6 +3 +3 +4

Change in O.N. of C is +4 – (+3) = +1 [*Loss of $1e^-$*]

Change in O.N. of Cr is +3 – (+6) = -3 [*Gain of $3e^-$*]

- *Equalize changes in oxidation numbers:*

Each $C_2O_4^{2-}$ loses 2 electrons ($C_2O_4^{2-}$ contains two carbon atoms), while each $Cr_2O_7^{2-}$ gains 6 electrons ($Cr_2O_7^{2-}$ contains two chromium atoms), i.e. For each $Cr_2O_7^{2-}$ reduced, three $C_2O_4^{2-}$ must be oxidized.

Thus, multiply Cr by 1 and C by 3 (inverse ratio):

$Cr_2O_7^{2-} + 3C_2O_4^{2-} \rightarrow 2Cr^{3+} + 6CO_2$

- *Balance oxygen atoms with $H_2O$:*

$Cr_2O_7^{2-} + 3C_2O_4^{2-} \rightarrow 2Cr^{3+} + 6CO_2 + 7H_2O$

- *Balance hydrogen atoms with $H^+$:*

$Cr_2O_7^{2-} + 3C_2O_4^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 6CO_2 + 7H_2O$

- *Check on the charges:*

$(-2) + 3(-2) + 14(+1) = 2(+3)$

$-2 - 6 + 14 = +6$

$+6 = +6$

### Balancing Half reactions in Alkaline solution

The following example illustrates the procedure for balancing half reactions containing *oxyanions* in *alkaline medium.*

Balance the following half reaction in alkaline medium: $Cr^{3+} \rightarrow CrO_4^{2-}$

- *Balance all the atoms except those of H and O.*

$Cr^{3+} \rightarrow CrO_4^{2-}$ [*Cr balanced*]

- *Assign oxidation numbers to atoms of elements that have changed:*

$Cr^{3+} \rightarrow CrO_4^{2-}$

O.N. +3 +6 [*Oxidation: Loss of electrons*]

- *Add appropriate number of electrons to balance electron gain or loss.*

Change in O.N. of Cr = (+6) – (+3) = +3 corresponds to *loss of 3 electrons.* Add $3e^-$ to the right, i.e.

$$Cr^{3+} \rightarrow CrO_4^{2-} + 3e^-$$

• *Add appropriate number of $H_2O$ molecules to balance oxygen atoms.*

Add $4H_2O$ to the left to balance O atoms on the right:

$$Cr^{3+} + 4H_2O \rightarrow CrO_4^{2-} + 3e^-$$

• *To balance hydrogen atoms: Add $H_2O$ molecules equal in number to the number of H atoms required, and at the same time, add the same number of $OH^-$ to the opposite side of the equation*

In the equation: $Cr^{3+} + 4H_2O \rightarrow CrO_4^{2-} + 3e^-$

There are 8 H atoms on the *left*; add 8 $H_2O$ to the *right* and simultaneously add 8 $OH^-$ to the *left*:

$$Cr^{3+} + 4H_2O + 8OH^- \rightarrow CrO_4^{2-} + 8H_2O + 3e^-$$

• *Subtract duplication of $H_2O$ on both sides*

There are $4H_2O$ on the left and $8H_2O$ on the right. The net equation is

$$Cr^{3+} + 8OH^- \rightarrow CrO_4^{2-} + 4H_2O + 3e^-$$

• *Check on the charges:*

$$+3 + 8(-1) = -2 + 0 + 3(-1)$$
$$+3 - 8 = -2 - 3$$
$$-5 = -5$$

**Solved Problem**

15 Consider the reaction represented by the following equation:

$$2MnO_{4\,(aq)}^- + 5C_2O_4^{2-}{}_{(aq)} + 16H^+ \rightarrow 2Mn^{2+}{}_{(aq)} + 8H_2O_{(l)} + 10CO_{2(g)}$$

Write down:

a. the species undergoing reduction giving reason;

b. the reducing agent giving reason;

c. the reduction half equation;

d. one observation made during the reaction.

*First, assign O.N. to atoms that have changed:*

$$\overset{+7}{2MnO_{4\,(aq)}^-} + \overset{+3}{5C_2O_4^{2-}{}_{(aq)}} + 16H^+ \rightarrow \overset{+2}{2Mn^{2+}{}_{(aq)}} + 8H_2O_{(l)} + \overset{+4}{10CO_{2(g)}}$$

a. $MnO_4^-$ *is reduced; oxidation number of Mn has decreased from +7 to +2.*

b. $C_2O_4^{2-}$ *is the reducing agent; oxidation number of C has increased from +3 to +4.*

c. $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

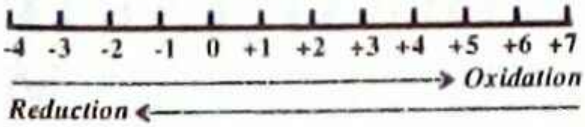
d. *(Any one of the following)*

- *The purple colour of $MnO_4^-$ turns colourless.*
- *A colourless and odourless gas is evolved.*

## Balancing Electron-transfer in Half reactions Using Oxidation Number [ON] Scale

The *oxidation number*, **ON** scale is a device that can be used to aid the balancing of *electron-transfer* in the equations of half reactions involving *oxyanions*, where the numbers of electrons gained or lost are not apparent.

The ON scale ranges from -4 to +7:




On the **ON** scale, a change in oxidation number, O.N. from the left to the *right* means an *increase* in O.N.; this is *oxidation* or *loss of electrons*, while a change in O.N. to the *left* means a *decrease* in O.N., which is *reduction* or *gain of electrons*.

**Examples**

**1.** A *half reaction* involving iron is;

$$\underset{\text{O.N.}}{\overset{}{Fe}} \rightarrow \underset{\overset{0}{}}{\overset{}{Fe^{2+}}} \quad \overset{}{+2}$$

The change in O.N. of Fe atom is from 0 to +2.
On the ON scale, it is an *increase* by 2 units to the *right*.
Hence, add $2e^-$ to the *right* of the equation:

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

**2.** A *half reaction* involving iodine is;

$$\underset{\text{O.N.}}{\overset{}{I_2}} \rightarrow \underset{\overset{0}{}}{\overset{}{2I^-}} \quad \overset{}{-1}$$

The change in O.N. of each iodine atom is from 0 to -1.
On the ON scale, it is a *decrease* by 1 unit to the *left*.
Hence, for the 2 iodine atoms, add $2e^-$ to the *left*:

$$I_2 + 2e^- \rightarrow 2I^-$$

**3.** Consider the following half equation:

$$\underset{\text{O.N.}}{\overset{}{Br^-}} \rightarrow \underset{\overset{-1}{}}{\overset{}{BrO^-}} \quad \overset{}{+1}$$

The change in O.N. of Br atom is from -1 to +1.
On the ON scale, it is an *increase* by 2 units to the *right*.
Hence, add $2e^-$ to the *right* of the equation:

$$Br^- \rightarrow BrO^- + 2e^-$$

**4.** Consider the following half equation:

$$\underset{\text{O.N.}}{\overset{}{ClO_3^-}} \rightarrow \underset{\overset{+5}{}}{\overset{}{Cl^-}} \quad \overset{}{-1}$$

The change in O.N. of Cl atom is from +5 to -1.
On the ON scale, it is a *decrease* by 6 units to the *left*.
Hence, add $6e^-$ to the *left* of the equation:

$$ClO_3^- + 6e^- \rightarrow Cl^-$$

**Revision Exercises**

**37** By the use of oxidation number method, give a balanced equation for the following reactions:

a. $NO_3^- + Cl^- + H^+ \rightarrow NO + Cl_2 + H_2O$

b. $ClO_3^- + Br^- \rightarrow BrO^- + OH^- + Cl^-$

**38** Consider the reaction represented by

$$xIO_3^- + yI^- + 6H^+ \rightarrow zH_2O + 3I_2$$

What are the values of *x*, *y* and *z* respectively?

**A.** 5, 3, 1. **B.** 5, 5, 3. **C.** 3, 1, 5. **D.** 1, 5, 3. [WAEC]

**Answers to Revision Exercises**

**5.** E **6.** D **20.** D **25.** A **26.** +1.21V
**30.** E **35.** E **38.** D

# 24

# •WAVE-PARTICULATE NATURE OF MATTER•

## 24.1 Introduction

This chapter describes the experiments that provided pieces of evidence to support the existence of *three subatomic particles* in the atom – *protons, neutrons and electrons*, and the arrangement of electrons in the atoms.

**Revision Exercises**

1. Name the three subatomic particles in an atom.
2. Give the composition of the nucleus of an atom.

## 24.2 Electrical Nature of the Atom

### Discovery of Electrons

***Sir J. J. Thompson*** (1897) discovered the existence of electrons in the atoms from his *cathode ray experiment*.

### Cathode ray experiment

When the gaseous form of a substance is introduced into a long glass-tube between two electrodes at extremely low pressure, and connected to a high voltage source, the gas becomes conducting. Luminous rays are emitted from the *cathode* moving to the *anode*. Hence, the tube is called *cathode ray tube* or *discharge tube* (figure 24.1).

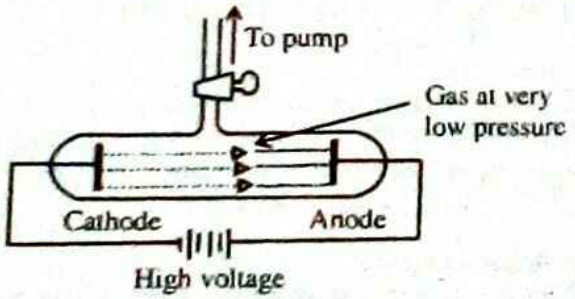



**Fig 24.1** *The Cathode ray Tube*

### Properties of Cathode rays

1. The rays are emitted at right angles to the electrodes.
2. They travel in straight lines with a high velocity.
3. The rays are deflected by electric and magnetic fields.
4. The rays flow from the cathode to the anode and are deflected towards the positive plate of an electric field (fig 24.2).

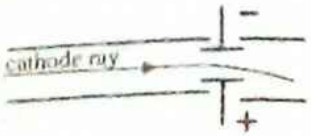



**Fig 24.2** *Effect of an electric field on cathode ray*

5. The rays rotate a small wheel placed in their path in a direction away from the cathode.
6. They cast a shadow of any object placed on their path, showing that the rays have *low penetrating power*. can only pass through an aluminium foil.
7. They heat a metal foil placed between the electrodes.
8. The rays have charge-to-mass ratio, e/m, of $1.76 \times 10^8$ C/g. *The value was found to be the same no matter the nature of the electrodes and the gas in the tube.* This observation confirms that *cathode rays are fundamental particles of matter*.

**Definition:** ***Cathode rays*** *are streams of negatively charged particles moving in straight lines with high velocities from the cathode to the anode.*

***Cathode rays*** are called ***electrons***.

### Observations and deductions from the properties of cathode rays

| | Observation | Deduction |
|---|---|---|
| 1 | *Rays are deflected by electric / magnetic fields* | *Rays consist of charged particles.* |
| 2 | *Rays are deflected to the positive plate of an electric field* | *Rays are negatively charged.* |
| 3 | *Rays rotate small wheel placed in their path.* | *Particles have mass and posses momentum* |
| 4 | *Rays cast shadow of an object placed on their path.* | *Rays have mass, and low penetrating power* |
| 5 | *Rays heat metal foil placed placed on their path* | *Rays conduct electric current* |

### Charge on an Electron

#### Oil-drop Technique

R. A. *Millikan* (1909) used the *oil-drop technique* to determine the value of the *charge on an electron* by measuring the strength of the current required to support an oil-drop that has captured one or more electrons. The value, which was found to be $1.60 \times 10^{-19}$ Coulombs was taken to be the value of the charge, *e*, on an electron.

An electron has only one unit of negative charge, written as $e^-$. When an atom captures one or more electrons, it becomes a negatively charged particle called *negative ion* or *anion*.

From the value of the *charge-to-mass* ratio by Thompson, ($e/m = 1.76 \times 10^8\ Cg^{-1}$), and that of the charge by Millikan ($e^- = 1.60 \times 10^{-19}$ C), the mass, *m* of an electron was found to be $9.11 \times 10^{-28}$ g, i.e.

$$m = \frac{1.60 \times 10^{-19}\ C}{1.76 \times 10^8\ Cg^{-1}} = 9.11 \times 10^{-28}\ g$$

#### Solved Problem

1. What deduction can be made from the observation that cathode rays cast a shadow of an object placed in their path?

*Cathode rays have mass, but cannot penetrate the object; instead, the rays are reflected.*

#### Revision Exercises

3a State two observations and corresponding conclusion that can be drawn from J. J. Thompson's cathode ray experiment.

b Name the particle generated in the cathode ray experiment. [WAEC]

4. State the deductions about the nature of cathode rays experiment in which it was observed that:

a. the rays are deflected towards the positive plate of an electric field.

b. the wheels of a small paddle are made to rotate by the rays.

5. Cathode rays cause an object placed behind a perforated anode to cast shadow on the screen. This observation shows that the rays

A. are positively charged. **B.** are negatively charged. C. have mass. **D.** travel in straight lines. [JAMB]

6. Mention the contribution of Millikan to the nature of the atom.

### Discovery of the Protons

**Goldestein** (1886) discovered the presence of *positively charged particles* in the discharge tube. They are produced when *electrons are removed from neutral gaseous atoms*. Such particles are called ***positive ions*** or ***cations***. They are attracted towards the negative cathode in the discharge tube.

When *positive ions* are allowed to pass through a perforated cathode, they form *positive rays*.

#### Properties of Positive rays

1. The positive rays are more massive than the cathode rays; hence, the entire mass of an atom is associated with its positive ion.
2. The charge-to-mass ratio of a positive ray is not constant; its value depends on the nature of gas in the discharge tube.
3. The *charge on a positive ion* ($+1.60 \times 10^{-19}$ C) is equal in magnitude but opposite in sign to that on an *electron* ($-1.60 \times 10^{-19}$ C).

The magnitudes of the charge on various positive ions were found to be $+1.60 \times 10^{19}$ C or an exact multiple of it, i.e. the relative charge on a positive ion can be +1, +2, +3, etc.

#### Hydrogen ion

When hydrogen atom loses its only electron, it forms a *positive ion*, $H^+$. The quantity of the charge on the ion is $+1.60 \times 10^{-19}$ C, while its charge-to-mass ratio, e/m is $9.58 \times 10^4\ Cg^{-1}$.

Since hydrogen ion, $H^+$, contains only *one proton* (*no neutron*), it is considered to be a fundamental particle; it is called ***proton***.

#### *Mass of a proton*

From the value of the *charge-to-mass* ratio of $H^+$, ($e/m = 9.58 \times 10^4\ Cg^{-1}$) and the value of the *charge* ($e^- = 1.60 \times 10^{-19}$ C), the mass, *m*, of a *proton* is $1.67 \times 10^{-24}$ g, i.e.

$$m = \frac{1.60 \times 10^{-19}\ C}{9.58 \times 10^4\ Cg^{-1}} = 1.67 \times 10^{-24}\ g$$

When the mass of a proton, $1.67 \times 10^{-24}$ g, is compared with that of an electron, $9.11 \times 10^{-28}$ g, a *proton is 1840 times heavier than an electron.*

### Discovery of Neutrons

***Lord Ernest Rutherford*** (1911) made the following observations:

1. The total mass of the protons and electrons in an atom was not equal to the actual mass of the atom, as obtained from the *mass spectrometer*.
2. The total mass of the protons in an atom accounted for about a half of its *nuclear mass*.

*Lord Rutherford*, therefore, suggested the existence of another type of particle in an atom.

***James Chadwick*** (1932) confirmed these observations after bombarding beryllium atoms with fast-moving alpha-particles. He discovered the existence of a new particle, which carries no charge, i.e. it is neutral, and has a mass almost equal to that of a proton. The new particle is called ***neutron***.

Recall that the total number of protons and neutrons in an atom is called ***mass number***, Z, and that only the naturally occurring hydrogen atom, called ***protium***, $^{1}_{1}H$, has *no neutron*. Except in the case of *protium*, the *number of neutrons* in an atom accounts for about a half of the *nuclear mass*, i.e. *mass number*, Z, of the atom.

**Revision Exercises**

7. Mention **one** property of the positive rays
8. Distinguish between cathode rays and positive rays
9. Which of the following scientists discovered the neutron? [WAEC]
   A. Ernest Rutherford B. J. J. Thompson
   C. James Chadwick D. R. A. Millikan

## 24.3 Discovery of the Nucleus

### Scattering of Alpha (α-) Particles

In the beginning, Sir J. J. Thompson described an atom as a uniform density ball of positively charged mass with electrons scattered randomly within the sphere, see figure 24.3. This *Thompson's model of the atom was rejected by other scientists.*



**Fig 24.3** *Thompson's model of the atom*

**Experiment on scattering of α-particles**

Lord Rutherford (1911) fired at a thin gold film with fast-moving *alpha particles*, and observed that almost all the *alpha particles*, 99.0%, passed through *without being deflected*, while a few *particles*, 1.0% were *deflected to various angles and directions, and even backward*, see figure 24. 4.

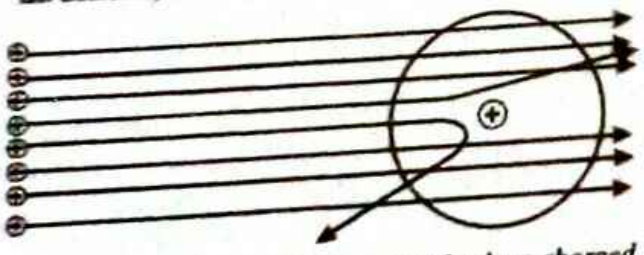


**Fig 24.4** *Deflection of alpha particles by a charged nucleus*

***Interpretation of the results***

**1. An atom consists of, predominantly, an empty space; hence, almost all the *α-particles* were able to pass through.**

**2. An atom has a *massive positive centre*, which occupies a very small space. Since *like charges repel*, the few *positively charged α-particles* that came very close to, or in direct contact with the *positive nucleus*, were those deflected to various angles and directions – due to repulsion.**

**Rutherford Model of the Atom**

**1. An atom contains a *small massive positive centre* called *nucleus*. The *nucleus* contains the *protons* and *neutrons*. *It is responsible for the entire mass of the atom*. The volume occupied by the nucleus is small compared to the entire volume of the atom.**

**2. The electrons rotate round the nucleus, in the same way that the planets rotate round the sun.**

**Rejection of Rutherford's Model of the Atom**

Scientists accepted the existence of the positive nucleus in an atom, but Rutherford's idea of *planetary* electrons was rejected.

*Reason:* Rutherford's model could not explain why electrons, being negatively charged and in continuous motion will not be losing energy, slow down, move spirally to the positive nucleus, and be *captured* by the nucleus, i.e. for *an atom to collapse.*

**Revision Exercises**

10 Describe the Rutherford model of the atom.
11 Distinguish between Thompson's model of the atom and that of Rutherford.

## 24.4 Bohr's Theory of the Atom

*Niel Bohr* (1913) proposed a theory to account for the existence of *energy levels* in the atom. His theory was based on *quantum theory*, instead of *electromagnetic theory*.

**Nature of Light and Electromagnetic Waves**

The mathematical relationship between the *velocity* of light, c, number of waves that passes through a point, i.e. *frequency*, ν and the wavelength, λ is:

*Velocity of light* = *wavelength* × *frequency*

$c\ (ms^{-1}) = \lambda\ (m) \quad \nu\ (s^{-1})$ ... 1

i.e. $c = \lambda\nu$ ... 2

or $\nu = c/\lambda$

Since the velocity of light, c is constant, then, wavelength, λ is inversely proportional to its frequency, ν, i.e. the longer the wavelength, the less the frequency, and vice-versa.

The units of wavelength, λ are *Angstrom*, Å, and *nanometer, nm*, which are small units of length.

$1\ Å = 10^{-8}\ cm = 10^{-10}\ m$. $1\ nm = 10\ Å = 10^{-9}\ m$.

The unit of frequency, ν is per second ($s^{-1}$).

### Experiment on Light Spectrum

When a beam of light is passed through a *prism*, it is dispersed, and when focused on a screen, it is separated into its component wavelengths, which form a ***visible rainbow*** with ***seven colours***: *Red, Orange, Yellow, Green, Blue, Indigo* and *Violet*. (*Memory aid*: ***ROYGBIV***).

The *visible region* is the only part of the *spectrum* our eyes can see. It is a *continuous spectrum*, *no complete separation of the colours* (fig 24.5).

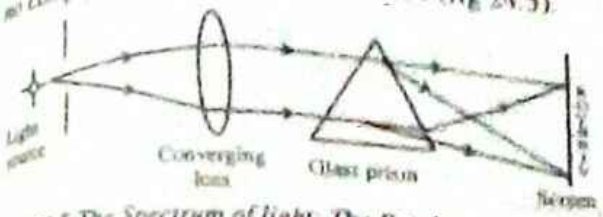



Fig 24.5 *The Spectrum of light: The Rainbow*

The following information can be obtained from *the visible spectrum*:

1. The *red* colour is the *least bent*, because it has *the longest wavelength* (or the *lowest frequency*), while the *violet* colour is the *most bent*, since it has *the shortest wavelength* (or the *highest frequency*).
2. It is a *continuous spectrum*, because *sunlight or white light is a mixture of all the wavelengths of light*. No colour has a definite wavelength; instead, each colour falls within a range. For instance, the wavelength range of red colour is 7500 – 6000 Å, while that of violet colour is 4500 – 4000 Å.
3. All radiations with wavelengths *longer* than the *red* colour is called ***infra-red*** (***IR***), while those radiations with wavelengths *shorter* than the *violet* colour are called ***ultraviolet*** (***UV***). Both the ***IR*** and *UV* radiations are *non-visible* types of electromagnetic radiations.

Modern equipment, called *spectrophotometer* is used for the detection of ***IR*** and ***UV*** radiations.

### Quantum Theory of Blackbody Radiation

***Light*** is that it is a *form of energy*.

**Experimental observation**:

When an object, such as a metal, is heated, it becomes *hot* and radiates heat. The intensity of the heat increases from ***red hot to white hot***, as temperature increases.

**Theoretical Explanation**

***Maxwell Planck*** (1901) used the ***quantum theory*** to explain the following observations:

1. The *change in heat intensity with temperature*.
2. The existence of a *set of lines* in the visible spectrum of hydrogen atom.

Planck postulated that radiant energy is composed of, and propagated in *small definite units*, or *small packets*, called *quanta* (singular ***quantum***) or ***photons***. The energy, E, associated with a *quantum* (or a *photon*) is directly proportional to its frequency, ν. The constant of proportionality is called the Planck's constant, h ($6.63 \times 10^{-34}$ *Js* (*joule second*)).

Mathematically, $E = h\nu$ ... 3

From equation 2, i.e. $\nu = c/\lambda$,

$\therefore E = hc/\lambda$ ... 4

According to the *quantum theory*, *a body (or matter) can only absorb or emit radiation in small definite quantity*, called *quantum* or *photon*, i.e. Energy = hν, or a whole number multiple, such as 2hν, 3hν, 4hν, etc.

### Light Emission by Elements

#### Emission spectrum of atomic Hydrogen

***Experimental observations***

1. When electricity is passed through hydrogen in a gas discharge tube at a low pressure, the molecules break up into atoms. These atoms emit electromagnetic radiations, which when analysed produced sharp lines with distinct colours at different wavelengths in the visible region of the spectrum. Each line is separate and sharp, and has its own colour at a discrete wavelength; hence, the spectrum is called *line emission spectrum* (fig. 24.7). It is unlike the *continuous spectrum of white light* (fig. 24.5).

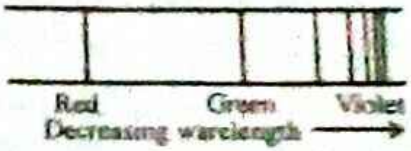



**Fig 24.7** *Line emission spectrum of hydrogen*

When various elements are heated in a flame or in an electric gas discharge tube, each element produces its own characteristic colour of light. For instance: Sodium vapour emits yellow light, that of calcium is brick-red, copper is green, while neon glows red.

Generally, every pure element produces its own unique set of lines. Hence, atomic emission spectra (singular: *spectrum*) can be used to identify various elements in a sample.

### Postulates of Bohr's theory of the Atom

In order to explain the emission spectrum of hydrogen, Bohr made the following assumptions:

1. The electrons in an atom exist in distinct energy levels, and never between energy levels. The energy levels are at definite distances from the nucleus.

2. The energy of an electron in a particular energy level has a fixed value, i.e. its *energy is quantized*, and differs from that of an electron in another level.

3. An electron continues to orbit round the nucleus in a particular energy level at a given temperature, without losing energy.

4. When an atom *absorbs* enough energy, its electrons are *promoted* from a *lower to a higher energy level. When an electron falls from a higher to a lower energy level, a quantum of radiation is emitted. The radiation produces a line in the emission spectrum of the element. The process whereby an electron moves from one energy level to another within the atom is called* **electronic transition**.

The *energy associated with a quantum of radiation in an electronic transition is the energy difference between the higher and lower energy levels.*

$$E_{photon} = E_{final} - E_{initial} = h\nu_{(final)} - h\nu_{(initial)} = h\Delta\nu$$

5. *When an electron is in the lowest energy level, i.e. the level nearest to the nucleus, it does not emit energy when orbiting round the nucleus.* For this reason, an electron cannot be captured by the nucleus, i.e. an atom cannot collapse.

***Theoretical explanation of the emission spectrum of hydrogen using quantum theory***

Figure 24.8 shows the energy levels in the atom of hydrogen, and the various electronic transitions responsible for the lines in the spectrum of its atom in figure 24.7. The following information can be obtained from figure 24.8.

1. The energy levels are assigned numbers, ***n***, starting from 1 to 2, 3, 4, etc. The first energy level, ***n*** = 1, is the nearest to the nucleus. It has the lowest energy; hence, the most stable. It is followed by the second energy level, n = 2, then, n = 3, n = 4, etc, with increasing energy. The space between two energy levels decreases as **n** increases.

2. Each electronic transition from a higher energy level, such as **n** = 2, 3, 4, etc, to the lowest energy level, **n** = 1, is accompanied by the emission of a quantum of radiation, which produces a line at a specific frequency. The various quanta of energy emitted produce a set of lines called ***Lyman series***. Similarly, all electronic transitions from higher energy levels to the second energy level, **n** = 2, produce another set of lines at specific frequencies; it is called ***Balmer series***. There are other sets of lines for hydrogen atom, which correspond to electronic transitions from higher energy levels to the third energy level, **n** = 3; it is called ***Paschen series***; then, to **n** = 4, **n** = 5, etc.

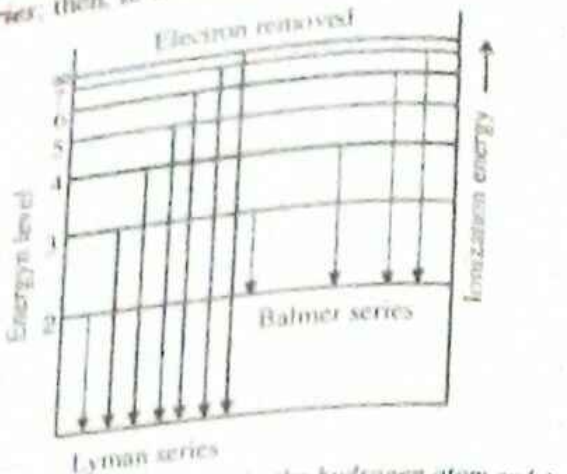



Fig 24.8 *The energy levels in the hydrogen atom and the electronic transitions responsible for the lines in its emission spectrum*

3. The lines obtained from all the transitions to the second energy level, ***n*** = 2 (***Balmer series***), appear in the *visible region* of the emission spectrum of hydrogen. Since more energy is released in all electronic transitions from higher energy levels to the first energy level, ***n*** = 1, i.e. ***Lyman series***, the lines corresponding to these high frequencies appear in the *ultraviolet region* of the spectrum.

The spectrum of hydrogen is the simplest; its atom has only one electron. For other elements with two or more electrons in their atoms, their emission spectra are very complex.

**Revision Exercises**

12 The lines observed in the simple hydrogen spectrum are due to emission of
A. electrons from the atom.
B. energy by proton transition.
C. energy by electron transition.
D. neutrons from the atom. [JAMB]

13 The idea of planetary electrons was that of
A. Bohr. B. Thompson.
C. Rutherford. D. Dalton. [JAMB]

14 Which electronic transitions are responsible for the lines in the Balmer series in the spectrum of hydrogen?

## 24.5 Wave-Particulate Character of an Electron

From the study of the atomic structure, ***de Broglie*** suggested that an electron, apart from being a particle, has a wave character (dual character). This is because a beam of electrons has mass and undergoes diffraction.

further studies on the atom show that electrons do not move in definite path like the earth orbits round the sun.

According to *Heisenberg Uncertainty Principle*: *it is impossible to know the exact position and velocity of a small moving body, such as an electron. Instead one can only give the probability of finding an electron in a given volume.*

*The region in space around the nucleus where there is a high probability of finding an electron is called orbital.* The distribution of electron density around the nucleus forms the *electron cloud*, which gives the shape and size of an orbital.

**Revision Exercises**

(a) Name the scientist that

a discovered the protons, b discovered the neutrons, c suggested the dual nature of an electron.

(b) The atomic theory model, which explains that electrons in an atom revolve round quantized energy levels is attributed to

A. Becquerel B. Bohr C. de Broglie
D. Rutherford E. Thompson [NECO]

(c) Define the term atomic orbital.

## 3.6 Quantum Numbers

The electrons in an atom can be identified by *four quantum numbers*. They are as follows:

1. Principal quantum number, $n$.
2. Angular momentum (Azimuthal) quantum no. $l$.
3. Magnetic quantum number, $m$.
4. Spin quantum number, $m_s$.

### 1. Principal Quantum Number, $n$

There are *energy levels* in an atom. Each energy level has its own *principal quantum number*, $n$, which is a positive integer: 1, 2, 3, 4, etc. The value of $n$ determines the relative energy of an electron, and its average distance from the nucleus.

These energy levels are associated with *electronic shells*, which are represented by capital letters K, L, M, N, etc. (See section 4.7).

| Energy Level, $n$ | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Shell symbol | K | L | M | N |

The value of $n$ determines the size of an orbital; the higher the $n$ value, the larger the orbital size.

### 2. Subsidiary (or Azimuthal) Quantum Number, $l$

Each *energy level* consists of *one or more energy sublevels*. Each *sublevel* has its own *sublevel quantum number*, $l$, which can take the values of 0, 1, 2, 3, 4, etc. Again, each *sublevel* has its own symbol: s, p, d, f, etc., usually written in small letters.

| Energy sublevel, $l$ | 0 | 1 | 2 | 3 |
|---|---|---|---|---|
| Sublevel symbol | $s$ | $p$ | $d$ | $f$ |

**Note:** The symbols *s*, *p*, *d*, and *f* are the first letters of the terms *sharp*, *principal*, *diffuse*, *and fundamental* respectively, that are used in describing spectral lines.

The number of *sublevels in an energy level* is determined by the possible values of the *sublevel quantum number*, $l$, and equals its principal quantum number, $n$. The *values of the $l$ start from zero up to a maximum of $(n - 1)$*, e.g.

| Energy level, | Energy sublevel value of $l$ | Energy sublevel |
|---|---|---|
| First, $n = 1$ | 0 | 1s |
| Second, $n = 2$ | 0, 1 | 2s, 2p |
| Third, $n = 3$ | 0, 1, 2 | 3s, 3p, 3d |
| Fourth, $n = 4$ | 0, 1, 2, 3 | 4s, 4p, 4d, 4f |

### 3. Magnetic Quantum Number, $m$

Each *energy sublevel* consists of *one or more orbitals*. The *number of orbitals* in a *sublevel* is equal to the mathematical formula $2l + 1$.

Each *orbital* has its own orientation in space. It is represented by a magnetic quantum number, $m$, which has values ranging from $+l$ to $-l$, including zero, e.g.

| Sublevel or Subshell | Value of $l$ | No. of orbitals $(2l + 1)$ | Values of magnetic quantum number, $m$ |
|---|---|---|---|
| s | 0 | 1 | 0 |
| p | 1 | 3 | +1, 0, -1 |
| d | 2 | 5 | +2, +1, 0, -1, -2 |
| f | 3 | 7 | +3, +2, +1, 0, -1, -2, -3 |

The *s-*, *p-*, *d-* and *f- sublevels* have one, three, five and seven orbitals respectively. When the *three p-orbitals*, the *five d-orbitals*, or the *seven f-orbitals belong to the same energy level, they have the same energy. Orbitals with the same energy* are called *degenerate orbitals*.

The maximum number of orbitals in an energy level is limited to $n^2$ (see Section 4.7)

### 4. Spin Quantum Number, $m_s$

The spinning of an electron about its own axis in an orbital is due to its magnetic property. There are two directions of spin: *clockwise* and *anticlockwise*. The spin is quantized, and designated by the ***spin quantum number***, which is either $+\frac{1}{2}$ or $-\frac{1}{2}$.

The number of possible directions of spin limits the maximum number of electrons in an orbital to *two*. The two electrons in an orbital spin in opposite directions, to minimize electronic repulsion.

The maximum number of electrons in an energy level (or shell) is limited to $2n^2$ (see Section 4.7).

**Solved Problem**

**5** List the **four** quantum numbers, and the main importance of each of them.

| | Quantum number | Importance |
|---|---|---|
| 1 | *Principal quantum number, n.* | *Determines the energy level, and distance from the nucleus.* |
| 2 | *Subsidiary (Azimuthal) quantum number, l.* | *Determines the number of energy sublevels) (subshells) in an energy level (shell).* |
| 3 | *Magnetic quantum number, m.* | *Determines the number of orbitals in a subshell.* |
| 4 | *Spin quantum number, s.* | *Describes the spin of an electron in an orbital.* |

**Revision Exercises**

**18** Name **three** scientists whose work gave evidence about the structure or nature of the atom. [WAEC]

**19** How many **a.** energy sublevels are in the L shell?
**b.** orbitals are in the M shell?

**20** Which quantum number divides shells into orbitals?
**A.** Principal. **B.** Azimuthal.
**C.** Magnetic. **D.** Spin. [JAMB]

**21** Copy and complete the table below:

| Energy sub-level | Maximum number of electrons | Number of orbitals present |
|---|---|---|
| *p* | | |
| *d* | | |
| *f* | | |

**22** With respect to quantum numbers, what does each of the following symbols or formulae represent?
**a.** $n$ **b.** $l$ **c.** $n^2$ **d.** $2l+1$ **e.** $2n^2$

## 24.7 Shapes of Orbitals

Each of the energy sublevels: *s*, *p*, *d* and *f*, has its own orbital with a characteristic shape. Only the shapes of the *s* and *p* orbitals are described here.

### 1. The *s-orbital*

The *s-sublevel* has only *one orbital*; it is called *s-orbital*. It is *spherically* symmetrical about the nucleus. Its size and energy depend on the value of *n*. The higher the *n* value, the larger the orbital size and the higher its energy. Hence, the s-orbital in the first energy level, K-shell, n = 1, i.e. 1s-orbital, has the smallest size, and the lowest energy.

The comparative sizes of the *s*-orbitals are:

1s < 2s < 3s < 4s, etc. (figure 24.9)

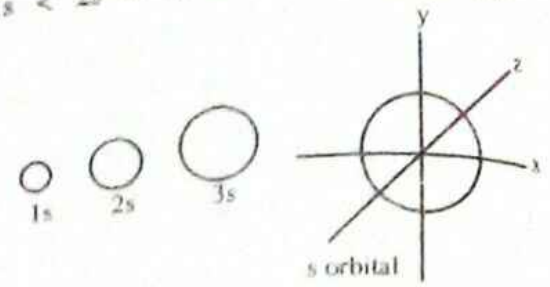



Fig 24.9 *Comparative sizes of the s-orbitals*

### 2. The *p-orbitals*

The *p-sublevel* has *three orbitals*; they are collectively called ***p-orbitals***. A *p-orbital* has a ***dumbbell*** shape (*figure-eight*) with the electron density concentrated on both sides of the nucleus (the *node*).

The three *p-orbitals* lie at right angles to one another, i.e. they are mutually orthogonal. They are designated $p_x$, $p_y$ *and* $p_z$ (figure 24.10).

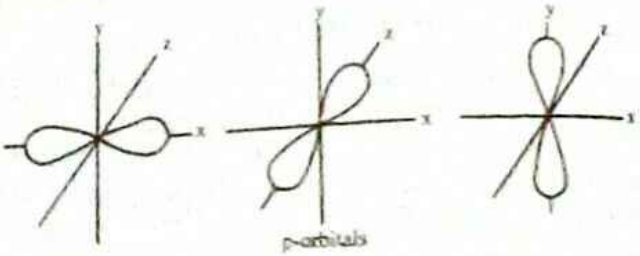



Fig. 24.10 *The p-orbitals*

The *three p-orbitals* in the *p-sublevel* of L-shell, n = 2, are designated $2p_x$, $2p_y$ *and* $2p_z$, while those in the M-shell, n = 3, are designated $3p_x$, $3p_y$ *and* $3p_z$. When the three *p-orbitals* are in the same energy level, they have the same energy, i.e. they are *degenerate orbitals*.

**Revision Exercises**

**23** Sketch the shape of a p-orbital.

**24** **a** Draw one of the orbitals, which is in the energy sub-level with three orbitals.
**b** State the shape of the orbital drawn in **a** above.

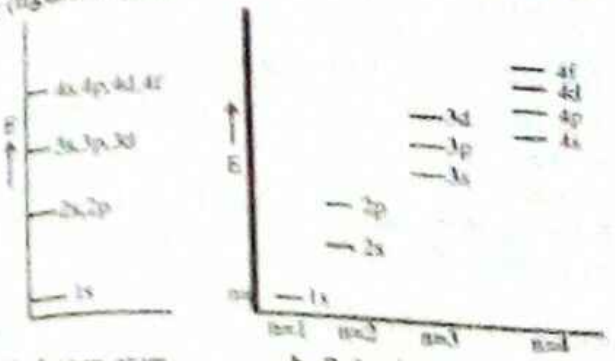
**25** Mention **TWO** types of orbitals that are called "degenerate orbitals". [NECO]

## 24.8 Energy Level Diagrams

Two different energy level diagrams can be used to describe the variation of energy in various orbitals.

### Type 1: Hydrogen atom

In an atom or ion with only one electron, as in hydrogen atom, the principal quantum number $n$ determines the energy. Here, all the orbitals in a given shell or energy level have the same energy. An increase in $n$ value leads to an increase in energy (figure 24.11).




a. *Hydrogen atom* b. *Poly-electron atom*

**Figure 24.11** *Relative energies of orbitals in the atom*

### Type 2: Polyelectron atom

In an atom with two or more electrons, the energy of an orbital is determined by the sum of the principal quantum number, $n$, and the energy sublevel quantum number, $l$, i.e. $(n + l)$. Here, all the orbitals in the same energy level do not have the same energy – unlike in a one-electron atom.

The order of increasing energy of orbitals within the same energy level is:

$$ns < np < nd < nf.$$

Hence, 2s orbital is of lower energy than 2p-orbitals, while the order of increasing energy in the third energy level, M-shell, n = 3, is: 3s < 3p < 3d.

The sequence of filling various atomic orbitals can be obtained from the two $(n + l)$ rules:

1. Energy of orbitals increases with increasing value of $(n + l)$.
2. When two orbitals have the same $(n + l)$ value, orbital with the lower $n$ value is of lower energy.

The order of increasing energy of some orbitals is:

**1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p**

Notice the following in the order above:

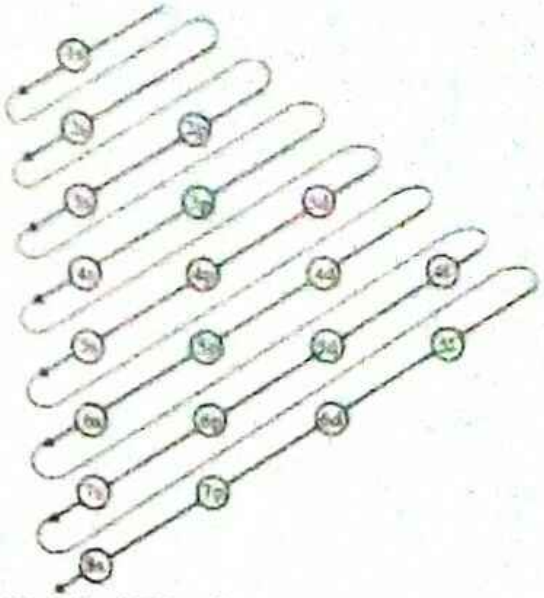
a. The 2p orbitals are of lower energy than the 3s orbital.

*Reason*: For the 2p-orbitals, $(n + l) = 2 + 1 = 3$, and for the 3s orbital, $(n + l) = 3 + 0 = 3$. Both of them have the same $(n + l)$ value. Since 2p has a lower $n$ value than 3s, then, 2p is of lower energy than 3s.

b. Although the 4s orbital is in the fourth energy level, it is of lower energy than the 3d orbitals, which are in the third energy level.

*Reason*: For the 4s-orbital, $(n + l) = 4 + 0 = 4$. For the 3d orbital, $(n + l) = 3 + 2 = 5$. Hence, the 4s orbital is of lower energy than the 3d orbitals.

Figure 24.12 gives a simple orbital filling diagram, which can be used to obtain the sequence in which various atomic orbitals can be filled.




**24.12** *Orbital filling diagram*

**Solved Problem**

2. Mention two differences between the 2s and 2p atomic orbitals.

**Solution** (*Any two of the following*)

- *The 2s orbital is of lower energy than the 2p orbital.*
- *The 2s orbital is spherical (or oval) in shape, while 2p orbital has a dumb-bell shape.*
- *There is only one type of 2s orbital, while there are three types of 2p orbitals.*

**Revision Exercises**

**26** Arrange the following orbitals in order of increasing energy: 2s, 3d, 3p, 4s [WAEC]

**27** What is $n + l$ rule? [$n$ = principal quantum number and $l$ = energy sublevel quantum number].

## 24.9 Quantum Numbers of Each Electron in an Atom

Recall that the distribution and spins of electrons in the atomic orbitals of the first twenty elements have been treated section 4.7(see Table 4.6).

The first electron in an orbital spins clockwise ↑, while the second electron spins anti-clockwise ↓.

### First Energy Level, n = 1 (K-shell)

The first energy level corresponds to the filling of the 1s orbital. Table 24.2 shows the electron configurations and the sets of four quantum numbers for the outermost (last) electron in the atom of each of the first two elements.

Notice that the sets of four quantum numbers for hydrogen, H, and helium, He, show that their outermost electrons are in the same energy level, $n$ = 1, within the same s-sublevel, $l$ = 0, in the same s-orbital, $m$ = 0, but of *opposite spins*, $m_s$, (+ ½ and - ½ respectively). In fact, it is impossible for two electrons in the same atom to have identical set of the four quantum numbers, they must differ in at least one quantum number.

**Table 24.2** *Quantum numbers of the electrons of atoms of elements in the first energy level*

| Element | Electronic configuration | Orbital 1s | Quantum Nos. of the Outer Electron | | | |
|---|---|---|---|---|---|---|
| | | | n | l | m | $m_s$ |
| $_1$H | $1s^1$ | ↑ | 1 | 0 | 0 | +½ |
| $_2$He | $1s^2$ | ↑↓ | 1 | 0 | 0 | - ½ |

### Second Energy Level, n = 2 (L-shell)

The second energy level corresponds to the filling of the 2s and 2p orbitals, occupied by eight elements, starting from boron, $_5$B to neon, $_{10}$Ne forming the second period. See Table 24.3 for their electron distributions.

**Table 24.3** *Quantum numbers of the electrons of atoms of elements in the second energy level*

| Element | Electronic Configuration | Electron Distribution In the Outer Orbitals | | | | Quantum Numbers of Outermost Electron | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 2s | $2p_x$ | $2p_y$ | $2p_z$ | n | l | m | $m_s$ |
| $_3$Li | $1s^2\ 2s^1$ | ↑ | | | | 2 | 0 | 0 | + ½ |
| $_4$Be | $1s^2\ 2s^2$ | ↑↓ | | | | 2 | 0 | 0 | - ½ |
| $_5$B | $1s^2\ 2s^2\ 2p^1$ | ↑↓ | ↑ | | | 2 | 1 | +1 | + ½ |
| $_6$C | $1s^2\ 2s^2\ 2p^2$ | ↑↓ | ↑ | ↑ | | 2 | 1 | 0 | + ½ |
| $_7$N | $1s^2\ 2s^2\ 2p^3$ | ↑↓ | ↑ | ↑ | ↑ | 2 | 1 | -1 | + ½ |
| $_8$O | $1s^2\ 2s^2\ 2p^4$ | ↑↓ | ↑↓ | ↑ | ↑ | 2 | 1 | +1 | - ½ |
| $_9$F | $1s^2\ 2s^2\ 2p^5$ | ↑↓ | ↑↓ | ↑↓ | ↑ | 2 | 1 | 0 | - ½ |
| $_{10}$Ne | $1s^2\ 2s^2\ 2p^6$ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | 2 | 1 | -1 | - ½ |

The electron distribution in the outer-shells of some atoms:

Carbon, $_6$C, $[1s^2]\ 2s^2\ 2p_x^1\ 2p_y^1$

Nitrogen, $_7$N, $[1s^2]\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$;

Oxygen, $_8$O, $[1s^2]\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$;

Fluorine, $_9$F, $[1s^1]\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$;

Neon, $_{10}$Ne, $[1s^2]2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$.

Neon atom is said to have an ***octet of electrons*** (four electron-pairs). Such atoms are quite stable.

### Third Energy Level, n = 3 (M-shell)

The third energy level corresponding to the filling of the 3s and 3p orbitals, which accommodate atoms of elements with atomic numbers 11 to 18, i.e. from sodium, $_{11}$Na to argon, $_{18}$Ar. Table 24.4 gives the electronic configurations and the sets of four quantum numbers for the outermost electrons in the atoms of elements in the third energy level.

**Table 24.4** *Quantum numbers of the electrons of atoms of elements in the third energy level*

| Element | Electronic Configuration | Electron Distribution In the Outer Orbitals | | | | Quantum Numbers of Outermost Electron | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 3s | $3p_x$ | $3p_y$ | $3p_z$ | n | l | m | $m_s$ |
| $_{11}$Na | $1s^2\ 2s^2\ 2p^6\ 3s^1$ | ↑ | | | | 3 | 0 | 0 | + ½ |
| $_{12}$Mg | $1s^2\ 2s^2\ 2p^6\ 3s^2$ | ↑↓ | | | | 3 | 0 | 0 | - ½ |
| $_{13}$Al | $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$ | ↑↓ | ↑ | | | 3 | 1 | +1 | + ½ |
| $_{14}$Si | $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$ | ↑↓ | ↑ | ↑ | | 3 | 1 | 0 | + ½ |
| $_{15}$P | $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$ | ↑↓ | ↑ | ↑ | ↑ | 3 | 1 | -1 | + ½ |
| $_{16}$S | $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$ | ↑↓ | ↑↓ | ↑ | ↑ | 3 | 1 | +1 | - ½ |
| $_{17}$Cl | $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3s^5$ | ↑↓ | ↑↓ | ↑↓ | ↑ | 3 | 1 | 0 | - ½ |
| $_{18}$Ar | $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | 3 | 1 | -1 | - ½ |

Notice that electronic configurations of elements from $_{11}$Na to $_{18}$Ar follow the same pattern as those of the elements from $_3$Li to $_{10}$Ne (see Table 24.3).

**Fourth Energy Level, n = 4 (N-shell)**

The fourth energy level corresponds to the filling of the 4s orbitals (see Table 24.5).

*Table 24.5 Quantum numbers of the electrons of atoms of elements in the fourth energy level*

| Element | Electronic Configuration | Electron Distribution In the Outer Orbital 4s | 4p$_x$ | 4p$_y$ | 4p$_z$ | Quantum Numbers of Outermost Electron n | l | m | m$_s$ |
|---|---|---|---|---|---|---|---|---|---|
| K | $1s^2\,2s^2\,2p^6\,3s^2\,3p^6 4s^1$ | ↑ | | | | 4 | 0 | 0 | + ½ |
| Ca | $1s^2\,2s^2\,2p^6\,3s^2\,3p^6 4s^2$ | ↑↓ | | | | 4 | 0 | 0 | - ½ |

The 3d orbitals are the next to be filled after 4s, being of lower energy than the 4p orbitals. Since there are five orbitals in the 3d subshell, the 3d orbitals are progressively filled by the next ten elements from scandium, $_{21}$Sc, to zinc, $_{30}$Zn. These elements form the *first transition series* in the periodic table. Their electronic configurations are discussed in section 35. 2.

**Solved Problem**

3. Mention the rule/principle that has been violated in each of the following electronic configurations, and write the correct configuration for each element.

a. $_5B$: $1s^2 2s^3$ [*Pauli's exclusion principle;* $_5B$: $1s^2 2s^2\,2p^1$]

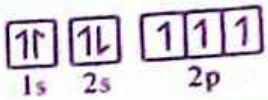
b. $_7N$: $1s^2\,2s^2\,2p_x^{\,2}\,2p_y^{\,1}$.
[Hund's rule; $_7N$: $1s^2\,2s^2\,2p_x^{\,1}\,2p_y^{\,1}\,2p_z^{\,1}$]

c. $_{10}$Ne: $1s^2\,2s^2\,2p^5\,3s^1$
[Aufbau principle; $_{10}$Ne: $1s^2\,2s^2\,2p^6$]

**Revision Exercises**

28 Name the **three** rules/principles, which governs the order in which electrons are accommodated in the shells of the atoms. [WAEC]

29 If the electronic configuration of an element is written as




which of the rule(s)/principle(s) is/are violated?

A. Aufbau principle
B. Aufbau principle and Hund's rule
C. Hund's rule
D. Pauli's exclusion principle [WAEC]

30 Which of the following is **NOT** true of 3d-orbitals?

A. It belongs to the quantum number n = 3.
B. It can be partially filled.
C. It contains a maximum of ten electrons.
D. It is in a lower energy level than 4s orbital.
E. Pairing of electrons in the orbital may occur. [N]

31 Write the electronic configuration of an element with atomic number 15, indicating the distribution of electrons in the energy sublevels, and thereafter, determine the number of unpaired electrons present.

**Answers to Revision Exercises**

5. C 9. C 12. C 13. C 16. B
19a 2; b 9 20. C 29. D 30. D

# 25

# •PERIODIC PROPERTIES OF THE ATOMS • PERIODICITY•

## 25.1 Introduction

The physico-chemical properties of an element depend on the electronic configuration of its atom. According to the *periodic law*: *The outer electron configurations of atoms recur periodically.*

Hence, *any property of the atom that varies with the electronic configuration exhibits periodicity.*

The following properties of the atoms exhibit *periodicity*: *atomic radius*, *ionic radius*, *ionization energy*, *electron affinity* and *electronegativity*.

**Revision Exercises**

1. State one importance of the electron configuration of an atom.
2. Mention three properties of the atom that exhibit periodicity.

## 25.2 Atomic Radius (Size)

The radius of an atom is the distance between the centre of the nucleus and the outermost shell of electrons.

Since a single atom cannot be isolated and its radius determined, the value assigned to the atomic radius of an element represents half of the internuclear distance of two adjacent atoms. These values are determined by the X-ray or electron diffraction method, and are expressed in Angstrom unit, Å. ($1Å = 10^{-10}$ m).

**Factors that determine Atomic size**

Two factors that determine the size of an atom:

1. *Nuclear charge*, i.e. the number of protons in the nucleus of the atom. There is *attractive force* between the positive nucleus and the electrons. Hence, *nuclear charge* tends to *decrease* atomic size.
2. *Screening* or *shielding effect*, i.e. effect due to the *repulsive force* between the electrons in the inner shells and those in the outer shells. Hence, *screening effect* tends to *increase* atomic size.

**Variation of atomic radius along the Period**

Consider the atomic radii of elements in the second period in the periodic table (see Table 25.1).

**Table 25.1** *Atomic radii of the elements in period 2 of the periodic table*

| Element | $_3$Li | $_4$Be | $_5$B | $_6$C | $_7$N | $_8$O | $_9$F | $_{10}$Ne |
|---|---|---|---|---|---|---|---|---|
| Nuclear charge | +3 | +4 | +5 | +6 | +7 | +8 | +9 | +10 |
| Shell configuration | 2,1 | 2,2 | 2,3 | 2,4 | 2,5 | 2,6 | 2,7 | 2,8 |
| Atomic radius, Å | 1.23 | 1.06 | 0.88 | 0.77 | 0.70 | 0.66 | 0.64 | - |

***Observation:*** There is a *decrease* in atomic radius from the alkali metal in group I to the halogen in group VII, from left to right across the period.

***Explanation:*** In period 2, there is only one inner shell of electrons (K-shell) in each of the elements. As the nuclear charge increases from lithium, Li (+3) to fluorine, F (+9), extra electrons are being added to the same outer shell. This increase in nuclear charge draws the electrons closer to the nucleus, thereby, decreasing the size of the atom.

Generally, an increase in nuclear charge decreeses the atomic radius when electrons are being added to the same outer shell.

The noble gases in group 0 are not assigned atomic sizes; since their outer shells are completely filled with electrons.

**Variation of atomic radius down the group**

Consider the alkaline metals of group I:

| Element | Atomic number | Shell configuration | Atomic size, Å |
|---|---|---|---|
| Li | 3 | 2, 1 | 1.23 |
| Na | 11 | 2, 8, 1 | 1.54 |
| K | 19 | 2, 8, 8, 1 | 1.96 |

**Observation**: There is a steady *increase* in atomic size as atomic number *increases* down the group.

**Explanation**: Down a group, there is an *increase* in the number of inner shells; the outer electrons are in shells that are far from the nucleus. Since the screening effect provided by the increase in the number of inner shells is greater than the effect due to an increase in nuclear charge, there is a steady increase in atomic size down the group.

**Solved Problem**

1. Explain why the atomic size of oxygen atom, $_8O$ is smaller than that of boron, $_5B$.

*Boron, $_5B$ (2, 3) and oxygen, $_8O$ (2, 6) are in the same period 2 in the periodic table. Because the nuclear charge of oxygen is higher than that of boron, the electrons are drawn closer to the nucleus in oxygen than in boron. Hence, the atomic size of oxygen is smaller.*

**Revision Exercises**

3. Mention two factors that determine the atomic size of an atom.
4. Explain why the atomic size of lithium atom, $_3Li$ is smaller than that of potassium, $_{19}K$.
5. Which of the following sets of elements are arranged in order of decreasing atomic size in the periodic table? A. $_6C$, $_4Be$, $_7N$, $_8O$ B. $_4Be$, $_6C$, $_7N$, $_8O$ C. $_8O$, $_7N$, $_6C$, $_4Be$ D. $_7N$, $_8O$, $_6C$, $_4Be$

## 25.3 Ionic Radius

*Ionic radius* are of two types: radius of a *cation* and radius of an *anion*. Like atomic radii, ionic radii are expressed in Angstrom unit, Å.

### Radius of a Cation

*A cation* is formed when a *neutral gaseous atom loses one or more electrons.*

Consider the removal of electrons from the atoms of lithium and magnesium:

$$Mg_{(g)} \rightarrow Mg^{2+}_{(g)} + 2e^-$$

Configuration: (2, 8, 2) (2, 8)

Radius, Å: (1.35) (0.60)

**Observation**: The cation, $Mg^{2+}$ is smaller in size than that of the corresponding neutral atom, Mg.

**Explanations:**

**1. *In term of number of shells of electrons***

The formation of a stable cation $M^{n+}$ with a noble gas configuration involves the complete removal of the outermost (valence) shell of electrons in the neutral atom M. Hence, the radius of the cation will be less than that of the neutral atom.

**2. *In term of effective nuclear charge***

*Effective nuclear charge is the difference between the numbers of protons and electrons in an ion.*

When an atom *loses one* or *more* electrons, there is an *increase in effective nuclear charge*, i.e., there are more protons than electrons in the ion. Under this condition, the *excess protons* draw the remaining electrons closer to the nucleus, thereby decreasing the size of the ion.

Table 25.2 gives the atomic and ionic radii of some elements.

**Table 25.2** *Atomic and ionic radii of some elements*

| Atom, M<br>Atomic radii, Å | $_3Li$<br>1.23 | $_{11}Na$<br>1.54 | $_{12}Mg$<br>1.35 | $_{13}Al$<br>1.18 |
|---|---|---|---|---|
| Cation, $M^{n+}$<br>Ionic radius, Å | $_3Li^+$<br>0.55 | $_{11}Na^+$<br>0.95 | $_{12}Mg^{2+}$<br>0.60 | $_{13}Al^{3+}$<br>0.50 |

### Radius of an Anion

An *anion* is formed when a *neutral gaseous atom gains* one or more electrons. Consider the addition of electrons to an atom of oxygen:

$$O_{(g)} + 2e^- \rightarrow O^{2-}_{(g)}$$

Configuration: (2, 6) (2, 8)

Radius, Å: (0.73) (1.40)

**Observation**: An anion $X^{n-}$, is larger in size than the corresponding neutral atom X, and vice versa.

**Explanation**: ***In term of effective nuclear charge***

When *one* or *more* electrons are added to the outermost shell of an atom, there is a *decrease in effective nuclear charge*, i.e., *there are more electrons than protons in the ion*. Under this condition, there is *less attraction* of the *added electrons* towards the nucleus, thereby *increasing* the size of the ion.

Table 25.3 gives the atomic and ionic radii of some elements.

**Table 25.3** *Atomic and ionic radii of some elements*

| Atom, X<br>Atomic radii, Å | $_8O$<br>0.73 | $_{17}Cl$<br>0.99 | $_{35}Br$<br>1.14 | $_{53}I$<br>1.33 |
|---|---|---|---|---|
| Anion, $X^{n-}$<br>Ionic radius, Å | $_8O^{2-}$<br>1.40 | $_{17}Cl^-$<br>1.81 | $_{35}Br^-$<br>1.95 | $_{53}I^-$<br>2.16 |

### Isoelectronic Ions

*Isoelectronic ions are ions (cations and anions) that have the same electron configurations (same number of electrons) but different atomic numbers (different number of protons).*

Consider the six ions in Table 25.4; they have the same electron configuration of neon, but carry different charges, due to difference in atomic numbers.

**Table 25.4** *Ionic sizes of some isoelectronic ions*

| Ion | $_7N^{3-}$ | $_8O^{2-}$ | $_9F^{-}$ | $_{11}Na^{+}$ | $_{12}Mg^{2+}$ | $_{13}Al^{3+}$ |
|---|---|---|---|---|---|---|
| Configuration | 2, 8 | 2, 8 | 2, 8 | 2, 8 | 2, 8 | 2, 8 |
| Nuclear charge | +7 | +8 | +9 | +11 | +12 | +13 |
| No. of electron | -10 | -10 | -10 | -10 | -10 | -10 |
| Effective nuclear charge | -3 | -2 | -1 | +1 | +2 | +3 |
| Size, Å | 1.71 | 1.40 | 1.36 | 0.95 | 0.60 | 0.50 |

Again, consider the ionic sizes of the *isoelectronic ions* in Table 25.4.

**Observations:**

1. The ions carry different charges.
2. There is a steady *decrease in ionic size as atomic number increases from left to right.*

**Explanations:**

1. The ions carry different charges because they have the same number of electrons but different nuclear charges.
2. As we move from left to right, there is an increase in effective nuclear charge; hence, ionic size decreases.

### Solved Problems

**2.** Explain why the atomic size of oxygen, $_8O$ is smaller than the ionic size of its anion, $_8O^{2-}$.

**Solution**

*When two electrons are added to oxygen atom, O (2, 6) to form the anion, $O^{2-}$ (2, 8), there is less attraction of the added electrons to the nucleus, thereby increasing the size of the anion.*

**3.** Which of the following does not have the electronic structure of $^{20}_{10}Ne$?

[$_8O$, $_9F$, $_{11}Na$, $_{13}Al$, $_{20}Ca$] [WAEC]

**A.** $Na^+$ **B.** $F^-$ **C.** $Al^{3+}$ **D.** $Ca^{2+}$ **E.** $O^{2-}$

**Solution**: ***D***. [$_{10}Ne = 1s^2\,2s^2\,2p^6$; $_{20}Ca^{2+} = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6$]

### Revision Exercises

**6.** Explain why the atomic size of lithium atom is more than that of its cation.

**7 a.** What are isoelectronic ions?

**b.** Give two examples, one each of a cation and an anion, that are isoelectronic with neon.

**8.** Which of the following pairs of species contain the same number of electrons?

[$_6C$, $_8O$, $_{10}Ne$, $_{11}Na$, $_{12}Mg$, $_{13}Al$, $_{17}Cl$]

**A.** $Mg^{2+}$ and $Al^{3+}$ **B.** $Cl^-$ and Ne

**C.** $Na^+$ and Mg **D.** C and $O^{2-}$ [WAEC]

**9.** Which of the following properties decreases down a group in the periodic table?

**A.** Atomic radius **B.** Electronegativity

**C.** Electropositivity **D.** Ionic radius [WAEC]

**10** Explain the term *effective nuclear charge*.

**11** Arrange the following ions in order of increasing size giving reasons: $Na^+$, $Mg^{2+}$, $Al^{3+}$.

[$_{11}Na$, $_{12}Mg$, $_{13}Al$] [WAEC]

## 25.4 Ionization Energy

### First Ionization Energy

The electrons in an atom are held to the nucleus by the electrostatic force of attraction between the nucleus and the electrons. However, when an atom absorbs sufficient energy, an electron can be completely removed from the atom. *The energy required to remove the outermost electron in an atom in gaseous state is called first ionization energy.*

*Ionization energy* can be measured by the use of the gas discharge tube. Its value is a measure of the degree of attraction the nucleus has for the electron removed. The stronger the attraction, the more the energy required to remove the electron from the atom, and vice versa.

Figure 25.2 is the graph of the first ionization energies of the first twenty elements in the periodic table. *Each value, represents the energy required to remove one mole of electrons from one mole of gaseous atoms to form one mole of gaseous ions:*

$$\underset{1\ \text{mol}}{Na(g)} \rightarrow \underset{1\ \text{mol}}{Na^+(g)} + \underset{1\ \text{mol}}{e^-};\quad \Delta H = +496\ \text{kJmol}^{-1}$$

The equation shows that one mole of gaseous sodium atoms absorbs 496 kJ of heat, in order to remove one mole of electrons, and form one mole of gaseous sodium ions.

### Factors that Determine Ionization Energy

**1. Atomic size and screening effect by inner electrons**

***Variation down the Group***: Consider the alkali metals in group I, see Table 25.2.

**Observation**: First ionization energy *decreases* with *increasing* nuclear charge down the group.

**Explanation**: Down a group, the electron to be removed is shielded by increasing number of inner shells of electrons. With increasing distance from the nucleus, less energy will remove the electron, since it will be weakly attracted by the nucleus.

**2. Nuclear Charge**

***Variation along the Period***: Consider the elements in the second period; Li to Ne, see Table 25.2.

**Observation**: There is a general *increase* in the first ionization energies.

**Explanation**: Along the period there is an *increase* in nuclear charge, and a *decrease* in atomic size. The electron to be removed is thereby strongly attracted by the nucleus; consequently, first ionization energy increases.

**3. Electronic Configuration of the Atom**

***a. Completely filled and half-filled sublevels***

***Variation along the Period***: Consider the elements in the third period; Na to Ar (see figure 25.1).

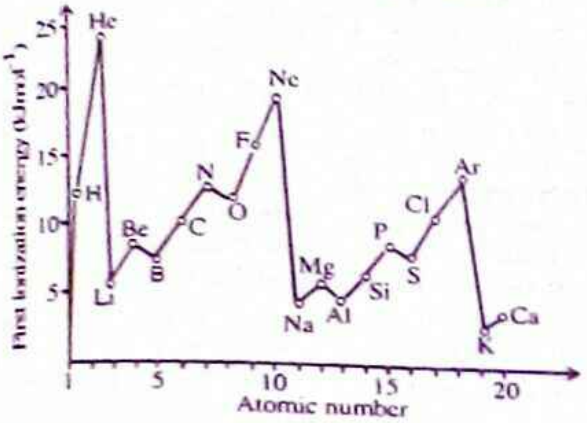



**Figure 25.2** *First ionization energies of the first twenty elements*

**Observation**: The *increase* in the first ionization energy is *irregular* along the period; the first ionization energies of magnesium and phosphorus are higher than expected.

**Explanation**: In magnesium, Mg ($1s^2 2s^2 2p^6 3s^2$), the electron to be removed is in the completely filled 3s sublevel. Because of the *extra stability* of completed sublevel, more energy is required to remove one of the paired electrons. Hence, the first ionization energy of magnesium is much higher than that of the element following it, aluminium.

Similarly, in phosphorus, P ($1s^2 2s^2 2p^6 3s^2 3p^3$), the electron to be removed is in the half-filled 3p sublevel that also has extra stability. Hence, the first ionization energy of phosphorus is much higher than that of the element following it, sulphur.

***b. Completely filled Shells: The Noble Gases***

Consider the group 0 element in the periodic table.

**Observation**: In each period, the noble gas (group 0) has the highest ionization energy.

**Explanation**: In noble gases, the outermost shells are completely filled with electrons; hence, their atoms are stable. A much higher energy is required to remove an electron from a completed shell.

## Periodicity in Ionization Energy

Figure 25.1 shows a plot of the first ionization energies of the first twenty elements. It is evident that the ionization energy of an element largely depends on its electronic configuration; hence, shows periodicity. The alkali metals occupy the *minima*, since they have low ionization energies, while the noble gases occupy the *maxima*, due to their extremely high ionization energies.

## Variation in Successive Ionization Energies

The energy required to remove successive electrons usually increases. Consider the successive ionization energies of element M in gaseous state:

I. $M \rightarrow M^+ + e^-$; $\Delta H = + E_1$ ($1^{st}$ Ionization energy)

II. $M^+ \rightarrow M^{2+} + e^-$; $\Delta H = + E_2$ ($2^{nd}$ Ionization energy)

III. $M^{2+} \rightarrow M^{3+} + e^-$; $\Delta H = + E_3$ ($3^{rd}$ Ionization energy)

Experimentally: $E_1 < E_2 < E_3 < \ldots < E_n$

Table 25.5 gives the successive ionization energies of three elements in period 3 of the periodic table. Generally, an atom continues to lose electrons until it acquires a noble gas configuration; after which, an extremely high energy will be required to remove another electron.

**Table 25.5** *Successive ionization energies ($kJmol^{-1}$)*

| Element | $1^{st}$ | $2^{nd}$ | $3^{rd}$ | $4^{th}$ | $5^{th}$ |
|---|---|---|---|---|---|
| Na | 496 | 4565 | 6912 | 9540 | 13360 |
| Mg | 738 | 1450 | 7732 | 10550 | 13620 |
| Al | 577 | 1816 | 2744 | 11580 | 15053 |

In Table 25.5, the first ionization energy of sodium, $_{11}Na$: $1s^2 2s^2 2p^6 3s^1$ (2, 8, 1), which corresponds to the removal of the outermost electron in the 3s orbital, (M-shell) is relatively low (496 $kJmol^{-1}$) when compared with the second ionization energy of 4565 $kJmol^{-1}$. *Reason*: Its second ionization energy corresponds to the removal of an electron from the completed L-shell of $Na^+$ (2,8). For this reason, group I elements form +1 ions only.

In magnesium, $_{12}Mg$ $(2, 8, 2)$, the first and second successive energies correspond to the removal of the two outermost electrons in the 3s sub-level and the formation of $Mg^{2+}$ $(2, 8)$, which is that of neon. The removal of another electron from $Mg^{2+}$ requires extremely high energy, hence, group II elements form $+2$ ions only.

For the same reason, aluminium atom, $_{13}Al$ $(2, 8, 3)$ $(1s^2 2s^2 2p^6 3s^2 3p^1)$, will lose its three valence electrons, to form $Al^{3+}$ $(2, 8)$. The removal of another electron from $Al^{3+}$ requires an extremely high energy, hence, group III elements form $+3$ ions only.

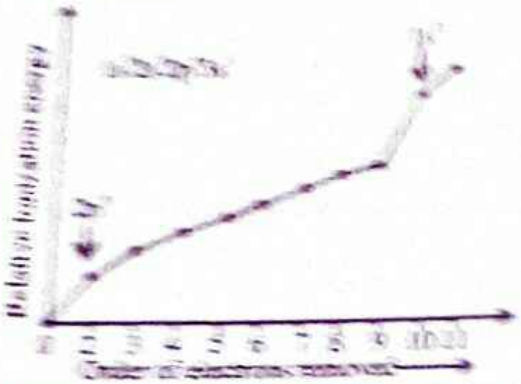



Fig. 25.2: Successive ionization energies of sodium atom.

Figure 25.2 shows a sketch of the variation of the successive ionization energies of sodium atom. The high jumps during the removal of the second and the tenth electrons correspond to the breaking into the noble gas configurations of neon and helium respectively.

### Metals and Non-metals

The properties of elements depend on their ionization energies. In their respective periods, the ionization energies of metals in groups 1, 2 and 3, are relatively low, i.e. they lose their valence electrons readily, to form cations.

Consequently, metals (excluding hydrogen) are on the left-hand side of the periodic table, while the non-metals are confined to the right-hand side.

### Solved Problems

**4.** How does *screening effect* affect the ionization energy of an atom across the period and down the group in the periodic table?

**Solution**

*Across a period:* Screening effect has no effect on ionization energy.

*Down the group:* Screening effect affects ionization energy. The trend down the group is:

∝ Screening effect increases. ∝ It increases atomic size.

∝ It decreases ionization energy.

**5.** P, Q, R and S are metals in the same group in the periodic table but in periods 3, 4, 5 and 6 respectively. Which of them loses electron least readily and why?

*Atom, P will lose its electron least readily.* **Reason:** In P atom, P will lose its electron least readily. **Reason:** In P atom, P will lose its electron least readily. **Reason:** In P atom, P will lose its electron least readily.

$Cl_{(g)} + e^- \rightarrow Cl^-_{(g)}$ ; $\Delta H = -349$ kJ mol$^{-1}$
1 mol 1 mol 1 mol

The equation shows that when one mole of gaseous atoms of chlorine accepts one mole of electrons, 349 kJ of energy is released.

### Factors that Determine Electron Affinity

**1. Nuclear charge**

***Variation across the period***

**Observation**: There is a general *increase* in electron affinity from left to right across the period.

**Explanation**: Across the period there is an *increase* in nuclear charge and a *decrease* in atomic size, leading to an *increase* in the nuclear attraction for the added electron.

The halogen atom has the highest electron affinity in their respective periods. This is because the addition of one electron to a halogen atom leads to the formation of an ion that has a stable noble gas configuration. Hence, the halogen atoms accept electrons with ease:

$F_{(g)} + e^- \rightarrow F^-_{(g)}$ ; $\Delta H = -333$ kJmol$^{-1}$
$(1s^2 2s^2 2p^5)$ $(1s^2 2s^2 2p^6)$

**2. Atomic size and screening effect**

***Variation down the Group***: Consider the halogens in group VII: (in kJ) F (-333); Cl (-349); Br (-325); I (-297)

**Observation**: Electron affinity *decreases* down the group with *increase* in nuclear charge.

**Explanation**: Down the group, the electron being added is shielded by increasing number of inner shells of electrons. With increasing distance from the nucleus, the nuclear attraction for the added electron decreases. Consequently, the tendency to accept electron decreases down the group.

The unexpected *low* electron affinity of fluorine is due to the repulsive forces between electrons packed in a small atom – compared to the larger chlorine atom.

Noble gases have zero electron affinity because their atoms do not accept electrons, since their outer shells are completely filled with electrons.

## Electron Affinity and Ionization Energy

Generally, *non-metals have high electron affinities*; they accept electrons readily to form anions, while *metals have low ionization energies*, i.e., they lose electrons readily to form cations.

Ionization energies remain one of the main factors that determine whether ionic or covalent bonds exist between atoms.

**Revision Exercises**

18 a. Explain the term *electron affinity*.
b. How does *electron affinity* varies down the group, and across the period in the periodic table?

19 Explain why the electron affinity of chlorine is more than that of bromine.

## 25.6 Electronegativity

*Electronegativity* is the *ability of an atom to attract shared pairs of electrons to itself in a molecule.*

It is more pronounced in heteronuclear molecules where two dissimilar atoms share one or more pairs of electrons. For instance: In hydrogen chloride, HCl, a pair of electrons is shared between the atoms of hydrogen and chlorine. In such a molecule, the electron density is more towards the more electronegative chlorine atom.

An atom of each element has its own *electronegativity*. Table 25.6 gives the electronegativity values of some elements. ***Linus Pauling*** (1950) introduced the ***electronegativity scale***.

**Table 25.6** *Electronegativity values of some elements*

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 2.1 H | | | | | | | - He |
| 1.0 Li | 1.5 Be | 2.0 B | 2.5 C | 3.0 N | 3.5 O | 4.0 F | - Ne |
| 0.9 Na | 1.2 Mg | 1.5 Al | 1.8 Si | 2.1 P | 2.5 S | 3.0 Cl | - Ar |
| 0.8 K | 1.0 Ca | | | | | 2.8 Br | - Kr |
| 0.8 Rb | 0.9 Sr | | | | | 2.5 I | - Xe |
| 0.7 Cs | 0.9 Ba | | | | | 2.2 At | - Rn |
| 0.7 Fr | 0.9 Na | | | | | | |

### Variation of Electronegativity

**Variation across the Period**

Consider period 2 elements, starting from lithium:

**Observation**: There is steady increase in electronegativity from left to right across the period.

**Explanation**: The steady increase in electronegativity is due to a steady increase in nuclear charge, and decrease in atomic size from left to right. Consequently, the halogen atom, fluorine, has the highest electronegativity in the period, due to the strong affinity for electron.

**Variation down the Group**

Consider the halogens in group VII.

**Observation**: There is a steady *decrease* in electronegativity down the group.

**Explanation**: The increase in atomic size due to the screening effect of inner shells of electrons decreases the nuclear attraction for shared electrons; hence, electronegativity decreases down the group.

The noble gases of group 0 are not assigned electronegativity values since they have completed shells of electrons.

### Electron Affinity and Electronegativity

The concept of *electron affinity should not be confused with that of electronegativity*. Electron affinity is a measure of the ability of an isolated gaseous atom to gain electrons; while electronegativity is a measure of the ability of an atom in a covalent molecule to attract shared electrons.

The concept of *electronegativity* is being wrongly used to describe the ease with which an atom *gains electrons* and becomes *negatively charged*. The opposite is *electropositivity*; a term being wrongly used to describe the ease with which an atom loses electrons and becomes *positively charged*.

Under these conditions, *electronegativity increases across the period and decreases down the group, while electropositivity decreases across the period and increases down the group.*

### Revision Exercises

20 Name the scientist that introduced the electronegativity scale.

21 Differentiate between electron affinity and electronegativity of an atom.

22 Arrange the following elements in order of decreasing electronegativity: $_{16}S$, $_{13}Al$, $_{11}Na$, $_{15}P$. [W]

23 Arrange the following elements in order of decreasing electronegativity: Al, Mg, Na, P, S, Si. [NECO]

24 A decrease in atomic size and an increase in nuclear charge across a period lead to

A. a decrease in covalency in bond formation.
B. an increase in chemical reactivity.
C. an increase in the tendency to lose electrons.
D. a decrease in electropositivity.

25 In order to remove one electron from a 3s-orbital of gaseous sodium atom, about 496 $kJmol^{-1}$ of energy is required. This energy is referred to as

A. electron affinity B. ionization energy
C. activation energy D. electronegativity. [JAMB]

## 25.7 Polarity of Chemical Bonds

### Application of Electronegativity

Electronegativity values can be used to predict the nature of chemical bonds between atoms:

1. If the electronegativity difference between the bonded atoms is very large, i.e., greater than 1.8, the chemical bond between the atoms will be *purely ionic*. This is true of the bonds between metals in groups I or II and non-metals in group VI or VII. Here, there is complete separation of charges – as in sodium chloride, $Na^+Cl^-$ and calcium oxide, $Ca^{2+}O^{2-}$, where the percentage ionic character is much greater than 50%.

2. If the electronegativity difference is moderate, i.e., between 0.4 and 1.6, there is sharing of electron-pairs; but the electron density is more towards the more electronegative atom. Such a bond is said to be *polar covalent*. For instance: In HCl molecule, the chlorine atom is more electronegative than the hydrogen atom. Hence, the electron density around the chlorine atom will be more than that of hydrogen atom, fig. 25.1.

In such a molecule, there will be *partial separation of charges*; the more electronegative atom acquires a partial negative charge, while the other atom becomes partially positive – as in $H^{\delta+}Cl^{\delta-}$.

In HCl, the percentage covalent character is 80%, while that of HF is 75%.

3. If the electronegativity difference is too small i.e., between 0.1 and 0.4, the bond will be covalent and weakly polar – as in BrCl, $BH_3$ and $CH_4$.

4. When two atoms of the same element combine, the electronegativity difference will be zero. The bond formed will be covalent, and there will be a uniform distribution of electron density around the atomic nuclei. Such a covalent bond will be *purely non-polar*. Examples are *homonuclear diatomic molecules* such as $H_2$, $O_2$, $N_2$ and $Cl_2$.

### Polarization in Covalent Bonds

*The uneven distribution or distortion of charges in a polar covalent bond due to uneven sharing of electrons is called polarization*. For instance: In HCl molecule, chlorine atom is more electronegative than hydrogen atom; hence, the electron density around chlorine atom is more than that of hydrogen atom. This makes the chlorine end to be *electron rich* and carries a *partial negative charge*, $\delta-$, while the hydrogen end is *electron poor*, and therefore, carries a *partial positive charge*, $\delta+$, see fig 25.3.

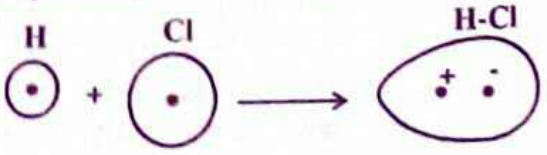



**Fig. 25.3**: *Electron density distribution in HCl molecule*

*The partial separation of charges in a polar covalent bond* is called *dipole*. The existence of a dipole makes a *polar covalent bond* to have a *part-ionic character*.

### Polarization in Ionic Bonds

Experimental studies have shown that *chemical bonds may not be purely ionic or purely covalent, because of polarization*.

In a purely ionic compound, the cation and anion are separate and spherical in shape, with charges uniformly distributed round their nuclei, fig 25.4a. If the electron density between the nuclei is increased, one of the ions must have been *polarized*, see fig 25.4b.



a. *Purely ionic* b. *Cation polarizes anion*

Fig 25.4 *Electron density distribution in an ionic compound*

### Fajan's Rule

The factors that promote polarization and hence, covalent characters in ionic compounds are summarized by the *Fajan's rule*, which state that:

*An ionic bond will exhibit covalent character if*

a. *either the cation or anion is highly charged,*

b. *the cation is small in size, and*

c. *the anion is large in size.*

**Explanation of the rule**: In an ionic compound, a cation tends to attract the electron cloud around the anion, i.e. a cation will polarize an anion.

The polarizing power of a cation and the polarizability of an anion depend on size and charge:

1. A cation with a small size and/or a high charge has a high charge density; hence, it is hard and has a high polarizing power.

For isoelectronic ions, the polarizing power of cations increases along a period and decreases down the group of the periodic table, e.g.

a. *For isoelectronic ions*: $Na^+ < Mg^{2+} < Al^{3+}$

*Increasing polarizing power →*

b. *For Group IA metals*: $Li^+ > Na^+ > K^+$

*← Decreasing polarizing power*

2. An anion with a large size and/or a high charge has a low charge density; hence, it is soft and readily polarized (or highly polarizable).

Among the halides the order of *increasing* polarizability is:

$$F^- < Cl^- < Br^- < I^-$$

*Increasing polarizing power →*

The least polarizable anion is $F^-$; the larger and the more polarizable (i.e. softer) anions are $Br^-$ and $I^-$, while $Cl^-$ is intermediate.

The polarization of an anion by a cation makes an ionic bond to be partially covalent. As the polarization of the anion increases, the covalent character of the ionic compound increases. Generally, all ionic bonds have some covalent character:

1. **Among NaCl, $MgCl_2$ and $AlCl_3$**: Since $Al^{3+}$ is the smallest and the most highly charged cation, $AlCl_3$ is the least ionic, followed by $MgCl_2$, while NaCl is the most ionic.

2. **Between $BeCl_2$ and $MgCl_2$**: $Be^{2+}$ is smaller in ionic size than $Mg^{2+}$; hence, $Be^{2+}$ has a higher polarizing power than $Mg^{2+}$. Consequently, $BeCl_2$ is less ionic than $MgCl_2$.

### Solved Problem

**6.** Which molecule will be more polar: HF or HCl? Explain.

*HF is more polar than HCl.*

*The electronegativity difference between hydrogen and fluorine atoms is more than that of hydrogen and chlorine atoms. This is because fluorine atom is more electronegative than chlorine atom.*

### Revision Exercises

**25** Explain the term *polarization*.

**26** Hydrogen chloride is described as a polar covalent molecule. Explain.

**27** What type of bond will be formed between elements P and Q if their electronegativity values are 0.8 and 4.0 respectively? [WAEC

**28** State the Fajan's rule.

**29** Which compound is more ionic: NaCl or $AlCl_3$? Explain, using the Fajan's rule.

## Answers to Revision Exercises

| | | | | |
|---|---|---|---|---|
| 5. B | 8. A | 9. B | 15. D | 16. C |
| 17. D | 24. D | 25. B | 29. NaCl | |

# 26

# •SHAPES OF MOLECULES AND IONS• •HYBRIDIZATION•

## 26.1 Introduction

The geometric shape of a molecule or ion describes the arrangement of its atoms in space.

Covalent molecules and molecular ions have definite shapes. *Reason:* Covalent bonds that hold the atoms in a molecule together are rigid and highly directional – unlike the ionic bonds that are non-directional.

The two theories employed in predicting molecular shapes are the *valence bond theory* and the *valence shell electron-pair repulsion theory*. The two theories are similar.

**Solved Problem**

1. Covalent molecules have definite shapes. Why?

*Definite shapes of covalent molecules are due to the fact that covalent bonds are rigid and highly directional.*

**Revision Exercises**

1. Explain the term *geometric shape of a molecule*.
2. Which type of chemical bond is non-directional?

## 26.2 Shapes Molecules and Ions

### Shapes of Diatomic Molecules

All diatomic molecules are linear, e.g. $H_2$, $F_2$, $Cl_2$, $O_2$, HF, HCl and CO.

• In the formation of hydrogen molecule, $H_2$, the half-filled s-orbitals of the two atoms overlap such that a pair of electrons is concentrated between the two atomic nuclei. It is an s-s bond, (fig. 26a).

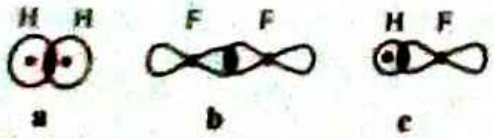



**Fig. 26.1** a. *The s-s bond in $H_2$ molecule*
b. *The p-p bond in $F_2$ molecule*
c. *The s-p bond in HF molecule*

• In the formation fluorine molecule, $F_2$, the half-filled $2p_z$-orbitals of the two atoms overlap such that a pair of electrons is concentrated between the two atomic nuclei. It is an p-p bond, (fig. 26b).

• In the formation of HF, the half-filled s-orbital of hydrogen atom, overlaps with the half-filled $2p_z$ orbital of fluorine atom so that a pair of electrons is concentrated between the two atomic nuc-lei. It is an s-p bond, (fig. 26c).

In the formation of the *s-s*, *p-p* and *s-p* bonds, the orbitals involved overlap along the internuclear axes of the orbitals, and are *collinear*. Such bonds are strong and highly directional. They are called σ (sigma) bonds.

### Shapes of Simple Polyatomic Molecules

The *central atom* controls the shape of a triatomic or polyatomic molecule. The *central atom* in such a molecule is the atom of the element present in the least number, or the atom that requires the highest number of electrons to complete its outermost shell. For instance:

• In $H_2O$, the oxygen atom, O is at the centre, since there is only one of it. Similarly, N is in the central atom in $NH_3$, while C is the central atom in $CO_2$ and $CH_4$.

• In HClO, monoxochlorate (I) acid, oxygen O is the central atom, since it requires two electrons to complete its outer shell of electrons, while H and Cl atoms require one electron each.

• It is possible for two or more identical atoms to be the central atoms – as in $H_2O_2$, where the two oxygen atoms are surrounded by the hydrogen two atoms, and in $C_2H_6$, where the hydrogen atoms surround the two carbons.

### Concept of Hybridization

When the central atom in a molecule uses the electrons from two different orbitals, the atomic orbitals redistribute their energies in order to produce a new set of orbitals of the same energy. This process, called *hybridization, is the mixing of atomic*

*orbitals of different energies in order to obtain a new set of orbitals of the same energy.*

The new set of orbitals is called *hybrid orbitals*. *Hybrid orbitals* are usually of the same length and strength. They are rigid and highly directional; hence, they determine the shapes of covalent molecules and their bond angles. Figure 26.2 illustrates *one hybrid orbital*.

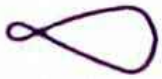


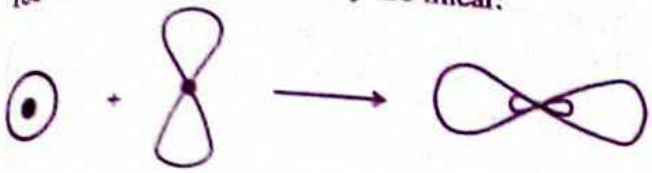
*Fig 26.2 A hybrid orbital*

**Types of hybridization in the s- and p-orbitals**

The three types of hybridization involving the s- and p-orbitals are: *sp*, $sp^2$ and $sp^3$ hybridizations.

**1. sp-hybridization:**

In *sp-hybridization*, *one half-filled s-orbital* and *one half-filled p-orbital* interact to form *two* identical orbitals, called *sp hybrid orbitals*, with axes at 180° to one another, i.e., they are linear:



*s-orbital* *p-orbital* *two sp hybrid orbitals*

***Formation of $BeCl_2$ molecule***

The ground state electron configuration of beryllium atom is $1s^2 2s^2$. In order to form covalent bonds, one of the 2s electrons is *promoted* into one of the three empty orbitals in the 2p-sublevel to give two unpaired electrons.

*The energy absorbed in order to promote an electron from one orbital to an empty orbital in a higher energy sublevel is called excitation energy.* The resulting electron configuration is called *excited state*.

Be: $1s^2 2s^2$ Be : $1s^2 2s^1 2p^1$

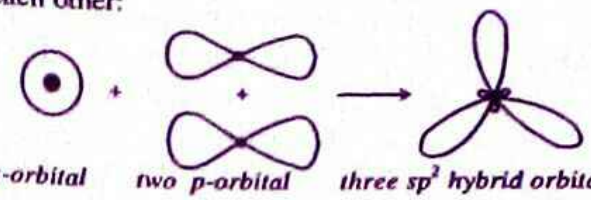


Ground state Excited state of Be

In the formation of $BeCl_2$, hybridization occurs between the half-filled 2s orbital and half-filled 2p orbital in the excited sate of beryllium atom, to produce two *sp* hybrid orbitals. The two hybrid orbitals then combine separately with the unpaired electron in each of the two chlorine atoms to give a *linear molecule*, with two σ covalent bonds and a *bond angle* of 180°: Cl–Be–Cl

**2. $sp^2$-hybridization**

In an *$sp^2$-hybridization*, *one half-filled s-orbital* and *two half-filled p-orbitals* interact to produce *three* identical *$sp^2$ hybrid orbitals*. The axes of the three orbitals lie in the same plane and at 120° to each other:

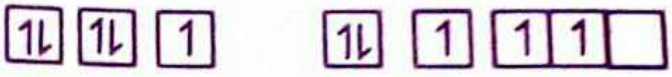


*s-orbital* *two p-orbital* *three $sp^2$ hybrid orbitals*

***Formation of $BH_3$ molecule***

The ground state electronic configuration of boron atom is $1s^2 2s^2 2p^1$. In order to form covalent bonds with three hydrogen atoms, one of the 2s electrons is *promoted* into one of the empty 2p orbitals to produce three unpaired electrons in the excited state of boron atom:

B: $1s^2$ $2s^2$ $2p^1$ B: $1s^2$ $2s^1$ $2p_x^1$ $2p_y^1$

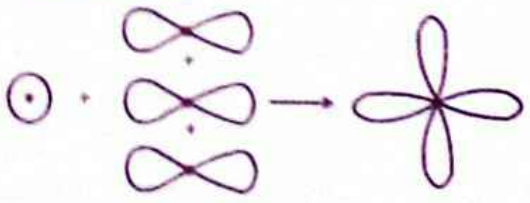


Ground state Excited state of Boron atom

In the formation of $BH_3$, hybridization occurs between the half-filled 2s orbital and the two half-filled 2p orbitals in the excites state of boron, to give three equivalent $sp^2$ hybrid orbitals. The three hybrid orbitals then combine separately with the unpaired electrons in the three hydrogen atoms to give boron hydride with three σ covalent bonds. The molecule is trigonal planar with a bond angle of 120°:

**3. $sp^3$-hybridization**

In *$sp^3$-hybridization*, *one s-* and *three p-orbitals* with one electron each interact to produce *four* equivalent *$sp^3$ hybrid orbitals*. In order to minimize electronic repulsion, the four *$sp^3$ hybrid orbitals* acquire a tetrahedral shape with a *bond angle* of 109.5° to each other:

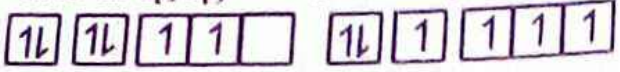


*s-orbital* *three p-orbital* *four $sp^3$ hybrid orbitals*

***Formation of methane, $CH_4$ molecule***

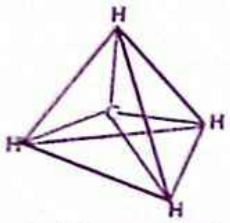
The ***ground state*** *electron configuration of carbon atom* is $1s^2\ 2s^1 2p^2$. In order to form *four* single covalent bonds with four hydrogen atoms, one of the 2s electrons is *promoted* to the empty $2p_z$ orbital, to give four unpaired electrons in the ***excited state*** *of carbon atom*:

C: $1s^2\ 2s^2\ 2p_x^1 2p_y^1$ C: $1s^2\ 2s^1\ 2p_x^1 2p_y^1 2p_z^1$



*Ground state* *Excited state*

In the formation of $CH_4$, hybridization occurs between the half-filled 2s orbital and the three half-filled 2p orbitals in the excited state of carbon to give four equal $sp^3$ hybrid orbitals. The four hybrid orbitals then combine separately with the unpaired electrons in the four hydrogen atoms to give methane that has four σ covalent bonds. The molecule has a *regular tetrahedron* shape with carbon at the centre and the hydrogen atoms at the four corners:




*Tetrahedral shape of methane*

## Hybridization involving Multiple Bonds

***1. Formation of double bond in ethene, $C_2H_4$***

In ethene, $H_2C{=}CH_2$, each carbon atom is $sp^2$ hybridized as in boron, i.e. each carbon atom has three $sp^2$ hybrid orbitals that are planar, and one unhybridized half-filled $2p_z$ orbital, which is at right angles to the axes of the hybrid orbitals.

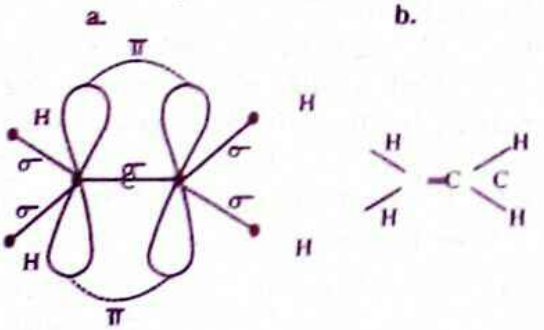



**Fig. 26.2** *Formation of a double bond in ethene*

Each carbon atom uses two of the three $sp^2$ hybrid orbitals to form σ-bonds with two hydrogen atoms, and the third in forming a σ-bond with each other. The un-hybridized $2p_z$ orbital on each carbon atom then, overlap side-by-side (laterally) above and below the plane to form another type of covalent bond called π (*pi*) *bond* (fig. 26.2a). This leads to the formation of a double covalent bond between the two carbon atoms in ethene (fig. 26.2b). A *double* covalent bond is composed of a relatively strong σ-bond and a relatively weak π-bond.

***2. Formation of triple bond in ethyne, $C_2H_4$***

In ethyne molecule, H—C≡C—H each carbon atom is *sp* hybridized as in beryllium, i.e. each carbon atom has two *sp* hybrid orbitals, which are linear and 180° to each other, and two unhybridized half-filled $2p_y$ and $2p_z$ orbitals, which are at right angles to each other and to the axes of the hybrid orbitals.

Each carbon atom uses one of the two $sp^2$ hybrid orbitals in forming a σ-bond with one hydrogen atom and the other in forming a σ-bond with each other; all the four atomic nuclei of the molecule are *collinear*. The unhybridized $2p_y$ and $2p_z$ orbitals on each carbon atom then, overlap side by side (laterally) above and below the plane to form two π (*pi*) *bonds* (fig 26.3a). This leads to the formation of a triple covalent bond between the two carbon atoms in ethyne (fig 26.3b).

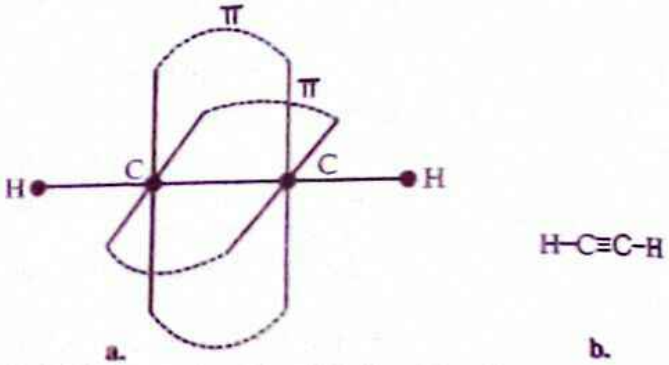



**Fig 26.3** *Formation of a triple bond in ethyne*

A *triple* covalent bond is composed of *one* relatively strong σ-bond and *two* relatively weak π-bonds.

### Solved Problem

**2.** Write the electronic configuration corresponding to *the excited state of nitrogen.*

**Solution:** Excited state of $_7N = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$

### Revision Exercises

3. What is *hybridization?*
4. State the **three** types of hybridization involving the *s* and *p* orbitals.
5. Write the electronic configuration corresponding to the excited state of carbon.
6. The hybridization of carbon atoms in ethene, $CH_2{=}CH_2$ is

   **A.** $sp^3$ **B.** sp **C.** $sp^2$ **D.** not possible.

7. State the type of hybridization and the bond angle in each of the following: **a.** $BH_3$ **b.** $BeCl_2$ **c.** $C_2H_6$

## Predicting Shapes of Molecules and Ions

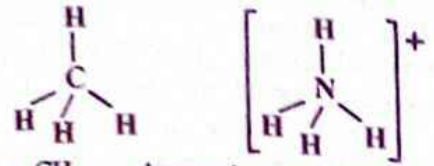
In order to identify the type of hybridization of the central atom and hence, the shape of a molecule or ion, the following procedure is suggested:

1. Identify the central atom in the molecule or ion.
2. Draw the electron-dot formula of the molecule or ion – indicating the electron-pairs used in bonding (bonding pairs) and those that are not used (lone-pairs) by the central atom.

### a. In $sp^3$ hybridization:

i. The central atom is bonded separately to *four* other atoms by σ-bonds (*four* bonding pairs); the shape is a *regular tetrahedral* with a bond angle of 109.5°. Examples: $CH_4$ and $NH_4^+$.

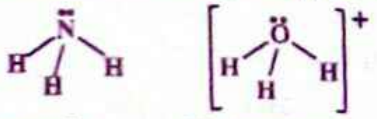
*Tetrahedral*



Methane, $CH_4$ Ammonium ion, $NH_4^+$

ii. The central atom is bonded separately to *three* other atoms by σ-bonds (*three* bonding-pairs) and has *one* lone-pair of electrons. The shape is a *distorted tetrahedral* (*pyramidal*) with a bond angle less than 109.5° due to the repulsive forces between bonding-pairs and lone-pairs of electrons, e.g. $NH_3$ (bond angle 107°), $H_3O^+$ and $PCl_3$.

*Distorted tetrahedral (Triagonal pyramidal)*



Ammonia Hydroxonium ion

iii. The central atom is bonded to *two* separate atoms by σ-bonds (*two* bonding-pairs) and has *two* lone-pairs of electrons. The shape is *bent* or *V-shape* with a bond angle much less than 109.5°, due to the repulsive forces between the two lone-pairs of electrons, and between the bonding-pairs and lone-pairs of electrons, e.g. $H_2O$ (bond angle 105°) and $H_2S$ (bond angle 92°).

***V-shape***



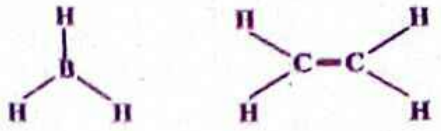
Water Hydrogen sulphide

The bond angle of $H_2S$ (92°) is less than that of $H_2O$ (bond angle 105°), due to the difference in the electronegativities of sulphur and oxygen.

### b. In $sp^2$ hybridization:

i. The central atom is bonded separately to *three* other atoms by σ-bonds (*three* bonding-pairs) without lone-pair; the shape is a *triangular planar* with a bond angle of 120°. Examples: $BH_3$ and $BCl_3$.

*Triangular planar*



Boron hydride Ethene

ii. The central atom is bonded separately to *three* other atoms by *two* σ-bonds and one double covalent bond, without lone pair of electrons; the shape is also *triangular planar* with a bond angle of 120° e.g. $H_2C{=}CH_2$, $COCl_2$ and $CH_3CO$. (In *ethene* each carbon atom is at the centre of a triangle.)

iii. The central atom is bonded separately to *two* other atoms by σ-bonds and has *one* lone-pair of electrons; the shape is *bent* or *V-shape* e.g. $SnCl_2$.

***V-shape***



Tin(II) chloride Sulphur(IV) oxide

iv. The central atom is bonded separately to *two* other atoms by *one* σ-bond and *one* double covalent bond, and has *one* lone-pair of electrons; the shape is also *bent* or *V-shape*, e.g. $SO_2$ and $NO_2$.

### c. In sp hybridization:

i. The central atom is bonded separately to *two* other atoms by the use of single σ bonds and has no lone pairs of electrons. The molecule is linear with a bond angle of 180°, e.g. $BeCl_2$.

*Linear*



Hydrogen cyanide Ethyne Carbon(IV) oxide

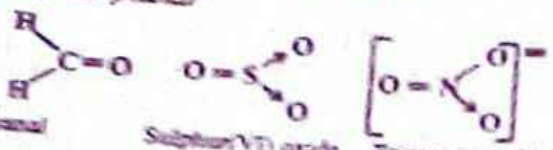
ii. The central atom is bonded separately to *two* other atoms by the use of *one* σ-bond and *one* triple covalent bond, and has no lone pairs of electrons. The molecule is linear with a bond angle of 180°, e.g. HCN, $C_2H_2$.

iii. The central atom is bonded separately to *two* atoms by *two* double covalent bonds; no lone pairs

of electrons. The molecule is linear with a bond angle of 180°, e.g. $CO_2$ and $CS_2$.

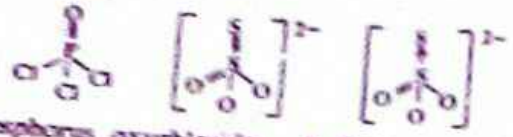
**Shapes of some molecules and ions**

*Triangular planar*



Methanal Sulphur(VI) oxide Trioxonitrate(V) ion

*Tetrahedral*



a. Phosphorus oxychlorides. b. Tetraoxosulphate(VI) ion. c. Trioxosulphatosulphate(IV) ion, $S_2O_3^{2-}$ [In $S_2O_3^{2-}$, the sulphur atom attached to the central sulphur atom is a neutral species; the bond is dative.]

**Solved Problem**

3. Which of the following has a linear structure?
I. $CO_2$ II. $C_2H_2$ III. $H_2O$ IV. $SO_2$
A. I only B. II only C. II and III only
D. I and II only E. I, II and IV only [NECO]

**Answer: D**

**Revision Exercises**

8 State the shape of each of the following species:
a. $CCl_4$: b. $NH_3$: c. $NH_4^+$: d. $CS_2$.

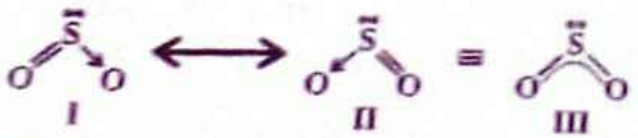
9 Consider the following molecules:
$CO_2$, $CH_4$, $NH_3$, $H_2O$.
In which molecule is the angle between two covalent bonds the a. least?; b. greatest?

10 State the bond angles in trigonal planar and pyramidal molecules.

## 26.3 Concept of Resonance

When a molecule cannot be represented by a single structure, the molecule is said to exhibit *resonance*. For instance: In $SO_2$ molecule, the sulphur atom forms a double covalent bond with one oxygen atom, and as a donor, forms a dative bond with the other oxygen atom.

Since the two oxygen atoms are occupying equivalent positions, the double bond can be between the sulphur and any of the two oxygen atoms – as shown in fig 26.4 I and II.



I II III

*Fig 26.4 Resonating structures of $SO_2$ molecule*

The two structures are said to be in *resonance* or are the *resonating* structures of $SO_2$ molecule. A two-way arrow (↔) is used to denote resonating structures. Usually, the true structure of a molecule exhibiting resonance is a hybrid of the resonating structures – as shown by structure III.

Other examples of molecules that exhibit resonance are $NO_2$ and $C_6H_6$ (benzene).

**Revision Exercises**

11 Explain the term *resonance*.

12 Give two examples of molecules that exhibit resonance.

## 26.4 Structures and Shapes of Solids

A *solid* is a substance that maintains its shape over a long period of time at a particular temperature. Some solids form *crystals* with definite shapes, while others are *amorphous* (*shapeless*), e.g. glass.

A *crystal* is a *solid with a definite shape*. The position a particle (atom, molecule or ion) occupies in a crystal is called *lattice point*. The pattern showing the arrangement of the particles is called *space lattice*, while the smallest number of particles in the space lattice, which describes the shape of the entire crystal, is called a *unit cell*.

The method used in establishing the structure of crystals is by the X-ray diffraction. The shape of a crystal can be cubic, tetragonal, hexagonal, octahedral, rhombic, etc.

The *five* types of bonding forces that hold matter in solid state are: *ionic*, *covalent*, *metallic*, *van der Waals forces* and *hydrogen bond*. There is a marked correlation between crystal structure and physical properties.

### Classes of Solids

There are *four* classes of solids: *ionic*, *covalent*, *metallic*, and *molecular*.

#### 1. *Ionic Solids*

*An ionic compound is composed of cations and anions*. These *ions* interlink in an alternating fashion to give a hard three-dimensional giant structure.

The shape of an ionic solid depends on the relative sizes of the cations and anions. For instance: In sodium chloride crystal, $Na^+$ and $Cl^-$ occupy the lattice points such that each $Na^+$ is surrounded by **six** $Cl^-$, and vice versa. The number is called *coordination number*. The NaCl lattice consists of a *face-centred cubic* system, fig 26.5.

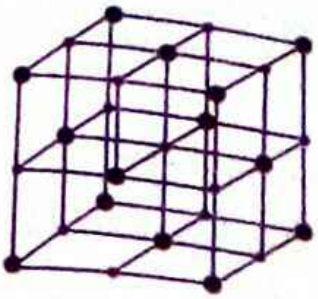


Fig 26.5 *Space lattice of NaCl*

**General Properties of Ionic Solids**

a. Ionic solids form crystals that are hard and stable, and with high melting points. This is because an ionic crysal is an infinite assembly of ions in three dimensions. For instance, sodium chloride crystals melt at 801°C.

b. They are brittle and do not conduct electricity in solid state, due to the strong cohesive force between the ions, which make them immobile.

c. They conduct electricity in fused or molten state, due to the mobility of the ions under this condition.

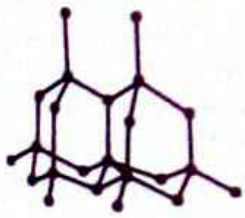
d. They are soluble in water to give aqueous solutions that are electrolytes.

*A solid substance that has a relatively high melting point, conducts electricity in molten state, and dissolves in water to give a conducting solution is an ionic solid.*

## 2. *Covalent Solids*

In a covalent solid, atoms of the same element occupy the lattice points. These atoms are linked, infinitely, by the strong covalent bonds, which are rigid and highly directional, to give a hard network solid. Diamond and graphite are examples of covalent network solids. They are the crystalline allotropes of carbon.

In diamond, carbon atoms that are $sp^3$ hybridized occupy the lattice points. It results in the formation of a single infinite three-dimensional interlocking molecule with a giant network crystal. Hence, diamond is hard, strong and with a melting point of about 3500 °C (fig. 26.6).



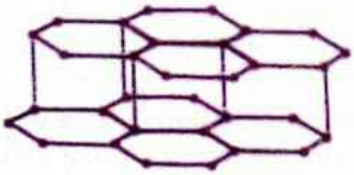


Fig 26.6 *Structure of diamond* Fig 26.7 *Structure of graphite*

In graphite, carbon atoms that are $sp^2$ hybridized occupy the lattice points. It results in the formation of planar infinite two-dimensional molecule with flat hexagonal network layer-lattice crystal (fig 26.7). See Section 30.2 for the properties and uses of diamond and graphite.

Sand, silicon(IV) oxide, $SiO_2$, is regarded as a covalent network solid. In the crystal, each silicon atom is covalently bonded to four oxygen atoms to produce a three-dimensional network crystal, which is hard and with a high melting point.

**General Properties of Covalent Solids**

a. Covalent solids are hard and strong, and with relatively high melting points.

b. They are insoluble in water, and non-conductors of electricity, except graphite.

## 3. *Metallic Solids*

Metallic solids are formed by elements that have the following properties: Low ionization energies, few valence electrons, and available empty valence orbitals. These properties are true of the elements in groups I, II and III, and the transition elements in the periodic table.

In a metallic solid, the lattice points are occupied by the positive nuclei of the metal atoms held together by *a sea of mobile electrons*.

**General Properties of Metals**

The physical properties of metals can be accounted for by their structures:

a. The free movement or mobility of their valence electrons accounts for the electrical and thermal conductivities of metals.

b. Metals are malleable and ductile, because metallic bonds are non-directional, while their valence electrons are mobile, and are able to move freely from one point to another within the lattice.

c. The bright metallic lustre in metals is due to the emission of light by the mobile valence electrons.

## 4. *Molecular Solids*

In a molecular solid, molecules occupy all the lattice points. Either the weak *van der Waals forces* or the stronger hydrogen bonds hold these molecules together.

***van der Waals bonds*** are intermolecular cohesive forces, which are formed between the following groups of molecules:

Atoms of *noble gases*, such as helium, neon and argon; *non-polar* molecules, such as $O_2$, $H_2$, $Br_2$, $O_3$, $P_4$, $S_8$, $CO_2$, $CH_4$, $CCl_4$ and wax; and *polar*

molecules, such as $SO_2$, $SO_3$ and HCl. The lattice structure is face-centred-cubic.

*van der Waals forces* are responsible for the liquefaction and solidification of noble gases, non-polarand polar molecules.

Molecular solids are soft and have low melting points. This is because *van der Waals* forces are extremely weak and non-directional. Such solids are sometimes referred to as *van der Waals solids*.

***Hydrogen bonds*** are intermolecular cohesive forces that operate between molecules in which atoms of hydrogen are covalently bonded to atoms of oxygen, nitrogen and fluorine (highly electronegative atoms) – as in HF, $H_2O$, $NH_3$, organic acids, alcohols, and amines. Such molecules are highly polar; the hydrogen atom acquires a partial positive charge, $\delta+$, while the electronegative atom becomes partially negative, $\delta-$.

*Hydrogen bonds* are formed when hydrogen atom that is covalently bonded to an atom of fluorine, oxygen or nitrogen in one molecule is attracted to an atom of fluorine, oxygen or nitrogen in another molecule. Fig 26.9 shows *hydrogen bonds*, in broken lines, between water molecules.

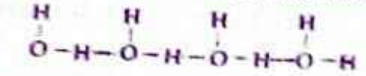


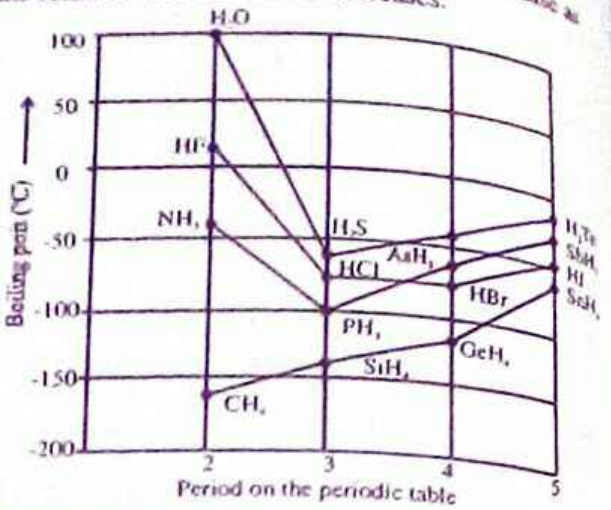
**Fig 26.9**: *Hydrogen bonds between water molecules*

*Hydrogen bonds* are more extensive in *ice* than in *water*. In water $H_2O(l)$, each oxygen atom is separately bonded to three hydrogen atoms by the use of two single covaleut bonds and one hydrogen bond (see fig 26.9); the shape is pyramidal. In ice $H_2O(s)$, each oxygen atom is separately bonded to four hydrogen atoms by the use of two single covalent bonds and two hydrogen bonds; the shape is *distorted tetrahedral*.

Molecular solids in which hydrogen bonds exist between their molecules are generally polar covalent; such molecules have higher boiling and melting points than expected.

### Evidence for Hydrogen bonding

Consider the boiling points (b.p.) of the hydrides of groups IV, V, VI and VII in the periodic table as shown below:




### *Comments on the curves*

1. Among the hydrides of group IV: $CH_4$, $SiH_4$, $GeH_4$ and $SnH_4$, there is a steady increase in boiling points as the relative molecular mass increases from $CH_4$ and $SiH_4$. This trend is as expected, since van der Waals forces of attraction increase as the relative molecular mass increases.

2. Among the hydrides of group VI, i.e. $H_2O$, $H_2S$, $H_2Se$ and $H_2Te$, the curve shows the expected increase in boiling point from $H_2S$ through $H_2Se$ to $H_2Te$. However, the boiling point of $H_2O$ is much higher than expected.

This observation is similar to those of the hydrides of groups V and VII, where the boiling points of $NH_3$ and HF are higher than expected. This is evidently a consequence of the strong intermolecular forces due to hydrogen bonds between the molecules of HF, $NH_3$ and $H_2O$.

3. Consider the molecules of $H_2O$ with relative molecular mass of 18, and $H_2S$ with relative molecular mass of 34. The boiling point of $H_2S$ is expected to be higher than that of $H_2O$, due to the higher relative molecular mass of $H_2S$; but because there are no hydrogen bonds between $H_2S$ molecules, it is a gas at room temperature, while $H_2O$ is a liquid at room temperature, due to hydrogen bonds between its molecules.

4. For the same reason, ammonia gas, $NH_3$ has a higher boiling point than phosphine, $PH_3$, while hydrogen fluoride, HF boils at a higher temperature than hydrogen chloride, HCl.

The high solubility of ammonia in water and the miscibility of alcohols and water are due to the formation of hydrogen bonds between their molecules, while the solubility of ionic compounds, such as sodium chloride, in water are due to the electrostatic force of attraction between the dipolar water molecules and the ions of NaCl.

5. If not for hydrogen bonding, water would have been a gas at room temperature, and that is to say, there would have been no life in this globe!

**Solved Problem**

4. Which of the following compounds exhibits hydrogen bonding? [WAEC]
A. $CH_3Cl$ B. $CH_3OH$ C. $CH_4$ D. $H_2S$
*Answer: B*

**Revision Exercises**

13 List *four* classes of solids with one example of each.
14 Non-polar molecules are held together by
A. van der Waals forces. B. hydrogen bonds.
C. covalent bonds. D. electromagnetic forces. [W]

## 26.5 Polarity of Molecules

### Dipole Moments

A *polar* covalent bond, **Y–X** has a *dipole*, since the bonded atoms have different electronegativities; with a partial negative charge, $\delta^-$, on the more electronegative atom and a partial positive charge, $\delta+$, on the other atom:

$$Y^{\delta+}–X^{\delta-}$$

The degree of polarity of a covalent bond is expressed in term of *dipole moment*, $\mu$. *Dipole moment increases as the electronegativity difference between the covalently bonded atoms increases.* Bond polarity increases as the dipole moment increases.

A *non-polar* covalent bond has *zero* dipole moment since there is no difference in the electronegativity of the bonded atoms.

### Shapes of Molecules and Polarity of Bonds

The *polarity* of a triatomic or polyatomic molecule depends on the shape of the molecule. The overall *dipole moment* of such a molecule is equal to the sum of all the individual bond dipoles within the molecule, e.g.

a. In $CO_2$, each of the carbon-oxygen double bond is polar, but the molecule has a *dipole moment* of zero, i.e. $CO_2$ molecule is non-polar. This is because the molecule is linear; the dipole moment of one C=O bond cancels the other, fig 26.10

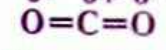



Fig 26.10 Shape of $CO_2$ molecule

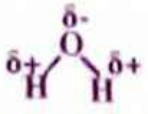
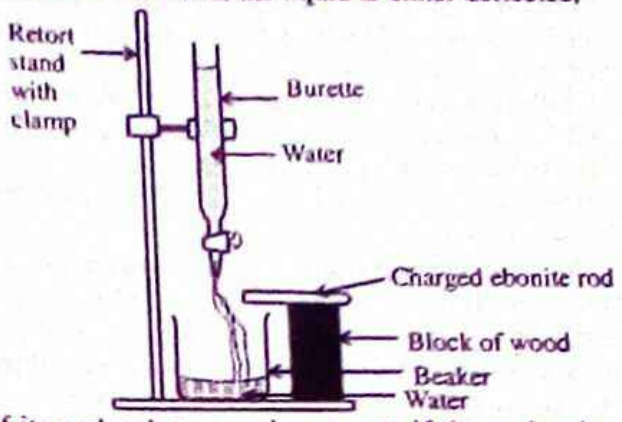



Fig 26.11 Shape of $H_2O$ molecule

b. The polarity of $H_2O$ molecule is because it is non-linear, i.e. *its dipole moment is not zero* – unlike that of $CO_2$. $H_2O$ molecule has a V-shape, fig 26.11.

### Testing the Polarity of a Liquid

When an ebonite rod, which is charged positively or negatively is brought close to a stream of a liquid from a burette, the liquid is either deflected,




if its molecules are *polar*, or not, if the molecules are *non-polar*, fig 26.12.

**Fig 26.12** *Testing the polarity of a liquid*

Generally, molecules with *non-symmetrical* shapes, such as $H_2O$ and $CHCl_3$ have *permanent dipoles*, and hence, *polar*; while those with *symmetrical* shapes, such as $CO_2$, $CH_4$ and $C_6H_6$ (benzene) will be *non-polar*.

**Revision Exercises**

15 In terms of dipole moment, distinguish between a polar molecule and a non-polar molecule.
16 The greater the difference in electronegativity between bonded atoms, the
A. lower the polarity of the bond.
B. higher the polarity of the bond.
C. weaker the bond.
D. higher the possibility of the substance formed being a molecule. [WAEC]
17 Carbon(IV) oxide is regarded as a non-polar molecule, despite the fact that the covalent bonds within the molecule are polar. Explain.

### Answers to Revision Exercises

6. C 14. A 16. B

# 27

# •RADIOACTIVITY AND NUCLEAR REACTIONS•

## 27.1 Introduction

*Nuclear chemistry* deals with the study of processes involving the *protons* and *neutrons* in the *nuclei* of atoms.

During *nuclear processes*, atoms of one element may be converted into atoms of other elements by any of the following *nuclear reactions*: *radioactive decay*, *nuclear disintegration*, *atomic fission* and *atomic fusion*.

*Nuclear reactions* differ from *chemical reactions*, which involve only the valence electrons in the atoms. Again, the heat liberated during any nuclear reaction is many thousands times greater than that of the most exothermic chemical reaction!

### Revision Exercises

1. What is nuclear chemistry?
2. Mention one process by which an atom of one element can be changed into that of another element.
3. Distinguish between a *nuclear reaction* and a *chemical reaction*.

## 27.2 Radioactivity

### Definition

***Radioactivity** is the spontaneous decay or disintegration of the nucleus of an atom with the emission of radiations and a large quantity of heat.*

*Radioactivity* is due to energy changes occurring within the nucleus of the atom. *Any substance capable of undergoing radioactivity is* **radioactive** e.g. uranium, radium, radon and carbon-14.

### Discovery of Radioactivity

A French physicist, ***Henri Becquerel*** (1895) observed that a certain uranium salt blackened a photographic film when placed together in the dark. He concluded that the uranium salt must have emitted certain radiations similar to the X-rays.

It was the turn of the *Curies* (*Pierre* and *Marie*) to investigate the properties of uranium. They discovered that uranium and its ores were radioactive, and that polonium and radium, which were isolated from uranium ores were also radioactive. In fact, radium was found to be two million times more radioactive than the same mass of uranium.

### Cause of Radioactivity

There are two classes of *naturally occurring* isotopes of elements: *stable* and *unstable* isotopes.

**a.** Atoms of *stable isotopes* consist of nuclei with approximately equal numbers of protons and neutrons. For instance: The two isotopes of chlorine have proton-to-neutron ratios of 17:18 and 17:20, while those of oxygen are 8 : 8, 8 : 9 and 8 : 10. Such isotopes are stable.

**b.** Atoms of *unstable isotopes* consist of nuclei with much more neutrons than protons. For instance: Uranium-238 with atomic number 92 has a nucleus of 92 protons and 146 neutrons. The nuclei of atoms of elements with atomic numbers greater than 83 are *unstable*.

The basis of radioactivity is the *instability* in isotopic atoms. An unstable isotope tends to become stable by emitting nuclear particles and radiations. Hence, an unstable isotope is radioactive; so also *artificial isotopes*.

### Revision Exercises

4. What is *radioactivity*?
5. Spontaneous emission of radiation by an unstable atomic nucleus is known as
   A. alpha emission. B. beta emission
   C. gamma emission D. radioactivity
   E. nuclear fission [NECO]
6. State the cause of radioactivity in isotopic atoms.

## 27.3 Radioactive Radiations

### Types of Radiations

Ernest *Rutherford* (1904), a physicist, studied the nature of radiations emitted during *radioactivity*; by subjecting the radiations from a small piece of uranium salt to a strong electromagnetic field. Three types of radiations were identified: **alpha** (α) rays, **beta** (β) rays and **gamma** (γ) rays.

He discovered that the *alpha* and *beta* rays were deflected in opposite directions by the magnetic field, while the *gamma* rays were not deflected at all, fig 27.1.

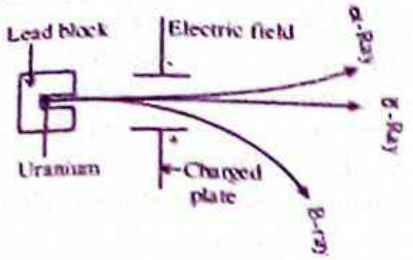



Fig 27.1

### Properties of the Radioactive Radiations

**1. Alpha (α) Rays**

a. Alpha rays consist of positively charged particles; hence, they are deflected towards the negative pole of the electromagnetic field.

b. They are massive; hence, only slightly deflected.

c. They have the longest wavelength; hence, the least energetic. They move with a velocity of about one tenth that of light, and have the *least penetrating power*: a sheet of paper or thin aluminium foil can stop them.

d. Being massive, they cause ionization on collision with particles on their path; they cause substances, such as *zinc blend*, ZnS, to fluorescence, i.e. glow brightly.

Naturally, α -particles have mass units of 4, and are regarded as the nuclei of helium atoms. They are represent-ed as $^{4}_{2}\alpha$ or $^{4}_{2}He$.

**2. Beta (β) Rays**

a. Beta rays consist of negatively charged particles; hence, they are deflected towards the positive pole of the electromagnetic field.

b. They are less massive than the α-particles; hence, more deflected towards the positive pole.

c. They have a shorter wavelength than the α-particles; hence, more energetic, move faster, and have a higher penetrating power than the α-particles. They will pass through a sheet of paper or an aluminium foil; only a 5 mm thick foil or a sheet of aluminium can stop them.

d. They have less ionizing effect than the α-particles.

A beta particle is called an *electron*. It has neither proton nor neutron. It nuclear symbol is $^{0}_{-1}\beta$ or $^{0}_{-1}e$.

**3. Gamma (γ) Rays**

a. They are electromagnetic radiations that have no mass or charge, i.e. they are neutral; hence, they are not deflected at all by the magnetic field.

b. They have the shortest wavelength; hence, the most energetic. They move at the velocity of light and have the *highest penetrating power*. They can only be stopped by 15 cm thick steel or lead block.

c. Gamma rays have the least ionizing power.

### Relative Energy of Radiations

When compared with X-rays, the order of increasing energy of the radioactive radiations is:

X-rays < α-rays < β-rays < γ-rays

*Increasing Energy* →

*Increasing Penetrating Power* →

### Detection of Radioactive radiations

Radioactive radiations are not only harmful; they are dangerous – being invisible. The following devices or instruments can be used to detect the radiations:

1. Geiger-Muller counters.
2. Wilson diffusion cloud chamber.
3. Scintillation counter.
4. Photographic plate.
5. Fluorescent screen coated with zinc sulphide, ZnS.

### Nuclear Symbols of Radiation Particles

Table 27.1 shows the nuclear symbols of various radiation particles. Note that the *mass number* **A**, is written as superscript, while the *atomic number* **Z**, is written as subscript.

**Table 27.1** *Nuclear Symbols of Nuclear particles*

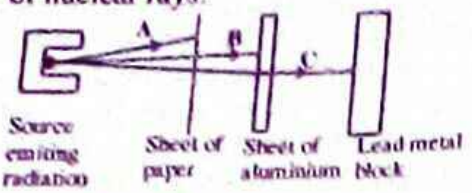
| | Particle | Symbol |
|---|---|---|
| 1. | Alpha particle; helium nucleus | $^{4}_{2}\alpha$ or $^{4}_{2}He$ |
| 2. | Beta particle; an electron | $^{0}_{-1}\beta$ or $^{0}_{-1}e$ |
| 3. | Proton; hydrogen nucleus | $^{1}_{1}p$ or $^{1}_{1}H$ |
| 4. | Neutron; neutral | $^{1}_{0}n$ |
| 5. | Positron; positive electron | $^{0}_{1}e$ |

**Solved Problems**

**1.** State **three** characteristics of beta particles. [WAEC]

**Solution** (*Any three of the following*)
- Beta particles are negatively charged.
- They are deflected towards the positive plate of an electric field. • They cause ionization in air.
- They are electrons . • They have negligible mass.

**2.** The diagram below illustrates the penetrating power of nuclear rays:




**a.** Identify **A**, **B** and **C**.

*A is an alpha ray; B is a beta ray; C is a gamma ray.*

**b.** If an electrostatic field is inserted between the source of rays and the sheet of paper, which of the rays will not be deflected and why?

**Solution:**

*Gamma ray will not be deflected, because it is neutral.*

**Revision Exercises**

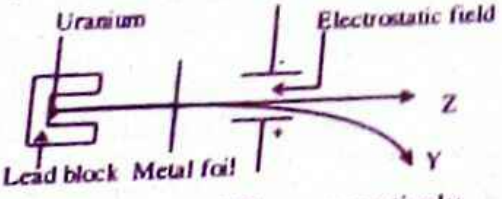
**7** Give the **three** types of radiations that are usually emitted by radioactive substances. [WAEC]

**8** List **three** characteristic properties of alpha particles.

**9** Gamma rays are produced when
- **A.** high velocity electrons are abruptly stopped in metals.
- **B.** energy changes occur within the nuclei of atoms.
- **C.** energy changes occur within the electronic structures of atoms.
- **D.** electrons are deflected in very strong magnetic fields.

**10** When a sheet of paper is placed in the path of a radioactive source, the radiation emitted, which passes through the paper consists of
- **A.** alpha and beta particles.
- **B.** alpha particles and gamma rays.
- **C.** beta particles and gamma rays.
- **D.** beta particles only. **E.** gamma rays only. [NECO]

**11** Study the diagram below:




**a.** The rays labeled Y and Z are respectively
- **A.** alpha and beta. **B.** beta and alpha.
- **C.** gamma and alpha. **D.** beta and gamma.

**b.** Which component of the emission from the uranium source was stopped by the metal foil?
- **A.** Gamma rays. **B.** Beta particles
- **C.** Alpha particles. **D.** X-rays. [WAEC]

**12** Write the nuclear symbols of each of the following:
**a.** an α-particle; **b.** β-particle; **c.** a proton;
**d.** a neutron; **e.** a positron.

**13** Name **three** devices for detecting radioactive emissions (radioactive detectors).

**14** Emission from radioactive substances can be detected by
- **A.** bomb calorimeter. **B.** Mass spectrometer.
- **C.** Geiger-Muller counter. **D.** X-ray equipment. [W]

## 27.4 Nuclear Reactions

*Nuclear reactions* occur in the nucleus of the atom of a radioactive element, due to energy changes.

As in a normal *chemical reaction*, a *nuclear reaction* can be represented by a *balanced nuclear equation*. The atoms of different isotopes of an element are called **nuclides**.

Consider the following *nuclear equations*:

1. $^{a}_{b}X + {}^{c}_{d}Y \rightarrow {}^{e}_{f}Z$ ...1
2. $^{g}_{h}M + {}^{i}_{j}Q \rightarrow {}^{k}_{l}R + {}^{m}_{n}T$ ...2

A nuclear equation is balanced if:

**a.** The sum of the *mass numbers* of the nuclides on the left is equal to those on the right, i.e.
In equation 1: $a + c = e$
In equation 2: $g + i = k + m$

**b.** The sum of the *atomic numbers* of the nuclides on the left is equal to those on the right, i.e.
In equation 1: $b + d = f$
In equation 2: $h + j = l - n$

**Worked Examples**

**3.** Balance the following nuclear equation, and hence, identify X:

$$^{14}_{7}N + X \rightarrow {}^{18}_{9}F$$

*Let the nuclear symbol of X be* $^{A}_{Z}X$, i.e.

$$^{14}_{7}N + {}^{A}_{Z}X \rightarrow {}^{18}_{9}F$$

Considering the mass numbers on both sides:

$14 + A = 18 \quad \therefore \quad A = 18 - 14 = 4.$

Considering the atomic numbers on both sides:

$7 + Z = 9 \quad \therefore \quad Z = 9 - 7 = 2.$

The nuclear symbol of the particle X is $^{4}_{2}X$; hence, X is an alpha particle.

**4.** Balance the following nuclear equation:

$$^{20}_{8}O + {}^{1}_{0}n \rightarrow {}_{10}Ne + {}^{0}_{-1}e$$

*Let A represent the mass number of Ne. In the equation:*
- Sum of the mass numbers on both sides must be equal

$20 + 1 = A + 0 \quad \therefore \quad A = 21$

- Sum of the atomic numbers on the left is $8 + 0 = 8$. For the sum of the atomic numbers on the right to be equal

$\Rightarrow$ 8, there must be 2 of $^{0}_{-1}e$; so that $10 + 2(-1) = 10 - 2$
$= 8$. Hence, the balanced equation of reaction is:

$$^{20}_{8}O + {}^{1}_{0}n \rightarrow {}^{21}_{10}Ne + 2\,{}^{0}_{-1}e$$

**Revision Exercises**

15 What are nuclides?

16 If an element X of atomic number Z and mass number Y is irradiated by an intense concentration of neutrons, the relevant nuclear equation is

A. $^{Y}_{Z}X + {}^{1}_{0}n \rightarrow {}^{Y+1}_{Z}X$

B. $^{Y}_{Z}X + {}^{1}_{0}n \rightarrow {}^{Y-1}_{Z+1}X$

C. $^{Y}_{Z}X + {}^{1}_{0}n \rightarrow {}^{Y}_{Z+1}X$

D. $^{Y}_{Z}X + {}^{1}_{0}n \rightarrow {}^{Y+1}_{Z-1}X$

E. $^{Y}_{Z}X + {}^{1}_{0}n \rightarrow {}^{Y+1}_{Z+1}X$

17 Balance the following and identify Q and R.

a. $^{28}_{13}Al \rightarrow {}^{28}_{14}Si + Q$

b. $^{14}_{7}N + R \rightarrow {}^{18}_{9}F$

18 Complete the following nuclear reactions:

a. $^{59}_{27}Co + {}^{1}_{0}n \rightarrow a + X$

b. $^{228}Ra \rightarrow {}_{86}Co + {}^{4}_{2}He$

19 State the values of p and q in the following equations:

$$2\,{}^{2}_{1}D \rightarrow {}^{1}_{1}H + {}^{p}_{q}T$$

20 What is the element Y in the following equation?

$$^{14}_{7}N + {}^{4}_{2}He \rightarrow {}^{1}_{1}H + Y$$

21 What is the value of $x$ in the following nuclear reaction equation?

$$^{11}_{5}B + {}^{251}_{98}Cf \rightarrow {}^{x}_{103}Lr + 3\,{}^{1}_{0}n$$

A. 241 B. 259 C. 261 D. 265 [WAEC]

## 27.5 Types of Nuclear Reactions

There are four types of nuclear reactions:

- *Radioactive decay*; • *Nuclear disintegration*;
- *Nuclear (atomic) fission*;
- *Nuclear (atomic) fusion.*

*Nuclear fission* and *nuclear fusion* are the two nuclear reactions that provide the so-called *nuclear energy*.

### 1. Radioactive Decay

*Radioactive decay* is a *natural radioactivity*. It is a nuclear reaction in which an *unstable* radioactive atom or *radioisotope*, on its own, *emits* an *alpha* or a *beta* particle (never both), in order to form an atom with a more stable nucleus.

**Alpha Decay in Heavy Nuclei**

When a radioactive atom *emits* or *loses* an alpha particle, it is said to undergo an *alpha decay*. It occurs in elements with atomic numbers greater than 83, e.g. isotopes of uranium, radium, thorium and radon:

• Uranium-238 decays by emitting an α-particle to form an isotope of thorium; the reaction is highly exothermic.

$$^{238}_{92}U \rightarrow {}^{234}_{90}Th + {}^{4}_{2}He + \text{heat}$$

**Note**: *When an atom emits or loses an α-particle, the new atom has an atomic number less by two and a mass number less by four.*

A nuclear reaction in which there is a change in the number of protons of the atom, i.e. atomic number, is called an *atomic transmutation reaction*. It leads to the formation of an atom of another element. *Atomic transmutation* reactions are peculiar to nuclear reactions.

• Similarly, thorium-234 undergoes an α-decay, to form radium-230;

$$^{234}_{90}Th \rightarrow {}^{230}_{88}Ra + {}^{4}_{2}He$$

**Beta Decay**

When a radioactive nuclide emits or loses a beta particle, it is said to undergo *beta decay*.

*Beta decays* are common among radioisotopes with atomic numbers less than 83. Such atoms have more neutrons than protons; hence, unstable. They emit β-particles in order to become more stable. For instance: Carbon-14 emits a beta particle to form nitrogen-14:

$$^{14}_{6}C \rightarrow {}^{14}_{7}N + {}^{0}_{-1}e$$

A close look at the above nuclear reaction shows that *when a neutron is transformed into a proton, a β-particle, i.e. an electron, is emitted*:

$$^{1}_{0}n \rightarrow {}^{1}_{1}p + {}^{0}_{-1}e$$

**Note**: *When an atom emits or loses a β-particle, the new atom has the same mass number as the original atom, but with an increase in atomic number by one.*

**Gamma Rays**

Generally, all radioactive substances emit gamma rays, but because these rays do not carry any charge, the mass number and the atomic number of the new atoms are not affected by their emission.

However, γ-rays are dangerous to living creatures; they damage the tissues.

**Worked Examples**

5. Identify the type of radiation emitted in the following:

$$^{125}_{53}I \rightarrow {}^{125}_{54}Xe + X$$

**Solution**

Let $^{A}_{Z}X$ represents the radiation particle emitted.

In order to balance the equation:

• The sum of the mass numbers on both sides must be equal, i.e. $125 = 125 + A$

$\therefore \quad A = 125 - 125 = 0.$

• The sum of the atomic numbers on both sides must be equal, i.e. $53 = 54 + Z$

$\therefore \quad Z = 53 - 54 = -1$

The nuclear symbol is ${}^{0}_{-1}X$; a beta particle is emitted.

**6.** An atom ${}^{238}_{92}X$ decays by alpha particle emission to give an atom Y. Write a balanced equation to represent the process.

${}^{238}_{92}X \rightarrow {}^{4}_{2}He + {}^{234}_{90}Y$

## 2. Nuclear Disintegration

*Nuclear disintegration* is an *artificial radioactivity* in which the nucleus of a non-radioactive atom, a stable isotope, is bombarded with nuclear particles, to produce an *artificial radioisotope* or cause *atomic transmutation*.

### a. Formation of Artificial Radioisotopes

An artificial radioisotope is obtained when a neutron or a γ-ray bombards a stable isotope:

#### i. Neutron Bombardment

• When a neutron bombards the atom of the stable non-radioactive uranium-238, radioactive uranium-239 is produced:

${}^{238}_{92}U + {}^{1}_{0}n \rightarrow {}^{239}_{92}U$

(non-radioactive) (radioactive)

• When the stable cobalt-59 captures a neutron bullet, radioactive cobalt-60 is obtained:

${}^{59}_{27}Co + {}^{1}_{0}n \rightarrow {}^{60}_{27}Co$

(non-radioactive) (radioactive)

#### ii. γ-ray Bombardment

• The stable beryllium-9 undergoes γ-ray bombardment to produce radioactive beryllium-8 with ejection of a neutron:

${}^{9}_{4}Be + \gamma \rightarrow {}^{8}_{4}Be + {}^{1}_{0}n$

### b. Atomic Transmutations

*Atomic transmutation* occurs when charged particles or fast-moving neutrons are used to bombard stable nuclei:

#### i. α-particle Bombardment

• When an α-particle bombards the atom of a stable non-radioactive nitrogen-14, radioactive oxygen-17 and a proton are produced:

${}^{14}_{7}N + {}^{4}_{2}He \rightarrow {}^{17}_{8}O + {}^{1}_{1}H + heat$

#### ii. Proton Bombardment

• ${}^{18}_{8}O + {}^{1}_{1}H \rightarrow {}^{17}_{9}F + \gamma\text{-rays} + heat$

• ${}^{7}_{3}Li + {}^{1}_{1}H \rightarrow 2{}^{4}_{2}\alpha + heat$

#### iii. Fast-moving Neutron Bombardment

• ${}^{14}_{7}N + {}^{1}_{0}n \rightarrow {}^{12}_{6}C + {}^{1}_{1}H$

**Solved Problems**

**7.** Explain clearly, the difference between the following reactions involving electron loss from lead:

${}^{211}Pb \rightarrow {}^{211}Bi + {}^{0}_{-1}e$

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

• ${}^{211}Pb \rightarrow {}^{211}Bi + {}^{0}_{-1}e$ *is a nuclear reaction in which an atom of Pb (lead) is converted to that of (Bi) bismuth by the emission of a beta particle.*

• $Pb \rightarrow Pb^{2+} + 2e^{-}$ *is a chemical reaction in which an atom of Pb loses two electrons to form lead (II) ion.*

**8.** What does the following equation illustrate?

${}^{238}_{92}U \rightarrow {}^{234}_{90}Th + {}^{4}_{2}He$

A. Artificial radioactivity. B. Nuclear fission.
C. Nuclear fusion. D. Radio-decomposition.
E. Spontaneous disintegration. [NECO]

**Solution:** *E*

**9.** If an element in group V of the periodic table undergoes an alpha emission, state with reasons to which group the product will belong.

*The product will belong to group III.*

*Since an alpha particle is emitted, the atomic number of the new element will decrease by two; hence, it will belong to group V less two, which is group III.*

**10** ${}^{23}_{11}Na + {}^{1}_{0}n \rightarrow {}^{24}_{11}Na$

The reaction above is an example of

A. nuclear fission B. nuclear fusion
C. artificial transmutation D. beta decay

**Solution:** *C* [JAMB]

## Revision Exercises

**22** Distinguish between an *alpha particle* and an *alpha decay*.

**23** The emission of a beta particle from the nucleus of ${}^{234}_{90}Th$ will produce

A. ${}^{234}_{91}Pa$ B. ${}^{238}_{88}Ra$ C. ${}^{230}_{90}Th$
D. ${}^{234}_{92}U$ E. ${}^{238}_{92}U$ [NECO]

**24** a Write a balanced equation for the bombardment of ${}^{7}_{3}Li$ with protons to produce ${}^{8}_{4}Be$ and γ-rays.

b Write an equation to represent β-decay of ${}^{24}_{11}Na$ to give Mg. [WAEC]

**25** The atomic number of an element increased by one after a radioactive decay. The element must have decayed by emitting

A. a proton B. an alpha particle.
C. a neutron. D. a beta particle. [JAMB]

26 Which of the following are **TRUE** of α-decay?
I. Mass number decreases by four.
II. Atomic number decreases by four.
III. Mass number does not change.
A. I and II only. B. II and III only.
C. I and III only. D. I, II and III. [JAMB]

27 If an element in group IV of the periodic table loses an alpha particle, to which group would the product belong ?

28 Alpha particle emission by $^{235}_{92}U$ produces element A. Beta particle emission by the particle A produces another element B. Element B also undergoes alpha particle emission to produce $^{227}_{89}Ac$. Write balanced equations to represent the above statement. [WAEC]

29 Which of the following has neither mass nor charge?
A. Alpha particle B. Deuterium
C. Gamma ray D. Neutron [WAEC]

30 a. Define the term *artificial transmutation*.
b. Give one example of an *artificial transmutation*.

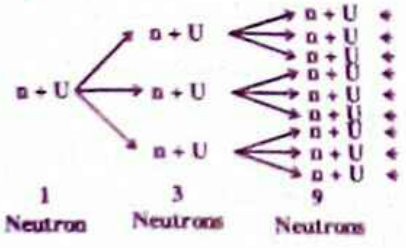
## 3. Nuclear Fission – A Chain Reaction

In a *nuclear fission*, the nucleus of an atom of a heavy radioisotope breaks into two nearly equal nuclei, with a release of a large quantity of heat and radiation, which can cause a temperature rise of over one million degrees centigrade. It is usually a chain reaction, e.g.

• When radioactive uranium-235 captures a fast-moving neutron, nuclear fission occurs; it leads to the formation of nuclei of strontium and xenon, three new neutrons and a large quantity of heat.

$$^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{90}_{38}Sr + {}^{144}_{54}Xe + 3{}^{1}_{0}n + \text{heat}$$

The uniqueness of this nuclear reaction is that *three new neutrons* are ejected during the process. Each of them goes to initiate the fission of another nucleus of uranium atom; leading to a *chain nuclear reaction*:




**Uses of Nuclear fission:** The process is used to generate electricity, and to produce new elements, radioisotopes, and nuclear bombs.

## 4. Nuclear Fusion

*Nuclear fusion is the opposite of nuclear fission.* In a *nuclear fusion, two or more light nuclei combine to produce a single heavier nucleus.*

Such a reaction occurs at extremely high temperatures, i.e., *nuclear fusion requires extremely high activation energy*. The reaction can only take place in the sun, or where there is *nuclear fission*, e.g.

• When the nuclei of hydrogen atoms undergo atomic fusion in the sun, α-particles together with positrons are emitted; the heat liberated is responsible for the sunlight energy we are enjoying on earth!

$$4{}^{1}_{1}H \rightarrow {}^{4}_{2}\alpha + 2{}^{0}_{1}e + \text{heat}$$

• In the man-made (artificial) hydrogen bomb, the nuclei of deuterium and tritium (both are isotopes of hydrogen) undergo nuclear fusion to produce α-particles, neutrons and a large quantity of heat:

$${}^{2}_{1}D + {}^{3}_{1}T \rightarrow {}^{4}_{2}\alpha + {}^{1}_{0}n + \text{heat}$$

Usually, the *heat energy released during nuclear fusion is greater than that of nuclear fission.*

**Uses of Nuclear fusion:** The process is used to produce new elements, radioisotopes, and atomic bombs.

### Solved Problem

**11** State one difference between atomic fission and atomic fusion.

**Solution** (*Any one of the following*)

| Nuclear Fission | Nuclear fusion |
|---|---|
| • A big nucleus splits into two nearly equal nuclei. | Smaller nuclei merge to form larger nuclei. |
| • Two or three neutrons are ejected. | No neutron is ejected. |
| • Heat liberated is less. | Much heat is liberated. |

### Revision Exercises

31 Define each of the following terms:
a. Nuclear fission; b. Nuclear fusion.

32 Balance the following equation and classify it as either nuclear fission or nuclear fusion:

$$^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{141}_{56}Ba + Kr + 3{}^{1}_{0}n$$

33 Find the value of m and n in the following nuclear reaction:

$${}^{1}_{1}H + {}^{m}_{n}T \rightarrow 2{}^{2}_{1}D$$

34 Which of the following statements are correct about nuclear fission?
I. The number of neutrons released exceeds the number that caused the fission.
II. New nuclei are formed.
III. Energy is produced.
IV. Smaller nuclei merge to form larger nuclei.
A. II, III and IV only. B. I, II and IV only.
C. I, II and III only. D. I, III and IV only.

## 27.6 Heat Liberated During Nuclear Reactions

In a *chemical reaction*, there is *conservation of mass*; there is *no conservation of mass* in a *nuclear reaction*. *Reason*. *Nuclear processes* are usually accompanied by *mass loss*, i.e. *total mass of product is less than total mass of reactants*. The large quantity of heat liberated is as a result of the conversion of the mass loss to heat e.g.

In the *nuclear fission* of uranium-235, there is a *mass loss* of 0.20 *g per mole*. The quantity of heat associated with the mass loss can be calculated from the Einstein equation: $E = mc^2$; where

E = energy in Joules,

m = mass loss in kilogram = $0.20 \times 10^{-3}$ kg,

c = velocity of light = $3.0 \times 10^8$ m $s^{-1}$.

Substituting: $E = 0.20 \times 10^{-3} \times (3.0 \times 10^8)^2$ kJ

$= 1.80 \times 10^{10}$ kJ.

### Revision Exercises

35 One of the features of the fission process is that
- A. its products are not radioactive.
- B. it leads to a chain reaction.
- C. neutrons are not released.
- D. the sum of the masses of the reactants equals the sum of the masses of the products. [JAMB]

36 In a nuclear fusion process, four protons each of mass $M_p$ were fused to produce a nucleus X of mass $M_X$. Which of the following equations is CORRECT? A. $4M_p > M_X$. B. $4M_p = M_X$ C. $4M_p < M_X$ D. $M_p = M_X$ [JAMB]

37 In a nuclear fusion experiment, the loss in mass amounts to $1.0 \times 10^{-6}$ kg. The amount of energy obtained from the fusion is
- A. $3.0 \times 10^{-4}$ J
- B. $3.0 \times 10^{-1}$ J
- C. $9.0 \times 10^{4}$ J
- D. $9.0 \times 10^{10}$ J [JAMB]

## 27.7 Half-life in Nuclear Processes

### What is Half-life?

The *half-life*, $t_{½}$ of a radioactive isotope is the time taken for a half of the original quantity to change or decay. The quantity can be in terms of *number of atoms*, its *mass*, *in grams*, etc.

Every radioactive element has its own half-life; it is constant for every decay process, and unaffected by temperature or pressure change. For instance:

The half-life of thorium-234 is 24 days. Suppose the *original mass* of pure thorium-234 $m$ = 100 g.

- In 24 days, 100 *g* of thorium decay to ½ of 100 *g*, i.e. mass left, $x_1$ = 50 g ... 1st half-life.
- In another 24 days, the mass left, $x_1$ = 50 g will decay to ½ of 50 g, or ½ of ½ of 100 g. i.e. mass left, $x_2$ = 25 g ... 2nd half-life
- In another 24 days, the mass left, $x_2$ = 25 g will decay to ½ of 25 g, or ½ of ½ of ½ of 100 g. i.e. mass left, $x_3$ = 12.5 g ... 3rd half-life.

It will be noticed that:
- In the 1st half-life, mass left, $x_1$ = ½ of $m$.
- In the 2nd half-life, mass left, $x_2 = (½)^2$ of $m$ or $(m/2^2)$.
- In the 3rd half-life, mass left, $x_3 = (½)^3$ of $m$ or $(m/2^3)$.
- In the nth half-life, mass left, $x_n = (½)^n$ of $m$ or $(m/2^n)$.

The general expression for a decay process is:

$$x = m/2^n$$

(where $m$ = initial quantity; $x$ = quantity left after a given *number of half-lives*, $n$).

$x/m$ = fraction that is left.

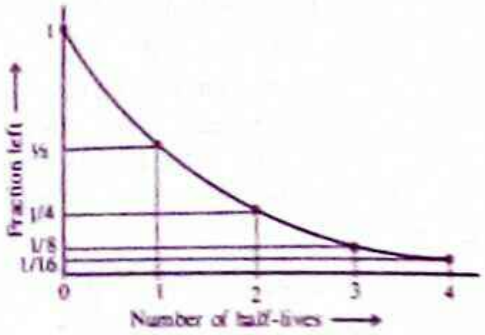
$(m - x)$ = quantity that has decayed.

$(m - x)/m$ = fraction that has decayed.

Number of half-lives, $n$ =

(Period of decay)/(Half-life)

Fig 27.3 shows the fractions of 1.0 *g* of radioactive thorium remaining after 1, 2, 3 and 4 half-lives. It is a first-order reaction, i.e., the rate of decay is directly proportional to the quantity of the reactant at a given time.




### Decay Constant

Radioactive isotopes decay according to first-order kinetics (see section 24.6). It can be shown that the quantity, 0.6931/*k*, is known as *half-life*; where *k* is the *decay (rate) constant*, i.e. $t_{½} = 0.6391/k$.

The half-life period of a radioactive element is a measure of the degree of radioactivity, and the relative stability of its atoms. The longer the half-life, the slower the rate of decay and the more stable the atoms of the element. Conversely, the shorter the half-life, the faster the rate of decay and the less stable the atoms of the element.

The decay process of a radioactive element is unaffected by physical and chemical changes. Table 27.2 gives the half-lives of some radioactive elements.

*Table 27.2 Half-lives of some radioactive elements*

| Element | Half-life, $t_{\frac{1}{2}}$ |
|---|---|
| Uranium-238 | $4.5 \times 10^9$ years |
| Radium-226 | 1,600 years |
| Thorium-234 | 24 days |
| Iodine-131 | 8 days |
| Polonium-214 | $1.50 \times 10^{-4}$ s |

**Solved Problems**

**12** The half-life of an element Z is 10 days. If there are 10 g of Z initially, what will be its mass after 40 days? [NECO]

A 40 g B 5 g C 2.5 g D 1.25 g E 0.63 g

**Solution:** *E*

*To find the mass left after 40 days of decay*

Given: Initial mass, $m = 10$ g;

No. of half-lives, $n = (40 \text{ days})/(10 \text{ days}) = 4$.

Required: To find the mass left, $x$.

Using the relationship, $x = m/2^n$ and substituting:

$x = 10/2^4 = 10/16 = 0.625$ g.

**13** A radioactive element has a half-life of 4 days. The fraction that has decayed in 16 days is

A. 15/16 B. 1/16 C. ¾ D. ¼ [JAMB]

**Solution:** *A*

*To find the fraction that has decayed, $(m - x)/m$:*

Given: No. of half-lives = (16 days)/(4 days) = 4.

Mass left, $x = m/2^n = m/2^4 = m/16$.

Hence, fraction left = $(m/16)/m = 1/16$

∴ fraction that has decayed = $(1 - 1/16) = 15/16$

Or *fraction that has decayed, $(m - x)/m$*

Substituting $x = m/16$;

$(m - x)/m = (15m/16)/m = 15/16$.

**14** Two radioactive elements M and N with half-lives of 50 years and 120 years respectively.

a. Which of the elements is more stable? *N.*

b. Give reason for your answer.

*N has a longer half-life than M.*

**15** Two equally toxic substances X and Y, which decay to non-toxic products were absorbed through the skin. If their half-lives are 8 minutes and 2 months respectively, which of them constitutes the greater health hazard? Explain your answer. [WAEC]

*X constitutes the greater health hazard.*

*The half-life of X (8 minutes) is shorter than that of Y (2 months). X decays faster and causes more damage within a shorter period than Y, which decays slowly and causes the same damage within a longer period.*

**Revision Exercises**

**38** What is meant by *half-life of a nuclide*?

**39** The half-life of $^{56}_{25}Mn$ is $9.3 \times 10^3$ seconds. What does the statement mean? [WAEC]

**40** Two radioactive elements Q and S have half-lives of 10 hours and 20 hours respectively. Therefore,

A. S decays faster than Q.

B. Q is twice as stable as S.

C. Q emits fewer particles than S.

D. S is more stable than Q. [WAEC]

**41** If 4 g of a radioactive material of half-life 10 days is spilled on a laboratory floor, how long would it take to disintegrate 3.5 g of the material?

A. 1¼ days B. 8¾ days

C. 30 days D. 80 days [JAMB]

**42** A radioactive substance has a half-life of 80 days. If the initial number of atoms in the sample is $6.00 \times 10^{10}$, how many atoms would remain at the end of 320 days?

A. $3.75 \times 10^9$ B. $7.50 \times 10^9$

C. $3.00 \times 10^{10}$ D. $5.63 \times 10^{10}$ [JAMB]

**43** If $1.20 \times 10^5$ atoms of a radioactive nuclide decade such that only $1.50 \times 10^4$ remained after 81 days. The half-life of the radioactive nuclide is

A. 21 days B. 27 days C. 54 days D. 81 days

**44** If the decay constant of a radioactive substance is 0.231 $s^{-1}$, the half-life is

A. 3.00 s B. 0.12 s

C. 0.33 s D. 1.50 s [JAMB]

## 27.8 Nuclear Reactor

A *nuclear reactor* is a device in which the large quantity of heat produced during *fission* reaction of a radioactive element is controlled to generate electricity.

In a *nuclear reactor*, an *atomic pile* made of *rods of uranium-235* serves as the *nuclear fuel* and the *source of energy*. The *rods of graphite*, which surrounds the rods of uranium acts as moderators: to slow down the fast-moving neutrons – without absorbing them – and make them available for the chain reactions.

Moveable rods of boron or cadmium are inserted between the rods of uranium-235, in order to absorb the neutrons and control the chain reactions, and hence, obtain a steady and continuous production of heat.

The nuclear reactor is made of a *thick concrete structure*, which acts as a shield, and provides protection against radioactive radiation fallouts.

The large quantity of heat produced in the reactor is used in heating water in the boiler, and the steam generated is used in driving turbines, which generate electricity.

In order to sustain a chain reaction, the quantity of uranium-235 must be large enough. The *quantity of a radioactive substance required to sustain a chain reaction* is called the *critical size*. Above the critical size, explosion is possible.

**Solved Problems**

**16** What is the function of each of the following in a nuclear reactor (atomic pile)?
Uranium; Graphite rods; Concrete structure.

*In a nuclear reactor, the function of*
- *Uranium: To serve as fuel and provide the required energy.*
- *Graphite rods: To serve as moderators – to slow down the neutrons produced.*
- *Concrete structure: To protect the reactor and provide a shield against radioactive radiations.*

**17** State the function of carbon of carbon(IV) oxide in a nuclear reactor. [WAEC]

*Solid carbon(IV) oxide, dry ice, is used as a coolant.*

**Revision Exercises**

**45** What is a *nuclear reactor*?

**46** Name the substance used as the fuel in a *reactor*?

**47** A radioactive solid is best stored
A. under paraffin oil. B. under ultraviolet light.
C. in a cool, dark cupboard.
D. in box lined with lead.

**48** Explain the term *critical size* in a nuclear reactor.

## 27.9 Uses of Radioactivity and Nuclear Reactions

### 1. In Nuclear Electric Power Plants

The large quantity of heat generated in a nuclear reaction is controlled, and used to produce steam that drives engines, in order to generate electricity.

### 2. In Atomic (Hydrogen) Bomb

Radioactive elements are made to undergo chains of nuclear reactions, and the huge quantity of heat is released uncontrolled. This is an example of a destructive use of nuclear energy.

### 3. In Radioactive Dating

Geologists make use of the half-lives of radioactive elements in dating geological remains, such as ancient tools. For instance: The quantities of uranium-238 in rocks are used to determine their ages. Similarly, in archeological dating, the half-life of carbon-14 enables the age of the remains of an organism, such as a plant, to be deduced by comparing carbon-14 content of a dead plant with that of a similar living plant.

### 4. In Gauging Thickness

The thickness of a material, such as a sheet of paper or a metal, can be estimated from the quantity of the beta or gamma radiation that penetrates the material.

### 5. In Studying Reaction Mechanism

- Radioactive elements, such as carbon-14 are used in following the paths of chemical reactions, and to determine the equilibrium positions in reversible reactions.
- Isotopic iodine can be used to study the rate at which the thyroid gland absorbs iodine.

### 6. As Tracers

Radioisotopes are used as tracers:
- In detecting leakages in pipelines.
- In chemical reactions.

### 7. In Medicine: Radiography/Radiotherapy

- Radioactive cobalt-60 emits penetrating gamma rays that are used in the treatment of cancer.
- Radioactive radon is used as a tracer in medical research – to detect body-defects.
- Radioisotopes emit gamma rays that kill bacteria; hence, used in sterilizing hospital instruments, and in pasteurization of foods.

### 8. In the Production of New Elements

Technicum (atomic number 43) and those elements with atomic numbers greater than 92 do not occur naturally; they are produced artificially by radioactivity.

### 9. In Agriculture

- Fertilizers containing radioactive phosphorus-32 are used in studying the uptake of tetraoxophosphate(V), $PO_4^{3-}$ from the soil by plants.
- Some radioisotopes are used in insecticides – for pest control.

**Revision Exercises**

**49** List **three** applications of radioactivity in different fields. [WAEC]

**50** The isotope used in dating technique is
A. $^{3}_{1}H$ B. $^{18}_{8}O$ C. $^{14}_{6}C$ D. $^{37}_{17}Cl$ [WAEC]

**51** I. Treatment of cancer
II. Detection of leakages in water mains
III. Detection of the ages of ancient tools.

IV. Preparation of drugs

Which combination of the above refers to the uses of radioactive isotopes?

A. I and II B. I, II and III C. I, II, III and IV D. II and III [JAMB]

Which of the following features of a human skeleton can be determined by carbon-dating?

A. Height. B. Mass. C. Age. D. Race. [WAEC]

Radioisotopes are used for the following EXCEPT

A. development of photographic films.

B. generation of electric power.

C. radio carbon dating.

D. sterilization of food and medical instruments.

E. tracers in chemical reactions. [NECO]

## 44.10 Health hazards in Radioactivity

During nuclear processes, alpha, beta and gamma particles are emitted. The absorption of these particles has damaging effects on human body:

- The absorption of beta particles affects the production of red blood cells in the bone marrow.
- Excessive absorption of the various radiations aids the decomposition of internal tissues, causes burns and cancer, reduces the number of blood cells, destroys genes, and finally causes death.
- Solid radioactive waste should not be disposed by burying (or *composting*, i.e. *use as manure*); such waste may decay, and contaminate the soil or release harmful radiations.

Human body should not be exposed to radioactive radiations for a long time.

### Solved Problem

**19** Give **one** advantage and **one** disadvantage of nuclear power generation over the use of fossil fuel.

**Answer**

*Advantage*: A relatively small quantity of uranium is required for nuclear power generation for a very long period, while a relatively large quantity of fossil fuel will only last for a short period.

*Disadvantage*: Nuclear power generation produces toxic wastes, while fossil fuel produces non-toxic wastes.

### Revision Exercises

**54** Which of the following pollutants is associated with genetic mutation? [WAEC]

A. Carbon(II) oxide B. Radioactive fallout

C. Biodegradable waste. D. Sulphur(IV) oxide.

**55** Which of the following is true of radioactivity?

I. It involves the transformation of a nucleus into another nucleus.

II. It gives out radiations.

III. Energy is given out during the process.

IV. The rate of radioactive decay is not affected by temperature and pressure.

A. I and II only. B. I and III only.

C. I, II and III only. D. I, II, III and IV. [WAEC]

**56** Give one reason why solid radioactive waste is not disposed by composting. [WAEC]

### Answers to Revision Exercises

| | | | | | |
|---|---|---|---|---|---|
| 5. D | 9. B | 10. B | 11a. D; b. C | | |
| 14. C | 16. A | 19. $p = 3$; $q = 1$ | | 21. B | 23. D |
| 25. D | 26. A | 27. Group II | | 33. C | 34. C |
| 35. B | 36. A | 37. D | 40. D | 41. C | 42. A |
| 43. B | 44. A | 47. D | 50. C | 51. C | 52. C |
| 53. A | 54. B | 55. D | | | |

# 28

# •HYDROGEN • HYDRIDES•

## 28.1 Introduction

### Atomic Structure

*Hydrogen*, **H** is the first element in the periodic table. Its atom is the simplest; it has a nucleus with only one proton – no neutron. Hence, its atom has only one electron that moves around the nucleus in the first energy level (K shell). Its orbital configuration is $1s^1$.

Under normal conditions of temperature and pressure, hydrogen exists as a discrete gaseous diatomic molecule, $H_2$ in which the two atoms are linked by a single covalent bond.

### Isotopes of Hydrogen

Hydrogen has three isotopes:

1. Common hydrogen, called ***protium***, $^1_1H$;
2. Heavy hydrogen; ***deuterium*** $^2_1H$ *(or* $^2_1D$*)*;
3. ***Tritium***, $^3_1H$, (or $^3_1T$).

*Protium* and *deuterium* are similar in chemical behaviours; they form water $H_2O$ and *deuterium oxide (heavy water)*, $D_2O$ respectively. *Tritium* is an unstable isotope of hydrogen; it is *radioactive*.

### Occurrence

Hydrogen does not occur in a free state in the atmosphere (except as volcanic gases); it occurs in combination with other elements – as compounds, such as water, acids and in almost all organic compounds.

The sun is about 90% hydrogen by mass, and the light being emitted by the stars is pure hydrogen.

### Revision Exercises

1. State the type of chemical bond between hydrogen atoms in a molecule of hydrogen.
2. Hydrogen exists in three forms with relative atomic masses of 1, 2 and 3.
   a. What name is given to this phenomenon?
   b. Name and write the nuclear symbols of the three forms.
   c. Which form of hydrogen is radioactive?

## 28.2 Preparation of Hydrogen

The following types of chemical reactions are used in the preparation of hydrogen gas:

### 1. Action of dilute acids on reactive metals

Hydrogen gas is liberated when a *metal* above it in the *activity series* reacts with a strong acid.

Potassium, sodium and calcium react explosively with dilute acids; hence, these metals are not suitable for the laboratory preparation of hydrogen.

The gas is conveniently prepared by the action of bench dilute tetraoxosulphate(VI) acid (2.0 *moles per* $dm^3$) on zinc metal. *Heat is not required.*

**Procedure and Observations**

- Zinc granules (*10.0 g*) are placed in a conical flask; then, the pieces of apparatus are set up as shown in figure 28.1.

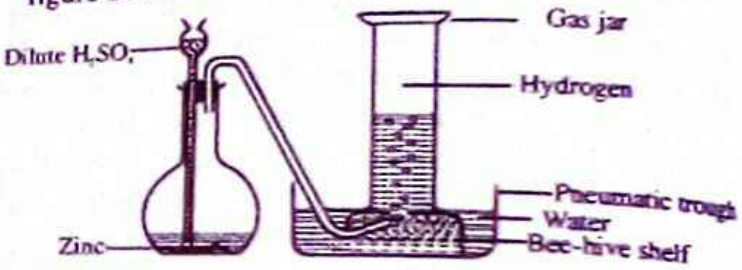



**Fig 28.1** *Laboratory preparation of hydrogen*

- The dilute $H_2SO_4$ is poured through the *thistle funnel* until the stem is just immersed in the acid.
- As the zinc metal dissolves in the acid, there is ***effervescence***; the gas evolved is colourless and odourless.
- The initial gas evolved should be allowed to escape with the air originally in the flask; then, the pure gas is collected over water.
- The resulting solution in the flask is colourless and warm (reaction is exothermic).

$$\underset{\text{(grey)}}{Zn_{(s)}} + \underset{\text{(colourless)}}{H_2SO_{4\,(aq)}} \rightarrow \underset{\text{(colourless)}}{ZnSO_{4\,(aq)}} + \underset{\text{(gas)}}{H_2\uparrow}$$

Whenever a gas is collected over water, it becomes *wet* by moisture (water vapour).

***To obtain dry hydrogen***

*Pure and dry hydrogen gas* is obtained by passing the gas through either a **U-tube** glass containing *fused* calcium chloride (as the *drying agent*), or

through a *Wolff (not wash) bottle* containing *concentrated* $H_2SO_4$ (as the *drying agent*) to absorb moisture. The gas is then collected by *upward delivery* (i.e. *downward displacement of air*) since it is *lighter than air*.

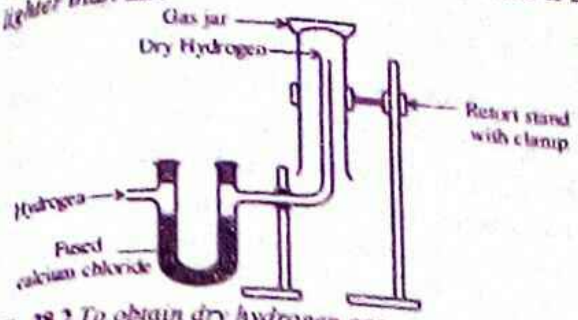



Fig 28.2 *To obtain dry hydrogen gas*

**Notes:**

a. Any metal above hydrogen in the *activity series* can be used. However, the reaction with potassium, sodium or calcium is highly explosive, while the reaction with iron or lead is very slow.

b. Both dilute hydrochloric acid (*2.0 moldm*$^{-3}$) can be used instead of dilute $H_2SO_4$. However, *dilute* or *concentrated* $HNO_3$ or *concentrated* $H_2SO_4$ is not suitable, because they are powerful oxidizing agents. The hydrogen gas produced will be oxidized to water.

c. When *dilute* $H_2SO_4$ is used, calcium metal is not suitable; because the insoluble $CaSO_4$ formed will coat the metal, and hence, stops the reaction.

$$Ca_{(s)} + H_2SO_{4\,(aq)} \not\longrightarrow \underset{\text{(white)}}{CaSO_{4\,(s)}} + H_{2\,(g)}$$

For the same reason, when calcium metal is used, *dilute* $H_2SO_4$ is not suitable; dilute HCl is used instead.

### 2. Action of cold water on a reactive metal

Potassium, sodium or calcium metal reacts with *cold* water to liberate hydrogen gas, and giving an alkaline solution. However, the reaction with potassium or sodium is very violent.

***Reaction with calcium metal***

- Place a small piece of calcium metal in a beaker of cold water; the metal sinks. A boiling tube full of water is then inverted over it.
- The metal dissolves with effervescence; the colourless and odourless gas evolved is hydrogen. It can be collected as shown in figure 28.3.
- As calcium dissolves, a white suspension of calcium hydroxide, which is slightly soluble in water is formed. Hence, if the water in the beaker is initially coloured with a few drops of methyl orange, the solution changes from *orange* to *yellow*. If phenolphthalein is used, the colour change is from *colourless* to *pink*. *Reason*: The resulting solution is alkaline.

$$Ca_{(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2\,(aq)} + H_{2\,(g)}$$

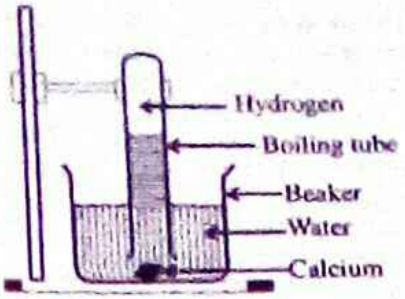



Fig 28.3 *Action of calcium on water*

### 3. Action of steam on red-hot iron

When excess of steam is passed over *red-hot* iron filings (or nails) placed in a combustion tube, the colourless and odourless gas evolved is hydrogen; it can be collected over water (see figure 28.4). The black residue left in the tube is iron(II, III) oxide, $Fe_3O_4$ (triiron tetroxide).

$$3Fe_{(s)} + 4H_2O_{\,(g)} \rightarrow Fe_3O_{4\,(s)} + 4H_{2\,(g)}$$

This method can be used to obtain a large quantity of hydrogen gas cheaply.

Metals, such as magnesium, aluminium and zinc, also react with steam to liberate hydrogen.

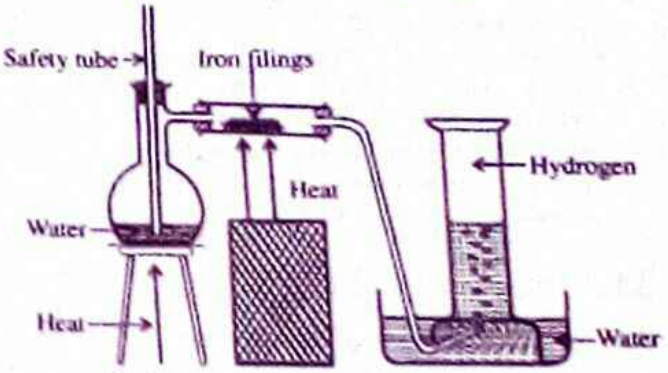



Fig 28.4 *Preparation of hydrogen from steam*

### 4. Action of alkali on some metals

Metals, such as zinc, aluminium, tin, lead and silicon – a semi-metal, react with a hot solution of NaOH or KOH to produce hydrogen gas and the corresponding salts:

- $Zn_{(s)} + 2NaOH_{(aq)} \rightarrow 2Na_2ZnO_{2\,(aq)} + 3H_{2\,(g)}$
- $2Al_{(s)} + 2KOH_{(aq)} + 2H_2O_{(l)} \rightarrow KAlO_{2(aq)} + 3H_{2(g)}$
- $Si_{(s)} + 2NaOH_{(aq)} + H_2O_{(l)} \rightarrow Na_2SiO_{3(aq)} + 2H_{2(g)}$

### 5. Action of water on metallic hydride

Sodium hydride, NaH or calcium hydride, $CaH_2$ reacts with water to produce hydrogen gas and an alkaline solution:

- $NaH(s) + H_2O(l) \rightarrow NaOH(aq) + H_2(g)$
- $CaH_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$

**Solved Problem 1**

State **four** observations in respect of the reaction between zinc granules and dilute $H_2SO_4$.

**Solution** *(Any four of the following)*

- *The metal, zinc, dissolves in the acid.*
- *There is effervescence or a gas is evolved.*
- *The gas is colourless and odourless.*
- *The resulting solution is colourless.*
- *The resulting solution is warm.*

**Revision Exercises**

3a. List **two** reactants in the laboratory preparation of hydrogen.

b. Name **two** drying agents that can be used to dry hydrogen gas.

4. Hydrogen is one of the products of the reaction between
   A. red hot iron filings and steam.
   B. copper and dilute hydrochloric acid.
   C. magnesium ribbon and cold water.
   D. trioxonitrate (V) acid and zinc. [WAEC]

5. Which of the following metals would react with both sodium hydroxide solution and dilute hydrochloric acid liberate hydrogen?
   A. Ca B. Cu C. Fe D. Zn [WAEC]

6. Which of the following metals will dissolve in aqueous sodium hydroxide ? [WAEC]
   A. Aluminium B. Copper C. Iron D. Silver

7. Write an equation to show how hydrogen can be obtained by the action of
   a. a dilute mineral acid on a metal;
   b. cold water on a metal;
   c. water on metallic carbide.

## 28.3 Properties of Hydrogen

### Physical Properties of Hydrogen

1. Pure hydrogen gas is colourless (invisible), and odourless.
2. It is insoluble in water.

When a gas jar of hydrogen is inverted over a trough or beaker of water, there will be no rise in water level in the jar.

3. It is less dense than air; it is the lightest gas.

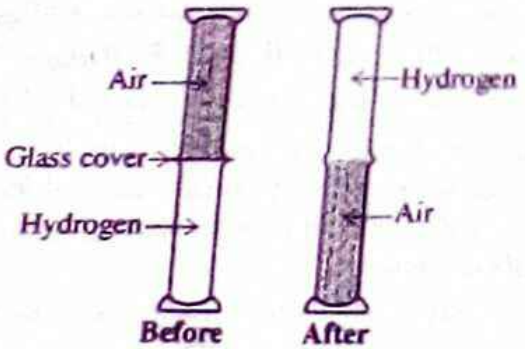



Fig 28.5 *Diffusion of hydrogen*

Invert a gas jar of air over a gar jar of hydrogen. After ten seconds, test each jar with a lighted splint.

*Observation: The gas in the upper jar explodes, showing the presence of hydrogen, while the gas in the lower jar burns normally, showing it contains air* (see fig 28.5).

*Reason:* Hydrogen gas is less dense than air; it is collected by upward delivery.

### Chemical Properties of Hydrogen

**1. Laboratory test for hydrogen**

Introduce a *lighted splint* into the gas jar.

*The gas explodes on mixing with air with the characteristic 'pop' sound.*

This is the *laboratory test* for hydrogen gas. The ***pop*** sound is due to the violent combination of hydrogen with oxygen in air, to produce steam.

**2. Action on litmus**

Introduce a damp (wet) blue or red litmus paper is into the gas jar

*There is no colour change; gas is neutral to litmus.*

**3. Combustion**

Dry hydrogen burns with a *pale blue flame* in air as a jet, when a lighted splint is applied

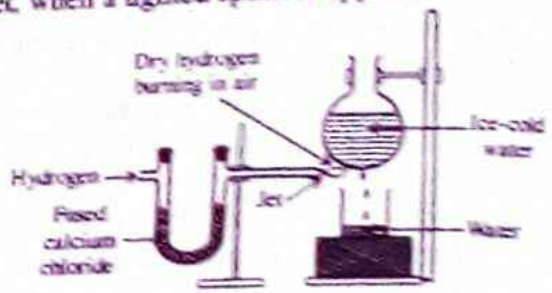



Fig 28.6 *Combustion of hydrogen*

When the flame is directed to a water-cooled surface, a colourless liquid is produced (fig 28.6). The liquid boils at 100 °C, and turns white anhydrous $CuSO_4$ powder to blue. The liquid is water.

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

**Note:** When a lighted splint is inserted into a gas jar of hydrogen (where there is no air) the light will be extinguished – showing that, although hydrogen burns in air, it will not allow a lighted splint to burn in it; i.e. it does not support combustion.

**4. Reducing Properties**

***a. Reaction with metal oxides:***

When hydrogen gas is passed over heated *oxide* of copper, zinc, iron, tin, lead or silver in a combustion tube, it *removes the oxygen*, leaving the metal as the residue. Hence, *hydrogen gas is a reducing agent.*

- $CuO(s)$ (black) $+ H_2(g) \rightarrow Cu(s)$ (brown) $+ H_2O(l)$
- $Fe_2O_3(s)$ (brown) $+ 3H_2(g) \rightarrow 2Fe(s)$ (grey) $+ 3H_2O(l)$

Hydrogen *cannot* reduce the oxides of sodium, $Na_2O$, potassium, $K_2O$ and calcium, $CaO$, because they are strongly ionic.

***b. Reaction with non-metals***

Hydrogen undergoes addition reaction with non-metals:

i. Hydrogen burns in a gas jar of chlorine, in the presence of sunlight as the catalyst, to produce hydrogen chloride gas.

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

It reacts similarly with bromine and iodine.

ii. When hydrogen is passed into a test tube of molten sulphur, a colourless gas with rotten-egg smell is evolved; the gas is hydrogen sulphide.

$$H_2(g) + S(s) \rightarrow H_2S(g)$$

iii. Hydrogen reacts with nitrogen at high pressure, at a moderate temperature, and in the presence of *finely divided* iron as a catalyst, to produce ammonia gas [Haber process].

$$3H_2(g) + N_2(g) \xrightarrow{Fe_{(s)}} 2NH_3(g)$$

In the above reactions, hydrogen is acting as a reducing agent; hence, behaving like a metal.

**5. Oxidizing Property**

Hydrogen reacts with highly reactive metals, such as sodium, lithium and calcium, to give the corresponding *hydrides*.

- $Na(s) + H_2(g) \rightarrow 2NaH(s)$
- $Ca(s) + H_2(g) \rightarrow CaH_2(s)$

Hydrogen is reduced; it is an oxidizing agent.

**6. Reactions with Hydrocarbons**

Hydrogen gas undergoes addition reactions with unsaturated hydrocarbons: alkenes and alkynes, to give the corresponding saturated alkanes, e.g

- $H_2(g) + C_2H_4(g) \rightarrow C_2H_6(g)$
  (ethene) (ethane)

**7. Reaction with Carbon(II) oxide**

Hydrogen reacts with carbon(II) oxide at 300 °C and high pressure, to give methanol, an alcohol.

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(l) \text{ (methanol)}$$

**Solved Problem**

2. When dry hydrogen was passed over lead(II) oxide, a greyish solid **J** was obtained.

a. Identify **J**. *J is lead metal.*

b. What type of reaction was involved in the formation of **J** from lead(II) oxide?

*It is a redox or displacement reaction.*

**Revision Exercises**

8 State **three** physical properties of hydrogen.

9 Write an equation to show the

a. reducing property of hydrogen;

b. oxidizing property of hydrogen.

10 State the observation and the product formed when hydrogen is passed into molten sulphur.

11 Which of the following oxides would be reduced when heated in a stream of hydrogen?

A. $K_2O$ B. $CaO$ C. $Na_2O$ D. $CuO$

## 28.4 Industrial Production

Hydrogen gas is produced on a large scale, for industrial use, by several methods:

**1. From Hydrocarbon – *Natural gas***

Methane, $CH_4$ is the main constituent of *natural gas*. It is passed with steam over nickel as catalyst at 800 °C and 30 atmospheres.

$$CH_4(g) + H_2O(g) \xrightarrow[\text{[800 °C; 30 atm]}]{Ni(s)} CO(g) + 3H_2(g)$$

More steam is passed, to convert carbon(II) oxide, CO to carbon(IV) oxide, $CO_2$.

$$CO(g) + 3H_2(g) + H_2O(g) \rightarrow CO_2(g) + 4H_2(g)$$

Carbon(IV) oxide is removed by passing the mixture through $KOH_{(aq)}$, leaving hydrogen gas.

**2. From *Water gas* [Bosch process]**

•*Water gas* is produced by passing *steam* over *white-hot* coke at about 1000 °C, to give a *mixture of carbon(II) oxide and hydrogen*, known as *water gas*.

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$$
[*Water gas*]

• More *steam* is then passed over the mixture, to obtain carbon(IV) oxide and more hydrogen.

$$CO(g) + H_2(g) + H_2O(g) \rightarrow CO_2(g) + 2H_2(g)$$
[*Water gas*]

• The carbon(IV) oxide is then removed by dissolving the mixture in water under pressure of 30 atmospheres, leaving only the hydrogen gas.

**3. By Electrolysis**

Hydrogen gas is obtained as a by-product at the cathode during the electrolysis of $NaCl_{(aq)}$, $NaOH_{(aq)}$, or dilute $H_2SO_{4(aq)}$ – called *electrolysis of acidulated water*. The processes are discussed in Section 22.4.

**4. From Cracking of Petroleum Products**

Hydrogen gas is obtained as a by-product in the *catalytic cracking of petroleum products* (see Section 39.5)

**Revision Exercises**

12 State **two** industrial sources of hydrogen. [WAEC]

13 What name is given to the process for the industrial production of hydrogen from water gas?

14 Using chemical equations only, state how hydrogen can be prepared through the Bosch process. [NECO]

## 28.5 Uses of Hydrogen

1. In filling weather balloons, because of its lightness (or very low density).
2. In the production of ammonia by Haber process.
3. In *oxy-hydrogen flame* – used in cutting preheated metals, because the mixture has a high heating value; it can produce a temperature of about 2500 °C. The reaction is highly exothermic.
4. In converting coal to crude oil.
5. In hardening vegetable oil to obtain *margarine*.
6. In the manufacture of plastics.
7. As a reducing agent – in the production of metals, such as copper and lead from their oxides.
8. In the manufacture of methanol.
9. In the synthesis of hydrochloric acid.
10. In the production of *water gas* and *coal gas* – used as industrial fuels.

**Solved Problem**

3. Explain why helium is preferred to hydrogen in filling balloons.

*Hydrogen is inflammable, i.e. it burns in the presence of air, while helium will not.*

**Revision Exercises**

15 State **five** uses of hydrogen.

16 Which property of hydrogen makes it suitable for
a. filling balloons; b. welding metals ?

## 28.6 Hydrides

Hydrogen combines with other elements to form binary ionic and covalent hydrides.

**1. Hydrides of Elements in Period 2**

The elements in Period 2 of the Periodic Table form a series of hydrides: LiH, $BeH_2$, $BH_3$, $CH_4$, $NH_3$, $H_2O$ and HF.

a. In LiH and $BeH_2$, hydrogen is more electronegative; the bonds have ionic character, but are covalent solids.

b. In $BH_3$, boron and hydrogen have similar electronegativity; the molecule is purely covalent.

c. In $CH_4$, carbon is more electronegative, but the bonds have no partial charges, the molecule is covalent and gaseous.

d. In $NH_3$, $H_2O$ and HF, the bonds are partially ionic with hydrogen atoms partially positive.

$NH_3$ is an alkaline gas; $H_2O$ is a neutral liquid, while HF is an acidic liquid. There exist hydrogen bonds between their molecules.

**2. Hydrides of Elements in Period 3**

Elements in Period 3 form a series of hydrides with the following formulae: NaH, $MgH_2$, $AlH_3$, $SiH_4$, $PH_3$, $H_2S$ and HCl.

a. In NaH(s), the bond is purely ionic with the formation of $Na^+H^-$ in the ionic solid.

b. In $MgH_2(s)$, the bonds are partially ionic, but it is a covalent solid, while $AlH_3$ is an unstable solid.

NaH, $MgH_2$ and $AlH_3$ react with water to liberate hydrogen gas and the corresponding hydroxides:

- $NaH(s) + H_2O(l) \longrightarrow NaOH(aq) + H_2(g)$
- $AlH_3(s) + 2H_2O(l) \longrightarrow Al(OH)_3(s) + 3H_2(g)$

c. $SiH_4(s)$ is covalent; it does not react with water.

d. In $PH_3(g)$, hydrogen and phosphorus have the same electronegativity; the molecule is covalent. It reacts with water to form a *weakly acidic solution*.

e. In $H_2S$ and HCl the covalent bonds are polar, with the hydrogen atoms partially positive. $H_2S$ dissolves in water to produce a weakly acidic solution, while HCl dissolves to form a strongly acidic solution.

Generally, on moving from the left to the right along a period in the Periodic Table, the hydrides of the elements change from ionic to covalent compounds. The variation is due to increase in electronegativity along the period.

**Revision Exercises**

17 Mention **two** binary compounds of hydrogen that are
a. gases at room temperature;
b. covalent solids; c. ionic solids.

18 Which physical property is common to $NH_3$, $H_2O$ and HF?

19 Name **one** binary compound of hydrogen in which the oxidation state of hydrogen atom is;
a. −1; b. +1.

**Answers to Revision Exercises**

4. A 5. D 6. A 11. D

# 29

# •OXYGEN • OXIDES • HYDROXIDES•

## 29.1 Introduction

### Atomic Structure and Bonding

Oxygen is the first element in group VI of the Periodic Table. Its atomic number is 8, and has an electron configuration of $1s^2 2s^2 2p^4$.

At room temperature and atmospheric pressure, oxygen exists as a *discrete gaseous diatomic molecule*, $O_2$; there is a double covalent bond between the two atoms.

### Occurrence

Oxygen is the most abundant element in the earth's crust; constituting about 50%. It exists naturally as gaseous diatomic molecules, and constitutes 21% by volume of air in the atmosphere.

It is also present in combination with other elements as in mineral ores, such as clay, limestone, and sand. It is about 90% by mass of water.

### Revision Exercises

1. State the type of bonding between the oxygen atoms in a molecule of oxygen.
2. Give the electron-dot formula for oxygen gas.
3. Which of the following does not contain element oxygen? Marble; rock salt; sucrose; sand.

## 29.2 Methods of Preparation

There are two common laboratory methods for the preparation of oxygen:

### 1. From potassium trioxochlorate(V)

***Experimental procedure***

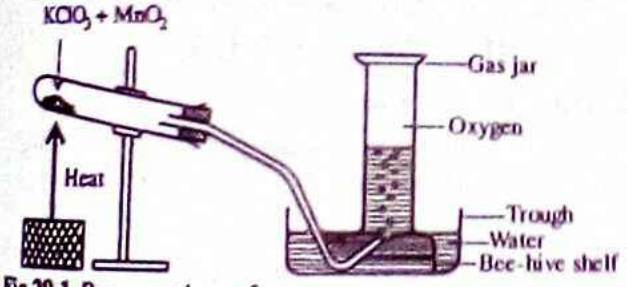



**Fig 29.1** *Preparation of oxygen*

**a.** A mixture of potassium trioxochlorate(V) (20 *g*) and black manganese(IV) oxide powder (5.0 g) is crushed, and placed in a boiling tube. The pieces of apparatus are then set-up as shown in figure 29.1.

**b.** Heat the mixture gently; a colourless and odourless gas is given off, which is collected over water.

$$2KClO_3\,(s) \xrightarrow[\text{heat}]{MnO_2\,(s)} KCl\,(s) + 3O_2\uparrow$$

***To show that manganese(IV) oxide is a catalyst***

**a.** At the end of the above experiment, weigh the $MnO_2$. Its mass will be found to be *the same as the quantity used initially, i.e. 5.0 g.*

**b.** Repeat the above experiment by heating $KClO_3$ (20 g) alone. It will be observed that *no gas will be given off until the temperature is about 400 °C.*

**c.** This observation shows that $MnO_2$ is a catalyst; it lowers the temperature at which oxygen is given off, and is not used-up in the reaction.

### 2. From hydrogen peroxide

**a.** Manganese(IV) oxide (5.0 g) is placed in a conical flask; then, the pieces of apparatus are set up as shown in figure 29.2. Heat is **not** required.

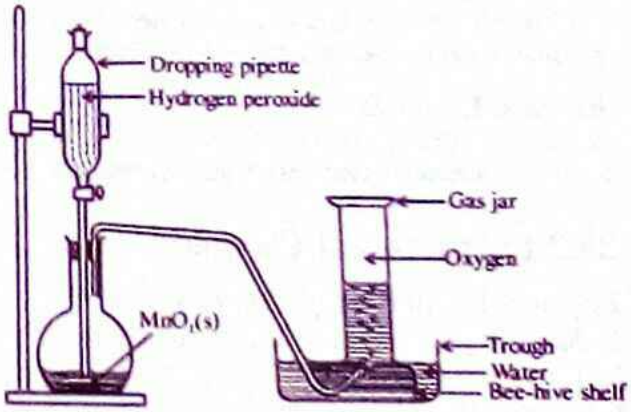



**Fig 29.2** *Preparation of oxygen from hydrogen peroxide*

**b.** Hydrogen peroxide (20% by volume) is added, drop-wise, through a dropping pipette, into the conical flask. There is immediate *effervescence*; the colourless and odourless gas evolved is collected over water.

$$2H_2O_2\,(l) \xrightarrow{MnO_2\,(s)} 2H_2O(l) + O_2\uparrow$$

***To obtain dry oxygen gas***

Dry oxygen gas is obtained by passing the gas through a *Wolff's (not wash) bottle* of concentrated $H_2SO_4$; the gas is then collected by *downward delivery* (or *upward displacement of air*); since pure oxygen is slightly denser than air (see figure 29.3).

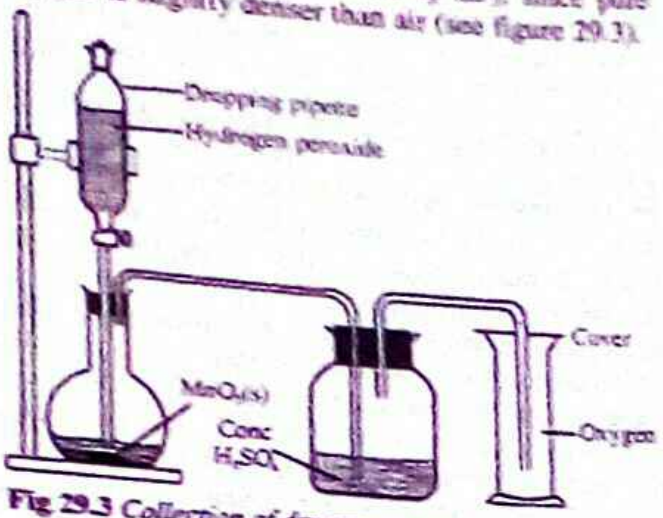



**Fig 29.3** *Collection of dry oxygen gas*

**Solved Problem**

1. Oxygen is evolved more rapidly when $MnO_2$ is heated with $KClO_3$. The test alone does not prove that the oxide is a catalyst. Why? [WAEC]

*At the end of the reaction, there is no change in the physical state, and the quantity of $MnO_2$ used.*

**Revision Exercises**

4. Mention a drying agent for oxygen.
5. Name a substance that can absorb oxygen.

## 29.3 Properties of Oxygen

### Physical Properties of Oxygen

1. Pure oxygen is colourless and odourless.
2. It is slightly denser than air.
3. It is slightly soluble in water.

### Chemical Properties

**1. Laboratory test:**

Insert a *glowing* splint into a gas jar of oxygen.

*It is be rekindled, i.e. brought black to life.*

**2. Action on litmus**

It has no effect on blue or red litmus paper, i.e. it is neutral to litmus.

**3. Combustion**

Oxygen supports combustion. Most elements burn in oxygen to produce the corresponding oxides.

**a. *Reaction with metals*:**

Metals, such as sodium, potassium, calcium, magnesium, aluminium and zinc burn brightly in oxygen, while iron, tin, lead and copper react slowly when heated. Metals, such as silver, gold and platinum do not react with oxygen.

Oxides of metals are generally basic.

**i. With sodium:**

Put a small piece of sodium metal in a deflagrating spoon; then, insert into a gas jar of oxygen.

*It burns brightly with a yellow flame, to produce white powdered sodium oxide.*

$$2Na_{(s)} + O_{2\,(g)} \rightarrow Na_2O_{(s)}$$




**ii. With magnesium:**

Insert magnesium ribbon held with a crucible tong into a gas jar of oxygen; *it burns rapidly with a white flash, to produce a white solid, magnesium oxide.*

$$2Mg_{(s)} + O_{2\,(g)} \rightarrow 2MgO_{(s)}$$

**iii. With iron:**

When red-hot iron wire is held in a gas jar of oxygen, *it burns slowly, to produce a black oxide, iron(II,III) oxide, $Fe_3O_4$.*

$$3Fe_{(s)} + 2O_{2\,(g)} \rightarrow Fe_3O_{4\,(s)}$$

**b. *Reaction with non-metals*:**

Non-metals, such as carbon, sulphur and phosphorus burn in oxygen to form acidic oxides: $CO_{2\,(g)}$, $SO_{2\,(g)}$ and $P_4O_{10\,(s)}$ respectively.

**4. Formation of Water**

Hydrogen burns violently in oxygen with a pale-blue flame, to produce water (see Section 28.).

$$2H_{2\,(g)} + O_{2\,(g)} \rightarrow 2H_2O_{(l)}$$

**5. Formation of Ozone:**

When a silent electric discharge is passed through oxygen, gaseous ozone, $O_3$ (trioxygen) is formed. The reaction is reversible:

$$3O_{2\,(g)} \rightleftharpoons 2O_{3\,(g)}$$

Ozone is an *allotrope* of oxygen.

***Allotropes*** are two or more different forms of the same element, in the same physical state. The phenomenon is called *allotropy*.

Other elements that exhibit allotropy are carbon, sulphur, and phosphorus.

**Revision Exercises**

6. List **three** physical properties of oxygen.

5. List **three** chemical properties of oxygen.
6. When hydrogen peroxide decomposes, the gas evolved
A. turns moist litmus paper to blue.
B. dissolves in water to produce an acid.
C. reacts with hydrogen to form water.
D. does not support combustion.
7. Write equation to show the combustion of sodium.

## 29.4 Industrial Production of Oxygen

Oxygen is produced, in large quantity, from the following sources:

### 1. From Liquefied Air

Oxygen is obtained industrially from atmospheric air by ***liquefaction***, followed by ***fractional distillation of the liquefied air***. The procedure is:

- Atmospheric air is purified by the removal of carbon(IV) oxide, water vapour, and dust.
- By successive heating and cooling at high pressure, the pure air becomes *liquefied* at -200 °C.
- The *liquefied air* is then fractionated by boiling. Nitrogen, being more volatile than oxygen, boils first at -196 °C, leaving oxygen, which is about 99.5% pure.

*Liquefied oxygen* is usually stored in cylinders; for medical and industrial use.

### 2. By Electrolysis

Oxygen, like hydrogen, is obtained during the electrolysis of dilute $H_2SO_4$ (see section 22.8)

**Revision Exercises**

10 State the **two** main physical processes involved in the manufacture of oxygen from air.
11 Outline the industrial production of oxygen from air.
12 The property used in the industrial preparation of nitrogen and oxygen from air is
A. density B. boiling point
C. solubility. D. rate of diffusion. [JAMB]

## 29.5 Uses of Oxygen

1. In *oxy-hydrogen flame*; for welding and cutting of metals. A mixture of hydrogen and oxygen burns to produce a temperature of about 2,500 °C.
2. In *oxy-ethyne flame*; for welding and cutting of steel. The reaction is highly exothermic.
3. In respiration by plants and animals.
4. As breathing aids in hospitals, high altitude flying.
5. A mixture of oxygen and helium is used in sea-diving.
6. In steel production by Linz-Donawitz (L-D) process.
7. Liquefied oxygen is used in explosives, and as propellant for rocket.

**Revision Exercises**

13 State **three** uses of oxygen.
14 Name two combinations of gases that are used for metal welding.

## 29.6 Oxides of Elements in Periods 2 and 3

### Structure and Bonding

Oxygen reacts with all the elements in Periods 2 and 3 (except noble gases) in the Periodic table to form one or more oxides.

1. The metals of groups I, II and III form ionic oxides with giant structures, e.g. $Li_2O$, BeO, $Na_2O$, MgO, and $Al_2O_3$ are ionic solids with high melting and boiling points. They conduct electricity when in molten states.
2. Oxides of boron $B_2O_3$ and silicon $SiO_2$ have giant *molecular* structures with strong covalent bonds. They have high melting points, but do not conduct electricity in molten states.
3. Other elements in Groups IV, V and VI form discrete covalent molecules, which are volatile e.g. $CO_{(g)}$, $CO_{2(g)}$, $NO_{2(g)}$, $N_2O_{(g)}$, $NO_{(g)}$, $OF_{2(g)}$, $P_4O_{10(s)}$, $SO_{2(g)}$, $SO_{3(l)}$ and $Cl_2O_{7(l)}$.

### Classification of Oxides

Based on their acid-base properties, there are four classes of oxides of elements in Periods 2 and 3: acidic, basic, amphoteric, and neutral.

**Table 29.1:** *Acid-base properties of s- and p-block elements*

| → increasing acidity | | | | | | | |
|---|---|---|---|---|---|---|---|
| Group | I | II | III | IV | V | VI | VII |
| Period 2 | Li | Be | B | C | N | O | F |
| Period 3 | Na | Mg | Al | Si | P | S | Cl |
| Period 4 | K | Ca | | | | | |
| | Basic oxides | | Amphoteric oxides | | | Acidic oxides | |

### 1. Basic oxides

Metals of Groups I and II form basic oxides e.g. $Li_2O$, $Na_2O$, MgO, $K_2O$ and CaO. They all dissolve in water to produce $OH^-$, i.e. they are alkalis:

$$MgO(s) + H_2O(l) \rightarrow Mg^{2+}(aq) + 2OH^-(aq)$$

**2. Acidic oxides**

Non-metals form acidic oxides (*acid anhydrides*), e.g. $B_2O_3$, $CO_2$, $NO_2$, $OF_2$, $P_4O_{10}$, $SO_2$, $SO_3$ and $Cl_2O_7$. They produce hydrogen ions in water, e.g.

$$CO_2(g) + H_2O(l) \rightarrow 2H^+(aq) + CO_3^{2-}(aq)$$

Silicon forms an insoluble acidic oxide, $SiO_2$. It reacts with a strong base to produce salt and water.

$$SiO_2(s) + 2NaOH(aq) \rightarrow Na_2SiO_3(aq) + H_2O(l)$$

Generally, acidic oxides are covalent.

Table 29.1 shows the trends in acidic and basic nature of oxides of s- and p-block elements.

**3. Amphoteric oxides**

The oxides of beryllium, BeO and aluminium, $Al_2O_3$ are *amphoteric*.

**4. Neutral oxides**

The neutral oxide are: CO, $N_2O$, and NO.

**Revision Exercises**

15 Mention one oxide in each case which
- a. reacts with NaOH and also with HCl;
- b. dissolves in water to give a pH of 11;
- c. is acidic but insoluble in water.

16 The oxides of the following elements form acid rain when dissolved in rain water EXCEPT
A. carbon B. lead C. nitrogen
D. phosphorus E. sulphur. [NECO]

17 Which of the following combinations of gases is used for metal welding?
I. Oxygen and ethyne; II. Hydrogen and ethyne;
III. Hydrogen and oxygen;
IV. Ethyne, hydrogen and oxygen.
A. I and II; B. III and IV;
C. I and III; D. II and IV.

## 29.7 Oxides and Hydroxides of Metals

### Chemical Properties

1. Metallic oxides are basic, because they undergo neutralization reaction with acids, e.g.

Powdered black copper(II) oxide dissolves in, and reacts with dilute tetraoxosulphate(VI) acid to give the corresponding salt:

$$\underset{\text{(black)}}{CuO(s)} + H_2SO_4(aq) \rightarrow \underset{\text{(blue)}}{CuSO_4(aq)} + H_2O(l)$$

2. Metallic oxides are insoluble in water, except $Na_2O$ and $K_2O$ that dissolve in and react with water to give soluble hydroxides. CaO and MgO are only slightly soluble in water

Soluble basic oxides are called *alkalis*; their aqueous solutions turn red litmus paper to blue, e.g.

- $Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$
- $MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(aq)$

3. Metallic hydroxides are insoluble in water (except those of NaOH and KOH).

Insoluble hydroxides are prepared by the action of sodium hydroxide solution on the corresponding soluble salt of the metal. The precipitate formed is filtered, washed with distilled water, and then dried between filter papers, e.g.

$$\underset{\text{(light green)}}{FeSO_{4(aq)}} + 2NaOH_{(aq)} \rightarrow \underset{\text{(dirty green)}}{Fe(OH)_{2(s)}} + Na_2SO_{4(aq)}$$

4. Ammonia gas dissolves in water to produce a weakly alkaline solution of ammonium hydroxide. The reaction is reversible.

$$NH_3(g) + H_2O(l) \rightarrow NH_4OH(aq)$$

5. Oxides and hydroxides of aluminium, zinc, lead and tin are amphoteric, i.e. they react with either an acid or a base to produce salt and water, e.g.

- $\underset{\text{(base)}}{PbO(s)} + 2\underset{\text{(acid)}}{HNO_3}(aq) \rightarrow Pb(NO_3)_2(aq) + H_2O(l)$
- $\underset{\text{(acid)}}{PbO(s)} + 2\underset{\text{(base)}}{NaOH}(aq) \rightarrow Na_2PbO_2(aq) + H_2O(l)$

6. Mercury, gold and platinum do not form hydroxides.

**Revision Exercises**

18 Classify each of the following oxides as acidic, neutral or amphoteric: $CO_2$; $SnO_2$; NO; $SO_2$;

19 Give the IUPAC name of $Na_2PbO_2$

20 Mention TWO insoluble bases. [NECO]

21 Mention TWO metals whose hydroxides do not exist. [NECO]

## 29.8 Ozone (Trioxygen)

### Nature and Occurrence

Ozone, $O_3$ is an allotrope of oxygen, $O_2$. It is found in the stratosphere (upper atmosphere) as a pale-blue gas. It shields the earth from the intense ultraviolet radiation of the sun.

### Methods of Formation

1. Ozone is formed when a silent electric discharge is passed through a tube of oxygen. The reaction is reversible and endothermic.

$$3O_2(g) \rightleftharpoons 2O_3(g) \quad \Delta H = +ve$$

2. It is also formed in the stratosphere by the action of ultraviolet light on molecules of oxygen.

In both cases, oxygen molecule dissociates into atoms, which then combine with oxygen molecules at high temperature to form ozonised oxygen:

$$O_2(g) \rightarrow 2O(g) \quad \text{.....step 1}$$
$$O(g) + O_2(g) \rightarrow O_3(g) \quad \text{.....step 2}$$

*Overall equation* of reaction:

$$3O_2(g) \rightleftharpoons 2O_3(g) \quad \Delta H = +ve$$

The formation of ozone from oxygen is an endothermic and a dynamic equilibrium process. At low temperatures, oxygen molecules are more stable, while at high temperatures ozone molecules are more stable.

### Physical Properties

1. Ozone is a pale-blue gas, which gives a blue liquid when liquefied at -112 °C.
2. It is poisonous, slightly soluble in water, but soluble in turpentine.
3. It makes mercury to wet glass.

### Chemical Properties

1. Ozone decomposes on standing at ordinary temperature; hence, it is more reactive than oxygen:

$$2O_3(g) \rightleftharpoons 3O_2(g) \quad \Delta H = -ve$$

2. It is a stronger oxidizing agent than oxygen; oxidizes sulphur (IV) oxide to sulphur (VI) oxide with liberation of oxygen.

$$\overset{+4}{SO_2}(g) + \overset{0}{O_3}(g) \rightarrow \overset{+6}{SO_3}(l) + O_2(g)$$

3. If ozone is passed into acidified solution of potassium iodide, iodine gas is liberated. It is a redox reaction:

$$KI_{(aq)} + O_{3(g)} + H_2SO_{4\,(aq)} \rightarrow K_2SO_{4\,(aq)} + H_2O_{(l)} + O_{2(g)} + I_{2(g)}$$

### Uses of Ozone

1. As a source of oxygen; to ventilate underground premises.
2. As a disinfectant; in purifying water and sewage.
3. As a bleaching agent.

### Revision Exercises

22 Use one word to describe the relationship between ozone and oxygen gas.

23 Write equation to show the formation of ozone from oxygen.

24 List one physical property and one use of ozone.

## 29.9 Hydrogen Peroxide

### Method of Preparation

Hydrogen peroxide is prepared by the action of dilute $H_2SO_4$ on powdered barium (IV) oxide (a peroxide) in a freezing mixture:

$$BaO_2(s) + H_2SO_4(aq) \rightarrow BaSO_4(s) + H_2O_2(aq)$$

The resulting mixture is thoroughly stirred; then, filtered, to obtain an aqueous solution of hydrogen peroxide.

### Physico-chemical Properties

1. Hydrogen peroxide is a colourless liquid with a characteristic antiseptic odour.
2. It decomposes at room temperature, using powdered $MnO_2$ or platinum wire as catalyst, to liberate oxygen.

$$\overset{+1\,-1}{2H_2O_2}(l) \xrightarrow{MnO_2} \overset{-2}{2H_2O}(l) + \overset{0}{O_2}(g)$$

It is an *auto-oxidation* or *disproportionation reaction.*

### 3. Oxidizing action

Lead(II) sulphide reduces hydrogen peroxide to *water.*

$$\overset{-2}{PbS}(s) + 4\overset{-1}{H_2O_2}(l) \rightarrow \overset{+6}{PbSO_4}(s) + 4\overset{-2}{H_2O}(l)$$

### 4. Reducing action

Hydrogen peroxide is oxidized to *oxygen* by lead (IV) oxide or silver oxide.

- $\overset{+4}{PbO_2}(s) + \overset{-1}{H_2O_2}(l) \rightarrow \overset{+2}{PbO}(s) + H_2O(l) + \overset{0}{O_2}(g)$
- $\overset{+1}{Ag_2O}(s) + \overset{-1}{H_2O_2}(l) \rightarrow \overset{0}{2Ag}(s) + H_2O(l) + \overset{0}{O_2}(g)$

### Uses of Hydrogen peroxide

1. It is used as an antiseptic.
2. In bleaching hair, teeth, and silk.
3. In the laboratory preparation of oxygen.

### Revision Exercises

25 Which of the following substances is a peroxide?
A. $Na_2O_2$ B. CuO C. $Pb_3O_4$ D. $Fe_2O_3$

26a Write equation to show the decomposition of hydrogen peroxide.

b What substance could be used in the laboratory to increase the rate of the reaction in a above?

27 Write an equation to show that hydrogen peroxide is an oxidizing agent.

28 List one use of hydrogen peroxide.

### Answers to Revision Exercises

8. C 12. B 16. B 17. C 25. A

# 30

# • CARBON AND ITS INORGANIC COMPOUNDS • FUELS •

## 30.1 Introduction

### Atomic Structure of Carbon

Carbon is the first element in group IV of the Periodic Table. (Other members of the group are silicon, germanium, tin and lead.) Its atomic number is 6, and has an electron configuration of $1s^2 2s^2 2p^2$.

Carbon atoms are able to *catenate*, i.e. join to one another by covalent bonds in a continuous fashion. The phenomenon is called *catenation*.

**Revision Exercises**

1. How many unpaired electrons are in the ground state electronic configuration of carbon, ${}_6C$?
2. What is catenation?

### Occurrence of Carbon

Carbon occurs in nature as a free element; the pure forms are diamond and graphite, which are usually mined. It also occurs in the impure forms as coke and charcoal.

Carbon follows oxygen as the second most abundant element in the human body. It occurs in the tissues of plants and animals; crude oil; in mineral *ores* such as marble, limestone and chalk; *seashells* and *eggshells*; and in organic matter of all kinds.

The most abundant compound of carbon is carbon(IV) oxide, $CO_2$, present in the atmosphere. Its other oxide is carbon(II) oxide.

**Revision Exercises**

3. Mention one pure and one impure forms of carbon.
4. Which of the following does not contain carbon?
   Marble; eggshell; air; quicklime; chalk.

## 30.2 Allotropes of carbon

### Allotropy

***Allotropy*** is defined as *the existence of an element in more than one form in the same physical state.* The *various forms are called* ***allotropes***.

The two *crystalline* allotropes of carbon are: ***diamond*** and ***graphite***.

### Diamond

**Structure and bonding**

In *diamond*, each carbon atom is at the centre of a regular tetrahedron and covalently bonded to *four* other atoms in a strong compact fashion. The covalent bonds between the atoms is continuous; it produces a single infinite tightly locked 3-dimensional giant (macro) molecule, which has a *network octahedral* structure (see figure 30.1a).

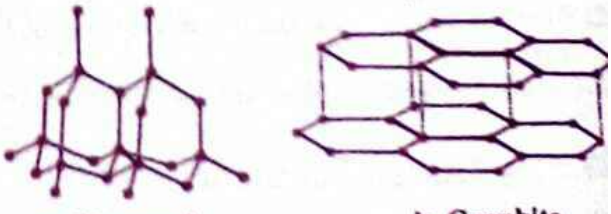
The rigidity of the structure is responsible for the hardness of diamond; it is the hardest known substance. Since the covalent bonds are strong and the molecule is compact, the melting point of diamond is very high.

**Physical properties of diamond**

1. Diamond is hard, colourless and transparent.
2. It forms *octahedral* crystals with high refractive index.
3. Its density is 3.5 $gcm^{-3}$, and melts at 3600 °C.
4. It does not conduct electricity, since all the four valence electrons per carbon atom are used in bonding, i.e. no mobile electrons.
5. It is insoluble in any solvent.

**Uses of diamond**

1. Because of its hardness, diamond is used in cutting glasses; in drilling rocks; in boring holes; in making bearings in engines; and as in abrasives, i.e. to smoothen rough surfaces.
2. Because of its high refractive index and amazing metallic lustre when cut, it is used in jewelries.



a. Diamond b. Graphite

**Fig 30.1** *Structures of diamond and graphite*

### Graphite

**Structure and bonding**

In *graphite*, each carbon atom is covalently bonded to *three* other atoms to produce an infinite two-dimensional *flat hexagonal layer* structure, which is strong and hard (see figure 30.1b above).

The flat hexagonal layers in graphite are held together by the weak van der Waals attractive forces, which allow movement of the planes parallel to each other; making graphite to be *soft* and *slippery*.

The fourth valence electron of each carbon atom in graphite is mobile, since it is not used in bonding; it accounts for its electrical conductivity.

**Physical properties of graphite**

1. Graphite forms soft, black and opaque *hexagonal* crystals, which are greasy to feel. The softness is due to the ability of the adjacent layers to slide over one another.
2. It is hard; its density is 2.3 $gcm^{-3}$, and melts at about 3500 °C
3. It conductors heat and electricity; due to the presence of mobile electrons in its atoms.
4. It is insoluble in any solvent.

Graphite is a non-metallic conductor; a *metalloid*.

**Uses of graphite**

1. Graphite is used as a *lubricant*, because it is soft, insoluble in water and heat resistant.
2. Used as inert electrodes during electrolysis, and for brushes of electric motors, being a good conductor of electric current.
3. When mixed with *clay*, graphite forms *lead*, which is used in making *lead pencils*. The hardness of a pencil depends on the amount of clay in the mixture. *Soft pencils* contain more of graphite, while *hard pencils* contain more of clay.
4. In making crucible; because of its high melting point.
5. In nuclear reactors; being soft and with a high melting point.
6. As black pigment in paints.

## Differences in Physical Properties of Diamond and Graphite

The structures of diamond and graphite account for the marked differences in their physical properties:

1. Diamond is harder and denser than graphite, because the atoms are bound together more tightly – making the molecule to be more compact.
2. Graphite is a conductor, while diamond is not.
3. Diamond forms octahedral crystals, while graphite forms hexagonal plates.
4. Diamond is transparent, while graphite is opaque.

**Solved Problem**

1. What are allotropes?

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

**Revision Exercises**

5. Define the term allotropy.
6. Mention the two crystalline allotropes of carbon.
7. What is the structure of: a. diamond? b. graphite?
8. List three physical properties of
   a. diamond; b. graphite.
9. Give the reason why diamond is hard, while graphite is soft.
10. Mention two uses of: a. diamond; b. graphite.
11. Which allotrope of carbon is a constituent of a lead pencil?
    A. Graphite B. Diamond
    C. Lampblack. D. Soot [JAMB]

## Amorphous forms of carbon

These are the *impure* forms of carbon. They have the structures of graphite, but are non-crystalline (shapeless). They are not true allotropes of carbon.

**1. Wood Charcoal**

*Wood is largely cellulose* – a compound of carbon, hydrogen and oxygen; with sulphur as an impurity.

*Wood charcoal* is obtained by burning *wood* in the absence (or limited supply) of air. It is a black solid, light, porous, brittle, and a good *adsorbent*.

It is used in *gas masks*, in order to *adsorb* liquefiable gases such as $NH_3$, $H_2S$, $Cl_2$, $SO_2$ and HCl; except $O_2$ and CO. Hence, when *wood charcoal* is placed in a gas jar containing a mixture of $NH_3$ and $O_2$ that has been collected over mercury, only $NH_3$ is adsorbed; the mercury level rises, leaving pure oxygen in the gas jar (figure 30.2).

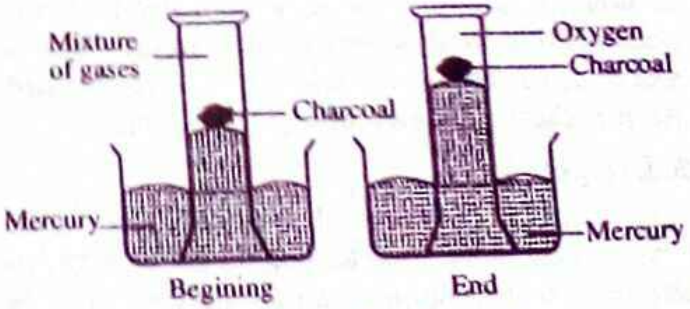



**Fig 30.2** *Adsorption of gases by charcoal*

When *wood charcoal* is treated with steam, its ability to *adsorb* gases increases, and become ***activated charcoal***.

*Activated charcoal* is used, industrially, in the purification of water – to filter suspended particles, and remove unpleasant taste, odour and colour; and to *adsorb* gases.

### 2. Coke

Coke is the residue obtained when *coal* is heated in the absence of air. It is a porous dark-grey solid used as a fuel, in the production of gaseous fuels, and extraction of metals.

### 3. Sugar Charcoal

*Sugar charcoal* is obtained when pure *sugar* (*sucrose or glucose*) is heated in the absence of air, or dehydrated by *concentrated* $H_2SO_4$. It is the purest form of charcoal.

- $\underset{\text{(sucrose)}}{C_{12}H_{22}O_{11(s)}} \xrightarrow{\text{Heat}} 12C_{(s)} + 11H_2O_{(g)}$
- $\underset{\text{(sucrose)}}{C_{12}H_{22}O_{11(s)}} \xrightarrow[(-11H_2O)]{\text{Conc } H_2SO_4} 12C_{(s)}$

**Note:** When *concentrated* $H_2SO_4$ is used as a *dehydrating agent*, it removes *elements of water* in the compound. It is a chemical process.

### 4. Animal Charcoal

*Animal charcoal* is obtained when *bones and refuse of animals* are heated in limited supply of air. Since animal bones contain calcium tetraoxophosphate(V) $Ca_3(PO_4)_2$, animal charcoal is, therefore, rich in tetraoxophosphate(V) ions $PO_4^{3-}$.

*Animal or bone charcoal is used to adsorb gases, and to remove colours (dyes) from coloured solutions.* For instance:

1. When extracts of sugar cane (brown sugar solution) is boiled with *animal or activated charcoal* and filtered, a colourless filtrate is obtained. On crystallization, it gives white crystals of sugar. Hence, animal charcoal is used in the industrial purification of sugar.
2. When a solution coloured with methyl orange or phenolphthalein is warmed with animal charcoal and then filtered, a colourless filtrate is obtained. Animal charcoal is a *decolorizing charcoal*.

### 5. Lampblack

*Lampblack* is obtained when gaseous or liquid hydrocarbon fuels, such as bottled cooking gas or kerosene are burned in limited supply of air. It is the *greasy black powder* or *soot* obtained inside the kerosene lamp.

*Lampblack* is often deposited in the exhaust pipe of a motor vehicle, due to incomplete combustion of petrol. It is used as fertilizer.

### 6. Carbon black

*Carbon black* is obtained when natural gas (mainly methane) is burned in an inadequate supply of air. It is not so greasy like lampblack.

*Carbon black* is used in producing carbon paper, printers' ink, black shoe-polish and typewriter ribbon. It is used as black pigments in paints, and is added to the rubber of motor vehicle tyres for colouration, and to reduce its wear and tear.

### Revision Exercises

12 List three amorphous forms of carbon and state one use of each of them.
13 Mention the property of wood charcoal that accounts for its use in gas masks.
14 What is *activated* charcoal?
15 State two uses of *carbon black*.

## Chemical Properties of Carbon

All the allotropic forms of carbon undergo identical chemical reactions as shown by the following:

### 1. Combustion of carbon

All the allotropic forms of carbon burn in oxygen with liberation of heat in two stages:

a. In excess air, there is complete combustion; carbon(IV) oxide is produced.

$$C(s) + O_2(g) \rightarrow CO_2(g) + \text{heat}$$

b. In a limited air supply, there is incomplete (or partial) combustion; carbon(II) oxide is formed.

$$2C(s) + O_2(g) \rightarrow 2CO(g) + \text{heat}$$

When a fixed mass of each of pure diamond and pure graphite is separately heated in excess oxygen in a combustion tube, the same quantity of carbon (IV) oxide will be produced in each case.

This shows that pure diamond and pure graphite contain 100 % carbon (no impurity).

### 2. Combination with a non-metal

When a mixture of carbon and powdered sulphur is strongly heated, they combine to produce liquid carbon(IV) sulphide – a poisonous liquid solvent.

$$C(s) + 2S(s) \rightarrow CS_2(l)$$

### 3. Combination with metals

Carbon combines with metals such as calcium, iron and aluminium at high temperatures to produce *carbides*:

- $Ca(s) + 2C(s) \rightarrow CaC_2(s)$
- $3Al(s) + 4C(s) \rightarrow Al_3C_4(s)$

### 4. Reducing actions of carbon

Because carbon combines readily with oxygen, it is an important *reducing agent*:

a. When heated with the an oxide of a *less electropositive metal* such as zinc, iron, tin, lead and copper, the free metal is obtained, e.g.

$C(s) + PbO(s) \rightarrow Pb(s) + CO(g)$

$3C(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + 3CO(g)$

Coke is extensively used industrially for the extraction of the above metals from their oxides.

b. When *hot air* is allowed to pass through red-hot coke, *producer gas* is produced:

$2C(s) + O_2(g) + 4N_2(g) \rightarrow 2CO(g) + 4N_2(g)$

[← From air →] [← Producer gas →]

c. When *steam* is passed through white-hot coke, *water gas* is produced.

$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$

[← Water gas →]

d. Hot concentrated $H_2SO_4$ is reduced to sulphur (IV) oxide when it is heated with coke.

$\overset{0}{C}(s) + \overset{+6}{H_2SO_4}(l) \rightarrow \overset{+4}{CO_2}(g) + \overset{+4}{2SO_2}(g) + 2H_2O(l)$

**Revision Exercises**

16 State one piece of evidence to show that both graphite and diamond are allotropes of carbon.

17 Write an equation for the reaction between coke and zinc oxide. Name the type of reaction.

18 Write an equation to show that carbon is a reducing agent.

**Solved Problems**

1. Explain why graphite is a conductor of electricity, while diamond, its allotrope, does not.

*In graphite each carbon atom has a mobile electron, which is not used in bonding and hence, delocalized in the entire structure; while in diamond, the four valence electrons in each carbon atom are used in bonding.*

2. Distinguish between *lampblack* and *carbon black*.

*Lampblack is obtained by burning kerosene in a limited supply of air, while carbon black is obtained by burning natural gas in a limited supply of air*

3. It is now known that carbon has an allotropic form called *fullerene*, containing molecules of formula $C_{60}$. Calculate the mass of one mole of these molecules. [C = 12]

*Molecular formula of fullerene is $C_{60}$. i.e. One molecule of fullerene contains 60 carbon atoms.*

*In terms of moles:*

*One mole of fullerene contains 60 moles of carbon.*

*Since 1 mole of carbon weighs 12.0 g,*

*∴ 60 moles of carbon weigh (60 × 12.0) g = 720 g.*

*Hence, the mass of one mole of fullerene = 720 g.*

**Note:** Molar mass of *fullerene* will be 720 $gmol^{-1}$.

**Revision Exercises**

19 Mention the respective properties of the following allotropes of carbon that account for their uses as indicated:

a. Diamond is used for drilling rocks.

b. Diamond is used as jewels;

c. Graphite is used as electrodes.

d. Graphite is used in slowing down neutrons in nuclear reactors.

20 Name the form of carbon used

a. in gas masks.

b. for adsorbing poisonous gases and purification of noble gases.

21 State two similarities and two differences between graphite and diamond.

22 Give the reason why graphite is a lubricant but diamond is not.

23 State the reason why diamond has a higher melting point than graphite.

24 Describe in outline how the following forms of carbon can be obtained:

a. Animal charcoal b. Sugar charcoal

c. Wood charcoal d. Lamp black.

## 30.3 Carbon(IV) oxide, $CO_2$

### Methods of Preparation

There are four classes of reactions in which carbon (IV) oxide is liberated:

1. Combustion of carbon or any organic compound in excess of oxygen or air e.g.

- $C(s) + O_2(g) \rightarrow CO_2(g)$
- $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

2. Decomposition of trioxocarbonate(IV) salts (except those of sodium and potassium), or hydrogentrioxocarbonate(IV) salts, by strong heat e.g.

- $CaCO_3(s) \rightarrow CaO(s) + CO_2\uparrow$
- $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2\uparrow$

3. Action of dilute mineral acid on a trioxocarbonate(IV) or hydrogentrioxocarbonate (IV) salt e.g.

- $Na_2CO_{3(s)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + H_2O + CO_2\uparrow$
- $KHCO_{3(s)} + HNO_{3(aq)} \rightarrow KNO_{3(aq)} + H_2O_{(l)} + CO_2\uparrow$

4. Fermentation of glucose by *enzyme zymase*

$C_6H_{12}O_6(aq) \xrightarrow{\text{zymase}} 2C_2H_5OH(aq) + 2CO_2(g)$

### Laboratory Preparation of $CO_2$ gas

Carbon(IV) oxide is conveniently prepared in the laboratory by the action of dilute hydrochloric acid (2.0 $moldm^{-3}$) on *marble chips*, calcium trioxocarbonate(IV).

**Procedure and Observations**

a. Marble chips (10.0 *g*) are placed in a flat-bottomed flask; then, the pieces of apparatus are set up as shown in fig 30.3.

b. Dilute HCl is added through the thistle funnel, until the stem is just immersed in the acid.

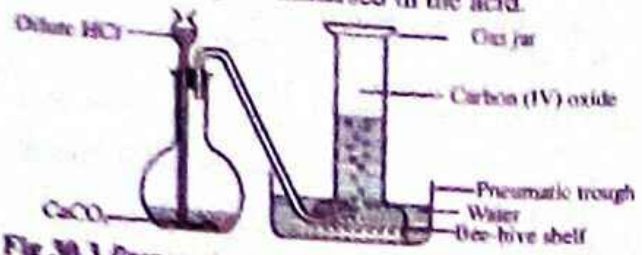



**Fig 30.3** *Preparation of carbon (IV) oxide*

c. There is effervescence as the marble chips dissolve in the acid. The gas evolved is colourless and odourless, and can be collected over water.

$$CaCO_3(s) + HCl(aq) \rightarrow CaCl_{2(aq)} + H_2O_{(l)} + CO_2\uparrow$$

d. Pure and dry carbon(IV) oxide is obtained by passing the gas through a solution of $KHCO_3(aq)$ to remove the acid impurity, HCl gas, and then, through concentrated $H_2SO_4$ (or fused $CaCl_2$) to dry the gas. It is then collected by downward delivery, being denser than air (see figure 30.3).

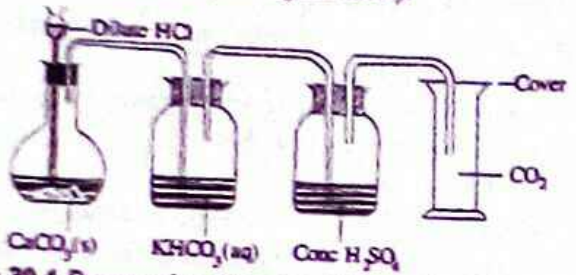



**Fig 30.4** *Preparation of pure and dry carbon(IV) oxide*

## Physical Properties of $CO_2$

1. Carbon(IV) oxide is colourless and odourless.
2. It is heavier than air.

Invert a gar jar of $CO_2$ over another gas jar with a burning candle (figure 30.5). The candle will soon be extinguished.

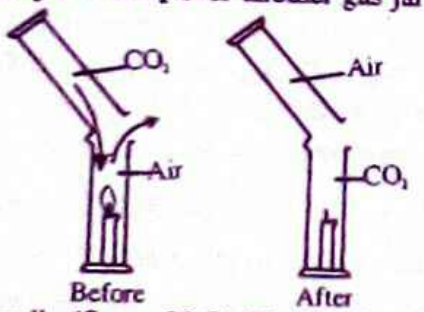



**Fig 30.5** *$CO_2$ is heavier than air*

*Reason*: $CO_2$ being denser than air displaces the air initially in the gas jar, then extinguishes the candle.

3. It does not support combustion.

Place a burning candle (or burning splint) in a gas jar of $CO_2$; it is extinguished.

4. Carbon(IV) oxide is easily liquefied at low temperatures with pressure higher than 5 atmospheres.

## Chemical Properties of $CO_2$

**1. Action on Water:**

Carbon (IV) oxide is soluble in water.

Invert a gas jar of $CO_2$ over a trough of water; the water level in the jar rises as the gas dissolves.

The solubility of $CO_2$ in water is in the ratio 1:1 by volume. It dissolves in, and reacts with water to give trioxocarbonate(IV) acid, $H_2CO_{3(aq)}$.

$$H_2O + CO_2 \rightleftharpoons H_2CO_{3(aq)} \rightleftharpoons 2H^+_{(aq)} + CO_3^{2-}{}_{(aq)}$$

Hence, $CO_2$ is the *acid anhydride* of $H_2CO_3$.

**2. Action on blue litmus:**

Pour about 5 $cm^3$ of distilled water into a gas jar of $CO_2$ and swirl. The resulting solution will turn blue litmus paper slightly red; $CO_2$ is acidic.

**3. Reaction with alkali – neutralization reaction**

• When $CO_2$ (an acidic oxide) is passed into a moderately concentrated NaOH or KOH solution, neutralization occurs to give a salt and water only.

$$CO_{2(g)} + 2NaOH_{(aq)} \rightarrow Na_2CO_{3(aq)} + H_2O$$

• When a large excess of the gas is used, an acid salt is formed.

$$Na_2CO_{3(aq)} + H_2O + CO_{2(aq)} \rightarrow 2NaHCO_{3(aq)}$$

**4. Oxidizing properties of $CO_2$**

**a. *Reaction with coke*:**

Pass $CO_2$ over red-hot coke; $CO_2$ is reduced to CO, a poisonous gas:

$$\overset{0}{C_{(s)}} + \overset{+4}{CO_{2(g)}} \rightarrow \overset{+2}{2CO_{(g)}}$$

**b. *Reaction with magnesium*:**

When burning magnesium ribbon is placed in a gas jar of $CO_2$, it continues to burn, to produce a mixture of white MgO and black carbon as the residues.

$$\overset{0}{2Mg_{(s)}} + \overset{+4}{CO_{2(g)}} \rightarrow \overset{+2}{2MgO_{(s)}} + \overset{0}{C_{(s)}}$$

In this reaction, magnesium is oxidized to its oxide, while $CO_2$ is reduced to carbon.

**5. Laboratory chemical test for $CO_2$ gas**

• Pass $CO_2$ into *limewater*. The solution turns milky, due to the precipitation of white $CaCO_3(s)$.

$$CO_2(g) + Ca(OH)_2(aq) \rightarrow CaCO_3(s) + H_2O(l)$$

• With an excess of $CO_2$ (or when $CO_2$ is passed into *lime water for a long time*), the milkiness disappears to give a colourless solution. This is due to the formation of $Ca(HCO_3)_2(aq)$; a water-soluble compound that causes temporary hardness.

$$CaCO_3(s) + H_2O + CO_2(g) \rightarrow Ca(HCO_3)_2(aq)$$

Hence, temporary hard water can be prepared in the laboratory by passing excess of $CO_2$ gas into *lime water*, to give a colourless solution of calcium hydrogentrioxocarbonate(IV), $Ca(HCO_3)_2$.

**Revision Exercises**

25 List the two reactants for the laboratory preparation of carbon(IV) oxide.

26 Draw a labelled diagram for the laboratory preparation of a dry sample of carbon(IV) oxide.

27 Give two physical and two chemical properties of carbon(IV) oxide.

28 Write an equation to show the oxidizing property of carbon(IV) oxide.

29 Describe the laboratory test for $CO_2$.

30 Describe what will be observed when $CO_2$ is passed into $Ca(OH)_2(aq)$ for a while, then in excess.

## Uses of Carbon(IV) oxide

1. Carbon(IV) oxide is used in fire extinguishers; being *heavier than air*, and *does not support combustion*.

*Liquid* carbon(IV) oxide fire extinguishers are used in putting out fires from *electrical installations* and *oils*.

2. Used in the production of aerated soft drinks, such as *Coca-Cola, 7-Up, and Pepsi-Cola*, because of its pleasant and refreshing acid taste.

3. It is used as effervescence in some health salts, such as *Andrew Liver Salt* or *Epson Salt*. It is responsible for their early effervescence when dissolved in water.

4. It is an essential ingredient in *baking powder*. *Baking powder is a mixture of* $NaHCO_3$ (*baking soda*), *tartaric acid, and cornstarch*. Its presence is necessary for loaves of bread to rise; it is responsible for the puffy nature of loaves of bread and cakes.

5. In the production of $Na_2CO_3$ by *Solvay process*.

6. It is necessary for photosynthesis.

The dissolved $CO_2$ gas in seawater provides seaplants with food for photosynthesis.

7. Solid carbon(IV) oxide is called ***dry ice***. It is used as a refrigerant in preserving perishable foods like meat, fish, and fruits, and in making ice cream. It is used as a coolant in nuclear reactor. It is called *dry ice* because it *sublimes* readily, without forming a liquid.

*Dry ice* has few advantages over the popular *ice*:

a. ***Dry ice*** produces a greater cooling effect than an equal mass of the common *ice* (***ice block***); *dry ice* can provide a temperature of -79 °C (194 K).

b. ***Dry ice***, *on warming, sublimes; unlike ice, that melts to produce water.*

**Caution:** *Never handle solid $CO_2$, dry ice, with the bare hand. It causes painful blisters similar to those caused by hot objects; since the process is highly endothermic.*

**Fire Extinguishers**

*The principle of fire extinguisher is based on the fact that $CO_2$ gas is heavier than air, and does not support combustion.*

***Soda-acid fire extinguisher*:**

When $CO_2$ is produced under pressure by the action of concentrated $H_2SO_4$ on $NaHCO_{3(aq)}$, and directed towards a *flame*, the foam produced by the gas forms a *blanket* over the *fire*, cuts off the supply of oxygen in air, and hence, prevents further burning.

$$NaHCO_{3(aq)} + H_2SO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + H_2O + CO_2\uparrow$$

**Caution:** *Never use water alone to extinguish fires from petrol, kerosene and oils; these liquids will float on water, and spread the fires!*

**Revision Exercises**

31 State four uses of carbon(IV) oxide.

32 What is *dry ice*?

33 What is the difference between *dry* ice and *ice* from water?

34 On what principle is *fire extinguisher* based?

**Solved Problems**

4. State the two properties of carbon(IV) oxide, which make it useful in extinguishing fire.

- *$CO_2$ does not support combustion.*
- *$CO_2$ is heavier than air.*

5. State what would be observed if $CO_2$ were passed through limewater for a long time.

*The limewater turns milky first, then, becomes a colourless solution..*

6. Give the reason why a piece of magnesium continues to burn inside a jar of $CO_2$, which does not normally support combustion.

*Burning magnesium is hot enough to remove oxygen from $CO_2$ in which it burns to form MgO.*

7. Explain the use of a solution of $Al_2(SO_4)_3$ together with a solution of $NaHCO_3$ in the *foam type* of fire extinguisher.

*$Al_2(SO_4)_3$ is a salt of a strong acid and a weak base: hence, it hydrolysis in water to produce an acidic solution. The acidic solution reacts with $NaHCO_3$ to liberate $CO_2$ gas in the form of foam under pressure.*

**Revision Exercises**

35 Name the gas formed when all forms of carbon burn in excess oxygen.

36 Write an equation for the reaction of carbon(IV) oxide with lime water.

37 How is temporary hard water prepared in the lab?

## 30.4 Carbon(IV) oxide/Oxygen cycle

The carbon(IV) oxide - oxygen cycle operates in nature in such a way that the percentages of carbon (IV) oxide (0.03 – 0.04%) and oxygen (21.0%) remain approximately constant in the atmosphere. This is due to the *balance* in the *rates of formation* and *consumption* of $CO_2$ in nature.

***Carbon(IV) oxide gets into the atmosphere*** through the following processes:

1. *Combustion of fuels*: Coal, wood, coke, petrol, kerosene, natural gas and other organic compounds burn in oxygen to produce $CO_2$(g).

$$C(s) + O_2(g) \rightarrow CO_{2(g)}$$

2. *During respiration in living things*: Foods in the form of starch and sugar are converted into glucose; which burns in oxygen to produce water vapour, carbon(IV) oxide and heat energy.

$$C_6H_{12}O_{6(aq)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(l)} + \text{heat}$$

3. *During decaying processes*, dead animals and plants decompose to produce carbon(IV) oxide by the action of bacteria.

4. *During fermentation process*, simple sugars, like glucose, is decomposed by an *enzyme* (*an organic catalyst*) called *zymase*, to produce carbon(IV) oxide, alcohol and heat energy.

$$C_6H_{12}O_{6(aq)} \xrightarrow{\text{zymase}} 2C_2H_5OH_{(aq)} + 2CO_{2(g)} + \text{heat}$$

***Carbon(IV) oxide is removed from the atmosphere*** through the following processes:

1. *During photosynthesis*: Green pigment in plants (*chlorophyll*) absorbs $CO_2$ from the atmosphere, in the presence of sunlight, and then, react with water in plants to *form glucose* and the *release of oxygen into the atmosphere*. The process is endothermic.

$$6CO_{2(g)} + 6H_2O_{(l)} + \text{heat} \rightarrow C_6H_{12}O_{6(aq)} + 6O_{2(g)}$$

2. When rain falls, the $CO_2$ in air dissolves in rainwater and waters in rivers, lakes, and seas. The resulting acidic solutions dissolve $CaCO_3$ in rivers and seas to form $Ca(HCO_3)_2$, which is used up by water-plants and animals – such as fishes, snails and crabs, to form their bones and shells, and also to cause temporary hardness in water:

$$CaCO_3(s) + H_2O + CO_2(g) \rightarrow Ca(HCO_3)_2(aq)$$

It should be noted that *respiration* process is the reverse of *photosynthesis*.

$$C_6H_{12}O_{6(aq)} + 6O_{2(g)} \underset{\text{(photosynthesis)}}{\overset{\text{(respiration)}}{\rightleftharpoons}} 6CO_{2(g)} + 6H_2O_{(l)} + \text{heat}$$

**Revision Exercises**

38 Name a process that

a. removes $CO_2$ from the atmosphere;

b. injects $CO_2$ into the atmosphere.

39 Write equation to show the formation of carbon(IV) oxide during respiration in human beings.

## 30.5 Carbon(II) oxide

Carbon(II) oxide is the other oxide of carbon. It is produced when carbon or any organic matter is burned in a *limited or inadequate supply of oxygen*:

$$2C(s) + O_2(g) \rightarrow 2CO(g) + \text{heat}$$

However, CO is unstable; it readily combines with hot air to form the more stable $CO_2$.

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

Generally, carbon(II) oxide is produced whenever there is an incomplete combustion of carbon and carbon-containing fuels.

### Laboratory Preparation of Carbon(II) oxide (*in the fume cupboard*)

#### 1. From crystals of ethanedioic acid

Carbon(II) oxide is conveniently prepared by the action of heat on a mixture of crystals of ethanedioic acid, $H_2C_2O_4 \cdot 2H_2O$ and concentrated $H_2SO_4$ held in a round-bottomed flask (see figure 30.6).

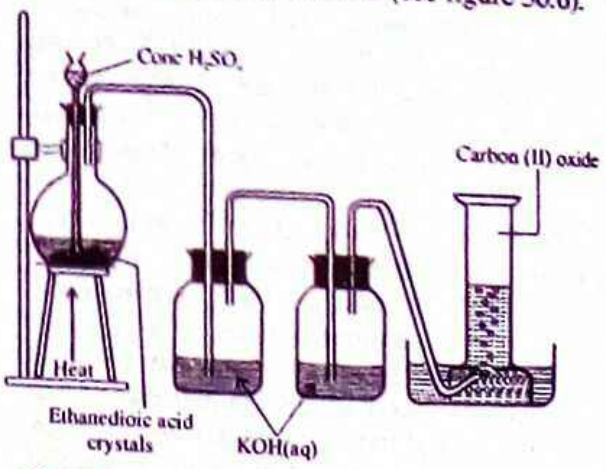



**Fig 30.6**

There is effervescence; the mixture of gases evolved is passed through two Woulff's bottles containing $KOH_{(aq)}$ – to absorb carbon(IV) oxide, while the remaining gas is then collected over water.

*Chemistry of Action*

a. When ethanedioic acid crystals are heated, they decompose to produce water and a mixture of gaseous carbon(II) oxide and carbon(IV) oxide.

$$H_2C_2O_4{\cdot}2H_2O_{(s)} \rightarrow 3H_2O(l) + CO_{(g)} + CO_{2(g)}$$

The role of conc $H_2SO_4$ is to remove *elements of water*, and hence, acts as a *dehydrating agent*.

b. When a mixture of CO and $CO_2$ is passed into KOH or NaOH solution, only $CO_2$ is absorbed – being an acidic oxide.

$$CO_{2(g)} + 2KOH_{(aq)} \rightarrow K_2CO_{3(aq)} + H_2O_{(l)}$$

**2. From crystals of sodium methanoate**

When concentrated $H_2SO_4$ is added to the crystals of sodium methanoate in a conical flask, there is effervescence; the colourless and odourless gas evolved is carbon(II) oxide. Heat is not required. The gas evolved is collected over water.

*Chemistry of action*

$$2HCOONa_{(s)} + H_2SO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + 2H_2O + 2CO\uparrow$$

Since carbon(II) oxide is the only gas evolved, the set-up does not require any Wolff's bottle.

When ethanoic acid is used in place of sodium methanoate crystals, the concentrated $H_2SO_4$ acts as a *dehydrating agent*:

$$HCOOH_{(l)} \xrightarrow[(-H_2O)]{H_2SO_4} CO_{(g)}$$

**3. Reduction of carbon(IV) oxide**

When carbon(IV) oxide is passed over heated coke or charcoal in a combustion tube, it is reduced to carbon(II) oxide (see figure 30.7).

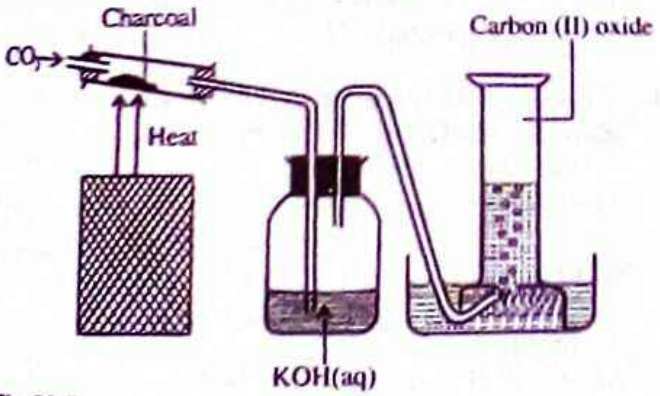



**Fig 30.7**

The unreduced $CO_2$ is removed by passing the gaseous mixture through KOH(aq). The remaining CO gas is then collected over water.

$$CO_{2(g)} + C_{(s)} \rightarrow 2CO_{(g)}$$

**Physical Properties of CO**

1. Pure CO gas is colourless and odourless.
2. It is slightly lighter than air.
3. Slightly soluble in water but insoluble in alkalis.
4. It is soluble in an ammoniacal solution of copper (I) chloride, $Cu_2Cl_2$.
5. The gas is poisonous; hence, it is prepared in the fume cupboard.

**Chemical Properties and Uses of CO**

**1. As a Fuel:**

Carbon(II) oxide burns in air with a pale-blue flame, to produce carbon(IV) oxide.

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

*The gas supports combustion.* Gaseous fuels such as *coal gas* and *water gas* contain carbon(II) oxide.

**2. Action on litmus**

Its aqueous solution has no action on litmus paper; it is a neutral oxide.

**3. As a Reducing Agent:**

Since carbon(II) oxide is readily oxidized to carbon(IV) oxide, it is a useful reducing agent:

a. A mixture of steam and carbon(II) oxide produces a mixture of carbon(IV) oxide and hydrogen:

$$CO_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)}$$

b. *With metallic oxides*: When carbon(II) oxide is passed over heated oxide of zinc, iron, tin, lead or copper, the free metal is obtained:

- $CO_{(g)} + ZnO_{(s)} \rightarrow Zn_{(s)} + CO_{2(g)}$
- $3CO_{(g)} + Fe_2O_{3(s)} \rightarrow 2Fe_{(s)} + 3CO_{2(g)}$

**Note:** *The product of combustion or oxidation of CO is $CO_2$: confirmed by its ability to turn limewater milky.*

4. Carbon(II) oxide combines with chlorine, using *finely* divided carbon as a catalyst to form carbonyl chloride, $COCl_2$ (phosgene): a poisonous liquid.

$$CO(g) + Cl_2(g) \rightarrow COCl_2(l)$$

5 Combines with nickel at 80 °C to form nickel carbonyl:

$$Ni(s) + 4CO(g) \rightarrow Ni(CO)_4(s)$$

At 180 °C, nickel carbonyl decomposes to give carbon(II) oxide:

$$Ni(CO)_4(s) \rightarrow Ni(s) + 4CO(g)$$

**6. In Organic Synthesis of Methanol:**

Carbon(II) oxide combines with hydrogen at 300 °C and high pressure, to give *methanol*, an alcohol:

$$CO(g) + 2H_2(g) \rightarrow \underset{\text{(methanol)}}{CH_3OH(l)}$$

### Effect of carbon(II) oxide on blood

Carbon(II) oxide, also known as *carbon monoxide*, is a dangerous gas; it is not only *invisible* (*colourless*) and odourless, it is also toxic or poisonous, when inhaled.

Ordinarily, *haemoglobin* of the red-blood cells carries oxygen in the form of *oxy-haemoglobin* to the body tissues. However, if carbon(II) oxide is inhaled *instead of oxygen*, it combines irreversibly with *haemoglobin* to form *carboxy-haemoglobin* that has a *cherry-red colour*, and prevents oxygen from being absorbed into the blood.

Lack of oxygen in the blood leads to suffocation, coma, and then, death. Hence, the following activities are dangerous:

1. Inhaling the gas from the exhaust of a motor vehicle, or an electric generating set.
2. Running a motorcar engine in a garage with the doors and windows closed;
3. Sleeping by charcoal fire in a poorly ventilated room.

This is because the fumes being produced during the combustion of fuels contain carbon(II) oxide.

### Revision Exercises

40 Mention two reagents required for the laboratory preparation of carbon(II) oxide.

41 Which of the following tests cannot be used to distinguish CO and $CO_2$ ?

A. Passing each gas over heated copper (II) oxide
B. Passing each gas through fresh lime water
C. Observing their colour and odour
D. Passing each gas into water and testing with litmus.
E. Comparing their diffusion rates through a porous plug.

42 State two physical properties of $CO_2$ which are similar to those of CO.

43 How does carbon (II) oxide react with
a. coke? b. oxygen? c. zinc oxide?

44 Write an equation to show the reducing property of carbon(II) oxide.

45 Why is CO described as a poisonous gas?

## 30.6 Calculations Involving Oxides of Carbon

### Mass-Mole Relationships

8 2.0 moles of pure marble react completely with an excess of dilute hydrochloric acid, calculate the mass of carbon(IV) oxide produced. [$CO_2$ = 44.0]

*To calculate the mass of $CO_2$*
It is mass-mole relationship.
From the balanced equation of reaction:

$$CaCO_3(s) + HCl(aq) \rightarrow CaCl_2 + H_2O + CO_2\uparrow$$
1 mol — 1 mol (44.0 g)

2 mol

1 mole of $CaCO_3$ produces 44.0 g (1 mol) of $CO_2$
∴ 2.0 mol of $CaCO_3$ produce (44.0 × 2.0) g $CO_2$
= 88.0 g of $CO_2$

### Mass-Mole-Gas volume Relationships

9. Calculate the volume of carbon(IV) oxide measured at s.t.p. produced when 1.0 *kg* of potassium hydrogen trioxocarbonate (IV) is totally decomposed by heat. [K = 39, O = 16, C = 12, H = 1; molar volume of gas at s.t.p. = 22.4 $dm^3$] [NECO]

*To calculate the volume of $CO_2$ liberated at s.t.p. by heating 1.0 kg of $KHCO_3$.*
This is mass-gas volume relationship.
Molar mass of $KHCO_3$ = 39 + 1 +12 + 48 = 100 $gmol^{-1}$
From the balanced equation of reaction:

$$2KHCO_3(s) \rightarrow K_2CO_3(s) + H_2O(g) + CO_2(g)$$
2 mol — 1 mol
(2 × 100) g — 22.4 $dm^3$

2 moles of $KHCO_3$ produce 1 mole of $CO_2$
i.e. (2 × 100 g) of $KHCO_3$ = 1 × 22.4 $dm^3$ of $CO_2$
∴ 1000 g (1.0 kg) of $KHCO_3$ = (22.4 × 1000/200)
= (22.4 × 5) $dm^3$
= 112 $dm^3$ of $CO_2$ at s.t.p.

10 In a soda-acid fire extinguisher, 1.00 kg of $NaHCO_3$ was completely used according to the reaction:

$$2NaHCO_{3(aq)} + H_2SO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + H_2O + 2CO_{2(g)}$$

Calculate the
a. amount of $H_2SO_4$ required for the reaction;
b. volume of $CO_2$ liberated at s.t.p.
[$NaHCO_3$ = 84; molar volume of gas at stp = 22.4 $dm^3$]

a. *To calculate the amount of acid required.*
Mass of $NaHCO_3$ used = 1.00 kg = 1000 g.
This is mass-mole relationship.
From the equation of reaction:
2 mol (2 × 84.0 g) $NaHCO_3$ ≡ 1 mol of $H_2SO_4$
∴ 1000 g of $NaHCO_3$ ≡ (1×1000)/(2 × 84)
= 5.95 mol of $H_2SO_4$

b. *To calculate the volume of $CO_2$ liberated.*
Mass of $NaHCO_3$ used = 1.00 kg = 1000 g.
From the equation of reaction:
2 mol (2 × 84.0 g) of $NaHCO_3$ ≡
2 mol (2 × 22.4 $dm^3$) of $CO_2$
∴ 1000 g of $NaHCO_3$ ≡ (2 × 22.4 × 1000)/(2 × 84)
= 267 $dm^3$ of $CO_2$ at s.t.p.

*Alternative method:*
Amount of $H_2SO_4$ used = 5.95 mol.
From the equation of reaction:
1 mol of $H_2SO_4$ ≡ 2 mol (2 × 22.4 $dm^3$) $CO_2$
∴ 5.95 mol $H_2SO_4$ ≡ 2 × 22.4 × 5.95
= 267 $dm^3$ of $CO_2$ at s.t.p.

**Revision Exercises**

46 What volume of $CO_2$ would be produced at s.t.p. if 25.0 g of $CaCO_3$ decomposes according to the following equation?

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

[$CaCO_3 = 100\ gmol^{-1}$; 1 mole of a gas occupies $22.4\ dm^3$ at s.t.p.]

A. $2.24\ dm^3$ B. $4.48\ dm^3$
C. $5.60\ dm^3$ D. $44.80\ dm^3$ [WAEC]

47 How many *grams* of $CaCO_3$ would be required to produce $4.50\ dm^3$ of $CO_2$ at s.t.p.?

Calculate the mass of carbon(IV) oxide produced.

48 Calculate the volume of carbon(II) oxide produced at s.t.p. by the dehydration of 9.20 g of methanoic acid.

## 30.7 Trioxocarbonate(IV) acid

Trioxocarbonate(IV) [Carbonic] acid, $H_2CO_3$ is a weak *dibasic* acid. It is obtained when carbon(IV) oxide combines with water. It is unstable; hence, never isolated:

$$CO_{2\,(g)} + H_2O \rightleftharpoons H_2CO_{3\,(aq)} \rightleftharpoons 2H^+_{(aq)} + CO_3^{2-}{}_{(aq)}$$

The acid forms both the normal and acid salts; the acid ionizes in two stages:

I. $H_2CO_{3(aq)} \rightleftharpoons H^+_{(aq)} + HCO_3^-{}_{(aq)}$

II. $HCO_3^-{}_{(aq)} \rightleftharpoons H^+_{(aq)} + CO_3^{2-}{}_{(aq)}$

**Revision Exercises**

49 Write equation to show the reaction of water with carbon(IV) oxide.

50 Is $H_2CO_3$ a weak or a strong acid? Explain.

## 30.8 Trioxocarbonate(IV) Salts, $CO_3^{2-}$

### Properties of the Salts

1. All trioxocarbonate(IV) salts are *insoluble*, except those of sodium, potassium and ammonium that are soluble in water.

2. Trioxocarbonate(IV) salts of potassium and sodium dissolve in water to produce alkaline solutions. This is because they are salts of a *strong base* and a *weak acid*; hence, they hydrolyse in water to produce alkaline solutions; e.g.

$$K_2CO_3(s) + 2H_2O \rightarrow \underset{\text{(strong)}}{2KOH(aq)} + \underset{\text{(weak)}}{H_2CO_3(aq)}$$

3. All trioxocarbonate(IV) salts, except those of potassium and sodium, decompose on heating, to liberate carbon(IV) oxide e.g.

- $ZnCO_{3\,(s)} \rightarrow ZnO_{(s)} + CO_{2\,(g)}$
- $(NH_4)_2CO_{3\,(s)} \rightarrow 2NH_{3\,(g)} + H_2O_{(g)} + CO_{2\,(g)}$

Note: *$Na_2CO_3$ and $K_2CO_3$ are not affected by heating.*

4. All trioxocarbonate(IV) salts react with dilute acids to liberate carbon(IV) oxide, e.g.

$$ZnCO_{3\,(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2\,(aq)} + H_2O_{(l)} + CO_{2\,(g)}$$

*Ionically:* $CO_3^{2-}{}_{(s)} + 2H^+_{(aq)} \rightarrow H_2O_{(l)} + CO_{2\,(g)}$

### 5. Chemical Tests for $CO_3^{2-}$ Salts

**a. Test on solid (Dry test):**

Put a small *solid* sample of the salt in a test tube, then, add few drops of dilute hydrochloric acid.

*There is a brisk effervescence; gas given off is colourless, odourless, turns moist blue litmus paper slightly red, and turns limewater milky. Gas is $CO_2$.*

**b. Test on solution (Wet test):**

To a few drops of the *solution of salt* in a test tube, add a few drops of barium chloride solution.

*A white precipitate is obtained:*

$$CO_3^{2-}(aq) + BaCl_2(aq) \rightarrow \underset{\text{(white)}}{BaCO_3(s)} + 2Cl^-{}_{(aq)}$$

*The precipitate dissolves in dilute HCl, to give a colourless solution..*

$$BaCO_{3\,(s)} + 2HCl_{(aq)} \rightarrow BaCl_{2\,(aq)} + H_2CO_{3\,(aq)}$$

**Revision Exercises**

51 Name one water-soluble and one water-insoluble trioxocarbonate (IV) salt.

52 Consider the general equation below:

$$X_aCO_3(s) \rightarrow X_aO(s) + CO_2(g)$$

The reaction will not occur when X is

A. Cu B. Na C. Mg D. Zn [WAEC]

### Preparation of *Soluble* $CO_3^{2-}$ Salts

1. Trioxocarbonate(IV) salt of potassium or sodium is prepared by passing an *excess of carbon(IV) oxide* into a solution of the alkali, to produce a white precipitate of sodium hydrogentrioxocarbonate(IV) salt; it is moderately soluble in water.

$$NaOH(aq) + CO_2(g) \rightarrow NaHCO_3(s)$$

The precipitate is filtered; then, heated to constant mass, to obtain *anhydrous* $Na_2CO_3$.

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

2. Ammonium trioxocarbonate(IV) is obtained by passing excess of carbon(IV) oxide into ammonia solution. The resulting solution is then concentrated, and crystallized.

$$2NH_3(g) + H_2O(l) + CO_2(g) \rightarrow (NH_4)_2CO_3(aq)$$

### Preparation of *Insoluble* $CO_3^{2-}$ Salts

**1. *By double decomposition method:***

An insoluble trioxocarbonate(IV) salt is prepared by the addition of an aqueous $Na_2CO_3$ to the aqueous solution of the required salt, e.g.

- $Na_2CO_{3(aq)} + CuSO_{4\,(aq)} \rightarrow \underset{\text{(pale green)}}{CuCO_{3\,(s)}} + Na_2SO_{4\,(aq)}$

• $Na_2CO_{3(aq)} + ZnCl_{2(aq)} \rightarrow ZnCO_{3(s)} + 2NaCl_{(aq)}$
(white)

2. Calcium trioxocarbonate(IV) is prepared by passing carbon(IV) oxide into limewater, in order to precipitate the salt, the mixture is then filtered.

$$Ca(OH)_{2(aq)} + CO_{2(g)} \rightarrow CaCO_{3(s)} + H_2O_{(l)}$$
(white)

### Uses of Trioxocarbonate (IV) Salts

• $Na_2CO_3$ is used in softening hard water; in making soap and glass; and as an alkali in acid-base titration.

• $CaCO_3$ is used in making quick lime, cement and glass; in agriculture (in *liming* the soil – to reduce acidity); and in the extraction of iron.

### Solved Problems

**11** Describe and explain the action of dilute hydrochloric acid on eggshells.

*When dilute hydrochloric acid is added to eggshells in a test tube, there is a brisk effervescence, the gas given off is colourless, odourless, and turns moist blue litmus slightly red. The gas turns limewater milky; gas is $CO_2$. These observations are consistent with the fact that eggshells contain $CaCO_3$ which reacts with the acid thus:*

$$CaCO_3(s) + HCl(aq) \rightarrow CaCl_{2(aq)} + H_2O_{(l)} + CO_2\uparrow$$

**12** Which pair of the following trioxocarbonate (IV) is soluble in water?

A. Potassium and zinc B. Sodium and potassium
C. Calcium and sodium D. Ammonium and Lead.

**Solution: *B*.**

### Revision Exercises

**53** Write a balanced equation to show action of heat on ammonium trioxocarbonate(IV).

**54** Mention one use of: a. $Na_2CO_3$; b. $CaCO_3$

## 30.9 Hydrogentrioxocarbonate(IV) Salts, $HCO_3^-$ [Acid Carbonates]

### Properties of $HCO_3^-$ salts

#### 1. Action of Heat

All hydrogentrioxocarbonate(IV) salts decompose, when heated, to give the normal salt, water vapour and carbon (IV) oxide, e.g.

$$2NaHCO_{3(s)} \rightarrow Na_2CO_{3(s)} + H_2O_{(g)} + CO_{2(g)}$$

#### 2. Laboratory tests for $HCO_3^-$ salts

**a. *Test on solid sample (Dry test)*:**

To the solid sample in a test tube, add a few drops of dilute hydrochloric acid.

*There is a brisk effervescence; gas given off is colourless, odourless, turns damp blue litmus paper slightly red, and turns limewater milky. The gas is $CO_2$.*

**b. *Test on solution of salt (Wet test)***

To a few drops of the solution of salt in a test tube, add few drops of barium chloride, $BaCl_2$ solution

*No visible reaction or no precipitate; but on heating the mixture, a white precipitate is formed.*

c. To a few drops of the solution in a test tube, add a few drops of phenolphthalein solution.

*The solution remains colourless or no change in colour, but on heating the mixture, the solution turns pink.*

### Preparation of $HCO_3^-$ salts

Hydrogentrioxocarbonate(IV) salts are prepared by passing a large excess of carbon(IV) oxide into a solution of the alkali, to form a white precipitate of the corresponding hydrogentrioxocarbonate(IV) salt; it is not highly soluble in water, e.g.

*In drops:* $2KOH_{(aq)} + CO_2 \rightarrow K_2CO_{3(aq)} + H_2O$

*In excess:* $K_2CO_{3(aq)} + CO_2 \rightarrow 2KHCO_{3(s)}$

**Note:** $NaHCO_3$ and $KHCO_3$ are less soluble than the other hydrogentrioxocarbonate(IV) salts. $Ca(HCO_3)_2$ and $Ba(HCO_3)_2$ exist in aqueous solution only.

### Uses of $HCO_3^-$ salt

$NaHCO_3$ is the most useful of all acid salts:

•It is an active component of *baking powder*.

•It is used in fire extinguishers.

•It is added to health salts and fizzy drinks to cause effervescence.

•Being weakly alkaline, it is used in *neutralizing* the acid injected by bees when they sting:

$$NaHCO_{3(aq)} + HCOOH_{(l)} \rightarrow HCOONa_{(aq)} + H_2O + CO_{2(g)}$$

• Also used in treating someone who has swallowed an acid or has acid burn – to neutralize the acid.

### Revision Exercises

**55** Name the active components of baking powder.

**56** The following compounds will decompose on heating except

A. $NaHCO_3$ B. $K_2CO_3$ C. $MgCO_3$
D. $Ca(HCO_3)_2$ E. $ZnCO_3$ [NECO]

**57** Describe one chemical test to distinguish between anhydrous $Na_2CO_3$ and $NaHCO_3$.

## 30.10 Fuels

### Definition and Classes of Fuels

A *fuel* is any substance that burns in air or oxygen to produce heat and light.

Most fuels are carbon and its organic compounds; hence, they burn to produce carbon(IV) oxide and sometimes water vapour, with the liberation of large quantities of heat and light.

The various classes of fuels are:
1. ***Solid fuels*** e.g. wood, coal and coke.
2. ***Liquid fuels*** e.g. petrol, kerosene, and alcohol (or methylated spirit)
3. ***Gaseous fuels*** e.g. producer gas, water gas, coal gas, natural gas, paraffin gas, and synthesis gas.
4. ***Human fuels*** e.g. food items in the form of fat and oil, protein, starch and sugar.
5. ***Atomic fuel*** e.g. uranium.

Every fuel has its own *energy (calorific) value*.

**Revision Exercises**

58 What is a fuel?

59 Mention two liquids and two gases that are fuels.

## Gasification of Coal
### *(Gaseous Fuels from Coal)*

The gaseous fuels that are extensively used for industrial and domestic purposes are: *water gas, producer gas, coal gas and synthesis gas.*

**1. Producer gas**

*Producer gas is a mixture of carbon(II) oxide and nitrogen.* It is produced in a furnace by passing *atmospheric air* through *red-hot coke* at about 1000 °C (fig. 30.8). The carbon(IV) oxide produced initially is reduced by more coke to carbon(II) oxide.

The overall reaction is *exothermic*. It is the heat generated that raises the temperature of coke.

$$\underset{}{2C(s)} + \underset{[\leftarrow \text{in air} \rightarrow]}{O_2 + 4N_2} \rightarrow \underset{(30\%)}{2CO(g)} + \underset{(70\%)}{4N_2(g)}$$

In *producer gas*, carbon(II) oxide, which is *combustible*, is about 30% by volume, while nitrogen, which is *incombustible*, is about 70% by volume of the mixture. The presence of *incombustible nitrogen reduces the heating value of producer gas.*

*Producer gas* is used in the industrial production of coal gas, steel and glass.

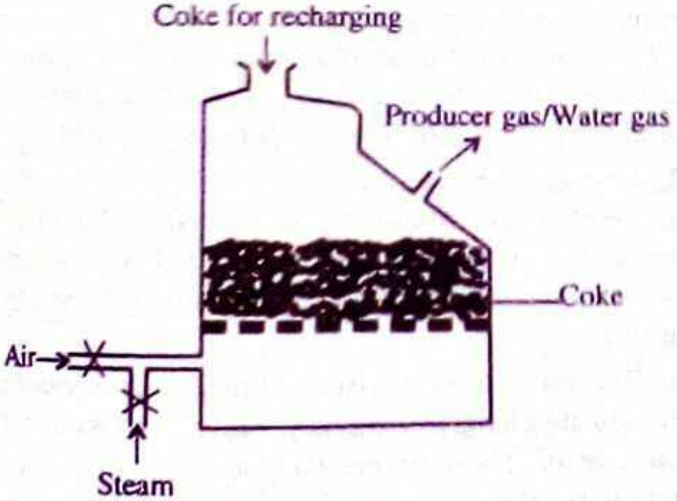



**Fig 30.8** *Production of Producer gas and Water gas*

**2. Water Gas**

***Water gas*** *is a mixture of carbon(II) oxide and hydrogen.* It is produced by passing *steam* through *white-hot coke* at a temperature between 1000 °C and 1200 °C.

$$\underset{}{C(s) + 2H_2O(g)} \rightarrow \underset{(50\%)}{CO(g)} + \underset{(50\%)}{H_2(g)}$$

The reaction is *endothermic* (heat is absorbed); hence, with time, the temperature of the coke falls. In order to raise the temperature to about 1200 °C again, hot air is passed over the coke (to obtain *producer gas*)[fig 30.8].

In *water gas*, each constituent of the mixture is 50% by volume. It is a more useful industrial fuel than *producer gas*, because both carbon(II) oxide and hydrogen in *water gas* are *combustible*.

*Water gas* is used in the production of hydrogen by *Bosch process*. (See Section 28.4).

Industrially, *producer gas* and *water gas* are produced, one after the other, in the same furnace – by passing steam and air alternately through coke; in order to maintain a temperature of about 1000 °C.

**3. Coal Gas**

*Coal gas* is the gaseous product of combustion of coal. It is a mixture of hydrogen (50%), methane (30%) and carbon(II) oxide (10%). Other constituents are ethane (5%) and impurities (5%) such as $H_2S$, $SO_2$, $CO_2$ and $N_2$.

*Coal gas* is widely used as an industrial and domestic fuel. It has more heating value than producer gas, since 95% of its constituents by volume are *combustible*.

**4. Synthesis Gas**

Like *water gas, synthesis gas* is *a mixture of carbon(II) oxide and hydrogen.* However, the mixture is obtained by passing *natural gas (methane) over steam or air in the presence of nickel catalyst.*

$$CH_{4(g)} + H_2O_{(g)} \xrightarrow{\text{Ni, 900 °C}} CO_{(g)} + 3H_{2(g)}$$

$$2CH_{4(g)} + O_{2(g)} \xrightarrow{\text{Ni, 900 °C}} 2CO_{(g)} + 4H_{2(g)}$$

## Separation of the Constituents of Producer gas and Water gas

*Producer gas* is a mixture of carbon(II) oxide and nitrogen, while *water gas* is a mixture of carbon (II) oxide and hydrogen. The two methods of separation are:

**1. Use of Nickel metal:**

When *producer gas* or *water gas* is passed over heated nickel, carbon(II) oxide is removed, due to

the formation of nickel carbonyl; leaving nitrogen, in the case of *producer gas*, and hydrogen, in the case *water gas*.

$$Ni_{(s)} + 4CO_{(g)} \rightarrow Ni(CO)_4 \text{ (Nickel carbonyl)}$$

Carbon(II) oxide can be recovered by decomposing the nickel carbonyl at 180 °C.

$$Ni(CO)_{4\,(g)} \xrightarrow{\Delta} Ni_{(s)} + 4CO_{(g)}$$

**2. Use of ammoniacal solution of $Cu_2Cl_2$**

Ammoniacal solution of copper(I) chloride, $Cu_2Cl_2$ will absorb CO in *producer gas* or *water gas*, leaving nitrogen or hydrogen, as the case may be.

**Solved Problem**

**13a** Name the gaseous fuels obtained when steam and air are passed over red-hot coke.

*Producer gas and water gas*

**b** Which of the fuels in a above has the lower heating ability? Give reason for your answer.

*Producer gas.*

*In producer gas (a mixture of nitrogen, 70% and carbon (II) oxide, 30%) only carbon(II) oxide is combustible; while in water gas (a mixture of carbon(II) oxide, 50% and hydrogen, 50%) both components are combustible. Hence, producer gas has the lower heating value.*

**Revision Exercises**

**60** What is meant by a fuel?

**61** State the components of each of the following:
**a.** water gas; **b.** producer gas; **c.** coal gas; **d.** synthesis gas.

**62** Describe how the components of water gas and producer gas can be separated.

**63** What name is given to the process for the commercial production of hydrogen from water gas?

**64** Give one reason why water gas and producer gas are usually prepared together in the same furnace. [W]

## 30.11 Coal

### Formation of Coal

***Coal*** is an important carbon-containing mineral, which is used as a fuel. It is formed by the gradual decay of plants vegetation, buried deep down the earth's crust.

On being subjected to *high temperature and pressure in the absence of air and moisture*, the vegetation undergoes various changes, passing through the following stages:

***Wood → Peat → Lignite → Bituminous coal → Anthracite***

*Peat, lignite, bituminous coal and anthracite* represent the various *types of coal*. They all contain carbon, hydrogen and oxygen; but the oxygen content is far less than that of *wood*.

*Anthracite* is the driest and the hardest form of coal; it contains the highest percentage of carbon, and *wood the lowest*. It is used as a domestic fuel, because of its high carbon content, and hence, has a high heating value.

Generally, *the higher the carbon content of a fuel, the higher is its heating or energy value.*

### Destructive Distillation of Coal

*Destructive distillation* is the process whereby a *solid matter is heated in the absence of air.*

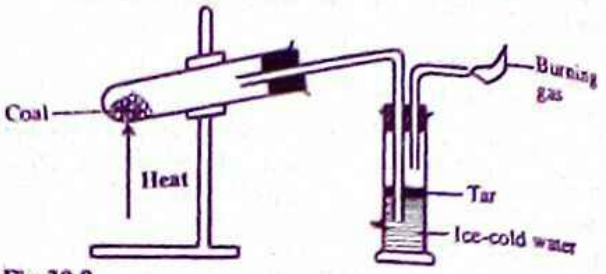



**Fig 30.9**

When coal is heated to about 1000 °C in the absence of air, it decomposes to give four products: *coal gas, ammoniacal liquor, coal tar and coke.*

*Coke* is the solid residue left after all the volatile products have been driven off. Part of the volatile products condenses on cooling, to give *ammoniacal liquor*, which flows on top of the *coal tar* – being lighter. The remaining part of the volatile products is the *coal gas*, which can be collected over water, as shown in figure 30.8.

### Compositions and Uses of Products

**1. Gaseous Products**

***Coal gas*** is the main gaseous product. It is a mixture of hydrogen, methane and carbon(II) oxide, with gaseous impurities such as ethane, hydrogen sulphide and carbon(IV) oxide.

Coal gas is used as an industrial fuel. The sulphur obtained from the hydrogen sulphide impurity is used in producing of tetraoxosulphate(VI) acid.

**2. Liquid Products**

**a.** ***Ammoniacal liquor*** is an aqueous solution of ammonia. On distillation, it gives ammonia, which when converted into ammonium salts, are used as fertilizers.

**b.** ***Coal tar*** is a thick viscous liquid, which can be fractionated to give *benzene, toluene, naphthalene and phenol*. These *by-products* are used in producing *nylon, plastics, explosives, dyes and drugs.*

c. *Pitch* is the black viscous residue obtained from the fractional distillation of coal tar.
It is used in road surfacing.

**3. Solid Products**

*Coke* is the main residue of destructive distillation of coal. It contains 70 – 90% carbon.

Its uses include: In the production of *producer gas* and *water gas*; as a reducing agent in the extraction of metals, such as iron; as an industrial and domestic fuel.

**Destructive Distillation of Wood**

When wood is subjected to destructive distillation, the four products are: *Wood charcoal*; *Pyroligneous acid* (liquid fraction, which is mainly a mixture of ethanoic acid, methanol, and propanone); *Wood tar*; and *Wood gas*.

**Revision Exercises**

66 Name **three** types of coal.
67 List **two** uses of coal.
68 What is destructive distillation?
69 Name **two** products obtained directly from the destructive distillation of coal.
70 Name the process by which benzene is obtained from coal tar.
71 The following industrial products are manufactured from chemicals derived from coal **except**
A. detergents B. dyes C. explosives
D. fertilizers E. plastics.
72 Name **two** products obtained directly from the destructive distillation of wood.

## 30.12 Combustion of Carbon-fuels

*Combustion* is the chemical reaction between a *gas* and a *substance*, which can be a *solid*, *liquid* or *gas*. Most *combustion* reactions involve *pure oxygen or oxygen in air*. The completeness of combustion depends on the quantity of oxygen available.

**1. Combustion of Methane (a hydrocarbon)**

Combustion of methane occurs under *three* different conditions:

**a. *In a limited or inadequate supply of air*:**
There is *incomplete* combustion; methane burns to form carbon as black soot.

$$CH_{4(g)} + O_{2(g)} \rightarrow C_{(s)} + 2H_2O_{(g)}$$

**b. *In a moderate supply of air*:**
*Incomplete* combustion occurs; it gives carbon(II) oxide and steam.

$$2CH_{4(g)} + 3O_{2(g)} \rightarrow 2CO_{(g)} + 4H_2O_{(g)}$$

**c. *In an excess of air*:**
There is *complete* combustion; steam and carbon (IV) oxide are produced.

$$CH_{4(g)} + 2O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(g)}$$

**2. Charcoal (or Coke) Fire**

There are *three* distinct combustion zones in a charcoal or coke fire. Each zone represents a particular chemical change (see fig. 30.10).

**Zone 1**: This is at the *base*, where there is an adequate supply of air. There is *complete* combustion; hence, carbon(IV) oxide is produced.

$$C_{(s)} + O_{2(g)} \rightarrow 2CO_{2(g)}$$

It is the hottest zone; the coke is *white* hot.

**Zone 2**: This is at the *centre* of the fire; there is *poor* supply of air. As the $CO_2$ goes up through the fire, it comes in contact with plenty of *red-hot* coke; it is therefore reduced to carbon (II) oxide.

$$CO_{2(g)} + C_{(s)} \rightarrow 2CO_{(g)}$$

Since there is a poor supply of air, the *red-hot* carbon also burns to produce carbon(II) oxide:

$$2C_{(s)} + O_{2(g)} \rightarrow 2CO_{(g)}$$

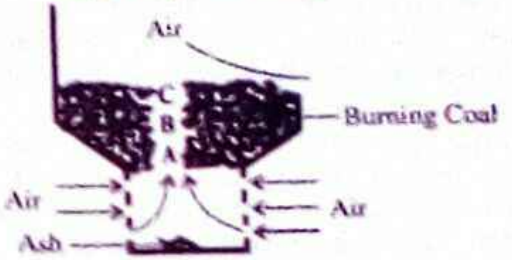



**Fig 30.10** *Production of Producer gas and Water gas*

**Zone 3**: It is at the *surface*; there is plentiful supply of air. Hence, the carbon(II) oxide burns with a pale blue flame to produce carbon(IV) oxide.

$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$$

If the air supply at the surface of the fire is *inadequate*, much of the smoke produced is the poisonous and dangerous carbon(II) oxide. This explain why it is necessary for plenty of air to be available during the burning of fuels, like wood and charcoal at homes, in order to prevent the production of carbon(II) oxide.

**Solved Problem**

**14** A sample of carbon is burnt in excess air at a rate of 0.50 g per second for 30 minutes.
a. Write a balanced equation for the reaction.
b. Determine the:
i. volume of carbon(IV) oxide produced at s.t.p.
ii. moles of oxygen used in the process at s.t.p.
[C = 12, O = 16.0, Molar volume, $V_m$ = 22.4 $dm^3$]

a. $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$

b. *First, calculate the mass of carbon burnt:*
*Mass of carbon burnt* = (0.5 × 30 × 60) g = 900 g.

$C_{(s)}$ + $O_{2(g)}$ → $CO_{2(g)}$
12 g (1 mol) ( 1 mol) 22.4 $dm^3$ (1 mol)

*i. To calculate volume of $CO_2$ produced at stp*
*From the equation of reaction:*
*12 g of carbon produce 22.4 $dm^3$ of $CO_2$ at stp;*
*∴ 900 g produce (22.4 × 900)/12 $dm^3$ = 1680 $dm^3$.*

*ii. To calculate the amount of $O_2$ consumed:*
*From the equation of reaction,*
*12 g of carbon require 1 mol of $O_2$ at stp;*
*∴ 900 g require (1 × 900)/12 mol = 75.0 mol.*

**Revision Exercise**

72 Write an equation to show the combustion of methane insufficient supply of air.

73 In *producer gas* carbon(II) oxide and nitrogen are present in the volume ratio of
A. 1 : 1 B. 1 : 2 C. 1 : 3 D. 2 : 1

## 30.13 The Flame

*A flame is a region of combustion that gives out both heat and light.* It is produced during the combustion of any fuel that contains carbon.

Most fuels burn to produce highly inflammable mixtures of gases, which when ignited bursts into flames, and accompanied by heat and light.

Every fuel has its own *ignition temperature*. The *ignition temperature* of petrol vapour is so low that it bursts into flame when there is a naked light. It is therefore dangerous to store petrol at homes.

### Structure of Flames

There are *two* types of flames: *luminous* and *non-luminous* flames.

A *candle flame* is a typical *luminous flame* with an *irregular shape*, while the *Bunsen burner* can be manipulated to produce either a *luminous flame* with an *irregular shape*, or a *non-luminous flame* with a *regular conical shape*.

### The Bunsen burner

The Bunsen burner was invented by a German chemist, Robert W. Bunsen (1855). It is a device or an instrument used in the laboratory as a source of heat, by burning a bottled gas.

The Bunsen burner consists of a metal *base* with an inlet for gas supply, and an outlet at the jet. It also has a metal *pipe* (or *stem*), which is screwed to the *base*. The *pipe* has two holes directly opposite one another at its lower end with a provision for a rotating metal *ring*, to open or close the holes, in order to regulate air supply to the jet.

### Luminous Flame in Bunsen burner or Candle

A *luminous flame* is produced when the *air holes* in the burner are *closed*. Under this condition, only the gas burns to give a flame, which is similar to that of *candle flame*. The burning *fuel* in a candle flame is *wax vapour*, which is a hydrocarbon.

A *luminous flame* has *four* zones:

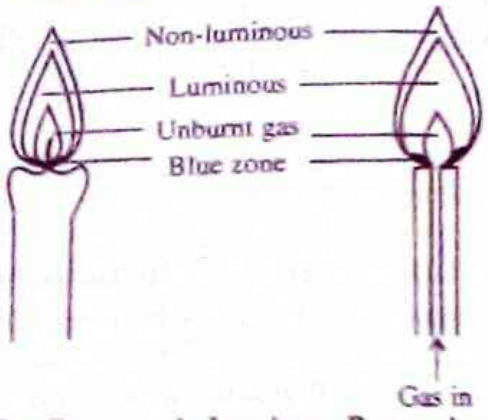
**Zone 1**: It is the large *yellow luminous zone*, due to the presence of particles of carbon that become incandescence, i.e. burn to give the yellow light.

It is a zone of *incomplete* combustion, due to *inadequate* air, it gives out carbon(II) oxide and soot. The presence of carbon particles can be detected by placing a white tile or a piece of paper in the luminous flame for a few seconds; a deposit of black soot will be obtained on the tile or paper.

**Zone 2**: It is a tiny *blue zone* of *complete* combustion; almost invisible. The carbon(II) oxide produced in the luminous zone burns in the surrounding air to produce carbon(IV) oxide.

**Zone 3**: It is the small *pale blue zone* at the *base* of the flame. It is a zone of *complete* combustion. Here, the carbon(II) oxide formed in the luminous zone burns in the surrounding air to produce $CO_2$.

**Zone 4**: It is a zone of unburned *wax vapour*. It is cold and colourless. There is no combustion here.




a. Candle b. Luminous Bunsen burner

**Fig 30.11** *Candle and Bunsen burner Flames*

### Non-luminous Bunsen Flame

The *non-luminous* Bunsen flame is produced when the *air holes in the burner are opened*. Under this condition, a mixture of gas and air is burning. It is usually blue in colour, conical in shape, noisy, steady, and much hotter than the *luminous* flame.

*Non-luminous* Bunsen flame has *three* zones:

**Zone 1**: It is the *outer* zone; a zone of *complete* combustion, due to *adequate* supply of air in the gas and from the surrounding. It is *pale blue*.

**Zone 2**: This is the *inner* zone. It is a small blue area of *incomplete* combustion, due to *inadequate* supply of air.

*Zone 3*: It is the *centre*; a small zone of unburned gas. It appears colourless, since no chemical reaction occurs here.

The *non-luminous* Bunsen flame can become *luminous* under the following conditions:

1. Presence of finely divided carbon particles that become incandescence when heated.
2. Increasing the pressure of the gas supply.
3. Pre-heating of the gas.

**Striking-back action of Bunsen burner flame**

When the *air holes* in the burner are *fully opened* and the *gas supply* is gradually *reduced*, the *flame burns faster*, moves downward, and burns at the jet with a small explosion. This action is called *striking-back*.

*Striking back* is caused by too much of oxygen in the gas-air mixture.

**The Hydrogen Flame**

The hydrogen flame is composed of *two* zones: *blue zone* of *complete* combustion and colourless zone of *unburnt gas*.

**Revision Exercises**

74 What is meant by a flame?

75 Draw a labeled diagram of each of the following to indicate the various zones:
a. A burning candle; b. Bunsen burner flame.

76 Distinguish between luminous and non-luminous flames.

77 Explain the ***striking back action*** of Bunsen flame.

## 30.14 Silicon

### Silicon as an Element

Silicon is directly below carbon in group IV of the Periodic Table. It has a shell configuration of 2, 8, 4 and orbital configuration of $1s^2 2s^2 2p^6 3s^2 3p^2$.

Silicon has a giant network molecular structure, like diamond. It has a high melting point of about 1400 °C, and is regarded as a metalloid – being a conductor of electricity.

### Occurrence of Silicon

Silicon occurs naturally as silicon(IV) oxide, $SiO_2$ called *silica* or *sand*. It also occurs as trioxosilicate (IV) salts.

It is the second most abundant element in the earth's crust; oxygen being the first.

### Compounds of Silicon and their Uses

**Silicon(IV) oxide, $SiO_2$**

It is called *silica* or *sand*. It is the most abundant compound of silicon, and another example of a compound with a giant network molecular structure. Thus, it is hard and brittle, and has a melting point of about 1700 °C. It is insoluble in water, and highly unreactive.

*Sand* is used in making laboratory glassware. A mixture of sand and cement, is used in making concrete.

**Silicon(IV) carbide, SiC**

It is obtained by fusing excess carbon with silica; the silica is reduced by carbon to form a hard and black solid called *carborundum*, SiC.

$$SiO_{2(s)} + C_{(s)} \rightarrow SiC_{(s)} + O_{2(g)}$$

Like diamond, powdered carborundum, SiC, is used as an abrasive – for making grinding wheels and sand-paper, which are used for smoothing hard and rough surfaces, and for sharpening cutlasses, and knives.

**Sodium trioxosilicate(IV), $Na_2SiO_3$**

Silicon(IV) oxide is weakly acidic; it reacts with fused NaOH slowly, to produce the salt and water:

$$SiO_{2\,(s)} + 2NaOH_{(l)} \rightarrow Na_2SiO_{3\,(s)} + H_2O_{(l)}$$

$Na_2SiO_{3(s)}$ dissolves in water to form a thick solution called ***water glass***; used in preserving eggs.

**Silica gel**

When $Na_2SiO_{3(s)}$ is treated with dilute hydrochloric acid, it produces a *gel*, which when heated, loses water and forms a hard and brittle blue solid called *silica gel*.

*Silica gel* has a great affinity for water or moisture; hence, it is used as a drying agent for gases, and as a *desiccant* for drying solids in the desiccators. It is also used in *column chromatography as the stationary phase*.

**Revision Exercises**

79 How many electrons are in the L shell of silicon, $_{14}Si$?

80 Why is silicon referred to as a metalloid?

81 Which compound is called silica?

82 Write an equation to show the reaction of silicon (IV) oxide with coke, and name the type of reaction.

83 State the *colour* and *one* use of each of the following: a. Silica gel; b. Silicon(IV) carbide

84 Write an equation to show that silicon(IV) oxide is acidic.

### Answers to Revision Exercises

11. A 41. C 46. C 47 20.1 *g* 48 4.48 $dm^3$
52. B 56. B 70. A 73. B

# 31

# •NITROGEN AND ITS COMPOUNDS• •PHOSPHORUS•

## 31.1 Introduction

### Structure and Bonding

Nitrogen, $_7N$ is the first element in group V of the Periodic Table; followed by phosphorus. Its orbital configuration is $1s^2\ 2s^2\ 2p^3$.

Nitrogen is a non-metal; it exists as a discrete diatomic molecule, $N_2$, in which the two atoms are linked by a triple covalent bond.

### Revision Exercises

1. Nitrogen (atomic number 7) is in which period of the Periodic Table?
2. State the type of chemical bond between the nitrogen atoms in a nitrogen molecule.

## 31.2 Nitrogen as an Element

### Occurrence of Nitrogen

Nitrogen is found free in air as a gaseous diatomic element, $N_2$. It occupies 80% (4/5) by volume of the atmosphere. It is found in combination with other elements in the earth's crust in the form of trioxonitrate(V) salts of sodium, potassium and calcium; and in plants and animals in the form of proteins and urea.

Nitrogen is found in combination with other elements, as in ammonia, $NH_3$ and hydrazine, $N_2H_4$. It forms oxides, oxy-acids and nitrides with metals.

### Revision Exercises

3. What is the volume of nitrogen in 1.0 $dm^3$ of air?
4. Which of the following does not contain element nitrogen? Cheese; ammonia; sugar; air.

### Laboratory Methods of Preparation

#### 1. From Atmospheric Air

• Atmospheric air is passed over red-hot copper metal in a combustion tube; in order to remove oxygen.

$$Cu_{(s)} + O_{2\ (g)} \rightarrow 2CuO_{(s)}$$

• It is then passed through aqueous NaOH, in order to absorb carbon(IV) oxide:

$$2NaOH_{(aq)} + CO_{2\ (g)} \rightarrow Na_2CO_{3\ (aq)} + H_2O_{(l)}$$

• The residual gas collected over water is nitrogen contaminated with a small quantity of noble gases (fig 31.1).

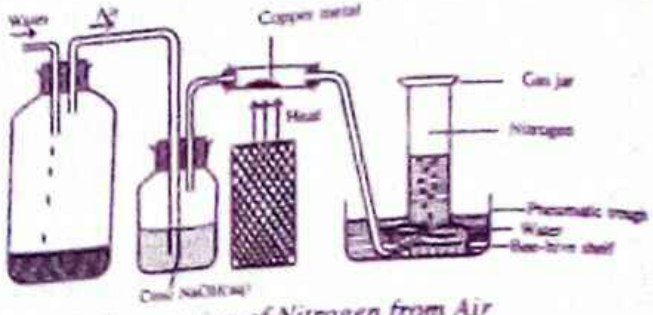



Fig 31.1 *Preparation of Nitrogen from Air*

Nitrogen obtained from the atmosphere is called *atmospheric* nitrogen. It is not pure – since it contains a small quantity of noble gases; hence, it is denser than chemically pure nitrogen.

#### 2. From ammonium dioxonitrate(III)

**Procedure:**

• A mixture of sodium dioxonitrate(III) (10.0 g) and ammonium chloride (7.0 g) dissolved in 100 $cm^3$ of pure water is placed in a round-bottomed flask (fig 31.2).

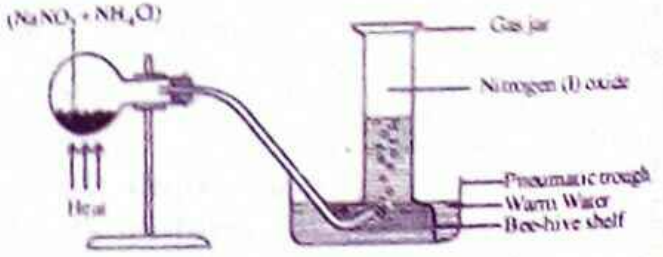



Fig 31.2 *Preparation of nitrogen from its compound*

• The mixture is heated gently; the colourless gas given off is collected over water.

**Chemistry of action**
The reaction goes in two stages:
First, ammonium dioxonitrate(III) is produced:

$$NaNO_{2\,(aq)} + NH_4Cl_{(aq)} \rightarrow NH_4NO_{2\,(aq)} + NaCl_{(aq)}$$

Then, it decomposes to produce nitrogen gas:

$$NH_4NO_{2\,(aq)} \rightarrow N_{2\,(g)} + 2H_2O_{(l)}$$

*Note: Ammonium dioxonitrate(III) is unstable. It should not be heated directly; the reaction is very rapid, and may lead to explosion.*

**3. From Ammonia gas**
Ammonia gas is passed over heated copper(II) oxide in a combustion tube to produce nitrogen gas, which can be collected over water.

$$3CuO_{(s)} + 2NH_{3\,(g)} \rightarrow 3Cu_{(s)} + 3H_2O + N_{2\,(g)}$$

## Physical Properties of Nitrogen

1. Pure nitrogen is colourless and odourless.
2. It is insoluble in water.
3. It is lighter than air.

## Chemical properties of Nitrogen gas

**1. Combustion**
Nitrogen gas is generally unreactive at ordinary temperatures and pressures. It does not burn, and does not support burning; it extinguishes a lighted splint.

**2. Action on Litmus papers**
It has no action on moist litmus paper; neutral to litmus.

**3. Reaction with Metals**
Magnesium ribbon burns in air to produce a mixture of magnesium oxide and magnesium nitride, a white solid.

$$2Mg_{(s)} + O_{2\,(g)} \rightarrow MgO_{(s)}\,(\text{white})$$

$$3Mg_{(s)} + N_{2\,(g)} \rightarrow Mg_3N_{2\,(s)}\,(\text{white})$$

Magnesium nitride decomposes on addition of water to liberate ammonia gas.

$$Mg_3N_{2(s)} + 6H_2O_{(l)} \rightarrow 3Mg(OH)_{2(aq)} + 2NH_{3(g)}$$

**4. Reaction with Non-metals**
a. Under conditions of high temperature and pressure, and in the presence of finely divided iron as catalyst, nitrogen combines with hydrogen, to produce ammonia. The reaction is reversible:

$$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$$

b. Nitrogen combines with oxygen, at high temperature and pressure, to produce nitrogen(II) oxide, an unstable colourless and odourless gas. The reaction is reversible:

$$N_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2NO_{(g)}$$

## Industrial Production of Nitrogen

Like oxygen, nitrogen is produced commercially from *liquefied air* (see Section 18.6). *Liquid air* is subjected to fractional distillation. During the process, nitrogen boils off first and is collected, since it has a lower boiling point (77 K) than oxygen.

## Uses of Nitrogen

1. In the production of ammonia by *Haber process*.
2. Liquid nitrogen is used as a refrigerant.
3. Since it is inert, and does not support combustion, nitrogen is used for the following purposes:

a. For prevention of fire.
b. As a diluent – to reduce combustion. Nitrogen is responsible for the low heating value of *producer gas*, and the low combustion rate of atmospheric oxygen.
c. Nitrogen provides inert atmosphere for food processing and packaging, and during some chemical reactions.

## Solved Problems

**1.** When powdered magnesium is heated to redness in a stream of nitrogen, magnesium nitride is formed.

a. Give the physical state, colour, and formula of magnesium nitride.
*Magnesium nitride is a white solid with the formula $Mg_3N_2$.*

b. Write an equation for the reaction.

$$3Mg_{(s)} + N_{2\,(g)} \rightarrow Mg_3N_{2\,(s)}$$

c. Calculate the amount, in mole, of magnesium nitride that can be obtained from 3.0 g of magnesium. [Mg = 24]
*Given: 3.0 g of Mg; Required: amount of $Mg_3N_2$*
*This is mass-mole relationship.*
*From the equation of reaction:*

$$3Mg_{(s)} + N_{2\,(g)} \rightarrow Mg_3N_{2\,(s)}$$
$$3\ mol \qquad\qquad 1\ mol$$
$$(3 \times 24)g$$

*$(3 \times 24)g$ of $Mg \equiv 1$ mol of $Mg_3N_2$*
*$\therefore$ 3 g of $Mg \equiv (1 \times 3)/(3 \times 24)$ mol*
*$= 0.0420$ mol of $Mg_3N_2$*

**2.** State how nitrogen can be obtained from $NH_3$
*By passing ammonia gas over heated copper(II) oxide; ammonia is oxidized to nitrogen.*

$$CuO_{(s)} + NH_{3\,(g)} \rightarrow 3Cu_{(s)} + H_2O + N_{2\,(g)}$$

**3.** How does nitrogen resemble or differ from $CO_2$ in its reaction with each of the following:

a. Lime water;
*Carbon(IV) oxide turns limewater milky, while nitrogen has no effect on lime water.*

b. Litmus solution;
*$CO_2$ turns damp blue litmus paper red, while nitrogen has no effect on litmus.*

c. A burning candle;
*Both of them will extinguish a burning candle.*

d. Burning magnesium;
*Burning magnesium will reduce $CO_2$ to carbon, and form magnesium nitride with nitrogen.*

- $2Mg_{(s)} + CO_{2\,(g)} \rightarrow 2MgO_{(s)} + C_{(s)}$
- $3Mg_{(s)} + N_{2\,(g)} \rightarrow Mg_3N_{2\,(s)}$.

**Revision Exercises**

5. Outline the laboratory preparation of nitrogen from atmospheric air.
6. Draw a labelled diagram for the laboratory preparation of pure nitrogen.
7. Nitrogen can be obtained in the laboratory from
   A. a solution of sodium trioxonitrate (V) and ammonium chloride.
   B. a solution of sodium dioxonitrate (III) and ammonium chloride.
   C. a solution of sodium dioxonitrate (III) and calcium chloride.
   D. concentrated tetraoxosulphate (V) and sodium trioxonitrate (V). [WAEC]
8. Name the process used in the commercial production of nitrogen.
9. What is the percentage by volume of nitrogen in air?

## 31.3 Ammonia, $NH_3$

### Structure and Bonding in Ammonia

Ammonia is a covalent molecule in which an atom of nitrogen shares a pair of electrons, separately, with three hydrogen atoms; it leads to the formation of a discrete molecule:

$$\begin{array}{c} H \\ | \\ H-N-H \end{array}$$

The molecule is polar, due to the large difference in the electronegativities of nitrogen and hydrogen.

At ordinary temperatures and pressures, $NH_3$ is a gas. The small amount of ammonia in the atmosphere, as an impurity, is due to the decay of nitrogenous matter (dead plants and animals) in air, and the burning of animal products, such as hairs, feathers, hoofs and horns.

Ammonia is a hydride of nitrogen; another hydride is hydrazine, $N_2H_4$.

### Laboratory Preparation of Ammonia

Ammonia gas is produced by the action of heat on a mixture of *an alkali* and *any ammonium salt*:

$$OH^- + NH_4^+ \rightarrow H_2O_{(l)} + NH_{3\,(g)}$$

**Procedure**

1. A mixture of slaked lime, calcium hydroxide (15.0 g) and ammonium chloride (20.0 g) is placed in a round-bottomed flask, and heated (fig 31.3).

$$Ca(OH)_{2\,(s)} + 2NH_4Cl_{(s)} \longrightarrow CaCl_{2\,(aq)} + 2H_2O_{(g)} + 2NH_3\uparrow$$

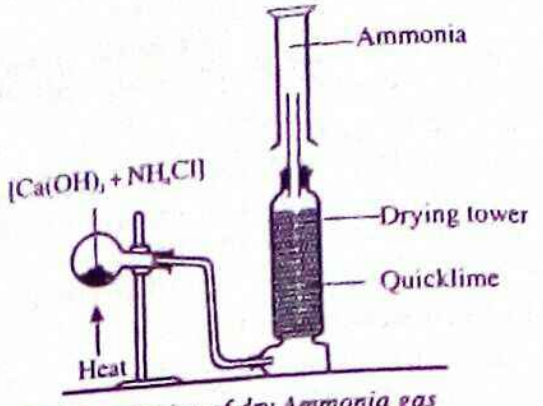



Fig 31.3 *Preparation of dry Ammonia gas*

2. The colourless gas evolved is passed through a tower of quick lime, calcium oxide, to dry the gas.
3. The gas is collected in a gas jar by upward delivery (i.e. downward displacement of air), since it is lighter than air.

**Precaution:** The neck of the flask must slope forward; in order to drive away the steam produced, and hence, prevent it from condensing into the hot glass flask.

**Notes:**

1. Common drying agents, such as concentrated $H_2SO_4$, fused calcium chloride, and phosphorus (V) oxide cannot be used to dry ammonia:
   - Conc $H_2SO_4$ reacts with $NH_3$ to produce a salt:
     $$H_2SO_{4\,(l)} + 2NH_{3\,(g)} \rightarrow (NH_4)_2SO_{4\,(s)}$$
   - Fused calcium chloride form a complex with $NH_3$
     $$CaCl_{2\,(s)} + 4NH_{3\,(g)} \rightarrow CaCl_2{\cdot}4NH_{3\,(s)}$$
   - Phosphorus(V) oxide (acidic) reacts with $NH_3$ (basic) to produce a salt:
     $$P_2O_{5\,(s)} + 6NH_{3\,(g)} + 3H_2O_{(l)} \rightarrow 2(NH_4)_3PO_{4\,(s)}$$
2. *Silica gel* is also a suitable drying agent for $NH_3$.

### Physical Properties of Ammonia gas

1. Ammonia, when pure, is a colourless gas with a characteristic *choking* smell.
2. It is lighter than air; hence, it is collected by upward delivery.
3. It is highly soluble in water. When a gas jar of ammonia is inverted over a beaker of water, there is an immediate rise in the water level in the jar. The high solubility of ammonia in water is due to hydrogen bonding between molecules of water and

ammonia. The gas can be used to demonstrate the *fountain experiment.*

4. Ammonia gas is readily liquefied; being polar, and with hydrogen bonds *between* the molecules.

## Chemical Properties of Ammonia gas

### 1. Reaction with Water

Ammonia gas dissolves in, and reacts with water to form an unstable ammonium hydroxide solution:

$$NH_{3\,(g)} + H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)}$$

The solution is *weakly alkaline*. A solution of ammonia gas in water is called *aqueous ammonia*, $NH_{3(aq)}$.

### 2. Action on Litmus

Ammonia gas turns *moist* red litmus paper blue; it is the only alkaline gas.

### 3. Reactions with Acids

Being an alkaline gas, ammonia neutralizes acids: it reacts with dilute $H_2SO_4$, a dibasic acid, under two conditions:

- With *excess acid*, an *acid salt* is formed;

$$NH_{3\,(g)} + H_2SO_{4\,(aq)} \rightarrow NH_4HSO_{4\,(aq)}$$

- With *excess ammonia*, a *normal salt* is formed;

$$2NH_{3\,(g)} + H_2SO_{4\,(aq)} \rightarrow (NH_4)_2SO_{4\,(aq)}$$

These reactions explain why concentrated $H_2SO_4$ cannot be used to dry ammonia gas.

### 4. Combustion of Ammonia gas

Dry ammonia gas burns in a supply of pure oxygen gas to produce nitrogen and water vapour.

$$4NH_{3\,(g)} + 3O_{2\,(g)} \rightarrow 6H_2O_{(l)} + 2N_{2\,(g)}$$

### 5. Reducing properties of ammonia gas

Ammonia acts as a reducing agent:

***a. With Copper(II) oxide***

When dry ammonia gas is passed over heated copper(II) oxide, ammonia is oxidized to nitrogen, while the black copper (II) oxide is reduced to a reddish-brown copper metal.

$$3CuO_{(s)} + 2NH_{3\,(g)} \rightarrow 3Cu_{(s)} + 3H_2O_{(l)} + 2N_{2\,(g)}$$

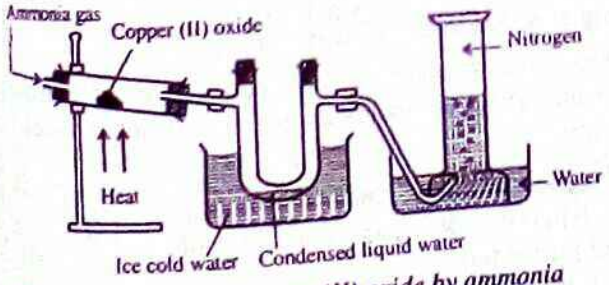



**Fig 31.4** *Reduction of copper(II) oxide by ammonia*

***b. With Chlorine gas***

When dry ammonia gas is passed into a gas jar of excess of chlorine (greenish-yellow gas), a colourless mixture of gases is obtained; ammonia is reduced to nitrogen, while chlorine is oxidized to hydrogen chloride.

$$2NH_{3\,(g)} + 3Cl_{2\,(g)} \rightarrow N_{2\,(g)} + 6HCl_{(g)}$$

If ammonia is in excess, the hydrogen chloride produced combines with more ammonia gas to form a dense white fume of ammonium chloride.

$$NH_{3\,(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)}$$

### 6. Laboratory chemical test for ammonia gas

When ammonia gas comes in contact with hydrogen chloride gas (from a reagent bottle of concentrated hydrochloric acid), *dense white fumes of ammonium chloride is formed.*

$$NH_{3\,(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)}$$

## The Fountain Experiment

The *fountain experiment* is used to show that some gases, such as $NH_3$, are *highly soluble in water.*

***Procedure and Observations:***

- A round-bottomed flask filled with dry ammonia is fitted with two glass delivery tubes, and then closed by the use of clips at A and B (fig. 31.5).
- The inverted flask is then placed in a beaker of water into which a few drops of phenolphthalein have been added (the solution remains colourless).
- The clip at A is slightly opened to allow a small volume of water to enter the flask, and then closed again. The ammonia gas in the flask dissolves in the water; the solution turns pink, and there is a sudden reduction of gas pressure in the flask.
- The clip at B is now opened; the reduced gas pressure in the flask forces water from the beaker through the delivery tube into the flask in the form of a ***fountain*** at C.

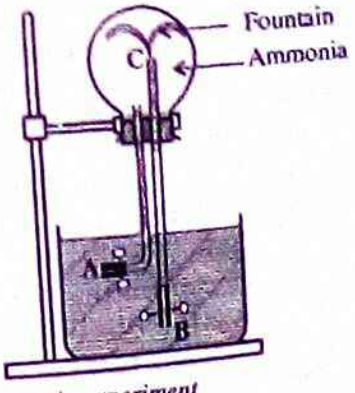



**Fig 31.5** *The fountain experiment*

### Industrial Production of Ammonia:

***The Haber process***

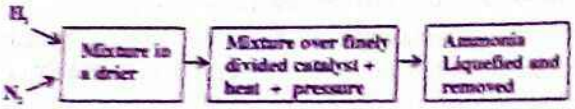
Ammonia is manufactured from its constituent elements by a process devised by a German chemist, Fritz Haber (1914).

- The raw materials used are: nitrogen (obtained from *liquefied air*), and hydrogen (obtained from *water gas* or *natural gas*).
- A mixture of dried nitrogen and hydrogen, in the ratio 1: 3 by volume is subjected to a high pressure of 200 – 250 atmospheres, at about 450 °C, and in the presence of *finely divided iron* as the catalyst; the reaction is exothermic and reversible.

$$N_{2\,(g)} + 3H_{2\,(g)} \underset{250\ atm.}{\overset{Fe,\ 450\ ^\circ C}{\rightleftharpoons}} 2NH_{3\,(g)}$$

- Under these conditions, about 20% ammonia is produced.
- Successive heating and cooling under pressure liquefy the ammonia produced, and the uncombined nitrogen and hydrogen are recycled.

***The flow chart for the production of ammonia***




### Other Industrial Sources of Ammonia

***1. From ammoniacal liquor***

Ammonia gas is obtained by the fractional distillation of ammoniacal liquor – a by-product of coal.

***2. From proteinous substances***

Ammonia gas is usually emitted when proteinous substances, such as feathers, hairs, hoofs and horns of animals are burned in a limited supply of air, and during the bacterial decay of dead plants and animals.

### Solved Problems

**4.** State and explain what will be observed when ammonia reacts with excess chlorine.

*The greenish-yellow chlorine turns colourless. This is due to the formation of a colourless mixture of nitrogen and hydrogen chloride.*

$$2NH_{3\,(g)} + 3Cl_{2\,(g)} \rightarrow N_{2\,(g)} + 6HCl_{(g)}$$

**5.** Which of the following gases is not used as a coolant? $N_2$; $O_2$; $NH_3$; $CO_2$

*Oxygen is not used as a coolant*

### Revision Exercises

**10** State the type of chemical bond between nitrogen and hydrogen atoms in a molecule of ammonia.

**11** Draw a well-labelled diagram for the laboratory preparation of a dry sample of ammonia. [NECO]

**12** List **two** reactants for the laboratory preparation of ammonia, and write an equation for the reaction.

**13** Explain why fused calcium chloride cannot be used to dry ammonia gas.

**14** Name **two** drying agents that can be used to dry ammonia gas. [WAEC]

**15** State **three** physical properties of ammonia.

**16** Explain why ammonia gas can be readily liquefied.

**17** Write an equation to show the reducing property of ammonia. [NECO]

**18** Describe **one** chemical test for ammonia gas.

**19** What property of ammonia makes it suitable for the *fountain experiment*?

**20** In the industrial production of ammonia:

a. What name is given to the process?

b. State one source of each of the starting materials.

c. What are the operating temperature and pressure?

## 31.4 Ammonia solution, $NH_3(aq)$

### Preparation of Ammonia solution

A solution of ammonia gas in water is called aqueous ammonia, $NH_3(aq)$.

$$NH_{3\,(g)} + H_2O_{(l)} \rightarrow NH_{3\,(aq)}$$

It is sometimes called ammonium hydroxide, since the solution ionizes slightly, to produce $OH^-$:

- $NH_{3\,(g)} + H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)}$
- $NH_4OH_{(aq)} \rightleftharpoons NH_4^+ + OH^-_{(aq)}$

Ammonium hydroxide exists as a solution only; it does not exist as a solid.

*Ammonia solution* is prepared by passing *ammonia gas* into water through an inverted funnel that is just touching the water surface. This is to prevent *sucking-back*, as the gas is highly soluble in water.

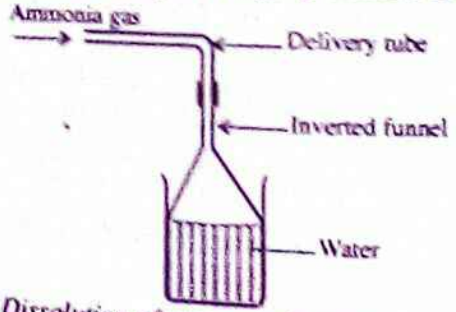



**Fig 31.6** *Dissolution of ammonia in water*

*Ammoniacal liquor*, an industrial source of aqueous ammonia, is obtained by the destructive distillation of coal (see Section 30.11).

### Properties of Ammonia solution

**1.** Ammonia solution is weakly alkaline; it turns red litmus blue.

**2.** It neutralizes acids to produce salts and water:

• Aqueous ammonia neutralizes hydrochloric acid to produce ammonium chloride solution.

$$NH_{3(aq)} + HCl_{(aq)} \rightarrow NH_4Cl_{(aq)}$$

• When $CO_{2(g)}$ is bubbled into $NH_{3(aq)}$, ammonium trioxocarbonate(IV) solution is obtained:

$$2NH_{3(aq)} + H_2O_{(l)} + CO_{2(g)} \rightarrow (NH_4)_2CO_{3(aq)}$$

3. Ammonia solution precipitates metal ions in solutions as *insoluble* hydroxides. Hence, it is used in the *qualitative* identification of cations.

**Procedure:**

*To an aqueous solution of the salt in a test tube, add aqueous ammonia in drops, then, in excess.*

**Expected Results:**

| Cation | Observation |
|---|---|
| $Zn^{2+}_{(aq)}$ | In drops, a *white gelatinous precipitate* of insoluble zinc hydroxide is formed: $Zn^{2+}_{(aq)} + 2NH_{3(aq)} + 2H_2O_{(l)} \rightarrow Zn(OH)_{2(s)} + 2NH_4^+{}_{(aq)}$ In excess $NH_{3(aq)}$, precipitate dissolves: $Zn(OH)_{2(s)} + 6NH_{3(aq)} \rightarrow [Zn(NH_4)_6]^{2+}_{(aq)} + 2OH^-_{(aq)}$ (Zinc hydroxide is amphoteric) |
| $Al^{3+}_{(aq)}$ | A *white gelatinous precipitate* is formed in drops, insoluble in excess ammonia: $Al^{3+}_{(aq)} + 3NH_{3(aq)} + 3H_2O_{(l)} \rightarrow Al(OH)_{3(s)} + 3NH_4^+{}_{(aq)}$ |
| $Pb^{2+}_{(aq)}$ | A *white precipitate* is formed in drops, insoluble in excess ammonia: $Pb^{2+}_{(aq)} + 2NH_{3(aq)} + 2H_2O_{(l)} \rightarrow Pb(OH)_{2(s)} + 2NH_4^+{}_{(aq)}$ |
| $Fe^{2+}_{(aq)}$ | A *green gelatinous precipitate* is formed in drops, insoluble in excess ammonia: $Fe^{2+}_{(aq)} + 2NH_{3(aq)} + 2H_2O_{(l)} \rightarrow Fe(OH)_{2(s)} + 2NH_4^+{}_{(aq)}$ |
| $Fe^{3+}_{(aq)}$ | A *brown gelatinous precipitate* is formed in drops, insoluble in excess $NH_{3(aq)}$: $Fe^{3+}_{(aq)} + 3NH_{3(aq)} + 3H_2O_{(l)} \rightarrow Fe(OH)_{3(s)} + 3NH_4^+{}_{(aq)}$ |
| $Cu^{2+}_{(aq)}$ | A *blue gelatinous precipitate* is formed in drops: $Cu^{2+}_{(aq)} + 2NH_{3(aq)} + 2H_2O_{(l)} \rightarrow Cu(OH)_{2(s)} + 2NH_4^+{}_{(aq)}$ Precipitate dissolves in excess $NH_{3(aq)}$ to give a ***deep blue*** solution of copper (II) tetraammine ions: $Cu(OH)_{2(s)} + 4NH_{3(aq)} \rightarrow [Cu(NH_3)_4]^{2+}_{(aq)} + 2OH^-_{(aq)}$ |

### Uses of ammonia gas and aqueous ammonia

1. Ammonia gas is used in refrigeration; since it can be liquefied easily.
2. In softening temporary hard water used in laundry; to prevent wastage of soap.
3. Used as a domestic cleaner – to neutralize acid in sweat.
4. In treating insect stings – to neutralize methanoic acid injected by the insects.
5. In the production of plastics by polymerization.
6. In the production of ammonium salts, fertilizers, and trioxonitrate(V) acid.
7. As a precipitating reagent for the identification of cations in aqueous solutions.

**Solved Problem**

6 Explain why ammonia solution is often applied to insect stings.

*Ammonia solution is a weak base, while insect stings contain methanoic acid, which a weak acid. It is applied for neutralization to occur.*

**Revision Exercises**

21 Give two uses of aqueous ammonia.

22 Name the process by which ammoniacal liquor can be obtained from coal.

23 What will be the pH of aqueous ammonia: less than 7, exactly 7, or greater than 7? Explain.

24 State what will be observed when aqueous ammonia is added to each of the following:
a. $Zn(NO_3)_2(aq)$; b. $Cu(NO_3)_2(aq)$;

## 31.5 Ammonium Salts

### Formation of Ammonium ion, $NH_4^+$

Ammonium ion, $NH_4^+$ is formed by the dative (or coordinate covalent) combination of a molecule of ammonia and hydrogen ion.

$$H^+ + NH_3 \rightarrow NH_4^+$$

Ammonium ion forms ionic compounds similar to monovalent metal ions such as $Na^+$, $Li^+$ and $K^+$, e.g. $NH_4Cl$ is ammonium chloride.

### Preparation of Ammonium salts

All ammonium salts are soluble in water; hence, they are prepared by crystallization method.

The method involves neutralization reaction; i.e. treatment of the appropriate acid with bench ammonia solution e.g.

### Preparation of Ammonium chloride crystals

The appropriate reagents and reaction:

$$NH_{3(aq)} + HCl_{(aq)} \rightarrow NH_4Cl_{(aq)}$$

**Procedure**

• Place about 100 $cm^3$ of bench hydrochloric acid in a beaker, and add bench ammonia solution from a reagent bottle into the acid with stirring.

• Continue the addition until the resulting solution turns red litmus paper blue; i.e. a slight excess of ammonia solution has been added to the acid.

• Boil the mixture, to expel excess ammonia gas.
• Concentrate the solution, then, crystallize.
• Filter and dry the crystals between filter papers, and store in the desiccator.

### Properties of Ammonium salts

**1. Solubility:**
All ammonium salts are soluble in water.

**2. Laboratory Test for Ammonium salts:**
Place any ammonium salt in a test tube, add any alkali, and heat the mixture.
*A colourless gas with choking smell is given off. The gas turns moist red litmus paper to blue, and produces dense white fumes with hydrogen chloride gas (from concentrated HCl reagent bottle). The gas is ammonia.*

$$NH_4^+ + OH^- \rightarrow H_2O_{(l)} + NH_3\uparrow$$

**3. Action of heat on ammonium salts**
All ammonium salts decompose when heated:
**a. Ammonium chloride** crystals decompose when heated in a test tube, to give a mixture of ammonia and hydrogen chloride:

$$NH_4Cl_{(s)} \rightarrow NH_{3\,(g)} + HCl_{(g)}$$

**b Ammonium trioxocarbonate(IV)** decomposes to give gaseous products; leaving no *residue*:

$$(NH_4)_2CO_{3\,(s)} \rightarrow 2NH_{3\,(g)} + H_2O_{(g)} + CO_{2\,(g)}$$

**c. Ammonium trioxonitrate(V)** decomposes, to give a mixture of nitrogen(I) oxide and steam – gaseous products:

$$NH_4NO_{3\,(s)} \rightarrow N_2O_{\,(g)} + H_2O_{(g)}$$

**d. Ammonium dioxonitrate(III)** decomposes, to give a mixture of nitrogen and steam:

$$NH_4NO_{2\,(s)} \rightarrow N_{2\,(g)} + H_2O_{(g)}$$
(unstable)

**e. Ammonium tetraoxosulphate(VI)** crystals decompose, when heated, to give ammonia gas and aqueous tetraoxosulphate(VI) acid:

$$(NH_4)_2SO_{4\,(s)} \rightarrow 2NH_{3\,(g)} + H_2SO_{4\,(aq)}$$

### Uses of Ammonium salts

1. $NH_4Cl_{(s)}$ ***(sal-ammoniac)*** is used in dry cells (batteries) and in solder flux (for soldering).
2. $(NH_4)_2CO_{3(s)}$ is used as a smelling salt – to stimulate human heart.
3. $NH_4NO_{3(s)}$ is used as fertilizers and as explosive.
4. $(NH_4)_2SO_{4(s)}$ is used as fertilizers.

### Revision Exercises

25 What type of reaction is involved in the conversion of ammoniacal liquor to $(NH_4)_2SO_4$ by dilute $H_2SO_4$?
26 State what is observed on warming ammonium trioxonitrate (V) with sodium hydroxide. [WAEC]
27 Explain why ammonium trioxocarbonate(IV) leaves no residue on being heated. [WAEC]
28 Why is nitrogen gas prepared from air is denser than the one prepared from $NH_4NO_3$?
29 Mention **one** use of an ammonium salt. [NECO]

## 31.6 Trioxonitrate(V) acid, $HNO_3$

### Oxy-acids of Nitrogen

Trioxonitrate(V) [*nitric*] acid, $HNO_3$ is one of the *oxy-acids* of nitrogen; the other is dioxonitrate(III) [*nitrous*] acid, $HNO_2$.

### Laboratory Preparation of $HNO_3$

**Procedure**
• Place a mixture of potassium trioxonitrate (V) crystals (20.0 g) and concentrated tetraoxosulphate (VI) acid (20.0 $cm^3$) in a retort flask and connect up the apparatus as shown in figure 31.7.

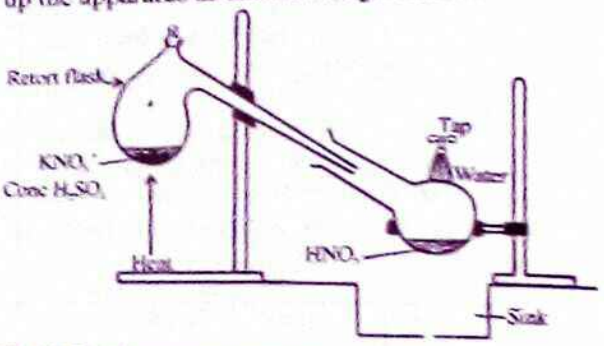



Fig 31.7 *Laboratory preparation of $HNO_3$*

• Heat the mixture gently, and collect the yellowish-brown fumes given off in a water-cooled round-bottomed flask.

$$KNO_{3\,(s)} + H_2SO_{4\,(l)} \rightarrow KHSO_{4\,(aq)} + HNO_{3\,(l)}$$

***Precautions***
• The entire apparatus should be made of glass, because $HNO_3$ is highly corrosive, and its vapour will attack rubber and wooden corks.
• The mixture should be heated gently, in order not to decompose the $HNO_3$ prepared. The yellowish-brown fumes observed is due to the decomposition of a small amount of $HNO_3$ to produce brown fume of nitrogen(IV) oxide, which dissolve in the acid to give it a yellowish-brown colour. The colour is removed by passing air into the solution.

### Physical properties of $HNO_3$

1. Pure $HNO_3$ is a colourless liquid; it is called ***aqua fortis*** (*strong water*).
2. Its density is 1.50 $gcm^{-3}$.
3. It boils at 85 °C under atmospheric condition.
4. It is miscible with water; the process is exothermic. (Care: Always *add acid to water*).

5. It is highly corrosive; it will attack skin, rubber, wooden corks, or any organic matter. Hence, *all-glass apparatus* must be used in the preparation.

## Chemical Properties of $HNO_3$

**1. As a dilute acid:** $HNO_3$ is a typical acid.

a. It turns blue litmus paper red.

b. It neutralizes bases to produce salts and water.

- $KOH_{(aq)} + HNO_{3(aq)} \rightarrow KNO_{3(aq)} + H_2O_{(l)}$
- $CuO(s) + 2HNO_{3(aq)} \rightarrow Cu(NO_3)_{2(aq)} + H_2O_{(l)}$

c. It liberates hydrogen gas only when it is very dilute, and with metals such as K, Na, Ca and Mg.

$$Mg_{(s)} + 2HNO_{3(aq)} \rightarrow Mg(NO_3)_{2(aq)} + H_{2(g)}$$

d. It liberates carbon(IV) oxide when treated with a trioxocarbonate(IV) or hydrogentrioxocarbonate (IV) salt.

- $Na_2CO_{3(s)} + 2HNO_{3(aq)} \longrightarrow 2NaNO_{3(aq)} + H_2O_{(l)} + CO_{2(g)}$
- $NaHCO_{3(s)} + HNO_{3(aq)} \longrightarrow NaNO_{3(aq)} + H_2O_{(l)} + CO_{2(g)}$

**2. As an Oxidizing Agent**

a. ***Reaction with metals***:

Unlike other strong acids, dilute $HNO_3$ is a strong oxidizing agent; hence, it does not liberate hydrogen gas with most metals:

i. With reactive metals, such as K, Na, and Ca: hydrogen gas is liberated with a *very dilute* $HNO_3$:

$$Ca_{(s)} + 2HNO_{3(aq)} \rightarrow Ca(NO_3)_{2(aq)} + H_{2(g)}$$

ii. With moderately reactive metals, such as Mg, Zn and Fe, the dilute $HNO_3$ is reduced to nitrogen (IV) oxide; hence, a brown gas is evolved. The hydrogen gas that would have been given off is oxidized to water.

$$Zn_{(s)} + 4HNO_{3(aq)} \rightarrow Zn(NO_3)_{2(aq)} + 2NO_{2(g)} + 2H_2O$$

iii. With less reactive metals, such as Pb and Cu, the products depend on its concentration:

I. When the acid is concentrated, $NO_2$ is liberated:

$$Cu_{(s)} + 4HNO_{3(aq)} \longrightarrow Cu(NO_3)_{2(aq)} + 2NO_{2(g)} + 2H_2O_{(l)}$$

II. When the acid is cold and half-diluted with water, NO gas is evolved:

$$3Cu_{(s)} + 8HNO_{3(aq)} \longrightarrow 3Cu(NO_3)_{2(aq)} + 2NO_{(g)} + 4H_2O_{(l)}$$

iv. Concentrated $HNO_3$ reacts slowly with Al, Fe, or Cr, and then stops. This is due to the formation of a protective layer of oxide on the metal surface; hence, the acid makes the metals passive.

v. Concentrated $HNO_3$ does not react with gold, Au and platinum, Pt.

b. ***Reaction with non-metals***:

Hot concentrated $HNO_3$ oxidizes carbon, phosphorus and sulphur to the corresponding oxy-acids:

- $C_{(s)} + 4HNO_{3(aq)} \rightarrow H_2CO_{3(aq)} + H_2O_{(l)} + 4NO_{2(g)}$
- $P_{(s)} + 5HNO_{3(aq)} \rightarrow H_3PO_{4(aq)} + H_2O_{(l)} + 5NO_{2(g)}$
- $S_{(s)} + 6HNO_{3(aq)} \rightarrow H_2SO_{4(aq)} + 2H_2O_{(l)} + 6NO_{2(g)}$

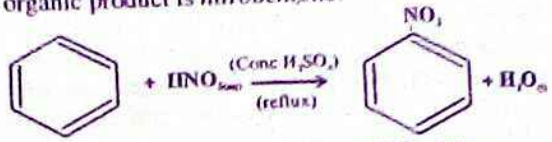
c. ***Reaction with iron(II) salts***:

Hot concentrated $HNO_3$ oxidizes *green* solution of iron(II) ions to *brown* solution of iron(III) ions.

$$\underset{\text{(green)}}{Fe^{2+}_{(aq)}} \rightarrow \underset{\text{(brown)}}{Fe^{3+}_{(aq)}} + e^-$$

d. ***Reaction with benzene: Nitration* reaction**

When concentrated $HNO_3$ is *boiled* with benzene using concentrated $H_2SO_4$ as the catalyst, the organic product is *nitrobenzene*:




$C_6H_{6(l)}$ (Benzene) $\qquad$ $C_6H_5{-}NO_{2(l)}$ (nitrobenzene)

**3. Dehydration of $HNO_3$**

When fuming trioxonitrate (V) acid is treated with $P_2O_5$ and the mixture is distilled, $N_2O_5$ is obtained as a white solid; $P_2O_5$ is a dehydrating agent:

$$2HNO_{3(aq)} + P_2O_{5(s)} \rightarrow 2HPO_{3(aq)} + N_2O_{5(s)}$$

**4. Thermal Decomposition of $HNO_3$**

When concentrated $HNO_3$ is strongly heated in a combustion tube, it decomposes to give a mixture of brown fumes of $NO_2$, water vapour, and oxygen:

$$4HNO_{3(l)} \rightarrow 2H_2O_{(l)} + 4NO_{2(g)} + O_{2(g)}$$

If the gaseous products are collected over water, the steam condenses and the $NO_2$ dissolves in the water – leaving only oxygen in the gas jar.

## Industrial Production of $HNO_3$:

***Catalytic Oxidation of Ammonia***

Large-scale production of trioxonitrate(V) acid is by the *catalytic oxidation of ammonia* obtained by the Haber process. The production goes through the following stages:

1. A mixture of pure and dry ammonia and purified air is passed over a platinum-rhodium catalyst in a chamber at about 8 atmospheres and 500 °C, to obtain nitrogen(II) oxide.

$$4NH_{3(g)} + 5O_{2(g)} \xrightarrow[\text{(8 atm; 500 °C)}]{\text{Pt-Rh}} 4NO_{(g)} + 6H_2O_{(g)}$$

The reaction is highly exothermic.

2. The nitrogen(II) oxide is cooled; then, reacts with more air, to form brown fumes of nitrogen (IV) oxide:

$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$$

3. The nitrogen(IV) oxide is passed through an absorption tower, where it dissolves in, and reacts with water and more air, to give the required trioxonitrate(V) acid.

$$4NO_{2\,(g)} + 2H_2O_{(l)} + O_{2\,(g)} \rightarrow 4HNO_{3\,(l)}$$

### Uses of Trioxonitrate(V) acid

1. Largely used in the manufacture of trioxonitrate (V) salts, which are mostly used as fertilizers.
2. In the manufacture of drugs, explosives – such as trinitrotoluene (TNT), and dynamites.
3. As a *nitrating agent* – in the production of dyestuffs.

### Solved Problems

7. Explain the differences in the reaction of zinc with dilute trioxonitrate(V) acid, and zinc with dilute hydrochloric acid.

*•When zinc reacts with dilute HCl, the acid is reduced to hydrogen; hence, a colourless gas is evolved:*

$$Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2\,(aq)} + H_{2\,(g)}$$

*•When zinc reacts with dilute $HNO_3$, the acid is reduced to nitrogen(IV) oxide; hence, a brown gas is evolved.*

$$Zn_{(s)} + 4HNO_{3\,(aq)} \rightarrow Zn(NO_3)_{2\,(aq)} + 2NO_{2\,(g)} + 2H_2O$$

*This shows that $HNO_3$ is a more powerful oxidizing agent than other strong acids.*

8. Explain why colourless concentrated trioxonitrate(V)acid turns yellow. [WAEC]

*The yellow colour is due to the presence of nitrogen(IV) oxide, which is produced when the acid decomposes.*

9. Name one industrial process in which platinum is used as a catalyst.

*Platinum is used in production of $H_2SO_4$ by contact process; in the production of $HNO_3$ from ammonia.*

### Revision Exercises

30 In the laboratory preparation of trioxonitrate(V) acid from trioxonitrate(V) salts, what other reagent is required? [WAEC]

31 Why is all-glass apparatus used in the laboratory preparation of trioxonitrate(V) acid? [NECO]

32 Explain the yellowish-brown colouration of trioxonitrate(V) acid prepared in the laboratory, and how the colour can be removed.

33 Write one equation in each case to illustrate the behaviour of $HNO_3$ as:

a. a typical acid; b an oxidjzing agent.

34 Which industrial process is used for converting ammonia to trioxonitrate (V) acid? [WAEC]

35 Give two large scale uses of $HNO_3$ [WAEC]

## 31.7 Trioxonitrate(V) Salts

### Solubility in Water

All trioxonitrate(V) salts are soluble in water.

### Methods of Preparation

All trioxonitrate(V) salts are soluble in water; hence, the salts are prepared by crystallization method, using the following types of reactions:

**1. By Neutralization reactions:**

Dilute $HNO_3$ is treated with the appropriate metallic oxide or hydroxide.

- $Ca(OH)_{2\,(aq)} + 2HNO_{3\,(aq)} \rightarrow Ca(NO_3)_{2\,(aq)} + H_2O_{(l)}$
- $CuO_{(s)} + 2HNO_{3\,(aq)} \rightarrow Cu(NO_3)_{2\,(aq)} + H_2O_{(l)}$

The resulting solution is concentrated, crystallized, and the crystals filtered and dried in the desiccator.

**2. From a trioxocarbonate(IV) salt:**

Dilute $HNO_3$ is treated with the appropriate trioxocarbonate (IV) salt in excess.

- $ZnCO_{3\,(s)} + 2HNO_{3\,(aq)} \longrightarrow Zn(NO_3)_{2\,(aq)} + H_2O_{(l)} + CO_{2\,(g)}$

The resulting mixture is filtered to remove excess trioxocarbonate(IV) salt. The filtrate is then concentrated, crystallized, and the crystals filtered and dried in the desiccator.

**3. From a Metal**

A metal, such as magnesium, zinc or copper, is treated with hot concentrated $HNO_3$.

- $Cu_{(s)} + 4HNO_{3\,(aq)} \longrightarrow Cu(NO_3)_{2\,(aq)} + 2NO_{2\,(g)} + 2H_2O$

The resulting mixture is filtered, to remove the metal in excess. The filtrate is then concentrated, crystallized, and the crystals filtered, and dried in the desiccator.

### Properties of Trioxonitrate(V) salts

1. All trioxonitrate(V) salts, when heated with concentrated $H_2SO_4$ produce trioxonitrate(V) acid.

$$NaNO_{3\,(s)} + H_2SO_{4\,(l)} \rightarrow NaHSO_{4\,(aq)} + HNO_{3\,(l)}$$

**2. Action of heat on trioxonitrate(V) salts**

**a. *K and Na:***

Trioxonitrate(V) salts of potassium and sodium decompose on heating, to give the corresponding dioxonitrate(III) and oxygen:

$$2KNO_{3\,(s)} \rightarrow 2KNO_{2\,(s)} + O_{2\,(g)}$$

This reaction shows that alkali metals have great affinities for oxygen.

**b. *Ca, Mg, Al, Zn, Fe, Sn, Pb and Cu:***

Trioxonitrate(V) of these metals decompose, when

heated, to give the corresponding metal oxides, nitrogen (IV) oxide and oxygen, e.g.

$$2Zn(NO_3)_{2\,(s)} \rightarrow 2ZnO_{(s)} + 4NO_{2\,(g)} + O_{2(g)}$$

*c. Hg and Ag:*

Trioxonitrate(V) of mercury or silver decomposes to give the metal, nitrogen (IV) oxide and oxygen:

- $Hg(NO_3)_{2\,(s)} \rightarrow Hg_{(l)} + 2NO_{2\,(g)} + O_{2\,(g)}$
- $2AgNO_{3\,(aq)} \rightarrow 2Ag_{(s)} + 2NO_{2\,(g)} + O_{2\,(g)}$

$AgNO_3(aq)$ decomposes in the presence of sunlight. Hence, the solution is usually stored in *amber-coloured* reagent bottles.

*d. $NH_4NO_3(s)$:* Crystals of ammonium trioxonitrate (V) decompose when heated, to give a mixture of nitrogen (I) oxide and steam – gaseous products:

$$NH_4NO_{3\,(s)} \rightarrow 2H_2O_{(l)} + N_2O_{(g)}$$

**3. Laboratory test for trioxonitrate(V) ions:**
***The Brown-ring Test***

**Wet test:** To the *solution* of the trioxonitrate(V) salt in a test tube, add fresh $FeSO_4$ solution. Then, with care and with the test tube in a slanting position, add concentrated $H_2SO_4$ down the side.

*A brown-ring of an unstable complex, $(FeSO_4)_2{\cdot}NO$, is formed between the acid (lower layer) and the aqueous solutions (upper layer).*

### Uses of Trioxonitrate (V) salts

1. $NaNO_3$ *(Chile saltpetre)*; used as a fertilizer.
2. $KNO_3$: In the manufacture of gunpowder (a mixture of carbon, sulphur and $KNO_3$).
3. $NH_4NO_3$: In the manufacture of explosives, and as fertilizers.

### Revision Exercises

37 What is the IUPAC name of $NaNO_2$?
38 What is the formula of aluminium trioxonitrate(V)?
39 Which of the following compounds will leave a metal residue when heated?
A. $Cu(NO_3)_2$ B. $AgNO_3$ C. $K_2CO_3$ D. $CaCO_3$
40 Which of the following salts would not decompose on heating? [WAEC]
A. $Zn(NO_3)_2$ B. $Pb(NO_3)_2$ C. $Na_2CO_3$ D. $CaCO_3$
41 Describe the laboratory test for trioxonitrate(V) ions, and mention the name given to the test.
42 Mention one use of a trioxonitrate(V) salt.
43 Name two trioxonitrate(V) compounds used as fertilizers. [WAEC]

## 31.8 Oxides of Nitrogen

The common oxides of nitrogen are:

- Dinitrogen(I) oxide, [Nitrous oxide], $N_2O(g)$;
- Nitrogen(II) oxide, [Nitric oxide], $NO(g)$;
- Nitrogen(IV) oxide, [Nitrogen dioxide], $NO_{2\,(g)}$.

Others are: dinitrogen(III) oxide, $N_2O_3$, a pale blue liquid at room temperature, and dinitrogen(IV) oxide, $N_2O_4$ a yellow liquid below room temperature, and dinitrogen(V) oxide, $N_2O_5$ that exists as an unusual white solid at room temperature..

### Revision Exercise

44 Give the IUPAC name of a. $N_2O_3$; b. $N_2O_5$.

## 31.9 Nitrogen(I) oxide, $N_2O$

### Methods of Preparation

1. Nitrogen(I) oxide is evolved when ammonium trioxonitrate(V) crystals are gently heated (to avoid explosion):

$$NH_4NO_{3\,(s)} \rightarrow 2H_2O_{(l)} + N_2O_{(g)}$$

2. It is conveniently prepared in the laboratory by the action of heat on a mixture of sodium trioxonitrate(V) and ammonium chloride (figure 31.8). The colourless gas evolved is collected over water.

$$NaNO_{3\,(aq)} + NH_4Cl_{(aq)} \rightarrow NaCl_{(aq)} + 2H_2O_{(l)} + N_2O_{(g)}$$

### Physical Properties of $N_2O$

1. $N_2O$ is a colourless gas with a sweet smell.
2. It produces *unconsciousness* in the body when inhaled; hence, it is popularly called *laughing gas*.
3. It is denser than air ($M_r[N_2O] = 44$).
4. It dissolves in cold water to give a neutral solution. It is insoluble in hot water.

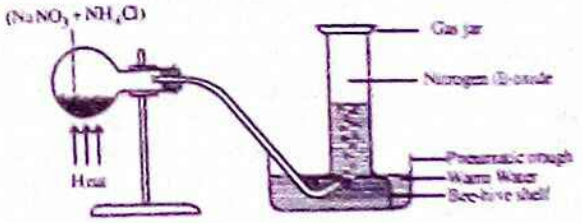



Fig 31.8 *Preparation of nitrogen (I) oxide*

### Chemical Properties of $N_2O$

**1. Combustion**

Nitrogen(I) oxide supports combustion, because it liberates oxygen gas on decomposition by heat.

$$2N_2O_{(g)} \rightarrow 2N_{2(g)} + O_{2(g)}$$

**a.** Nitrogen(I) oxide, like oxygen, rekindles a brightly glowing splint; but unlike oxygen, it does not produce brown fumes with nitrogen(II) oxide.

**b.** A burning candle burns brighter in a gas jar of nitrogen(I) oxide, to produce a colourless and odourless gas, that turns limewater milky.

$$C_{(s)} + 2N_2O_{(g)} \rightarrow CO_{2\,(g)} + 2N_{2\,(g)}$$

c. Burning sulphur continues to burn in a gas jar of $N_2O$, with a blue flame, to produce a colourless gas with pungent smell, gas is sulphur (IV) oxide:

$$S_{(s)} + 2N_2O_{(g)} \rightarrow SO_{2\,(g)} + 2N_{2\,(g)}$$

d. Phosphorus burns in a jar of $N_2O$ with a yellow flame to produce dense white fumes of phosphorus (V) oxide:

$$2P_{(s)} + 5N_2O_{(g)} \rightarrow P_2O_{5\,(g)} + 5N_{2\,(g)}$$

e. When $N_2O$ is passed over red-hot copper in a combustion tube, the residue is black copper(II) oxide, and nitrogen as the residual gas:

$$Cu_{(s)} + N_2O_{(g)} \rightarrow CuO_{(s)} + 2N_{2\,(g)}$$

### Uses of $N_2O$

Nitrogen(I) oxide (*laughing gas*) is used in dentistry and in surgery as an anaesthetic.

### Comparing and Contrasting $O_2$ and $N_2O$

1. Oxygen is colourless and odourless, while $N_2O$ is colourless and with a sweet smell.
2. Both gases support combustion, and rekindle a glowing splint.
3. $O_2$ produces brown fumes with NO gas, while $N_2O$ does not
4. Both gases react with Cu metal to produce black CuO; that of $N_2O$ is accompanied with $N_2$ gas.

### Revision Exercises

45 Which oxide of nitrogen is formed when ammonium trioxonitrate (V) crystals are heated?
46 Write equation to show the action of heat on crystals of $NH_4NO_3$.
47 In the reaction: $Cu_{(s)} + N_2O_{(g)} \rightarrow CuO_{(s)} + 2N_{2\,(g)}$ Identify the oxidizing and reducing agents.
48 What is the popular name for nitrogen (I) oxide?
49 Give one similarity and one difference between oxygen and nitrogen(I) oxide.
50 Give one use of nitrogen(I) oxide.

## 31.10 Nitrogen(II) oxide, NO

### Method of Preparation of NO

When moderately concentrated trioxonitrate(V) acid is poured on copper turnings, there is effervescence; the colourless and odourless gas given off is nitrogen(II) oxide:

$$3Cu_{(s)} + 8HNO_{3\,(aq)} \longrightarrow 3Cu(NO_3)_{2\,(aq)} + 2NO_{(g)} + 4H_2O_{(l)}$$

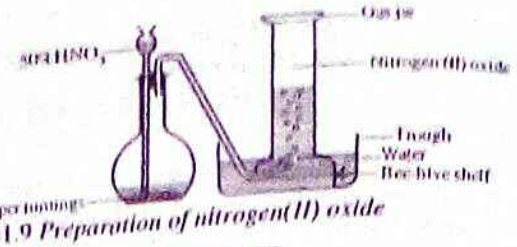



Fig 31.9 *Preparation of nitrogen(II) oxide*

### Physical Properties of NO

1. Pure nitrogen (II) oxide is colourless with an unknown smell.
2. It is insoluble in water, and has no action on blue or red litmus; the gas is neutral.
3. It does not support combustion.

### Chemical Properties of NO

1. Nitrogen(II) oxide is unstable in air; it combines readily with oxygen in air to produce brown fumes of $NO_2$.

$$2NO_{(g)} + O_{2\,(g)} \rightarrow 2NO_{2\,(g)}$$

This reaction explains why its smell is unknown.

2. When the gas is bubbled into a fresh solution of $FeSO_4$ in dilute $H_2SO_4$, an unstable brown complex is formed – as in the *brown ring test*.

$$2FeSO_{4\,(aq)} + NO_{(g)} \rightarrow (FeSO_4)_2{\cdot}NO_{(aq)}$$

3. Unlike $N_2O$, NO is stable to heat. It can only produce dense white fumes of $P_2O_3$ with *brightly* burning phosphorus

$$4P_{(s)} + 10NO_{(g)} \rightarrow 2P_2O_{3\,(g)} + 5N_{2\,(g)}$$

### Revision Exercises

51 Under what conditions do copper turnings react with $HNO_3$ to produce nitrogen (II) oxide?
52 Mention the colour of the complex formed when nitrogen(II) oxide is bubbled into a solution of acidified $FeSO_4$.

## 31.11 Nitrogen(IV) oxide, $NO_2$

### Methods of Preparation

Nitrogen(IV) oxide is given off in the following types of reactions:

**1. Action of heat on the trioxonitrate(V) salt of Cu, Mg, Al, Zn, Fe, Sn, Pb or Cu (heavy metals)**

*From $Pb(NO_3)_{2(s)}$:*

• Place about 5.0 *g* of the crystals of the salt in a dry boiling tube, and connect up the apparatus as shown in figure 31.10.

- Heat the test tube gently; the crystals break up with the characteristic *crackling* sound.
- Heat strongly; melting occurs, and a brown nitrogen(IV) oxide gas, mixed with oxygen is given off.




Fig. 31.10 *Preparation of nitrogen(IV) oxide*

- The gas is liquefied in a U-tube placed in *a freezing mixture of ice and common salt*, while oxygen is collected over water.

$$2Pb(NO_3)_{2\,(s)} \rightarrow 2PbO_{(s)} + 4NO_{2\,(g)} + O_{2\,(g)}$$

**2. Action of concentrated $HNO_3$ on a metal**

When a mixture of concentrated $HNO_3$ and copper turnings is heated, the metal dissolves with effervescence, to liberate reddish-brown fumes of $NO_2$.

$$Cu_{(s)} + 4HNO_{3\,(aq)} \longrightarrow Cu(NO_3)_{2\,(aq)} + 2NO_{2\,(g)} + 2H_2O$$

**3. Action of concentrated $H_2SO_4$ on a trioxonitrate(V) salt**

When a mixture of concentrated $H_2SO_4$ and any trioxonitrate(V) salt is heated strongly, the salt dissolves with effervescence, to form reddish-brown fumes of nitrogen(IV) oxide:

$$4NaNO_{3\,(s)} + 2H_2SO_{4\,(l)} \longrightarrow 2Na_2SO_{4\,(aq)} + 2H_2O_{(l)} + 4NO_{2\,(g)} + O_{2\,(g)}$$

### Physical Properties of $NO_2$

1. $NO_2$ is a reddish-brown gas with a pungent smell; it is poisonous.
2. It is denser than air, and readily liquefied at 20 °C to a yellow liquid, dinitrogen(IV) oxide, $N_2O_4$.

### Chemical Properties of $NO_2$

1. **Action on litmus:** It turns *moist* blue litmus paper red. It is an acidic gas.
2. **Reaction with water:** It dissolves in, and reacts with water to give two acids:

$$2NO_{2\,(g)} + H_2O_{(l)} \rightarrow HNO_{2\,(aq)} + HNO_{3\,(aq)}$$

Hence, $NO_2$ is *a mixed anhydride* of the two acids.

- When mixed with air, nitrogen(IV) oxide reacts with water to produce trioxonitrate(V) acid.

$$4NO_{2\,(g)} + 2H_2O_{(l)} + O_{2\,(g)} \rightarrow 4HNO_{3\,(l)}$$

3. **Reaction with alkalis:** When $NO_2$ is passed into aqueous NaOH or KOH, a mixture of two salts and water are produced.

$$2NO_{2\,(g)} + 2NaOH_{(aq)} \rightarrow NaNO_{2(aq)} + NaNO_{3(aq)} + H_2O_{(l)}$$

4. **Decomposition:** $NO_2$ will support the combustion of red-hot copper or iron, or burning magnesium or phosphorus at very high temperatures to decompose the gas and pro-duce nitrogen:

$$4Cu_{(s)} + 2NO_{2(g)} \rightarrow 4CuO_{(s)} + N_{2(g)}$$
$$3Fe_{(s)} + 2NO_{2(g)} \rightarrow Fe_3O_{4(s)} + N_{2(g)}$$

5. **Dimerisation:** When the reddish-brown fume of $NO_2$ is cooled to a low temperature (about 100 °C), it turns colourless – due to the formation of dinitrogen (IV) oxide, its dimer.

$$2NO_{2\,(g)} \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} N_2O_{4\,(g)}$$

On further cooling to about 20 °C, $N_2O_4$ forms a pale yellow liquid.

6. **Reaction with nitrogen(II) oxide:** When a mixture of NO and $NO_2$ is cooled below freezing point, nitrogen(III) oxide, $N_2O_3$, is obtained as a pale blue liquid:

$$NO + NO_2 \rightarrow N_2O_{3(l)}$$

7. **Laboratory Test for $NO_2$:**

Insert a *moist starch-iodide paper* into a gas jar of $NO_2$. *The paper turns blue-black.*

This is due to the liberation of iodine, which turns starch blue-black.

**Solved Problem**

9. State what is observed when lead(II) trioxonitrate(V) crystals are heated strongly, and the residue is allowed to cool.

*The crystals decompose with a crackling sound, and melting occurs. A reddish-brown gas is given off, leaving a residue, which is red when hot, and turns yellow on cooling.*

**Revision Exercises**

53 Write an equation to show that nitrogen(IV) oxide is a mixed-anhydride.

54 Write an equation to show the reaction of nitrogen (IV) oxide with aqueous KOH.

55 Name the gas evolved when nitrogen(IV) oxide is passed into burning phosphorus.

56 The gas evolved by heating a mixture of ammonium chloride and sodium dioxonitrate(III) is

A. $N_2$ B. $NH_3$ C. $N_2O$ D. NO E. $NO_2$

57 Describe a chemical test for nitrogen(IV) oxide.

## 31.12 Oxidation States of Nitrogen

Nitrogen exits in various oxidation states as illustrated in the following examples:

| Oxidation State | Example |
|---|---|
| −3 | $NH_3$, $Mg_3N_2$, $Li_3N$ |
| 0 | $N_2$ |
| +1 | $N_2O$ |
| +2 | NO |
| +3 | $HNO_2$, $NCl_3$, $N_2O_3$, $NO_2$ |
| +4 | $NO_2$, $N_2O_4$ |
| +5 | $HNO_3$, $N_2O_5$, $NO_3$ |

**Revision Exercises**

**58** Name **one** acidic and **one** neutral oxides of nitrogen.

**59** What is the oxidation state of nitrogen in each of the following?

a. $NH_3$ b. $NaNO_3$ c. $NCl_3$ d. $N_2$

**60** Which of the following oxides of nitrogen has oxidation number of +1?

A. $KNO_3$ B. $N_2O$ C. $N_2O_3$ D. NO [WAEC]

**61** An oxide of nitrogen contains 70% of oxygen.

a. Determine its empirical formula. [N = 14; O = 16]

b. If the relative molecular mass of the oxide is 92, deduce its molecular formula.

c. To what class of oxides does it belong? [WAEC]

**62** Which of the oxides of nitrogen support the combustion of phosphorus? [NECO]

## 31.13 The Nitrogen Cycle: Nitrogen Fixation

Nitrogen is an essential element in the formation of proteins in plants and animals. Unfortunately, it cannot be used directly in its free gaseous state, except in the form of trioxonitrate(V) salts (*nitrates*).

There are various processes through which atmospheric nitrogen is converted into trioxonitrate(V) salts in the soil; the processes are called *fixing* or ***fixation of nitrogen***.

1. When there is thunderstorm or lightning, electric discharges are produced, during which atmospheric nitrogen and oxygen combine to form unstable and colourless nitrogen(II) oxide:

$$N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$$

The NO gas readily combines with more oxygen, to form brown fumes of $NO_2$.

$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$$

The nitrogen(IV) oxide dissolves in rainwater in the presence of oxygen, to produce a very dilute solution of $HNO_3$, which falls as *acid rain*.

$$4NO_{2(g)} + 2H_2O_{(l)} + O_{2(g)} \rightarrow 4HNO_{3(l)}$$

2. Plants absorb trioxonitrate (V) salts through the roots for the formation of proteins. When animals and man eat these plants, the proteins are utilized in the formation of flesh, and the excess is excreted as urea – in urine and faeces.

When plants and animals die and decay, the bacteria in the soil decompose the proteins into organic compounds of nitrogen, which are then converted into ammonia and ammonium salts, by *putrefying* bacteria.

A portion of the ammonium salts, in alkaline medium, is oxidized into trioxonitrate(V) salts by *nitrifying* bacteria, while the remaining portion, in acidic medium, is oxidized to nitrogen, by *denitrifying* bacteria. The nitrogen eventually goes back into the atmosphere. This is the process that compensates for the loss of atmospheric nitrogen.

3. The roots of leguminous plants, such as groundnuts and beans, contain nitrogen-fixing bacteria, which convert atmospheric nitrogen directly into proteins.

4. *Manure* and nitrogenous fertilizers are being added to the soil periodically, in order to replace nitrogen that has been used up by crops or plants.

The nitrogen cycle operates in nature such that the percentage of nitrogen in the atmosphere remains constant.

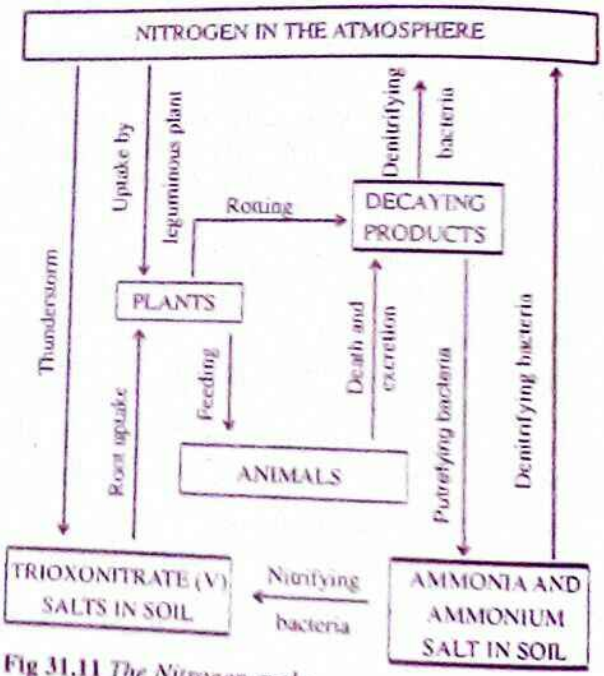



Fig 31.11 *The Nitrogen cycle*

**Revision Exercises**

**63** Name *one* process, which converts atmospheric nitrogen to trioxonitrate(V) in the soil.

**64** Describe briefly, the ways in which plants obtain their supplies of nitrogen from natural sources.

**65** Explain the formation of trioxonitrate(V) acid in the nitrogen *cycle*.

## 31.14 Phosphorus

### Phosphorus as an Element

*Phosphorus* is the element directly below nitrogen in group V of the Periodic Table. Its electron configuration of 2, 8, 5 shows that there are five valence electrons in its atom, while its orbital electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^3$ shows that each of its *p*-orbitals is half-filled, i.e. phosphorus has *three unpaired* electrons.

Phosphorus is a solid non-metal. It exists as discrete tetratomic molecules, $P_4$ and exhibits oxidation numbers of -3, +3 and +5 in its compounds.

### Occurrence of Phosphorus

Phosphorus is a very reactive non-metal; hence, it is never found in free uncombined state. It is found in the earth's crust, largely, as *ores*, such as calcium tetraoxophosphate(V), $Ca_3(PO_4)_2$ and *apatite*, $CaF_2.3Ca_3(PO_4)_2$. It is also present as tetraoxophosphate(V) in living matter – bones and teeth.

### Allotropes of Phosphorus

Phosphorus exhibits allotropy; the two commonest allotropic forms are the *white* and the *red*. The *white* phosphorus is more popular.

### White Phosphorus

It is a soft, silvery-white and waxy solid. It exists as discrete tetratomic molecules, $P_4$ in which each atom is covalently bonded to three separate atoms, to produce a tetrahedral structure.

- White phosphorus is highly reactive; it smoulders and glows when exposed to air.
- It is soluble in organic solvents, but inactive and insoluble in water; hence, it is usually stored under water – since it has a low ignition temperature.
- It is highly toxic (poisonous); it causes serious burns when in contact with the skin.
- It is unstable; when heated to about 250 °C, it changes to the more stable red allotrope.

### Red Phosphorus

It exists as red powder in which discrete tetratomic molecules, $P_4$ combine repeatedly, to form a long chain of tetratomic *macromolecules*.

- Red phosphorus is less reactive than the white allotrope.
- Like the white allotrope, it is insoluble in water.
- However, it is denser, insoluble in organic solvents, and non-toxic.
- When heated to about 290 °C, it sublimes; its vapour condenses to produce the white allotrope.

### Revision Exercises

66 Which element is above phosphorus in the Periodic Table?

67 How many electrons are in the L shell of phosphorus?

68 Mention the elements in *apatite*.

69 Define allotropy, and mention the two allotropic forms of phosphorus.

70 State the atomicity of phosphorus.

71 Calculate the mass of one mole of phosphorus, $P_4$ [P = 31]

### Chemical Properties of Phosphorus

#### 1. Combustion

**a. *In Air*:**

Phosphorus bursts into a dazzling flame on exposure to air, to form two oxides:

i. In excess dry air or oxygen, it produces dense white fumes of phosphorus (V) oxide, which on cooling forms a white solid.

$$P_{4(s)} + 5O_{2(g)} \rightarrow P_4O_{10(s)}$$

*or*

$$4P_{(s)} + 5O_{2(g)} \rightarrow 2P_2O_{5(s)}$$

ii. In a limited supply of air or oxygen, phosphorus(III) oxide is formed.

$$P_{4(s)} + 3O_{2(g)} \rightarrow P_4O_{6(s)}$$

*or*

$$4P_{(s)} + 3O_{2(g)} \rightarrow 2P_2O_{3(s)}$$

**b. *In Oxides of Nitrogen*:**

Oxides of nitrogen, such as $N_2O$, NO and $NO_2$, will support the combustion of burning phosphorus to produce dense white fumes of $P_2O_5$ and nitrogen gas (see Sections 31.9, 31.10 and 31.11 above).

#### 2. Reaction with Chlorine

a. Phosphorus burns in chlorine to produce a mixture two chlorides:

i. In a limited supply of chlorine, phosphorus(III) chloride is produced as a colourless liquid.

$$P_{4(s)} + 6Cl_{2(g)} \rightarrow 4PCl_{3(l)}$$

*or*

$$2P_{(s)} + 3Cl_{2(g)} \rightarrow 2PCl_{3(l)}$$

ii. In excess chlorine, phosphorus(V) chloride is formed as a white solid.

$$P_{4(s)} + 10Cl_{2(g)} \rightarrow 4PCl_{5(s)}$$

*or*

$$2P_{(s)} + 5Cl_{2(g)} \rightarrow 2PCl_{5(s)}$$

b. When chlorine gas is bubbled into liquid phosphorus(III) chloride, phosphorus(V) chloride is formed as a white solid:

$$PCl_{3(l)} + Cl_{2(g)} \rightarrow PCl_{5(s)}$$

#### 3. Reaction with Metals

When a mixture of phosphorus and a metal, such as potassium, sodium, calcium or aluminium is

heated, the corresponding metallic phosphide is formed as a white solid.

- $P_{(s)} + 3Na_{(s)} \rightarrow Na_3P_{(s)}$
- $2P_{(s)} + 3Ca_{(s)} \rightarrow Ca_3P_{2\ (s)}$
- $P_{(s)} + Al_{(s)} \rightarrow AlP_{(s)}$

Metallic phosphides are ionic; they are composed of the metal ions and phosphide ions, $P^{3-}$.

**4. Reducing action of phosphorus**

When phosphorus is treated with hot concentrated trioxonitrate(V) acid, it is oxidized to tetraoxophosphate(V) acid, and the acid is reduced to nitrogen(IV) oxide.

$$\underset{0}{P_{(s)}} + 5\underset{+5}{HNO_{3\ (aq)}} \rightarrow \underset{+5}{H_3PO_{4\ (aq)}} + H_2O_{(l)} + 5\underset{+4}{NO_{2\ (g)}}$$

**Revision Exercises**

72 Describe with an equation how phosphorus(V) oxide is obtained.

73 Mention the gas evolved by the action fuming concentrated $HNO_3$ on phosphorus.

## 31.15 Compounds of Phosphorus

### Hydride of Phosphorus

Phosphine, $PH_3$ is analogous to ammonia, $NH_3$. It is a colourless gas, poisonous, and smells like rotten fish. It is usually produced when a mixture of phosphorus and an alkali is heated.

Unlike ammonia, it is only slightly soluble in water; the solution is not alkaline. This is because hydrogen bonds are not formed between its molecules and water.

In $PH_3$, phosphorus atom is in the oxidation state of -3.

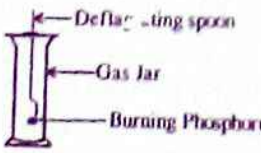
### Chlorides of Phosphorus

Phosphorus forms two chlorides: $PCl_3$ and $PCl_5$.

*Phosphorus(III) chloride* is a colourless liquid.

- It is formed when phosphorus is warmed in dry chlorine gas:

$$2P_{(s)} + 3Cl_{2\ (g)} \rightarrow 2PCl_{3\ (l)}$$




- It fumes in moist air, and react with water to form trioxophosphate(III) acid.

$$2PCl_{3\ (l)} + 3H_2O_{(l)} \rightarrow H_3PO_{3\ (aq)} + 3HCl_{(aq)}$$

- It reacts with the hydroxyl group, **-OH**, in organic compounds, such as alcohols and carboxylic acids, to form the corresponding chloroalkanes and acid chlorides e.g.

- $3CH_3CH_2\underline{OH}_{(l)} + 2PCl_{3\ (l)} \rightarrow CH_3CH_2\underline{Cl}_{(aq)} + H_3PO_{3\ (aq)}$
- $3CH_3CO\underline{OH}_{(l)} + 2PCl_{3\ (l)} \rightarrow CH_3CO\underline{Cl}_{(aq)} + H_3PO_{3\ (aq)}$

In these reactions, the chlorine atom, -Cl, has replaced the hydroxyl groups, -OH.

*Phosphorus(V) chloride* is a pale-yellow solid; it sublimes when heated.

- It is prepared by the action of chlorine on $PCl_3$; the reaction is reversible.

$$PCl_{3(l)} + Cl_{2(g)} \rightleftharpoons PCl_{5(s)}$$

- It is also obtained by treating phosphorus with an excess of chlorine.

$$2P_{(s)} + 5Cl_{2\ (g)} \rightarrow 2PCl_{5\ (s)}$$

- It fumes in moist air, and is hydrolyzed in water to produce trioxophosphate(V) acid, $H_3PO_4$.

$$2PCl_{5\ (l)} + 4H_2O_{(l)} \rightarrow H_3PO_{4\ (aq)} + 5HCl_{(aq)}$$

- Like $PCl_3$, $PCl_5$ reacts with the hydroxyl groups, **-OH** in organic compounds, such as alcohols and carboxylic acids, to form the corresponding chloroalkanes and acid chlorides, with the liberation of hydrogen chloride gas:

- $3CH_3CO\underline{OH}_{(l)} + 2PCl_{5\ (l)} \rightarrow CH_3CO\underline{Cl}_{(aq)} + POCl_{3\ (aq)} + HCl\uparrow$

This reaction is used as the *chemical test* to confirm the presence of the hydroxyl group, -OH in organic compound, such as alcohols and carboxylic acids.

### Oxides of Phosphorus: $P_2O_3$ and $P_2O_5$

Phosphorus forms two oxides: phosphorus(III) oxide, $P_4O_6$, a dimer of $P_2O_3$, and phosphorus(V) oxide, $P_4O_{10}$, a dimer of $P_2O_5$.

***Phosphorus(III) oxide*** is a white volatile solid.

- It is formed when phosphorus is burned in a limited supply of air or oxygen.

$$P_{4\ (s)} + 3O_{2\ (g)} \rightarrow P_4O_{6\ (s)}$$

- It is an acid anhydride; it dissolves in water to form trioxophosphate(III) acid.

$$P_4O_{6\ (s)} + 6H_2O_{(l)} \rightarrow 4H_3PO_{3\ (aq)}$$

***Phosphorus(V) oxide*** exists as a white powder.

- It is formed when phosphorus burns in an excess of dry air or oxygen.

$$P_{4\ (s)} + 5O_{2\ (g)} \rightarrow P_4O_{10\ (s)}$$

- It is an acid anhydride; it dissolves in water to form tetraoxophosphate(V) acid.

$$P_4O_{10\ (s)} + 6H_2O_{(l)} \rightarrow 4H_3PO_{4\ (aq)}$$

• Because of its affinity for moisture, and being deliquescent, it is used as a *drying agent* for gases and solids.

• $P_2O_5$ will dehydrate fuming $HNO_3$ to give $N_2O_5$, as a white solid:

$$2HNO_{3\,(aq)} \xrightarrow[(-H_2O)]{P_2O_{5\,(s)}} N_2O_{5\,(s)}$$

• It is also used as a *dehydrating agent* in organic reactions. For instance: when heated with ethanol, ethene, a gaseous hydrocarbon, is obtained:

$$C_2H_5OH_{\,(l)} \xrightarrow[(-H_2O)]{P_2O_{5\,(s)}} C_2H_{4\,(g)}$$

### Oxy-acids of Phosphorus

The two common oxy-acids of phosphorus are $H_3PO_3$ and $H_3PO_4$; they are typical mineral acids. Others are $HPO_3$ and $H_4P_2O_7$.

***Trioxophosphate (III) acid*** is a weak *dibasic* acid. It ionizes in water to form $H_2PO_3^-$ and $HPO_3^-$ only; it does not produce $PO_3^{3-}$ in water.

***Tetraoxophosphate(V) acid*** is a strong *tribasic* acid. It ionises in water to form $H_2PO_4^-$, $HPO_4^{2-}$ and $PO_4^{3-}$. Hence, it forms a series of two different *acid salts* and a normal salt: $Ca(H_2PO_4)_2$, $CaHPO_4$ and $Ca_3(PO_4)_2$.

### Revision Exercises

74 Explain why ammonia is readily liquefied while phosphine is not.

75 Which chloride of phosphorus is a liquid at room temperature?

76 Calculate the amount (in moles) of chlorine that would be produced from 5.10 g of phosphorus(V) chloride. [ P = 31, Cl = 35.5 ] [WAEC]

77 Name the oxide of phosphorus used as a drying agent.

78a Which of the oxides of nitrogen can be prepared by distilling a mixture of fuming trioxonitrate(V) acid and phosphorus(V) oxide? [NECO]

b Write an equation for the reaction in 4a above.

79 Give the IUPAC names of

a. $H_2PO_4^-$ b. $HPO_4^{2-}$ c. $H_4P_2O_7$

80 Consider the mineral acid $H_3PO_4$.

a. Give the IUPAC name;

b. State the basicity.

c. Write an equation for its reaction with excess calcium hydroxide solution.

81 Which of the following acids is formed from $P_2O_3$, if the rest are formed from $P_2O_5$?

A. $HPO_3$ B. $H_4P_2O_7$ C. $H_3PO_4$ D. $H_3PO_3$

## 31.16 Uses of Phosphorus and Its Compounds

1. ***Phosphorus*** is used in the production of tetraoxophosphate(V) and trioxophosphate(III) acids.

2. ***Red phosphorus*** mixed with a combustible *antimony sulphide*, is specifically used in coating the sides of matchboxes.

**Note:** *Matchstick heads are coated with a mixture of an oxidizing agent and an abrasive.*

3. ***$Ca_3(PO_4)_2$ in ores and bone-ash*** is used as fertilizers. Being insoluble in water, it is converted into the soluble form by reacting it with concentrated $H_2SO_4$ to give a fertilizer called ***super phosphate***, which is a mixture of $Ca(H_2PO_4)_{2(s)}$ and $CaSO_{4(s)}$.

4. ***$(NH_4)_3PO_4$*** is used as a fertilizer.

5. ***Organic compounds of phosphorus*** are used in insecticides, pesticides, rat-poisons and as weed-killers.

### Revision Exercises

82 Give the IUPAC names of the following:

a. $Ca_3(PO_4)_2$ b. $Ca(H_2PO_4)_2$ c. $(NH_4)_3PO_4$

83 State one use of a named compound of phosphorus.

84 Which compound of phosphorus is present in animal charcoal?

85 What is the percentage by mass of

a. phosphorus in $Ca_3(PO_4)_2$?

b. nitrogen in $(NH_4)_3PO_4$?

### Answers to Revision Exercises

7. B 9 80.0% 39. B 40. C 56. A
60. B 61a. $NO_2$; b. $N_2O_4$ 70 4 71 124 g
76 0.0844 *mol* 81. D 85a 20.0%; b. 20.8%

# 32

# •SULPHUR AND ITS COMPOUNDS•

## 32.1 Introduction

The element sulphur, like element oxygen, is in Group VI in the Periodic Table.

Its shell structure is 2, 8, 6; while its orbital configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$.

**Revision Exercise**

1. An element X has sixteen protons in its nucleus.
   a. In which period of the Periodic Table is X?
   b. How many electrons are in the L-shell of X?
2. Name an element in the same group with oxygen (atomic number 8) in the Periodic table.

## 32.2 Sulphur as an Element

### Occurrence of Sulphur

Sulphur occurs in a free elemental state as a yellow solid, and in sulphide ores, such as copper pyrite, $CuFeS_2$; iron pyrite, $FeS_2$; zinc blend, ZnS; copper glance, $Cu_2S$; and galena, PbS. It is also present in *gypsum*, calcium tetraoxosulphate(VI) dihydrate $CaSO_4 \cdot 2H_2O$.

It is present in the atmosphere, in traces, in the form of hydrogen sulphide – a pollutant from crude oil, rotten eggs, and combustion of coal.

Sulphur is found, largely, in America.

### Extraction of Sulphur: Frasch Process

Extraction of sulphur is carried out by a process designed by Herman Frasch (1891).

The procedure is as follows:

1. Three concentric steel pipes are driven through the earth's crust down to the sulphur bed.
2. *Super-heated water* at about 180 °C is pumped down, under pressure, through the outer pipe, to melt the sulphur.
3. *Hot compressed air* is blown down through the inner pipe, to force the molten sulphur and water through the middle pipe (see figure 32.1).

The molten sulphur is allowed to cool and solidify in tubular moulds, to produce ***roll sulphur***, which is 99.5% pure. Elemental sulphur obtained directly by extraction is called *roll* sulphur.

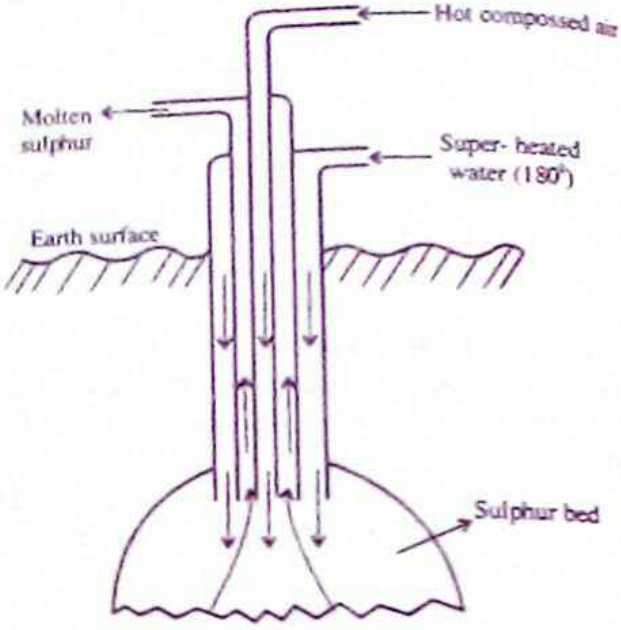



Fig 32.1 *Extraction of Sulphur*

**Revision Exercises**

3. Give the physical state and colour of sulphur.
4. Mention two ores of sulphur.
5. a Draw a labelled diagram for the extraction of sulphur.
   b Sate the function of each of the following in the extraction of sulphur:
   i Hot compressed air; ii Super-heated water.
6. What is *roll* sulphur?

### Allotropes of Sulphur

Sulphur exists in *two allotropic crystalline* forms, called *rhombic* and *monoclinic* sulphur, and in *one amorphous* form, called *plastic sulphur*.

### Crystalline forms

#### 1. Rhombic (α-) sulphur

It is obtained by dissolving *roll sulphur* in liquid carbon(IV) sulphide, placed in a beaker in a fume cupboard.

The solvent is allowed to evaporate, to produce yellow translucent octahedral crystals (fig 32.2a).

It is a yellow stable solid at room temperature; forms octahedral crystals that contain molecules

with rings of eight sulphur atoms, $S_8$; melts at 114 °C; has a density of 2.06 $gcm^{-3}$; and soluble in carbon(IV) sulphide.

**2. Monoclinic or Prismatic (β-) sulphur**

It is prepared by dissolving *roll sulphur* in methylbenzene (toluene) held in a beaker, and warming the solution on a water bath.

On cooling, transparent and needle-like crystals of monoclinic sulphur are formed along the walls of the beaker (fig 32.2b).

It is a yellow stable solid above 96 °C; forms thin needle-shape crystals that contain molecules with rings of eight sulphur atoms, $S_8$; melts at 120 °C; has a density of 1.96 $gcm^{-3}$; and soluble in carbon (IV) sulphide.

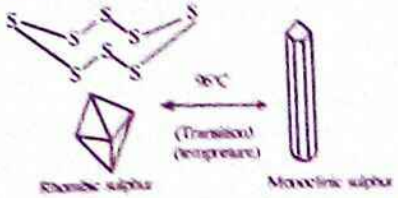



Fig 32.2 a b

## Characteristics of the crystalline forms

1. The two crystalline allotropes are pure sulphur, and undergo the same chemical reactions.
2. They are both soluble in carbon(IV) sulphide.
3. They have different shapes, densities, and melting points.
4. *Rhombic* sulphur is stable below 96 °C. Above 96 °C, it changes into *prismatic* sulphur. Similarly, *prismatic* sulphur is stable above 96 °C; below 96 °C, it changes into *rhombic* sulphur. Hence, the *transition temperature* is 96 °C.

## Amorphous sulphur

**Plastic sulphur**

It is a super-cooled liquid. It is obtained by pouring molten *roll* sulphur into cold water continuously, to produce non-crystalline and elastic sulphur.

Although it is a pure form of sulphur, its molecules contain different numbers of sulphur atoms. It is slightly soluble in carbon(IV) sulphide, $CS_2$.

Non-crystalline sulphur is usually produced during chemical reactions as an almost white powder.

## Revision Exercises

7. What is allotropy?
8. Name two elements, apart from sulphur, which exhibit allotropy.
9. a. Name two allotropes of sulphur.
   b. State two differences between the two allotropes.
10. What is the transition temperature of the two crystalline allotropes of sulphur?
11. Name the crystalline allotrope of sulphur that is stable at room temperature.
12. Why is plastic sulphur said to be amorphous?
13. Describe the formation of *plastic* sulphur.

## Physical Properties of Sulphur

1. Sulphur is a yellow non-metallic solid, it exhibits allotropy.
2. It sublimes to give *flowers of sulphur, when heated in the absence of air.*
3. It is insoluble in water, but soluble in $CS_2(l)$.
4. A non-conductor of heat and electricity.
5. When heated in the absence of air, *roll sulphur* undergoes the following changes:
   - It melts at 115 °C to form an *amber-coloured* mobile liquid.
   - At about 160 °C, the liquid becomes viscous and darker in colour.
   - Near its boiling point, it becomes mobile again and reddish brown in colour.
   - At its boiling point of 444 °C, it gives off a brown vapour.

This characteristic behaviour of sulphur is due to the existence of two allotropes of liquid sulphur at different temperatures.

## Chemical Properties of Sulphur

**1. Combustion in Air:**

Sulphur burns in air with a blue flame to produce a colourless gas with irritating smell that turns blue litmus paper to red; the gas is sulphur(IV) oxide

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

**2. Reaction with Hydrogen**

When hydrogen gas is bubbled into molten sulphur in a test tube, a colourless gas with a characteristic rotten-egg smell is evolved; the gas is hydrogen sulphide:

$$H_2(g) + S(l) \rightarrow H_2S(g)$$

**3. Reaction with Carbon**

When a mixture of carbon and sulphur is heated in an electric furnace, the vapour produced condenses to form a poisonous and inflammable liquid called carbon(IV) sulphide:

$$C(s) + S(s) \rightarrow CS_2(l)$$

**4. Reactions with Metals**

Sulphur combines directly with most metals to produce the corresponding *anhydrous sulphides*:

a. When a mixture of iron filings and powdered sulphur is heated, in the absence of air, a dark-

grey mass of iron(II) sulphide is produced:

$$Fe(s) + S(s) \rightarrow FeS(s)$$

**b.** A mixture of *liquid* mercury and *powdered* sulphur, on stirring, produces mercury(II) sulphide, *without heating*.

$$Hg(l) + S(s) \rightarrow HgS(s)$$

**5. Sulphur as a reducing agent:**

**a.** When sulphur powder is warmed with concentrated $H_2SO_4$, it is oxidized to sulphur(IV) oxide, while the acid is reduced to sulphur(IV) oxide also:

$$\overset{0}{S_{(s)}} + 2H_2\overset{+6}{S}O_{4(aq)} \rightarrow 2H_2O_{(l)} + 3\overset{+4}{S}O_{2(g)}$$

**b.** When warmed with concentrated $HNO_3$, sulphur is oxidized to tetraoxosulphate(IV) acid:

$$S_{(s)} + 6HNO_{3(aq)} \rightarrow H_2SO_{4(aq)} + 2H_2O_{(l)} + 6NO_{2(g)}$$

**Revision Exercises**

**14** What is *flower of sulphur*?

**15** If sulphur is dissolved in carbon(IV) sulphide and the solution is allowed to evaporate, the allotrope of sulphur formed is

**A.** plastic sulphur **B.** amorphous sulphur
**C.** rhombic sulphur **D.** monoclinic sulphur
**E.** colloidal sulphur. [WAEC]

**16** What are the products of reaction of sulphur with concentrated tetraoxosulphate(VI) acid?

**17** Under what condition does mercury react with sulphur?

## Uses of Sulphur

**1.** Sulphur is used in the large-scale production of tetraoxosulphate(VI) acid, and in the production of the following: Carbon(IV) sulphide – used as a solvent and pesticide; in gunpowder and matches; dyestuffs; sulphur drugs and ointments; fungicides, insecticides and germicides.

**2.** In vulcanizing rubber; it makes raw rubber to become hard, tough and elastic, and hence, suitable for making tyres.

**3.** In the production of calcium hydrogentrioxosulphate(IV), $Ca(HSO_3)_2$, used in bleaching wood-pulp for making newsprints.

**Revision Exercises**

**18** State **three** uses of sulphur.

**19** Sulphur is used for the following **except**

**A.** coating of steel to prevent rusting.
**B.** manufacture of dyes.
**C.** manufacture of tetraoxosulphate (VI) acid.
**D.** prevention of growth of fungi.
**E.** vulcanization of rubber. [NECO]

# 32.3 Hydrogen sulphide gas

## Occurrence

Hydrogen sulphide gas is produced, naturally, by decaying animals and plants – due the action of certain bacteria on proteinous substances, such as rotting eggs. It is also produced during combustion of coal, and from sulphur-containing crude oil.

Hydrogen sulphide is present in the atmosphere as a pollutant responsible for the tarnishing of ornamental metals, such as silver – due to the formation of an insoluble surface coating of the sulphide.

## Laboratory Preparation of $H_2S$ gas *(in the fume cupboard)*

Hydrogen sulphide gas is prepared by the action of moderately concentrated hydrochloric acid on *ground* iron(II) sulphide.

**Procedure**

**1.** *Ground* iron(II) sulphide (20.0 *g*) is placed in a conical flask. Moderately concentrated hydrochloric acid (or bench reagent) is added by the use of a thistle funnel or a dropping funnel (figure 32.3).

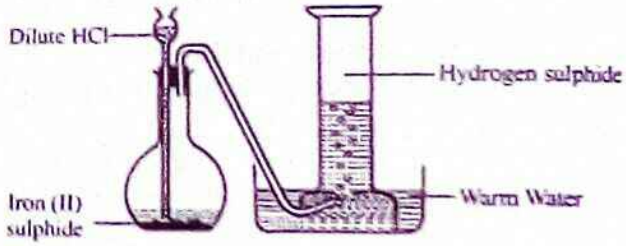



**Fig 32.3** Preparation of $H_2S$

**2.** As the iron(II) sulphide dissolves in the acid, there is effervescence; the colourless gas evolved is collected over *warm* water.

$$\underset{\text{(grey)}}{FeS_{(s)}} + \underset{\text{(colourless)}}{2HCl_{(aq)}} \rightarrow \underset{\text{(dirty green)}}{FeCl_{2(aq)}} + H_2S\uparrow$$

***To obtain dry hydrogen sulphide***

Dry hydrogen sulphide is obtained by passing the gas through a U-tube containing anhydrous calcium chloride as the drying agent, to absorb moisture. The gas is then collected by *downward delivery*; since it is heavier than air (fig. 32.4).

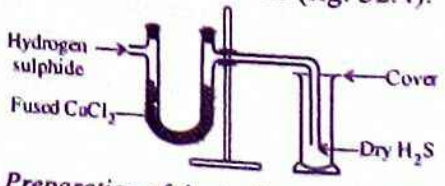



**Fig 32.4** *Preparation of dry hydrogen sulphide*

**Notes:**
1. *Ground* or *powdered* FeS(s) reacts faster than *sticks* of FeS(s), because of its larger surface area.
2. Concentrated $H_2SO_4$ cannot be used to dry $H_2S$; silica gel can be used.

## Physical Properties of $H_2S$

1. Pure hydrogen sulphide is colourless, and has a characteristic *rotten egg* smell.
2. It is soluble in *cold* water, but insoluble in *warm* water.
3. It is denser than air ($M_r[H_2S] = 34$); hence, it is collected by downward delivery of gas.
4. It is poisonous; hence, it is prepared in the fume cupboard.

## Chemical Properties of $H_2S$

### 1. Action on Litmus

Hydrogen sulphide turns *moist* blue litmus paper to red; the gas is *weakly* acidic.

### 2. Combustion in Oxygen

$H_2S$ burns with blue flame in air or oxygen:

a. In a limited supply of air, sulphur powder is deposited

$$2H_2S_{(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} + S_{(s)}$$

b. In an excess or plentiful supply of air, sulphur (IV) oxide is produced.

$$2H_2S_{(g)} + 3O_{2(g)} \rightarrow 2H_2O_{(g)} + 2SO_{2(g)}$$

### 3. Acid Properties

Hydrogen sulphide is an acidic gas:

a. Dissolves in cold water to produce hydroxonium ions:

$$H_2S_{(g)} + 2H_2O_{(l)} \rightarrow 2H_3O^+_{(aq)} + S^{2-}_{(aq)}$$

Hence, the solution will turn blue litmus paper red; the solution is weakly acidic.

b. It is *dibasic* (*diprotic*); neutralizes alkalis to produce both the normal and acid sulphides:

i. With *excess* alkali, a normal sulphide is formed:

$$2NaOH_{(aq)} + H_2S_{(g)} \rightarrow Na_2S_{(aq)} + 2H_2O$$

ii. With *excess* gas, an acid sulphide salt is formed:

$$NaOH_{(aq)} + H_2S_{(g)} \rightarrow NaHS_{(aq)} + H_2O$$

### 4. Laboratory Tests for $H_2S$

a. Pass hydrogen sulphide into an aqueous solution of a lead(II) salt, e.g. lead(II) ethanoate solution:
*A black precipitate of lead(II) sulphide is formed:*

$$\underset{\text{(colourless)}}{Pb^{2+}_{(aq)}} + H_2S_{(g)} \rightarrow 2H^+_{(aq)} + \underset{\text{(black)}}{PbS(s)}$$

b. Insert a strip of test paper soaked into a solution lead(II) ethanoate into a gas jar (or test tube) containing $H_2S$:
*The paper turns black*; due to *the formation of PbS*.

$$\underset{\text{(colourless)}}{Pb^{2+}_{(aq)}} + H_2S_{(g)} \rightarrow 2H^+_{(aq)} + \underset{\text{(black)}}{PbS(s)}$$

### 5. Reducing Properties of $H_2S$

Hydrogen sulphide gas is a *reducing agent*:

a. When $H_2S$ gas is bubbled into a solution of concentrated $H_2SO_4$, the acid is *reduced* to sulphur.

$$\overset{-2}{3H_2S_{(g)}} + \overset{+6}{H_2SO_{4(aq)}} \rightarrow 4H_2O_{(l)} + \overset{0}{4S_{(g)}}$$

*This reaction explains why concentrated $H_2SO_4$ cannot be used to dry $H_2S$ gas.*

b. When $H_2S$ gas is passed into a solution of concentrated trioxonitrate(V) acid, the acid is *reduced* to give brown fumes of nitrogen(IV) oxide, while the gas is *oxidized* to give a deposit of sulphur.

$$\overset{-2}{H_2S_{(g)}} + \overset{+5}{2HNO_{3(aq)}} \rightarrow 2H_2O_{(l)} + \overset{+4}{2NO_{2(g)}} + \overset{0}{S_{(s)}}$$

c. When excess $H_2S$ is bubbled into an acidified $KMnO_4$ solution, the *purple* solution is *reduced* to *colourless solution*, with a *deposit of sulphur*.

• Insert a strip of filter paper soaked into a solution of acidified $KMnO_4$ into a gas jar of $H_2S$; the paper is *decolourised*, and *yellow sulphur is deposited*.

$$\underset{\text{(purple)}}{2KMnO_{4(aq)}} + 5H_2S_{(g)} + 3H_2SO_{4(aq)} \rightarrow \underset{\text{(colourless)}}{K_2SO_{4(aq)} + 2MnSO_{4(aq)}} + 8H_2O + \underset{\text{(yellow)}}{5S_{(s)}}$$

d. When $H_2S$ is bubbled into an acidified $K_2Cr_2O_7$ solution, the *orange* solution is *reduced* to a *green* solution of chromium(III) salt, with a *deposit of sulphur*:

$$\underset{\text{(yellow)}}{K_2Cr_2O_{7(aq)}} + 3H_2S_{(g)} + 4H_2SO_4 \rightarrow K_2SO_{4(aq)} + \underset{\text{(green)}}{Cr_2(SO_4)_{3(aq)}} + 7H_2O_{(l)} + \underset{\text{(yellow)}}{3S_{(s)}}$$

e. When $H_2S$ is passed into a *brown* solution of iron(III) chloride, the solution turns *pale green* of iron(II) chloride with a deposit of yellow sulphur:

$$\underset{\text{(yellow)}}{2FeCl_{3(aq)}} + H_2S_{(g)} \rightarrow \underset{\text{(green)}}{2FeCl_{2(aq)}} + \underset{\text{(yellow)}}{S_{(s)}} + 2HCl_{(aq)}$$

f. When a gas jar of $H_2S$ is inverted over a gas jar of chlorine (a *greenish-yellow* gas), the mixture turns *colourless*, due to the formation of hydrogen chloride gas, and *a deposit of yellow sulphur*:

$$\underset{\text{(greenish-yellow)}}{H_2S_{(g)} + Cl_{2(g)}} \rightarrow \underset{\text{(colourless)}}{2HCl_{(g)}} + \underset{\text{(yellow)}}{S_{(s)}}$$

g. A mixture of $H_2S$ and *moist* $SO_2$ deposits yellow sulphur:

$$\overset{-2}{2H_2S_{(g)}} + \overset{+4}{SO_{2(g)}} \rightarrow 2H_2O_{(l)} + \overset{0}{3S_{(s)}}$$

*This reaction shows that $H_2S$ is a more powerful reducing agent than $SO_2$.*

**b.** When an aqueous solution of $H_2S$ is exposed to sunlight, the solution turns turbid, due to the atmospheric oxidation of $H_2S$ to sulphur.

$$\underset{-2}{2H_2S_{(aq)}} + \underset{0}{O_{2(g)}} \rightarrow \underset{-1}{2H_2O_{(l)}} + \underset{0}{2S_{(s)}}$$

**Note:** When $H_2S$ gas is acting as a *reducing agent*, it is *oxidized* to sulphur.

### 6. Precipitating Reactions

Hydrogen sulphide is used in qualitative analysis as a *precipitating reagent*, because most metallic sulphides are insoluble and coloured. Hence, $H_2S$ gas can be used to confirm the presence of certain cations in neutral, acidic, or alkaline solution.

**Test:** To the *solution of the substance*, pass $H_2S$ gas until it is in excess.

**a.** *In an alkaline or neutral solution:* Zinc ions are precipitated as a white sulphide, while iron(II) ions are precipitated as black iron(II) sulphide.

$$\underset{\text{(colourless)}}{Zn^{2+}_{(aq)}} + H_2S_{(g)} \rightarrow \underset{\text{(white)}}{ZnS_{(s)}} + 2H^+_{(aq)}$$

**b.** *In an acidic solution:* $Pb^{2+}$, $Cu^{2+}$, and $Ag^+$ are precipitated as black sulphides:

$$\underset{\text{(blue)}}{Cu^{2+}_{(aq)}} + H_2S_{(g)} \rightarrow \underset{\text{(black)}}{CuS_{(s)}} + 2H^+_{(aq)}$$

### Solved Problem

1. When $H_2S$ gas is bubbled into acidified solution of $KMnO_4$ in a test tube, a yellow precipitate is formed.

**a.** Name the precipitate.
*The yellow precipitate is sulphur.*

**b.** State the function of $KMnO_{4\,(aq)}$ in the reaction.
*$KMnO_{4\,(aq)}$ is the oxidizing agent.*

**c.** Give another substance that will react similarly with hydrogen sulphide gas.
*Acidified solution of $K_2Cr_2O_7$*

### Revision Exercises

20 State two physical properties of $H_2S$ gas.
21 What is the characteristic odour of $H_2S$ gas, and why is it prepared in the fume cupboard?
22 Write a balanced equation for the reaction of hydrogen sulphide with sodium hydroxide solution.
23 Give one reaction in to show the property of hydrogen sulphide as a precipitating agent.
24 State the observations when hydrogen sulphide reacts with solution of iron(III) chloride.
25 What property of hydrogen sulphide does each of the following reactions illustrate ?
   a. $H_2S + Cl_2 \rightarrow 2HCl + S$
   b. $Cu(NO_3)_2 + H_2S \rightarrow CuS + 2HNO_3$
   c. $KOH + H_2S \rightarrow KHS + H_2O$
26 State what would be observed when $H_2S$ is bubbled into acidified $K_2Cr_2O_7$ solution.
27 Describe one chemical test for $H_2S$.

### The Kipp's Apparatus: Gas Generator

The Kipp's apparatus is a device used for the intermittent supply of gases that can be produced by the action of an aqueous solution of an acid (*a liquid*) on a metal or a salt (*a solid*) *without heating*, e.g. $H_2$, $CO_2$, HCl, $SO_2$ and $H_2S$.

**To generate hydrogen sulphide gas**
***(In the fume cupboard or outside the laboratory)***

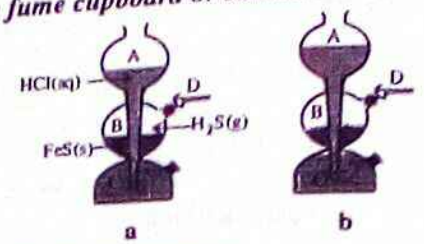



**Fig 32.5** *The Kipp's apparatus*

1. The *solid*, *coarse* iron(II) sulphide is put in **B** while the *liquid*, moderately concentrated hydrochloric acid, is added through **A** into **C**.
2. As the *liquid* comes in contact with the *solid*, effervescence occurs; $H_2S$ gas is given off, and can be obtained through tap **D** (figure 32.5a).
3. When the gas is no longer required, tap **D** is closed. The pressure generated by the gas forces the acid out of **B** down into **C**, then, into **A** (fig 32.5b).
4. Tap **D** is opened when the gas is required.

### Revision Exercises

28 Name the laboratory equipment used for the intermittent production of hydrogen sulphide.
29 Name two gases, apart from hydrogen sulphide, that can be generated by the Kipp's apparatus.

## 32.4 Sulphides, $S^{2-}$

### Physical Properties of Sulphide salts

#### 1. Solubility in Water

All sulphides are *insoluble* in water, except those of potassium, sodium, calcium and ammonium.

#### 2. Colours of Sulphides:

- $K_2S$, $Na_2S$ and CaS form white crystals, while $(NH_4)_2S$ crystals are yellow.
- ZnS is white; FeS is dark-grey, while the PbS, CuS and MgS) are black.

### Preparation of Sulphides

Sulphides are prepared by some of the usual chemical reactions used for the preparation of salts:

#### 1. By Direct Combination

Sulphur combines readily with most metals to form the corresponding *anhydrous sulphides*, e.g.

Action of heat on a mixture of iron filings and powdered sulphur produces *anhydrous* iron(II) sulphide, as a black solid:

$$Fe_{(s)} + S_{(s)} \rightarrow FeS_{(s)}$$

**2. By Crystallization**

*Soluble* sulphides are obtained by neutralization of *the appropriate alkali* with $H_2S$ gas, followed by crystallization, e.g.

When $H_2S$ gas is bubbled into lime water, an aqueous solution of calcium sulphide is obtained.

$$Ca(OH)_{2(aq)} + H_2S_{(g)} \rightarrow CaS_{(aq)} + 2H_2O_{(l)}$$

The solution is partially evaporated, followed by crystallization, to obtain white crystals of CaS.

**3. By Precipitation**

*Insoluble* sulphides are obtained by passing *excess* $H_2S$ gas into an aqueous solution of the appropriate salt; it leads to the precipitation of the corresponding sulphide of the cation, e.g.

When $H_2S$ is passed into a solution of a copper(II) salt, a black precipitate of the sulphide is obtained:

$$\underset{\text{(blue)}}{CuSO_{4(aq)}} + H_2S_{(g)} \rightarrow \underset{\text{(black)}}{CuS_{(s)}} + H_2SO_{4(aq)}$$

The precipitate is filtered, and then, dried.

## Laboratory Tests for Sulphides

**1. Test on solid (*Dry test*)**

Put the solid sample of the sulphide in a test tube, then, add a dilute mineral acid, such as $HCl_{(aq)}$.

*There is effervescence; gas evolved is colourless with a rotten egg smell; turns damp blue litmus paper to red; and blackens lead(II) ethanoate paper. Gas is $H_2S$:*

$$FeS_{(s)} + 2HCl_{(aq)} \rightarrow FeCl_{2(aq)} + H_2S_{(g)}$$

**2. Test on a solution (*Wet test*)**

To the solution of the sulphide salt in a test tube, add a few drops of lead(II) ethanoate solution.

*A black precipitate of lead(II) sulphide is formed:*

$$Pb^{2+}_{(aq)} + S^{2-}_{(aq)} \rightarrow PbS_{(s)} \text{ (black)}$$

## Uses of Sulphide salts

1. Most sulphide salts are used in paints.
2. Zinc sulphide, ZnS is used in coating electric fluorescent tubes.

## Revision Exercises

30 State **two** methods of preparing zinc sulphide.

31 State the colour and physical state of each of the following:

**a.** ZnS; **b.** $H_2S$; **c.** PbS; **d.** $(NH_4)_2S$

32 Mention **one** use of sulphide salts.

## 32.5 Sulphur(IV) oxide, $SO_2$

### Oxides of Sulphur

The two oxides of sulphur are sulphur(IV) oxide, $SO_2$ and sulphur(VI) oxide, $SO_3$. At room temperature, $SO_2$ is a gas, while $SO_3$ is a colourless liquid.

### Occurrence of Sulphur(IV) oxide

Sulphur(IV) oxide is formed during the combustion of sulphur and coal fuels. It is present in the atmosphere as a dangerous pollutant.

### Laboratory Preparation of $SO_2$

***(In the fume cupboard)***

Sulphur(IV) oxide is evolved in the following types of reactions:

1. Action of a dilute mineral acid on a trioxosulphate(IV) salt.
2. Action of hot concentrated tetraoxosulphate(VI) acid on certain metals and non-metals.

**1. From a Trioxosulphate(IV) salt**

**a.** Crystals of sodium trioxosulphate(IV) (20.0 g) are placed in a flat-bottomed flask, and moderately concentrated HCl is added through a thistle funnel. The mixture is then heated.

**b.** As the salt dissolves in the acid, there is effervescence. The colourless gas evolved is dried by passing it through concentrated tetraoxosulphate (VI) acid (or anhydrous calcium chloride).

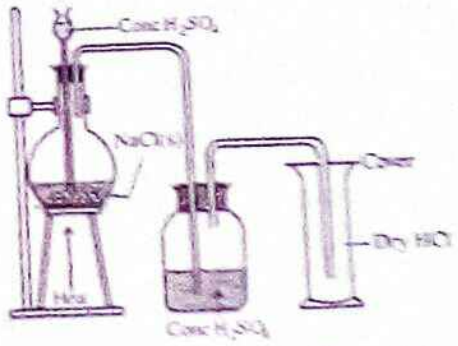



Fig 32.6 *Preparation of dry sulphur(IV) oxide*

**c.** The gas is collected by *downward delivery*; it is heavier than air (fig 32.6).

$$Na_2SO_{3(s)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + H_2O_{(g)} + SO_2\uparrow$$

**2. From concentrated tetraoxosulphate(VI) acid**

The same set-up in figure 32.3 is used; but with copper turnings (20.0 g) and concentrated $H_2SO_4$.

$$Cu_{(s)} + 2H_2SO_{4(aq)} \rightarrow CuSO_{4(aq)} + 2H_2O + 3SO_2\uparrow$$

**Note:** *Sulphur, carbon, silver, or mercury can be used instead of copper.*

**Industrial Production of $SO_2$**

Sulphur(IV) oxide is produced, commercially, by the combustion of powdered *roll sulphur* in air.

$$S_{(s)} + O_{2\,(g)} \rightarrow SO_{2\,(g)}$$

The gaseous product is stored in cylinders, under pressure, for industrial use.

**Physical Properties of $SO_2$**

1. Pure sulphur(IV) oxide is a colourless gas with a characteristic choking smell.
2. It is denser than air ($M_r(SO_2) = 64$).
3. It is very soluble in water, hence, can be used to demonstrate the *fountain* experiment.
4. It can be liquefied at low pressures.
5. It is poisonous, prepared in the fume cupboard.

**Chemical Properties $SO_2$**

1. **Action on moist litmus**

$SO_2$ turns moist blue litmus paper red. It is acidic.

2. **As an anhydride**

$SO_2$ dissolves in water to produce trioxosulphate (IV) acid; a weak unstable dibasic acid.

$$SO_{2(g)} + H_2O_{(l)} \rightarrow H_2SO_{3\,(aq)}$$

Hence, $SO_2$ gas is an anhydride of $H_2SO_{3(aq)}$.

3. **Combustion:** $SO_2$ gas does not burn in air.

4. **Reaction with Alkalis**

Being acidic, $SO_2$ neutralizes an aqueous alkali, to produce an acid salt, or a normal salt.

a. With excess gas, an acid salt is produced:

$$NaOH_{(aq)} + SO_{2\,(g)} \rightarrow NaHSO_{3\,(aq)}$$

b. With excess alkali, a normal salt is formed:

d. When $SO_2$ gas is passed into a solution of concentrated $HNO_3$, the acid is reduced to brown nitrogen(IV) oxide gas.

$$2HNO_{3\,(aq)} + SO_{2\,(g)} \rightarrow H_2SO_{4\,(aq)} + 2NO_{2\,(g)}$$

e. When the gas is passed into chlorine water, the solution is reduced to hydrochloric acid;

$$SO_{2(g)} + Cl_{2\,(g)} + H_2O_{(l)} \rightarrow H_2SO_{4\,(aq)} + 2HCl_{(aq)}$$

f. When oxygen is bubbled into a water-solution of sulphur(IV) oxide, $SO_2$ is oxidized to dilute tetraoxosulphate(VI) acid:

$$2SO_{2\,(g)} + 2H_2O_{(l)} + O_{2\,(g)} \rightarrow 2H_2SO_{4\,(aq)}$$

g. It reduces lead(IV) oxide to a lead(II) salt:

$$PbO_{2\,(s)} + SO_{2\,(g)} \rightarrow PbSO_{4\,(s)}$$

h. It reduces the brown fumes of nitrogen(IV) oxide to a colourless nitrogen(II) oxide.

$$NO_{2\,(g)} + SO_{2\,(g)} \rightarrow SO_{3\,(g)} + NO_{(g)}$$

**6. Oxidizing Properties of $SO_2$**

Unlike $H_2S$, $SO_2$ can act as an oxidizing agent:

a. Burning magnesium continues to burn in sulphur (IV) oxide, to produce a mixture of white magnesium oxide and yellow sulphur powder:

$$\underset{0}{2Mg(s)} + \underset{+4}{SO_2(g)} \rightarrow \underset{+2}{2MgO(s)} + \underset{0}{S(s)}$$

b. When passed into a gas jar of hydrogen sulphide, the product of oxidation and reduction is the same yellow sulphur powder:

$$\underset{+4}{SO_{2\,(g)}} + \underset{-2}{2H_2S_{(g)}} \rightarrow 2H_2O_{(l)} + \underset{0}{3S_{(s)}}$$

*This reaction shows that $SO_2$ is a stronger oxidiz-*