CHM 001: Access Chemistry

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Course Guide

Introduction

Welcome to this chemistry course. We suppose that many of you are taking this course because you want to strengthen your background in chemistry. Armed with this strong background in chemistry, you can then proceed to advanced programmes in chemistry. The training of biologists, geoscientists, medical doctors, nurses, soil scientists, food scientists, chemical engineers, petroleum engineers and many others requires that students in those areas have a good exposure in chemistry.

We have packaged this chemistry course in such a way that you will learn chemistry using a technique peculiar to the open learning system. This technique has been adopted by the National Open University of Nigeria in most of the courses offered to students.

You will here learn the content of this chemistry course at a reasonable pace. You will need to master the language chemists use to describe the world around us. The language is simple, interesting and specific to the subject, chemistry.

We wish you success with the course and hope that you will find it both interesting and useful.

What you will learn in this course

This course is titled "foundation chemistry". It assumes that you had taken a chemistry course before but probably you did not make the grade you desired. So you are re-taking the course with the aim of doing better. There is no doubt therefore that you are familiar with the language of chemistry.

In this present course, you will be presented information in chemistry in a structured way to make learning easier. All the units follow the same pattern and so after the first few units, the rest will become easy to follow. The whole range of senior school certificate examination (SSCE) syllabus has been covered in this course.

Learning Outcomes-Aims and Objectives

The broad aims of this foundation chemistry course can be summarised thus. The course aims to provide you with chemistry content that will be sufficient for you to have the equivalent of the SSCE. Thus you will have solid foundation in chemistry which will enable you go into an advanced science course needing a background of chemistry.

The objectives of this course are set out below. On completion of the course, you should be able to:

1. Distinguish between chemistry and the other science subjects.
2. Discuss the role of chemistry in our every day living.
3. Apply the language of chemistry in describing the world around you.
4. Carry out simple chemical calculations.
5. Identify chemical process in what goes on in your environment.

Course Materials

Three different sets of course materials are provided:

- A Course Guide which spells out the broad details of the foundation chemistry course including the aims and objectives.

- The Study Units with detailed learning information. Each study unit has a set of performance objectives along with other relevant learner guide.

There are forty five (45) study units grouped into three main sections referred to as volumes:

Volume One: General and Physical Chemistry

Volume Two: Physical and Inorganic Chemistry

Volume Three: Organic Chemistry.

- A set of recommended chemistry textbooks is listed at the end of each study unit.

Table of Contents

Volume Two: Physical and Inorganic Chemistry

Volume One

General Physical Chemistry

Unit 1

Elementary Units in Chemical Reactions

1.0 Introduction

Chemistry is the study of matter and chemists in their investigations, study the properties and transformations of matter. Many materials that we use everyday, directly or indirectly are products of chemical research and examples of useful products of chemical reactions are limitless.

What then is matter? **Matter is anything that has mass and occupies space.** Matter is classified into solid, liquid and gas.

- Solids have fixed shapes and sizes. Glass, sand and most metals are examples of solids.
- Liquids have fixed volumes but no fixed shapes. Liquids take the shape of the containing vessel. Water and kerosene are examples of liquids.
- Gases flow and fill the entire space available. Air and cooking gas are examples of gases.

The above classification is commonly referred to as physical classification. Matter can also be classified into elements, compounds and mixtures. This latter classification is referred to as chemical classification. It is remarkable that all these substances, solids, liquids, gases, elements, compounds and mixtures are built up from simple basic units.

What is the basic unit of matter?
What are the building blocks of matter and what laws govern the interaction of matter?
The above are some of the questions that will be answered in this unit.

1.1 Objectives

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

- Define atoms, molecules, elements and compounds.
- Differentiate between atoms and molecules as well as elements and compounds.
- Explain why matter is said to be electrical in nature.
- State the postulates of Dalton's atomic theory and explain modifications to it.
- List and give relative masses and charges of the subatomic particles.
- State the laws of chemical combinations.
- Write chemical symbols and formulae for common elements and compounds.
- Determine chemical formulae from experimental data.
- Write and balance simple chemical equations.

1.2 Elements, Compounds and Mixtures

An element is a pure substance, which cannot be split up into simple substances by a chemical reaction. A pure substance that can be broken down into elements is called a compound. There are over 100 chemical elements. Some occur naturally as free elements, mixed with other elements or compounds. Some are very rare, while most occur in combined state in compounds.

The table 1.1 below gives a list of some elements and their total abundance either as free elements or in combined states.

Table 1.1 List of some elements and their abundance

Element	Abundance in percentage by mass
Oxygen	49.1
Silicon	26.1
Aluminium	7.5
Iron	4.7
Calcium	3.4
Sodium	2.6
Hydrogen	0.88
Chlorine	0.19
Carbon	0.09

Elements can be broadly classified into two groups, metals and non-metals. Examples of metals are copper and iron. The general characteristics of metals are lustre, good conductor of heat and electricity. Metals can be rolled and hammered into sheets and drawn into wires. They are used for roofing and electrical cables respectively. All metals are solids at room temperature except mercury which is a liquid at room temperature. About 75 percent of the elements are metals. Unlike metals, non metals do not have characteristic lustre. Many are gases at room temperature and others are solids except bromine which is a red brown liquid at room temperature.

Non metals are non-conductors of heat and electricity. They cannot be rolled into sheets or drawn into wires like the metals. Oxygen, nitrogen, carbon and iodine are examples of non metals.

- A compound is formed when two or more elements combine chemically in fixed proportion by mass. The properties of compounds are different from those of the elements from which they are formed. A lot of energy is often required to split compounds into the constituent elements. There are limitless number of compounds. Sodium chloride, (common salt), water and calcium trioxocarbonate(iv), (marble) are examples of compounds.
- A mixture is a physical combination of elements or compounds. The composition of a mixture varies and the components are separated by physical methods. Such physical methods include, heating, cooling, dissolution, filtration and distillation. Air and petroleum are examples of mixtures.

1.3 The Particulate Nature of Matter

1.3.1 The concept of atoms and molecules

Experiments show that very small quantities of matter have the same chemical properties or characteristics as larger ones of the same type e.g. a small iron nail and a big iron rod have the same chemical characteristics. For example both will rust when exposed to air and moisture and both will conduct heat and electricity.

- The smallest unit of an element that has the properties and characteristics of the element is the atom. The atom is the smallest unit of an element that can take part in a chemical reaction.
- The molecule is the smallest unit of a compound that has the characteristics of the compound. It is the smallest unit of the compound that can take part in a chemical reaction. The atom is to the element as molecule is to the compound.
- The behaviour of matter is explained using the above concept and chemical reactions are explained as combinations and rearrangement of atoms. The basic unit of matter in chemical reactions is the atom. Atoms and molecules are the building blocks of matter.

1.3.2 The atomic theory and chemical reaction

A theory is a tested proposal to explain an observed statement of facts. A theory serves as a guide to new experiments. When proved incorrect or inadequate by experiment, a theory is discarded or modified so that new experimental facts can be accounted for. This latter statement is true of Dalton's atomic theory. Dalton's atomic theory form the basis of theory of the atom. It has been modified in the light of new experimental facts about the atom. The postulates of Dalton's atomic theory are:

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

Some important modifications to the theory are:

- Matter is composed of more fundamental particles, some of which are electrically neutral, some carry positive charge and some negative charge. This implies that the atom is divisible.
- All atoms of the same element are not identical. The existence of atoms of the same element having different masses have been proved with the use of an instrument called mass spectrometer. Atoms of the same element having different masses are called isotopes.
- The smallest particle of an element that can take part in a chemical change is still the atom and in a chemical change atoms are neither created nor destroyed. Irrespective of masses, atoms of the same element have same chemical properties.

1.3.3 The constituents of the atom

Matter is electrical in nature. Evidences for this assertion came from results of experiments of early scientists like Faraday, Thompson and Millikan. The negatively charged particle in matter is the electron. It has negligible mass. The proton is the positively charged particle. It carries the same magnitude of charge as the electron and is very much heavier than the electron. The third particle is the neutron, a neutral particle with a mass approximately equal to that of the proton. These three particles are constituents of the atom except the hydrogen atoms that do not contain neutrons.

The number of each particle present in the atom varies from one element to another. For the atom (matter) to be electrically neutral, the number of protons must equal the number of electrons. Atoms of the same element will have the same number of protons and electrons but may have different numbers of neutrons. Such atoms will have different masses and are called **isotopes.**

Particle	Relative Mass	Relative Charge
Electron	5.5×10^{-4}	-1
Proton	1.00 727	+1
Neutron	1.00867	0

1.3.4 Relative atomic and molecular masses

Chemistry is a quantitative science and it is always desired to know the relative masses of substances that react as pure elements or compounds. The measurement of masses of atoms is not possible because they are very small. Their masses can however be compared to give relative atomic and molecular masses of elements and compounds. The relative atomic mass of an element is the mass of one atom of the element compared to one-twelfth (1/12) of the mass of one atom of carbon - 12 isotope.

On this scale 1 atom of carbon-12 isotope is given a mass of 12 atomic mass units. With the use of the mass spectrometer it has been possible to determine fairly accurately the relative atomic masses of elements.

The relative molecular mass of a compound is the sum of the relative atomic masses of the elements present in the chemical formula of the compound.

1.3.5 Chemical symbols and formulae

Chemical symbols and formulae are abbreviations used to represent elements and compounds. A chemical equation uses these symbols and formulae to summarise a chemical reaction. Chemical symbols consist of the first one or two letters of the name of the element. Some symbols do not correspond with the elements names; these symbols are derived from the Latin names of the elements. It is important that you know the symbols for as many of the common elements as possible. Table1.3 gives some examples of chemical symbols of elements.

Table 1.3 Elements, symbols and relative atomic masses

Element	Symbol	Relative atomic mass
Hydrogen	H	1.00797
Oxygen	O	15.9998
Chlorine	Cl	35.453
Sodium	Na	22.990
Iron	Fe	55.847
Magnesium	Mg	24.305
Zinc	Zn	65.38
Cobalt	Co	58.933
Copper	Cu (cuprium)	64.456
Lead	Pb (plumbuim)	207.19
Gold	Au(Aurium)	196.967

Hydrogen, oxygen and chlorine elements exist in nature as diatomic molecules. i.e. units consisting of two atoms that are chemically bound together. The latin names for copper, lead and gold are in bracket. The formula of a compound gives the proportion of the different elements present in the compound by mass. By the law of constant composition the proportion by mass of the different elements present is fixed for a pure sample of the compound irrespective of the method of preparations.

Example 1.1

Analysis of 1.630g pure sample of a compound of calcium and sulphur gives 0.906g Ca and 0.724 sulphur.

$$\% \text{Ca} = \frac{\text{mass of Ca x 100}}{\text{mass of sample}} = \frac{.906 \text{ x } 100}{1.630} = 55.6\%$$

$$\% \text{S} = \frac{\text{mass of sulphur}}{\text{mass of sample}} \text{ x } 100$$

$$= \frac{.724}{1.630} = 44.4\%$$

Relative mass of Ca and S in the compound

$$= \frac{55.6}{\text{Relative atomic mass of Ca}} : \frac{44.4}{\text{relative atomic mass of S.}}$$

$$= \frac{55.6}{40} : \frac{44.4}{32}$$

$$= 1.39 : 1.39$$

i.e. 1 : 1

The formula of the compound is CaS.

Having determined the relative atomic mass of the elements that make up the compound, you can proceed to determine the empirical formula of the compound. Since the relative masses of the elements in a compound depend partly on the masses of the atoms and also on the relative number of each atom of each element involved in the combination to form the compound.

Example 1.2

2.83g of a compound of lead (Pb) and surphur gives 2.45g lead and 0.38g sulphur. Determine the formula of the compound.

$$\% \text{Pb} = \frac{2.45}{2.83} \text{ x } 100 = 86.6$$

$$\% \text{ S} = \frac{0.38}{2.83} \text{ x } 100 = 13.4$$

Relative number of Pb : S

$$= \frac{86.6}{207} : \frac{3.4}{32}$$

$$= 0.418 : .419$$

i.e 1 : 1

Formula of compound is PbS.

Now determine a formula of a compound of calcium, carbon and oxygen with 40 percent Ca, and 48 percent oxygen.

1.3.6 Other laws of chemical combination

In the previous section, the law of constant composition (proportion) is stated. Two more laws will be discussed in this section.

(a) The law of conservation of matter

This states that matter is neither created nor destroyed in a chemical reaction. A consequence of this law is that a chemical equation must always be balanced to account for all atoms present on the reactant side, and on the product side of the reaction.

For example

$$2H_2 + O_2 \rightarrow 2H_2O$$
$$2Na + Cl_2 \rightarrow 2NaCl$$
$$H_2 + Cl_2 \rightarrow 2HCl$$
$$2CO + O_2 \rightarrow 2CO_2$$

(b) The law of multiple proportions

This states that when two different compounds are formed from the same two elements e.g. (CO and CO_2 or SO_2 and SO_3) the masses of one element which react with a fixed mass of the other are in a ratio of small whole numbers.

Example 1.3

Analysis of two compounds of carbon shows that 1.33g oxygen combines with 1.00g of carbon, while in the second 6.64g oxygen combines with 2.49g of carbon. Show that this is in agreement with the law of multiple proportion.

For the 1st compound

1.00g carbon combines with 1.33g oxygen

For the second compound

2.49g carbon combines with 6.64g oxygen

$\frac{2.49g}{2.49g}$ carbon will combine with $\frac{6.64}{2.49g}$ g oxygen

1.00g carbon will combine with 2.667g oxygen.

Ratio of O mass combining with 1.0gC

$= 1.33 : 2.667$

$\approx 1 : 2$ simple ratio.

1.4 Chemical Reactions and Equations

A chemical reaction involves the reshuffling of atoms from one set of combinations to another. In the reshuffling, one compound is converted to another. The smallest units that can take part in chemical reactions are the atoms and molecules. A chemical equation is often used to summarise the reaction that has taken place. A chemical equation gives the reactants and products of the reaction and the quantities of the reactants and products in correct ratio in accordance with the law of conservation of matter. Sometimes chemical equations give the physical states of the reactants and products.

(s) for solid
(l) for liquid
(g) for gas
(aq) for aqueous (solution in water)

The equation does not give you the rate of the reaction, the energy effect and the conditions necessary for the reaction to occur.

1.5 Conclusion

A chemical reaction involves elements, compounds and mixtures and leads to rearrangement or reshuffling of atoms. The elementary particles that form the basic units of elements and compounds in chemical reactions are atoms and molecules. Though atoms are composed of more fundamental particles, they are not split in chemical reactions. Dalton's atomic theory is the basis of modem atomic theory and explains satisfactorily the laws that govern chemical reactions of elements and compounds. Atoms and molecules are the building blocks of matter. The atom has a substructure of its own. This is the subject of the next unit.

1.6 Summary

- The concept of atoms and molecules is introduced and explained.
- Dalton's atomic theory is discussed and the modification in the light of new experimental evidences highlighted.
- The atom has a substructure of its own and it is electrical in nature.
- In chemical reactions, atoms are not split but are reshuffled. They are neither created nor destroyed.
- Pure compounds contain fixed proportions of elements by mass.
- A chemical equation is a summary of the reaction.
- Chemical symbols and formulae allow for summary of a reaction in short hand form. A chemical equation must be balanced for the law of conservation energy to be satisfied.
- Chemistry is a quantitative science and as such, amounts of matter used in reactions must be known. The relative atomic and molecular masses allow us to see on the atomic level, the relative amounts of reactants to products in chemical reactions.

Tutor-Marked Assignments

(c) Calculate the percentage by mass of hydrogen in the following compounds:
   (i) water (H_2O) (ii) Hydrogen sulphide (H_2S) (iii) hydrogen chloride (HCl) and
   (iv) methane (CH_4)

2. (a) What are isotopes?
   (b) Natural chlorine consists of 75 percent of chlorine-35 and 25 percent of chlorine-37 isotopes. Calculate the relative atomic mass of chlorine element.
   (c) Explain why matter is neutral though it contains negative particles in its structure.

1.8 References

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Osei Yaw Ababio (2002). *New School Chemistry.* Onitsha Africana-Fep Publishers.

Unit 2

Electronic Configuration 1 – Static Model

2.0 Introduction

In the last unit the concept of atoms and molecules was introduced and discussed. Dalton's theory proposed that atoms are indivisible units of matter. The atom is the smallest unit of matter that can take part in a chemical change. Dalton's atomic theory satisfactorily explained the laws of chemical combination but could not explain why substances react the way they do. Why is oxygen able to react with maximum of two atoms of hydrogen as in water? Why do some elements exist only as diatomic molecules? Why are some elements very reactive and some inert? Dalton's law could not explain electrolysis neither could it explain the different masses of atoms of the same element.

Today we believe that the atom has a substructure of its own. The atom consists of much smaller particles that we call protons, neutrons and electrons. The relative masses and charges of these particles are given in unit 1.

What are the evidences in support of this new picture of the atom? How many of these particles are present in the atom of elements? How are these particles arranged in the atom? These are some of the questions that will be answered in this unit.

2.1 Objectives

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

- Discuss the scientific evidences for the electrical nature of the atom.
- Give the number of subatomic particles in atoms of given elements.
- Recall the relative masses and charges of the subatomic particles.
- Define isotope
- Explain the nuclear model of the atom proposed by Rutherford.
- State the limitations of Rutherford's theory.
- Explain the origin of electronic energy levels in atoms.
- Write electronic shell configuration for elements and ions.

2.2 The Electrical Nature of the Atom

2.2.1 Historical evidences

A very early evidence for the electrical nature of the atom came from Faraday. The result of Faraday's experiment on electrolysis showed that chemical change could be caused by the passage of electricity through aqueous solutions of chemical compounds. This evidence was closely followed by the discharge tube experiment. A heated metal cathode emitted negatively charged particles. This beam of particles is called cathode rays and the particles are the electrons.

J.J. Thompson worked on cathode rays and confirmed that they are negatively charged. Their charge mass ratio was determined and found to be -1.76×10^{8} coulomb/g^{-1}. R. A. Millikan determined the electronic charge in his famous oil drop experiment in 1908. The charge of the electron is -1.602×10^{19} coulomb. The mass of the electron was calculated. It is 9.11×10^{-28}g.

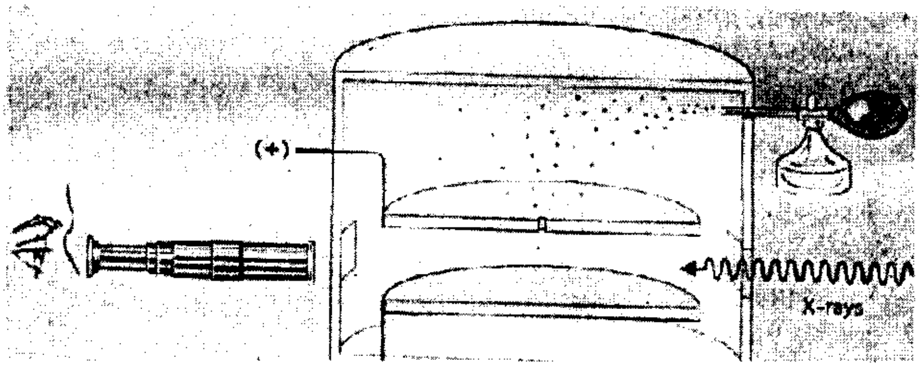


Fig. 2.1: Millikan oil drop experiment

The atom is electrically neutral, so it is reasonable to expect positively charged particles in the atom. The existence of positively charged particles was confirmed in a modified version of the set up used by J. J. Thompson by another scientist by name Goldstein. The charge/mass ratio of the positive particles are much smaller than for the electrons. The largest charge/mass was for hydrogen ion (H^+) which now represents the fundamental particle of positive charge in the atom. The proton is about 1835 times as heavy as the electron and carry a charge equal but of opposite sign to that of the electron. Protons and electrons are present in all atoms.

The evidence of radioactivity by H. Becquerel further demonstrated the existence of subatomic particles. Becquerel observed that certain substances spontaneously emit radiations. The most important of these radiations are the alpha, beta and gamma radiations. Chadwick later confirmed the existence of a neutral particle in the atom and called this a neutron. This neutron has a mass approximately equal to that of the proton.

Table 2.1: Properties of subatomic particles

Particles	**Mass**	**Charge**		
	Grams	a.mu	Coulombs	electron charge
Proton	1.67×10^{-24}	1.007274	$+1.602 \times 10^{-19}$	+ 1
Neutron	1.68×10^{-24}	1.008665	0	
Electron	9.11×10^{-28}	.000549	-1.602×10^{-19}	−1

2.2.2 Atomic and mass numbers

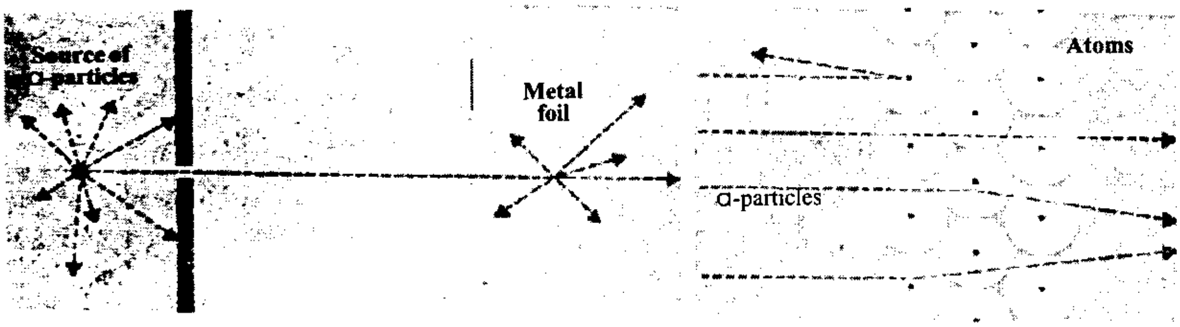
Atoms of different elements have varying numbers of protons, electrons and neutrons. The atomic number is the number of protons in an atom of the element and for a neutral atom, the atomic number is also the number of electrons. The sum of the number of protons and neutrons is the mass number.

Isotopes are atoms of the same element with different mass numbers. We shall see in the subsequent units that the chemical property of an element depends on the number as well as the arrangement of the atomic electrons. This explains why atoms of the same element with different masses have the same chemical properties. $^{12}_{6}C$ and $^{14}_{6}C$ These are isotopes of carbon, mass number 12 and 14 and neutron numbers 6, and 8 respectively.

2.3 Atomic Models

2.3.1 The nuclear atom

The presence of subatomic particles posed challenge to early scientists. It was necessary to propose a model for the atom. J. J. Thompson proposed that the atom could be viewed as positive matter in which electrons are uniformly distributed to make it neutral at every point. This view was dropped because of the findings of two other scientists, Rutherford and Marsden. They bombarded a thin gold foil with fast moving alpha particles. They found that most of the alpha particles pass through the foil undeflected. Some were deflected as large angles while very few were sent back on their paths. Alpha particles are positively charged and many of them passing through the foil undeflected suggested that most of the gold foil was empty space.



(a) (b)

Fig. 2.2: Scattering of α-particles by a metal foil. (b) Deflection of α-particles by atomic nuclei

Rutherford, using the findings in the above experiment proposed a model for the atom. He proposed that the atom consisted of a tiny positively charged nucleus. The nucleus is centrally placed in the atom and the electrons surround it. The very small number of deflections of alpha particles suggest that the nucleus occupies a very small portion of the atom. For heavy particles such as the alpha particle to be so deflected suggests that the nucleus is a centre of heavy mass and positive charge. The protons and neutrons occupy the nucleus while the electrons are arranged around the nucleus and move in orbits around it, as planets around the sun. This is Rutherfords nuclear model of the atom.

By counting the number of alpha particles deflected in various directions, Rutherford was able to show that the diameter of a nucleus is about 1/100,000 times the diameter of the atom.

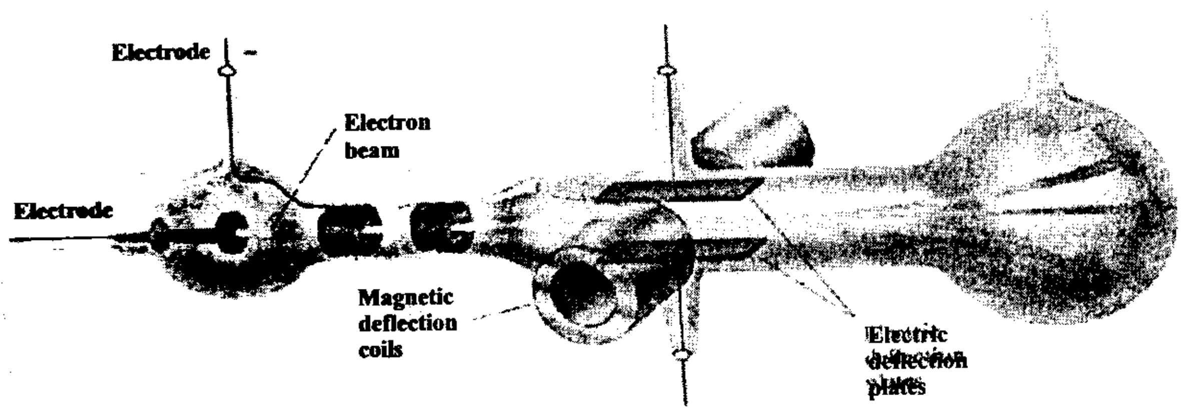


Fig. 2.3: Schematic of a discharge tube. When a voltage is applied across electrodes that are sealed in a partially evacuated glass tube, the space between the electrodes glows.

2.3.2 Electronic energy levels

A major problem of Rutherford's model of the atom is that the electron (–vely charged) rotating around the nucleus (+vely charged) will lose energy continuously because of the electrostatic force of attraction of the nucleus on the electrons. This is not observed in practice. Infact energy absorption and emission by elements is discontinuous.

Have you ever seen the rainbow in the sky? The colours you see range from violet to red with no sharp line separating one colour from the other. This is a continuous spread of colours and is called a continuous spectrum. The different colours are component colours of light. In the laboratory the separation of light into its component colours also happens when light passes through a glass prism.

Light from the vapour of an element does not give a continuous spectrum. Each element has its own characteristic bright lines in particular positions. This is a line spectrum suggesting that light energy absorption or emissons by elements is only at particular energies characteristic of the element.

On the basis of the above observations Niel's Bohr proposed a model for the atom in which electrons move round the nucleus only in allowed orbits numbered serially. The orbit closest to the nucleus is assigned number 1 and is the orbit of lowest energy. Allowed transitions are transitions from one orbit to another and will lead to emission or absorption of the energy difference between the orbits.

In the light of Bohr's model, there are electronic energy levels in atoms corresponding to different orbits of electron motion that are allowed. These energy levels are sometimes referred to as electron shells and designated K, L, M, N etc. corresponding to orbit numbers 1, 2, 3, 4, etc respectively.

Bohr's model gave satisfactory explanation of the hydrogen spectrum. The theory is limited however in its explanation for multi electron atoms. The wave mechanical treatment of the atom overcomes this limitation of Bohr's theory and is the subject of a subsequent unit.

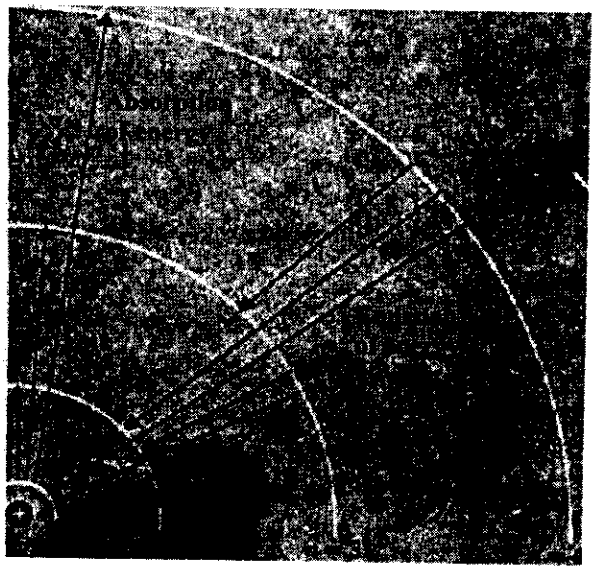


Fig. 2.4: The radii of Bohr's orbits.

2.3.3 Electronic configuration

Electronic configuration gives the arrangement of electrons in the energy levels in the atom. In the ground state (most stable state of lowest energy) of the atom, electron assignment to energy levels is according to the following rules:

- the order of filling is K → L → M → N etc. The first shell is filled first before filling the second
- the K shell can accommodate maximum of 2 electrons
- the L shell can accommodate maximum of 8 electrons.
- the M shell accommodates 18 electrons.

  When 8 electrons are accommodated into the M shell however, there is extra stability and the next 2 electrons go into the N shell. Subsequently any electron goes into the M shell until it contains the maximum of 18 electrons.
- there are higher energy levels that accommodate a larger number of electrons than the K, L, M shells.

Table 2.2: Electron arrangement in some elements

Element	Symbol	Atomic number	Arrangement of electrons
Hydrogen	H	1	1
Helium	He	2	2
Lithium	Li	3	2, 1
Berylium	Be	4	2,2
Nitrogen	N	7	2, 5
Oxygen	O	8	2, 6
Fluorine	F	9	2, 7
Neon	Ne	10	2, 8
Sodium	Na	11	2, 8, 1
Magnesium	Mg	12	2, 8, 2
Aluminium	Al	13	2, 8, 3
Silicon	Si	14	2, 8, 4
Sulphur	S	16	2, 8, 6
Chlorine	Cl	17	2, 8, 7
Argon	Ar	18	2, 8, 8
Calcium	Ca	20	2, 8, 8, 2

The electronic structure 2, 8,1 denotes 2 electrons in the K shell, 8 in the L shell and 1 in the M shell. Study the above table and note the following:

(a) He and Ne; each has full shell of electrons and are both inert gases.

(b) F and Cl; each has one electron short of a full electron arrangement.

(c) H and Na; each has one electron outside a full shell electron arrangement. These pair of elements with similar electron arrangements also have similar chemical properties.

Now give the electron arrangement for each of the following:

Carbon (6) Phosphorus (15) and potassium (19)

Which of the elements in the table will have similar chemical properties with phosphorus.

Note

Isotopes have the same number of electrons and therefore have the same electron arrangement. Their chemical properties are the same.

2.3.4 Ion formation

An ion is formed when an atom gains or loses electron.

e.g. H^+, F^- Na^+. The proton number is not affected by ion formation but the electron number increases or decreases.

Ion	Electron number	Electron arrangement
Li^+	2	2
F^-	10	2, 8
O^{2-}	10	2, 8
Mg^{2+}	10	2, 8
Cl^-	18	2, 8, 8
Ca^{2+}	18	2, 8,8

You will observe that these ions have closed or full shell electron arrangements and are stable ions. This observation and the full shell arrangements for the inert gases, suggest that a full shell electron arrangement is a stable electron arrangement.

2.4 Conclusion

Matter is electrical in nature. This is supported by results of experimental investigations by early scientists. Three fundamental particles are present in the atom. The positive charge and mass are in a small centre of the atom. This centre is the nucleus and is surrounded by electrons moving round in allowed orbits of fixed energy. Electron assignment to these energy levels show that elements with similar properties have similar electron arrangement. The noble (inert) elements have closed shell electron arrangement suggesting that a closed shell arrangement of electrons is a stable configuration. This observation is used to explain chemical bonding.

2.6 Summary

- The historical evidences for the electrical nature of the atom are many. Some of these evidences are revealed and discussed in this unit.
- Rutherford proposed a nuclear model for the atom. This model was modified by Bohr who proposed electronic energy levels, sometimes referred to as electronic shells around the nucleus.
- The electrons are accommodated into these shells starting with the shell of lowest energy.
- The rules for electron arrangement allow for elements with similar properties to have similar electronic configuration.
- The inert elements have closed shell electron arrangement.
- Ions are formed when atoms gain or lose electrons. Stable ions also have closed shell electron arrangement.

2.7 Tutor-Marked Assignments

1. (a) State the contribution of Dalton and Rutherford to atomic theory.

   (b) Explain the limitations of Rutherford's model of the atom and show how Bohr's modification improved on Rutherford's model.

2. (a) Give the shell electron arrangement in the following elements. The atomic numbers are in brackets
Be (4) Mg (12) K (19) Si (14) and Cl (17)

(b) Which of the listed elements in (a) above are likely to:
   - (i) be metals.
   - (ii) be non-metals
   - (iii) have similar properties with carbon.
   - (iv) form univalent ion of the type X^-.
   - (v) have divalent ion of the type M^{2+}.

2.8 References

Bajah, S. T., Teibo, B. O., Onwu G. and Obikwere A. (2002). *Senior Secondary Chemistry Textbook 2.* Lagos. Longman Publishers.

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Unit 3

The Nucleus and Radioactivity

3.0 Introduction

The nucleus is the centre of positive charge and mass in an atom. The number of positive charges in the nucleus of a neutral atom determines the number of electrons that surround the nucleus. The arrangement of the electrons around the nucleus determines the chemical properties of the element.

Presently there is no theory that predicts the stability of the nucleus but a number of empirical observations suggest that the presence of neutrons account partly for nuclear stability. Except for the hydrogen atom, all nuclei contain neutrons. As the proton number increases, the neutron number also increases. For heavy elements the neutron number far exceeds the proton number in the nucleus.

e.g. ${}^{208}_{82}\mathrm{Pb}$ has 82 protons and 126 neutrons.

Are all nuclei stable? Can nuclei react? What happens when a nucleus is unstable? Can a stable nucleus be made unstable? These are some of the questions to be answered in this unit.

3.1 Objectives

At the end of this unit you should be able to:

- State some empirical observations suggesting that neutrons are partly responsible for nuclei stability.
- Define radioactivity.
- Balance nuclear reaction equation.
- List the three types of radiations from a radioisotope giving their relative charges and masses.
- Show the path of nuclear radiations in an electric field.
- Define fusion and fission
- List some uses of radioactivity.
- Explain why radioactive wastes are dangerous.

3.2 The Nucleus

The nucleus occupies a very small volume of the atom. According to Rutherford the nucleus is about 1/100,000 times the size of the atom. Except for hydrogen all elements have more than one proton in their nuclei. From your knowledge of elementary magnesium in Physics, you learnt that like charges repel each other whereas unlike charges attract each other.

How then can particles of the same charge stay so close in the nucleus without repelling. As mentioned in the introduction, no theory predicts nuclear stability. Empirical observations suggest that neutrons are partly responsible for nuclear stability. Listed below are these observations:

- All nuclei except hydrogen contain neutrons.
- As proton number increases neutron number also increases and far exceeds proton number for heavy elements.
- For some elements certain neutron-proton combination are unstable.
- Some neutron-proton combination are more abundant than others for the same element.

Table 3.1 gives some naturally occurring isotopes of carbon and oxygen and their abundance.

Table 3.1: Naturally occurring isotopes

Element	Isotope	Natural abundance
Carbon	$^{12}_{6}C$	98.89
	$^{13}_{6}C$	1.11
	$^{14}_{6}C$	trace
Oxygen	$^{16}_{8}O$	99.758
	$^{17}_{8}O$	0.038
	$^{18}_{8}O$	0.204

3.3 Nuclear Reactions

Nuclear reactions involve changes in the composition of nuclei leading to the conversion of one element to another. Contrary to the postulate of Dalton, an element is destroyed and a new one is created, when a radioactive element like uranium disintegrates.

Like in simple chemical reactions symbols are used to summarise the nuclear reaction in an equaiton. A nuclear reaction equation must be balanced to account for all particles and charge.

$$\text{e.g. } ^{238}_{92}U \rightarrow ^{234}_{90}Th + ^{4}_{2}He$$

Uranium 238, the uranium isotope having an atomic mass of 238 is radioactive. It breaks down emitting particles of Thorium and Helium.

3.3.1 Radioactivity

Some nuclei are unstable and will spontaneously emit radiations. This is called radioactivity and is an example of a nuclear reaciton.

Very heavy metals with atomic number greater than 83 are radioactive. Some isotopes of light elements are also radioactive. A radioactive isotope is called a **radioisotope**. Examples of radioisotopes are

$$^{238}_{92}U \quad \text{and} \quad ^{14}_{6}C$$

Radioisotopes decay at different rates. The half-life is a measure of the stability of a radioisotope.

Half life is the time it takes for half of the radioactive substance to decay. $^{14}_{6}C$ and $^{238}_{92}U$ have half lives of 5570 and 4.47 x 10^9 years respectively. They are very stable compared to $^{23}_{11}Na$ and $^{214}_{84}P_o$ with half lives of 60 seconds and 101 microseconds respectively.

Some stable isotopes of elements can be made radioactive.

$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{14}_{6}C + ^{1}_{1}P$$

The above is a reaction that occurs instantly in the nature by the bombardment of cosmic neutrons upon nitrogen. It helps to keep $^{14}_{6}C$ activity constant in the atmosphere.

3.3.2 Nuclear radiations

A radioactive element in its decay emits radiations. These radiations are mainly of three types. They are called alpha (α); Beta (β) and gamma (γ) rays. The properties of α, β and γ rays are summarised in the table 3.2. α, β and γ radiations are detected when they pass through an electric or magnetic field.

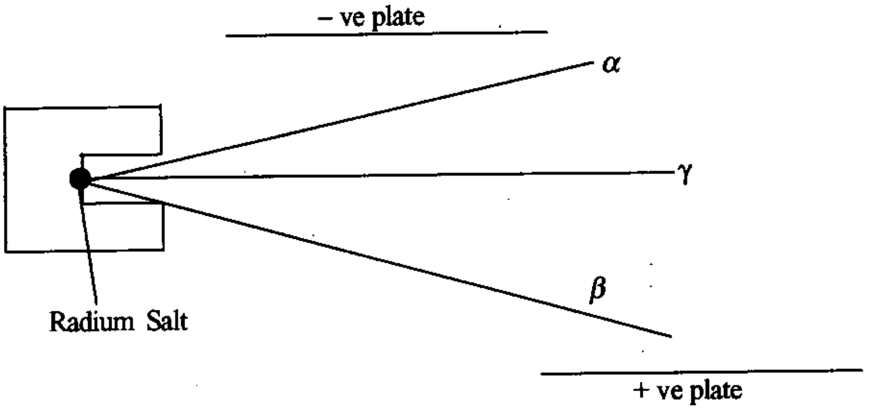


Fig. 3.1: Radiations

Table 3.2: Alpha (α), Beta (β) and gamma (γ) radiations

Alpha (α)	Beta (β)	gamma (γ)
(i) positively charged	negatively charged	no charge
(ii) they are helium nuclei $^{4}_{2}He$	they are electrons $^{0}_{-1}\beta$	electromagnetic radiation
(iii) deflected towards a –ve pole	deflected towards a +ve pole	no effect of electric field.
(iv) low penetrating power (absorbed by a thin sheet of paper).	higher penetrating power	very high penetrating power (absorbed by thick lead block).
(v) high ionising power on gases	low ionising power on gases	very low ionising power on gases

The decay of heavy radioisotopes is usually accompanied by the emission of all the three types of radiations. Decay of light radio isotopes is usually accompanied by one or at most two of the three radiations.

3.3.3 Nuclear fusion

This is a process in which two or more light nuclei combine to form a heavier nucleus with a release of energy. **Nuclear fusion reactions require very high temperatures**. Because of the very high temperatures in sun, fusion reactions are believed to occur and are responsible for the very high thermal energy that comes from the sun.

$${}^{2}_{1}H + {}^{2}_{1}H \rightarrow {}^{4}_{2}He + \text{energy}$$

The above is suspected to be one of the reactions occurring in the sun. The energy from a fusion reaction initiates more reactions. If not controlled, can lead to explosion.

3.3.4 Nuclear fission

Nuclear fission is a process in which the nucleus of a heavy element is spilt into two nuclei of nearly equal mass with a release of energy and radiation.

$${}^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{236}_{92}U \rightarrow {}^{140}_{54}Xe + {}^{93}_{38}Sr + 3\,{}^{1}_{0}n \quad \text{energy}$$

This fission process is initiated by the absorption of a neutron. The reaction releases three neutrons which can initiate more fission reactions. This is an example of a **chain reaction**. If the chain reaction is not controlled the fission reaction can become explosive. The energy from fission reactions are not as high as in fusion and the reactions in fission do not require very high temperatures to initiate. There are fission reactors used in generating electricity.

3.3.5 Other examples of nuclear transformation reactions.

Nuclear transformation implies changing one element to another by the reactions of atomic nuclei. These reactions are many. Many isotopes of elements have been prepared by this method and used in chemical, biological and medical researches.

$${}^{14}_{7}N + {}^{4}_{2}He \rightarrow {}^{17}_{8}O + {}^{1}_{1}H$$

$${}^{27}_{13}Al + {}^{4}_{2}He \rightarrow {}^{30}_{15}P + {}^{1}_{0}H$$

For heavy elements, neutron bombardment is more common because they are neutral and are not repelled by nuclei with the use of particle accelerators. Some heavy elements have been produced by the radioactive action of alpha particles, i.e. Helium atom.

$${}^{238}_{92}U + {}^{4}_{2}He \rightarrow {}^{239}_{94}Pu + 3\,{}^{1}_{0}n$$

3.4 Uses of Radioactivity

Radioactivity has a large number of uses which include

- Treatment of cancer.
- Sterilising hospital equipment and instruments.
- Controlling the thickness of paper, metals and plastics.
- Controlling the filling of packets and containers.

- Tracing movement of a substance in a process.
- Source of energy as in fission.
- Radioactive dating e.g. carbon dating.

3.5 Hazards of Radioactivity

Gamma radiation is used to destroy cancerous cells. This is one use gamma radiaiton is put into. F-radiation also destroys healthy cells as well and too much exposure to it can do more harm than good. The extent of damage depends on the energy and type of radiation. The effect of radiation is also cumulative and small doses over a long period of time will also cause serious damage to biological systems.

Radioactive waste is very dangerous and must be disposed properly to avoid unnecessary exposure to its hazards.

3.6 Conclusion

The nucleus is sterilised in part by the presence of neutrons. Nuclear reactions unlike chemical reactions which involve valence electrons, nuclear reactions involve protons and neutrons. Nuclear reactions are much more exothermic than chemical reactions.

Many atomic nuclei are unstable. Some occur naturally and some are man-made. Unstable nuclei emit radiations with characteristic properties. The emitted radiations find application in various fields of human endeavour but also pose danger to users and non users alike. Radioactive waste must be properly disposed to avoid unwanted effects. Radioactive materials must always be handled with care.

3.7 Summary

This unit discusses the properties and applications of the nucleus.

- When nuclei react they are transformed in the reactions.
- Unstable nuclei decay to give out three major types of radiations with characteristic properties. The radiations have properties that make them detectable.
- Reactions of atomic nuclei in fission and fusion processes are important because of the high energies involved.
- Fission reactors are used to generate electricity.
- Radioactivity is used in medicine, agriculture, industry, engineering and chemical research laboratories.
- The emitted radiations can lead to unwanted efects in biological systems.
- The environment must be protected by proper disposal of radioactive waste.

3.8 Tutor-Marked Assignments

1 (a) List the three types of radiations emitted by radioisotopes and show how they are differentiated in an electric field.

(b) Fill in the missing nuclei in the following nuclear equations.

(i) $^{70}_{30}Zn \rightarrow ^{0}_{-1}e + ?$

(ii) $^{137}_{57}La + ^{4}_{2}He \rightarrow ^{1}_{1}P + ?$

2 (a) List four uses of radioactivity

(b) Give some empirical observations suggesting that neutrons are partly responsible for nuclear stability.

(c) How many protons, neutrons and electrons are present in the following

$$^{60}_{27}Co \; , ^{43}_{19}K \quad \text{and} \quad ^{55}_{26}Fe$$

3.9 References

Bajah, S. T., Teibo, B. O., Onwu, G. and Obikwere A., (2002). *Senior Secondary Chemistry Textbook 2* Lagos Longman Publishers.

Osei Yaw Ababio, (2002). *New School Chemistry.* Onitsha. Africana-FEP Publishers.

Unit 4

Chemical Bonding 1: Electrovalent, Covalent and Co-ordinate Covalent

4.0 Introduction

When elements combine, compounds are formed. The forces that hold atoms together in compounds are called chemical bonds. The combination of chemical elements to give a compound is a chemical reaction. Some elements are very reactive and exist in nature only in combined states, e.g. sodium in sodium chloride (common salt) and calcium in calcium trioxocarbonate (marble). Few elements are relatively unreactive and exit rarely as free elements. They are called noble or rare elements, e.g. no compound of helium, argon and neon exists. Most elements have intermediate reactivity and exist as free elements as well as in chemical compounds e.g. carbon occurs as graphile and diamond as well as in petroleum and many organic compounds. There are some non metallic elements that exist only as diatomic molecules in the free state. These elements also occur in combined states.

In the previous unit, you were shown that arrangement of electrons in atoms showed some correlation between electron arrangement and properties.

Li (2, 1), Na (2,8,1), K (2,8,8,1) all have similar configuration with one electron each in their outermost shell. They are metals. F (2,7) and Cl(2,8,7) all need one electron to complete their outermost electron shell. They are non-metals. The inert or noble elements He (2), Ne (2,8), Ar (2,8,8) all have complete shell arrangement of electrons. The electron arrangement in stable ions of metals and non metals also show that complete shell of electrons is a stable configuration e.g. Na^+ (2,8), F^- (2,8) and O^{2-} (2,8).

In chemical bonding therefore elements tend to attain the noble or inert gas configuration. There are many types of bonds but in this unit, you will focus on three types:

- electrovalent
- co-valent
- co-ordinate covalent.

4.1 Objectives

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

- Explain electrovalent and covalent bonding.
- Write electron dot formulae for compounds.
- List properties of electrovalent and covalent compounds.
- State the octet rule.

- Explain the importance of noble gas configuration on chemical bonding.
- Predict the type of bonds between atoms.
- Explain the difference between covalent and co-ordinate covalent bonding.

4.2 Electrovalent (Ionic) Bonding

When atoms interact for bond formation only the outermost parts of the atoms are in contact and so only the outer electrons in the outermost shell (valence electrons) are involved. The outermost shell electron arrangement is therefore very important in determining the type of bond. Electrovalent bonding involves electron transfer from the valence shell of one atom to the valence shell of the other.

One atom loses electrons to become positively charged and the other gains electrons to become negatively charged. **The positively and negatively charged ions are called cations and anions respectively.** The ionic bond results from the attraction between these oppositely charged ions. This type of bonding is usually between metals and non-metals.

e.g. Li and F

$$\mathrm{Li} \longrightarrow 2,1$$

$$\mathrm{F} \longrightarrow 2,7$$

$$\mathrm{Li} \longrightarrow \mathrm{Li^+}\ (2) + e$$

$$\mathrm{F}, +e \longrightarrow \mathrm{F^-}\ (2,8)$$

$$\mathrm{Li^+} + \mathrm{F^-} \longrightarrow \mathrm{Li^+}\ [\,:\overset{\bullet\bullet}{\underset{\bullet\bullet}{\mathrm{F}}}:\,]^-$$

The formula of LiF written as above is the electron dot formula (Lewis structure). The brackets around the fluorine are intended to show that all eight electrons are the exclusive property of the fluoride ion (F). Another example is the bond between sodium and chlorine.

$$\mathrm{Na}\ (2, 8, 1) \longrightarrow \mathrm{Na^+}\ (2, 8) + e$$

$$\mathrm{Cl}\ (2, 8, 7) + e \longrightarrow \mathrm{Cl^-}\ (2, 8, 8)$$

$$\mathrm{Na^+} + \mathrm{Cl^-} \longrightarrow \mathrm{Na^+}[\,:\overset{\bullet\bullet}{\underset{\bullet\bullet}{\mathrm{C}\ell}}:\,]$$

As can be seen from the examples, the loss and gain of electrons result in inert gas configurations for the cation and anion. Except for helium, He (2) the inert gas configuration corresponds to eight electrons in the outershell. The electronic theory of valency as postulated by Kossel and Lewis 1716 was prompted by the remarkable stability of the rare gas elements. This stability is associated with the presence in the atoms of a group of eight electrons in the outer shell. This completeness appears to be the source of stability in rare gases.

The tendency for atoms to have eight electrons in their outermost shell (is explained by the octet rule). The octet rule states that:

- atoms tend to gain or lose electrons until there are eight electrons in their valence shell.

Note that the rule does not always hold. In cases like these, other stable configurations explain ion stability. The number of bonds to a particular atom depends on the number of electrons gained or lost to attain stable configurations for example.

$$\mathrm{Ca}\ (2, 8, 8, 2) \longrightarrow \mathrm{Ca^{2+}}\ (2, 8, 8) + 2e$$

$$2Cl\,(2, 8, 7) + 2e \longrightarrow 2\,Cl^-\,(2, 8, 8)$$

$$Ca^{2+} + 2Cl^- \longrightarrow Ca^{2+}\left[\bullet\overset{\bullet\bullet}{\underset{\bullet\bullet}{Cl}}\bullet\right]^{-1} \left[\bullet\overset{\bullet\bullet}{\underset{\bullet\bullet}{Cl}}\bullet\right]^{-1}$$

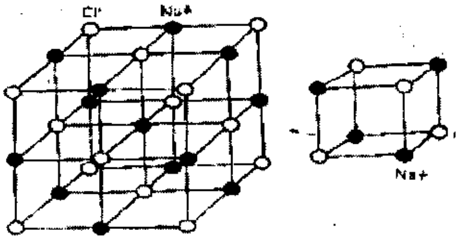
$$Ca^{2+} + 2Cl^- \longrightarrow CaCl_2$$

Now explain the bonding between sodium and oxygen. Write the formula of the compound.

4.2.1 Structure of electrovalent compounds

It is incorrect to speak of a molecule of an ionic compound like NaCl or LiF. Ionic compounds are usually solid consisting of regular arrangement of equal number of positive and negative charges. For Lif and NaCl there will be equal numbers of cations and anions.

This regular arrangement of cations and anions in the solid crystal is called the lattice. The structure of sodium chloride is illustrated in the Fig 4.1



chlorine ion, Cl⁻
sodium ion, Na⁺

The basic unit of
the crystal lattice

Fig 4.1 Lattice structure in sodium chloride

4.2.2 Properties of electrovalent compounds

Electrovalent compounds are

(i) usually crystalline solids,
(ii) generally soluble in water but generally insoluble in organic solvents like ether or kerosene,
(iii) usually high melting point compounds,
(iv) good conductors of electricity when molten or in aqueous solution but not when solid.

It is easier to explain the binding forces in the union between sodium ion and chloride ion, in the formation of sodium chloride since their opposite ionic charges attract each other. Its however difficult to comprehend the manner of bondage between non ionic or non polar atoms.

4.3 Covalent Bonding

It is easier to explain the binding forces in the union between sodium ion and chloride ion, in the formation of sodium chloride since their opposite ionic charges attract each other. Its however difficult to comprehend the manner of bonding between non ionic or non polar atoms.

Lewis, 1916, came up with a tenable explanation, suggesting that non ionic molecular compounds arise from the sharing of electrons among atoms, resulting in a form of bonding which was called the covalent bond. This type of bonding involves sharing of electron pairs rather than complete transfer. The shared electron pair/s is/are contributed by the two atoms involved in the bonding. The binding force results from the attraction of the shared electron pairs by the nuclei of the atoms involved in the bonding. This type of bonding is between non metals. Look at the following examples.

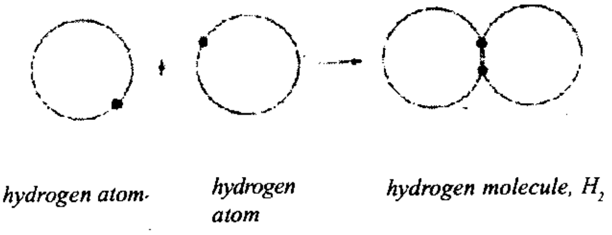


Fig 4.2: Formation of covalent hydrogen molecule

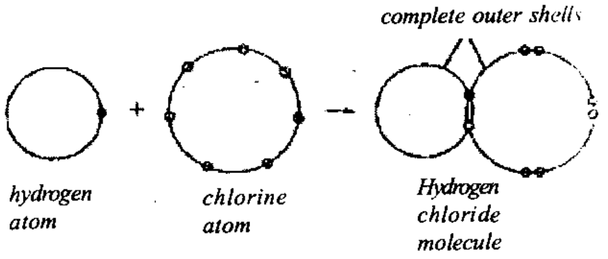


Fig 4.3 Shared electrons in hydrogen chloride

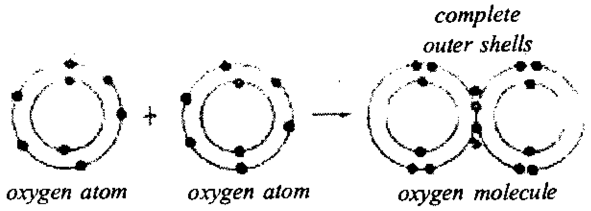


Fig 4.4 Formation of covalent oxygen molecule

An electron pair constitutes a bond and two pairs constitute a double bond as in the oxygen molecule. The number of electron pairs shared depend on the number of electrons each atom must share to attain an inert gas configuration. Covalent compounds form molecules and depending on the intermolecular forces between the molecules they may be gas (O_2, H_2 HCl) or liquids (Br_2 H_2O) or low boiling solids (candle wax).

4.3.1 Properties of covalent compounds

Covalent compounds are

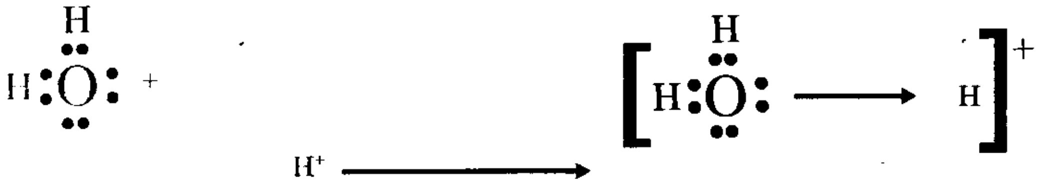
(i) mostly liquids or gases,
(ii) generally low melting when they are solids,
(iii) generally not very soluble in water,
(iv) generally soluble in organic solvents,
(v) non conductors of heat and electricity unless they dissolve to form ions e.g. HCl

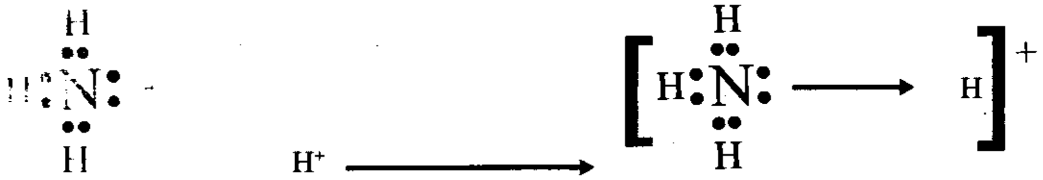
4.4 Co-ordinate (Dative) Covalent Bonding

In a covalent bond the shared electrons are donated and controlled by both atoms that are involved in the bonding. This is not the case with co-ordinate covalent bond. One atom donates the electron pairs but both atoms control the donated pair/s.

Once a coordinate covalent bond is formed it is not different from ordinary covalent bond. The electron pair is attracted by both nuclei of the bonded atoms. For this type of bond to be formed, one atom must have a lone pair/s of electrons. (Lone pairs are electron pairs that are not used in bonding to other atoms) The other atom must have a vacancy in its valence shell to accept the lone pair. The bond formation also results in inert gas configuration for both atoms.

Let us look at the formation of the hydronium ion and the ammonium ion, H_3O^+ and NH_4^+

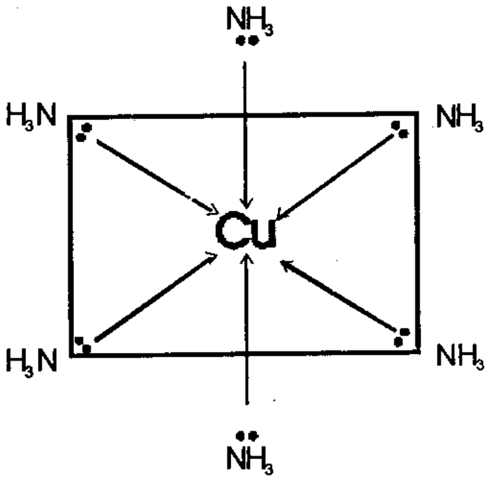




Note that the positive charge is now controlled by the entire molecule. The dative bond cannot be differentiated once formed but sometime to indicate the presence of a dative bond in the molecule we indicate with arrow the direction of electron donation (→) The arrow points towards the acceptor atom.

Co-ordinate covalent bonding is common with metal complexes. The molecules donating the electron pairs are called ligands and the metal ion the central atom.

E.g. The formation of the ammonia complex with copper ions in solution. The octet rule



does not apply here. Why? It is a complex ion and has charges located on a group of atom.

4.5 Conclusion

In this unit we have discussed two major types of bonding; the electrovalent and covalent bonding. The properties of a compound depend on the type of bond between the constituent of atoms.

Electrovalent compounds consist of cations and anions in their solid structure. When an ionic solid dissolves in water or is melted, these ions become free. This explains why ionic compounds are good electrolytes when molten or in solution. Most covalent compounds are gases at room temperature because they consist of molecules held together by weak intermolecular forces. Dative bonding is an important type of bonding that helps to explain the structure and properties of additive compounds and complex ions.

4.6 Summary

- An ionic bond is the electrostatic force that bonds opposite ions together.
- A covalent bond is as a result of attraction between shared electron pairs and nuclei of the atoms involved in the bonding.
- In bond formation elements attain inert or stable configuration.
- Electrovalent bonding is between metals and non metals but covalent bonding is between non metals.
- A Lewis structure is very useful in chemical bonding because it shows the arrangement of the valence electrons of the atoms in a bond.
- For the formation of a dative bond, one atom must have lone pairs of electrons to donate, and the other atom must have available vacancy in the outer shell to accommodate the donated electrons. Water and ammonia have lone electron pairs and take part in dative bonding with the hydrogen ion. Dative bonding is a special type of covalent bonding.

4.7 Tutor-Marked Assignments

1. (a) Define the following:
    (i) cation, (ii) anion, (iii) ionic compound and (iv) valence electrons.

   (b) Magnesium burns in oxygen to give a compound.
    (i) Explain the bonding between magnesium and oxygen.
    (ii) Write the formula of the compound.
    (iii) Calculate the percentage of oxygen in the compound.

2. (a) State the octet rule.
   (b) Explain its significance in covalent bonding.
   (c) You are given the following : KCl, HBr, Cl_2, NH_3, BF_3
    State with reasons in each case, the compounds
    (i) that will conduct electricity when melted.
    (ii) that will dissolve in water to produce ions.
    (iii) with lone pairs of electrons.
    (iv) that can accept a lone electron pair.

4.8 References

Bajah, S. T., Teibo, B. O., Onwu, G. and Obikwere A. (2002). *Senioir Secondary Chemistry Textbook 1,* Lagos. Longman Publishers.

Osei Yaw Ababio, (2002). *New School Chemistry.* Onitsha. Africana-Fep. Publishers.

Unit 5

Chemical Bonding II: Metallic and Intermolecular Bonding

5.0 Introduction

There are three major types of bonds, electrovalent, covalent and metallic. Each bond type gives characteristic properties to the compounds that are formed.

In a previous unit we discussed electrovalent and covalent bonding. While electrovalent bonding is between metals and non metals, covalent bonding is between non-metals. In the formation of electrovalent and covalent bonds valence electrons play very important roles and each valence shell of the bonded atoms attain inert gas stable configuration. For metal- metal bond, the valence electrons are so few that electron sharing to attain electron octet is not possible. Electrovalent bonds cannot be formed as metals tend to lose electrons and not accept them. A negatively charged metal ion is not possible.

How then do we explain bonding in metallic solids? How can we explain the fact that metallic solids are good conductors of heat and electricity? What major differences are there in the structures of ionic and metallic solids? The above questions will be answered in this unit. We shall also explain the origin of intermolecular forces that hold covalent molecules together in the bulk sample and account for their special properties.

5.1 Objectives

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

- Explain metallic bonding.
- Account for metallic properties.
- List metallic properties.
- Explain dipole-dipole interaction.
- Account for properties of covalent compounds.
- Explain hydrogen bonding.
- Account for the high boiling point of water compared to hydrogen sulphide.

5.2 Metallic Bonding

Metals usually have 1, 2, or 3 electrons in their **valence shells**

Li (2, 1) or $1s^2 2s^1$

Na (2, 8, 1) or $1s^2\ 2s^2\ 2p^6\ 3s^1$
Mg (2, 8, 2) or $1s^2\ 2s^2\ 2p^6\ 3s^2$
Al (2, 8, 3) or $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

In metallic bonding each metal atom contributes its valence electrons to form a 'cloud' or 'sea' of delocalised electrons. These electrons do not belong to any particular metal atom but will circulate freely through the metal lattice. **The electrostatic attraction between the positive cores that form the metal lattice and the 'sea' or 'cloud' of electrons constitute the metallic bond.** The above explanation of metallic bonding implies that the lattice forms a single large crystal. This accounts for the high strength of metals. There is no direction to metallic bond and so the metallic lattice can be distorted easily by hammering and drawing. Metals are malleable and ductile. The free moving electrons conduct heat and electricity by their movement.

The strength of the metallic bond depends on the attraction of the electron cloud to the positive cores in the metal lattice. The metallic bond strength increases with the number of valence electrons each metal contribute into the electron 'cloud'. Take the example of

Mg (2, 8, 2) $1s^2\ 2s^2\ 2p^6\ 3s^2$
Na (2, 8, 1) $1s^2\ 2s^2\ 2p^6\ 3s^1$

Sodium is a softer metal than magnesium because for sodium only one valence electron per atom but for magnesium two electrons are donated per atom to the electron cloud.

Following the above argument compare the strength of the metallic bonding in magnesium with that in aluminium (13).

For metals in the same group of the periodic table, metallic strength decreases down the group. The increase in atomic size down the group is not accompanied by any increase in electron cloud strength. This listed properties of metals are explained by the metallic bonding just explained.

- High tensile strength.
- Malleable and ductile.
- Conductor of heat and electricity.
- High density.
- Solid at room temperature except mercury that is a liquid at room temperature.
- Usually have shiny surface (lustre)

Now explain why metals have these three listed properties.

(i) High strength (ii) ductility (iii) High density

5.2.1 Uses of metals

The use of a metal for a particular application depends on a number of factors which include cost, availability, durability and performance. Table 5.1 gives the uses of some metals and the reasons for such uses.

Table 5.1 **Uses of pure metals**

Metal	Use	Reason for use
Copper	electrical cables	excellent conductor of electricity and very ductile.
Tin	coating tin cans	not poisonous
Aluminium	kitchen foil	very malleable

5.3 Intermolecular Bonding

The ionic and covalent bonds represent very strong interactions between atoms in a compound. In addition to these bonds there are other weaker attractive forces that exist between atoms and molecules. The existence of these weak attractive forces explains a number of physical properties of some compounds. Because these forces are usually between molecules they are called intermolecular forces. For example Van der Waal's forces, dipole-dipole attractions and hydrogen bonding.

5.3.1 Van der Waal's forces

Van der Waal's forces exist even between uncombined atoms and non polar molecules. A non polar molecule is one in which the electron pair for bonding is equally shared by the atoms involved in the bond formation. Examples of non polar molecules are N_2, Cl_2, H_2, O_2 etc i.e covalent bond between two identical atoms is a non polar bond. Non polar bond may also exist between unlike atoms if they have the same electronegativity. For example CO_2.

The movement of electrons around an atom can lead to a momentary shift of more electrons to one side of the molecule than the other. During this shift an imbalance in charge exists with one side of the molecule slightly positive and the other slightly negative. The positive end will attract the negative end of another molecule close to it. This attraction constitute a bond. This attractive force may be strong but because it is for a short time its effect is generally very small.

The magnitude of this force increases with increasing number of electrons. This force is present between all molecules atoms and ions. Its effect can be very large when there are many electrons in the molecules or atoms. Take the case of the halogens (Group VII elements) fluorine, chlorine are gases, bromine is a liquid while iodine is a solid. Remember all of them exist as diatomic molecules and are only bonded together by van der waal forces, Van der Waal's forces are attractions between molecules which happen because of creation of temporary dipoles in all molecules. The very large number of electrons in bromine and Iodine allows for substantial cohesive force between bromine and iodine molecules making bromine liquid and iodine solid at room temperature. Van der Waal's forces is sometimes called induced dipole- induced dipole attraction.

5.3.2 Dipole-dipole attractions

Covalent bonding between atoms of different elements will result in a polar bond. The shared electron pair will be more under the control of the more electronegative atom. Take the example of HCl. Chlorine is more electronegative than hydrogen. The shared pair of electron is controlled more by Chlorine. The chlorine end of the molecule will be slightly negative and the hydrogen end slightly positive e.g. HCl, $H^{\delta+} - Cl^{\delta-}$. The positive end of one hydrogen chloride molecule will attract the negative end of another molecule. This is dipole-dipole attraction. Though dipole-dipole interactions are not as substantial as full ion-ion interactions, they are stronger than Van der Waal's forces.

The table 5.2 gives the normal boiling points of covalent compounds. Dipole interactions are only about one percent as strong as covalent and ionic bonds.

Table 5.2 Boiling points of covalent compounds

Compound	Chemical formula	B.pt (K) ΔH_{vap}
Hydrogen	H_2	20
Nitrogen	N_2	77
Oxygen	O_2	90
Iodine	I_2	458
Bromine	Br_2	332
Water	H_2o	373
Hydrogen chloride	HCl	188
Hydrogen bromide	HBr	206
Chlorine	Cl_2	239
Hydrogen sulphide	H_2S	223

The following are important observations from the table.

(i) The boiling points of non polar compounds are very low compared to polar compounds.

(ii) The boiling point increases with molecular mass for polar and non polar compounds.

$B_{pt}\ H_2 < B_{pt}\ O_2 \qquad B_{pt}\ HCl < B_{pt}\ HBr$

(iii) The boiling point of H_2O is abnormally high compared to those of other hydrides e.g. HCl, HBr, H_2S.

5.3.3 Hydrogen bonding

Hydrogen bonding is a special type of dipole-dipole interaction which occurs when hydrogen is bonded to very small electronegative elements like N, F and Oxygen. In combination with these small electronegative elements, hydrogen carries a substantial positive charge. The attraction of this positive end with the negative end of another molecule will constitute a strong bond. This bond is the hydrogen bond. Hydrogen bond is about 5 to 10 times stronger than ordinary dipole-dipole interaction. It is not as strong as ordinary covalent bonds between atoms in a compound.

Hydrogen bonding is responsible for water being a liquid at room temperature rather than a gas. Hydrogen bonding explains the high boiling point of water compared to hydrogen sulphide (see table 5.2). Hydrogen bonding explains why hydrofluoric acid is a weaker acid than hydrochloric acid.

5.4 Conclusion

From our discussion on chemical bonding, you can see that almost all atoms have the ability to combine with other atoms to form compounds. No wonder the number of compounds are limitless. In this unit the types of bonding discussed are interatomic and intermolecular bonding.

The metallic bonding is one of the major types of interatomic bonding and it explains very well the observed properties of metallic solids. Weak bonding exists between molecules, atoms and ions as a result of instantaneous shift in electron distribution around atoms in compounds. This weak bonding can be substantial leading to solid structure of covalent compounds at room temperature. Covalent bonding between unlike atoms will always lead to unequal share of bond electrons. Attraction between polar ends of molecules also account for the cohesive force between polar molecules, when the polar bond is between hydrogen and small electronegative elements. The cohesive energy of the dipole-dipole interaction can be very substantial. This may lead to abnormal behaviour of such compounds.

5.5 Summary

- Metallic bonding is explained and used to account for properties of metals.
- Intermolecular forces are discussed and used to explain properties of polar and non polar compounds.
- Hydrogen bond is a very important dipole-dipole interaction that explains the behaviour of some compounds of hydrogen with small electronegative elements.
- Hydrogen bonding is present in water. It explains why water is a liquid instead of a gas at room temperature.

5.6 Tutor-Marked Assignments

1 (a) Give a description of the bonding between the atoms in a molecule of water.
  (b) Explain hydrogen bonding in water.

2 (a) Explain the type of bonding in magnesium metal.
  (b) Explain and account for the following properties of magnesium.
    (i) High tensile strength and density.
    (ii) Malleability and ductility
  (c) Compare and contrast magnesium with sodium chloride.

5.7 References

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Unit 6

Periodic Table I: Classification of Elements

6.0 Introduction

There are 103 known elements, some of which are familiar and others are rare. Recall that atoms are built of particles of three kinds: protons, neutrons and electrons. The nucleus of each atom is made of protons and neutrons. The number of protons (the atomic number) determines the electric charge of the nucleus, and the total number of protons and neutrons (the mass number) determines its mass. In a neutral atom the number of electrons surrounding the nucleus is equal to the atomic number.

The chemical and physical properties of an element are governed by the number and arrangement of the electrons. Several attempts have been made since 1817 to group elements together based on recurring properties such as atomic weight. The most important step in the development of the periodic table was published in 1869 by Dmitri Mendelyeev, who made a thorough study of the relation between the atomic weights of the elements and their physical and chemical properties. **The word periodic means recur at regular interval.**

The initial arrangement has now been largely replaced following new knowledge about electronic structure of atoms. The present periodic table is based on the recurrence of characteristic properties when elements are arranged in order of increasing atomic number.

6.1 Objectives

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

- Identify the groups and periods of elements in the periodic table.
- List the first few members of each group.
- Identify the blocks of elements.
- State general trends of some characteristics of elements.

6.2 The Periodic Law and Periodic Table

The periodic law states that the properties of the chemical elements are not arbitrary, but depend upon the structure of the atom and vary with the atomic number in a systematic way. In other words, the properties of the elements are the periodic function of their atomic number. When elements are systematically arranged in order of increasing atomic number, certain characteristics recur at regular intervals.

The periodic recurrence of properties of the elements with increasing atomic number can be clearly shown by arranging the elements in a table, called the periodic table of the elements. The periodic table shows the arrangement of elements in seven horizontal rows and eight vertical columns as shown in table 6.1

Table 6.1 Periodic Table

Group / Period	IA	IIA											IIIA	IVA	VA	VIA	VIIA	0
1	^{1}H																^{1}H	^{2}He
2	^{3}Li	^{4}Be	**Transition Elements**										^{5}B	^{6}C	^{7}N	^{8}O	^{9}F	^{10}Ne
3	^{11}Na	^{12}Mg	IIIB	IVB	VB	VIB	VIIB	VIIIB	VIIIB	VIIIB	IB	IIB	^{13}Al	^{14}Si	^{15}P	^{16}S	^{17}Cl	^{18}Ar
4	^{19}K	^{20}Ca	^{21}Sc	^{22}Ti	^{23}V	^{24}Cr	^{25}Mn	^{26}Fe	^{27}Co	^{28}Ni	^{29}Cu	^{30}Zn	^{31}Ga	^{32}Ge	^{33}As	^{34}Se	^{35}Br	^{36}Kr
5	^{37}Rb	^{38}Sr	^{39}Y	^{40}Zr	^{41}Nb	^{42}Mo	^{43}Tc	^{44}Ru	^{45}Rh	^{46}Pd	^{47}Ag	^{48}Cd	^{49}In	^{50}Sn	^{51}Sb	^{52}Te	^{53}I	^{54}Xe
6	^{55}Cs	^{56}Ba	^{57}La	^{72}Hf	^{73}TA	^{74}W	^{75}Re	^{76}Os	^{77}Ir	^{78}Pt	^{74}Au	^{80}Hg	^{81}Ti	^{82}Pd	^{83}Bi	^{84}Po	^{85}At	^{86}Rn
7	^{87}Fr	^{88}Ra	^{89}Ac															

Inner Transition Elements

Lanthanides	^{58}Ce	^{59}Pr	^{60}Nd	^{61}PM	^{62}Sm	^{63}Eu	^{64}Gd	^{65}Tb	^{66}Dy	^{67}Ho	^{68}Er	^{69}Tm	^{70}Yb	^{71}Lu
Actinides	^{90}Tb	^{91}Pa	^{92}U	^{93}Np	^{94}Pu	^{95}Am	^{96}Cm	^{97}Bk	^{98}Cf	^{99}Es	^{100}Fm	^{141}Md	^{102}No	^{102}Lr

6.3 Description of the Periodic Table

The periodic table contains rows of elements called periods and columns of elements called groups. The horizontal rows of the periodic table consist of a very short period (containing hydrogen and helium, atomic number 1 and 2), two short periods of 8 elements each, two long periods of 18 elements each, a very long period of 32 elements, and an incomplete period. The elements in the period have the same number of shells and the number of valence electrons increases progressively by one across the period from left to right. For example, members of period 2 are Li, Be, B, C, N, O, F and Ne with 3, 4, 5, 6, 7, 8, 9, and 10 electrons respectively.

For all members of the period the additional electron is added to the second shell hence the name period 2. In general, every period starts with an element containing one electron in its outermost shell (e.g. Li, Na, K) and ends with an element whose outermost shell is completely filled (e.g. He, Ne, Ar - the noble or inert elements). The properties of elements change in a systematic way through a period. For example the first members of each period are all light metals that are reactive chemically, and this metallic character decrease across the periods which ends with unreactive inert gases.

The elements that appear in a vertical column belong to the same group or family. They have the same number of outer electrons or valence electrons and have closely related physical and chemical properties. The groups IA and IIA elements are usually placed at the left side of all the periods and IIIA, IVA, VA, VIA VIIA and O (sometimes called VIIIA) elements are at the right side. The central elements of the long periods, called the representative elements have properties differing from those of the elements of the short periods. The transition metals are placed in groups IIIB, IVB, VB, VIB,VIIB, VIIIB, IB and IIB.

The very long periods (6 and 7) are compressed into the table by removing fourteen elements each, called the inner transition or rare-earth metals (Z=58 to Z = 71 ⟶ lanthanides; and Z = 90 to Z = 103 ⟶ actinides) and representing them separately below the table. The lanthanides, which are in period 6, starting from lanthanum (La) and ending with Lutetium (Lu) are rare metals that show a great resemblance to one another

The actinides, which are in period 7, starting with actinium (Ac) are known as **artificial elements** because they do not occur naturally but are formed during nuclear reactions. They are unstable and short-lived.

6.3.1 The periods

The periods are numbered from 1 to 7 and the elements in the same period have the same number of electron shells. Period 1 elements have one electron shell (K); period 2 elements have two electron shells (K,L); period 3 elements have three electron shells (K,L,M); etc. The number of valence electrons in the atoms of the elements in the same period increase progressively by one from left to right.

Across a given period, there is a progressive change in chemical properties. For example, metallic properties decrease across the period while non-metallic characteristics increases. The first three members of any period (Groups 1 to 3), except period 1 are metals while those of Group 4 to 7 and 0 are non-metallic in behaviour. Using period 3 as an illustration, sodium, magnesium and aluminium are metallic and form mainly ionic compounds and basic oxides. To the right of the period, phosphorus, sulphur and chlorine are non-metallic and form mainly covalent compounds and acidic oxides.

6.3.2 The main groups

The elements in groups IA to VIIA and group O are generally referred to as the main Group elements. Hydrogen is placed in group IA for convenience only because of the single electron but does not have similar characteristic with other members of the group.

(a) Group IA, the alkali metals: Lithium (Li), Sodium (Na), Potassium (K), etc are light metals which are very reactive chemically e.g.reacts vigorously with cold water to liberate hydrogen gas. The atoms of each element have only one electron, which they readily donate and are strong reducing agents. They react by losing this valence electron to form ionic or electrovalent bonds. The alkali metals are excellent conductors of electricity because the valence electrons are mobile. $Na \longrightarrow Na^+ + e^-$

The alkali metals are made by electrolysis of the molten hydroxides or chlorides. Because of their reactivity especially with water, the metals must be kept in an inert atmosphere or under oil.

Sodium metal catches fire when in contact with water, so avoid dropping it in the sink in the laboratory

The metals are useful chemical reagents in the laboratory, and they find industrial use in the manufacture of organic chemicals, dyestuffs and tetraethyl lead (the anti-knock agent in gasoline). Sodium is used in sodium - vapour lamps, and because of its high heat conductivity, in the stems of valves of airplane engines, to conduct heat away from the valve head.

(b) Group IIA; the alkaline - earth metals: The metals of group IIA are beryllium (Be) magnesium (Mg), calcium (Ca) etc and are much harder and less reactive than the alkali metals. They have two electrons in their outermost shell and react essentially by forming divalent ionic bonds. The compounds of all the alkaline - earth metals are similar in composition; they form oxides MO, hydroxides $M(OH)_2$, trioxocarbonates MCO_3, etc.

$$Ca \longrightarrow Ca^{2+} + 2e^-$$
$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$$

(c) Group IIIA: Boron (B) is a **metalloid**-intermediate properties between metals and non-metals; whereas aluminium (Al) and other members of the group are metals. Members of the group are trivalent since each of its atoms has three valence electrons and forms electrovalent compounds.

$$Al \longrightarrow Al^{3+} + 3e^-$$

Aluminium the only familiar element of the group reacts with steam at 600°C to give hydrogen gas. The oxide and hydroxide of aluminium are amphoteric - they have both acidic and basic properties.

$$Al(OH)_3 + \underset{\text{an acid}}{3H_2SO_4} \longrightarrow Al_2(SO_4)_3 + 3H_2O$$

$$Al(OH)_3 + \underset{\text{a base}}{NaOH} \longrightarrow NaAl(OH)_4$$

(d) Group IVA: Carbon (C), Silicon(Si), germanium (Ge), Tin (Sn) and Lead (Pb) are members of this group. Their atoms each has four valence electrons and tend to form covalent compounds. Carbon is a non-metal, silicon and germanium are metalloids while tin and lead are metals showing a gradation from non-metallic to metallic character on going down the group.

Carbon and silicon form more stable +4 state compounds (CO_2 and S_1O_2 - Sand) while tin and lead form more stable +2 state compounds (SnO and PbO). The compounds of carbon and hydrogen called hydrocarbons form a large class of organic compounds used as fuels e.g.butane (C_4H_{10}), hexane (C_6H_{14}).

(e) Group VA: Nitrogen (N) and phosphorus (ρ) are the familiar members of this group. Their atoms each has five valence electrons and show two common valence of 3 and 5. Both of them are non-metals. They are electron acceptors in their reactions and form several oxides e.g.

$$N_2O_3, \quad N_2O_5, \quad P_4O_6, \quad P_4O_{10}$$

The oxides are acidic and they react with water to form acids

$$N_2O_5 + H_2O \longrightarrow 2HNO_3 \text{ (trioxonitrate (v) acid)}$$

Nitrogen and phosphorus react with hydrogen to form ammonia (NH_3) and phosphine (PH_3).

(f) Group VIA: Oxygen (o) and sulphur (s) are the familiar members of this group and are both non-metals. They are electron acceptors and are oxidising agents e.g.

$$2Mg + O_2 \longrightarrow 2MgO$$
$$2Na + S \longrightarrow Na_2S$$

The elements do not attack water but combine with hydrogen to give water and hydrogen sulphide

$$2H_2 + O_2 \longrightarrow 2H_2O$$
$$H_2 + S \longrightarrow H_2S$$

(g) Group VIIA: Fluorine (F), Chlorine (Cl), bromine (Br) and Iodine (I) are the members of this group. They are commonly called halogens. They are all non-metals and highly reactive. Their atoms each has seven valence electrons and they are electron acceptors. The halogens show great similarity in their properties e.g.

(i) all are non-metals gases.

(ii) they exist as diatomic molecules e.g. I_2, Cl_2.

(iii) They form ionic compounds when they react with metals but form covalent compounds with hydrogen.

$$2Na + Cl_2 \longrightarrow 2NaCl \quad \text{ionic}$$
$$H_2 + Br_2 \longrightarrow 2HBr \quad \text{covalent}$$

(iv) their hydrides are soluble in water to give acids

$$HBr(g) + H_2O \longrightarrow \underset{\text{acidic}}{H_3O^+ + Br}$$

(v) their reactivity decreases down the group e.g. while fluorine reacts explosively with hydrogen even in the dark, chlorine reacts slowly in diffuse light, bromine reacts slowly in bright light and iodine reacts incompletely even in bright light.

Group O: Helium (He), Neon (Ne), Argon (Ar), are the familiar members of this group which are commonly referred to as rare gases or noble gases. They have no bonding electrons because the outermost shell is completely filled hence the group name zero. The rare gases are therefore unreactive and exist freely as monoatomic molecules in the atmosphere (about 1% of the composition of air).

Members of the group exhibit similar properties which are different from those of the halogens that come before them and alkali metals that come after them. This is a confirmation that the end of a period has been reached.

6.3.3 The transition elements

This is a collection of elements with very similar behaviour and are usually placed between Groups II and III of the periodic table. All the transition elements have the following characteristics.

(a) They are metals with high tensile strength and high melting point.

(b) They exhibit variable valencies.

(c) They form coloured ions.

(d) They have the ability to form complex ions.

(e) Several of them show catalytic ability. e.g. manganese and nickel

6.4 Conclusion

In this unit you have learned the periodic classification of elements. You should have learned that when elements are arranged in order of increasing atomic number, certain properties recur at regular intervals. Furthermore, you should have learned that the periodic table of elements serve to justify the trend of behaviour exhibited by elements.

6.5 Summary

What you have learned in this unit concerns the arrangement of elements in groups and periods based on their atomic number and properties. It has served to introduce you to the periodic Table. The units that follow shall use the **atomic *orbital model*** to further justify the classification and explain the gradation of properties of elements based on the periodic table.

6.6 Tutor-Marked Assignments

(a) What is the atomic and mass number of an element?

(b) Define the periodic law of elements.

(c) From the elements carbon, oxygen, neon, sodium, magnesium, aluminium, sulphur, chlorine and argon, name two which are
    (i) in the same group (ii) in the same period (iii) reactive metals
    (iv) able to form acidic oxides (v) inert.

6.7 References

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Unit 7

Electronic Configuration II: Atomic Orbital Model

7.0 Introduction

For a long time, it was believed that electrons were orbiting the nucleus in the same way the planets orbit the sun. You have learned in unit 2 about the contributions of Rutherford and Bohr to atomic structure in order to obtain a model of the atom. Their contributions went a long way to explain some of the observation about the atom. The Rutherford's model of an atom as consisting of a central positively charged nucleus and the negatively charged electrons some distance away from the nucleus, is still acceptable. However, classical electromagnetic theory denies the possibility of any stable electron orbits around the nucleus.

In Bohr's model of the atom, the electron was restricted to being found in a definite regions i.e. it had to be found in that orbit and nowhere else. In the Wave Mechanics Model, however, there is a slight chance that the electron may be located at distances other than in the restricted orbits. Despite this, we still accept Bohr's scheme for quantisation of energy in the atom and that the lowest energy level of the atom is the most stable state.

Although Bohr's contribution was remarkable, particularly his quantisation of energy, theory to explain the spectral lines for hydrogen atom; it has the following limitations:

(a) The Bohr model failed to account for the frequencies of the spectral lines for complex atoms other than hydrogen.

(b) The model also failed to satisfactorily explain why the Rutherford's atom did not collapse as predicted by the theory of electromagnetic radiation.

The present day picture of the atom is based on wave mechanical or quantum mechanical treatment. The treatment reflects on the wave-nature of the electron and the quantisation of energy in the atom. Although these treatments are fundamentally mathematical in nature, it describes the electron as point charge and that the density of the cloud at a specified point gives only the probability of finding electrons at that point.

We shall look at how this new thinking will help our understanding of the atom and the observed relation between electronic arrangement in atoms and the chemical behaviour of elements.

7.1 Objectives

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

- Describe the quantum theory of atomic orbitals.
- Illustrate the shapes of the electron clouds corresponding to s – and p – orbitals.

- Write electronic configurations of atoms based on the orbital model.
- Relate the electron configuration of atoms to the classification of elements in the periodic table.

7.2 Quantum Theory of Atomic Orbitals

In the quantum model, the atom is still believed to consist of a central nucleus and orbiting electrons but the physical picture of the atom is by far different from the models proposed by Rutherford and Bohr. The quantum theory attempts to understand how electrons are arranged in the atom based on wave and quantum mechanics treatment. The electron is visualised as a point charge. The density of this point charge varies in different locations around the nucleus and gives a measure of the probability of finding the electron at a specified point.

The region or space, around the nucleus, in which an electron in a given energy level is most likely or probable to be found is defined as an orbital. So rather than describing a fixed Bohr orbit in which electrons are located, the modern theory gives a probability description of atomic orbitals. The results of the quantum mechanical treatment of the atom is summarised below.

7.2.1 The principal quantum number (n)

You will recall that in the Bohr's model, each orbit is denoted by the principal quantum number. This designation is retained in the quantum model but to represent distinct energy levels and not shells or orbits. In otherwords, the quantum model recognises different quantised energy levels around the nucleus. Each principal quantum number (n) corresponds to a particular energy level and has integral values of 1, 2, 3, 4, etc. The principal quantum number n = 1 represent the lowest energy level that an electron can occupy. Electron with the largest ('n') value has the most energy and occupies the highest energy level; and therefore the most easily removable or ionisable electron. The maximum possible number of electrons in an energy level is given by $2n^2$. ($n \geq 1$).

7.2.2 The subsidiary or azimuthal quantum number, (*l*)

This subsidiary quantum number shows how many energy sub-levels are present in each electronic energy level. The subsidiary quantum number, *l*, has integral values ranging from 0, 1, 2, ... (n–1). The sub-levels with *l* = 0, 1, 2, 3, are usually referred to s–, p–, d– and f– sub-levels respectively.

7.2.3 The magnetic quantum number, (M)

The magnetic quantum number (*m*) gives the number of orbitals present in each sub-energy level and has integral values ranging from – *l* ...0 ....+ *l*. For example, when *l* = 2, *m* has the values –2, –1, 0, 1, 2, i.e. the *l* = 2 sub-level (d-sublevel) has five orbitals; when *l* = 1, *m* has the values –1, 0 1 i.e. the *l* = 1 sub-level (p – sub-level) has three orbitals (See Table 7.1)

7.2.4 The spin quantum number (s)

The spin quantum number, (s) describes the fact that each orbital can only hold a maximum of two electrons with opposite spin. Their spin states are denoted by the spin quantum numbers –½ and +½.

Table 7.1 Atomic energy levels and sub-levels

Value of *n*	Values of *l*	Number of sub-levels	Names of the sub-levels
1	0	One	*s*
2	0 and 1	Two	*s* and *p*
3	0, 1, and 2	Three	*s*, *p*, and *d*
4	0, 1, 2 and 3	Four	*s*, *p*, *d*, and *f*

7.3 The Shape of Atomic Orbitals

Contrary to Bohr's postulate, electrons do not move around the nucleus in definite paths, infact it is impossible to accurately determine the path of the electron. Rather, the location of electron is defined in terms of probabilities which is described by the orbital. **A region in space where there is a high probability of finding an electron in an atom is called an orbital.** The density cloud of the electrons defines the shape of the orbital.

The electrons that move about to produce a spherical symmetrical cloud around the nucleus is an s-electron residing in an s-orbital. The p-electrons move about three axes, x, y and z that are at right angles to one another, producing a dumb-bell cloud around the nucleus along each axes. They are called the p-orbitals and are distinguished from each other by Px, Py and Pz in line with the direction of the electron cloud. Fig. 7.2 shows the shapes of the S, Px, Py and Pz orbitals. The geometrical representation of the d and f orbitals are more complex and beyond the scope of this programme.

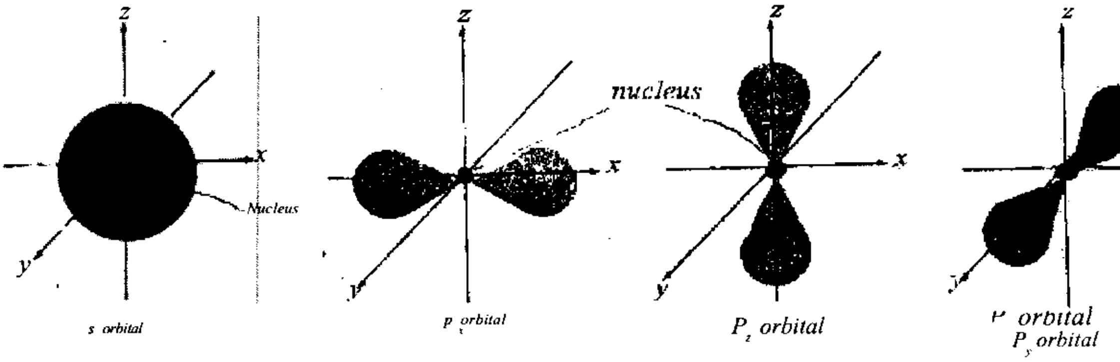


Fig 7.2: Geometrical representation of s- and p- orbitals

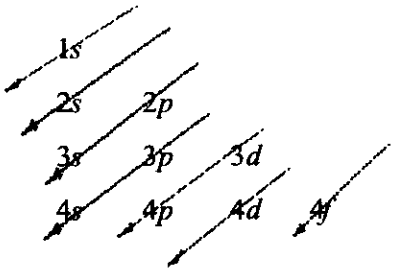
7.4 Electronic Configuration of Atoms – Orbital Model

The quantum treatment essentially deals with the arrangement of electrons in atoms. However, before we can apply the quantum numbers to express the electronic configuration of atoms, there are two important rules that you should be familiar with.

(a) Pauli Exclusion Principle states that two electrons in the same atom cannot have the same values for all four quantum numbers. The principle simply means two electrons in an atom cannot behave in an identical manner.

(b) Hund's Rule; states that, in the filling of orbitals, electrons occupy each energy level singly before electron pairing takes place.

The way in which electrons are arranged in an atom is determined by the order of the sub-levels on a scale of increasing energy level. This is so because electrons are found in the lowest possible energy level, the ground state which is the most stable state of an atom. A simple representation of the orbitals on an energy scale is given in Fig. 7.3



1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 4f – increasing energy

Fig. 7.3; Atomic orbitals on an energy scale.

The maximum number of electrons in each sub-level is determined by the number of orbitals present in the sub-level bearing in mind that each orbital can take a maximum of two electrons with opposite spin. Table 7.2 gives the number of orbitals and maximum number of electrons in each sub-level.

Table 7.2: The number of orbitals and maximum electrons in the sub-level

Value of l	**Name of sub-level**	**Values of m**	**Number of values of m**	**Number of orbitals**	**Maximum number of electrons**
0	*s*	0	One	One	2
1	*p*	1, 0, –1	Three	Three	6
2	*d*	2, 1, 0, –1, –2	Five	Five	10
3	*f*	3, 2, 1, 0, –1, –2, –3	Seven	Seven	14

Starting with hydrogen, which has an atomic number of 1, the electron occupies the 1s sub-level and this process of electronic occupation continues with increased atomic number according to the order of increasing orbital energy levels. To keep a check on the spin of the electron, arrows of opposite spins are used to distinguish two electrons in an orbital. Table 7.3 gives the electronic configuration of the first ten elements using the four quantum numbers.

Table 7.3 Electronic configurations of the atoms of elements using the four quantum numbers.

Element	**Atomic number**	**The four quantum numbers**				**Maximum electrons in sub-levels**	**Maximum electrons in principal levels**	**Configuration of atoms in ground state**				
		Principal	***Subsidiary***	***Magnetic***	***Spin***			1s	2s	2p		
Hydrogen	1	$n = 1$	$l = 0$	$m = 0$	± ½	2 *s* electrons	2	↑				
Helium	2							↑↓				
Lithium	3		$l = 0$	$m = 0$	± ½	2 *s* electrons		↑↓	↑			
Beryllium	4							↑↓	↑↓			
Boron	5							↑↓	↑↓	↑		
Carbon	6	$n = 2$		$m = 1$	± ½		8	↑↓	↑↓	↑	↑	
Nitrogen	7		$l = 1$	$m = 0$	± ½	6 *p* electrons		↑↓	↑↓	↑	↑	↑
Oxygen	8							↑↓	↑↓	↑↓	↑	↑
Fluorine	9			$m = -1$	± ½			↑↓	↑↓	↑↓	↑↓	↑
Neon	10							↑↓	↑↓	↑↓	↑↓	↑↓

7.5 Electronic Configuration and Periodic Classification of Elements

One of the advantages of the electronic configuration of elements using quantum numbers is that it showed the basis for the periodic classification of element. In other words, the key to the periodicity of elements lies in the electronic configurations of their atoms.

The orbital arrangement of electrons clearly showed the great usefulness of the Period Table as it explains the groups and characteristic properties of elements. The correlations between electronic configuration and the physical and chemical behaviour of elements will be discussed in details in subsequent units. Table 7.4 shows the electronic configurations of the first twenty elements of the Periodic Table.

Table 7.4: The electronic configurations of the first twenty elements of the Periodic Table

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

7.6 Conclusion

In this unit you have learned about the quantum mechanical treatment of the electronic structure of the atom. This is a follow up to what you learned about Rutherford and Bohr models of the atom. You should have also learned that the position of electrons can be defined only in terms of the probability of finding it in a region in space referred to as orbitals. Furthermore, you learned about the four quantum numbers used for characterising an electron. You need to be aware of how to write the orbital electronic configurations of elements based on these four quantum numbers.

7.7 Summary

What you have learned in this unit concerns the quantum treatment of electrons in atoms and how each of the four quantum numbers can be used to fully characterise an electron. It has served to introduce you to orbital electronic configuration. The unit on Period Table II shall build upon this treatment of the electrons in the atoms of elements.

7.8 Tutor-Marked Assignments

1. (a) Write the electronic configuration of:

   (i) Aluminium (ii) Calcium (iii) Argon (iv) Oxygen (v) Carbon

   (b) Using electronic configuration account for the occurrence of periods and groups in the Periodic Table.

   (c) Define orbitals and sketch the s– and p– orbitals.

7.9 References

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Unit 8

Periodic Table II: Gradations of Atomic Properties

8.0. Introduction

The periodic table consists of elements arranged in groups and periods based on their atomic number. The number of electrons in a neutral atom of an element gives the atomic number. The electrons occupy electronic shells. The elements in any period have the same number of electronic shells and the number of valence electrons increases progressively by one across the period from left to right. When elements are arranged in this way, it was observed that the properties of elements recur at regular intervals. That is, the properties of the elements are a periodic function of their atomic number. The periodic properties give rise to vertical columns of groups or families of elements with the same number of outer or valence elements. The elements in any group have closely related physical and chemical properties. One great advantage of this, is that it is only necessary to learn the properties of each group rather than the properties of each individual element.

Recall that the Bohr theory of shells was the basis for the arrangement of electrons in atoms. Recent discoveries about the atoms have necessitated a revision of this idea. The electrons in atoms are now believed to occupy regions in space around the nucleus called orbitals rather than fixed shells. Orbitals are simply regions in space around the nucleus where the probability of finding an electron is high, they are usually denoted by s,p,d, and f- orbitals.

8.1 Objectives

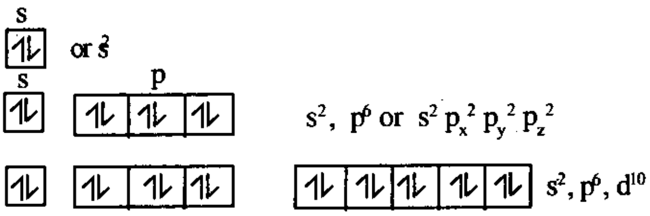
At the end of this unit, you should be about to:

- Explain the general trend in periodic properties down a group and across a period based on electronic configuration.
- Define atomic radii, ionic radii, ionization energy electron affinity and electronegativity.
- Explain the trend of the above properties within the periodic table.

8.2 Brief Revision of the Electronic Configuration

Electrons in atoms occupy various energy levels(n) and sub-energy levels (s,p,d,f - orbitals). Recall the Pauli's exclusion principle and Hund's rule in the arrangement of electrons in the energy levels. The summary below will refresh your memory.

Energy level	Number of sub-levels
1	s
2	s,p
3	s,p,d
etc	etc



For example, sodium with atomic number 11 will have the electronic structure $1s^2\ 2s^2\ 2p^6\ 3s^1$; magnesium with atomic number 12, $1s^2\ 2s^2\ 2p^6\ 3s^2$ and so on.

8.3 Electronic Configuration and the Periodic Table

The chemical and physical properties of an element are governed by the number and arrangement of the orbital electrons, that is, by the atomic number. The modern periodic classification (The Periodic Table) groups atoms of the element according to their electronic configurations.

Elements with one s electron in their outer shell are called Group I (the alkali metals) and elements with two *s* electrons in their outer shell are called Group II (the alkaline earth metals). These two groups are known as the *s* block elements, because their properties result from the presence of *s* electrons. Elements with three electrons in their outer shell (two *s* electrons and one *p* electron) are called Group III, and similarly Group IV elements have four outer electrons, Group V elements have five outer electrons, Group VI elements have six outer electrons and Group VII elements have seven outer electrons. Group 0 elements have a full outer shell of electrons so that the next shell is empty; hence the group name. Groups III, IV, V, VI, VII and 0 all have *p* orbitals filled and because their properties are dependent on the presence of *p* electrons, they are called jointly the *p* block elements.

In a similar way, elements where *d* orbitals are being filled are called the *d* block, or transition elements. In these, *d* electrons are being added to the penultimate shell (one shell before the outer shell). Finally, elements where *f* orbitals are filling are called the *f* block, and here the *f* electrons are entering the antepenultimate (or second shell from the outer shell) shell.

A summary of the block arrangement of elements based on the outermost energy levels for s- and p- block elements; and the orbitals being filled for d- and f- block elements.

Group I	One s electron	S- block
Group II	two s electrons	
Group III	two s electrons + one p electron	P- block
Group IV	two s electrons + two p electrons	
Group V	two s electrons + three p electrons	
Group VI	two s electrons + four p electrons	
Group VII	two s electrons + five p electrons	
Group O	two s electrons + six p electrons	

Transition Elements: d-orbitals being filled with electrons - d-block Inner Transition Elements: f-orbitals being filled with electrons - f- block (Lanthanides and Actinides)

Table 8.1 Periodic Table

	s block												p block					
Group / Period	I	II											IIIA	IVA	VA	VIA	VIIA	0
1	^{1}H																^{1}H	^{2}He
2	^{3}Li	^{4}Be											^{5}B	^{6}C	^{7}N	^{8}O	^{9}F	^{10}Ne
3	^{11}Na	^{12}Mg	d block										^{13}Al	^{14}Si	^{15}P	^{16}S	^{17}Cl	^{18}Ar
4	^{19}K	^{20}Ca	^{21}Sc	^{22}Ti	^{23}V	^{24}Cr	^{25}Mn	^{29}Fe	^{27}Co	^{28}Ni	^{29}Cu	^{30}Zn	^{31}Ga	^{32}Ge	^{33}As	^{34}Se	^{35}Br	^{36}Kr
5	^{37}Rb	^{38}Sr	^{39}Y	^{40}Zr	^{41}Nb	^{42}Mo	^{43}Tc	^{44}Ru	^{45}Rh	^{46}Pd	^{47}Ag	^{48}Cd	^{49}In	^{58}Sn	^{51}Sb	^{52}Te	^{53}I	^{54}Xe
6	^{55}Cs	^{56}Ba	^{57}La	^{72}Hf	^{73}Ta	^{74}W	^{75}Re	^{74}Os	^{77}Ir	^{78}Pt	^{79}Au	^{80}Hg	^{81}Ti	^{80}Pd	^{83}Bi	^{84}Po	^{85}At	^{86}Rn
7	^{87}Fr	^{88}Ra	^{89}Ac															

f block

Lanthanides	^{58}Ce	^{59}Pr	^{98}Nd	^{61}Pm	^{92}Sm	^{63}Eu	^{94}Gd	^{85}Tb	^{96}Dy	^{97}Ho	^{98}Er	^{99}Tm	^{78}Yb	^{71}Lu
Actinides	^{98}Th	^{91}Pa	^{92}U	^{93}Np	^{94}Pu	^{95}Am	^{96}Cm	^{97}Bk	^{98}Cf	^{99}Es	^{198}Fm	^{101}Md	^{102}No	^{183}Lr

In the periodic table (Table 8.1) the elements are arranged in order of increasing atomic number, that is in order of increased nuclear charge, so that each element contains one more orbital electron than the preceding element. Instead of listing the 103 elements, the periodic table arranges them into several rows or periods, in such a way that each row begins with an alkali metal and ends with an inert gas. The sequence in which the various energy levels are filled determines the number of elements in each period, and the periodic table can be divided into four main regions according to whether the *s,p,d* or *f* levels are being filled.

1st period	1*s*			elements in this period =	2
2nd period	2*s*		2*p*	elements in this period =	8
3rd period	3*s*		3*p*	elements in this period =	8
4th period	4*s*	3*d*	4*p*	elements in this period =	18
5th period	5*s*	4*d*	5*p*	elements in this period =	18
6th period	6*s*	5*d*	6*p*	elements in this period =	32

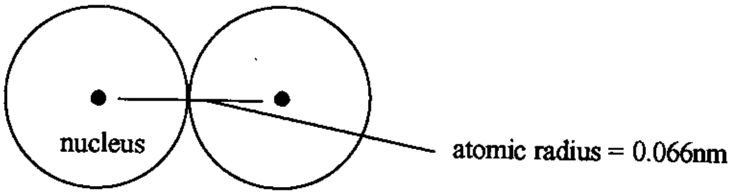
This form of the periodic table has many advantages. The similarity of properties within a group and the relation between the group and the electron structure is emphasized. The *d* block elements are referred to as the transition elements since they are situated between the *s* and *p* blocks. Hydrogen and helium differ from the rest of the elements because there are no *p* orbitals in the first shell. Helium obviously belongs to Group O, the inert gases, which are chemically inactive because their outer shell of electrons is full. Hydrogen is more difficult to place in a group. It could be included in Group I because it has one *s* electron in its outer shell, or in Group VII because it is one electron short of a complete shell. Hydrogen is included in both these groups in the periodic table, although it resembles neither the alkali metals nor the halogens very closely. The unique properties of hydrogen are largely due to the extremely small size of hydrogen atoms. Thus there is a case for placing hydrogen in a group on its own, or omitting it from the periodic table altogether.

8.4 The Periodic Table and Atomic Properties

We learned that physical and chemical properties of the elements vary periodically with the atomic number. The periodic table therefore provides an organized structure to the knowledge and understanding the chemistry of the elements. Apart from this, there is also a variation of atomic properties of elements in the periodic table. Some of these properties are atomic and ionic sizes, ionization energy, electron affinity and electronegativity.

8.4.1 Atomic size

The atom is a very small entity and so it is difficult to determine its size i.e. distance from the center of the nucleus to the outermost orbital. However with the aid of modem techniques such as X-ray and electron diffraction, it is possible to determine the distance between covalently bonded atoms. For example, the distance between the nuclei of oxygen atoms in an oxygen molecule is 0.132nm, so the atomic radius of an oxygen atom is approximately 0.066nm. **The atomic radius or sizes of any atom is taken to be one-half the distance of closest approach between the nuclei of atoms in the elemental substance.**



oxygen atom + oxygen atom = oxygen molecule

Fig 8.1 Atomic radius of oxygen

Atomic size decreases from left to right across a period in the periodic table. In other words, as the atomic number increases across any period, the size of the atom decreases. Recall that as we move across a period one electron is added increasingly from one element to the next and the electrons are being added to the same shell at about the same distance from the nucleus. At the same time, protons are also being added to the nucleus. Increase in the number of proton, increases the nuclear charge which progressively exert a stronger attraction upon the electrons around it and would pull them towards the nuclei. As the nuclear charge increases with atomic number across a period, the attractive force exerted by the nucleus on the outermost electrons of the atom increases hence the atomic radius or size decreases across a period. For example, on moving from Lithium to beryllium, the number of charges on the nucleus is increased by one, so that all the orbital electrons are pulled in closer to the nucleus. In a given period, the alkali, metal is the largest atom and the halogen the smallest. Table 8.2 shows the atomic radii (in nm) of the first twenty elements of the Periodic Table.

Table 8.2: Atomic radii of the first twenty elements

Group / Period	1	2	(nm)	3	4	5	6	7	0
1	H ● 0.037							H ● 0.039	He ● 0.049
2	Li ● 0.152	Be ● 0.111		B ● 0.088	C ● 0.077	N ● 0.070	O ● 0.066	F ● 0.064	Ne ● 0.070
3	Na ● 0.186	Mg ● 0.160		Al ● 0.143	Si ● 0.117	P ● 0.110	S ● 0.104	Cl ● 0.099	Ar ● 0.094
4	K ● 0.231	Ca ● 0.197							

On descending a group in the periodic table such as lithium, sodium, potassium etc, the atomic size increases due to the effect of extra shells of electrons being added; this outweighs the effect of increased nuclear charge. Recall the lithium in period 2 has two shells; sodium in period 3 has three shells while potassium in period 4 has four shells. In general, as we go down the group, atomic size increases with atomic number (see Table 8.2).

8.4.2 Ionic radius

Ions of elements are formed when atoms lose or gain electron. The size of an ion called ionic radii is different from atomic sizes. Ionic sizes are measured in electrovalent compounds.

The ionic radius of a given compound is the distance between the centre of one ion and the centre of its nearest neighbour of opposite charge.

A positive ion is formed by removing one or more electrons from an atom. When this happens, the number of positive nuclear charge is more than the number of negative electronic charge, hence the electrons are pulled in. *A positive ion is therefore smaller than the corresponding atom and the more electrons removed (that is, the greater the charge on the ion), the smaller it becomes* e.g.

Atomic radius Na = 0.186nm
Ionic radius Na^+ = 0.116nm

Atomic radius Fe = 0.139nm
Ionic radius Fe^{2+} = 0.090nm
Ionic radius Fe^{3+} = 0.076nm

When a negative ion is formed, one or more electrons are added to an atom. The number of positive nuclear charge is now less than the number of negative electronic charge hence the pull on the electrons is reduced. In general, ionic radii of negative ions are greater than the corresponding atomic radii i.e. negative ions are bigger than the corresponding atom e.g.

Atomic radius Cl = 0.099
ionic radius Cl^- = 0.128

8.4.3. Ionization energy

If energy is supplied to an atom, electrons may be promoted to a higher energy level. If sufficient energy is supplied, the electron may be completely removed, giving a positive ion. The energy required to remove the most loosely bound electron from each atom in a mole of gaseous atom, producing one mole of gaseous ion is called **ionization energy** (KJ mol^{-1}). Since it is possible to remove one, two or three.... electrons from most atoms there is a first second or third... ionization energy (I.E.).

$$M \xrightarrow{1^{st}\ I.E} M^{+} \xrightarrow{2^{nd}\ I.E} M^{2+} \xrightarrow{3^{rd}\ I.E} M^{3+} \longrightarrow$$

The factors influencing the ionization energy are the

(a) size of the atom which is a measure of the outermost electron from the nucleus.

(b) charge on the nucleus - as nuclear charge increases, the attraction for outermost electron increases, and so more energy is required to ionise .

(c) screening effect of inner electron shells - the outermost electrons are repelled by all the other inner shell electrons and prevented from experiencing the full attraction of the positively charged nucleus.

Across a period, the first ionization energy increases as atomic number increases since the atomic radius decreases. As the distance decreases, the attraction of the positive nucleus for the electron will increase, hence more energy is required to remove the outermost electron hence the ionization energy will increase. Note that the screening effect remain almost the same across a period since electrons are added to the same shell. Table 3 shows the first ionization energies of the first twenty elements.

Table 8.3 First Ionization Energies of the Elements (KJ mol^{-1})

Table 8.2: Atomic radii of the first twenty elements

Group / Period	1	2		3	4	5	6	7	0
1	H • 1311								He ● 2372
2	Li ● 520	Be • 899		B • 801	C • 1086	N • 1403	O • 1410	F • 1681	Ne ● 2080
3	Na ● 496	Mg • 737		Al ● 577	Si ● 786	P ● 1012	S ● 999	Cl • 1255	Ar ● 1521
4	K ● 419	Ca ● 590							

The first ionization energies of the elements in the first two short periods are shown in Fig. 8.2. These show a general upward trend from Li to Ne and from Na to Ar. The values for Ne and Ar are the highest in their periods because it requires a great deal of energy to break a stable filled shell of electrons. There are several irregularities. The high values for Be and Mg are attributed to the stability of a filled *s* level. The high values for N and P indicate that a half-filled *p* level is also particularly stable. The values for B and /Al/ are lower most loosely bound electron from each atom in a mole of gaseous atom, producing one mole of gaseous ion is called **ionization energy** (KJ mol^{-1}). Since it is possible to remove one, two or three.... electrons from most atoms there is a first second or third... ionization energy (I.E.).

$$M \xrightarrow{1^{st}\ I.E} M^{+} \xrightarrow{2^{nd}\ I.E} M^{2+} \xrightarrow{3^{rd}\ I.E} M^{3+} \longrightarrow$$

The factors influencing the ionization energy are the

(a) size of the atom which is a measure of the outermost electron from the nucleus.

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4	K • 419	Ca • 590							

The first ionization energies of the elements in the first two short periods are shown in Fig. 8.2. These show a general upward trend from Li to Ne and from Na to Ar. The values for Ne and Ar are the highest in their periods because it requires a great deal of energy to break a stable filled shell of electrons. There are several irregularities. The high values for Be and Mg are attributed to the stability of a filled *s* level. The high values for N and P indicate that a half-filled *p* level is also particularly stable. The values for B and /*Al*/ are lower because removal of one electron leaves a stable filled *s* shell, and similarly with O and S a stable half-filled *p* shell is left.

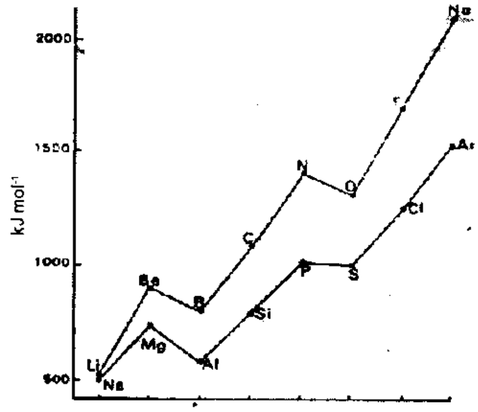
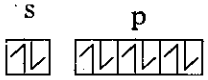
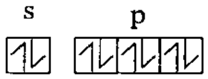


Fig 8.2. First ionization energies of the elements in the first two short periods.

Filled s level e.g. Be $1s^2$ $2s^2$
Mg $1s^2$ $2s^2$ $2p^6$ $3s^2$



Half-filled p level e.g. N $1s^2$ $2s^2$ $2p^3$
P $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^3$



Completely full - inert gas structure
e.g.Nc $1s^2$ $2s^2$ $2p^6$
Ar $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$

In general, the ionization energy decreases on descending a group because an extra shell of electron is added which also help to screen the outer electron from the nucleus. This trend is shown with the alkali, metals from Li(520) to Na(496) to K(419).

8.4.4 Electron affinity

Electron affinity has to do with the gain of electrons to form negative ions while ionization deals with loss of electrons to form positive ions. *The energy released when an extra electron is added to a neutral gasesous atom to form a univalent negative ion is termed the electron affinity.* Since energy is given off in the process, electron affinity has a negative value. Electron affinities depend on the size and effective nuclear charge of the atom. Moving from left to right across a period, electron affinities decreases (i.e. increase in negative value), expect for the noble gases which have positive values. Down a group of the periodic table, electron affinities increase (i.e. decrease in negative value). The reason for the observed trend is that atoms with smaller atomic radii tend to have a stronger attraction for electrons and thus form negative ions more readily.

Element			Energy ($kJ\ mol^{-1}$ negative value)
Li	→	Li^-	57
Na	→	Na^-	21
Al	→	Al^-	26
P	→	P^-	60
S	→	S^-	200
Cl	→	Cl^-	348

8.4.5 Electronegativity

The tendency of an atom in a molecule to attract bonded electrons to itself is termed the *electronegativity of the atom.* Generally, small atoms attract electrons (due to closeness of the nucleus) more than large ones and are therefore more electronegative. Atoms with nearly filled shells of electrons will tend to have higher electronegativity (because of the desire to have a stable filled shell) than those with sparsely occupied shells.

The electronegativities of elements decrease down a group and increase across a period. The reason for the trend is that down the group, atomic size increases and effective nuclear charge decreases hence electron attracting power (electronegativity) of the atom decreases. From left to right of a period, the opposite effect is observed, atomic size decreases and effective nuclear charge increases, these combine to increase electronegativity. The most electronegative elements are the reactive non-metals (e.g. Fluorine) at the top right-hand corner of the periodic table while the least electronegative elements are the reactive metals (e.g. caesium) at the bottom left-hand corner of the period table.
(See Table 8.4)

Table 8.4: Electronegativity volume

Group / Period	1	2		3	4	5	6	7	0
1	H • 2.1							H • 2.1	He
2	Li • 1.0	Be • 1.5		B • 2.0	C • 2.5	N • 3.0	O • 3.5	F • 4.0	Ne •
3	Na • 0.9	• 1.2		Al • 1.5	Si • 1.8	P • 2.1	S • 2.5	Cl • 3.0	Ar •
4	K • 0.8	Ca • 1.0							
5	Rb 0.8								
6	Cs 0.7								

8.5 Conclusion

In this unit you have learned a number of periodic properties that is evident when elements are arranged as a periodic function of atomic number. You should have also observed how this periodic properties vary down a group and across the period of a Periodic Table. You need to be aware of the reasoning behind the observed trend.

8.6 Summary

What you have learned in the unit concerns the classification of elements in the Periodic Table based on electronic configuration of atoms. It has served to introduce you to the variation of atomic properties - atomic size and radius, ionization energy, electron affinity and electronegativity, in the Periodic Table.

8.7 Tutor-Marked Assignments

1.(a) Use the electronic configuration to explain the occurrence of periods and groups in the Periodic Table.
(b) Define ionization energy and electronegativity and explain their trends in the Periodic Table.

8.8 References

1 (a) Osei Yaw Ababio (2002), *New School Chemistry* Onitsha. Africana-Fep Publishers.

Unit 9

Mole Concept 1

9.0 Introduction

Though it is possible to compare the masses of atoms, they are too small to be weighed. A chemical reaction takes place always between large number of reactant particles. The products that are formed also contain a large number of product particles. Chemists therefore use a large number of particles as a base unit when comparing amounts of different substances reacting or are formed in chemical reactions. This basic unit is the mole and the mole concept is one of the most important concepts in Chemistry. The mole concept is applicable to all chemical processes. In this unit the mole will be defined and the concept applied to chemical calculations involving masses and volumes of chemical substances.

9.1 Objectives

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

- Define the mole.
- Recall Avogadro Number.
- Calculate molar mass from formula mass.
- Calculate percentage of elements in compounds with given formulae.
- Establish mole ratios of reactants and products in reaction.
- Calculate yield and percentage yield.
- Recall molar volume of gas at S.T.P.
- Use the above in calculations involving gases.

9.2 The Mole Defined

The mole is the amount of any substance that contains as many elementary particles as there are atoms in 0.012kg of carbon-12. Now 0.012kg of carbon - 12 contains the Avogadro number of atoms, so one mole of a substance is that amount which contains Avogadro number of particles. The elementary particles may be molecules, atoms, ions, electron etc and must be specified. Avogadro number has been determined experimentally and is 6.02×10^{23}. A very large number indeed. A mole of a substance therefore provides a quantity of material that can be measured for use in the laboratory.

1 mole $\equiv 6.02 \times 10^{23}$ particles

9.3 The Mole and the Molar Mass

The atomic mass of an element is the mass of one atom of the element relative to the mass of one atom of Carbon-12 which by convention is given a mass of 12.00 a.m.u.

$$6.02 \times 10^{23} \text{ atoms of C-12} \equiv 12\text{g}$$

$$1 \text{ atom of C-12} \equiv \frac{12\text{g}}{6.02 \times 10^{23}}$$

Take helium (relative atomic mass 4) as our first example.

$$\text{mass of 1 atom of He} = \frac{4}{12} \times \frac{12}{6.02\times10^{23}} \text{ g}$$

$$\text{mass of 1 mole He} = \frac{4 \times 12}{12} \times \frac{6.02 \times 10^{23}}{6.02 \times 10^{23}}$$

$$= 4\text{g}$$

Take oxygen (relative atomic mass 15.99)

$$\text{mass of 1 atom of O} = \frac{15.999 \times 12}{12 \times 6.02 \times 10^{23}} \text{ g}$$

$$\text{mass of 1 mole O atoms} = \frac{15.999 \times 6.02}{12 \times 6.02 \times 10^{23}} \times 10^{23} \times 12 \text{ g}$$

$$= 15.999\text{g}$$

It follows from the above calculation that the mole can also be defined as the quantity of a substance whose mass in grams is numerically equal to the atomic, molecular or formular mass of the substance. The molar mass of a compound is the number of grams of the compound needed to make up one mole of the compound i.e. contains 6.02×10^{23} molecules of the compound.

With this new definition of the mole you can calculate the number of

(i) moles
(ii) particles
(iii) atoms etc in a given mass of a substance of known formula.

Table 9.1 Some substances and their molar masses

Substance	Formular	Formular mass	Molar mass (g)
Hydrogen gas	H_2	2.0	2.0 g
Magnesium	Mg	24.0	24.0g
Methane	CH_4	18.0	18.0g
Water	H_2O	18.0	18.0g
Common salt	NaCl	58.5	58.5g

Example 1

Calculate the following for 4.5g of water:

(i) number of moles.
(ii) number of water molecules.
(iii) mole and number of oxygen atoms.
(iv) mole and number of hydrogen atoms.

Solution

(i) Formula of water is H_2O
formula mass = 2 (1) + 16 = 18g
$\therefore$ molar mass of water = 18g
18g of water = 1 mole

$\therefore$ 4.5g of water = $\frac{1}{18} \times 4.5$mol
= 0.25 mol

(ii) 1 mole $\equiv 6.02 \times 10^{23}$ particles
$\therefore$ 0.25 mole $\equiv 6.02 \times 10^{23} \times 0.25$ molecules of water
= 1.505×10^{23} molecules.

(iii) Formula of water = H_2O
mole of O = mole of water = 0.25
number of O atoms = $0.25 \times 6.02 \times 10^{23}$
= 1.504×10^{23} atoms

(iv) From the formula mass H_2O
mole H atoms = 2 x mole of water = 0.50 mol
Number of H atoms = $0.50 \times 6.02 \times 10^{23}$
= 3.01×10^{23} atoms
You can also convert amount (in moles) to mass (m gram).

Example 2

What is the mass of 2 moles of ammonia gas (NH_3) with the following relative atomic mass of atoms,
N= 14 H=1

Solution

formula mass of NH_3 = 14 + 3 (1)
= 17
molar mass = 17g
1 mole has a mass of 17g
$\therefore$ 2 moles = 17g x 2 = 34g

9.4 Finding the Formula of a Compound

This involves the calculation of the quantities of the elements involved in the formation of the compounds. The concept of a mole is central in this type of calculations.

Example 1

0.24g Magnesium is burnt in oxygen. The mass of the magnesium oxide is found to be 0.40g

Determine (i) the formula of magnesium oxide
(ii) the molar mass of magnesium oxide.

Solution

Mass of oxygen in magnesium oxide
= 0.40 - 0.24 = 0.16g,
0.24g Mg combines with 0.16g O
OR (multiply x 100 to remove the decimal point)
24g Mg combines with 16g O to form
40g of magnesium oxide.

mole of magnesium = $\frac{24}{24} = 1$

mole of Oxygen = $\frac{16}{16} = 1$

∴ 1 mole of magnesium combines with 1 mole of oxygen in magnesium oxide
∴ Formula = MgO
molar mass = 24 + 16 = 40g.

Example 2

Zinc oxide is found by chemical analysis to contain 80.3 percent (by mass) of zinc and 19.7 percent of oxygen.
Determine the formula of zinc oxide.

Solution

Assuming we analyse 100g sample.
80.3g Zn and 19.7g O

mole of Zn = $\frac{80.3}{65.4} = 1.23$

mole O = $\frac{19.7}{16.00} = 1.23$

1.23 mol of zn combines with 1.23 mol of oxygen

∴ 1 mol of Zn combines with I mol of oxygen
formula = ZnO.

Example 3

2.00g mercury combines with 0.71 chlorine gas to form 2.7g of mercury chloride. What is the simplest formula of mercury oxide.

Solution

2.00g Hg combines with 0.71g chlorine

mole Hg $= \frac{2.00}{200} = 0.01$

mole Cl $= \frac{0.71}{35.5} = 0.2$

.01mol Hg combines with .02 mol Cl

1 mol Hg will combine with $\frac{1.0 \times 0.02}{0.01} = 2$

formula = $HgCl_2$

9.5 Calculating the percentages of elements in a compound

Example 1

Calculate the percentage of oxygen in water.

Solution

formula of water H_2O

formula mass = 2 + 16 = 18g

mass of 1 mole = 18g.

% oxygen = $\frac{16}{18} \times 100 = 88.9$

Example 2

Calculate the percentage of nitrogen in ammonium nitrate fertilizer formula NH_4NO_3

Solution

NH_4NO_3 formula mass $= 14 + 4\,(1) + 14 + (16)\,3$

$= 14 + 4 + 14 + 48$

$= 80$

molar mass = 80 g

mass of nitrogen/formula mass = 28

% Nitrogen = $\frac{28}{80} \times 100$

= 35 percent

9.6 Using Empirical Formula to Calculate Unknown Atomic Mass of an Element

Example 1

The empirical formula of non metallic oxide is XO_2 where *X* stands for the chemical symbol of the element with unknown atomic mass. 0.80g of *X* is burnt in oxygen and the mass of the metal oxide found to be 1.60g. Given that the atomic mass of oxygen is 16, determine the atomic mass of *X*.

Solution

Mass of oxygen in the compound = 1.60 − 0.80
= 0.80g

mole of oxygen = $\frac{0.80}{16}$ = 0.05

from the formula XO_2
ratio X : O is 1:2
2 mol O combine with 1 mole *x*
0.05 mol O will combine with 0.05 x ½
= 0.025 mol X

0.025 mol X ≡ 0.8g

1 mol X = $\frac{0.8}{0.025}$ = 32g

molar mass is 32

9.7 The Mole in Chemical Reactions (Yield and percentage yield)

The above is very important in chemistry because it allows for calculation of yields expected even before an experiment is carried out. A balanced chemical equation of the reaction is all that is required.

$FeO_{(s)} + CO_{(g)} \longrightarrow Fe_{(s)} + CO_{2(g)}$

mole ratio of reactant of product
1 : 1 1 : 1

1 mole FeO + 1 mole CO ⟶ 1 mole $Fe_{(s)}$ + 1 mole $C0_{2g}$ or in terms of masses.
72g FeO + 28g CO ⟶ 56g Fe + 44g CO_2

Suppose we require to produce 2.8g $Fe_{(s)}$

mole Fe(s) required = $\frac{2.8}{56}$ = 0.05

mole FeO needed as reactant
= 0.05 x 72 = 3.6g
mole CO = 0.05 x 28 = 1.4g

9.7.1 Calculation of percentage yield

In most reactions the conversion of reactant to product is not often complete. The percentage yield gives the ratio of the experimental yield to a theoretical yield assuming complete reaction.

Take the last example

Suppose 3.6g of FeO reacts with enough CO(g), and only 2.2g of Fe(s) is formed.

$$\%yield = \frac{\text{yield from experiment}}{\text{yield expected}} \times 100$$

$$= \frac{2.2}{2.8} \times 100$$

$$= 78.571\%$$

9.7.2 Molar volume for gases

At a temperature of 273 and pressure of 1 atmosphere commonly called (STP), a mole of any gas occupies a volume of 22.4 dm^3. This is called molar volume.

1 mole of a gas occupies a volume of 22.4dm^3 at S.T.P.
Now consider the reaction in the last section.

$FeO_{(s)} + CO_{(g)} \longrightarrow Fe_{(s)} + CO_{2(g)}$
At S.T.P.
22.4 dm^3 of $CO_{(g)}$ ≡ 1 mole $CO_{(g)}$
22 4 dm^3 $CO_{2(g)}$ ≡ 1 mole CO_{2g}

Example 1

Calculate the volume of CO required at S.T.P. to react completely with 3.6g FeO.

$FeO_{(s)} + CO_{(g)} \longrightarrow Fe_{(s)} + CO_{2(g)}$

mole ratio FeO : CO = 1:1

Mole FeO in 3.6g FeO = $\frac{3.6}{72} = 0.05$

mole CO needed = 0.05
Volume CO needed at S.T.P.
= 0.05 x 22.4 dm^3
= 0.112dm^3

Example 2

What mass of Fe(s) is formed by complete reaction of 5.6dm^3 of CO at S.T.P. in the above reaction.

Solution

mole CO = $\frac{5.6}{22.4}$ = 0.25 mole

mole ratio
FeO: CO: Fe(s) = 1 : 1 : 1
∴ mole Fe formed = 0.25
mass of Fe = 0.25 x 56
= 1.4g

9.8 Conclusion

From the many examples considered in this unit, you will agree that the mole concept is a very useful tool in chemical calculations. In the next unit the use of mole concept in volumetric analysis and solution preparations will be discussed. Learn to use the mole concept and you will be in a position to solve a mole of problems.

9.9 Summary

The mole is defined and applied to chemical calculations. The mole concept is applicable to gas reactions as well as reactions with solid and liquid substances. The mole is a measurable quantity of substance and is more relevant to experiments in quantitative analysis.

9.10 Tutor-Marked Assignments

1.(a). Give the number of moles of atoms in the following:
60g Carbon, 6.4g O_2 and 10.00g Ca

(b) What is the mass of the following?
(i) 3.5 moles of Oxygen molecules
(ii) 0.05 mole of CaC_2

2.(a) What is percentage of water of crystallisation in $CuSO_4.5H_2O$ and $Na_2CO_3.10H_2O$

(b) 5.4g of carbon burns in excess oxygen. Calculate
(i) mole and mass of CO_2 formed
(ii) volume of CO_2 at S.T.P.

3. The percentage composition by mass of a compound of sodium, sulphur and oxygen are 18.2,12.7 and 19.1 percent respectively. Water of crystallisation is 50 percent (by mass). Determine the formula of the compound.

9.11 References

Bajah, S.T., Teibo B.O., Onwu, G. and Obikwere A. (2002). *Senior Secondary Chemistry Textbook 1.* Lagos. Longman Publishers.

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Unit 10

Mole Concept II

10.0 Introduction

In the last unit, the mole was defined and the mole concept used in calculations. The mole concept is particularly useful in predicting yield and calculating yield from experiments. This is very important for industrial or laboratory processes that involve reversible reactions. Yield and yield percent calculations allow chemists to assess the efficiency of chemical processes and look for ways of improvement where applicable and possible.

In this unit we continue our discussion of the mole concept. Applications in solution preparation, volumetric analysis and electrolysis will be the focus. More calculation using the mole concept to assess the efficiency of some processes will also be discussed.

10.1 Objectives

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

- Apply mole concept to calculate solution concentration.
- Define molar and molal solutions.
- Describe the preparation of a molar solution.
- Calculate amount of substance in solution in moles and in grams.
- List more applications of the mole concept.
- Calculate concentration of an unknown solution from titration data.
- Apply the mole concept to prepare dilute solution from concentrated solutions.
- Define the Faraday and relate it to the mole.

10.2 Mole Concept in Solutions

10.2.1 The molar and molal solutions

A solution that contains one mole of solute in 1.0 dm^3 of the solution is called a **molar solution.** A molar solution is prepared by dissolving one mole of the solute in small amount of the solvent and then make the solution up to 1.0 dm^3 in a standard volumetric flask. A molar solution can also be prepared from amount less than or equal to one mole of the solute.

Example

It is required to prepare 250.00 cm^3 of 1.0 mol dm^{-3} solution of glucose ($C_6 H_{12} O_6$).

Calculate

(i) mole of glucose required

(ii) mass of glucose required.

Solution

molar mass of glucose = 6(12) + 12(1) + 6(16)g

= 180g

for a molar solution of glucose $1dm^3$ contains 1.0 mol

$250cm^3$ will contain $= \frac{1.0 \times 250}{1000}$

= 0.25 mol

(i) 0.25 mol glucose is required

(ii) mass of glucose = mol x molar mass

= 0.25 x 180

= 45g

A molal solution contains 1 mole in 1kg of the solvent

A molal solution is prepared by dissolving 1 mole of the solute in 1000g of solvent. The solute and solvent are weighed and mixed in the stated proportions. The final volume of solution is immaterial.

Note

From the definitions and methods of preparation, both solutions are not the same. The preparation of solutions in volumetric (titrimetric) analysis is done in standard volumetric flasks and solution concentrations are expressed in mol dm^{-3}

Not all solutions are molar solutions. The concentration of a solution is calculated from the amount of solute and the volume of solution.

Example

Calculate the concentration of a solution containing 8.0g NaOH in $500cm^3$ of solution in

(i) g/dm^3 (ii) mol dm^{-3}

Solution

8g NaOH in $500cm^3$

$8.0 \times \frac{1000}{500}$ g will be in $1000cm^3$ of solution

16.0g will be in $1000cm^3$ of solution

concentration (g/dm^3) = 16.0

(ii) concentration (mol dm^{-3}) $= \frac{g/dm^3}{\text{molar mass}}$

$= \frac{16.0}{(23 + 16 + 1)} = \frac{16}{40}$

$= 0.4\ moldm^{-3}$

10.2.2 Calculation of mole and mass in solution

When the concentration of a solution is expressed in $moldm^{-3}$, it is possible to calculate the amount in moles and grams of the solute in a volume of solution.You must remember that though a solution has one concentration, the amount of solute will be different for different volumes of the solution. A volume of sea water will taste the same whether you test a cup of it or a bucket or a drop. The amount of salt you recover from sea water however depends on the volume of sea water evaporated.

Example

Calculate the amount of sodium chloride recoverable from (i) 1.0dm^3 (ii) 10dm^3 (iii) 3 drums of sea water.

(1 drum – 50dm^3). Concentration of sodium chloride in the sea water is 0.43 moldm^{-3}. Na = 23, Cl = 35.5

Calculate the amount in (a) mole and (b) g dm^{-3}.

Solution

(a) (i) 1.0 dm^3 contains 0.43 mol/Nacl.

(ii) 10.0 dm^3 contain 0.43 x 10 = 4.3 mol NaCl

(iii) 3 drums = 3 x 50dm^3 = 150 dm^3

150.0dm^3 contain 0.43 x 150

= 64.5 mol NaCl

(b) (i) Amount in g = mole x molar mass

= 0.43 x 58.5

= 25.16g

(ii) Amount in g = 4.3 x 58.5

= 251.6g

(iii) Amount = 64.5 x 58.5 g

= 3773.3g

= 3.77 kg

10.3 The Mole Concept in Volumetric Analysis

10.3.1 Determination of concentration of a solution

The solution of unknown concentration is titrated with a standard solution (a solution of known concentration). From the average titre the calculation of the concentration is done using mole concept.

Example

25.0 cm^3 of 0.10 mol dm^{-3} sodium hydroxide solution requires 21.5cm^3 ethanoic acid solution for complete neutralisation using phenolphthalein indicator. Calculate the concentration of the ethanoic acid solution in (i) mol dm^{-3} and (ii) g/dm^3. Equation of the reaction is NaOH + CH_3 COOH ® $CH_3COONa + H_2O$

Solution

Mole ratio NaOH: CH_3COOH = 1:1

$$\text{Mole NaOH} = \frac{\text{Conc (mol dm}^{-3}\text{) x V(cm}^3\text{)}}{1000}$$

$$= \frac{0.10 \times 25}{1000} = 2.5 \times 10^{-3}$$

Because mole ratio is 1:1

mole $CH_3COOH = 2.5 \times 10^{-3}$

2.5×10^{-3} mole CH_3COOH is in $21.5cm^3$ of solution

$\therefore \frac{2.5 \times 10^{-3} \times 1000}{21.5}$ mol CH_3COOH is in 1.0 dm^3 of solution

concentration ($moldm^{-3}$) = 0.116

concentration (g/dm^3) = $moldm^{-3}$ x molar mass

= 0.116 x 60

= $6.96gdm^{-3}$

10.3.2 Determination of percentage purity

The mole concept can be applied in volumetric analysis for the determination of percentage purity of an acid or an alkali sample

Example

5.0g of sodium hydroxide dissolved in $1.0dm^3$ of solution. $25.0cm^3$ of the solution requires 24.9 cm^3 of a 0.10 $moldm^{-3}$ trioxonitrate (v) acid for complete neutralisation using methyl orange indicator.

Calculate the percentage purity of the sodium hydroxide sample. Equation of the reaction is

$$NaOH_{(aq)} + HNO_{3\,(aq)} \longrightarrow NaNO_{3(aq)} + H_2O\,(l)$$

mole ratio NaOH: HNO_3 = 1:1

mole $HNO_3/24.9cm^3$ = $\frac{24.9 \times 0.10}{1000}$

= 2.49×10^{-3}

$\therefore$ mole $NaOH/25.0cm^3$ = 2.49×10^{-3}

mole $NaOH/1000cm^3$ = $\frac{2.49 \times 10^{-3} \times 1000}{25}$

= 0.0996 $moldm^{-3}$

g/dm^3 (NaOH) = .0996 x molar mass (NaoH)

= .0996 x 40

= 3.984g

Percentage purity = $\frac{\text{amount calculated}}{\text{amount dissolved}} \times 100$

= $\frac{3.984}{5.0} \times 100$

= 79.68

10.3.3 Mole concept in solution dilution

Many times it is required to make a dilute solution from a relatively concentrated solution of the same substance in the same solvent. Mole concept allows for calculation to know how much solvent must be added to get the required concentration. Dilution becomes the only way of making dilute solution of common acids that are available commercially as concentrated acids e.g. H_2SO_4, HCl and HNO_3.

Example

A bottle of commercial tetraoxosulphate (vi) acids reads 98 percent w/w, specific gravity 1.84, molar mass 98g

Calculate the volume of this commercial acid sample required to prepare 2.0dm^3 of a 0.05 mol dm^{-3} solution.

Solution

98% w/w implies 98g H_2SO_4 in 100g of solution.

98g H_2SO_4 are in 100g of commercial acid

98g H_2SO_4 are in $\frac{100}{1.84}$ cm^3 of concentrated acid

$$\text{Note that specific gravity} = \frac{\text{mass of substance}}{\text{mass of an equal volume of water}}$$

$$= \frac{\text{mass of substance}}{\text{volume of substance}}$$

This means that specific gravity is numerically the same as density. Recall

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

$$\therefore \quad \text{volume} = \frac{\text{mass}}{\text{density}}$$

98g H_2SO_4 are in $\frac{100}{1.84}$ cm^3

$\therefore$ $\frac{98 \times 1000 \times 1.84}{100}$ g H_2SO_4 are in 1000 cm^3

1803.2g H_2SO_4 are in 1000cm^3

$$\text{Concentration (moldm}^{-3}) = \frac{\text{g/dm}^3}{\text{molar mass}}$$

$$= \frac{1803.2}{98}$$

$$= 18.4 \text{ moldm}^{-3}$$

Mole of acid required for the preparation of 2.0dm^3 of 0.05 mol dm^{-3} solution

= moldm^{-3} x Volume (dm^3)

= 0.05 x 2 = 0.10 mol dm^{-3}

For the concentrated acid.

18.4 mol are present in 1000 cm^3

$$\text{0.10 mol will be present} = \frac{0.10}{18.4} \times 1000$$

$$= 5.435 \text{ cm}^3$$

This latter part of the calculation can be done using the formula

$M_c V_c = M_d V_d$ M_c – concentration of commercial acid
V_c – volume of commercial acid
M_d – concentration of dilute acid
V_d – volume of dilute acid.

Substituting

$$18.4 \times V_c = 0.05 \times 2000 \text{ cm}^3$$

$$V_c = \frac{0.05 \times 2000 \text{ cm}^3}{18.4}$$

$$= 5.435 \text{ cm}^3$$

Note that $M_c V_c$ = millimoles of concentration acid
$M_d V_d$ = millimoles of dilute acid

By equating the millimoles, the volume of the concentrated acid required is calculated.

Example

What volume of water must be added to 200cm^3 of a 0.04 mol dm^{-3} solution to dilute it 0.25 moldm^{-3}?

Solution

Using the millimole equation

$$M_c V_c = M_d V_d$$

$$V_d = \frac{M_c V_c}{M_d}$$

$$V_d = \frac{0.40 \times 200}{0.25}$$

$$= 320 \text{ cm}^3$$

Volume of water to be added

$$= 320 - 200$$

$$= 120 \text{ cm}^3$$

10.4 The Mole Concept in Electrolysis

10.4.1 The mole concept and the Faraday

During electrolysis chemical reactions occur and substances are discharged or liberated at the electrodes. The Faraday is quantity of charge carried by 1 mole (6.02×10^{23}) of electrons. A Faraday liberates or discharges 1 mole of a univalent ion like H^+

$$H^+ + e \rightarrow H$$

A mole H^+ will require a mole of electrons to form a mole of H atoms

Example

Calculate the charge on an electron given that Faraday's constant is 96500 coulombs.

Solution

By definition

$$96500 \equiv 6.02 \times 10^{23} \times e$$ where *e* is the electronic charge

$$e = \frac{96500}{6.02 \times 10^{23}} = 1.603 \times 10^{-19} \text{ coulombs}$$

10.4.2 The mole concept and the efficiency of an electrolytic process

This can be assessed by comparing amount of reaction that occurred at the electrode with the quantity of electricity passed. In these calculations the Faraday is used as base unit of electricity.

Example

4,825 coulombs of electricity passed in an electrolysis process. The volume of hydrogen gas liberated was 0.50 dm^3 at S.T.P. Calculate the efficiency of the electrolysis process. (Faraday constant = 96500 coulombs)

(Hint 1 Faraday of electricity should liberate 1.0g H_2 gas). Molar volume of gas = 22.4 dm^3 at S.T.P.

Solution

$$1 \text{ Faraday} \equiv 6.02 \times 10^{23} \text{ electrons} = 96\,500 \text{ coulombs}$$

For this process

1 Faraday liberates 1.0g H_2 gas

$$1 \text{ Faraday liberates } \frac{1.0}{2.0} \times 22.4 \text{ dm}^3\ H_2 \text{ at S.T.P}$$

$$= 11.2 \text{ dm}^3$$

$$4825 \text{ coulombs} = \frac{4825}{96500} \text{ Faraday} = 0.05 \text{ Faraday}$$

1 Faraday liberates 11.2 dm^3 at S.T.P.

.05 Faraday should liberate .05 x 11.2

$$= 0.56 \text{ dm}^3 \text{ at S.T.P.}$$

$$\text{The efficiency of the process} = \frac{\text{Volume } H_2 \text{ liberated}}{\text{Theoretical volume}}$$

$$= \frac{0.50}{0.56}$$

$$= 0.89$$

% efficiency = 89 percent.

10.5 Conclusion

This unit concludes the discussion and applications of the mole concept. More applications of the concept will still be in subsequent units. It is hoped that the examples in these two units will assist you in subsequent units where you will be required to use the concept in calculations.

10.6 Summary

The applications of the mole concept in solution preparation, volumetric analysis and electrolysis are discussed and illustrated with appropriate examples. The mole concept is used to asses the efficiency of an electrolytic process.

10.7 Tutor-Marked Assignments

1. (a) Calculate the number of moles of sodium hydroxide in
    - (i) 2.4g of the solid
    - (ii) $50 cm^3$ of 0.1 mol dm^{-3} solution.
    - (iii) 5.3×10^{14} NaOH particles

   (b) Calculate the mass of Na_2CO_3 in $100 cm^3$ of 0.05 mol dm^{-3} Na_2CO_3 solution.

2. A solution contains 2.82 g of MOH in $500 cm^3$ of solution, where M is a metal of unknown atomic mass. $25.0 cm^3$ of the solution of MOH require $25.1 cm^3$ of 0.10 mol dm^{-3} HCl solution for complete neutralisation. Calculate the atomic mass of and identify M.

10.8 References

Bajah, S. T., Teibo, B. O., Onwu, G and Obikwere, A. (2002).*Senior Secondary Chemistry Textbooks 1 & 2*. Lagos. Longman Publishers.

Osei Yaw Ababio (2002). *New School Chemistry* (New Edition). Onitsha. Africana-FEP Publishers.

Unit 11

The Kinetic Theory and States of Matter

11.0 Introduction

In unit 1 you learnt that matter is made up of tiny particles, called atoms or molecules. No one has ever seen an atom or a molecule. None of the most powerful microscopes known to us can help us see such particles. Matter exists in three states. These states are solid, liquid and gas. Ice, water and steam are good examples of these states. Let us take a state like the solid state. The particles in the solid are tightly connected together by forces of cohesion.

The forces holding the particles of a solid restrict their movement, so that they are held in fixed positions. Solids have definite shapes and volumes and are very difficult to compress. Liquids are hard to compress, have no definite shape but posses definite volumes. A gas occupies the whole volume of the container, has no definite shape and is very compressible.

Can you explain why if a bottle of perfume is opened at one end of a room, the smell is perceived all over the room?

The kinetic theory explains the differences in the behaviour of matter in different states. The changes that occur when matter is heated are also explained by the theory.

11.1 Objectives

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

- State the kinetic theory.
- List some natural phenomena that support the theory.
- Use the kinetic theory to explain melting, vaporisation and evaporation.
- Define melting and boiling points.
- Sketch and explain a typical heating or cooling plot.

11.2 The Kinetic Theory

The word 'kinetic' describes motion or movement. The kinetic energy of a body is the energy it possesses as a result of its motion. The higher the velocity of a body, the higher its kinetic energy.
Can you now explain why accidents with very fast moving bodies (cars, stones etc) are very fatal?

11.2.1 The postulate of the kinetic theory

The postulate of the kinetic theory is this, that the particles of matter (atoms or molecules) are continually moving and so possess kinetic energy. In any given sample of matter, some molecules have very high energies while some have very low kinetic energies. The average kinetic energy of the particles increases with increasing temperature of the matter.

11.2.2 The kinetic theory and practical evidences

(a) **Measurement of molecular velocities with the help of scientific instruments**

Scientists have been able to measure velocities of molecules and detect their exact positions at definite times.

(b) **Natural phenomena**

(i) **Brownian motion**

This is the irregular movement of suspended particles caused by constant collision with molecules of the suspending medium. A suspension of sulphur powder in water when viewed under a microscope will demonstrate Brownian motion. Brown was the first scientist to observe this behaviour, hence the name Brownian motion.

(ii) **Diffusion**

Diffusion describes the movement or spread of substances from a region of high to low concentration. Diffusion occurs in solids, liquids and gases. A drop of liquid bromine in a closed jar of air vaporises and spreads evenly throughout the jar. A crystal of a soluble coloured solid when dropped in water will after sometime colour the entire volume of water.

e.g. $CuSO_4.5H_2O$ (blue in colour). Diffusion is fastest in gases and slowest with solids.

(c) **Osmosis**

This is a special type of diffusion that involves movement of water particles. The swelling of bean seed in water is an example of osmosis.

All the above evidences confirm that particles of matter are in motion as postulated by the kinetic theory.

11.3 The Kinetic Theory and The States of Matter

The particles of matter in a solid are closely packed and firmly held together by strong forces of attraction. Because of the strong cohesive force, the particles are held in fixed positions and can only rotate or vibrate about a mean position. This explains why solids have definite shapes and volumes and are very difficult to compress e.g. iron, ice, candle.

The particles in the liquid state are further apart than in the solid. The kinetic energy of the liquid particles is higher and particles are not fixed in positions. There is some motion that allows the liquid to maintain a fixed volume but no fixed shape e.g. ethanol, water and kerosene.

In the gas state the particles are in constant random motion in all directions at very high velocities. There is virtually no force of attraction between the particles explaining why a gas diffuses freely filling all available space. A gas has no definite shape or volume. The large empty spaces between the gas particles explain why gases are very compress

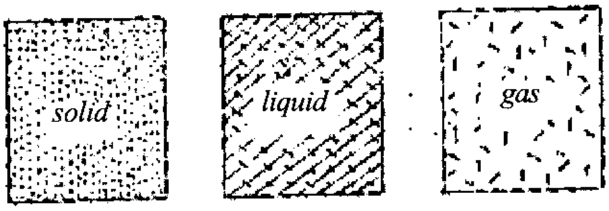

Fig 1.1 Model of the three states of matter

11.4 The Kinetic Theory and Change of State

In the previous section we learnt that solid particles are fixed in positions by strong forces. On the other hand gas molecules are in perpetual and random motion at very high velocities because of lack of cohesive forces between the particles. When solid matter is heated, the average kinetic energy of the particles increases and changes in the nature of matter occurs from solid-liquid-gas

11.4.1 Melting and melting point

Heating increases the average kinetic energy of the solid particles. At a temperature characteristic of a particular solid, the particles that are fixed in position acquire sufficient energy (kinetic energy) to overcome the cohesive force keeping them in fixed positions. So the solid gradually change to the liquid form. *The temperature at which this happens is called the melting point of the solid and the phenomenon is called melting.* The melting point is characteristic of the solid and is often used as a criterion of purity for the solid substance. A pure solid will have a sharp melting point i.e. the temperature of the solid/liquid mixture remains constant until the melting process is completed.

11.4.2 Vaporisation and boiling point

The heating of liquid matter leads to increase in the average kinetic energy of liquid particles. As the temperature increases the particles acquire sufficient energy to overcome the cohesive energy of the liquid state. The particles become free, move more randomly independent of each other. The liquid has gradually been turned to gas (vapour). This is vaporisation. *The temperature at which there is massive vaporisation from within the bulk of the liquid is the boiling point.* At the boiling point, vapour molecules escape from the inside of the containing vessel to the surrounding space. The temperature of the vapour/liquid mixture remains constant until all the liquid is vaporised. The boiling point is also a criterion of purity for liquid substances. Again pure liquids have a sharp boiling point. For instance the boiling point of water is 100C but vaporisation can take place below that temperature.

11.4.3 Evaporation

There is a decrease in liquid volume as a result of loss of vapour molecules during vaporisation. This is evaporation. Evaporation is most rapid at the boiling because the liquid particles have maximum kinetic energies. Evaporation also occurs at temperatures below the boiling point. This is most likely when a liquid sample is placed in an open container. The high energy particles on the liquid surface can vaporise into the surrounding space. The loss of high energy particles from the liquid surface will result in a decrease in the liquid volume as well as a decrease in the average kinetic energy of the liquid sample.

What is the effect of evaporation below the boiling point on liquid temperature?

11.4.4 Sublimation

Certain substances (e.g. ammonium chloride and solid carbon(iv) oxide) do not melt when they are heated but change directly from a solid to a gas. When the gas cools it returns directly to the solid state. This process is called *sublimation* and is a useful method for separating a mixture of substances when only one of the substances sublimes, e.g. ammonium chloride and sodium chloride.

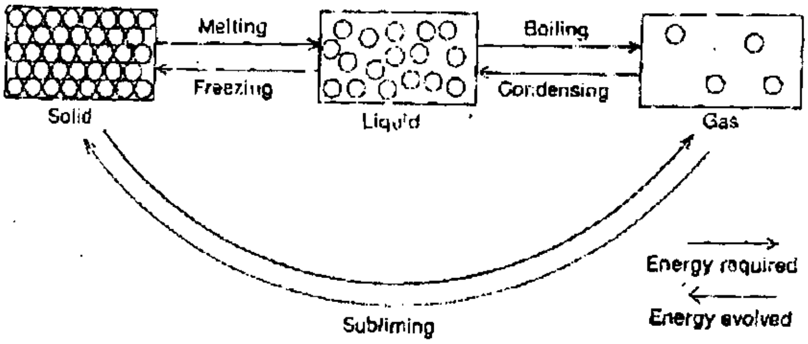

Fig 11.2 States of matter and their interconversion

11.5 Heating and Cooling Graphs

These are plots of temperature change (average kinetic energy change) with the time of heating or cooling. Fig 11.3 shows the graph obtained when a sample of ice is heated with a steady source of energy. This is a typical heating graph.

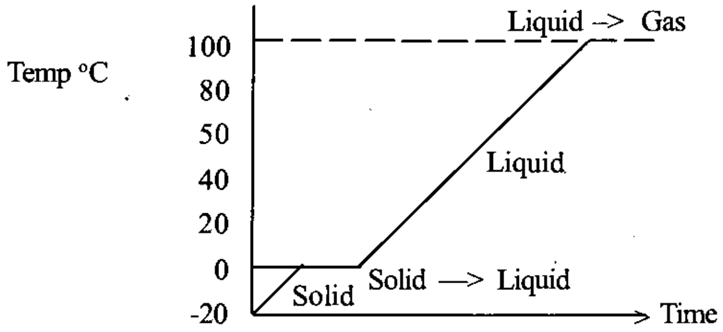

Fig 1.1.3 Heating water

When a change of state is taking place e.g. solid-liquid or liquid - (vapour) gas, the temperature remains constant despite the continue supply of heat. This energy which is not used to raise the temperature is called the **latent heat** (of vaporisation and the latent heat of fusion at the boiling and melting points respectively). The latent heat is used to supply the particles energy to overcome the cohesive forces in the liquid or solid state. When the substance cools the reverse changes occur. As the vapour condenses and the liquid freezes the lalent heats are evolved.

11.6 Conclusion

In this unit you learnt about the states of matter and the changes that occur when matter is heated. With virtually no attractive force between the gas particles you should expect the physical behaviour of gases to be much different from those of the solids and liquids. This special behaviour of gases will be the subject of the next two units.

11.7 Summary

Matter exists in three states; solid, liquid and gas. When matter is heated change of state occurs. The kinetic theory explains this as the result of the higher average kinetic energy of the particles at the higher temperature. Melting and boiling occur at temperature characteristics of the matter. These temperatures are called melting and boiling point respectively.

11.8 Tutor-Marked Assignments

1(a) Differentiate between
- (i) melting and freezing
- (ii) vaporisation and condensation

2(a) Explain the effect (if any) of the sample size on a typical heating or cooling graph.

(b) The boiling points of substances A,B,C,D are 100,60,20, and 300°C respectively. Arrange A,B,C,D in the order of increasing melting point . Give a reason for your order of arrangement.

11.9 References

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Unit 12

The Gas Laws (I): Boyle's and Charles' Laws and the General Gas Equations

12.0 Introduction

In the previous unit the kinetic theory was used to explain the physical nature of the different states of matter as well as the changes that occur when matter is heated. Can you recall the following as explained in that unit? Melting point, boiling point, vaporisation and condensation.

You will also recall that particles in the gas state are in random motion in all directions and at very high speed with virtually no force of attraction between the particles. The physical behaviour of a gas is very much different from those of the solid and liquid. This physical behaviour of gases was investigated by early scientists and that led to the establishment of gas laws named after them. There is a need therefore to increase the postulates of the kinetic theory to account for the special behaviour of gases.

This is the first of two units on gases and you will learn about Boyle's law and Charles' law and the general gas equation. Statement of the gas laws will be examined and the gas behaviour as established by each law explained by the kinetic molecular theory.

12.1 Objectives

By the end of this unit you should be about to:

- State the postulates of the kinetic molecular theory for gases.
- State the Boyle's and Charles' laws for gases.
- Illustrate Boyle's and Charles' laws graphically.
- Use the kinetic molecular theory to explain Boyle's and Charles' laws.
- Derive the general gas equation from Boyle's and Charles' laws.
- Carry out calculations based on the three gas laws.
- Explain the effect of temperature and pressure on the volume of a gas

12.2 The Kinetic Molecular Theory of Gases

Two assumptions are made about gases in the kinetic theory:

(i) There is virtually no force of attraction between gas molecules

(ii) Gas molecules move independent of each other.

These assumptions are only true for an ideal gas. An idea gas is also often referred to as a perfect gas.

Real gases in general do not quite follow the assumptions made for an ideal gas. They constitute what is called the kinetic molecular theory. They specifically deal with the gas molecules. These following six statements describe the behaviour of an ideal gas:

1. A gas consists of small identical particles called molecules moving randomly in all directions colliding with each other and also with the walls of the containing vessel.
2. There is no force of attraction between the gas molecules.
3. Molecular collisions are perfectly elastic i.e. no energy is lost when molecules collide with each other or with the container wall.
4. The volume of gas molecules is negligible compared to the container volume.
5. The collisions of gas molecules with the container walls give rise to what is called the gas pressure.
6. The temperature of the gas is directly proportional to the average kinetic energy of the molecules.

- Which of the above will not always be true for a real gas?
- Can you predict the conditions under which a real gas can be assumed to behave ideally?

12.3 Boyle's Law

12.3.1 Statement of Boyle's law

Boyle's law states that at a constant temperature the volume of a given mass of gas is **inversely proportional** to the pressure.

Note: The words in bold typeface is the statement of the law. Boyle's law describes the relationship between the pressure and volume of a gas at constant temperature.
Mathematically

$V \propto \frac{1}{P}$ at constant temperature

OR V = Volume and P = Pressure of gas

$V = \frac{k}{P}$ where k is the constant of proportionality.

$PV = k$

Boyle's law can also be stated mathematically as $P_1 V_1 = P_2 V_2$
P_1 is the pressure when gas volume is V_1 and P_2 is the pressure when gas volume is V_2.
The above implies that the product of the pressure and volume is always a constant. What this means is that as the gas pressure increases, the volume decreases and vice versa as long as the temperature is constant.
Boyle's law can also be presented graphically

Fig. 12.1 P ---->

From the above graphical illustration, you see that as pressure increases, the volume decreases.

Fig. 12.2 P or V

This figure shows that the product of presure and volume is contant

Consider the equation in the form $PV = k$

The equation can be written as $P = \frac{k}{V}$

The above equation is the mathematical representation of the alternative statement of Boyle's law:

The pressure of a given mass of gas is inversely proportional to the volume provided the temperature is constant.

Examples

1. At 25°C and 750mm Hg pressure the volume of a given mass of oxygen is $520cm^3$. Calculate the gas volume when the pressure is increased to 760mm Hg pressure at constant temperature.
2. A gas occupies a volume of $1.20dm^3$ at 25°C and 760 mm Hg pressure. What will be gas pressure when the gas expands into $2.80dm^3$ container at the same temperature?

Answers

1. Let P_1 = 750mmHgand $V_1 = 520cm^3$
   P_2 = 760mmHgand V_2 = ?
   using $P_1V_1 = P_2V_2$

   $$\frac{P_1V_1}{P_2} = V_2$$

   $$\frac{750 \times 520}{760} = V_2 = 513\ cm^3$$

2. Let P_1 = 760mm Hg V_1 = $1.20dm^3$
   P_2 = ? V_2 = $2.80dm^3$

   Using $P_1V_1 = P_2V_2$

   $$\frac{P_1V_1}{V_2} = P_2$$

   $$\frac{760 \times 1.20}{2.80} = P_2 = 326mm\ Hg$$

12.3.2 How kinetic theory explains Boyle's Law

According to the kinetic molecular theory of gases an increase in pressure of the gas implies an increase in the number of molecular collisions per unit area of the containing vessel. You will also recall that for a fixed mass of gas at constant temperature, the number and the average kinetic energy of the molecules remain constant for the number of molecular collisions per unit area of the containing vessel to increase under a condition of fixed mass and average kinetic energy of the gas molecules, the area and therefore the volume of the containing vessel must decrease. This implies that an increase in gas pressure is accompanied by a corresponding decrease in the gas volume. The reverse of the above is true when the gas pressure is reduced at constant temperature.

12.4 Charles' Law

12.4.1 Charles' law and the kelvin temperature scale

The term temperature is a measure of the degree of hotness or coldness of a body. The celsius or centrigrade (^{0}C) scale is the most used temperature scale in scientific work. The volume of matter generally increase with increasing temperature but the increase is most pronounced for gases.

- Can you recall the name of the instrument used to measure temperature?

  Charles study on gases show that the volume of a gas increases by 1/273 of its volume at 0^0C for every 1^0C rise in temperature.

Mathematically stated

$$V_T = Vo + \left(\frac{T}{273}\right) Vo$$

V_T = Volume of the gas at T°C
V_0 = Volume of gas at 0°C.

According to the above equation, a gas has zero volume at - 273°C. This temperature at which the gas volume is theoretically zero is the lowest temperature that can be reached. It is called the **absolute zero** temperature. The Kelvin temperature scale represented with a capital K has this temperature (-273) as its starting point and measures temperatures upwards from it.

Recall the relationship between temperature and the average kinetic energy of gas molecules and explain why it is assumed that the average kinetic energy of gas particles at -273°C is zero.

The Celsius and the Kelvin (absolute) scales are related by the equation.

$$T(K) = t^oC + 273$$

Let us now try using the above formula to complete the table below.

t°c	T(K)
20	–
–	325
–15	–
77	–
–	40

In calculations involving the gas laws, temperature readings must be converted to the Kelvin scale.

Note: Temperatures on the Kelvin scale are in K units with no degree sign.
e.g. 40K and 374K

12.4.2 The statement of Charles' law

Charles' law states that for a fixed mass of gas, the volume is directly proportional to the absolute temperature provided the pressure remains constant.

Mathematically

$V \propto T(K)$ V – Volume of gas

OR T – Kelvin temperature

$V = kT$ Where k is a constant.

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

OR

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$ where V_1 is the volume at T_1 and V_2 is the volume at T_2

Charles' law can also be stated in an alternative form when the gas volume is constant and pressure changes with temperature. In this case $P \propto T$; $P=kT$; $= k\ \frac{P}{T}$ * $= \frac{P_1}{T_1}\ \ \frac{P_2}{T_2}$

at constant volume, the pressure of a fixed mass of gas is directly proportional to the Kelvin temperature. Charles' law can also be presented graphically as shown below.

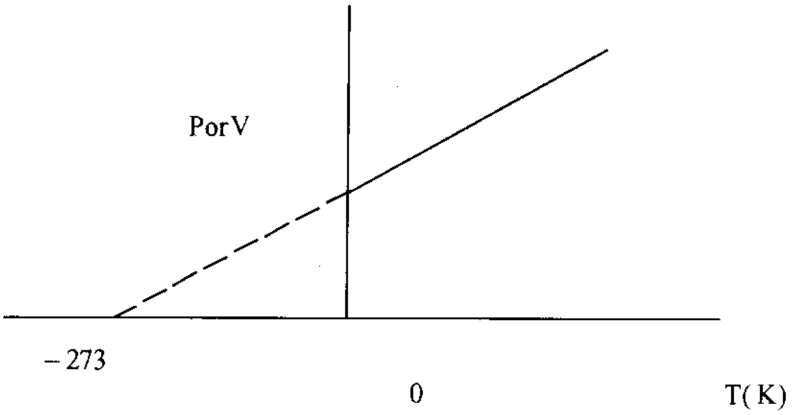

Fig 12.3

We can now solve this problem

At 27°C the volume of mass of helium gas is 1.85dm³. At what temperature will the volume be 2.25dm³ if pressure is kept constant.

$V_1 = 1.85dm^3$

$T_1 = 273+17 = 300K$

$T_2 = ?$

$V_2 = 2.25dm^3$

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

$$V_1T_2 = V_2\ T_1;\ T_2 = \frac{V_2T_1}{V_1} = \frac{2.25 \times 300}{1.85}$$

$= 364.9K$

Assignment

The pressure of a mass of oxygen gas at 25°C is 78.5mm Hg in a 1.0dm^3 container. What pressure will the gas exert when the temperature is increased to 40°C without any change in the volume.?

12.4.3 How the Kinetic theory explains Charles' law

According to the kinetic molecular theory, an increase in gas temperature leads to increase in the average kinetic energy of the gas molecules. This will result in more random motion of the molecules. For a fixed mass of gas, the number of gas molecules is constant and at constant pressure of gas the number of collisions per unit area of the containing vessel is also constant. The only way for the pressure to remain constant despite the increase in the random motion and more collisions of particles with the wall of the container is for the area and therefore the volume of the container to increase. This implies that an increase in the temperature of the gas at a constant pressure leads to a corresponding increase in the gas volume.

In the alternative, consider the case when the volume of a fixed mass of gas is kept constant and the temperature is increased. At the higher temperature, the more random motion of the gas molecules will lead to more molecular collisions per unit area on the wall of the container and thus increase in the gas pressure.

12.5 The General Gas Equation

A gas sample is described completely by four quantities: the amount, the temperature, pressure and volume. According to Boyle's and Charles' laws both pressure and temperature can affect the volume of a gas.

According to Boyle's law

$V \propto \frac{1}{P}$ and according

to Charles' law $V \propto T$

when both T and P change for a gas sample $V \propto \frac{T}{P}$; or $V = \frac{kT}{P}$

$$PV = kT; \quad \frac{PV}{T} = k$$

$$\therefore \quad \frac{PV}{T} = k \text{ (constant)}$$

Sometime the above is given as

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

The last is the general gas equation and is Boyle's and Charles' law combined. For one mole of gas, the constant of proportionality (k) in the general gas equation is the molar gas constant (R) and the general gas equation then reads;

$PV = RT$. For n moles of gas the equation has the form

$PV = nRT$.

The value and units of the gas constant R depends on the units of P, V, and T.

P in atm.

V in dm^3

T in K

From the general gas equation

$$PV = nRT$$

and $R = \frac{PV}{nT}$

The value of R is 0.082 atm dm^3 K^{-1} mol^{-1} when pressure is in atmosphere, volume in dm^3 and temperature in Kelvin. But when pressure is in Nm^{-2}, volume in m^3 and temperature in Kelvin, the value of R is 8.31 JK^{-1} mol^{-1} (Joules per degree Kelvin per mole).

Example

1. A mass of oxygen gas occupies a volume of 2×10^4 cm^3 at a pressure of 1.01×10^5 Nm^{-2} and temperature of 17°C. Calculate the volume when the pressure is increased to 1.35×10^5 Nm^{-2} and the temperature changed to 43°C.

Solution

$P_1 = 1.01 \times 10^5\ Nm^{-2}$ $\qquad P_2 = 1.35 \times 10^5\ Nm^{-2}$

$T_1 = 273 + 17 = 300K$ $\qquad T_2 = 273 + 43 = 316K$

$V_1 = 2 \times 10^4\ cm^3$ $\qquad V_2 = ?$

Using the general gas equation in the form

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$ and making V_2 the subject of the formula

$$V_2 = \frac{P_1V_1T_2}{T_1P_2}$$

Substituting values we have

$$V_2 = \frac{1.01 \times 10^5 \times 2 \times 10^4 \times 316}{300 \times 1.35 \times 10^5} = 1.58 \times 10^4\ cm^3$$

12.6 Conclusion

In this unit the physical behaviour of an ideal (perfect) gas is summarised in the assumptions of the kinetic molecular theory of gases. Some of the assumptions of the theory may not always be true for real gases, explaining why real gases sometimes deviate from ideal behaviour. The quantities, pressure, temperature, volume and amount (mole) are important in measurements and calculations involving gases. These parameters describe the behaviour of the gas and a change in one of them will result in modification of their behaviour.

12.7 Summary

This unit presents the kinetic molecular theory of gases. The theory is used to explain Boyle's and Charles' laws. Apart from giving the statements of the two laws they are graphically illustrated and employed in simple calculations

The general gas equation was derived from Boyles and Charle's laws. Note that in calculations involving the gas laws, the Kelvin temperature is used.

12.8 Tutor-Marked Assignments

1. Identify two assumptions in the Kinetic theory that can account for observed deviations of real gases from ideal behaviour
2. Calculate the pressure of 0.20 mole oxygen gas placed in a 5.0dm^3 vessel at 25°C. State the effect if any on (i) the pressure (ii) the volume (iii) the number of moles, when the gas is heated.

12.9 References

Osei Yaw Ababio (2002) *New School Chemistry.* Onitsha African-Fep Publishers.

Unit 13

The Gas Laws II Dalton's, Graham's, Avogadro's and Gay Lussac's laws

13.0 Introduction

In unit 12 the ideal or perfect gas is described in the postulates of the kinetic theory. The ideal or perfect gas does not exist. It is only hypothetical.

Real gases deviate from ideal behaviour and do not obey the gas laws perfectly. Imagine a real gas subjected to low temperatures and very high pressures. The gas molecules are compressed into a very small volume and are not very energetic. Intermolecular forces of attraction e.g. Vander waals and dipole-dipole attractions come into play between the gas molecules. The volume of gas molecules will also become significant when compared with the space occupied by the gas.

In this unit you will learn more about gas behavior in Dalton's, Graham's, Avogadro's and Gay Lussac's laws. These laws are also adequately explained by the kinetic theory and like the previous ones, are obeyed perfectly by ideal gases only. Most real gases however obey these laws with very little deviations at ordinary laboratory conditions of temperature and pressure.

13.1 Objectives

At the end of this unit you should be able to:

- Account for deviations of real gases from ideal behaviour.
- State the statement of the laws of Dalton, Graham, Avogadro and Gay Lussac.
- What Avogadro constant is and relate it to the mole.
- Use Gay Lussac's law to predict the volume of a gaseous product in a gas reaction.
- Apply the laws of Dalton, Graham, Avogadro and Gay Lussac in simple calculations.
- Explain why gases diffuse faster than liquids and solids.

13.2 Dalton's Law

13.2.1 Dalton's law of partial pressures

Dalton's law states that the total pressure exerted by a mixture of gases in a container is equal to the sum of the partial pressures of the gases present in the mixture provided no chemical reaction occurs.

The partial pressure of a gas in a mixture is the pressure the gas would exert if it occupies the total volume of the mixture alone. Mathematically for a mixture of three gases A, B, C in a container.

$P_{Total} = P_A + P_B + P_C$ where P_{Total} is the total pressure of the mixture and P_A, P_B, P_C are the partial pressures of A, B and C respectively.

Recall the general gas equation PV = nRT

For gas A, $P_AV = n_A RT$

For gas B, $P_BV = n_B RT$

For gas C, $P_CV = n_C RT$ where n_A, n_B and n_C are the number of moles of A, B and C in the mixture.

$P_{Total}V = (n_A + n_B + n_C) RT$ and

$P_A = x_A P_{Total}$, $P_B = x_B P_{Total}$ and $P_C = x_C P_{Total}$ where x_A, x_B and x_C are the mole fractions of A, B , and C in the mixture. It follows from the above that the partial pressure of a gas in a mixture is equal to the product of total pressure and the mole fraction of that gas in the mixture.

Dalton's law finds application in calculations and determination involving volumes of gases that contain water vapour as the case in the laboratory preparations of gases that are collected over water e.g H_2, O_2 and N_2.

Example

A 1.0dm^3 gas jar contains 0.02 mole oxygen and 0.125 mole nitrogen at 27°C

Calculate,

(a) the partial pressures of oxygen and nitrogen.

(b) the total pressure of the gas mixture R = 0.082 litre atm K^{-1} mol^{-1}

Recall the general gas equation

$$PV = nRT$$

$$P = \frac{n\ RT}{V} \qquad T = 273 + 27 = 300K$$

(a) For O_2 ; $PO_2 = \frac{0.02\ (.082) \times 300}{1.0}$

$= 0.492$ atm

For N_2; $PN_2 = \frac{0.125\ (.082) \times 300}{1}$

$= 3.075$ atm

(b) $P_{Total} = PO_2 + PN_2$

$= 0.492 + 3.075$

$= 3.567$ atm

13.2.2 How the Kinetic theory explained Dalton's Law

When two or more gases mix without a chemical reaction, each gas behaves independently of the other since there are no attractive forces between the molecules. Each gas will exert its own pressure on the container wall. The total pressure of the gas mixture will therefore be the sum of the pressures of the gases in the mixture.

13.3 Graham's Law of Diffusion

Diffusion is a natural phenomenon. It involves the movement of particles through a medium from a region of high particle concentration to a region of lower particles concentration. Diffusion occurs in all the states of matter. By virtue of the very high kinetic energy of gas particles, diffusion is fastest in gases.

Graham's law expresses the relationship between the rate of diffusion of a gas (R) to its vapour density and explains why the law is called Grahams's Law of diffusion. **The law states that at a constant temperature and pressure, the rate of diffusion of a gas is inversely proportional to the square root of its density.**

Mathematically;

$R \alpha \frac{1}{r}$ where R is the rate of diffusion and r the gas density.

From the above relationship the higher the density of the gas the slower it will diffuse. When the rates of diffusion for two gases 1 and 2 are compared or divided the equation becomes

$\frac{R_1}{R_2} = \sqrt{\frac{\rho_2}{\rho_1}}$ where R_1 R_2 are rates and ρ_1 ρ_2 are densities respectively

Graham's law can also be stated in terms of the relative molar masses of the gases

$$\frac{R_1}{R_2} = \sqrt{\frac{M_2}{M_1}}$$

The rate of diffusion is inversely related to the time of diffusion i.e. the higher the rate of diffusion, the shorter the time for a given mass of gas to diffuse. It follows from the above that

$\frac{R_1}{R_2} = \sqrt{\frac{t_1}{t_2}}$ where t_1 t_2 are the the times for the same mass of gases 1, 2 to diffuse under the same conditions.

Assignment

It takes 20 minutes for a given mass of oxygen to diffuse through an opening. How long will it take the same mass of the following gases to diffuse through the same opening under the same conditions of temperature and pressure?

(i) SO_2 (ii) CO_2 (iii) H_2S (iv) NO_2

13.4 Avogadro's Law and its Applications

This law states that equal volumes of all gases at the same temperature and pressure contain the same number of molecules.

Avogadro's law provides information on all number of molecules in a given volume of gas and allows for change over from statements relating volumes of gases to statements relating to the number of molecules or moles.

e.g. $H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)}$

1 vol of $H_{2(g)}$ reacts with 1 volume of $Cl_{2(g)}$ to give 2 volumes of $HCl_{(g)}$. Applying the Avogadro's law this implies that 1 mole of $H_{2(g)}$ reacts with 1 mole of $Cl_{2(g)}$ to give 2 moles of $HCl_{(g)}$. Application of the law as above has allowed for the establishment of formulae for gases. At $0^\circ C$ and 760 mmHg pressure, 22.4dm^3 of any gas contains approximately 6.02×10^{23} molecules i.e. 1 mole of gas molecules. $0^\circ C$ and 760 mmHg pressure are referred to as standard temperature and pressure (S.T.P) respectively and 22.4 dm^3 is the molar volume of gas at S.T.P.

13.5 Gay Lussac's Law of Combining Volumes

This law states that when gases react, they do so in volume, which bear a simple ratio to another and to other products (if gaseous) provided temperature and pressure remain constant.

Applying Avogadro's law, Gay Lussac's law can also be restated as follows:

When gases react they do so in small whole numbers of molecules of reactants to produce small whole numbers of the products provided temperature and pressure remain constant.

e.g.	$N_2(g)$	+	$3H_2(g)$	$\longrightarrow$	$2NH_3(g)$
Gay Lussac:	one volume		three volumes		two volumes
Avogadro:	one molecule		three molecules		two molecules

From the above, a balanced equation that can be written for the reaction provided there is no unidentified products is

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

Assignment

In the contact process for the production of tetraoxosulphate (vi) acid, a step of the production process involves the oxidation of sulphur (iv) oxide gas to sulphur (vi) oxide gas. 2 volumes of the lower oxide reacts with 1 volume of oxygen to give 2 volumes of the higher oxide

(a) Use Gay Lussac's and Avogadro's law and write a balanced chemical equation for the reaction.

(b) Calculate the volume of oxygen gas required at S.T.P. to completely react with 6.4g of sulphur (iv) oxide.

13.6 Conclusion

This unit concludes our discussion on gases and gas behaviour though the theory used in explaining the laws talks of an ideal or a perfect gas. Most real gases obey the gas laws at normal laboratory conditions with very little deviation. Understanding gas behaviour should help us to manage, control and improve our environment for better living. Remember that the earth is surrounded by air which is a mixture of gases.

13.7 Summary

- This unit presented to you four gas laws: Dalton's, Graham's, Avogadro's and Gay-Lussac's.
- Statements of these laws are recalled and interpreted mathematically and applied to numerical problems.
- The concept of standard temperature and pressure and the molar volume are introduced.
- Diffusion in the gas phase is a very rapid process and explains why gases mix.
- Provided there is no chemical reaction, each gas in a mixture behaves independently of the other.

Can you relate the above statement to the air in our environment?

13.8 Tutor-Marked Assignments

1. $50.0cm^3$ of nitrogen gas was collected over water at 17°C and 770 mmHg pressure. Calculate the volume of the dry gas at S.T.P. Saturated vapour pressure of water at 17°C is 14 mmHg.
2. 0.30g of a vapour of a volatile liquid occupies a volume of $0.062dm^3$ at 27°C and 757 mmHg. Calculate the molar mass of the liquid substance.

13.9 References

Bajah, S. T., Teibo, B. O., Onwu, G and Obikwere, A. (2002). *Senior Secondary Chemistry Textbook 1*. Lagos. Longman Publishers.

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Unit 14

Liquids

14.0 Introduction

In unit 11 the general physical features of the solid, liquid and gas state of matter were highlighted. According to the Kinetic theory the liquid particles have lower average Kinetic energy than the gas and movement is a intermediate between those of the solid and the gas. Liquid particles are much wider apart and are held by weaker forces of attraction than in the solid state.

You will recall from the heating curve that, when solid matter is heated it changes to the liquid form at the melting point. The cooling of the vapour (gas) also results in liquid formation, the process is called condensation. The liquid state is therefore an intermediate state between the solid and gas states. Liquids are fluids, like gases. They flow and can be poured from one container to another. Unlike gases they have fixed volumes and are uncompressible.

- Now list some differences and similarities between solids and liquids.

In this unit, the liquid state is revisited with a view to highlight and explain some concepts about liquids and the liquid state.

14.1 Objectives

At the end of this unit you should be able to:

- List some properties of liquids that make them resemble gases.
- Define saturated vapour pressure.
- List factors that affect the saturated vapour pressure of liquids.
- Define boiling and boiling point.
- Define the term 'normal boiling point'.
- Describe a method to determine the boiling point of a liquid.

14.2 The Vapour Pressure of Liquids

You will recall that a liquid sample consists of molecules with varying Kinetic energies. Some particles have very high energies while some have low energies. Now consider a liquid sample placed in a closed container in the laboratory. Some energetic particles that are close to the liquid surface will vaporise and constitute a vapour pressure above the liquid. This pressure builds up until the space above the liquid is saturated with vapour. When this happens a dynamic equilibrium is set up between the liquid particles in the vapour and the liquid phase.

The pressure of the vapour under this equilibrium condition is called the **saturated vapour pressure** (SVP) of the liquid. It is the maximum vapour pressure of the liquid at that temperature. The SVP is not dependent on the liquid volume in the container and it increases with increasing temperature Fig14.1

– Try and explain this increase with temperature using the Kinetic theory.

Liquids with strong intermolecular forces generally have low saturated vapour pressure than those with weak intermolecular forces.

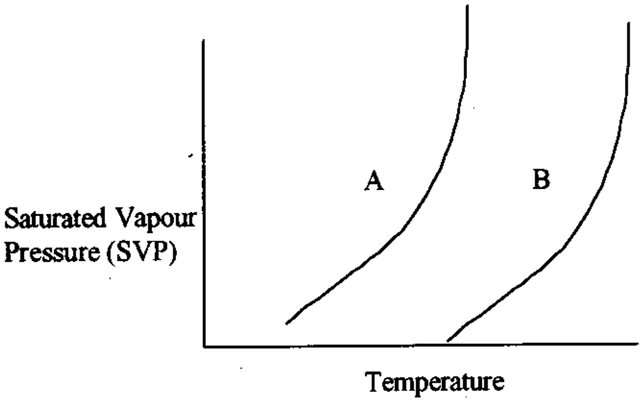


Fig 14.1: Change of saturated vapour pressure with temperature.

14.3 Boiling and Boiling Point

The atmosphere around us exerts a pressure on all objects on the earth surface. The pressure of the atmosphere is called atmospheric pressure. Its value decreases with altitude (height above sea level). This implies that the atmospheric pressure on top of a high mountain is less than at the base.

A heated liquid is also acted upon by the atmospheric pressure but as it is heated, its saturated vapour pressure increases, opposing the downward effect of the atmospheric pressure. At a particular temperature characteristic of the liquid, the saturated vapour pressure becomes equal to the atmospheric pressure. At this temperature vaporisation becomes most rapid and bubbles of vapour form even from the interior of the liquid. This is boiling and the temperature is called boiling point. By definition **the boiling point is the temperature at which the saturated vapour pressure of the liquid equals the prevailing atmospheric pressure.**

The above definition does not allow for a reference point of measurement because the atmospheric pressure is not a constant at every point on the earth's surface. This is because the atmosphere contains many gases including water vapour. It is thus a mixture and depending on the place in the earth and the conditions, its composition is not always the same. The normal (standard) boiling point of a liquid is the temperature at which its saturated vapour pressure equals 760mmHg is called 0 atmosphere pressure. The normal boiling point of water is 100°C but because the atmospheric pressure in Zaria is slightly less than 760mmHg water boils at less than 100°C. Measurements show that water boils at 98°C in Zaria. Do you know at what temperature water boils in your locality?

The saturated vapour pressure of acetone at 20°C is much higher than that of water at the same temperature which liquid will have the higher boiling point, water or acetone? Give reasons for your answer.

14.4 Boiling Point - A Criterion of Purity

Most substances in nature exist in the inpure state. For instance polluted water poses danger to the public therefore water is purified before drinking. In the study of chemistry, purification techniques, are studied. Now recall some of the purification techniques taught in Unit 1.

Even after purification, a test of purity is important so as to ascertain the success of the purification process. For liquid sample, boiling point is used to ascertain the purity of a liquid sample. A pure liquid has a fixed boiling point i.e. the boiling is always at a fixed and constant temperature provided the external pressure is constant.

- What will be the effect of pressure increase on the boiling point of a pure liquid?

Until all the liquid is vaporised at the boiling point the liquid/vapour mixture will maintain a constant temperature.

14.5 Methods of Boiling Point Determination

Several methods have been developed for determining the boiling point of liquids. Here we shall consider two methods. The first is used for liquids with non poisonous vapours while the second, is used for liquids with poisonous vapours.

The easiest method is to insert a thermometer into a boiling liquid in an open glass container. The temperature must be read with the thermometer inside the boiling liquid. This method can be used for liquids whose vapoured are not poisonous or offensive. The distillation method is recommended for liquids with poisonous or offensive vapour.

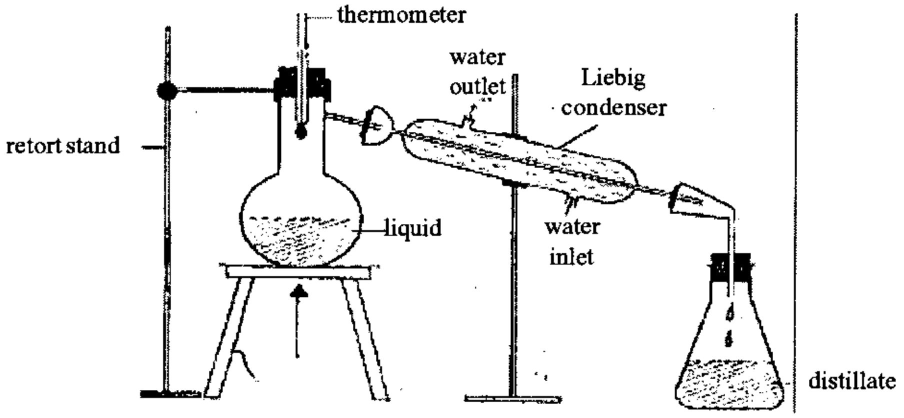


Fig 14.2 Simple distillations

The liquid is placed in the flask labelled A. When the flask is heated the satured vapour pressure of the liquid increases until it becomes equal to the pressure above the liquid. Boiling occurs and the thermometer records the temperature of the liquid/vapour mixture for liquids that are flammable the heating must be done electrically or indirectly using a liquid bath. For liquids with boiling points lower than 100°C, a water or steam bath may be used.

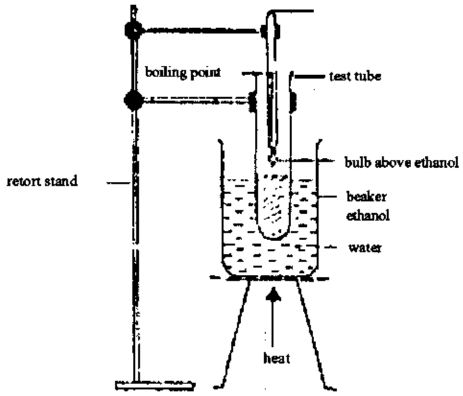


Fig 14.3 Determination of boiling point of alcohol

14.6 Conclusion

In this unit you are presented with some facts about the liquid state of matter. Liquids, like gases, are used daily in domestic and commercial ventures. The saturated, vapour pressure of a liquid expresses its relative volatility. A liquid with very high normal boiling point is less volalite than one of low boiling point. Volatile liquids are stored in **air tight containers** more so when the vapour is poisonous or offensive. e.g. perfumes, petrol, kerosene, mercury and laboratory chemiclas that are liquids.

14.7 Summary

- The liquid state is presented and its intermediate nature between the solid and gas explained. Concepts such as, saturated vapour pressure, boiling and boiling points are explained.
- Normal boiling point is defined. Values of normal boiling points can be used to ascertain the relative volatility of liquids.
- Boiling point is a (criterion) of purity for liquids. A pure liquid boils at a constant and fixed temperature provided the external pressure is constant.

- Methods of boiling point determination are discussed.

14.8 Tutor-Marked Assignments

1. The saturated vapour pressures of four liquids A, B, C, and D are 45, 15, 135 and 75 mm Hg at 25°C respectively.
    (a) Arrange the liquids in the order of increasing boiling points.
    (b) Arrange in the order of increasing volatility. Give reasons for the order of arrangement.

2. Define the terms
    (a) normal boiling point
    (b) differentiate between boiling and boiling point.

14.9 References

Bajah, S.T., Teibo, B.O., Onwu, G. and Obikwere A. (2002).*Senior Secondary Chemistry Textbooks Lagos* Longman Publishers.

Unit 15

Solids

15.0 Introduction

In unit 11, the general features of the solid state are highlighted and explained using the kinetic theory. You will recall that the closeness and low average kinetic energy of solid particles allow for strong attractive forces keeping particles in fixed positions. Solid matter therefore occurs naturally in different shapes and sizes e.g. small stones and big rocks and mountains.

Scientists have also synthesised, modified, shaped and reshaped solid mater e.g. polymetric materials such as resins, fibres, rubbers and plastics are available in various shapes, sizes and colours: plastic buckets, cups etc, textile materials, electrical parts: plugs; cables and sockets, motor vehicle and machinery parts are just few examples. Unlike the gas and liquid matter that require containers for storage and moving them from place to place, solid matter is the easiest to handle and move around. The following are some of the very important use of solids; support, shelter, for movement and for food

In this unit, the focus is on the solid state. Classification, properties and particle arrangement are also discussed. The significance of solid melting point and its use as criterion of purity for the solid are also discussed. In particular the structures of the element, carbon, diamond and graphite forms are fully discussed.

15.1 Objectives

At the end of this unit you should be able to:

- List some use of solid matter.
- Identify the different classes of solids.
- List some properties of the different types of solids.
- Compare and contrast the properties of diamond and graphite.
- Describe a simple experiment to determine the melting point of a solid.
- Recall that the melting point is a criterion of purity.

15.2 Solid Classification

Solids are classified as crystalline or amorphous by virtue of the order in particle arrangement.

Crystalline solids are built from simple structural units which repeat themselves in three dimensions to give the solid its characteristic geometric form. Most metal and ionic solids are **crystalline** in nature.

Other solids such as glass, rubber and plastics do not have definite geometrical forms and are called **amorphous**. The regular and repeated arrangement of particles in the crystalline form a pattern called the crystal lattice.

15.3 Solid Properties

Solids are generally characterised by hardness/firmness and high mechanical strength. The mechanical strength of any solid material is determined by the type of bonds holding the particles in position in the solid structure. The type of force in turn depends on the chemical nature of the units that occupy the fixed position in the lattice. Solids are grouped into four classes based on the nature of the **intermolecular forces** between the particles of the solid matter.

15.3.1 The molecular solid

The **lattice points** in molecular solids are occupied by molecules which do not carry any charge. The forces holding the molecules together are of two types, the dipole-dipole interaction for polar molecules and Van der waals forces which are the non-polar molecules. You will recall that these forces i.e. the dipole-dipole and Van der Waals forces are relatively weak forces. This is why molecular solids are usually soft and of very low melting points. The lack of electrical charge in the structure makes them non conductors. They are used mainly as insulators. Examples of compounds that form molecular solids are ammonia, ice water, candle wax and carbon(iv) oxide. Many molecular solids are liquids or gases at normal laboratory temperatures and pressures. Water for instance is a liquid and carbon(iv) oxide is a gas at normal laboratory temperature.

15.3.2 The metallic solid

The lattice points in the metallic solid is occupied by the positive core of the metallic atom surrounded by an electron cloud. The force of attraction here is electrostatic between the positive metal cores and the electron cloud. This electrostatic force is strong and is responsible for the compact structure of metals and their very high boiling and melting points. The **mobility** of the electron cloud under the influence of heat and electricity accounts for the high thermal and electrical conductivities of metals. Examples of metallic solids are copper, iron, lead, aluminium and zinc.

Can you now explain the following?

- An aluminium spoon when placed in hot water soon feels hot to the hand.
- Exposed electrical cables when touched or stepped on can lead to shock or death.

Apart from the high thermal and electrical conductivities, metallic solids are malleable and ductile i.e. can be beaten into shapes and drawn into thin wires e.g. copper wires and aluminium doors.

15.3.3 The ionic solid

The units occupying the lattice points in ionic solids are positive and negative ions. There is very strong attraction between the positive and negative ions. In the solid structure each ion is surrounded by as many ions as possible of the opposite charge leading to a giant assembly of ions held together in a rigid structure. Ionic solids are characterised by the following properties

(i) High melting and boiling points.

(ii) They are non conductors of electricity in the solid state but conduct when molten or in solution.

(iii) Because the energy to separate the ions is relatively high, ionic solids are hard and brittle. Examples of ionic solids are NaCl, KCl, KNO_3 and $CuSO_4$.

- Why do ionic solids conduct electricity in the molten state or in solution and not in the solid form?

15.3.4 The covalent solid

The lattice points in covalent solids are occupied by atoms linked together by a continuous system of covalent bonds. The shared electrons between the atoms in the lattice result in strong bonding between the atomic nuclei. Examples of covalent solids are diamond, graphite and quartz (SiO_2). When all the valence electrons are involved in bonding as in diamond and quartz, the solid will not conduct electricity. In some arrangement where all valence electrons are not used in bonding as in graphite, electrical conductivity is possible because the free electrons move under the influence of applied electrical potential.

15.4 The Structure of Diamond and Graphite

You will recall that diamond and graphite are allotropes of carbon

- What are allotropes?

Both of them are also covalent solids but while diamond is hard, have very high density and melting point, graphite is soft, less dense and have a much lower melting point. In both diamond and graphite, the lattice points are occupied by carbon atoms. In diamond, carbon atoms are tetrachedrally bonded using Sp^3 hybridised orbitals. All the four valence electrons of carbon are used in bonding resulting in a rigid three dimensional network. This accounts for the very hard nature of diamond. Diamond is the hardest substance known. It cannot be cut by any other substance, hence it is used in cutting glass and metals.

In the graphite structure however, each carbon atom is linked to three others using Sp^2 hybridised orbitals. The carbon atoms are arranged in layers one above the other. The layers are held together by weak van der waal forces. Graphite has a relatively high melting point and it is less dense than diamond. The presence of mobile electrons in the crystal lattice makes graphite a good conductor of electricity.

Recall that carbon has four valence electrons and only three are used in bonding in graphite but all the four electrons are used in diamond. Graphite is used as an inert electrode in electrolysis. The layered structure of graphite allows one layer to slide over another easily acounting for the lubricating property of graphite. Unlike oil, it is non-sticky and is usually used on bicycle chains and for bearings of some motor cars.

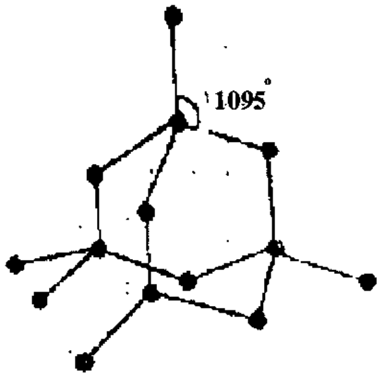


Fig. 15.1: Structure of diamond

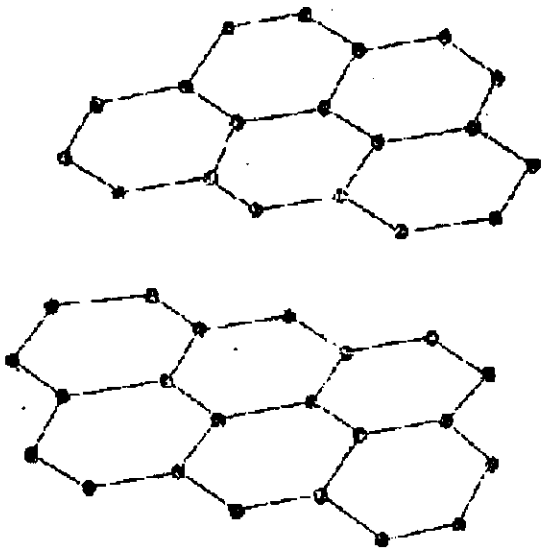


Fig. 15.2: Hexagonal rings in graphite

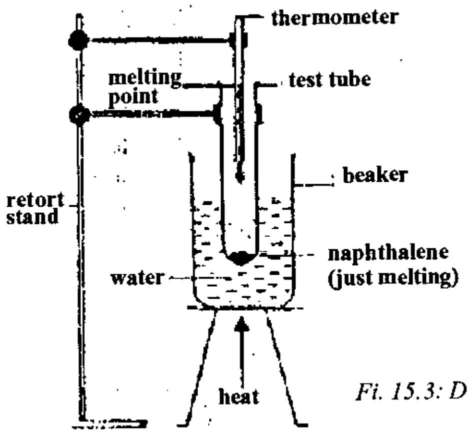
Some properties of diamond and graphite are summarised in the table 15.1

Property	Diamond	Graphite
1. Appearance	Colourless, transparent solid, sparks when cut	Black opaque with metallic lustre
2. Crystalline structure	Three dimensional network	Two dimensional network
3. Density	Very dense	Less dense
4. Hardness	Hardest natural substance known	Soft
5. Electrical conductivity	Non conductor	Good conductor
6. Chemical activity	Inert unreactive	More reactive
7. Uses	(i) used as a precious jewel	1. dry lubricant
	(ii) drilling rocks and cutting glass	2. electrodes in electrolysis.
	(iii) to sharpen tools	3. used in 'lead' pencil
	(iv) pivot supports in precision instruments	4. black pigment in paints
	(v) dies for drawing wires	5. neutron moderator in atomic reactors

15.5 Melting and Melting Point

Heating of solid matter increases the average kinetic energy of the particles. You will recall that at a particular temperature characteristic of the solid the particles will acquire sufficient energy and overcome the attractive forces holding them in fixed positions. At this temperature the solid structure collapses and a liquid is formed. This is the melting point. As earlier explained in unit 11, melting of a pure solid sample occurs at a constant temperature and is a test of purity.

The melting point of a solid sample is determined by the capillary tube method. A small amount of the solid sample is put in a glass capillary tube. The capillary tube is attached to a thermometer using a rubber band. The capillary tube is heated in a transparent liquid bath and the temperature at which the solid starts melting is noted. For a pure solid sample, this temperature remains constant until all solid is melted.



Fi. 15.3: Determination of melting point of naphthalene

Electrically operated melting point apparatus can also be used but the equipment is fairly expensive. The apparatus is fitted with a thermometer. It also has apartments for placing the capillary tube. After the capillary tube containing the solid sample is put into the apparatus, the apparatus is switched on. As the solid heats up, the process is monitored through a magnifying glass in front of the apparatus until melting occurs.

15.6 Conclusion

In this unit you have learnt that the physical behaviour of the solid is not only determined by the particle arrangement but also on the nature of the particles that occupy the lattice points which in turn determines the type and strength of the intermolecular forces holding the particles in the solid. Solids with weak intermolecular forces have low melting points while those with strong cohesive forces have fairly high melting points.

Solids are used for a variety of applications and the choice of a solid for a particular application must be only after its physical and chemical behaviour have been properly investigated. Where a solid must be used pure, the melting point determination offers a way of ascertaining its purity.

15.7 Summary

In this unit, the solid state is presented. The important roles of solids in our daily life were highlighted. Solids are classified according to the degree of order in the particle arrangement and the type of particles that occupy the lattice points. The ionic, covalent, metallic and molecular solids are discussed and their physical properties explained in relation to the nature of the particles in the solid structure. The melting point is again presented and its use as a criterion of purity emphasised.

Graphite and diamond are discussed, their structures and properties compared and contrasted. Their uses differ and these uses are presented as part of the study.

15.8 Tutor-Marked Assignments

1. Explain the following observations
   (a) Chlorine (Cl_2) is a gas while bromine is a liquid and iodine is a solid at normal laboratory temperatures and pressures.
   (b) Diamond is hard but graphite is soft.
2. List some uses of graphite and diamond.

15.9 References

Osei Yaw Ababio (2002) *New School Chemistry*. Onitsha. Africana-FEP Publishers.

Volume Two

Physical and Inorganic Chemistry

Unit 1

Energy and Energy Changes in Chemical and Physical Processes (1)

1.0 Introduction

Energy is the capacity or ability to do work. Energy appears in different forms, some of which are kinetic, potential, chemical, (heat), electrical and light. The conversion of energy from one form to another occurs all the time in natural and man-made activities. Some examples of energy conversions are:

- Food (a form of chemical energy) is converted to heat when digested. You will recall that nutritionists talk of caloric value of classes of food.
- Fuel (petrol, diesel) also a form of chemical energy is converted to heat when it burns and then to mechanical energy for motion.
- A stone dropped from a height possesses potential energy which is converted gradually to kinetic as it falls and finally to heat when it hits the ground. In all energy conversions, energy is conserved. **The law of conversion of energy states that energy is neither created nor destroyed in its transformation.**

Every matter has its own characteristic energy when energy is converted from one form to another, whether in a physical or chemical process, an energy will accompany the process.

1.1. Objectives

In this unit, let us consider energy changes in chemical and physical processes and their relevance to energy source for industrial and domestic use.

1.2 Energy Changes in Chemical Processes

1.2.1 Heat content and heat of reaction

The energy a chemical substance possesses as a result of its structure and physical state is called its heat content or enthalpy. The change in energy that accompanies a chemical reaction is called the heat of reaction. In energy calculation, enthalpy and enthalpy change are given the symbols H and DH respectively.

The absolute value of the heat content cannot be measured for a chemical substance but the heat or enthalpy change can be measured or calculated.

For a chemical reaction

DH reaction = $H_p - H_R$ where H_p and H_R are the enthalpies of the product and reactant respectively. For reactions involving many reactants and products the equation becomes

$\Delta H_{reaction} = \Sigma H_p = \Sigma H_R$ where Σ means summation

1.2.2 Exothermic and endothermic reactions

A chemical reaction is either accompanied by evolution or absorption of heat. Evidence of heat evolution is an increase in temperature. The reaction vessel is warm or hot to the hand. This is the exothermic reaction. For the endothermic reaction the temperature decreases and the reaction vessel feels cold to the hand because of heat absorption from the surroundings.

Recall the equations

$$\Delta H_{reaction} = H_p - H_R \text{ and}$$

$$\Delta H_{reaction} = \Sigma H_p - \Sigma H_R$$

When the total heat content of the products is less than that of the reactants the enthalpy change (ΔH) is less than zero i.e. (ΔH) is –ve. The difference in the heat contents is given off to the surrounding. An exothermic reaction is a reaction in which heat is given off and ΔH is –ve. For the endothermic reaction ΔH is + ve i.e. $H_p > H_R$ and heat is absorbed from the surroundings. An endothermic reaction is a reaction in which heat is absorbed and ΔH is + ve

1.2.3 Energy level diagrams

The energy change in a chemical or physical process can be represented on a plot of potential energy change against time of reaction. This type of diagram is called an energy level diagram. Fig 1.1

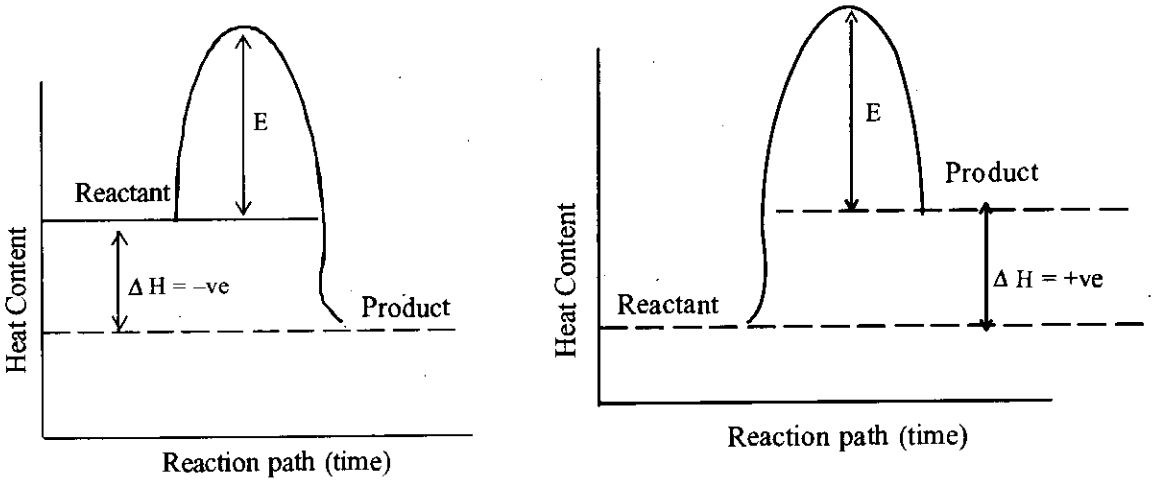


Fig 1.1 (a) Exothermic reaction (b) Endothermic reaction

The energy change marked E on the diagrams is known as the activation energy. The activation energy is the minimum energy needed by the reactant before reaction can occur. All reactions whether exothermic or endothermic require the activation energy.

When reactions take place between molecules or atoms, it usually involves the breaking of old bonds between atoms or molecules and the formation of new ones. These processes are not consecutive but occur simultaneously, at which point an activated complex is said to be formed. The activated complex is a temporary phase of the reactants whose duration is extremely brief.

1.2.4 The standard state

Enthalpy and enthalpy change depend on the temperature and pressure of the reaction. The reference point of enthalpy and enthalpy calculations is 25°C (298K) and 760 mm Hg pressure (1 atmosphere) for gas reactions and a concentration of 1.0 moldm^{-3} for reactions in solution. The heat change measured under the conditions stated above is called the standard heat (enthalpy) change. It is given the symbol $\Delta H°$. The enthalpy at standard state is given the symbol $H°$. The standard enthalpy change of a reaction is the amount of heat evolved or absorbed when a chemical reaction occurs between molar quantities of the reactant as represented in the equation of the reaction under standard conditions. It is given the symbol $\Delta H°_{reaction}$.

The standard enthalpy of a compound is its heat content at standard state. The standard enthalpy of pure elements in their normal state is zero. The latter statement implies that for $H_{2(g)}$, Na(s), C(s), etc H^0 is 0.

1.2.5 Thermochemical equations

The heat contents of reactants and products of a reaction depends not only on their chemical structures but also on their physical states. Earlier in this unit, we learnt that temperature and pressure affect the enthalpy and enthalpy change of reactions, hence the standard state is defined as a reference point. The following is a list of factors that can affect the enthalpy of a compound.

(i) Amount of reactants and products: The heat of a reaction is proportional to the amount of reactants used up or products formed. The enthalpy change (ΔH) is normally given per mole of a reactant or a product.

(ii) A change of temperature or pressure for gases: It is therefore very necessary to state the temperature and pressure of measurement if different from the standard state.

(iii) The physical state of the reactants and products: It is important to state the physical state of the reactants and products. The physical state is indicated as subscript after the chemical symbols of reactants and products as (g) for gas (*l*) for liquid and (s) for solid. For a salt or ion in solution the symbol ((aq) is used.

(iv) The concentration of the salt or ions in solution: Because of the stated factors that can affect the enthalpy of compounds, it is required that a chemical reaction must be represented correctly in energy calculations.

The chemical reaction equation which gives the physical states of the reactants and products as well as the heat change that accompanies the reaction is called the **thermochemical equation** for the reaction

e.g. $C_{(s)} + O_{2(g)} \longrightarrow CO_2 \; \Delta H = -393 \text{kJmol}^{-1}$

$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O(l) \; \Delta H = -285.6 \text{kJmol}^{-1}$

$NaCl_{(aq)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)} \; \Delta H = -13.6 \text{kJmol}^{-1}$

1.3 Types of Heat of Reaction

Reactions are of many types. In this section, the heat change will be defined and named accordingly for formation, combustion, neutralisation and solution. The standard heat is defined in each case.

1.3.1 Standard heat (enthalpy) of formation ΔH^0_f

The standard enthalpy of formation of a compound is the heat evolved or absorbed when one mole of the compound is formed from its elements in their normal state under standard conditions.

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$$
$$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(g)}$$

Can you explain the following about the above reactions?

(i) The heat change differs for the two reactions.

(ii) The heat evolved is less for the second reaction.

For a given chemical compound there is only one chemical equation that fits the above definition of heat of

formation. Now write the chemical equations for the formation of $CO_{(g)}$ and Ca $CO_{3(s)}$.

Heat of formation is useful in the calculation of heat of reaction.

$$\Delta H^0_{reaction} = \Sigma \Delta H^0_f \text{ of products} - \Sigma \Delta H^0_f \text{ of reactants}$$

Example

Calculate the heat change (ΔH^0) for the reaction

$C_2H_{2(g)} + 2H_{2(g)} \longrightarrow C_2H_{6(g)}$ given that ΔH^0_f values are -1256kJ and –84.7 kJ for $C_2H_{2(g)}$ and $C_2H_{6(g)}$ respectively.

1.3.2 Standard heat (enthalpy) of combustion ΔH°C

This is the heat evolved when 1 mole of the compound is completely burnt in oxygen under standard conditions. Note here that combustion reactions are exothermic reactions. Combustion reactions are very important since they form the main source of energy for industrial and domestic purposes. Even the food we eat supply us energy. It is burnt off during digestion. Heat of combustion is useful in the calculation of heat of formation and reaction

$$\Delta H^0_f = \Sigma \Delta H^0_c \text{ of reactants} \longrightarrow \Sigma \Delta H^0_c \text{ of products}$$

1.3.3 Standard heat (enthalpy) of Neutralisation, ΔH^0_{neu}

This is the amount of heat evolved when 1 mole of H^+ from an acid reacts with 1 mole OH from an alkali to form a mole of water under standard conditions.

$$\Delta H^0_f = \Sigma \Delta H^0_{neu} \text{ of reactants} \longrightarrow \Sigma H^0_{neu} \text{ Products}$$

so,

$$\Delta H^0_{reaction} = \Sigma \Delta H^0_{neu} \text{ of reactants} \longrightarrow \Sigma \Delta H^0_{neu} \text{ of Products}$$

Neutralisation is the reaction of an acid with an alkali to give salt and water only. Strong acids and bases are strong electrolytes. They ionise completely in solution. For such acids and bases, neutralisation is the reaction of H^+ and OH^- to give water

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

This is why the heat of neutralisation is essentially constant for strong acids and bases.

For example

$$HNO_{3(aq)} + KOH_{(aq)} \longrightarrow KNO_{3(aq)} + H_2O_{(l)}$$
$$\Delta H = -57.3 \text{ kJmol}^{-1}$$

$$HCl_{(aq)} + Na\,OH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$$
$$\Delta H = -57.1 \text{ kJmol}^{-1}$$

Weak acids and bases are weak electrolytes and are only partially dissociated in solution. Part of the energy of neutralisation is expended to effect complete dissociation. This is why the heat of neutralisation for weak acid or weak base reaction is lower than for the strong acid and base combination.

e.g. $NH_4OH_{(aq)} + HCl_{(aq)} \longrightarrow NH_4Cl_{(aq)} + H_2O_{(l)}$

$\Delta H = -51.5 \text{ kJ mol}^{-1}$

1.3.4 Standard heat (enthalpy) of solution. ΔH^0_{soln}

Dissolution is a physical process in which a solute mixes homogeneously with a solvent. e.g. sugar solution or brine (solution of common salt in water).

The separation into solute and solvent is by physical methods. For the recovery of the solute, evaporation is used and for solvent recovery simple distillation is used.

For an ionic solid dissolving in water, a two step process occurs.

1. Lattice breaking which resulting in the formation of $Na^+_{(g)}$ and $Cl^-_{(g)}$. This process is an endothermic process. The energy required is the lattice energy ($\Delta H^0_{lattice}$) ΔH is + ve.
2. The free ions are attracted to water, molecules and they become hydrated. This process releases energy. It is exothermic and ΔH –ve.

These two steps describe the dissolution process and the resultant heat of solution depends on the relative magnitude of the lattice energy and hydration energy.

The process is represented as in the equations.

$$\begin{tikzcd}
NaCl_{(s)} \arrow[r, "\text{lattice energy}", "\Delta H_{lattice}"'] & Na^+_{(g)} + Cl^-_{(g)} \arrow[d, "\begin{array}{l}\text{Heat of hydration}\\ +H_2O\\ \Delta H_{hydration}\end{array}"] \\
 & Na^+_{(aq)} + Cl^-_{(aq)}
\end{tikzcd}$$

$$\Delta H_{soln} = \Delta H_{lattice} + \Delta H_{hydration}$$

The dissolution process will release heat energy (exothermic) if $\Delta H_{hydration} > \Delta H_{lattice}$ otherwise the dissolution process will be an endothermic process.

The standard heat of solution is the heat (enthalpy) evolved or absorbed when one mole of a substance is dissolved in so much water that dilution results in no change in heat. For a mole of the solid as stated in the definition, the lattice energy $\Delta H_{lattice}$ is a constant but the hydration energy increases with dilution. Diluting a concentrated solution will therefore lead to further heat change called the heat of solution. At very high dilution when the ions have been completely hydrated, further dilution will not lead to heat change because both $\Delta H_{lattice}$ and $\Delta H_{hydration}$ are constant

1.3.5 Enthalpy of change of state

There are three main physical transformations that can occur for a given substance. These are the solid —> liquid, liquid —> gas and solid —> gas called melting, vaporisation and sublimation respectively. The molar heat of fusion (ΔH_{fusion}) is the heat energy required to convert a mole of the solid to the liquid at its melting point. The molar heat of vaporisation (ΔH_{vap}) is the heat energy required to convert a mole of the liquid to the vapour at boiling point. The molar heat of sublimation ΔH_{sub} is the heat energy required to convert a mole of the solid to gas at the same temperature.

These heats are represented as shown

$$\begin{tikzcd}
\text{Solid} \arrow[r, "\text{melting}", "\Delta H_{fusion}"'] \arrow[dr, "\text{Sublimation}", "\Delta H_{sub}"'] & \text{liquid} \arrow[d, "\begin{array}{l}\Delta H_{vap}\\ \text{vaporisation}\end{array}"] \\
 & \text{gas}
\end{tikzcd}$$

$$\Delta H_{sub} = \Delta H_{fusion} + \Delta H_{vaporisation}$$

1.4 Determination of the Heat of Reaction

The measurement of absolute enthalpies of compounds is not possible but enthalpy changes can be measured in the laboratory. The measurement of heat changes that accompany reactions is called calorimetry and calorimetry experiments are done in specially insulated containers called calorimeters.

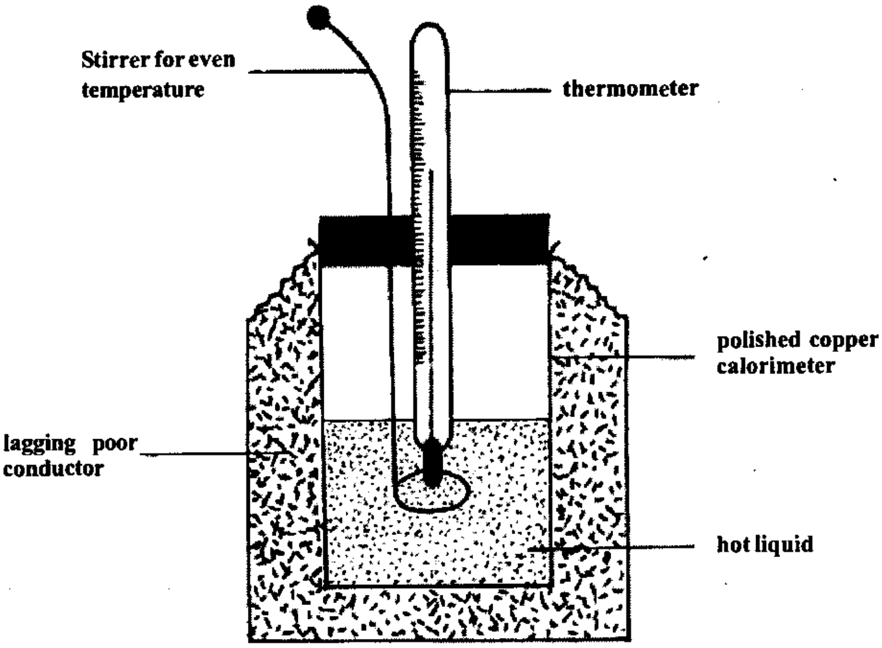


Fig 1.2: Calorimeters

The words calorimetry and calorimeter come from the word calorie. A calorie is the amount of heat energy required to raise the temperature of one gram of water through 1^0 centigrade. The SI unit of heat is the joules (J) and one calorie is equivalent to 4.2 joules. Calorimeters are of many types. The bomb calorimeter is a fairly sensitive calorimeter used in the measurement of heat of combustion.

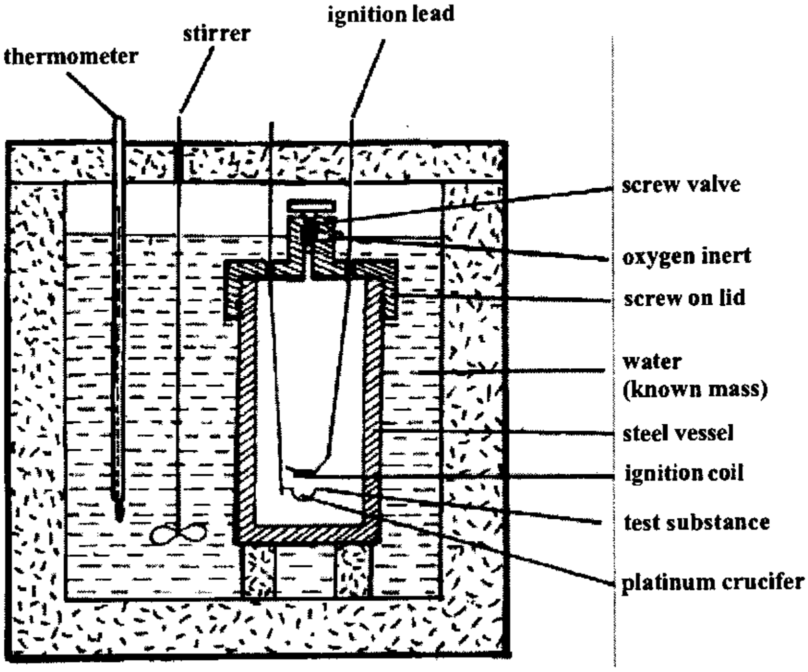


Fig 1.3 A bomb calorimeter

Simple and less sensitive calorimeters can be adapted for the measurement of small heat changes such as in neutralisation reactions and solutions. These adapted calorimeters must be well insulated and measurement must be as fast as possible to reduce errors. Fig 1.4 shows an adapted calorimeter for the determination of heat of neutralisation.

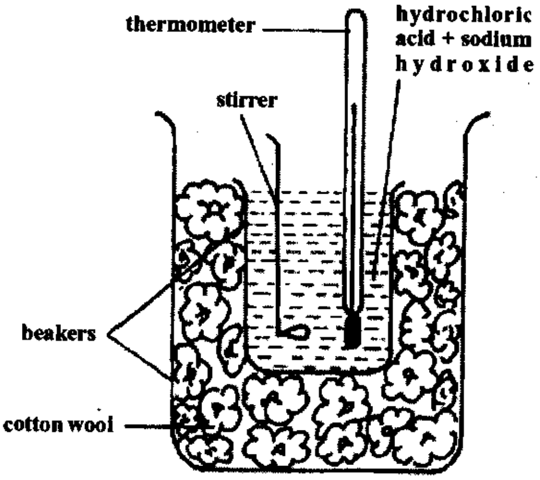


Fig 1.4: Determination of the heat of neutralization

In all calorimetry experiments the major measurement is the temperature change that accompanies the reaction of a known amount of the reactants in a calorimeter of known heat capacity (Heat capacity is the heat energy required to raise the temperature through 1°C). The heat change (enthalpy) is calculated by equating the heat energy gained by the calorimeter and its contents to the heat given off or absorbed in the reaction. Many calorimetry experiments are done at temperature and pressures different from the standard state.

The heat of many reactions cannot be measured directly because of experimental difficulties. The nature of the reactants, the rate of the reaction and the magnitude of the heat are some of these difficulties e.g. some reactions are explosive in nature because of the large amount of heat that accompanies them while some are too slow for any accurate measurements to be possible.

$$Na_{(s)} + H_2O_{(l)} \longrightarrow NaOH_{(aq)} + H_{2(g)}$$

This reaction is explosive because of the large heat of reaction. Where the heats cannot be measured, they can be calculated from the heats of formation or the heats of combustion of the reactants and products.

Recall

$$\Delta H_{\text{Reaction}} = \Sigma \Delta H_f \text{product} - \Sigma \Delta H_f \text{reactant}$$

Or

$$\Delta H_{\text{reaction}} = \Sigma \Delta H_c \text{ of reactants} - \Sigma \Delta H_c \text{ of products.}$$

Values of heat of formation and combustion for compounds are available in literature.

1.5 Conclusion

Every change, whether physical or chemical is accompanied by energy change. The amount of energy change depends on the amount of substance, the chemical nature as well as the physical state of the substances involved and the temperature and pressure if gases are involved. The standard state is described as 25°C, 760mm Hg and 1.0 moldm^{-3} for solution.

1.6 Summary

- Heat is a form of energy.
- The heat content of a body is called its enthalpy while the heat change that accompanies a process is called the enthalpy change.

- The different types of heat are defined and explained.
- Thermochemical equations are very important for heat calculation and the endothermic and exothermic reactions are defined and illustrated.

1.7 Tutor-Marked Assignments

1. Define the following: enthalpy, enthalpy change, exothermic reaction, endothermic reaction and heat of formation.
2. (a) Calculate the heat change that accompanies the given reactions at standard state

   $CH_{4(g)} + Cl_{2(g)} \longrightarrow CH_3Cl_{(g)} + HCl_{(g)}$

   (b) Calculate the heat change for the reverse reaction

   $CH_3Cl_{(g)} + HCl_{(g)} \longrightarrow CH_{4(g)} + Cl_{2(g)}$

   ΔH^0_f of $CH_{4(g)}$ $CH_3Cl_{(g)}$ and $HCl_{(g)}$ are

   –74.9, –83.7 and –9.20 $kJmol^{-1}$ respectively.

(c) Illustrate the reaction in (a) on an energy level diagram.

1.8 References

Osei Yaw Ababio (2002). *New School Chemistry*. Onitsha. Africana-FEP publishers.

Units 2

Changes in Chemical and Physical Processes (II). The Free Energy and Spontaneous Reactions

2.0 Introduction

The word spontaneous means voluntary or occurring without external influence or assistance. A spontaneous reaction can therefore be defined as a reaction that occurs without external aid or incitement. For example sodium metal reacts explosively with water. This is why sodium metal is kept in oil to avoid contact with water. Calcium carbide commonly called carbide by welders is kept away from water. This is also to stop the spontaneous reaction of carbide with water.

In unit 1 you learnt the different forms of energy and the energy changes in physical and chemical processes. The concept of heat content (enthalpy) was introduced and chemical changes were classified as exothermic or endothermic processes depending on whether heat evolution or absorption accompanied the reactions.

Now you will look at some examples of process that have been studied.

$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)} \quad \Delta H = -285.6\ \text{kJmol}^{-1}$$

$$\Delta H = -285.6\ \text{kJ mol}^{-1}$$

$$NH_4NO_{3(s)} + H_2O_{(l)} \longrightarrow NH_4^+{}_{(aq)} + NO_3^-{}_{(aq)}$$

$$\Delta H = 26.5\ \text{kJ mol}^{-1}$$

The first process, the reaction of hydrogen with oxygen is an exothermic reaction but yet the reaction of hydrogen with oxygen is not a spontaneous reaction. Recall that for a reaction to occur in a jar of hydrogen gas, a spark must be introduced i.e reaction is aided to occur. Another example is the reaction of nitrogen and oxygen which is also an exothermic reaction. These two gases N_2 and O_2 are present in the air and no reaction occurs. The reaction of nitrogen and oxygen will not occur at ordinary temperature.

The second process, the dissolution of ammonium trioxonitrate (v) is an endothermic reaction. When the solid dissolves, the beaker cools down appreciably. This process, though endothermic occurs spontaneously. Ice melts when removed from the freezer compartment and placed outside spontaneously but it is an endothermic process. The above examples and many others suggest that enthalpy data alone are not sufficient to predict whether a change will be spontaneous or not.

In this unit a new concept is introduced for reactions which when considered together with the enthalpy change will enable us predict more accurately the direction of a spontaneous process.

2.1 Objectives

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

- Define entropy and entropy change.
- Calculate entropy change from suitable data.
- Predict qualitatively the entropy changes for reactions and processes.
- Explain the concept of free energy.
- Predict the direction of a spontaneous change from values of entropy and enthalpy change and temperature.
- Recall the equation $\Delta G = \Delta H - T\Delta S$

2.2 Entropy and Entropy Change

Entropy is a measure of the disorder of a system. The greater the disorder the greater the entropy. The entropy change is the measure of the change in disorder that accompanies a chemical of physical process. The entropy and entropy change are given the symbols S and ΔS respectively. Similar to enthalpy.

$\Delta S_{\text{reaction}} = S_p - S_R$ and for many reactants and products

$\Delta S_{\text{reaction}} = \Sigma S_p - \Sigma S_R$

For a process that is accompanied by greater disorder the entropy increases and ΔS is positive. When a process is accompanied by less disorder (more order) the entropy decreases and ΔS is negative. The change in entropy is a driving force behind reactions and processes. It is a measure of the capacity for a spontaneous change. Entropy is measured in units of energy. The SI unit is the joules.

Entropy is affected by many factors

(i) *The physical state:* The solid state with its ordered structure has the least entropy while the gas state has the highest. The liquid is intermediate.

$$\text{Ice} \longrightarrow \text{water} \qquad \Delta S + \text{ve}$$
$$\text{Water} \longrightarrow \text{Steam} \qquad \Delta S + \text{ve}$$

Solid – liquid, liquid – gas and solid – vapour transitions are accompanied by increased entropy.

(ii) *Temperature:* The higher the temperature, the higher the average kinetic energy of the particles, the more the random motion and collisions leading to greater disorder. Entropy increases with increasing temperature. For a gas sample when there is a change of temperature and pressure the entropy change depends on the volume change. Entropy increases with increasing volume of a gas sample.

(iii) *Change in the number of gas molecules:* There is more random motion in a gas than in a liquid or solid. The more the number of gas molecules resulting from a reaction the greater the entropy of such a reaction.

e.g.

$$N_2O_{4(g)} \longrightarrow 2NO_{2(g)} \quad \Delta S + \text{ve}$$
$$CaCO_{3(s)} \longrightarrow CaO + CO_{2(g)}$$
$$\Delta S + \text{ve}$$
$$H_2 + \tfrac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)} \quad \Delta S - \text{ve}$$
$$Na_{(s)} + H_2O_{(l)} \longrightarrow NaOH_{(aq)} + H_{2(g)} \quad \Delta S + \text{ve}$$

(iv) Mixing: There is more disorder in a mixture of samples than in each of the pure samples. When a solid dissolves in a liquid entropy increases (ΔS + ve). When two gases mix, there is also increase in entropy.

2.3 Free Energy and the Free Energy Change

Free energy is defined as the energy that is available to do work. Free energy is related to the enthalpy and entropy.

$G = H - TS$ where G is the free energy and H, S and T are enthalpy, entropy and the absolute temperature for a change, physical or chemical at a constant temperature.

$\Delta G = \Delta H - T\Delta S$. For the standard state

$\Delta G^o = \Delta H^o - T\Delta S^o$ where $T = 298K$

The free energy determines whether a reaction will occur spontaneously or not. For a spontaneous change ΔG is less than zero i.e ΔG – ve. When ΔG is greater than zero (ΔG +ve) the process is not spontaneous. Such reactions will occur by supplying a driving force e.g. by heating. At equilibrium $\Delta G = 0$

Note the $T\Delta S$ term which is a measure of the total entropy change at the temperature of the reaction.

2.4. Applications of the Free Energy Equation

Five cases will be considered.

2.4.1 An exothermic reaction accompanied by an increase in entropy.

For the above type of reaction

ΔH is – ve and ΔS is + ve

e.g. $2Na_{(s)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)}$

$CaC_{2(g)} + H_2O_{(l)} \longrightarrow CaO_{(s)} + C_2H_{2(g)}$.

The reactions above are exothermic reactions and are accompanied by greater disorder. The free energy change for such reactions at any temperature is less then zero i.e even at absolute zero temperature ΔG is still less than zero. The reactions are always spontaneous. The only way to prevent such reactions would be to keep the reactants apart. This is why carbide and sodium are kept away from water.

2.4.2 An endothermic reaction accompanied by a decrease in entropy

Here ΔH is + ve and ΔS is – ve. It follows that ΔG must be positive. The reaction is therefore unlikely to occur. The reverse of the reactions will serve as

$NaOH_{(aq)} + H_{2(g)} \longrightarrow Na_{(s)} + 2H_2O_{(l)}$

$CaO(s) + C_2H_{2(g)} \longrightarrow CaC_{2(s)} + H_2O_{(l)}$

For the above reactions even at absolute zero, ΔG is greater than zero. They are not spontaneous.

2.4.3 An exothermic reaction accompanied by a decrease in entropy

For the above group of reactions.

ΔH is – ve and Δs is – ve

water $\longrightarrow$ Ice ΔH–ve

steam $\longrightarrow$ water ΔH – ve

In both processes ΔH is – ve and ΔS is –ve. The disorder decreases as a result of the processes. Because ΔS is –ve.

– $T\Delta S$ is + ve and ΔH is – ve. For such processes there is an equilibrium temperature when $\Delta G = 0$. This is case when $T\Delta S = \Delta H$

$T_{eq} = \frac{\Delta H}{\Delta S}$ T_{eq} – equilibrium temperature

Above T_{eq}, ΔG is + ve and the processes are non spontaneous. Below T_{eq} the ΔG is – ve and the processes are spontaneous. The tendency for a spontaneous process decreases with increasing temperature for the process. The equilibrium temperatures are the melting and boiling points respectively.

2.4.4. An endothermic reaction accompanied by an increase in entropy

The ΔH is + ve and ΔS is + ve

$$NH_4NO_{3\,(s)} + H_2O_{(l)} \longrightarrow NH_4^+{}_{(aq)} + NO_3^-{}_{(aq)}$$

Ice $\longrightarrow$ water

Because $\Delta S > O$

$- T\Delta S < O$ but ΔH is +ve. There is an equilibrium temperature (T_{eq}) as in the last example.

$$T_{(eq)} = \frac{\Delta H}{\Delta S}$$

Above T_{eq} ΔG is –ve and the reactions are spontaneous. Below $T_{(eq)}$ the ΔG is +ve and the reactions are non-spontaneous reaction. The tendency for a spontaneous reaction increases with increase in temperature. Solubility of ammonium trioxonitrate (v) increases with increasing temperature. For this reaction to have occurred spontaneous at laboratory temperature suggests that the equilibrium temperature is below the laboratory temperature. In the case of the ice → water reaction the equilibrium temperature is the melting point which is about O°C. Because the laboratory temperature is above O°C, the melting process is spontaneous and occurs as soon as the ice is removed from the freezer and placed outside in the laboratory.

2.4.5 A reaction in which the enthalpy change is zero

For some reactions the enthalpy is very negligible. The driving force for such reactions is the entropy change alone. When the reaction is accompanied by an increase in entropy the reaction is spontaneous.

2.5. Conclusion

Enthalpy factor alone cannot be used to predict the spontaneity of a physical or chemical process. The entropy also contributes to the driving force of reactions. The free energy is a better and more reliable predictor of spontaneity of reactions. The free energy gives us the net energy that is available to do work. A knowledge of the free energy change of a reaction at a particular temperature can assist in creating favourable condition for preventing reactions or making reactions occurs. Some chemicals are kept at very low temperatures in the laboratory and some are kept away from other chemicals or even moisture to prevent reactions that will lead to unpleasant results.

2.6 Summary

- The spontaneous reaction is defined and the concepts of entropy and free energy introduced.
- Factors that will affect the entropy and entropy change are enumerated.
- The concepts of free energy is used to explain the spontaneity or otherwise of reactions.
- The temperature effect on the spontaneity of reactions is also explained.

2.7 Tutor-Marked Assignments

1. (a) Explain the terms entropy and entropy change
   (b) Will the entropy change increase, decrease or remain the same for the listed reactions?
      (i) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$
      (ii) $2CO_{(g)} + O_{2(g)} \longrightarrow 2CO_{2(g)}$
      (iii) $HCl_{(g)} + NH_{3(g)} \longrightarrow NH_4Cl_{(s)}$
      (iv) $2HCl_{(aq)} + Na_2CO_{3(aq)} \longrightarrow 2NaCl_{(aq)} + H_2O_{(l)} + CO_{2(ag)}$
      (v) $C_2H_{4(g)} + H_{2(g)} \longrightarrow C_2H_{6(g)}$

In each case give a reason for your answer.

2. (a) Predict and explain the effect of temperature and pressure on the spontaneity of the following process/reaction.
   (i) water ⟶ ice
   (ii) water ⟶ stream
   (iii) $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$
   $\Delta H = -92kJ\ mol^{-1}$

2.8 References

Bajah, S. T., Teibo, B. O., Onwu G. and Obikwere, A. (2002) *Senior Secondary Chemistry Textbook 2.* Lagos. Longman Publishers.

Osei Yaw Ababio, (2002). *New School Chemistry.* Onitsha. Africana-FEP Publishers.

Unit 3

Chemical Kinetics (I) – Rates of Reactions

3.0 Introduction

In units 1 and 2 we discussed energy, energy effects and the spontaneous reaction. You are now aware that you can not rely solely on enthalpy data to predict the direction of a spontaneous change. There are also well known and studies reactions predicted to be spontaneous by free energy calculations, but yet are not observed to occur. Let us look at the reaction

$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$$

This reaction though predicted to be spontaneous by free energy calculations will not occur until a spark is introduced into the mixture of hydrogen and oxygen. Some processes are found to occur instantaneously while some are slow and may go on for years. Mixing aqueous solutions of sodium chloride and silver trioxonitrate (v) results in instantaneous precipitation of silver chloride but the transformation of one rock salt to another is a continuous and slow process.

In this unit we shall focus on chemical reactions and try to answer the questions of how fast a reaction goes and what factors affect the rate of a reaction.

3.1 Objectives

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

- Explain what happens when a chemical reaction occurs.
- Describe some methods of monitoring reaction rate.
- Enumerate the factors affecting reaction rate.
- Identify the method of monitoring the rate of a reaction when the chemical equation is given.

3.2 Rate of a Chemical Reaction

3.2.1 Meaning of rate of reaction

When a chemical reaction occurs, reactant bonds are broken and new bonds form. The result is that product appears as the reactant disappears. **The rate of the reaction is the amount (moles) of a reactant converted or product formed per unit time of reaction.**

$$\text{Rate of reactions} = \frac{\text{Change in concentration of reaction of product}}{\text{Time taken for the reaction}}$$

For the reaction $Mg_{(s)} + 2HCl_{(aq)}$ ® $MgCl_{2(aq)} + H_{2(g)}$, the rate can be expressed in four different ways which are:

(i) rate of consumption (disappearance) of Mg(s),
(ii) rate of consumption (disappearance) of HCl(aq),
(iii) rate of formation of $MgCl_2(aq)$,
(iv) rate of formation of $H_2(g)$.

3.2.2. Monitoring the rates of chemical reactions

·Monitoring involves making series of measurement carefully·with a view to establish or prove relationship. The relationship here is the effect of concentration on the rate of a reaction. For a given chemical reaction the choice of a method or property for monitoring the rate depends on the nature of the reactants and products.

Now let us use this reaction as an example.

$$Zn_{(s)} + 2HCl_{(aq)} \longrightarrow ZnCl_{2(aq)} + H_{2(g)}$$

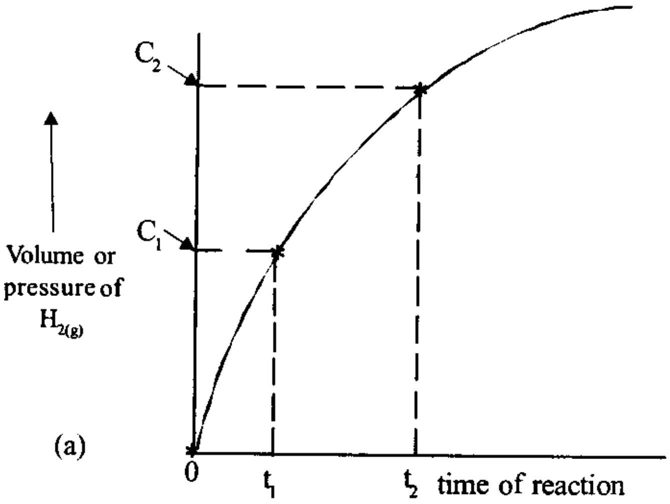
In the laboratory two methods can be used to monitor this reaction rate effectively.

(i) You measure the volume or pressure of $H_2(g)$ and make a plot of gas volume or gas pressure against the time of reaction. A graduated syringe can be fixed to the reaction vessel. Note in this case it is the concentration of the product you are measuring.

If concentration of product at $t = 0 = C_0$
$t_1 = C_1$
$t_2 = C_2$

Where t = 0 when you are starting the measurement.
t = 1 when you measure firstly (say) after 5 mins.
t = 2 when you measure secondly (say) after 10 mins.

(ii) Titration of HCl(aq) an acid with a standard solution of an alkali (NaoH) to monitor the change in the acid concentration with the time of reaction. The results from these two methods are illustrated in fig. 3.2.



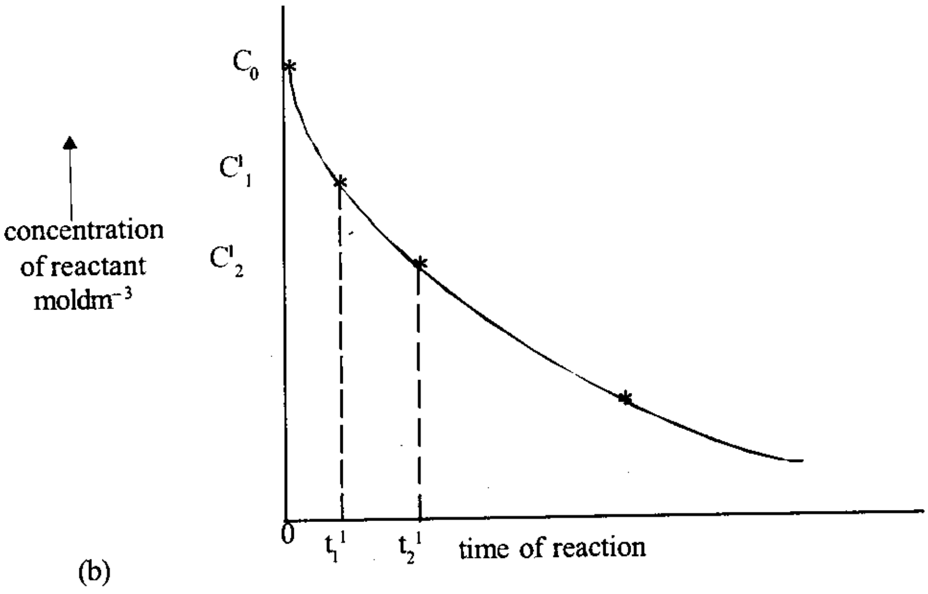


Fig 3.2

The average rate of the reaction can be calculated at t_1 t_2 and $t_1{}^1$, $t_2{}^1$

$$\text{Average rate} = \frac{\text{change in product/reactant concentration}}{\text{time}}$$

using the first curve (a)

$$\text{Average rate at } t_1 = \frac{C_1 - O}{t_1 - O}$$

$$\text{Average rate at } t_2 = \frac{C_2 - O}{t_2 - O}$$

The product concentration is zero at the beginning of the reaction.

Using the second curve (b)

$$\text{Average rate at } t_1{}^1 = \frac{C_0 - C_1^1}{t_1{}^1 - O}$$

$$\text{Average rate at } t_2{}^1 = \frac{C_0 - C_2^1}{t_2{}^1 - O}$$

Where C_0 is the initial concentration of the acid. You can see from the calculations and the curves that the average rate is not constant and decreases as the time of reaction increases.

$$\frac{C_1}{t_1} - \frac{C_2}{t_2} \quad \text{and} \quad \frac{C_0 - C_1{}^1}{t_1} \qquad \frac{C_0 - C_2^1}{t_2^1}$$

Implying that the reactant and product concentrations change most rapidly with time at the beginning. The graphs are steepest at the beginning. The steepness of each graph decreases with the time of reaction and approaches a zero value close to the end of the reaction. This agrees with observation. Gas effervescence from a solid/liquid reaction as in the case of $Zn_{(s)} + HCl_{(aq)} \longrightarrow ZnCl_{2(aq)} + H_{2(g)}$ is very vigorous at the beginning of the reaction, becoming less and less vigorous until the reaction finally stops.

3.2.3 Methods of monitoring the rates of reactions

You will recall that the purpose of monitoring is to establish or prove a relationship.

Now you will reconsider the reaction;

$$Zn_{(s)} + 2HCl_{(aq)} \longrightarrow ZnCl_{2(aq)} + H_{2(g)}$$

Two methods of monitoring the rate were discussed earlier. Can you recall these methods. The two methods you just recalled are also applicable to many reactions with similar features as the above reaction. There are many reactions however, to which these methods are not applicable.

Take for example

$$BaCl_{2(aq)} + Na_2SO_{4(aq)} \longrightarrow BaSO_{4(s)} + 2NaCl(aq)$$

This is a reaction in which no gas is involved but a precipitate forms as the reactants are used up. The amount of precipitate formed could serve as a method of monitoring its rate. A choice of method for a reaction must therefore be done after careful study of the physical and chemical nature of the reactants and products. Listed below are methods that could be used to monitor rates in some specific situations. The property that is changing in each method must change proportionately with the amount of a reactant or product in the reactions.

(i) Decrease in the mass of the reaction system as a gaseous product escapes.

(ii) Measurement of volume or pressure of a gaseous product or reactant.

(iii) Amount of precipitate formed.

(iv) Colour intensity. This method is used when a coloured product is formed from colourless reactants or a coloured reactant is converted to a colourless product.

(v) Changes in the pH of the reaction medium. This is applicable when an acid or base is used up or produced in the reaction.

(vi) Titration of a product or reactant with an appropriate reagent.

(vii) Increase or decrease in total pressure or volume for a gas reaction. Recall Avogadro's law. A change in the number of molecules of gas in a reaction will lead to a change of pressure or volume. Now suggest a method each to monitor the rates of these reactions.

(i) $CaCO_{3(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$

(ii) $2SO_{2(g)} + O_{2(g)} \longrightarrow 2SO_{3(g)}$

3.3 Factors that Affect Reaction Rates

Some reactions are very fast while some are slow. The rates of many reactions are changed markedly when the condition of the reactions are altered. Many factors will affect the rate of a chemical reaction. It is important that when studying the effect of one factor on the rates, the others are kept constant. In this way the effect of each factor can be assessed and if possible quantified. Here are factors that can affect the rate of a chemical reaction.

3.3.1 Nature of the reactant

In a chemical reaction, bonds are broken in the reactant. Reactants that are strongly bonded are not very reactive because of the high energy needed to initiate the reaction. The reaction of the form

$$M + HCl_{(aq)} \longrightarrow MCl_{(aq)} + H_2$$

occurs only slowly with iron, rapidly and vigorously with zinc and magnesium and there is no evidence of reaction with gold.

The reaction of solid sodium hydroxide with aqueous hydrochloric acid is not very fast but the reaction of aqueous solutions of the two react instantaneously. The reaction of potassium tetraoxomanganate(vii) with Fe^{2+} in acid is instantaneous at room temperature. The same potassium tetraoxomanganate (vii) solution will not react with aqueous sodium oxalate ($Na_2C_2O_4$) unless the reaction container is first heated. All the above are evidences of the reactant nature on the reaction rate.

3.3.2. Concentration of the reactant

The rate of a homogeneous reaction is affected by the concentration of the reactants. Homogeneous here means that the reactants are in the same physical state. i.e all reactants are either in solution or they are all gases. Note here that solid-solid reactions are very unlikely.

3.3.3 Temperature

Reactions are usually faster at elevated temperature. Many reactions that are slow at room temperature have their rates markedly increased when the temperature is increased. For good results, experiments to monitor the rate must always be at a constant temperature. For a 10°C rise in temperature the rate of a reaction may double.

3.3.4 Pressure/volume for gases

Pressure affects the rate of gas reactions only. For reactions of the solids or liquids, pressure has little or no effect at all. For a gas at a constant temperature, a pressure increase leads to a decrease in volume resulting in higher concentration and a faster reaction. The reverse is the case when the pressure is reduced.

Recall that for a gas

$$PV = nRT$$

$$\frac{P}{RT} = \frac{n}{V}$$

$$\frac{P}{RT} = C$$

$$\therefore P \propto C$$

P – pressure
V – volume
T – temperature
N – number of mole
R – gas constant
C – concentration

As pressure increases at constant temperature $\frac{P}{RT}$ increases i.e. concentration increases.

3.3.5 Surface area

For a reaction occurring between reactants in different physical states, the rate depends on the area of contact between the two states. When the area of contact increases the rate also increases. A lump of lead metal for example reacts very slowly with oxygen gas. When the lead is in powder form, its reaction with oxygen is much faster. This is because of the large area of contact of oxygen gas with the powdered lead.

3.3.6 Catalyst

A catalyst is a substance which when added to a reaction system increases the rate of the reaction but is not used up and does not change its chemical nature at the end of the reaction. Catalysts are usually specific in character i.e they act on a particular reaction. Only a small amount of the catalyst is often needed for the reaction. Can you remember the catalyst used in the laboratory preparation of oxygen from potassium trioxochlorate (v) ($KClO_3$). Now give the name of the catalyst. A catalyst can have its efficiency increased by substances that are not necessarily catalysts for the reaction. Remember Al_2O_3 promotes the efficiency of the iron catalysts in the Haber process.

3.3.7 Light

Some chemical reactions are light sensitive. Some of these reactions will not occur in the absence of light while the rates of some are only increased in the presence of light. The decomposition of hydrogen peroxide is accelerated by light. This is why it is kept in brown bottles. Next time you visit a pharmacy shop, request to be shown a bottle of hydrogen peroxide and confirm this. The reaction of methane (CH_4) with chlorine will of not occur without light. Reactions that are sensitive to light are called **photochemical reactions**. Photosynthesis reaction is another example of a photochemical reaction.

3.4 Conclusion

The rate of a reaction tells us how fast a reaction goes and many factors affect it. The rate of a reaction can therefore be controlled by appropriate choice of reaction conditions. Monitoring the rates of a reaction must always be at constant temperature for reproducible results. A choice of method for monitoring the rate depends on the physical and chemical nature of the reactants and products and must only be after proper study of the reaction.

3.5 Summary

The rate of a reaction is defined and the different methods of monitoring reaction rates enumerated. The change of reactant concentration with time of reaction was explained and illustrated on rate curves. The factors affecting reaction rates are enumerated and explained.

3.6 Tutor-Marked Assignments

1. For the reaction

$$2SO_{2(g)} + O_{2(g)} \xrightarrow[\text{catalyst}]{V_2O_5} 2SO_{3(g)} \qquad DH - 180\ \mathrm{kJ\ mol^{-1}}$$

(a) State and explain the effect of temperature and pressure on the reaction rate

(b) Suggest and explain a method of monitoring the reaction rate.

2. (a) Explain the term rate of reaction

(b) For the reaction

$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$$

State the factors that will affect the reaction rate

(c) A 10.0g Ca CO_3 sample was heated for 4.5mins. The weight of the chip reduced to 6.25g. Calculate the rate of the reaction in

(i) mol $CaCO_3$ used up/min

(ii) mol CaO formed/min

3.7 References

Bajah, S. T., Teibo, B. O., Onwu G. and Obikwere A. (2002). *Senior Secondary Chemistry Textbook 2.* Lagos. Longman Publishers.

Osei Yaw Ababio (2002) *New School Chemistry.* Onitsha. Africana-FEP Publishers.

Unit 4

Chemical Kinetics (II) – Collision Theory and the Activation Energy

4.0 Introduction

In unit 3, the rate of a reaction is defined and factors that affect the rate enumerated and discussed. Factors like temperature, concentration, nature and catalyst will affect the rate of all homogeneous reactions. Other factors like pressure, light and surface area are specific for some types of reaction. One method of expressing reaction rate is the rate of formation (production) of products. The rate at which a product forms from a reaction is of economic importance in industries and factors are always made to bear on reactants (raw materials) not only to improve quality or yield alone but also to increase production rate and reduce time of labour.

In this unit a theory called the collision theory will be discussed and used to explain why some of the enumerated factors in unit 3 have so much effect on the rates of reactions. The concept of activation energy of a reaction and its effect on the rate will also be discussed.

4.1 Objectives

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

- Explain the concept of activation energy.
- Draw energy level diagrams to explain the concept of activation energy.
- Explain and illustrate the effect of catalyst on the activation energy.
- Explain the effects of factors on rate using collision theory.
- Explain why chemical reactions occur at different rates.

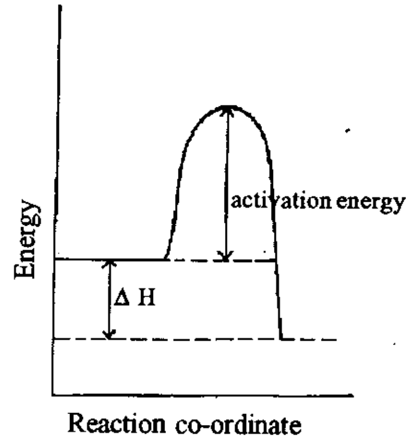
4.2 Activation Energy and the Reaction Rate

In a chemical reaction, bonds are broken and formed. An initial energy input is always required to start the reaction. This input of energy activates the reactant molecules to start reacting. This minimum energy that is needed to start a reaction is called the activation energy.

When the reactant molecules acquire the activation energy they form a high energy particle called the activated complex. The activated complex is relatively more unstable than the reactant or product particles because of its high energy. It readily decompose to give the product or the reactant. All chemical reactions whether exothermic or endothermic require the activation energy. Reactions with fairly high activation energies are usually very slow at ordinary temperatures while those with small activation energies are very fast. When the activation energy is very high the reaction may not occur except an external source of energy is supplied to activate the reactant molecules. The reaction of hydrogen and oxygen gas is an example of such reactions with relatively high activation energy. The reaction occurs only after a spark is introduced into the gas mixture. When a catalyst is added to a reaction mixture the activation energy is lowered and the rate of the reaction increases. The figures 4.1 (a, b, c) illustrate the concept of activation energy for the exothermic and endothermic reaction and the effect of catalyst on the activation energy of the reaction.

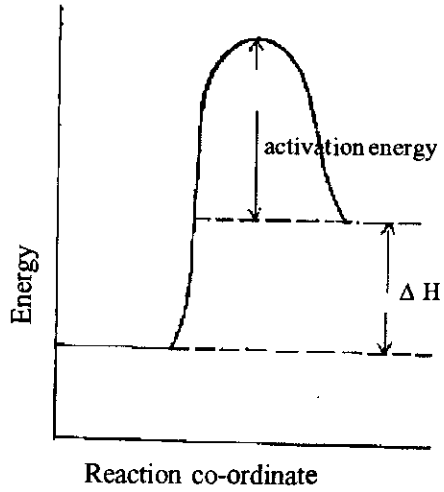
Fig. 4.1

(a)



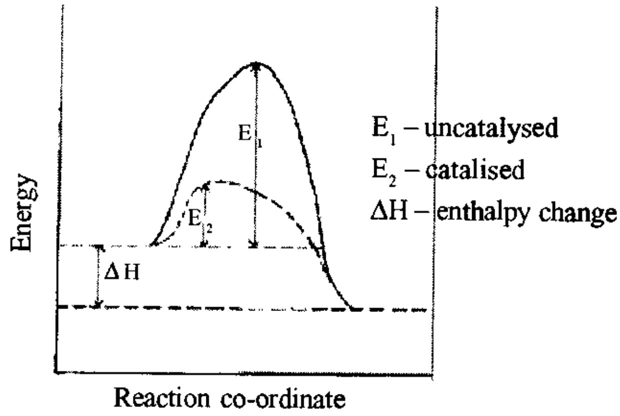
Reaction profile for the exothermic reaction

(b)



Reaction profile for the endothermic reaction

(c)



Reaction profile for a reaction with and without a catalyst

4.3 The Collision Theory

4.3.1 The collision theory discussed

The collision theory assumes that for a reaction to occur the reactant particles must collide. Not all collisions will lead to reaction but only collisions of particles that have sufficient energy to overcome the activation energy. The collisions that lead to reaction are called **effective collisions**. The reaction rate is determined by the rate of collision as well as the fraction of effective collisions. The rate of a reaction increases with number of collisions as well as the fraction of effective collisions. The collision theory can be used to explain the effects of the factors enumerated earlier on the reaction rate.

4.3.2 The collision theory and the nature of the reactant

The reactant nature determines the type of bonds that must be broken before products can be formed. The type of bond depends on the compound. A reactant with very strong bonds in its molecules will not react as fast as one with weak bonds because it will require a higher activation energy. You will recall that the higher the activation energy the slower the reaction and vice versa.

4.3.3 The collision theory and the reactant concentration

When the reactant concentration is increased, the number of colliding particles per unit volume increases. This will lead to more collisions and therefore increase in reaction rate.

4.3.4 The collision theory and temperature

An increase in temperature of the reacting molecules has a two fold effect.

(i) The particles now have higher average kinetic energies. This will increase the fraction of effective collisions because particles collide with higher energies.

(ii) Because of the higher average kinetic energy, there is increase in random motion which will result in more collisions.

The net effect is that the number of collisions and fraction of effective collisions increase. This will lead to a higher rate of reaction. Fig. 4.2 gives the normal distribution of kinetic energies between particles at two different temperatures

T_1 and T_2 with $T_2 > T_1$

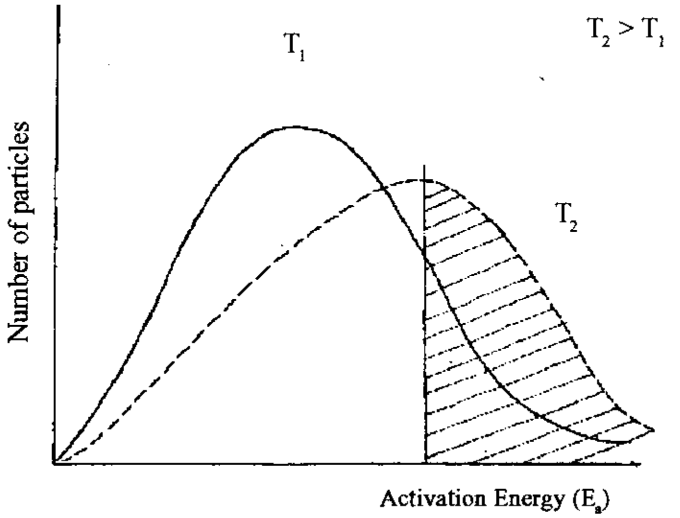


Fig 4.2 Kinetic energy

Enthalpy distribution among reacting particles at two temperatures T_1 and T_2. The shaded area under each curve represents the proportion of reactant that have sufficient energy to cause reactions. There are more molecules at T_2 that have sufficient energy. Recall that only collisions between molecules with energy equal to or greater than Ea can lead to reaction.

4.3.5 The collision theory and pressure

As the pressure of the gas increases the volume decreases. The particles are now closer together and will make more collisions. This will lead to higher rate of reaction.

4.3.6 The collision theory and catalyst

The catalyst lowers the activation energy of the reaction. More molecules will now have sufficient energy to overcome this small activation energy. The fraction of effective collisions increases and rate of reaction also increases. The catalyst effect on the activation energy is illustrated in Fig. 4.1

4.4 Conclusion

All reactions, whether exothermic or endothermic require activation energy. The very fast nature of some reactions, suggest that their activation energies are very small. Slow reactions such as that between hydrogen and oxygen, nitrogen and oxygen require very high activation energies and do not even occur unless they are given energy to start. The collision theory is able to account for the effect of many factors on the rate of the reaction.

4.5 Summary

The concept of activation energy is discussed. The activation energy of a reaction has a bearing on its rate. Fast reactions have small and slow ones have very high activation energies.

- The collision theory is discussed. The theory is used to explain the effect of nature of reactant, concentration of reactant, temperature, catalyst and gas pressure on the rate of reaction.
- The effect of temperature as explained by the theory is two fold. Temperature increases the number of collisions and the fraction of effective collisions. This may explain in part why rate experiments are so sensitive to temperature change. You will recall that reaction rate may double for every 10°C rise in temperature.

4.6 Tutor-Marked Assignments

1. What do you understand by the following: reaction rate, energy level diagram, activation energy and activated complex?
2. (a) Explain the effect of a catalyst on the rate of a reaction and draw energy level diagram to illustrate its effect on the reaction profile.

   (b) List three properties of a good catalyst.

4.7 References

Bajah, S. T., Teibo, B. O., Onwu, G. and Obikwere A. (2002). *Senior Secondary Chemistry Textbook 2.* Lagos. Longman Publishers.

Osei Yaw Ababio (2002). *New School Chemistry.* Onitsha. Africana-FEP Publishers.

Unit 5

Chemical Equilibrium (I)

Reversible Reactions and Lé Chatelier's Principle

5.0. Introduction

Matter is continually changing. These changes are as a result of chemical and physical processes. The melting of ice, burning of fuel, burning of magnesium, digestion of food, respiration, making of soap or detergent, dissolving of sugar in water and many laboratory preparations are all examples of processes which result in changes in matter.

- Can you add more to the above list? Now add five more examples.

Most chemical reactions can only go in one direction. Take for example the reaction of magnesium with dilute hydrochloric acid.

$$Mg_{(s)} + 2HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + H_{2(g)}$$

There is no way the reverse reaction can occur. Hydrogen will not react with magnesium chloride, under any condition to produce magnesium and hydrochloric acid. **This is an example of an irreversible reaction.**

Some reactions, however, are reversible. **A reversible reaction is a reaction that can go in either direction depending on the conditions of the reaction.** There are a number of common examples of reversible reactions. The extent to which the reactants are converted to products in reversible reactions will be discussed. The effects of certain factors on the extent of reaction will also be discussed and explained.

5.1 Objectives

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

- Give some examples of reversible reactions.
- Write chemical equations for reversible reactions.
- Define the equilibrium state and list its characteristics.
- State the equilibrium law.
- Write equilibrium constant expressions for reactions.

- State Lé chatellier's principle.
- Use Lé chatelier's principle to explain the effects of concentration change, pressure, temperature on the equilibrium position and the equilibrium constant of a reversible reaction.

5.2. Reversible Reactions

Reversible reactions are reactions that do not proceed to completion and the conversion of the products to reactants is also possible under a set of reaction conditions. They are represented by $\rightleftharpoons$ between the reactants and the products. Reactions in which the reactants go virtually to give products and there is no tendency for products to revert to the reactants are **irreversible reactions**. They are represented by $\longrightarrow$ between the reactants and the products.

The reaction of magnesium with dilute hydrochloric acid, the precipitation of silver chloride when aqueous solutions of silver nitrate and sodium chloride are mixed and the reaction of aqueous solutions of acid and alkali are examples of **irreversible reactions.**

$$Mg_{(s)} + 2HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + H_{2(g)}$$

$$AgNO_{3(aq)} + NaCl_{(aq)} \longrightarrow AgCl_{(s)} + NaNO_{3(aq)}$$

$$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(aq)}$$

5.2.1 Common examples of reversible reactions

(a) Heating of hydrated copper (II) tetraoxosulphate (vi) crystals.

$$CuSO_4 .5H_2O_{(s)} \rightleftharpoons CuSO_{4(s)} + 5H_2O_{(l)}$$

When the hydrated salt is heated, water vapour is given off. The blue colour of the hydrated salt changes to white and the crystals turn to powder. When a few drops of water are added to the cold white powder, the blue colour returns as the hydrated salt is formed.

(b) Heating ammonium chloride crystals

$$NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$$

When ammonium chloride crystals are heated the salt dissociates into ammonia gas and hydrogen chloride gas. As the gases cool, they recombine to form the solid. One test for ammonia gas is to hold the stopper of a concentrated hydrochloric acid near the source of ammonia. A dense white fume of ammonium chloride is formed.

(c) Formation of calcium hydrogen trioxocarbonate(iv)

When excess carbon (iv) oxide is bubbled through lime water ($Ca(OH)_{2(aq)}$ an initial white precipitate turns clear as calcium hydrogen trioxocarbonate (iv) is formed. When this solution is heated, the precipitate returns as the insoluble calcium trioxocarbonate(iv) forms.

$$CaCO_{3(s)} + H_2O_{(l)} + CO_2 \rightleftharpoons Ca(HCO_3)_{2(aq)}$$

(d) Reaction of iron with steam.

When steam is passed over heated iron a slow reaction occurs producing hydrogen gas and an oxide of iron. The reverse reaction also occurs when hydrogen is passed over the heated oxide.

$$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$$

5.2.2 Reversible reactions and the equilibrium state

When a chemical reaction occurs spontaneously, it continues until a state of dynamic equilibrium is reached in which both the forward and reverse reactions are taking place at the same rate. The concentrations of the reactants and products no longer change with time. The reaction is said to be at equilibrium or that **a state of equilibrium has been reached.** This equilibrium can only be established in a sealed system, where no chemicals can enter or leave the system. **Such a system is called a closed system,** The equilibrium state remains unless it is disturbed. The equilibrium state can be approached from the reactant or product direction. The equilibrium state is a dynamic state in which there is no net change in properties such as the density or concentration of the various parts of the system.

At the equilibrium state the **free energy** change is equal to zero ($\Delta G = 0$)

Recall $\Delta G = \Delta H - T\Delta S$

If $\Delta G = 0$

$\Delta H = T_{eq}\Delta S$ $\quad T_{eq}$ equilibrium temperature

$$\Delta S = \frac{\Delta H}{T_{eq}}$$

The entropy change that accompanies the reversible reaction can be calculated if the enthalpy change is known.

5.2.3 The reversible reaction and the equilibrium constant

There is a fixed relationship, at a given temperature, between the molar concentration of the products and the reactants in the equilibrium mixture. The above is the equilibrium law.

For a reaction of the form

$A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$ $\quad k_c$ – concentration equilibrium constant

$$k_c = \frac{[C]\ [D]}{[A]\ [B]}$$

[ ] molar concentration

From the above you see that the equilibrium constant (k_C) is an index of how far the reaction goes in the direction of $C_{(g)}$ and $D_{(g)}$. **Very high value of k_C implies that the reaction goes virtually to completion. Very small values of k_C implies that the reaction does not go far in favour of $C_{(g)}$ and $D_{(g)}$**

The equilibrium constant for the reverse reaction.

$$C_{(g)} + D_{(g)} \rightleftharpoons A_{(g)} + B_{(g)}$$

$$k_c = \frac{[A_{(g)}]\ [B_{(g)}]}{[C_{(g)}]\ [D_{(g)}]}$$

The equilibrium constant of the reverse reaction is the reciprocal of the requilibrium constant of the forward reaction.

Now let us look at real reactions.

(a) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

$$k_c = \frac{[HI_{(g)}]^2}{[I_{2(g)}]\ [H_{2(g)}]}$$

(b) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

$$k_c = \frac{[NH_{3(g)}]^2}{[N_{2(g)}]\ [H_{2(g)}]^3}$$

Note that the molar concentrations are raised to the power of the reactant coefficient in the equation. A correctly balanced equation is required to enable you write the correct equation for k_c.

Now write the equilibrium constant equation for the reaction.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

For gas reactions we can also write the equilibrium constant expression using the **partial pressures of the gases**

For example

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$$k_P = \frac{[P_{HI_{(g)}}]^2}{[P_{H_{2(g)}}]\ [P_{I_{2(g)}}]}$$ P – partial pressure

k_p and k_c are not equal but are related. Recall that for a gas, pressure is directly proportional to the concentration. The units of k_c and k_p depend on the particular reaction that is considered.

For example

$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$, k_c and k_p have no unit because the number of molecules is the same on reactant and product side.

For the decomposition reaction

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

k_c and k_p will have units of mol dm^{-3} and Nm^{-2} or mm Hg (i.e. pressure unit)

$$k_c = \frac{[NO_{2(g)}]^2}{[N_2O_{4(g)}]}$$

$$k_P = \frac{[P_{NO_{2(g)}}]^2}{[P_{N_2O_{4(g)}}]}$$

– The equilibrium constant is related to the free energy change of the reaction

$\Delta G = \Delta G^o + RT \ln K$ ΔG^o – free energy standard

At equilibrium $\Delta G = O$ and

$\Delta G^o = - RT \ln k$

5.3 Factors Affecting an Equilibrium State

The position of equilibrium can be altered by changing the conditions. The effect on the equilibrium state caused by a change of certain condition of the reaction is predicted by Le Chatelier's principle.

5.3.1 Lé Chatelier's principle

This principle states that for a system in equilibrium if any change is made to the conditions, the equilibrium will alter so as to oppose the change.

It can also be stated that if a system in equilibrium is subjected to a constraint, it will adjust to annul or nullify the effect of the constraint.

The above principle governs the behaviour of equilibria and the changes in condition that could be altered include temperature, pressure (for gases) and concentration of either the products or reactants.

5.3.2 Lé Chatelier's principle and temperature effect

If the temperature is **increased** the reaction will move in the direction that uses up heat i.e. the **endothermic** reaction is favoured. For a **decrease** in temperature the **exothermic** reaction is favoured. Note here that the reaction is in dynamic equilibrium and the forward and reverse reactions can occur. If the forward reaction is exothermic, the reverse reaction will be endothermic and vice versa. A change in temperature will therefore favour the forward or the reverse reaction. The value of the equilibrium constant will increase for the endothermic reaction but dercrease for the exothermic reaction.

e.g. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}, \Delta H -ve$

k_c decreases with increasing temperature.

5.3.3 Lé Chateliers principle and pressure change

This applies only to gaseous reactions. If the pressure is increased at constant temperature, the system will move in the direction of reduced volume.

Recall Boyle's Law: $P_1V_1 = P_2V_2$

The direction of reduced volume is the direction of small number of gas molecules. Recall Avogadro's law, equal volumes of gases at the same temperature contain same number of molecules. The smaller number of molecules will have the smaller volume.

e.g. $2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$

Increase pressure will favour the forward reaction and a decrease pressure will favour the reverse, **when there is no change in the number of gas molecules pressure will have no effect.**

5.3.4 Lé Chatelier's principle and concentration change

If the concentation of one substance is increased, the reaction will move in the direction to use up the added substance. If the added substance is a reactant, the reaction will move in the product direction and if it is a product, the movement will be in favour of the reverse reaction. If the concentration of one substance is reduced the reaction will move in the direction to produce more of the substance removed. If the removed substance is a reactant, the reverse reaction is favoured but if the product is removed the forward reaction is favoured.

Based on the above, most equilibrium reactions have been made to go virtually to completion by the removal of products as they are formed.

5.4 Effect of Catalyst on Reversible Reactions

A catalyst reduces the activation energies for both the forward and reverse reactions. The catalyst does not change the enthaply change of the reaction. In the presence of the catalyst the reactants and products are not changed. The catalyst only increases the rate of the reaction. The equilibrium constant is not changed but the time to get to the equilibrium position is reduced in the presence of a catalyst.

5.5. Conclusion

All chemical processes tend to a state of dynamic equilibrium which can only be attained in closed systems. Several industrial processes involve reversible reactions. For such reactions it is important to get optimum conversion of reactants to products. The conditions of the reaction system will affect the position of equilibrium and the economic of the process and must therefore be tailored to guarantee maximum yield possible. The use of a catalyst does not increase the extent of conversion but will only decrease the time of the process.

5.6. Summary

- A reversible reaction is defined and contrasted with irreversible ones.
- Common examples of reversible reaction are given for proper understanding of the concept.
- The characteristics of the equilibrium state are discussed and equilibrium constant expression written and explained for some reactions.
- Certain factors, temperature, pressure and concentration will affect the equilibrium position of a reaction but only the temperature will change the value of the equilibrium constant.
- For the endothermic reaction k_c increases with increasing temperature but for the exothermic reaction a decrease in k_c accompanies a temperature increase. The catalyst does not change the position of equilibrium but it makes the approach to equilibrium faster.

5.7. Tutor-Marked Assignments

1. (a) What is a reversible reaction? Give two examples

   (b) Explain the effect of the following on the equilibrium position and the equilibrium constant of the reaction, $N_{2(g)} + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H\text{–ve}$

      (i) temperature

      (ii) pressure

      (iii) catalyst

2. (a) State Lé chatelier's principle

   (b) Write the equilibrium expressions for the following gas reaction

      (i) $2NH_{3(g)} + 3Cl_{2(g)} \rightleftharpoons 6HCl_{(g)} + N_{2(g)}$

      (ii) $Cl_{2(g)} \rightleftharpoons 2Cl_{(g)}$

   (c) The dissociation constant for the acid HX is 1.3×10^{-5} at 298K.

Calculate the standard free energy change (ΔG^o) for the acid dissociation.

When the acid dissociates the following equilibrium is set up.

$$HX_{(aq)} \rightleftharpoons H^+_{(aq)} + X^-_{(aq)}$$

$$R = 8.314\ Jmol^{-1}\ K^{-1}$$

5.8 References

Bajah, S. T., Teibo, B. O., Onwu G. and Obikwere, A. (2002). *Senior Secondary Chemistry Textbook 2.* Lagos. Longman Publishers.

Osei Yaw Ababio (2002). *New School Chemistry* Onitsha. Africana-FEP Publishers.

Unit 6

Chemical Equilibrium (II) Applications

6.0 Introduction

In unit 5 we learnt that a reversible reaction tends to a state of dynamic equilibrium. At equilibrium there is a fixed relationship between the molar concentrations of the reactants and products. This last statement is the equilibrium law and the fixed relationship is the equilibrium constant for the reaction at the given temperature. A change of reaction conditions such as temperature, pressure and concentration affect a reaction at equilibrium. The effect of these changes in reaction conditions on the equilibrium is explained by Lé Chatelier's principle.

Many industrial processes involve reversible reactions and optimum conversion of the reactants to products is desired at minimum cost. The conditions of the reactions chamber can greatly affect the position of equilibrium and hence the economy of the process. The Haber process for the production of ammonia and the contact process for the production of tetraoxo-sulphate (vi) acid are examples. In both cases there is a consideration of the best way of achieving a good yield of products at minimum cost. These two applications will be discussed in this unit.

The equilibrium law has been applied to many reactions in solution. These reactions include, acid-base dissociation in water, salt hydrolysis, buffer solutions, solubility product and common ion effect. The application of the equilibrium law to some of the above reactions will also be the subject of this unit.

6.1 Objectives

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

- Recall some applications of Lé Chatelier's principle in the Haber and contact processes.
- Explain common ion effect.
- Arrange acids/bases in order of strength when ka values are known.
- Calculate pH of acid or alkaline solutions.
- Use the concept of hydrolysis to explain the basic and acidic behaviour of some salt solutions.
- Explain the action of buffer solutions.
- Recall one practical application of common ion effect.

6.2 Applications of the Equilibrium Law to Gas Reactions

6.2.1 The Haber process

In the Haber process ammonia gas is produced from nitrogen and hydrogen gases. In this large scale production of ammonia, the mixture of one part nitrogen and three parts hydrogen is compressed to very high pressures (200 – 1000 atmospheres) and passed through the catalyst chamber at 450-500°C. The catalyst is iron mixed with aluminum oxide (alumina). The alumina promotes the action of the iron as a catalyst.

$$N_{2(g)} + 3H_{2(g)}, \overset{\text{catalyst}}{\rightleftharpoons} 2NH_{3(g)}, \Delta H - Ve$$

The industrial conditions for the Haber process are explained by Lé chatelier's principle.

- Very high pressures because the reaction is accompanied by a decrease in volúme.
- A temperature of 450 – 500°C. The reaction is exothermic and a lower temperature would increase the yield of ammonia. The rate of the reaction is however too low at lower temperatures.
- The iron catalyst is used for the equilibrium to be established more quickly.

Even with the above industrial conditions the yield of ammonia is only 10-15 percent. The reaction is pushed in the forward direction for more ammonia formation by removing the ammonia as it is formed. Recall that when the product concentration is decreased, an equilibrium reaction shifts in the product direction to form more product.

6.2.2 The contact process

Large scale production of tetraoxosulphate (vi) acid is by the contact process. The main reaction is the catalytic oxidation of sulphur (iv) oxide gas to sulphur (vi) oxide gas. This is a reversible reaction accompanied by evolution of heat (exothermic).

$$2SO_{2(g)} + O_{2(g)} \overset{\text{catalyst}}{\rightleftharpoons} 2SO_{3(g)} \Delta H - Ve$$

The catalyst is vanadium (v) oxide (V_2O_5).

The mixture of sulphur (iv) oxide and excess oxygen (air) is first purified and dried. The dry pure mixture of gases is passed through the catalyst chamber at a temperature of about 450°C and at atmospheric pressure. The industrial conditions are also explained by Le Chatelier's principle.

- Atmospheric pressure is used though an increased pressure should improve the yield. The yield at this low pressure is about 98 percent and a higher pressure effect will be negligible.
- A temperature should improve the yield because the reaction is exothermic. The yield is fairly high at this temperature and a lower temperature will decrease the rate of the reaction.
- The catalyst helps to reduce the time of the process.

Two methods are used to push the reaction in favour of the product.

- The product $SO_{3(g)}$ is removed as it is formed.
- Excess oxygen is used.
- Now explain why the use of excess oxygen will push the reaction in favour of the product.

6.3 Applications of the Equilibrium Law to Aqueous Equilibria

6.3.1 Dissociation of weak acids and bases

The dissociation of a weak acid or base in water is a reversible reaction. The extent of dissociation is expressed in the acid/base dissociation constant (k_a or k_b). For the acid HA and base MOH in aqueous solution.

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

H^+ is called the hydroxonium ion

for the base MOH

$$MOH_{(aq)} \rightleftharpoons M^+_{(aq)} + OH^-_{(aq)}$$

$$k_c = \frac{[H_3O^+]\,[A^-]}{[HA]\,[H_2O]}$$

$$k_c[H_2O] = \frac{[H_3O^+]\,[A^-]}{[HA]} = k_a$$

For the base MOH

$$\frac{[M^+][OH^-]}{[MOH]} = k_b$$

k_a, k_b are the acid and base dissociation constants respectively. The acid or base strength is determined by the extent of dissociation. Acids/bases that are strongly ionised will have high dissociation constants. Acids/bases with low dissociation constants are weak acids/bases.

The table gives K_a, K_b values for some acids and bases.

Acid/base	*k_a/k_b values*
CH_3COOH	1.8×10^{-5}
HF	6.5×10^{-4}
HCN	3.1×10^{-8}
NH_3	1.8×10^{-5}
CH_3NH_2	3.7×10^{-4}

Can you arrange the above acids in the order of increasing strength?

Which base is the stronger base?

NH_3 or CH_3NH_2? For strong acids and bases dissociation is assumed to be complete.

6.3.2 Dissociation of water and the pH scale

Water dissociates slightly to give

$$H_2O(l) \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

$$k_c = \frac{[H^+][OH^-]}{[H_2O]}$$

Can you now explain why water conducts electricity?

$k_c\,[H_2O] = [H^+][OH^-] = k_w$

k_w is often called the ion product of water. At 25°C (298K)

$k_w = 10^{-14}$ and for pure water $[H^+] = [OH^-]$

At 25°C, $[H^+] = [OH^-] = 10^{-7}$

Because of the very small values of $[H^+]$ and $[OH^-]$ an acidity scale called the pH scale is used

$pH = -\log H^+$

For pure water $pH = -\log 10^{-7}$

$= 7$

In like manner we define

$pOH = -\log [OH^-]$

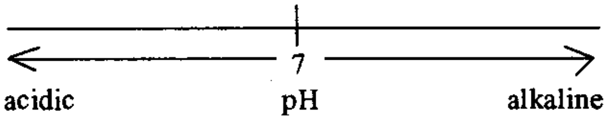
for water $pOH = 7$

$pH = pOH = 7$ for water at 25°C.

and $pH + pOH = 14$ at the same temperature.

When an acid dissolves in water the (H^+) increases and $pH < 7$ but when a base dissolves $[OH^-]$ increases $pOH < 7$ or $pH > 7$

On the pH scale therefore, acid solutions have pH < 7 while alkaline solutions have pH > 7



Example:

Calculate the pH of 0.001 HC*1* solution

HC*1* is a strong acid

$HCl_{(aq)} \longrightarrow H^+_{(aq)} \longrightarrow Cl^-_{(aq)}$

$[H^+] = .001 mol\ dm^{-3}$

pH $= -\log H^+$

$= -\log .001$

$= 3$

Now calculate pH for .005 $H_2SO_4(aq)$

6.3.3 Hydrolysis of salts

A solution of an acid will turn blue litmus red while alkaline solution turns red litmus blue. Some salt solutions are acidic or alkaline to litmus. This is because of hydrolysis of the salts. For example, a solution of sodium ethanoate turns red litmus blue and a solution of ammonium chloride turns blue litmus red. The above observation is explained by a reversible reaction occurring between the salts and water which leads to alkaline or acidic behaviour. $CH_3COONa_{(aq)} + H_2O_{(1)} \rightleftharpoons CH_3COOH_{(aq)} + NaOH_{(aq)}$. Because sodium hydroxide is a strong base and CH_3COOH is a weak acid, the solution is alkali i.e. the alkali has an upper hand.

for NH_4Cl

$NH_4Cl_{(aq)} + H_2O_{(1)} \rightleftharpoons NH_4OH_{(aq)} + HCl_{(aq)}$

HCl is a strong acid but NH_4OH is a weak alkaline (base). The acid has the upper hand and the resulting solution is acidic to litmus. The concept of hydrolysis is very helpful in explaining such observations as above and also in making proper choice of indicator for acid-base titrations.

6.3.4 Buffer Solutions

Buffer solutions are solutions of a weak acid or base and one of its salts.

These solutions possess the ability to resist pH change when small amounts of acid or base are added to them. Examples of buffers are ethanoic acid and its sodium salt and ammonia solution and ammonium chloride. The first example is acid buffer and the second is an alkaline buffer. The capacity of buffer solutions to resist change of pH is explained by reversible reactions in the acid-salt mixture.

Take for example the buffer with ethanoic acid and its sodium salt. The following reactions occur.

$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$ weak acid

$CH_3COONa_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$ highly dissociated

When a small amount of H^+ is added to the buffer solution the weak acid equilibrium is reversed and un-dissociated CH_3COOH is formed. This will have little effect on the CH_3COO^- in solution because of CH_3COO^- from the second reaction. Similarly when OH^- is added the reaction $OH^- + H^+ \longrightarrow H_20$ occurs (H^+) is reduced and the acid equilibrium shifts in the forward direction. This produces more CH_3COO^- but not enough to make much difference because of the large concentration of CH_3COO^- from the salt dissociation.

Buffer solutions are important in reactions that occur only at constant hydrogen ion concentration (pH). They are very important in the body because most of body metabolism occurs only at constant pH.

6.3.5 Common ion effect

A saturated solution is one in which no more of solute will dissolve in the solvent at that temperature. A saturated solution is in equilibrium with excess solid in solution.

Take the example of a saturated calcium chloride solution

$CaCl_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2Cl^-_{(aq)}$

If to this solution is added some sodium chloride crystals (Nacl), the NaCl also furnishes Cl^- in solution

$NaCl_{(aq)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$

Cl^- is the common ion in this example. The additional Cl^- ions in solutions will shift the $CaCl_2$ equilibrium in the reverse direction. More solid will come out i.e solubility of $CaCl_2$ decreases: ***The common ion effect can be defined as the decrease in solubility caused by the presence of an ion of a salt that is added to the solution of the salt from an external source.***

An industrial application of common ion effect is in the soap industry. Soap is produced by treating oil or fat with sodium hydroxide. Fat or oil + NaOH ⟶ Soap + Propane 1,2,3, triol.

'Soap is the sodium salt of a fatty acid. Soap is fairly soluble producing Na^+ and the anion of the fatty acid. Addition of sodium chloride (NaCl) to the soap solutions will introduce Na^+ as common ion. The effect is that the solubility of the soap is reduced and more solid soap precipitates out. The yield of soap is by this method increased. This is called salting out of soap. It is a practical application of common ion effect.

6.3.6 Solubility product

For sparingly soluble salts the solubility product is an index of solubility. Salts with high value of solubility product are more soluble than others with low solubility product values.

Take the example of a saturated AgCl solution.

$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$

$$k_c = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

$$k_c[AgCl] = [Ag^+][Cl^-] = k_{sp}$$

k_{sp} is the solubility product of AgCl. The importance of the solubility ion concept lies in its bearing upon precipitation from solution of metal ions.

The solubility product of AgCl at 25°C is 1.1×10^{-10} mol^2dm^{-6}. In any aqueous solution the product of the molar concentration of Ag^+ and Cl^- in solution cannot exceed this value. If for silver chloride the product of the concentrations is made to exceed this value. Adding a salt with a common ion or mixing solutions with high ion concentrations of Ag^+ and Cl^- ions will result in precipitation of the salt.

Example

The solubility product of AgCl is 1.1×10^{-10} at 25°C. Explain why precipitation occurs when a drop of $0.01 moldm^{-3}$ NaCl is added to $10.0cm^3$ of $0.10moldm^{-3}$ $AgNO_3$ solution in a test tube.

Answer:

$AgNO_3 \longrightarrow Ag^+_{(aq)} + NO^-_{3\,(aq)}$

Dissociation is assumed complete

$[Ag^+] = .10$

$[NO_3^-] = .10$

For AgCl to be precipitated

$[Ag^+][Cl^-] > 1.1 \times 10^{-10}$

$$[Cl^-] > \frac{1.1 \times 10^{-10}}{0.1} = 1.1 \times 10^{-9}$$

The amount of Cl^- is so small that a tiny drop of $0.01 moldm^{-3}$ sodium chloride solution will give precipitate. You will recall that this is a test for chlorides.

6.4 Conclusion

Reversible reactions are many. This unit is a demonstration of the equilibrium law and Lé Chattelier's principle. When applied to industrial processes, reaction conditions are chosen to get optimum yield of products. The application of the equilibrium law to aqueous equilibrium has led to developments of many concepts like acid dissociation constant, common ion effect, solubility product and the pH scale. These concepts are used to explain and quantify some observations in chemical analysis.

6.5 Summary

- The Haber and contact processes are discussed.
- Lé Chatelier's principle is used to justify the reaction conditions for optimum yield of product.
- Applications of the equilibrium law and Lé Chatelier's principle to aqueous equilibria are enumerated and explained.

6.6 Tutor-Marked Assignments

1. The following reaction conditions are used in the Haber process.
   (i) Pressure 200 atmospheres
   (ii) Temp 450°C
   (iii) Catalyst Iron

Justify the above reaction conditions. (Ammonia production is from H_2 and N_2 and the process is exothermic)

2. Explain the following observations
   (a) An aqueous solution of $FeCl_3$ is acidic to litmus but a solution of Na_2CO_3 is alkaline to litmus.
   (b) Explain the terms.
      (i) Salting out
      (ii) Common ion effect
      (iii) Solubility product

6.7 References

Bajah, S.T., Teibo, B.O., Onwu G. and Obikwere A., (2002). *Senior Secondary Chemistry Textbook 2* Lagos, Longman Publishers.

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Unit 7

Acids, Bases and Salts : General Properties

7.0 Introduction

The concept of acids and bases is one of the most important and useful concepts in chemistry. Many chemical reactions are classified as acid-base reactions on the basis of the many theories that have been proposed.

Acids, bases and salts are compounds that we see, touch and use in our every day life at home. We use common salt (sodium chloride) everyday in seasoning our food and sterilising fruits and vegetables. We use soap everyday in washing. Many of our food items contain these compounds. Citrus fruits like oranges and lemon contain citric acid and lactic acid is present in milk. Sodium chloride, tetraoxosulphate(vi) acid and calcium trioxocarbonate(iv) and many others are important raw materials in the chemical industry.

Water is one of the most abundant chemical in nature and serves as a good solvent for many substances both ionic and covalent. Most acids dissolve in water to produce ions. This is also true of bases and salts. They are electrolytes. In this unit, we investigate the properties of acids, bases and salts and explain some of their behaviour in chemical reactions.

7.1 Objectives

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

- Define acid, base and salt.
- Describe some methods of preparation of each.
- List some properties and uses of each.
- Explain hygroscopy, deliquescence and efflorescence.
- Differentiate between a weak and a strong acid.
- Explain why acid/base solutions conduct electrically.

7.2 Acids

7.2.1 Definition, examples and preparation

An acid can be defined as a compound,

(i) containing hydrogen which can be replaced directly or indirectly by a metal;

(ii) that produces $H^+(H_3O^+)$ (hydroxonium ion) as the only positive ion in aqueous solution.

$$H^+ + H_2O \longrightarrow H_3O^+$$

By the above definitions HNO_3, H_2SO_4 CH_3COOH are acids. HNO_3 and H_2SO_4 are sometimes referred to as inorganic or mineral acids while CH_3COOH is referred to as an organic acid — Now add more acids to the list of acids.

Acids are generally prepared by the following methods.

(a) Action of water on acid anhydride (acidic oxides) e.g.

$$H_2O + SO_2 \longrightarrow H_2SO_3 \text{ trioxosulphate(iv) acid}$$
$$H_2O + N_2O_5 \longrightarrow 2HNO_3$$

(b) Displacement of a more volatile acid from its salt.

$$2KCl + H_2SO_4 \longrightarrow K_2S0_4 + 2HCl$$

(c) Oxidation of petroleum hydrocarbons

$$2C_3H_8 + 4O_2 \longrightarrow 3CH_3COOH + 2H_2O \quad \text{ethanoic acid.}$$

(d) Ethanoic acid can also be prepared by the reaction of lead (ii) ethanoate with hydrogen sulphide.

$$Pb(CH_3COO)_2 + H_2S \longrightarrow PbS_{(s)} + 2CH_3COOH$$

(e) Direct reaction of the elements

$$\text{e.g. } H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)}$$

The first reaction requires a catalyst. The catalyst used is activated charcoal.

7.2.2 General properties of acids

Acids generally have sour taste and are corrosive. An aqueous solution of an acid turns blue litmus paper red. The chemical properties include

(a) Reaction with metals to liberate hydrogen gas e.g. $Zn + 2HCl_{(aq)}$, $\longrightarrow ZnSO_4 + H_2$

(b) Liberate $C0_2$ from trioxocarbonates and hydrogentrioxocarbonates

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2O$$

(c) Neutralise bases or alkalis to form salt and water only.

$$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$$
$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$$
$$CaO + 2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O$$

7.2.3 Uses of acids

(a) In manufacture of dyes, fertilizers, paints, detergents and salts.

(b) They serve as solvents and electrolytes.

(c) As preservatives.

(d) For refining gasoline and lubricating oils.

(e) In dissolving metals.

7.3 Bases

7.3.1 Definition examples and preparation

A base is defined as a compound which produces OH^- as the only negative ion in aqueous solution.

A more general definition is that a base neutralises an acid to form salt and water only. A soluble base is called an alkali.

By the above definition CaO, NaOH $Ca(OH)_2$ are bases.

Bases are prepared by the listed methods.

(a) Burning of metallic elements in oxygen

$$4Na + O_2 \longrightarrow 2Na_2O$$
$$2Mg + O_2 \longrightarrow 2MgO$$

(b) Decomposition of carbonates.

$$CaCO_3 \xrightarrow{heat} CaO + CO_2$$
$$CuCO_3 \longrightarrow CuO + CO_2$$

(c) Alkaline solutions are prepared by dissolving metallic oxides in water.

$$Na_2O + H_2O \longrightarrow NaOH(aq)$$
$$CaO + H_2O \longrightarrow Ca(OH)_2(aq)$$

(d) Direct reaction of electropositive metals with water.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$
$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$$

7.3.2 General properties of bases

Bases have bitter taste and appear slippery or soapy to touch. Their solutions will turn red litmus blue. Bases liberate ammonia gas when warmed with an ammonium salt.

$$NH_4Cl + NaOH \longrightarrow NaCl + NH_3 + H_2O$$
$$(NH_4)_2SO_4 + 2KOH \longrightarrow K_2SO_4 + 2NH_3 + 2H_2O$$

7.3.3. Uses of bases

(a) In manufacture of dyes, paper, soap etc.

(b) Some are used as drying agents.

(c) Calcium hydroxide is used for making mortar, plaster of paris (POP) and cement. It is also used in sugar refining and neutralisation of soil acidity.

(d) Milk of magnesia is a suspension of magnesium hydroxide in water. It is used as a mild laxative and antacid in tooth pastes to neutralise acidity in the mouth.

7.4 Salts

7.4.1 Definition, examples, and preparation

A salt is formed when a base is neutralised by an acid. A salt consists of a metallic and acidic radicals.

Examples are NaCl, $NaNO_3$, Na_2SO_4, KCl etc.

Salts are prepared by the listed methods.

(a) Neutralisation of a base by an acid.

(b) Reaction of an acid with a reactive metal

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

(c) Reaction of an acid with a trioxocabonate(iv)

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

(d) Reaction of soluble salts to produce an insoluble salt.

$$AgNO_{3(aq)} + NaCl_{(aq)} \longrightarrow AgCl_{(s)} + NaNO_{3(aq)}$$
$$BaCl_{2(aq)} + Na_2SO_{4(aq)} \longrightarrow BaSO_{4(s)} + 2NaCl_{(aq)}$$

(e) **Direct combination of a gas with metal**

$$2Na_{(s)} + Cl_2 \longrightarrow 2NaCl$$
$$2Fe + 3Cl_2 \longrightarrow FeCl_3$$

7.4.2 Types of salts

(a) Normal Salt

This is the salt formed when all the replaceable hydrogens in the acid have been completely replaced by a metal.

e.g. $NaCl$, Na_2SO_4, $Ca(NO_3)_2$

(b) Acid salts

These are formed when the replaceable hydrogens in the acid are partially replaced by a metal. They are produced by partial neutralisation of acids with more than one replaceable hydrogens.

They are acidic to litmus e.g. $NaHSO_4$ $NaHCO_3$ is alkaline to litmus because of hydrolysis.

(c) Basic salts

They are formed when there is partial replacement of the hydroxyl ions in a metallic hydroxide by an acid. They are formed as a result of partial neutralisation of a base.

$$Zn(OH)_2 + HCl \longrightarrow ZnOHCl + H_2O$$
$$Ba(OH)_2 + HCl \longrightarrow BaOHCl + H_2O$$

They are alkaline to litmus.

(d) Double salts

Double salts are formed when two salts crystallise from solution in definite proportion by mass.

e.g. $K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$

from K_2SO_4 and $Al_2(SO_4)_3$. They combine the chemical properties of the two salts.

(e) Complex salts

These are salts of complex ions.

e.g. $K_3Fe(CN)_6$, $Cu(NH_3)_4SO_4$

Recall that complex ions are formed by coordinate covalent bonding of metal ions with covalent molecules that can donate lone pair of electrons for binding. These covalent molecules are called ligands.

(f) Hydrated salts

These are salts that contain water of crystallisation e.g. $Na_2CO_3 . 10H_2O$, $CuSO_4 . 5H_2O$. The water of crystallisation is chemically bonded to the salt.

On heating or on exposure, some hydrated salts lose their water of crystallisation.

7.5 General Characteristics of Acids, Bases and Salts

7.5.1 Ionisation

Acids, bases and salts ionise in aqueous solution to produce ions. They are all electrolytes. Acids and bases which are completely ionised in solution usually water are strong acids or bases e.g. HNO_3, HCl, $NaOH$, KOH and H_2SO_4. Weak acids and bases are partially ionised in solution e.g. NH_4OH. The extent of ionisation is given by the acid or base dissociation constant which has been discussed in an earlier unit (i.e. Unit 6).

Strong acids and bases are strong electrolytes and weak acids and bases are weak electrolytes. Very soluble salts ionise readily in solution and are strong electrolytes but sparingly soluble salts are weak electrolytes. Because acids ionise and increase the H^+ concentration in water, the pH of acid solutions is less than 7. Bases that dissociate in water increase the hydroxide ion concentration in water. The pH of base solutions is greater than 7. Salts solutions are generally neutral to litmus. Some however show acidic or basic behaviour because of hydrolysis. Recall that hydrolysis is part of an earlier unit i.e. Unit 6.

7.5.2 Deliquescence

This is a phenomenon whereby substances absorb moisture and form solution. Substances that show this behaviour are called **deliquescent compounds.**

e.g. Na OH, KOH, NaCl, $MgCl_2$ and $CaCl_2$.

They have great affinity for water and are sometimes used as drying agents, e.g. fused calcium II chloride.

7.5.3 Hygroscopy

Hygroscopic compounds absorb moisture without forming solution when exposed to the atmosphere. They have very strong affinity for water and are used as drying agents.

e.g. CuO, CaO, and concentrated H_2SO_4. They are sometimes called **dessiccants.**

7.5.4 Efflorescence

Efflorescence is a phenomenon whereby a hydrated salt loses all or part of its water of crystallisation when exposed to the atmosphere. An example is $Na_2CO_3 . 10H_2O$. This salt loses nine molecules of water of crystallisation when exposed and is converted to the mono hydrate

$$Na_2CO_3 . 10H_2O \longrightarrow Na_2CO_3H_2O + 9H_2O$$

7.6 Conclusion

The acid-base concept used in this unit is based on ease of hydrogen ion or hydroxyl ion loss in solution which is the Arrhenius concept. With this concept, so many chemical compounds are classified as acids, bases and salts.

There are two more acid base theories not discussed here which when considered will allow many more compounds to be classified as acids, bases or salts. It is hoped that after studying this unit you now understand and appreciate these compounds more.

7.7 Summary

- Acids, bases and salts are defined, examples are given and the methods of preparation discussed. Their uses are also enumerated.
- Some general characteristics are discussed in relation to their uses as electrolytes and drying agents.

7.8 Tutor-Marked Assignments

1. You are supplied with $0.01 moldm^{-3}$ solutions of A, B, C, D, and E with pH values of 2, 12, 3.5, 6.5 and 9 respectively.
    (a) Arrange the solutions in order of increasing H^+ concentration.
    (b) Which of the solutions will turn litmus from red to blue?
    (c) Which of them is likely to be a solution of a strong acid? Explain.

(d) Explain what happens when equal volumes of A and B are mixed. What is the pH of the mixture?

2 (a) Give two characteristics reaction each of an acid and a base.

(b) Give the product of the given reactions.

(i) $CuCO_3 \longrightarrow$

(ii) $CuCO_{3(s)} + HCl_{(aq)} \longrightarrow$

(iii) $CH_3COOH + Ca(OH)_2 \longrightarrow$

7.9 References

Bajah, S. T., Teibo, B. O., Onwu G. and Obikwere A. 2002. *Senior Secondary Chemistry Textbook 2.* Lagos. Longman Publishers.

Osei Yaw Ababio (2002). *New School Chemistry* Onitsha. Africana-FEP Publishers.

Unit 8

Acids, Bases and Salts: Applications in Volumetric Analysis

8.0 Introduction

In unit 7, acids and bases are presented and their nature and characteristics described.

In this unit the study of acids and bases is extended to quantitative work. In volumetric (titrimetrics) analysis, accurate measurements of volumes of reacting acids and bases are carried out and used to determine how much of the acid or base is present in the sample that is being analysed. Acid-base (neutralisation) reactions are used in volumetric analysis because they fulfil the following conditions.

(a) They are simple reactions that can be expressed by simple chemical equations.

(b) Their reactions are complete and are in equivalent or stoichiometric proportions (mole ratio).

(c) Their reactions are instantaneous especially when both are in solution.

(d) There is a marked change in the pH of the solution at the equivalence point.

(e) Indicators are available to signal the end point of the reaction.

In this unit we consider titration of free acids and bases. The use of sodium trioxocarbonate in acid-base titration is explained. What is the chemical nature of acid-base indicators? Why are they used in acid-base titration? Why do we need to make a choice of an indicator for particular reactions? These are questions that will be answered as we go through the unit.

8.1 Objectives

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

- Define standard solution and standard substance.
- List properties of a standard substance.
- Calculate amount in moles of an acid in a volume of solution.
- Carry out acid-base titration.
- Make correct choice e.g indicator for titration.
- Recall indicator colours in acid and alkaline solutions.
- Differentiate between the end point and the equivalence point of a titration.
- List apparatus for volumetric analysis.
- Explain why Na_2CO_3 is used in acid-base reactions.

8.2 Solutions

8.2.1 Types of Solutions

Solutions used in titrimetic analysis can be classified into two types: the saturated and unsaturated solutions. The saturated solution is one which contains at a given temperature, as much solute as it can hold in the presence of excess solute. A saturated solution is in dynamic equilibrium with the excess solid (Solute) e.g.

$$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$$

An unsaturated solution is one which contains less solute than it can hold at the given temperature. The concentration of a solution is expressed in $moldm^{-3}$, that is the number of moles of solute in ldm^3 of solution. The concentration of a saturated solution of a solute in a solvent gives the solubility of that solute in the solvent at the given temperature. Solutions used in titrimetric analysis are mostly unsaturated solutions. For acids or bases that are very soluble in water, e.g. $Ca(OH)_2$, titration of their saturated solutions with standard acid or alkali is often used to determine their solubility.

8.2.2 Standard solutions

A standard solution is a solution of known concentration. It may be prepared by dissolving a known weight of a pure sample of the substance in a known volume of solution. The solution so prepared is often referred to as a primary standard solution.

Example

10.6g of pure anydrous Na_2CO_3 was dissolved in $250cm^3$ of solution. Calculate its concentration in $moldm^{-3}$

($Na_2 CO_3$ = 106)

Solution

$$\text{Mole } Na_2 CO_3 = \frac{m}{M} = \frac{10.6}{106} = 0.1$$

0.1 mole $Na_2 CO_3$ dissolves in $250cm^3$

$$\therefore 0.1 \times \frac{1000}{250} \text{ mole will dissolves in } 1000cm^3$$

$$= 0.40mol$$

Concentration = 0.40 $moldm^{-3}$

Some substances cannot be obtained in the pure form e.g. NaOH because it absorbs moisture (hygroscopic) and CO_2 from the atmosphere. A solution of NaOH prepared must be titrated with an acid of known concentration before its exact concentration is known. Such a solution whose concentration is known exactly after a titration with another solution of known concentration is called a **secondary standard solution.**

8.2.3. Primary standard substances

You will recall that in the last section 8.2.2, a primary standard solution is prepared using a pure sample of the substance. You will also recall that sodium hydroxide cannot be obtained in very pure form. Substances that can be obtained in very pure form and are used for preparing primary standard solutions are called **primary standard substances**. Apart from being obtained pure a primary standard substance must also satisfy the following conditions.

(a) Easy to obtain dry and purify if necessary.

(b) Be unaltered in air during weighing maintain its composition, not hygroscopic nor oxdised by air or affected by CO_2.

(c) Its reaction with other reagents must be stoichiometric and instantaneous

(d) Be readily soluble. Can you now appreciate why NaOH is not used as primary standard?

8.2.4 Preparing a standard solution

Step 1: Get the solute and solvent in very pure form. If there is need, purify and dry.

Step 2: Weigh out with a good chemical balance, the calculated weight of the solute required.

Step 3: Dissolve solute in small amount of solvent in a beaker transfer into a volumetric flask.

Step 4: With a wash bottle, rinse the beaker many times with distilled water (solvent) and add washings to the volumetric fask.

Step 5: Make the volumetric flask to the mark with solvent and shake well and then stopper.

The steps are represented in the illustration below

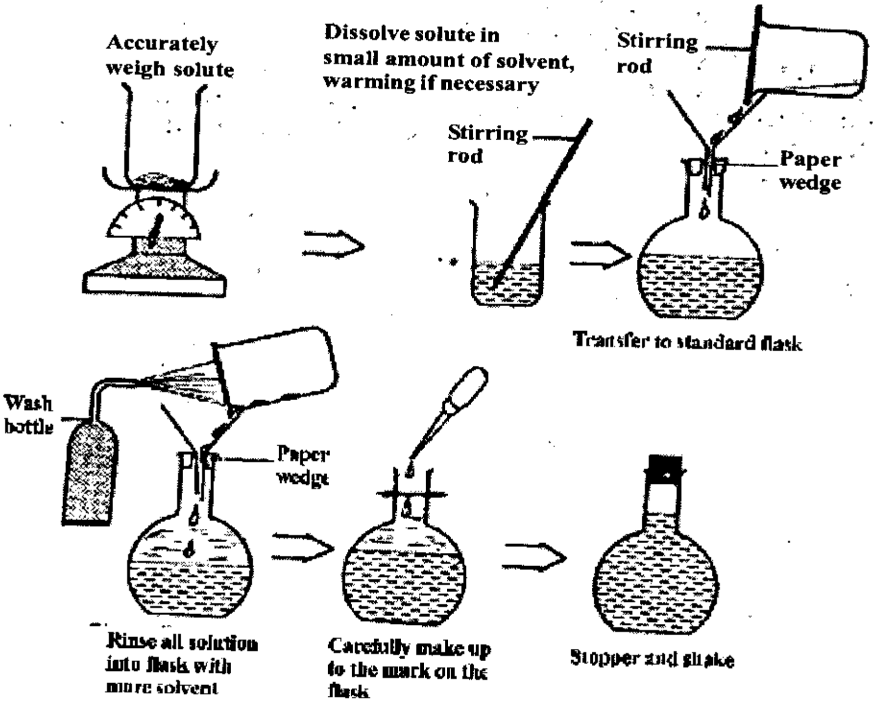

Fig. 8.1: Preparing a standard solution

8.3 Acid-Base Titration

8.3.1 The equivalence points and the end point of a titration

For a given acid-base reaction there is always an equivalent amount of acid that will just neutralise an amount of base or vice versa. The point during the titration when this equivalent amount bas been added is the equivalence point. For example: 25.0cm^3 of 0.10 $moldm^{-3}$ is titrated against 0.10 $moldm^{-3}$ HCl. The equivalence point is 25.0cm^3 because the acid and base are of equal concentration.

The purpose of adding indicator is to detect this equivalence point. **The point at which the indicator changes colour is the end point.** The end point and the equivalence point will be the same or very close if the choice of indicator is correct. If not the indicator may give signal of end point when the reaction is far away from the equivalence point. This will lead to error in the determination of acid or base concentration. You can now see why the choice of indicator is important in titrimetic analysis.

8.3.2 Acid-base indicators

Acid-base indicators are organic compounds that behave as weak acid and bases. They have different colours in acid and alkaline solutions.

Table 8.1 Common acid-base indicators

Indicator	*Colour Change acid/alkaline*	*pH range of colour range*
Litmus	red/blue	5.0 – 8.0
Methyl orange	red/yellow	3.1 – 4.4
Phenolphlthaleen	colourless/pink	8.3 – 10.0
Methyl red	red / yellow	4.2 – 6.3

As you can see from the table, there is a range of pH over which the colour range occurs for each indicator. A knowledge of this and the relative strengths of the acid and base titrated allow for a good choice of indicator for the acid-base reaction.

8.3.3 Neutralisation curves and choice of indicator

This is a plot of pH against the volume of base during a titration

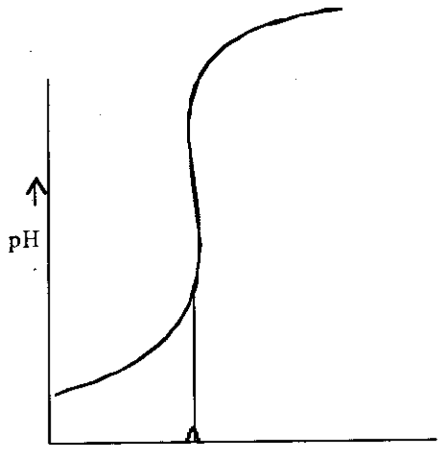

Fig 8.2 Volume of NaOH added

Neutralisation curve for a strong acid/strong base titration. The change in pH near the equivalence point enables us to select an indicator that will give the least titration error. The curve shows that near the equivalence point the rate of change of pH is very rapid. For the strong acid-strong base reaction any of the indicators in the table will give a sharp end point because only one drop or two of alkali causes the pH to move over the whole vertical portion of the curve.

For the weak acid-strong base titration, (ethanoic acid and sodium hydroxide) the hydrolysis of the salt makes the solution to be alkaline at the equivalence point. Phenolphthalein is the choice of indicator because its colour change is in the alkaline range. When a strong acid is titrated against a weak base, at the equivalence point the salt hydrolysis makes the solution acidic. Methyl orange or methyl red are the suitable indicators for such reactions.

8.3.4. The use of sodium trioxocarbonate (IV) in acid-base titrations

Sodium trixocarbonate is the salt of a weak acid and strong base. In aqueous solution the salt is hydrolysed.

$$Na_2CO_{3(aq)} + H_2O_{(l)} \rightleftharpoons 2\,Na^+_{(aq)} + 2OH^-_{(aq)} + H_2\,CO_{3(aq)}$$

As the OH^- reacts to give water the equilibrium reaction moves in the forward direction until all the sodium carbonate has hydrolysed. The reaction can go in parts.

$$Na_2\,CO_{3(aq)} + HCl_{(aq)} \longrightarrow Na\,Cl_{(aq)} + NaHCO_{3(aq)}$$
$$NaHCO_{3(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2\,CO_{3(aq)}$$

At the equivalence point because of the weak acid H_2CO_3 the solution is weakly acidic.

$$H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$$

Methyl orange is used as indicator for the titration.

8.4 Calculations in Volumetric Analysis

Example 1

	Rough	*1st Titration*	*2nd Titration*	*3rd Titration*
	cm^3	cm^3	cm^3	cm^3
Burette reading (final)	23.50	23.80	23.30	24.60
Burette reading (initial)	1.00	1.70	1.10	2.40
Volume of HCl used	22.50	22.10	22.20	22.20

Titration results

The result from HCl/NaOH titration is presented in the table. The acid concentration is 0.10mol dm^{-3} and the sodium hydroxide solution contain s1.10g NaOH in 250cm^3 of solution. Use the above titration result to calculate the percentage purity of the NaOH sample used. The pipette volume is 25.0 cm^3

Equation of the reaction

$$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$$

mole ratio NaOH: HCl = 1: 1

$$\text{mole of HCl} = \frac{M_{HCl} \times V_{HCl}}{1000} \qquad \text{M - concentration (mol dm}^{-3}\text{)} \quad \text{V - average titre}$$

$$V = \frac{22.10 + 22.20 + 22.20}{3}$$
$$= 22.17\text{cm}^3$$

Take average of titre values, that are within 0.2cm^3. These titres are called concordant titres.

$$\text{mole of HCl} = \frac{0.10 \times 22.17}{1000} = 2.217 \times 10^{-3}$$

mole of NaOH = 2.217×10^{-3} because the mole ratio = 1:1

$$\text{mole NaOH} = \frac{M_{NaOH} \times V_{NaOH}}{1000}$$

$$M_{NaOH} = \frac{1000 \text{ x mole NaOH}}{V_{NaOH}}$$

$$= \frac{1000 \text{ x } 2.217 \text{ x } 10^{-3}}{25}$$

$= 0.08\,867$

$= 0.0\,887$ (3sig figs.)

calculation of concentration in g dm^{-3}

concentration (g dm^{-3}) = concentration mole dm^{-3} x molar mass

= .0887 x 40 (molar mass of NaOH)

= 3.548g

= 3.55g (3 sig fig) of pure NaOH.

The solution contains 1.10g/250cm^3.

$$\text{concentration (g } dm^{-3}\text{) of impure NaOH} = \frac{1.10 \text{ x } 1000}{250}$$

= 4.40g

$$\text{The \% purity} = \frac{\text{mass of pure}}{\text{mass of impure}} \text{ x } 100$$

$$= \frac{3.55}{4.40} \text{ x } 100$$

= 80.7%

Example 2

	Rough	*1st Titration*	*2nd Titration*	*3rd Titration*
	cm^3	cm^3	cm^3	cm^3
Burette reading (final)	26.80	43.30	17.10	34.10
Burette reading (initial)	10.00	26.80	0 .50	17.50
Volume of HCl used	16.80	16.50	16.60	16.60

The table gives the result from the titration of a saturated solution of $Ca(OH)_2$ with 0.05 mol dm^{-3} HNO_3 solution at 25°C. The pipette capacity is 25.0cm^3. Calculate the solubility of $Ca(OH)_2$ at 25°C in

(i) moldm^{-3} (ii) gdm^{-3}

Solution

$$\text{Average titre} = \frac{16.50 + 16.60 + 16.60}{3}$$

= 16.57cm^3

Equation of reaction

$$Ca(OH)_2 + 2HNO_3 \longrightarrow Ca(NO_3)_2 + 2H_2O$$

mole ratio 1:2 $Ca(OH)_2 : H_2NO_3$

mole HNO_3 in average titre $= \frac{16.57 \times 0.5}{1000}$

$= 8.285 \times 10^{-3}$

mole $Ca(OH_2)$ $= \frac{8.285}{2} \times 10^{-3}$

$= 4.143 \times 10^{-3}$

Concentration of $Ca(OH)_2$ in mol dm^{-3}

$= \frac{\text{mole } Ca(OH)_2 \times 1000}{25.0}$

$= \frac{4.143 \times 1000 \times 10^{-3}}{25}$

$= .166$ mol dm^{-3}

concentration is dm^{-3} $= .166 \times$ molar mas

$= .166 \times (40 + 34)$

$= 12.3$ gdm^{-3}

Recall that the concentration of a saturated solution of a solute is the solubility of the solute in the solvent.

Solubility of $Ca(OH)_2$ $= 0.166$ mol dm^{-3}

or 12.3g dm^{-3}

8.5 Conclusion

In this unit, we have defined and explained terms and concepts that are related to solutions and acid –base reactions in water. The use of acid-base reactions are many but only two are discussed. Those not discussed which include, the determination of water of crystallisation of hydrated acids or salts and the determination of molar mass of unknown acids are equally important. You will realize that apart from the experimental aspect by acid-base analysis which must be done with good precision, interpretation of data is equally important. A good knowledge of the mole concept is required for proper handling of results from acid-base reactions.

8.6 Summary

- Acid-base reactions require solutions of known concentrations that are prepared from substances of high purity called standard substances. Na_2C0_3 is a standard substance but NaOH is not.
- Solution can be saturated and unsaturated. Most solution used in volumetric analysis are unsaturated. The solubility of a sparingly soluble base or acid can be determined by titrating its saturated solution with standard acid or base.
- The percentage purity of acids-bases can also be determined using acid-base reactions.
- The mole concept is applied in the calculations. Note that concentration can be expressed in many units. Only two units, $moldm^{-3}$ and gdm^{-3} are used in this unit.
- Indicators are important in titrimetric analysis.

Tutor-Marked Assignments

1. Define the following:
   (i) standard solution (ii) saturated solution, (iii) primary standard substance
   (ii) List three characteristics of a primary standard substance.
2. (a) Calculate the concentration of KOH solution prepared by dissolving 5.45g in 1.0 dm^3 of solution.
   (b) Calculate the volume of 0.1 mol dm^{-3} HCl solution that will neutralize 25cm^3 portion of the solution.
3. (a) List two characteristics of a good acid-base indicator.
   (b) Explain why Na_2CO_3 is
      (i) alkaline to litmus
      (ii) used in acid-base titration.

8.8 References

Bajah, S. T. Teibo, B. O., Onwu G. and Obikwere A. 2002. *Senior Secondary Chemistry Textbook 2.* Lagos. Longman Publishers.

Osei Yaw Ababio (2002). *New School Chemistry* Onitsha. Africana-FEP Publishers.

Unit 9

Electrolysis And Redox Reactions

9.0 Introduction

Matter is electrical in nature because it contains protons and electrons which carry positive and negative electricity respectively. The flow of free electrons constitute an electric current and a steady flow of current supplies electric energy. Many of the material comforts we enjoy today come from the use of current electricity. Electricity plays a large part in our world that it would be difficult to imagine life without it. The working of appliances such as radio, television, computers, refrigerators, irons, fans and many others is possible as a result of electric energy.

Recall the law of conservation of energy which states that energy can neither be created nor destroyed in any process. It is just changed from one form to another. Electric energy can be converted to chemical energy. This is the case when the passage of electricity through matter leads to a chemical reaction. Chemical energy can also be converted to electrical energy. This is the case in torch, calculator and car batteries.

In this unit some chemical reactions that occur as a result of passage of electric energy through matter will be discussed and explained.

What are the factors that determine the type and amount of product? Why are some reactions preferred to others?

What type of chemical reactions occur to produce electricity in car batteries?

These are some of the questions that will be answered as we go through this unit.

9.1 Objectives

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

- Explain and give examples of electrolytes and non electrolytes.
- Explain electrolytic conduction.
- Define electrolysis.
- Recall products from some electrolysis of salts.
- Define oxidation, reduction, oxidising and reducing agent.
- Explain how oxidation numbers are assigned.
- Define electrochemical cell.
- Compare and contrast electrolytic and electrochemical cells.

9.2 Electrolysis

This is the process by which the passage of an electric current through a solution or molten compound liberates one or more free elements.

9.2.1 Electrolytes and non electrolytes

Electrolytes are substances which either in molten or aqueous solution allow the passage of an electric current. Ionic solids consist of positive and negative ions held together in a rigid framework by electrostatic forces. When dissolved in water or melted, the ions become free. These free ions can carry charge from one point to another. Examples are sodium chloride and calcium chloride. Some covalent compounds, when they dissolve in water are dissociated into ions. These will also conduct electricity. e.g HCl and NH_3.

$$HCl_{(g)} + H_2O_{(l)} \longrightarrow H_3O^+ + Cl^-.$$

H_3O^+ is the hydronium ion. Substances like NaCl and HCl that for all practical purpose are completely dissociated are called **strong electrolytes.** Some substances like ethanoic acid (CH_3COOH) which dissociates partially in solution are called **weak electrolytes**. Substances that do not conduct electricity either in molten or aqueous solution are called **non-electrolytes**. Non – electrolytes are usually covalent or organic compounds. Examples are sugar and ethanol.

9.2.2 Electrolytic conduction and electrolysis

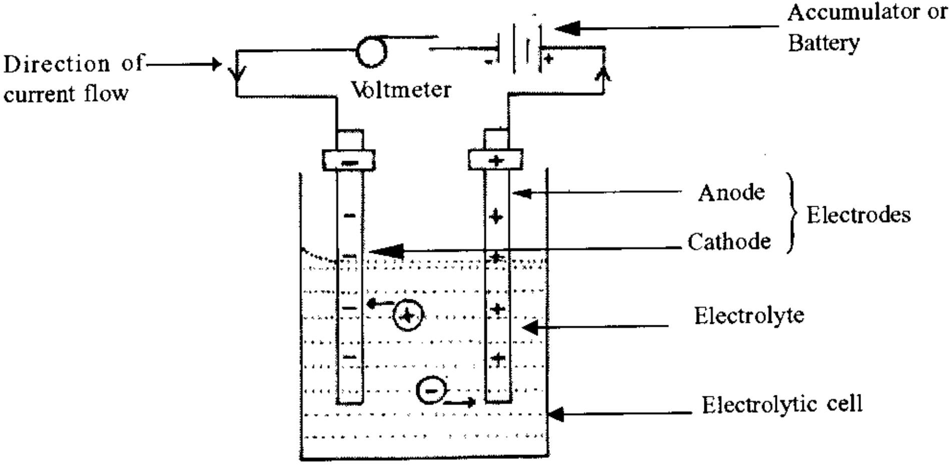

Fig. 9.1 An Electrolytic cell (Voltameter)

The above is an electrolytic cell commonly called **voltameter**. Now we shall explain the functions of the labelled parts of the voltameter. The electrodes are conductors, wires, rods, graphite through which electric current enters and leaves the electrolyte. The **anode** is the +ve electrode through which current enters the electrolyte. Note that it is connected to the positive terminal of the battery.

The **cathode** is the negative electrode through which current leaves the electrolyte. It is connected to the negative terminal of the battery. Both the anode and cathode are called electrodes. When the battery is switched on, the positive ions migrate toward the negative electrode and the negative ions move toward the positive electrode. This movement of ionic charges through the liquid brought about by application of electricity is called **electrolytic conduction.**

When the ions of the liquid electrolyte come in contact with the electrodes, chemical reactions occur. At the anode (+ve electrode), the –ve ions lose electrons. This is **oxidation.**

At the cathode (-ve electrode), the +ve ions gain electrons. This is **reduction**. The liquid will continue to conduct electricity only as long as these reactions at the electrodes continue. The electrons that are deposited at the anode are eliminated from the solution to maintain a constant supply of electrons at the cathode. As the electrons flow through the exterior wire, ions flow through the solution.

Take for example the electrolysis of molten sodium chloride, the ions present are. Na^+ and Cl^-.

At the anode $Cl^- \longrightarrow Cl + e$

$Cl + Cl \longrightarrow Cl_2$ gas

At the cathode

$Na^+ + e \longrightarrow Na_{(s)}$

The net result is that NaCl has been split into Na solid and Cl_2 gas.

9.2.3 Preferential discharge of ions during electrolysis

The product at the electrodes during electrolysis depend on a number of factors

(a) Nature of the electrode

Certain electrodes take part in electrolytic reactions and must be used with caution. Platinum and graphite electrodes are inert electrodes and do not take part in electrolytic reactions. They are safer to use to avoid unwanted results.

(b) Concentration of the ions of the electrolyte

Increase in the concentration of any ion in the electrolyte increases the chance of its discharge especially when they are close in the electrochemical series. The electrochemical series gives the order of discharge of ions from solution. This factor is important for mixed electrolyte or for aqueous solutions of electrolytes. Recall that water also ionizes to give H^+ and OH^-. Water is a weak electrolyte. e.g for $NaCl_{(aq)}$

Cations are $Na^+ + H_3O^+$

Anions $\longrightarrow Cl^-\ OH^-$

Na^+ is too far from H^+ on the electrochemical series so H^+ is discharged as $H_{2(g)}$ at the cathode and Cl_2 at the anode.

(c) Position on the electrochemical series

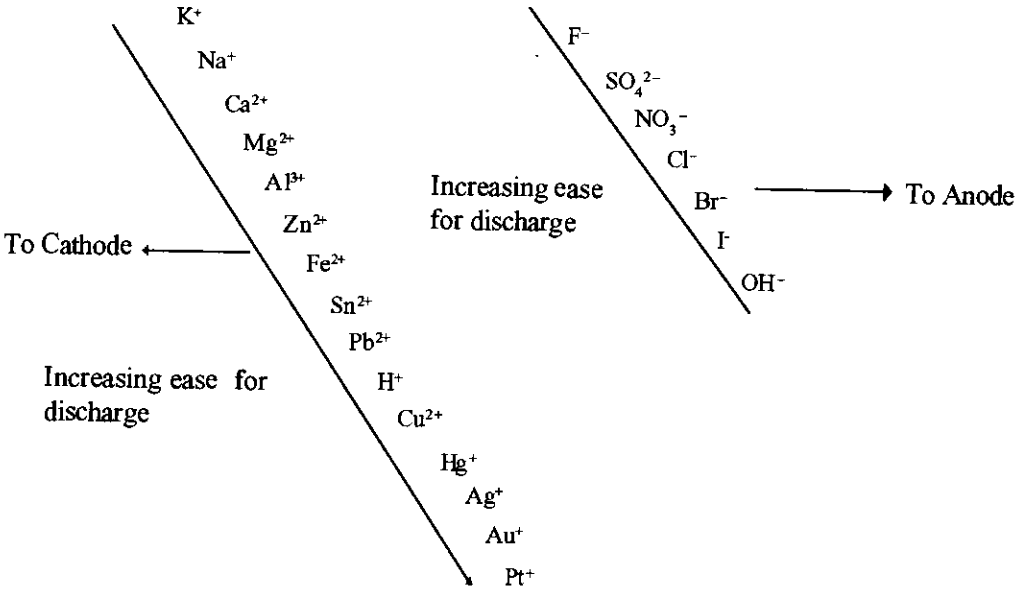

Fig 9.2 Electrochemical/Reactivity Series

All other factors being constant, ions that are lower is the series will be discharge in preference to any other above in the series. The electrochemical series is the arrangement of cations and anions in the order they are discharged during electrolysis.

9.2.4 Examples of electrolysis of some salts

Let us illustrate what we have discussed so far with examples: the electrolysis of copper (ii) tetraoxosulphate (iv) and sodium chloride solutions using platinum or carbon electrodes. The ions present in sodium chloride solutions are Na^+, H_3O^+ which both migrate to the cathode and Cl^- and OH^- which migrate to the anode.

At the cathode H_3O^+ is preferentially discharged and at the anode the Cl^- is discharged

$H_3O^- + e \longrightarrow H_2O + H$ are cathode reactions

$H + H \longrightarrow H_{2(g)}$

$Cl \longrightarrow Cl + e$ are anode reactions

$Cl + Cl \longrightarrow Cl_{2\,(g)}$

$H_{2(g)}$ is given off at the cathode and chlorine gas at the anode.

The cations, present in $CuSo_4$ solution are Cu^{2+}, H_3O^+. Copper is lower than hydroden in the electrochemical series. It is discharged in preference to the hydrogen.

At the anode the anions are OH^- and SO_4^{2-}. The OH^- is much lower in the series than SO_4^{2-}. It is discharged in preference to the SO_4^{2-}. The result is deposition of copper at the cathode and liberation of oxygen at the anode.

$CU^{2+}_{(aq)} + 2e \longrightarrow Cu_{(s)}$

$4OH^-_{(aq)} \longrightarrow O_{2(g)} + 2H_2O_{(l)}$

Some more examples of electrolysis of salts are given in the table 9.1

Table 9:1 Products at the electrodes during the electrolysis of some salt

Salt	*Type of electrode*		*Product at the*	
	cathode	*anode*	*cathode*	*anode*
• Molten sodium chloride	Carbon	Carbon		
• Very dilute sodium chloride solution	Carbon	Carbon	$H_{2(g)}$	$O_{2(g)}$
• Concentrated sodium chloride solution	Carbon	Carbon	$H_{2(g)}$	$Cl_{2(g)}$
• Concentrated sodium hydroxide solution	Platinum or carbon	Platinum or Carbon	$H_{2(g)}$	$O_{2(g)}$
• Dilute sodium hydroxide solution	Carbon	Carbon	$H_{2(g)}$	$O_{2(g)}$
• Dilute tetraoxosulphate (vi) acid	Carbon	Carbon	$H_{2(g)}$	$O_{2(g)}$

Using the information provided in the table, explain why the concentrations of $H_2SO_{4(aq)}$ and $NaOH_{(aq)}$ increase during electrolysis of dilute $H_2SO_{4(aq)}$ and $NaOH_{(aq)}$ respectively.

9.3 Redox Reactions

9.3.1 Oxidation and reduction

Oxidation is defined as:

(a) addition of oxygen to a substance.

(b) removal of hydrogen from a substance.

(c) loss of electrons.

(d) increase in oxidation number.

Oxidation numbers are numbers given to elements in the free and combined states according to a set of rules. Oxidation number allows us to keep track of electrons during chemical reactions. It is the charge that an atom of the elements would have if both electrons of each bond were assigned to the more electronegative element. Elements are assigned zero oxidation numbers in their elemental forms.

Reduction is also defined as

(a) removal of oxygen

(b) addition of hydrogen

(c) gain of electrons

(d) decrease in oxidation number

Oxidation and reduction reactions always occur together. Recall that during electrolysis oxidation occurs at the anode and reduction at the cathode. The substance that accepts electrons is the oxidizing agent while the one that donates the electrons is the reducing agent.

9.3.2 Assignment of oxidation number

Oxidation is defined in the last section. Now we want to recall the rule for assigning oxidation numbers and use same to assign oxidation numbers to some elements in compounds.

The rules are:

(i) all atoms of elements in uncombined state have zero oxidation number. e.g. Na in $Na_{(s)}$, H in $H_{2(g)}$.

(ii) in simple ions, e.g Na^+, Zn^{2+} Al^{3+} etc, the oxidation number is the charge on the ions.

(iii) the sum of the oxidation numbers must add up to zero for compounds and to the net charge on the ions if it is a complex ion

(iv) hydrogen and all alkali metals have +1 oxidation number in their compounds. Hydrogen has a –1 oxidation number in hydrides

(v) the oxidation number of oxygen is –2 in its compound except in peroxide where it is –1.

We now want to apply the rules to simple examples. $H_{2(g)}$ (H), NaCl(Cl), H_2SO_4(S), $HClO_4$(Cl) and SO_3^{2-} (S). Assign oxidation numbers to the elements in bracket in the given compounds or ions. For H_2, the oxidation number of H is zero (rule i)

NaCl – the rule assigns +1 to Na, Cl must therefore have an oxidation number of –1 (rule ii)

H_2SO_4(S). Let the oxidation number of S be x.

$$+2 + x - 8 = 0 \text{ (rules (iii) iv vi)}$$

$$x = +6$$

Oxidation number of sulphur in H_2SO_4 is +6. This is why the IUPAC name is tetraoxosulphate (vi) acid. Now complete by assigning oxidation numbers for Cl in $HClO_4$ and S in SO_3^{2-}

9.3.3 Redox reactions and the electrochemical cell

In the previous section you learnt that oxidation-reduction reactions occur together and they involve loss and gain of electrons respectively. It is possible to have an arrangement in which the electron formed by the oxidation process are made to flow through a conductor (copper wire) to the reduction site. This flow of electrons will constitute an electric current a demonstration of the conversion of chemical energy to electrical energy. This type of arrangement is called an **electrochemical cell** or **galvanic cell**. An example of a galvanic cell is the Daniel cell which makes use of the following redox reaction.

$$CuSO_{4(aq)} + Zn_{(s)} \longrightarrow ZnSO_{4(aq)} + Cu_{(s)}$$

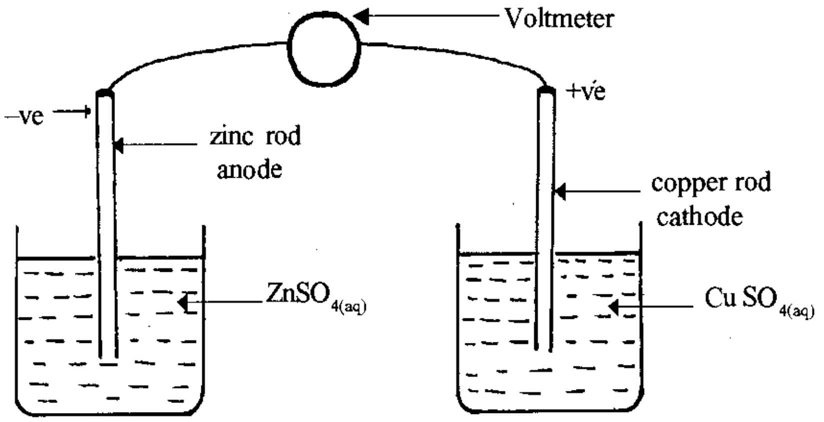

Fig 9.3 Electron transfer in a redox reaction

For a 1.0 mol dm^{-3} solutions of the electrolytes solutions at 298k the voltmeter will record about 1.10 volts. The reactions that occur are $Zn \longrightarrow Zn^{2+} + 2e^-$ at the anode

$Cu^{2+} + 2e \longrightarrow Cu_{(s)}$ cathode.

Note here again that oxidation is at the anode and reduction at the cathode. 1.10 volts is called the **electromotive force** (emf) of the cell. The emf is the electric potential difference between the electrodes.

9.3.4 Comparison of the electrolytic and electrochemical cells

This comparison is given in the table 9.2, the differences and similarities are highlighted.

Table 9.2: Comparison of the electrolytic and electrochemical cells

Electrolytic Cell	*Electrochemical Cell*
• Chemical decomposition occurs by passage of electricity through an electrolyte solution	Electricity is generated by chemical reaction within the cell.
• Electrical energy is converted to chemical energy	Chemical energy is converted to electrical energy
• The anode is the positive electrode	The anode is the negative electrode
• Oxidation occurs at the anode	Oxidation occurs at the anode
• The cathode is the negative electrode	The cathode is the positive electrode
• Reduction occurs at the cathode	Reduction occurs at the cathode
• Eelctrons flow from anode to cathode	Electrons flow from anode to cathode

9.4 Conclusion

The transformation of energy from electrical to chemical and vice versa has important consequences that are beneficial to humanity. The application of electrolysis are mainly in industries and natural phenomena such as corrosion. You can now understand why torch batteries supply electrical energy. You will also appreciate the importance of electrolysis when we look at the applications in the next unit.

9.5 Summary

- The transformation of electrical energy to chemical energy has been explained in electrolysis. Examples of electrolysis of salt are given.
- Redox reactions form the basis of the conversion of chemical energy to electrical.
- The electrochemical cell has been explained, compared and contrasted with the electrolytic cell.

9.6 Tutor-Marked Assignments

1.(a) Arrange the following compounds in the order of increasing conductivity. Give reasons to explain your order of arrangement.

Dilute ethanoic acid solution, distilled water, dilute trioxonitrate (v) acid solution and sugar solution. All solutions are in water.

(b) Give the oxidation number of sulphur in the following $S_{(s)}$, H_2S, H_2SO_4, SO_2, H_2SO_3, and Na_2SO_4.

2. Write the ionic equation for the reaction of zinc powder and copper trioxonitrate (v) solution

(b) State with reason which substance is

(i) oxidised

(ii) reduced

(c) Describe with a well labelled sketch the electrochemical cell that can result from above redox reaction.

9.7 References

Bajah, S. T. Teibo, B. O., Onwu G. and Obikwere A. 2002. *Senior Secondary Chemistry Textbook 2.* Lagos. Longman Publishers.

Osei Yaw Ababio (2002). *New School Chemistry* Onitsha. Africana FEP Publishers.

Unit 10

Practical Applications of Electrolysis

10.0 Introduction

The passage of an electric current through molten or aqueous solutions of electrolytes results in chemical reactions. This is electrolysis, widely used in industrial processes. The process is expensive because of the large quantities of electricity required. Despite this disadvantage it is used in electroplating, metal extraction from their ores, preparation of chemical compounds and purification of copper metal.

Corrosion of iron and steel which we call rusting is of special economic importance. In this unit corrosion will be explained using the concept of electrolysis and the methods of preventing corrosion discussed. The quantitative aspect of electrolysis will also be considered and Faraday's laws stated and applied in simple calculations.

10.1 Objectives

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

- List some applications of electrolysis.
- Explain some applications of electrolysis.
- Apply Faraday's laws to simple calculations.
- Define and explain corrosion.
- Enumerate and explain methods of preventing rusting of iron or steel.

10.2 Industrial Applications of Electrolysis

10.2.1 Purification of copper (refining)

Copper occurs naturally as the impure element. Even when produced by smelting copper pyrites ($CuFeS_2$) in a blast furnace the copper obtained is still not one hundred percent pure. The copper must be further refined for many of its industrial uses particularly in the electrical engineering industry where copper of extremely high purity is needed. The impure copper called blister copper is purified by electrolysis.

The impure copper is made the anode while the cathode is a thin sheet of pure copper. The electrolyte is copper (II) tetraoxosulphate (vi). At the cathode copper is preferentially discharged because it is lower than hydrogen on the electrochemical series. Recall that the electrochemical series is defined and used in unit 9

$$Cu^{2+}_{(aq)} + 2e \longrightarrow Cu_{(s)}$$

At the anode neither the OH^- nor SO_4^{2-} is discharged but copper goes into solution because it requires less energy than the discharge of the ions.

$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e$$

The net effect is that copper goes into solution at the anode and it is deposited at the cathode. The anode dissolves away as the copper ions go into solution. The impurities are not dissolved and fall to the base of the tank. The copper obtained is of very high purity.

10.2.2 Electroplating

Electroplating involves forming a very thin coat of one metal on the surface of another. This may be for protection or for decorative purposes. The article to be coated is made the cathode and the metal that will form the coat is made the anode. The electrolyte is a solution of the salt of the metal that will form the coat. e.g. silver plating a steel rod, the steel rod is made the cathode and pure silver is made the anode. The electrolyte is silver trioxonitrate (V) solution.

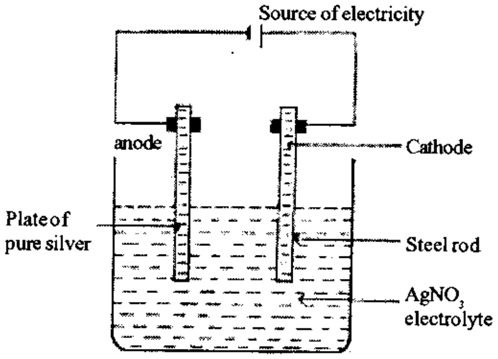

Fig. 10.1 *Silver plating a steel rod*

During electrolysis, silver is deposited at the cathode and silver goes into solution at the anode.
Cathode reaction.

$$Ag^+ + e \longrightarrow Ag_{(s)}$$

Anode reaction

$$Ag_{(s)} \longrightarrow Ag^+ + e$$

The concentration of the electrolyte remains virtually constant throughout the process. For good results, the surface of the metal to be plated must be clean and grease free. In place of silver other metals could be used. Electroplating prevents rusting and improves the appearance of the finished product.

10.2.3 Isolation of elements or extraction of ores

Reactive metals such as aluminium, sodium and potassium are prepared from their molten chloride or hydroxide by electrolysis – (you will recall that these metals are high on the electrochemical series). Oxygen and chlorine gases are also prepared by electrolysis of their aqueous sodium salts.

Aluminium finds many important uses as a structural metal because of its strength and light weight. The commercial availability of aluminium has been made possible through the process of electrolysis. The electrolytic process of extraction of aluminium makes use of a solution of aluminium oxide (alumina) in cryolite Na_3AlF_6. The electrolytic cell is an iron container lined with graphite. The graphite lining serves as the cathode and the anodes are graphite rods dipping into the electrolyte solution.
At the cathode Al is deposited

$$Al^{3+} + 3e \longrightarrow Al_{(s)} \text{ reduction.}$$

At the anode oxygen gas is liberated

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

$$O + O \longrightarrow O_2$$

The electrolyte must be kept at very high temperatures (950°C) by heating electrically. This process is therefore very expensive.

10.2.4 Preparation of sodium hydroxide

Sodium hydroxide is an important raw material in many industries. The soap, paper and chemical industries and many other use sodium hydroxide. Sodium hydroxide is manufactured industrially by the electrolysis of brine using inert electrodes

$$NaCl_{(aq)} \longrightarrow Na^+ + Cl^-$$
$$H_2O \longrightarrow H^+ + OH^-$$

At the cathode $H_{2(g)}$ is liberated and at the anode $Cl_{2(g)}$, is given off. The net effect is that the brine solution becomes more and more alkaline. The net reaction is the formation of sodium hydroxide from brine.

10.3 Quantitative Electrolysis

The amount of products liberated or deposited at the electrodes during electrolysis is quantified and compared using Faraday's laws of electrolysis. Consider an electrolysis process in which silver ions are discharged

$$Ag^+ + e \longrightarrow Ag_{(s)}$$

For a mole of silver to be deposited, it would mean that a mole of silver ions have picked a mole of electrons. The electronic charge is 1.602×10^{-19} coulomb (Recall Millikans oil drop experiment). For 1 mole of electron the total charge is computed from the product of the electronic charge and Avogadro's constant. This quantity of charge that deposits a mole of Ag^+ and any other monovalent ion at the electrode is called the Faraday (F) after Michael Faraday who first noted this relation.

$F = Ne$ N - Avogadro constant

$= 6.023 \times 10^{23} \times 1.602 \times 10^{-19}$ e – electronic charge

≈ 96500 coulombs (C) – To discharge a mole of a divalent ion at the electrode, two Faradays of charge are required and for a trivalent ion, three Faradays. This can be applied to both anions and cations and it is an application of the mole concept in electrolysis.

Faraday's laws are two. The first law states:

The amount of substance deposited or liberated at the electrodes during electrolysis is directly proportional to the quantity of electricity passed.

$m = Eit$ m – mass deposited (g)

E – electrochemical equivalent of the element

i – current (amperes)

t - time (seconds)

E is a constant for the particular ion discharged and is usually very small

For silver $E = 1.118 \times 10^{-3} g\,C^{-1}$ and

For hydrogen $E = 1.045 \times 10^{-5} g\,C^{-1}$

For many calculations E is not required. The mole concept is used when the faraday constant is given.

Example

Calculate the amount of silver deposited by the passage of a current of 2.0 amp for 2 hours through a silver voltameter, What volume of oxygen (STP) will be liberated by the same quantity of electricity?

$F = 96500C$ Ag = 108

Solution

$Ag^+ \quad + e \quad Ag_{(s)}$

1 F will deposit 108g silver

Quantity of electricity

$Q = it$

$Q = 2.0 \times 2 \times 60 \times 60$

$= 1 4400 C$

96500C deposits 108g

$$14400C \text{ will deposit } \frac{14400}{96500} \times 108$$

$= 16.1 g$

For the hydrogen voltameter

$2H^+ . + 2e \longrightarrow H_{2(g)}$

2 x 96500 C liberates 1 mole H_2 = 22.4dm^3 at STP

$$14400 \text{ C will liberate } \frac{14400}{2 \times 96500} \times 22.4 \text{ dm}^{-3}$$

$= 1.67 \text{ dm}^3$

Faraday's second law allows for comparison of the relative amounts of elements liberated or deposited by the same quantity of electricity. **The law states that when the same quantity of electricity is passed through solutions of different electrolytes, the amount in moles of the elements is inversely proportional to the charges on the ions.**

Let us consider the discharge of

Ag^+, Ca^{++}, Na^+ and Al^{3+} by 1 Faraday of electricity.

For Ag^+, 1 mole $Ag_{(s)}$ is deposited

For Ca^{2+}, 0.5 (½) mole $Ca_{(s)}$ is deposited

For Na^+, 1 mole $Na_{(s)}$ is deposited

For Al^{3+}, 0.33 (1\3) mole is deposited

The amount in moles is inversely proportion to the charge on the ion.

Example

The passage of 2.0 amp current for sometime through a silver voltameter deposits 8.05 g of silver.

Calculate the mass of copper that will be deposited by the same quantity of electricity. (Ag = 108Cu = 64)

Solution

For silver

$Ag+ \quad + \quad e \longrightarrow Ag_{(s)}$ univalent

For $Cu^{2+} \quad + \quad 2e \longrightarrow Cu_{(s)}$ divalent

$$\text{mole Ag deposited} = \frac{8.05}{108}$$

$= 7.45 \times 10^{-2}$

mole Cu deposited $= \frac{7.45}{2} \times 10^{-2}$

$= 3.725 \times 10^{-2}$

mass of Cu deposited $= 3.725 \times 10^{-2} \times 64$

$= 2.38g$

10.4 Corrosion of Metals

In the previous unit the electrochemical series is used to explain the preferential discharge of ions during electrolysis. Many metals react with water and oxygen in the air and are said to corrode. Corrosion can be related to the electrochemical series. The very reactive metals, sodium and potassium react rapidly with oxygen and water and are usually stored in liquid paraffin to prevent their corrosion.

Iron in the form of steel is an important engineering material. It is used in the construction of bridges, fly overs and store houses. It is also used in the automobile industry. Iron and steel are very prone to corrosion. For iron and steel this is called rusting. Rusting is of special economic importance. The mechanism and prevention of corrosion is discussed in the next section.

10.5 Rusting of Iron

Rusting is caused by the action of oxygen and water vapour on iron or steel. Rust is hydrated iron (III) oxide with varying composition and can be expressed as $xFe_2O_3 . yH_2O$. Iron does not rust in the absence of oxygen and moisture. An iron nail put in a test tube where air and moisture are excluded will not rust. Rusting is electrolytic in character and is accelerated by the presence of dissolved salts in solution. This is why iron or steel parts of machineries rust faster near the sea. Where the atmosphere is polluted with gases like CO_2, H_2S, SO_2 which can dissolve and increase electrolytic conduction, the rate of rusting is also accelerated.

10.6 Methods Used to Prevent Corrosion

Many methods are used to prevent iron and steel from rusting. All methods attempt to prevent air and moisture from getting to the iron or steel surface. The methods are

(a) Painting

This can be by spraying, dipping or brushing. Provided the paint surface is not broken the iron will not rust.

(b) Plastic Coating

The plastic layer prevents oxygen and water from getting to the iron surface. This type of protection is used for draining racks in the kitchen. When the plastic breaks rusting sets in.

(c) Greasing or Oiling

This will also prevent contact with air and water. It is a very good method for treating moving parts that are made of iron.

(d) Galvanizing

The iron product is coated with zinc. The zinc coating can be by spraying or dipping. If the zinc coating is scratched rusting will not take place, instead of iron to rust, it is the zinc that is affected because it has a higher discharge potential than iron.

$$Fe^{2+} + 2e \longrightarrow Fe_{(s)} \quad E^{o} = -0.44v$$

$$Zn^{2+} + 2e \longrightarrow Zn_{(s)} \quad E^{o} = -0.76v$$

(e) Coating with tin

This type of coating is used for food cans. Zinc coating cannot be used because zinc is poisonous. If the tin coating is scratched and the bare steel is exposed rusting will take place. This is because the discharge potential of iron is higher than that of tin.

$$Fe^{2+} + 2e \longrightarrow Fe_{(s)} \quad E^{o} = -0.44v\ Fe_{(s)}$$
$$Sn^{2+} + 2e \longrightarrow Sn_{(s)} \quad E^{o} = -0.14v\ Sn_{(s)}$$

(f) Sacrificial cathodic protection

This is very similar to what happens when iron is galvanized. This method is used for protecting ship body from rusting. In the presence of dissolved salt and gases in sea water, rusting is much faster. To prevent ship body from rusting, blocks of a suitable metal are strapped to the steel body of the ship. The metals used are more reactive than steel and are sacrificed in place of the iron.

(g) Electroplating

Using electrolysis a thin coating of nickel can be deposited on the iron. This may be followed by another thin layer of chromium to give a nice shining surface e.g. car'bumpers and electric kettles.

10.7 Conclusion

Though electrolysis process is an expensive one, it is the only method of extracting reactive metals from their salts. e.g. Na, K, and Al. It is a method used to obtain high quality copper for electrical engineering purposes. Metal surfaces are protected from corrosion by electroplating and finished metal products have been made more appealing by electroplating.

Corrosion is of economic importance and the methods of prevention are many. The quantitative aspect of electrolysis as given by Faraday's laws allows for calculations of expected yields from electrolysis processes.

10.8 Summary

- The application of electrolysis are discussed and explained.
- The laws of electrolysis as given by Faraday are used in sample calculations
- The mole concept is introduced and used.
- Corrosion of metals is general and rusting of iron in particular are discussed.
- Methods of preventing rusting of iron are enumerated and explained.

10.9 Tutor-Marked Assignments

1. By means of an appropriate example in each case, explain the following application of electrolysis.
   (a) purification of metals
   (b) electroplating.
2. The passage of a current 3.0 amp for 6.0 hours through a water voltameter liberates 3.76 dm^3 of O_2 at the anode at (S.T.P.) Determine Faraday's constant.

10.10 References

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Unit 11

Carbon and Its Compounds

11.0 Introduction

Carbon is a non-metal that has been known for a very long time under the names charcoal, soot and diamond. It is the sixth most abundant element in the universe. Carbon exists naturally in the elemental states as diamond, graphite and coal; and in the combined state as petroleum, wood, natural gases and mineral deposits. The common mineral deposits of carbon are the metallic trioxocarbonates (IV) such as limestone (calcium trioxocarbonates (IV) and dolomite (Magnesium trioxocarbonates (IV)). Carbon as carbon (IV) oxide, CO_2, constitutes 0.03% of the atmosphere. The carbon found in coal, petroleum, wood and natural gases are used essentially as source of fuels for energy supply.

Carbon is also an essential constituent of all living things. The study of the millions of carbon compound in living (organic) organism forms a separate branch of chemistry known as 'organic chemistry'. Organic compounds will be treated in separate units of this programme. Our concern in this unit is the chemistry of carbon as an element and its non-organic compound such as the oxides, sulphides, carbides, trioxocarbonates (IV) and hydrogen trioxocarbonates (IV) which are in the domain of in organic chemistry.

You will recall that carbon has six electrons with an electronic configuration of $1s^2\ 2s^2\ 2p^4$ and is therefore placed in group 4 and period 2 of the periodic Table. The energy required to lose its four outermost electrons or gain four electrons to form a stable configuration is enormous, therefore carbon combines essentially by forming four covalent bonds with other elements. Chemically, carbon is not very reactive element and that is why it exist naturally as elemental carbon in various forms e.g. diamond, graphite, coal, charcoal and carbon black.

11.1 Objectives

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

- Recognise the uniqueness of carbon as an element.
- Define allotropy and describe the various allotropic forms of carbon.
- Enumerate the important inorganic compounds of carbon.
- Describe the characteristics of some carbon compounds.
- Explain the carbon cycle.

11.2 Allotropes of Carbon

The existence in the same physical state of two or more structural form of an element is known as allotropy. Carbon exhibit allotropy. Diamond and graphite are two allotropic forms of crystalline carbon. The others like coal, coke, charcoal, lamp-black, sugar charcoal and animal charcoal are amorphous or non-crystalline forms of carbon.

11.2.1 Diamond

Diamond exists naturally in South Africa, Brazil, India, and Venezuala. It is the purest form of naturally occurring carbon and is commonly obtained as a colourless solid, which can be transformed into brilliant gem. The structure of diamond consist of an infinite array of carbon atoms covalently bonded. The diamond crystal is octahedral in shape.

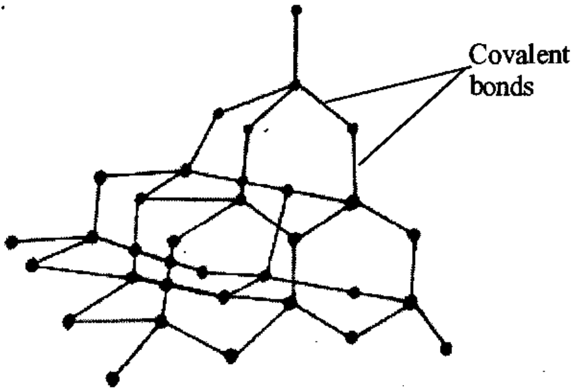

Fig. 11.1 The Structure of Diamond

The network structure gives diamond its great strength and high melting temperature. Diamond is the hardest substance known. It is a poor conductor of heat and electricity. Diamond is resistant of chemical attack. Since diamonds are dense and hard, they are used industrially in drills for mining, as abrasives sharpen very hard tools, and for cutting glass and metals. They are also used as pivot supports in precious instruments and as dies for drawing wires. Its high refractive index and dispersion power give it a sparkling brilliance when it is cut and polished making it valuable as jewellery.

11.2.2 Graphite

The structure of graphite consists of hexagonal sheets of covalently bonded carbon atoms. The sheets are held together by weak intermolecular forces in parallel layers. Graphite occurs naturally as an opaque black solid called plumbago, which is formed by the action of volcanic heat on coal deposits. It is found as deposit in Austria, China, West Germany, Madagascar and Srilanka.

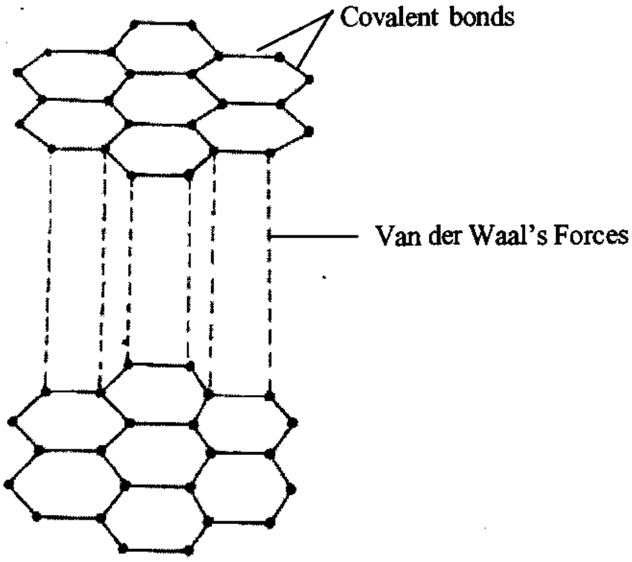

Fig 11.2 The Structure of Graphite

Graphite can also be artificially produced by heating coke at a high temperature in an electric furnace.

Because graphite is in sheets, it is soft and slippery. Although it has a high melting point, it is less dense than diamond. Graphite is relatively inert chemically but can be oxidized under suitable conditions. Unlike diamond, graphite is a good conductor of electricity because of the presence of mobile electrons within the sheets. The electrons exist since only three of the four valence electrons of each carbon atom in the graphite crystal are involved in bond formation.

Graphite is an excellent dry lubricant. This is because its layered structure allows one layer to slide over another easily. Unlike oil, it is non volatile and not sticky. It is usually used on bicycle chains and for the bearings of some motor cars. When mixed with oil it forms a high temperature lubricant. Being a good conductor of electricity and is often used as electrodes in electroplating and batteries. A non-conductor can be made conductive by coating it with graphite. Because graphite is soft and marks paper, it used to make pencils. It is used as black pigment in paint.

11.2.3 Amorphous (or non-crystalline) carbon

Carbon exists in several other forms which have no definite crystalline structure. They are not considered as true allotropes of carbon. Apart from coal, which is naturally occurring, all the other amorphous forms of carbon can be prepared in various ways.

(a) Coal was formed from vegetation protected from complete decay by water-washed earth deposit. Decomposition occurred gradually under pressure and in the absence of air. Carbon (IV) oxide, methane and water were liberated, leaving behind a material that contained a very high percentage of carbon. During this process of carbonization, the vegetable material was converted in stages into peat, lignite (or brown coal), bituminous (or soft) coal, and finally anthracite (or hard coal) which is about 95% pure carbon. Impurities present may include nitrogen, sulphur and phosphorus. Coal is used mainly as a fuel to generate power for steam engines, factories and electrical plants. It is also used for making various chemicals e.g. benzene, methane. Nigeria has a large coal deposit in Jos, Plateau State and Enugu, Anambra State. There are large lignite deposits in Onitsha and Asaba.

(b) Coke is obtained by heating bituminous coal to very high temperatures in the absence of air to burn off the volatile constituents. This process is referred to as the destructive distillation of coal. Coke is used mainly as a fuel as it burns with practically no smoke and leaves very little residue. It is an important industrial reducing agent, used in the extraction of metals, e.g. iron from their ores. It is also used in the production of gaseous fuels, like water gas and producer gas and for the manufacture of graphite, calcium carbide, silicon carbide and carbon (IV) sulphide.

(c) Carbon black (soot) is made by heating carbon containing materials in a limited supply of air to give finely divided particles of carbon. Lamp-black is obtained from vegetable of lamp oils, while carbon black itself obtained from coal gas, natural gas or fuel oils. Carbon black is used in manufacturing tuber tyres, black shoe polish, printer's ink, typewriting ribbons and carbon paper.

(d) Charcoal can be made by burning wood, nut shells bones, sugar and even blood. Wood charcoal, the most common, is prepared by burning wood in a limited supply of air.
Sugar charcoal is formed when sugar is dehydrated i.e. 'the hydrogen and oxygen it contains are removed in the form of water either by burning the sugar in a limited supply of air or by the action of concentrated tetraoxosulphate(VI) acid. It is the purest form of amorphous carbon.
Animal charcoal is produced when bones and animal refuse are burnt in limited supply of air. Charcoal has a very porous structure and allows molecules of gases and dyes to adsorb or adhere to its internal surfaces. Thus, it is a good adsorbent particularly when activated. Wood charcoal is used in gas-masks for adsorbing poisonous gases. It is also used for the purification of the noble gases and the recovery of industrial solvents. Similarly, animal charcoal, is used in removing the brown colour from crude sugar and colourizing petroleum jelly. Like coal, wood charcoal is also used mainly as a domestic fuel in Nigeria.

11.3 General Properties of Carbon

(a) All the different allotropes of carbon are black solids or greyish-black except diamond which is colourless when pure.

(b) All the allotropes have high melting point, about 3,500°C.

(c) Carbon is insoluble in all common solvents e.g. water, petrol, alkalis, acids and carbon (IV) sulphide. This characteristic explains why carbon deposit in motor engines have to be mechanically removed-decarbonization of motor engines.

11.4 Chemical Properties of Carbon

Carbon is not a very reactive element. Its compounds are formed by covalent bonding and most of them are stable. Carbon forms single or multiple covalent bonds with itself and other elements such as hydrogen, oxygen, nitrogen and sulphur. The unique ability of carbon to form long chains and rings of carbon-carbon bonds (known as catenation) enables it to have numerous compounds. The molecules range from small to extremely large ones and most of them are organic in nature and therefore beyond the scope of this unit.

All the allotropes of carbon have similar chemical properties; however diamond and graphite are less reactive than the amorphous form.

11.4.1 Combustion reactions

Carbon burns in excess oxygen to produce carbon (IV) oxide only, although the temperature required differ for the allotropic forms.

$C(s) + O_2(g) \longrightarrow CO_2\,(g)$

When the supply of air is limited, combustion may not be complete. Carbon (II) oxide is formed instead of carbon (IV) oxide

$2C(s) + O_2(g) \longrightarrow CO(g)$

Charcoal Fires: *In countries like Nigeria and Ghana, charcoal is used extensively for making fires. As the charcoal burns, carbon (IV) oxide and carbon (II) oxide are formed at various levels inside the charcoal pot, depending on the level of oxygen supply.*

Some of the reactions involved are:

$2CO + O_2 \longrightarrow CO_2$

$CO_2 + C \longrightarrow 2CO$

$C + O_2 \longrightarrow CO_2$

The carbon (II) oxide that are not oxidized and escapes to the atmosphere is dangerous if the area around the fire is not well ventilated because the gas is poisonous.

11.4.2 Combination reactions

Carbon combines directly with certain elements such as sulphur, hydrogen, calcium and aluminium at very high temperatures usually greater than 500°C.

$C(s) + S(s) \longrightarrow CS_2(l)$ carbon (IV) sulphide

$C(s) + 2H_2\,(g) \longrightarrow CH_4(g)$ methane

$2C(s) + Ca(g) \longrightarrow CaC_2\,(s)$ Calcium Carbide

$3C(s) + 4Al(s) \longrightarrow Al_4C_3\,(g)$ aluminum carbide

11.4.3 Carbon as reducing agent

Carbon is a strong reducing agent i.e. as oxygen acceptor. It reduces the oxides of less active metals such as iron and copper; at high temperatures.

$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$

$2CuO + C \longrightarrow 2Cu + CO_2$

At high temperatures, carbon can also reduce steam to hydrogen and carbon (IV) oxide.

$C + H_2O \longrightarrow CO + H_2$

11.4.4 Reactions with strong oxidizing agents

When carbon is heated with concentrated trioxonitrate(V) acid or concentrated tetraoxosulphate(VI) acid, it is oxidized to carbon(IV) oxide.

$C_{(s)} + 4HNO_{3(aq)} \longrightarrow 2H_2O(l) + 4NO_{2(g)} + CO_{2(g)}$

$C_{(s)} + 2H_2SO_{4(aq)} \longrightarrow 2H_2O(l) + 2SO_{2(g)} + CO_{2(g)}$

11.5 Oxides of Carbon

Carbon forms two types of oxides, carbon(IV) oxide, CO_2, and carbon(II) oxide CO. Both oxides are obtainable as products of the combustion of carbon.

11.5.1 Carbon(IV) Oxide

Carbon(IV) oxide constitute about 0.03% by volume of air and is also found, in very small quantity, dissolved in water. In the earth crust, carbon(IV) oxide is found as metallic trioxocarbonates(IV) and hydrogen trioxocarbonate(IV) e.g. in limestone regions and coral reefs. Carbon (IV) oxide is very important to green plants which use it to produce food substances e.g. starch, by the process of photosynthesis.

(a) *Preparation:* Carbon(IV) oxide is prepared in the laboratory by the action of dilute hydrochloric acid or trioxonitrate(V) acid on metallic trioxocarbonate(IV) or hydrogen trioxocarbonate.

$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$

$CaCO_3 + 2HNO_3 \longrightarrow Ca(NO_3) + H_2O + CO_2$

$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$

Action of heat on metallic trioxocarbonate(IV) except those of sodium and potassium, or the hydrogen trioxocarbonates(IV) of sodium, and potassium; is also used for the production of carbon(IV) oxide

$CaCO_3 \longrightarrow CaO + CO_2$

$2NaHCO_3 \longrightarrow Na_2O + H_2O + 2CO_2$

Carbon(IV) oxide is obtained industrially as by-product in the fermentation process and manufacture of quicklime (CaO) from limestone ($CaCO_3$).

(b) *Physical properties*

(i) CO_2 is a colourless, odourless and tasteless gas.

(ii) It is about 1.5 times denser than air.

(iii) It is moderately soluble in water

(iv) It turns damp blue litmus paper red because CO_2 dissolves in water to form an acidic oxide, trioxocarbonate(IV) acid.

(v) It can readily be liquefied and solidified (-78°C). Solid CO_2 is known as cardice or dry ice.

(c) *Chemical properties*

(i) CO_2 does not burn nor does it support combustion. However burning magnesium, decomposes CO_2 leaving behind carbon deposit and magnesium(II) oxide ash.

$CO_2 + 2Mg \longrightarrow 2MgO + C$

(ii) CO dissolves in water to form trioxocarbonate(IV) acid (soda water). It is a weak acid.

$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$

(iii) CO_2 reacts directly with alkalis e.g. NaOH, to form trioxocarbonates(IV).

$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$

In the presence of excess, CO_2, the trioxocarbonate (IV) is converted to hydrogen trioxocarbonate(IV)

$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$

When CO_2 is passed through the alkali, calcium hydroxide (limewater), the lime water turns milky due to the precipitation of insoluble calcium trioxocarbonate(IV). This reaction is used to test for CO_2.

$$\underset{\text{limewater}}{Ca(OH)_2} + CO_2 \longrightarrow \underset{\text{insoluble}}{CaCO_3} + H_2O$$

However, when excess gas is bubbled, the milkiness disappears leaving a clear solution because the insoluble trioxocarbonate(IV) is converted to soluble hydrogen trioxocarbonate(IV).

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$$

(d) *Uses*

(i) Many fire extinguishers use carbon(IV) oxide to put out fires as the gas does not support combustion. Being heavier than air, it envelops the burning material and cuts off the oxygen supply. Carbon(IV) oxide is more effective than water in putting out petrol or oil fires because these materials float on water.

(ii) Carbon(IV) oxide is used in the manufacture of:
- Sodium trioxocarbonate(IV) (washing soda) by the Solvay process.
- Sodium hydrogentrioxocarbonate(IV).
- Lead (II) trioxocarbonate(IV).
- Urea and ammonium tetraoxosulphate(VI) – important fertilizers.

(iii) Yeast and baking powder are used in baking to produce carbon (IV) oxide which causes the dough to rise, making dough 'light'.

(iv) Solid carbon(IV) oxide i.e., dry ice is used as a refrigerant for perishable goods, e.g. ice-cream. On warming, it sublimes and provides a lower temperature. Gaseous carbon (IV) is used to preserve fruits. Carbon(IV) oxide is also used as a coolant in nuclear reactors.

(v) Carbon(IV) oxide is used to give carbonated (aerated) drinks a pleasant and refreshing taste e.g. Coca-cola, pepsi-cola, beer, cider, wine and champagne. 'Soda-water' drink is a solution of CO_2 gas in water under pressure.

(vi) Green plants use CO_2 during photosynthesis.

11.5.2 Carbon(II) Oxide

CO is produced by the incomplete combustion of carbon compounds, such as octane, C_8H_{18}, found in petrol.

$$2\,C_8H_{18(l)} + 17O_{2(g)} \longrightarrow 16CO_{(g)} + 18H_2O_{(l)}$$

CO occurs in traces as an impurity in the air. The percentage may increase in cities where the gas is released in the exhaust fumes of motor cars, and in industrial areas due to the combustion of fuels. It is a poisonous gas and as little as 0.5% of it in the air may lead to death. As the gas has no colour or odour, its presence is difficult to detect, so it is very dangerous.

(a) *Preparation:* Carbon(II) oxide is prepared by passing carbon (IV) oxide over red-hot carbon

$$CO_2 + C \longrightarrow 2CO$$

It can also be prepared by dehydrating methanoic acid, HCOOH, or ethanedioc acid, $C_2H_2O_4$, using concentrated tetraoxosulphate(VI) acid, which act as dehydrating agent.

$$HCOOH \xrightarrow[-H_2O]{\text{Conc. } H_2SO_4} CO$$

$$C_2H_2O_4 \xrightarrow[-H_2O]{\text{Conc. } H_2SO_4} CO_2 + CO$$

The preparation of CO must be done in a fume cupboard as the gas is poisonous.

In the latter reaction, the CO_2 is removed by passing gaseous products through concentrated sodium hydroxide.

(b) *Physical Properties*

(i) Carbon (II) oxide is a colourless, tasteless and odourless gas.

(ii) It is insoluble in water, but dissolves in a solution of ammoniacal copper (I) chloride.

(iii) It is slightly less dense than air.

(iv) It has no effect on litmus

(c) *Chemical Properties*

(i) As a reducing agent: Carbon (II) oxide is a strong reducing agent. It reduces some metallic oxides to metals and is itself oxidized to carbon (IV) oxide.

$$PbO_{(s)} + CO_{(g)} \longrightarrow Pb_{(s)} + CO_{2(g)}$$

It also reduces steam to hydrogen

$$H_2O + CO \longrightarrow CO_2 + H_2$$

(ii) .It burns in air with a blue flame to give carbon(IV) oxide

$$2CO + O_2 \longrightarrow 2CO_2$$

(iii) Carbon (II) oxide poisoning is as a result of its reaction with haemoglobin in the red blood cells and thus prevents the haemoglobin from transporting oxygen in our body. Death resulting from CO poisoning occur when the supply of oxygen to the body become inadequate because the carrier haemoglobin is not available for this purpose.

(d) *Uses*

(i) CO is used as reducing agent in the extraction of metals e.g. iron from its ores.

(ii) CO is an important constituent of gaseous fuels like producer gas ($CO + N_2$) and water gas ($CO + H_2$).

(f) *Fuel Gases*

These are gas mixtures produced by heating coke with oxygen or steam. All the raw materials coke, air and water are cheap and readily available.

(i) When hot coke combines with oxygen of the air, the product is a gaseous mixture, of one-third carbon (II) oxide and two-third nitrogen by volume, called producer gas. The formation of producer gas is exothermic.

$$\underset{\text{coke}}{2C} + \underbrace{O_2 + 4N_2}_{\text{form air}} \qquad \underbrace{\underset{\text{2 volumes}}{2CO} + \underset{\text{4 volumes}}{4N_2}}_{\text{Producer gas}} + \text{heat}$$

Producer gas has a low heating power because it contains about 67% non-combustible nitrogen and 33% carbon (II) oxide. However, it is inexpensive and is widely used to heat furnaces retorts e.g. in the manufacture of zinc, steel and glass. It is also a source of nitrogen for the manufacture of ammonia (Haber process).

(ii) When hot coke combine with steam, the product is a gaseous, mixture, of equal volumes of carbon (II) oxide and hydrogen, called water gas. The formation of water gas is endothermic.

$$\underset{\text{coke}}{C} + \underset{\text{steam}}{H_2O} \longrightarrow \underbrace{\underset{\text{1 volume}}{CO} + \underset{\text{1 volume}}{H_2}}_{\text{water gas}} - \text{heat}$$

During the process, the coke quickly cools to a temperature too low for reaction if heat is not supplied externally. Industrially both producer gas and water gas are made in the same plant, known as the producer, by passing air and steam alternately through the heated coke. The heat produced when producer gas is formed is sufficient for water gas formation.

Water gas is used to manufacture hydrogen and as an important industrial fuel (both CO and H_2 burn in air releasing a lot of heat).

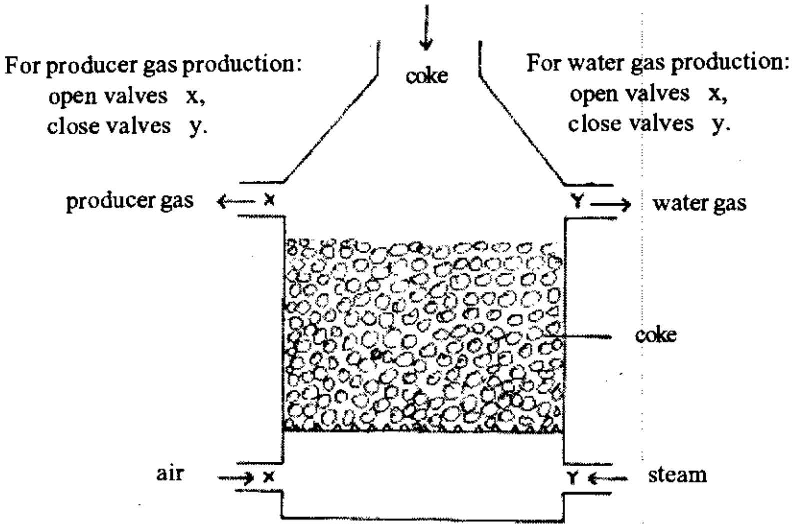

Fig. 11.3 Production of fuel gases

11.6 Trioxocarbonates (IV) and Hydrogen Trioxocarbonate (IV)

Trioxocarbonates (IV) and hydrogen trioxocarbonates (IV) are inorganic compounds of carbon. When carbon(IV) oxide dissolves in water to produce trioxocarbonates (IV) acid, which is a weak dibasic acid.

$$CO_2 + H_2O \longrightarrow H_2\,CO_3 \text{ (trioxocarbonate (IV) acid)}$$

$$H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-} \text{ weak acid}$$

The acid reacts with certain free metals e.g. zinc, metallic oxides e.g. CaO and alkalis e.g. NaOH to form trioxocarbonate (IV) salts. Metallic trioxocarbonates are usually found as natural ores or deposits e.g. limestone ($CaCO_3$), dolimite ($MgCO_3$)

$$Zn + H_2CO_3 \longrightarrow ZnCO_3 + H_2$$

$$CaO + H_2CO_3 \longrightarrow CaCO_3 + H_2O$$

$$2NaOH + H_2CO_3 \longrightarrow Na_2CO_3 + 2H_2O$$

Trioxocarbonate (IV) salts are of two types:

- the normal trioxocarbonate (IV) MCO_3 and
- the acidic hydrogen trioxocarbonate (IV) $MHCO_3$

11.6.1 Preparation of soluble trioxocarbonate (IV) salt

The water soluble trioxocarbonate (IV) salts are sodium, potassium and ammonium trioxocarbonate (IV). They are commonly prepared by passing carbon (IV) oxide through a solution of the corresponding alkali.

$$2MOH + CO_2 \longrightarrow M_2CO_3 + H_2O$$

(where M = Na, K or NH_4).

11.6.2 Preparation of insoluble trioxocarbonate (IV) salts

Most metallic trioxocarbonate (IV) are insoluble in water. The general methods for preparing them are:

(a) reaction of a base e.g. $Ca(OH)_2$; metals e.g. Zn; or metallic oxide e.g. MgO; with trioxocarbonate (IV) acid

$$Ca(OH)_2 + H_2CO_3 \longrightarrow CaCO_3 + 2H_2O$$

$$Zn + H_2CO_3 \longrightarrow ZnCO_3 + H_2$$

$$MgO + H_2CO_3 \longrightarrow MgCO_3 + H_2O$$

(b) displacement of the trioxocarbonates of the water soluble sodium trioxocarbonate e.g.

$$Na_2CO_3 + CaCl_2 \longrightarrow CaCO_3 + 2NaCl$$

$$Na_2CO_3 + 2AgNO_3 \longrightarrow 2Na_2NO_3 + Ag_2CO_3$$

The insoluble trioxocarbonates are precipitated out.

11.6.3 Hydrogen trioxocarbonate (IV) salts

These are the acid salts of trioxocarbonate (IV) acid formed when a metal or ammonium radical replaces one of the two hydrogen atoms in the molecule. They are soluble in water. However, the hydrogentrioxocarbonates (IV) of ammonium, potassium and sodium can be isolated as solids. Calcium hydrogentrioxocarbonate (IV) is responsible for hardness in water.

Hydrogentrioxocarbonates (IV) may be prepared by passing CO_2 through a solution of the corresponding hydroxides or trioxocarbonates (IV) e.g. NaOH or Na_2CO_3

$$NaOH + CO_2 \longrightarrow NaHCO_3$$

$$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$$

11.6.4 Properties of trioxocarbonates (IV) salts

(a) Action of heat – All trioxocarbonate (IV) salts except those of sodium, potassium and barium, decompose on heating to liberate carbon (IV) oxide.

$$ZnCO_3 \longrightarrow ZnO + CO_2$$

$$2Ag_2CO_3 \longrightarrow 4Ag + 2CO_2 + O_2$$

$$(NH_4)_2CO_3 \longrightarrow 2NH_3 + CO_2 + H_2O$$

All hydrogen trioxocarbonates (IV) also decompose on heating the solid or solution to give carbon (IV) oxide, water and the corresponding trioxocarbonates (IV).

$$2KHCO_3 \longrightarrow K_2CO_3 + H_2O + CO_2$$

(b) All trioxocarbonate (IV) and hydrogen trioxocarbonate (IV) salts react with dilute acids to form carbon (IV) oxide water and a salt.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

$$Ca(HCO_3)_2 + 2HCl \longrightarrow CaCl_2 + 2H_2O + 2CO_2$$

11.6.5 Uses of some important trioxocarbonate (IV) salts

(a) Na_2CO_3 is used in the manufacture of glass, soap and detergents, as well as in the production of pulp and paper.

(b) $NaHCO_3$ is used in baking powder to liberate CO_2 gas, which helps the dough to "rise" during baking. It is also used as medicine to relieve indigestion e.g. in Andrews liver salts. It is used in dry-powder fire extinguishers.

(c) $CaCO_3$ is used in the production of cement, chalk and important industrial chemicals e.g. CaO, NH_3.

11.7 Carbon Cycle in Nature

Carbon is being continuously circulated in nature by a series of changes known as the Carbon Cycle. Atmospheric carbon (IV) oxide forms the vital link between the various carbon compound in the cycle. The level of carbon (IV) oxide in the air is kept at about 0.03% by volume and this is achieved through a natural balance between its rate of formation and its rate of removal from the atmosphere.

Some of the processes that liberate CO_2 into the atmosphere are:

(a) the respiration of living organism in which glucose is converted to CO_2

$$\underset{\text{glucose}}{C_6H_{12}O_6} + 6O_2 \longrightarrow 6CO_2 + H_2O + \text{energy (respiration process)}$$

(b) Combustion of carbon containing substances e.g. petrol, wood, coal, butane gas.

$$\underset{\text{petrol}}{2C_8H_{18}} + 25O_2 \longrightarrow 16CO_2 + 18H_2O$$

(c) Decomposition of organic materials e.g. plants and animals and trioxocarbonates(IV) salts.

Some of the processes that remove CO_2 from the atmosphere are:

(i) photosynthesis in plants for the production of food

$$6CO_2 + 6H_2O + \text{energy} \longrightarrow C_6H_{12}O_6 + 6O_2 \text{ (photosynthesis process)}$$

(ii) the sea and other water bodies act as reservoirs for carbon(IV) oxide when it dissolves in them.

(iii) it is stored as part of bone, shells in living organism and in trioxocarbonate ores or deposits.

Increased human activities are upsetting the delicate natural balance that keeps the CO_2 level fairly constant in the atmosphere. These activities are

(a) an increase in the combustion of fossil fuels in industries, homes and vehicles; and

(b) deforestation so that the forest which release carbon (IV) oxide into the atmosphere are much reduced in size.

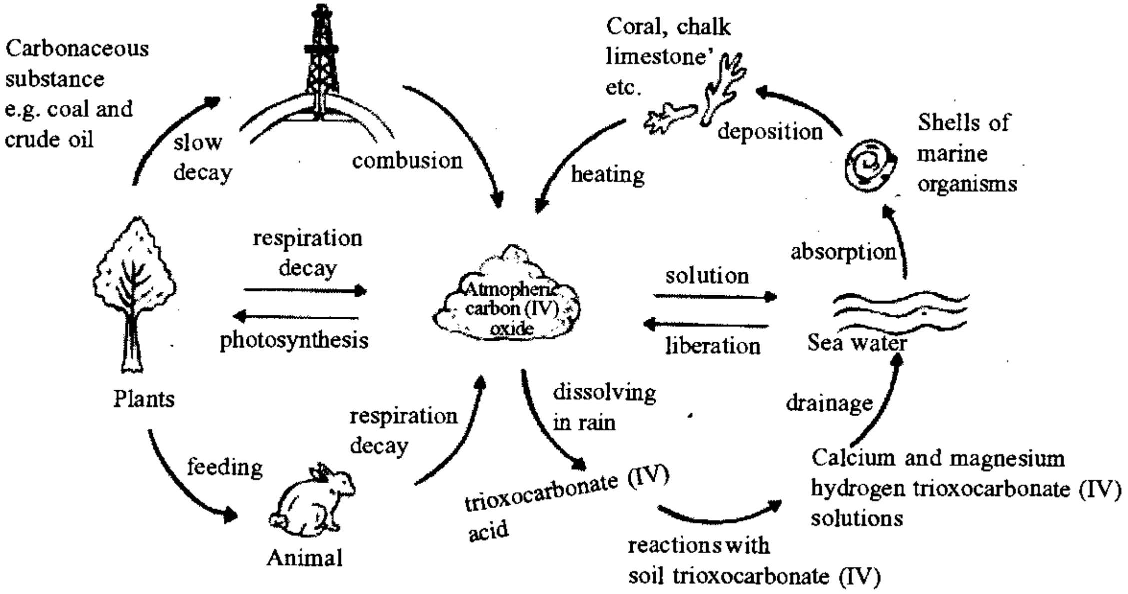

Fig. 11.4 Carbon cycle

The consequence of disturbing the CO_2 balance is the greenhouse effect, a gradual warming of our planet, which will lead to melting of the polar cap and submergence of coastal lands on earth.

11.8 Conclusion

In this unit you have learned about carbon and its inorganic compounds. You should have learnt that carbon exists in several allotropic forms and form very stable compounds in its reactions. Carbon exists naturally in the free state, and as oxides and trioxocarbonates(IV). Furthermore, you should have learnt about the delicate balance of carbon that needs to be maintained. If our earth is to remain stable.

11.9 Summary

What you have learned in this unit concerns the chemistry of carbon and its oxides and trioxocarbonates (IV). It has served to introduce you to the inorganic compounds of carbon.

11.10 Tutor–Marked Assignments

(a) Write equations to show how carbon (II) oxide is formed from (i) carbon (IV) oxide (ii) ethanedioic acid

(b) Write short note on
  (i) fuel gases,
  (ii) carbon cycle.

(c) Write the equation for the reaction if calcium trioxocarbonates
  (i) on heating
  (ii) on addition of dilute hydrochloric acid

11.11 References

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Unit 12

The Chemistry of Important Industrial Gases

12.0 Introduction

In previous units, our study of the kinetics theory of gases and the physical studies of solids and liquids have introduced you to the three states of matter. Solids and liquids are things we see around us. They are composed of molecules that are held together by forces that enable them take up definite shapes or volumes.

The presence of gases can only be inferred based on colour, odour or using our sense of feeling. This is because gas molecules have much kinetic energy and move about in all directions at great speed, hence they have no definite shape.

The atmosphere around us is filled with air, which is composed of gases, namely oxygen, nitrogen, carbon (IV) oxide and the noble gases. The sun and the stars are said to contain gases e.g. ozone, hydrogen. Gases are essential component of our existence e.g. oxygen for respiration in animals and carbon (IV) oxide for photosynthesis in plants; and are also important industrial chemicals e.g. Sulphur (IV) oxide for the manufacture of tetraoxosulphate (VI) acid; and carbon (II) oxide and hydrogen as reducing agents and fuels for some industrial processes.

This unit will be dedicated to the study of some important gases especially those required on a large scale in the industry. We shall look at the general characteristics of gases, the methods of preparation, particularly in large quantities and the several uses of the gases. The characteristics and uses of important non-gaseous compound like hydrochloric acid, trioxonitrate (V) acid and tetraoxosulphate (VI) acid; derived from these gases, will also be discussed. It is hoped that at the end of this unit, you will come to appreciate the importance of gases just like solids and liquids that we see around us.

12.1 Objectives

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

- Recall the general characteristics of all the gas treated in this unit.
- Describe the industrial preparation of all the gases.
- Enumerate the uses of all the gases.
- Describe the general characteristics, method of preparation and uses of mineral acids derived from these gases.

12.2 Hydrogen

Hydrogen is the lightest of the elements. Hydrogen constitutes about 1% of the earth crust. However, it is found free only in very small amounts (0.01%) in the atmosphere and in volcanic gases, although large amounts occur in the sun and the stars. Hydrogen is, however, widely distributed in combination with other elements e.g. in water, natural gas, petroleum. It is also a constituent of most other organic substances e.g. proteins, carbohydrates and fats, which are essential components of all living things.

Hydrogen gas is one of the most widely used gases in industry for producing fuels (e.g. kerosene, petrol etc), fertilisers, solvents, explosives and plastics. Hydrogen is an unusual element. It has a single valence electron like the Group I alkali metals, but hydrogen exists, as a diatomic gas with non-metallic properties. On the other, the hydrogen atom is one electron less than having a noble gas configuration just like the halogens in Group VII. In the periodic table, hydrogen is usually placed in Group I for convenience, although in reality can be considered to form a family of its own.

Laboratory preparation of hydrogen

Hydrogen can be prepared in the laboratory by any of these three methods, namely:

(a) action of zinc on dilute hydrochloric acid or tetraoxosulphate (VI) acid

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

(b) action of Zinc or Aluminium with Sodium hydroxide

$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$$

$$2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2$$

(c) action of iron on steam

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

12.2.1 Industrial Preparation of hydrogen

When required on a commercial level, hydrogen can be prepared by a variety of methods, of which the production from hydrocarbon-based sources has become very important.

(a) **From water gas (Bosch Process)**

Large quantities of hydrogen is prepared from cheap raw materials, namely water and coke (coal). Steam is passed over red-hot coke at about 1,200°C to give a mixture of carbon (II) oxide and hydrogen, known as water gas. The water-gas is then mixed with more steam and passed over a catalyst, iron (III) oxide or chromium (III) oxide at 450°C. The carbon (II) oxide which is a poisonous gas, in the water-gas is converted to carbon (IV) oxide with further yield of hydrogen.

$$\underset{\text{steam}}{H_2O} + \underset{\text{coke}}{C} \xrightarrow{100^0C} CO + H_2(\text{water gas})$$

$$\underbrace{CO + H_2}_{\text{water gas}} + \underset{\text{steam}}{H_2O} \longrightarrow CO_2 + 2H_2$$

The carbon (IV) oxide is removed by passing the gaseous products through water and potassium hydroxide. Any unreacted carbon (II) oxide is absorbed in an ammoniacal solution of copper (I) ethanrate.

(b) **From hydrocarbon sources**

These routes have gradually replaced the Bosch process because it utilises cheaper hydrocarbons e.g. methane, propane from natural gas and petroleum. Methane (obtained from natural gas) is mixed with steam and heated to about 900°C over a nickel catalyst. The mixture of hydrogen and carbon (II) oxide produced is known as **synthesis gas**.

$$\underset{\text{methane}}{CH_4} + \underset{\text{steam}}{H_2O} \longrightarrow \underbrace{CO + 3H_2}_{\text{synthesis gas}}$$

The 'synthesis gas' is mixed with more steam and passed over iron (III) oxide as catalyst at 450°C. This second stage is exactly the same as the water gas-steam reaction in the Bosch process.

A second industrial process for hydrogen production is to start with petroleum. The gases obtained from the oil refining process, mainly hydrocarbons, are treated with steam in the presence of nickel catalyst.

$$\underset{\substack{\text{propane}\\\text{(from}\\\text{Petroleum)}}}{C_3H_8} + 6H_2O \xrightarrow[\text{heat}]{\text{Nickel}} 3CO_2 + 10H_2$$

The carbon (IV) oxide is removed as in the Bosch process.

(c) **By electrolysis**

Hydrogen is obtained as a by-product in the electrolysis of brine for the manufacture of sodium hydroxide and chlorine.

12.2.2 Uses of hydrogen

(a) In the manufacture of ammonia in the Haber process.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

The ammonia is converted to trioxonitrate (V) acid, which is then used in the manufacture of fertilizers, explosives, plastics, drugs and dyes.

(b) Hydrogen is used to harden (i.e. hydrogenation) vegetable oils (e.g. palm oil, cotton seed oil, corn oil, soyabean oil) to give solid fats. The solid fats are used for the soap and candle industries and as margarine for food.

(c) Catalytic hydrogenation of coal produces a petroleum like oil mixture called **synthetic petroleum,** which can be fractionally distilled to obtain petrol, lubricants etc. This petrol is more expensive to produce than the 'ordinary petrol' and is used only in countries with plenty of coal but no petroleum.

(d) Hydrogen is a constituent of many gaseous fuels e.g. water gas and coal gas. Liquid hydrogen is used as a rocket fuel.

(e) Hydrogen releases a lot of heat when it burns hence it is used in oxy-hydrogen flames to produce high temperatures of 4,000 to 5,000°C. This flame is used in the welding of aluminium or high-chromium/iron alloys.

12.3 Oxygen

Oxygen is the life-sustaining gas. Oxygen gas constitutes, about 21% by volume of the atmosphere and is reasonably soluble in water to support marine life. It is by far the most abundant element on earth and about 60% of all atoms in the earth's crust are oxygen atoms.

Oxygen in the atmosphere is being consumed by the respiration process however the percentage remains fairly constant due to the process of photosynthesis, whereby green plants release oxygen back to the atmosphere.

The oxygen atom, with an atomic number of 8, has 6 electrons in its outer orbital and is in Group VI of the periodic table. Oxygen is a very active element and therefore does not exist in the elemental form but form a variety of ionic (e.g. MgO) and covalent (e.g. O_2 and H_2O) compounds. Oxygen gas supports the combustion of many substances. Non-metals like, carbon, sulphur and phosphorus burn in oxygen to form acidic oxides.

$$C + O_2 \longrightarrow CO_2$$
$$S + O_2 \longrightarrow SO_2$$
$$4P + 5O_2 \longrightarrow 2P_2O_5$$

Metals like sodium, calcium and magnesium burns in oxygen to form basic oxides

$$4Na + O_2 \longrightarrow 2Na_2O$$
$$2Ca + O_2 \longrightarrow 2CaO$$
$$2Mg + O_2 \longrightarrow 2MgO$$

Laboratory preparation of oxygen

Oxygen gas is prepared in the laboratory by two methods namely:

(a) Thermal decomposition of salts rich in oxygen e.g. $KClO_3$;

$$2KClO_3 \xrightarrow[\substack{MnO_2\\ \text{catalyst}}]{\text{heat}} 2KCl + 3O_2$$

(b) Decomposition of peroxides e.g. H_2O_2

$$2H_2O_2 \xrightarrow{\text{heat}} 2H_2O + O_2$$

12.3.1 Industrial preparation of oxygen

The principal source of oxygen is air, which is a mixture of gases. The efficient industrial process for obtaining oxygen from air is a two-stage process

(a) **Liquefaction of air**

Air, in its natural form, is filtered to remove dust and then passed through sodium hydroxide solution to remove carbon (IV) oxide present in air. It is then compressed to a pressure of about 200atm, cooled and allowed to escape rapidly through a fine jet into an expansion chamber. The sudden expansion further cools the air. The cooled air is used to cool the air, coming into the expansion chamber. When the cold, compressed air coming into the expansion chamber is cold enough, liquefaction occurs and liquid air is obtained.

(b) **Fractional distillation of liquid air**

The liquid air obtained is then passed into a fractionating column for distillation. Nitrogen, which is more volatile than oxygen, distills out first, at a temperature of - 196°C and is collected as liquid nitrogen. At a temperature of -183°C, the oxygen distills out and is collected as liquid oxygen. Liquid oxygen is stored in strong steel cylinders until when it is required for use.

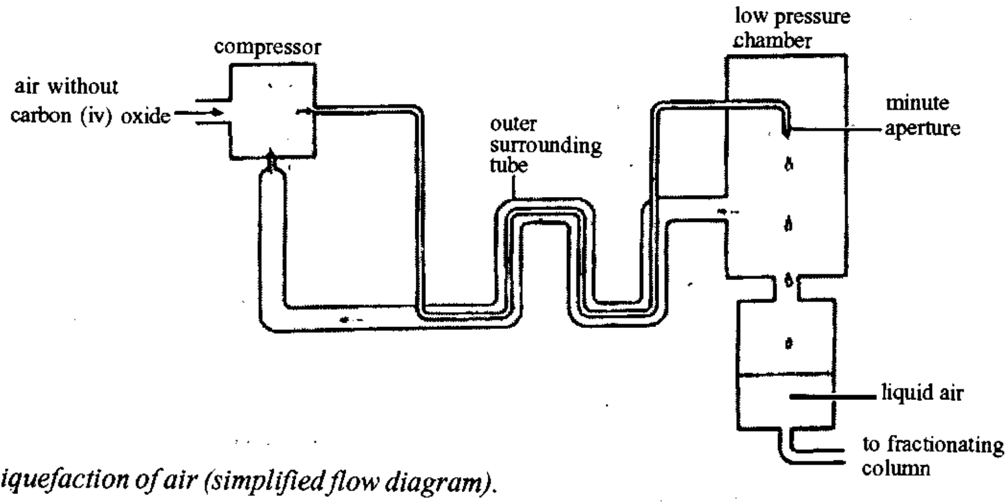

Fig 12.1 Liquefaction of air (simplified flow diagram).

12.3.2 Uses of oxygen

Naturally, oxygen is used to sustain life, as oxygen gas for respiration, and constituent of water and several biologically important molecules e.g. carbohydrates proteins, fats etc. In addition, oxygen is useful in many other ways.

(a) Oxygen is used to aid breathing by hospital patients with respiratory problems and those in surroundings with little or no air e.g. high-altitude, pilots, high-mountain climbers and deep-sea divers.

(b). Because oxygen readily supports combustion, it is used in oxy-hydrogen and oxy-acetylene flames to obtain high temperatures for welding purposes.

(c) Liquid oxygen and fuels are used as propellants for space rockets.

(d) Oxygen is used in the steel industry for the removal of carbon, sulphur and phosphorus impurities from pig iron.

(e) Oxygen is used in the manufacture of important chemicals such as tetroxosulphate (VI) acid, trioxonitrate (V) acid and ethanoic acid.

12.4 Nitrogen

Nitrogen exists mainly in air and is the most abundant element in air as it constitutes 78% of the earth's atmosphere. Like oxygen, it is one of the most important substances on earth, as it is an essential element of every living thing. Specifically, it is part of the protoplasm, the substance of living cell and of proteins, the building blocks of living things.

Nitrogen, as the diatomic molecule, is very stable and relatively inert. Its presence in air in this form is very important because it dilutes the oxygen to the point where combustion, respiration and oxidation occur reasonably slow in nature. Otherwise ignition and fire may occur indiscriminately. The inertness of nitrogen is also utilized in industry as some drugs and goods are packaged under nitrogen to prevent oxidation. Nitrogen gas is used as one of the gases to fill electric light-bulbs because it does not react with the tungsten filament, even when hot.

In the combined form, nitrogen occurs abundantly in the earth's crust as trioxonitrate (V) salts and in organic matter such as protein, urea and vitamin B compounds. Plants obtain their proteins by absorbing soluble trioxonitrate (V) salts through their roots. As plants remove nitrogen from the soil to make proteins, the soil becomes infertile and the trioxonitrate (V) salts are replaced by using nitrogen fertilizers such as ammonium trioxonitrate (V) and diammonium tetraoxosulphate (VI).

Laboratory preparation of nitrogen

Nitrogen is prepared in the laboratory by several methods.

(a) From air, by removing the other constituents of air : Carbon (IV) oxide and oxygen are removed by passing air through sodium hydroxide and heated copper turnings respectively. The nitrogen obtained by this method contains about 1% by volume of rare gases as impurities and is denser than pure nitrogen.

(b) Decomposition of ammonium dioxonitrate (III), NH_4NO_2: Thermal decomposition of this unstable salt solution made by mixing ammonium chloride and sodium dioxonitrate (III) in solution, gives nitrogen.

$$\begin{array}{lcl} NH_4Cl + NaNO_2 & \longrightarrow & NH_4NO_2 + NaCl \\ & & \quad \big\downarrow \text{heat} \\ & & N_2 + 2H_2O \end{array}$$

(c) From ammonia : Nitrogen is liberated when ammonia is oxidised by hot copper (II) oxide

$$2NH_3 + 3CuO \longrightarrow 3Cu + 3H_2O + N_2$$

12.4.1. Industrial preparation of nitrogen

Nitrogen is manufactured by the fractional distillation of liquid air as described in section 12.3.1 of this unit. The nitrogen distilled out at - 196°C; however the nitrogen so obtained contains about 1% argon and oxygen. The oxygen is removed by passing the mixture over heated copper. Nitrogen is stored in steel cylinders and sold as liquid nitrogen or as the compressed gas.

12.4.2 Uses of nitrogen

(a) Nitrogen is used in the manufacture of ammonia and thence trioxonitrate (V) acid and trioxonitrate(V) fertilisers. Ammonia is manufactured industrially by the Haber process - direct combination of hydrogen and nitrogen (as described in section 12.2.2 of this unit). Most of the ammonia is used to make nitrogen fertilizer e.g. diammonium tetraoxosulphate (VI) and ammonium trioxonitrate (V).

(b) Liquid nitrogen is used as a cooling agent

(c) Because of its inert nature, nitrogen is used

- as a carrier gas in gas chromatography
- in industrial processes involving easily oxidizable chemicals e.g. metal transistors.
- as preservative to prevent rancidity (due to the oxidation of fats) in packaged foods.

12.5 Chlorine

Chlorine is the most important member of the halogen family found in Group 7 of the Periodic Table. Each halogen atom has seven valence electrons and are all very reactive non-metals. Due to their reactive nature, the halogens are dangerous and so are not found free in nature, but are usually found combined with metals. Chlorine is a greenish yellow gas. It is usually found in nature in the combined form as chlorides. The most abundant of these is sodium chloride or common salt, which is found both in the sea and as salt deposits. Sea water containing high concentration of sodium chloride is called brine.

Laboratory preparation of chlorine

Chlorine is prepared in the laboratory by the oxidation of concentrated hydrochloric acid with a strong oxidising agent such as manganese (IV) oxide, potassium tetraoxomanganate (VII) or lead (IV) oxide.

$$4HCl + MnO_2 \xrightarrow{heat} MnCl_2 + 2H_2O + Cl_2$$

$$KMnO_4 + 16HCl \longrightarrow MnCl_2 + KCl + 8H_2O + 5Cl_2$$

Industrially, chlorine is manufactured by the electrolysis of brine or the chlorides of molten sodium, magnesium or calcium. This process has been discussed extensively in the unit on electrolysis.

Chlorine is widely used as

(a) a bleaching agent for cotton, linen and wood-pulp.

(b) a germicide in the sterilization of water for domestic and industrial use and in the treatment of sewage.

(c) in the manufacture of organic solvents (e.g. trichloromethane, $CHCl_3$; tetrachloromethane, CCl_4).

- chloroethene (use for making polychloroethene, PVC, plastic);
- bleaching agents (e.g. bleaching powder and sodium oxochlorate (I) use in dye works and (laundries);
- potassium trioxochlorate (V): use for making matches and fireworks; and sodium trioxochlorate (V); a weed killer
- hydrochloric acid.

12.6 Oxides of Sulphur

There are two oxides of sulphur, sulphur (IV) oxide and sulphur (VI) oxide; both of which are gases.

12.6.1 Sulphur (IV) oxide

Sulphur (IV) oxide is often found in volcanic gases coal, which contains sulphur in the combined form, produces sulphur (IV) oxide when burned. The presence of large amounts of sulphur (IV) oxide in the atmosphere is one of the major causes of **acid rain.**

Sulphur (IV) oxide is produced industrially by burning sulphur or metallic sulphides in air or oxygen.

$$S + O_2 \longrightarrow SO_2$$

$$FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

Sulphur (IV) oxide is a strong reducing agent, in the presence of water, due to the formation of the trioxosulphate (IV) ion, SO_3^{2-}, which readily donates electrons to an oxidizing agent e.g. tetraoxomanganate (VII) ion MnO^-_4, and heptaoxodichromate (VI) ion; $Cr_2O_7^{2-}$

$$SO_2 + H_2O \rightleftharpoons H_2SO_3 \rightleftharpoons 2H^+ + SO_3^{2-}$$

It decolurises an acidified $KMnO_4$ solution by reducing it to manganese (II) tetraoxosulphate (VI).

$$2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + H_2SO_4$$

It changes the colour of acidified $K_2Cr_2O_7$ solution from reducing orange Cr (VI) to green Cr (III).

$$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

A solution of sulphur (IV) oxide in water bleaches both natural and artificial dyes; because of reducing power.

$$\text{Dye} + SO_2 + H_2O \longrightarrow (\text{Dye-O}) + H_2SO_4$$

In the presence of a stronger reducing agent e.g. hydrogen sulphide or carbon; sulphur (IV) act as oxidising agent

$$SO_2 + 2H_2S \longrightarrow 2H_2O + 3S$$

$$SO_2 + C \longrightarrow CO_2 + S$$

12.6.2 Uses of sulphur (IV) oxide

(a) Its most important use is in the manufacture of sulphur (VI) oxide which is the precusor compound for the manufacture of tetraoxosulphate (VI) acid.

(b) It is used as a bleaching agent for wool, silk, sponges, and wood pulp during paper making.

(c) It is used as a germicide and a fumigant e.g. for destroying termites, moulds and bacteria.

(d) It is used as preservatives for food especially dried fruits and grains.

12.6.3 Sulphur (VI) oxide

Sulphur (VI) oxide is prepared industrially by direct combination of sulphur (IV) oxide and oxygen. The conditions for good yield of sulphur (VI) oxide are

- use of a catalyst such as vanadium (V) oxide or platinized abestos.
- a temperature of 400 - 450°C and
- a slight pressure.

$$2SO_2 + O_2 \xrightarrow[450^{\circ}C]{V_2O_5} 2SO_3$$

This is part of the contact process for the manufacture of tetraoxosulphate (VI) acid.

12.7 Conclusion

You have learned in this unit the characteristic, methods of industrial preparation and uses of important gases. You should also have learned about characteristics, industrial production and uses of mineral acids derived from these gases. This has served to introduce you to several important chemicals used in the laboratory and industry.

12.8 Summary

What you have learned in this unit concerns the gases, hydrogen, oxygen, nitrogen, chlorine and the oxides of sulphur. You have learned about their general behaviour; sources, both natural and synthetic; and uses.

12.9 Tutor-Marked Assignments

1. (a) Describe the industrial preparation of oxygen and nitrogen from air.
   (b) Enumerate the uses of oxygen gas.

12.10 References

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Unit 13

Metals I: General Characteristics

13.0 Introduction

Elements are normally broadly divided into metals and non-metals although there is no clear line of division between the two groups. It is known that elements which easily lose electrons exhibit metallic characteristics. The characteristics shown by metals used to distinguish them from non-metals. Metals, in general, have a quite different appearances, the metallic lustre or the way in which light is reflected on its surface.

Another way in which metals are different from non-metals is in electrical and thermal conductivities. Metals are generally good conductors while non-metals are poor or non conductors.

The periodic classification of elements shows that in the Periodic Table, metallic character decreases and non-metallic character increases from left to right across any period. This is because decrease in atomic size and increase in nuclear charge across a period prevent the elements from losing electrons readily. In Period 3 for example, metallic character decrease from sodium to magnesium to aluminium while the remaining elements silicon, phosphorus, sulphur, chlorine and argon are non-metals. Metallic character of elements increases down the group of the Periodic Table because the tendency to lose electrons increases as atomic size increases down the group. For example, in Group IA the order of metallic character is Be < Mg < Ca < Sr < Ba.

Metals are of great practical importance to man. The development of automobiles, airplanes, jet motors, skyscrapers, and several other objects characteristic of modern civilization and general progress in technology is a result of progress in the science of metals.

13.1 Objectives

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

- Enumerate the characteristic properties that distinguish metals from non-metals.
- Explain metallic properties in terms of their nature of bonding.
- Explain the chemical reactivities of metals.
- Discuss the general extraction methods of metals.
- Name common metal alloys and their uses.

13.2 Physical Properties of Metals

The physical properties of metals can be explained using the nature of bond (metallic bonding) between the atoms. Some of these characteristics are

(a) Metals have high electrical and thermal conductivity i.e. good conductors, because of the mobile nature of their valence electrons.

(b) Metals have a lustrous shiny appearance. All metals except copper and gold are silvery in colour. The high lustre of metals is because the valence electrons can absorb energy from light and then re-emit it when the electron drop back from its excited state to its original energy level.

(c) Metals are malleable i.e. can be hammered into sheets e.g. gold leaves; and are ductile i.e. can be drawn into wire. Metals show these characteristics because of the fairly uniform attraction between the mobile valence electrons and the ions formed. Metals can therefore be stretched or drawn out into various shapes because the ions and electrons can move into other positions without breaking up the metallic structure.

(d) Metals are hard and strong because of the binding action of the electrons which hold the atoms in a close-packed lattice structure. Some metals, however, do not show this property, e.g. sodium and potassium are light, soft metals and mercury is a liquid at room temperature.

Non-metals generally exist as covalent molecules held together by weak Vander Waal's forces and they do not exhibit these metallic characteristics. Carbon, a non-metal, is an exception because it exists as diamond which is a hard solid and as graphite, which is a good conductor. Some elements like silicon and boron show some metallic characteristics and are referred to as metalloids - intermediate between metals and non-metals.

13.3 Chemical Properties of Metals

The chemical properties of any element are controlled by the number of valence electrons present in their atomic structure. The tendency to lose electrons depends on the ionization energy. Since it is easier to remove an electron from a large atom than from a small one, metallic character increases as we descend the groups and decreases from left to right of the period, of the periodic table. This ionization pattern is used to define metals and non-metals.

(a) Ionization ability

Metals are electropositive because of their tendency to lose electrons when supplied with energy

$$M \longrightarrow M^+ + e^-$$

The stronger this tendency, the more electropositive and more metallic an element is. Metals are generally electron donors and non-metals are electron acceptors. Metallic atoms have few valence electrons, between one to three.

$$Na \longrightarrow Na^+ + e^- \quad \text{(univalent)}$$

$$Ca \longrightarrow Ca^{2+} + 2e^- \quad \text{(divalent)}$$

$$Al \longrightarrow Al^{3+} + 3e^- \quad \text{(trivalent)}$$

When metals ionise this way, the positive ions formed chemically combine with negative ions, formed by non-metals when they gain electrons, to give ionic or electrovalent compounds.

(b) Reducing ability

Electron donors are reducing agents. Metals are reducing agents because they tend to donate their electrons readily during chemical reaction. The donated electrons are accepted by oxidising agents usually non-metals.

$$\underset{\text{reducing agent}}{2Ca} + \underset{\text{oxidising agent}}{O_2} \longrightarrow 2Ca^{2+}O^{2-}$$

(c) Reaction with acids

Metals which are more electropositive than hydrogen react with mineral acids e.g. HCl, H_2SO_4, HNO_3 and displace the hydrogen ion, H^+ of the acid.

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

The reaction can be simplified into an oxidation and reduction (redox) processes

$$Zn \longrightarrow Zn^{2+} + 2e^- \quad \text{oxidation}$$

$$2H^+ + 2e^- \longrightarrow 2H \longrightarrow 2H_2 \quad \text{reduction}$$

(d) Formation of oxides

Several metals react with oxygen to form basic oxides which are ionic compounds. Basic oxides that are water soluble form alkalis e.g.

$$4Na + O_2 \longrightarrow 2Na_2O_{(s)}$$

$$Na_2O_{(s)} + H_2O \longrightarrow 2Na^+OH^-_{(aq)}$$

The rate of reaction depends on the reactivity of the metals. Sodium rapidly tarnishes in air, magnesium and calcium tarnish in moist air while iron, aluminium, zinc and tin are oxidised in moist air to form the oxides.

$$4Fe + 3O_2 \longrightarrow 2Fe_2O_3 \quad \text{(rusting process)}$$

Non-metallic oxides are covalent compounds which are acidic e.g. CO_2, SO_3 or neutral e.g. CO, oxides.

13.4 Occurrence of Metals in Nature

More than eighty of the known elements are metals. Metals are widely distributed in the earth's crust either as compounds or in the free metallic state. The state in which metals exist in nature depends on the reactivity of the metals.

Chemically active metals such as sodium, potassium, calcium and magnesium, are usually found combined with other elements. They exist as chlorides, trioxocarbonate(IV), which are stable compounds. Base metals such as zinc, lead and copper, are only moderately reactive and hence exist in nature as oxides or sulphides. The so-called noble metals such as silver and gold, are unreactive and therefore exist in the free or uncombined state.

Majority of the metals are found as minerals in combined form with almost fixed composition and mixed with earthy materials e.g. sand. This natural form of existence of metals are called ores. e.g. Bauxite and cryolite for aluminium; limestone and marble for calcium.

The chemically active metals are mainly used as alloys. The base metals are found in everyday use, because of their cheapness e.g. iron, tin, zinc; while the noble metals are mainly used because their pleasing appearance and as monetary standard because of their high cost.

13.5 Electrochemical or Activity Series

Metals generally contain few valence electrons which they readily donate or give up to form positive ions. The tendency to donate electrons vary from metal to metal and as a result metals can be arranged in series according to their comparative tendencies to give up their valence electrons (i.e. their electropositivity). This is the electrochemical or activity series.

The relative position of a metal in the series indicates the chemical reactivity of the metal and the chemical properties of its compounds. The most active metals form very stable compounds and their ores are chlorides or trioxocarbonates(IV) e.g. potassium, calcium. The base metals form compounds of intermediate stability and their ores are oxides or sulphides or sometimes trioxocarbonates (IV) e.g. iron and zinc. The least active metals, the noble metals usually occur in free state.

Table 13.1 shows the activity series of metals and their properties.

Table 13.1: Activity Series of Metals showing their Properties

Metal	***Electro-positivity***	***Chemical activity***	***Combustion***	***Action with water***	***Action with dilute acids***	***Action with concentrated acids***			***Action with other metallic salts.***
						HCl	H_2SO_4	HNO_3	
Potassium *K*	*Decreasing electropositivity*	*Decreasing chemical activity*	Burns readily in air to form the oxide	Displace hydrogen from cold water	React to form hydrogen and a salt (Al reacts only with dilute HCl)	React to form hydrogen and a salt	React to form SO_2	React to form NO_2	Each metal will displace a metal lower in the series from a solution of lower metal
Sodium *Na* Calcium *Ca*									
Magnesium *Mg* Aluminium *Al*				Displace hydrogen from steam at red heat				No reaction Forms *NO* No Reaction	
Zinc *Zn* Iron *Fe* Tin *Sn*			Form the oxide when heated in air						
Lead *Pb* Copper *Cu* Mercury *Hg*				Do not react with cold water or steam	No reaction (Pb reacts with dilute HNO_3 to form the oxides of Nitrogen)				
Silver *Ag* Gold *Au*			No action			No Reaction	No Reaction	No reaction	

Table 13.2 Summarises the activity series of metals and the gradation of some properties of their compounds.

Table 13.2: Activity series of metals showing the nature of some of their compounds.

Activity series of metals	*Reactions of the oxide*			*Characteristic of*			***Solubility of sulphide***	***Solubility of chlaride***
	with water	***with heat***	***with carban***	***hydraxide***	***trioxocarbonate (IV)***	***trioxonitrate(V)***		
Potassium *K*	Dissolve to form hydroxides	Stable to heat	Not reduced when heated.	Soluble in water; stable to heat	Soluble in water; stable to heat.	Decomposed to dioxonitrate (III) and O_2 by heat	Soluble in water;	Soluble in water; except $PbCl_2$ which is insoluble in cold water but slightly soluble in warm water
Sodium *Na*								
Calcium *Ca*								
Magnesium *Mg*	Insoluble			Insoluble in water except $Ca(OH)_2$ which is sparingly soluble; decomposed to the oxide by heat	Insoluble in water; decomposed to the oxide and CO_2 by heat; $Al_2(CO_2)_3$ does not exist	Decomposed to the oxide, NO_2 and O_2 by heat	Insoluble in water; soluble in dilute HCl	
Aluminium Al								
Zinc *Zn*			Reduced to the metal when heated					
Iron *Fe*								
Tin *Sn*								
Lead *Pb*								
Copper *Cu*								
Mercury *Hg*		Decomposed to the metal				Decomposed to the metal, NO_2 and O_2 by heat.		Insoluble in water
Silver *Ag*							Insoluble in water and dilute HCl	
Gold *Au*				Hydroxides do not exist	Insoluble; decomposed to the metal, CO_2 and O_2 by heat			

13.6 Extraction of Metals

The method of extraction of a metal from its ores depends on the ease with which compounds of the metal can be reduced to the metal. Reducing agents or electron donors are used to supply the electrons required to convert the metallic ion to the metal. Compounds of chemically active metals cannot be reduced by common reducing agents such as carbon and hydrogen; rather they are reduced by electrolysis. The ores of the less active base metals are normally first decomposed to their oxides before reduction with carbon.

Mineral ores are commonly found associated with earthy materials and therefore a preliminary preparation is often required before extracting, the metal. The ores are preliminarily prepared by

(a) Concentration - the ore may be separated from the earthy material by washing in a stream of water to leave behind the heavier ores e.g. tin ore or shaken with oil and water, and the one floated e.g. zine ore or magnetic separation e.g. copper ore.

(b) Roasting - oxide ores are easier to handle during metal extraction than sulphides or trioxocarbonates(iv) ores. All non oxide ores are usually converted to the oxide by roasting it in air.

13.6.1 Electrolytic reduction

The most electropositive metals at the top of the activity series e.g. K, Na Ca and Mg, are obtained from their ores by electrolytic reduction. The ores are commonly stable chlorides and trioxocarbonate(IV) and their electrolysis is a very powerful redox process. The ore is used as the electrolyte and the cathode acts as the reducing half-cell which supply electrons to convert the metallic ion to the free metal.

Electrolytic processes are expensive to install and maintain. They are used only when the thermal and chemical reduction of the ores are difficult to achieve.

13.6.2 Chemical reduction

The less reactive base metals, e.g. lead, zinc, iron and tin are extracted from their ores by chemical reduction. This reduction process can be achieved by:

(a) reducing oxides of metals with coke (carbon) or carbon(II) oxide

$$ZnO + C \longrightarrow Zn + CO$$

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

(b) oxidation of sulphide ores to the oxide which is then reduced by coke

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$

$$2PbO + C \longrightarrow 2Pb + CO$$

In both methods, the carbon combines with the oxide ions to release the electrons required for the reduction of the metal ions.

$$C + O^{2-} \longrightarrow CO + 2e^-$$

$$Zn^{2+} + 2e^- \longrightarrow Zn$$

$$Fe^{2+} + 2e^- \longrightarrow Fe$$

$$Pb^{2+} + 2e^- \longrightarrow Pb$$

13.6.3 Thermal reduction

Non-oxide ores are reduced by heating the ore in air to give the free metals. Mercury is obtained by heating mercury (II) sulphide in air

$$HgS + O_2 \longrightarrow Hg + SO_2$$

Table 13.3 summarises the common ores and methods of extraction of metals based on their positions in the activity series.

Table 13.3 Activity series of metals and methods of metal extraction

Metal	Reactivity	Most common ore	Method of extraction
Potassium K Sodium Na	Very reactive	Chlorides	Electrolysis of fused hydroxides and chlorides
Calcium Ca Magnesium Mg		Chlorides and trioxocarbonates (IV)	Electrolysis of fused chlorides
Aluminium Al		Oxides	Electrolysis of oxides
Zinc Zn Iron Fe Tin Sn Lead Pb	Moderately reactive	Oxides, trioxocarbonates(IV) and sulphides	Roasting of trioxocarbonates (IV) and sulphides to form oxides; reduction of oxides by carbon or carbon (II) oxide
Copper Cu	Least reactive	Sulphides	Roasting in air
Mercury Hg			Heating in air
Silver Ag Gold Au		Free element	Mined as free elements

13.7 Conclusion

In this unit you have learned about metals particularly the nature of their existence in the earth's crust. You should have also learned about the physical and chemical properties of metals which are dependent on the number of valence electrons present. Furthermore, you should have learned how metals are arranged based on chemical reactivity and this has served as a guide to the reductive method suitable for the extraction of the metals from its ores.

13.8 Summary

What you have learned in this unit is that metals are found in nature either as compounds known as ores or in the free state. That metals can be arranged in order of their comparative electropositivities which has served to determine which choice of electrolytic, chemical or thermal reduction as the methods for the extraction of metals. The unit that follows shall build on these general characteristics of metals.

13.9 Tutor-Marked Assignments

(a) Name two metals which will not liberate hydrogen gas from dilute tetraoxosulphate (VI) acid.

(b) Give two common ores and methods of extraction of Mg, Zn and Cu.

(c) Write short notes on

  (i) Preliminary preparation of ores

  (ii) Chemical reduction process in extraction of metals.

13.10 References

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Unit 14

Metals II - The Transition Metals

14.0 Introduction

You will recall that the periodic table placed some elements between group II and group III called **transition elements**. Transition or d-block elements are so called because their position in the periodic table is between the s- and p- block elements, and their properties are transitional between the highly reactive metallic elements of the s-block, which typically form ionic compounds, and the elements of the p-block which are largely non-metallic forming covalent compounds.

In the d-block the penultimate shell, that is, the orbital next to the outermost orbital, of electrons is being expanded from eight to eighteen by the addition of d-electrons. The term transition element is used only for an element which has partially or incompletely filled d-orbitals. They occupy three rows or periods; (Periods 4, 5 and 6 of the periodic table) with ten elements in each row. All transition elements are metals of great economic importance. Table 14.1 shows the d-block transition metals.

Table 14.1 The transition elements

Period	4	1st transition series	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Period	5	2nd transition series	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Period	6	3rd transition series	La	Hf	Ta	W	Re	Os	Ir	Pt	Aw	Hg
Number of electrons			1	2	3	4	5	6	7	8	9	10

The first transition series metals from scandium (Sc) to zinc (Zn) in period 4 are the primary focus of this unit and they are particularly important in industry. Metals in this series include titanium (Ti), vanadium (v), chromium (Cr), Manganese (Mn), Iron (Fe), cobalt (Co), nickel (Ni) and copper (Cu). The transition metals have very similar properties and are quite different from the reactive s-block metals of Groups I and II.

14.1 Objectives

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

- List and write the electronic configuration of members of the first transition series.
- Compare the characteristics of transition metals with those of the s-block metals.
- Explain the peculiar properties of transition metals.
- Recall the industrial uses of the first transition series metals.

14.2 Electronic Configuration of 1st transition series metals

Recall that the energy level diagram of atomic orbitals is 1s<2s<2p<3s<3p<4s<3d<4p. Thus for elements having atomic numbers 1 to 18, the electrons are filled normally into the orbitals. This ends with Argon whose electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$. The next element, potassium (atomic number 19) and 19th electron goes into the 4s orbital which is of a lower energy than the 3d. For calcium (atomic number 20), the 20th electron goes to complete the 4s orbital. Next is scandium (atomic number 21), the first transition element, the 21st electron goes into the 3d orbital, which is the next available orbital in terms of the energy level diagram. The filling of the 3d orbital continue from scandium to zinc giving the first transition series. Thus, the outer 4p orbitals of the elements from scandium to zinc are not filled because of their higher energy levels, while the inner or penultimate 3d orbitals are preferentially filled since they are at lower energy levels. Table 14.2 gives the electronic configuration of the s-block and d-block metals of Period 4.

Table 14.2 Electronic configuration of s- and d- block metals of Period 4

Element	**Electronic configuration**										
s-block	*1s*	*2s*	*2p*	*3s*	*3p*	*3d*					*4s*
K	2	2	6	2	6						1
Ca	2	2	6	2	6						2
d-block											
Sc	2	2	6	2	6	↓					2
Ti	2	2	6	2	6	↓	↓				2
V	2	2	6	2	6	↓	↓	↓			2
Cr	2	2	6	2	6	↓	↓	↓	↓		1
Mn	2	2	6	2	6	↓	↓	↓	↓	↓	2
Fe	2	2	6	2	6	↓↑	↓	↓	↓	↓	2
Co	2	2	6	2	6	↓↑	↓↑	↓	↓	↓	2
Ni	2	2	6	2	6	↓↑	↓↑	↓↑	↓	↓	2
Cu	2	2	6	2	6	↓↑	↓↑	↓↑	↓↑	↓↑	1
Zn	2	2	6	2	6	↓↑	↓↑	↓↑	↓↑	↓↑	2

NOTE: There are five 3d orbitals. Each of these can only accommodate two electrons with opposite spins.

Chromium and copper atoms have only one electron in their 4s orbitals. This is as a result of the special stability associated with halfly or fully filled sub levels. The $3d^5$ and $3d^{10}$ electronic configuration of chromium and copper respectively show that the five 3d orbitals are singly or doubly filled.

14.3 Physical Properties of 1st Transition Series Metals

(a) All the transition elements are typical metals with high boiling and melting points. They are hard, dense and lustrous e.g. Iron, copper, zinc. They have good mechanical properties - malleable and ductile.

(b) They are generally good conductors of heat and electricity e.g. copper and iron.

These properties of transition metals can be explained in terms of strong metallic bonding. In addition to the 4s electrons, the 3d electrons in the atoms of these metals are available for metallic bonding. The extra electrons make the metallic bonds in the transition elements very strong. In comparison, the corresponding s-block metals, potassium and calcium, in the same period are soft and of lower melting point. The metallic bonds in s-block metals, which have only one or two available electrons for bonding, are not as strong as those in d-block metals, with extra 3d electrons.

The atomic size of the d-block metals also affects their properties. In comparison, both the s-block and d-block metals in period 4 have atoms with the same number of principal energy levels (n=1,2,3,4) but the transition metals have larger atomic number. As a result, the atoms of the transition metals are smaller than those of the s-block metals. For example, Iron (atomic number 26) atom with a +26 nuclear charge will have a stronger attraction on its electrons and pull them closer (decrease atomic size) than potassium (atomic number 19) with a +19 nuclear charge. This difference is reflected in their atomic sizes - iron (0.12nm) and potassium (0.20nm).

The combined effects of strong metallic bonds and small atomic sizes accounts for the high boiling and melting points, densities and tensile strengths of the transition metals. The melting points of manganese and zinc are comparatively lower because their atoms have half-filled and fully-filled d-orbitals respectively. This electronic arrangement give stability to the atoms, hence the d-orbital electrons are not available for metallic bonding. Table 14.3 summarises some properties of the first transition metal series.

Table 14.3: Some properties of the first transition series metals

←s-block→←———— d-block ————→

Property	Potassium	Calcium	Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc
Atomic Number	19	20	21	22	23	24	25	26	27	28	29	30
Outer electronic Structure	$3d^04s^1$	$3d^04s^2$	$3d^14s^2$	$3d^24s^2$	$3d^04s^2$	$3d^04s^2$	$3d^04s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s^1$	$3d^{10}4s^2$
Configuration M^{2+}	-	$3d^04s^0$	-	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$
Configuration M^{3+}	-	-	$3d^84s^0$	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	-
Relative atomic Mass	39.1	40.08	44.956	47.90	50.942	51.996	54.938	55.847	58.933	58.710	63.54	65.37
Density(gcm^{-3})	0.86	1.54	3.1	4.43	6.67	7.188	7.21	7.869	8.70	8.902	8.94	7.13
Melting point(K)	337	1118	1814	1933	2163	2130	1517	1808	1768	1728	1356	693
Boiling point(K)	1048	1760	3104	3560	3653	2943	2235	3023	3134	3003	2840	1180
Atomic radius (nm)	0.20	0.17	0.14	0.13	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.13
Ionic radius (nm) M^{2+}	-	0.094	-	0.090	0.088	0.084	0.080	0.076	0.074	0.072	0.070	0.074
Ionic radius (nm) M^{3+}	-	-	0.081	0.076	0.074	0.069	0.066	0.064	0.063	0.062	–	–

The densities of transition metals increase across the series because their relative atomic masses increase progressively while the atomic sizes remain fairly constant since electrons are being filled into the 3d penultimate shell.

14.4 Chemical Reactivity

The chemical reactivity of elements is dependent on their outermost electrons. In the s-block and p-block the chemical properties of the elements in a given period vary (e.g. from metal to non-metals) from left to right. For the transition metals this does not happen simply because electrons are added progressively to the inner d-orbitals and not the outermost orbitals, as in the s-block and p-block elements. The nuclei of transition metals have a stronger pull on their electrons than the nuclei of s-block metals. The s-block metals, therefore, have lower ionization energies and are more reactive than the transition metals.

(a) They do not react with cold water like the alkali metals. They however react with steam at high temperatures.

$$3Fe_{(s)} + 4H_2O_{(g)} \longrightarrow Fe_3O_4 + H_2$$

$$Zn + H_2O \longrightarrow ZnO + H_2$$

(b) They are oxidised when exposed to air or heated to red hot. In damp air, iron rusts to form a reddish brown layer of hydrated iron (III) oxide - this can be observed on iron roofing sheets of our houses.

$$4Fe + 3O_2 \xrightarrow{H_2O(\text{moisture})} 2Fe_2O_3\ 3H_2O\,(\text{rust})$$

(c) Iron, cobalt and nickel react with dilute mineral acids e.g. HCl, H_2SO_4, to give hydrogen gas because they are higher than hydrogen in the electrochemical series.

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$

All the transition metals react with concentrated acids to form the corresponding salt. Copper reacts with either dilute or concentrated trioxonitrate (V) acid to form blue copper (II) trioxonitrate (IV) solution

$$Cu + 2HNO_3 \longrightarrow \underset{\text{blue}}{Cu(NO_3)_2} + H_2$$

14.5 Variable Oxidation States

One of the most striking features of the transition metals is that they exhibit variable valency. Many of the metals show a wide range of valencies e.g. Fe^{3+} and Fe^{2+}; Cu^{2+} and Cu^{+}; V^{3+} and V^{4+}. This is in contrast to the S-block metals, where the single valency always equals the group number. The variable oxidation states shown by transition metals is because the 3d electrons are available for bond formation. The term oxidation state is usually preferred to valency. All the metals show an oxidation state of +2 which can be associated with the loss of the two outermost s-electrons from the neutral atom.

The oxidation states shown by the transition metals may be related to their electronic structures as shown in Table 14.4

Table 14.4

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Electronic * Structure	d^1S^2	d^2S^2	d^3S^2	d^5S^1	d^5S^2	d^6S^2	d^7S^2	d^8S^2	$d^{10}S^1$	$d^{10}S^2$
Oxidation States				I					I	
	II	II	II	(II)	(II)	(II)	(II)	(II)	(II)	(II)
	(III)	III	III	(III)	III	III	III	III	III	
		(IV)	(IV)	IV	(IV)	IV	IV	IV		
			(V)	V	V	V	V			
				VI	VI	VI				
					VII					

** inner energy orbitals not shown* ( ) *commonest oxidation states*

Thus Sc could have an oxidation number of (+II) if both *s* electrons are used for bonding and (+III) when two *s* and one *d* electrons are involved. Ti has an oxidation state (+II) when both s electrons are used for bonding, (+III) when two s and one d electrons are used and (+IV) when two s and two d electrons are used. Similarly, V shows oxidation numbers (II), (III), (IV) and (V). In the case of Cr, by using the single s electron for bonding we get an oxidation number of (+I); hence by using varying numbers of d electrons oxidation states of +(II), (III), (IV), (V) and (VI) are possible. Mn has oxidation states (II), (III), (IV), (V), (VI) and (VII).

Recall that the oxidation state of any element can be worked out from the molecular formula of its compounds. For example the oxidation state of Mn in $KMnO_4$ is:

$K^+ = +1$

$4O^{2-} = 4 \times (-2) = -8$

Since it is neutral, positive and negative charges must balance, hence remaining positive charge is +7

i.e. $+1 + x - 8 = 0$

$x = 8 - 1 = +7$

which is the oxidation state of Mn.

The lower oxidation states of the transition metals occur in ionic compounds and tend to form reducing agents e.g. Cr^{2+} salts, and basic oxides e.g. $Mn^{2+}O^{2-}$. The higher oxidation states are found in covalent compounds (sharing electrons) and tend to form oxidising agents e.g. $K_2Cr_2O_7 \longrightarrow$ Cr(VI) and acidic oxides e.g. $Mn_2O_7 \longrightarrow$ Mn (VII). Compounds of transition metals with intermediate oxidation states form amphoteric oxides.

14.6 Complex ion formation

Transition metals form many coordination compounds, complex ions, in contrast to the s- and p- block elements. **A complex ion has a central positive ion linked by a cluster of several other ions or molecules called ligands.** The number of ligands is referred to as the coordination number. The bonding between the central metal ion and the ligands may be either predominantly electrovalent or predominantly coordinate. The ligands act as electron donors. Examples of ligands are $:NH_3$, H_2O: CN^-.

For example the blue complex ion, tetraamine copper (II) ion $[Cu(NH_3)_4]^{2+}$ in which the central ion, Cu^{2+}, is coordinately bonded to four ammonia a molecules as ligands.

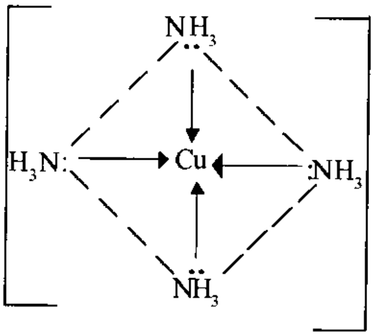
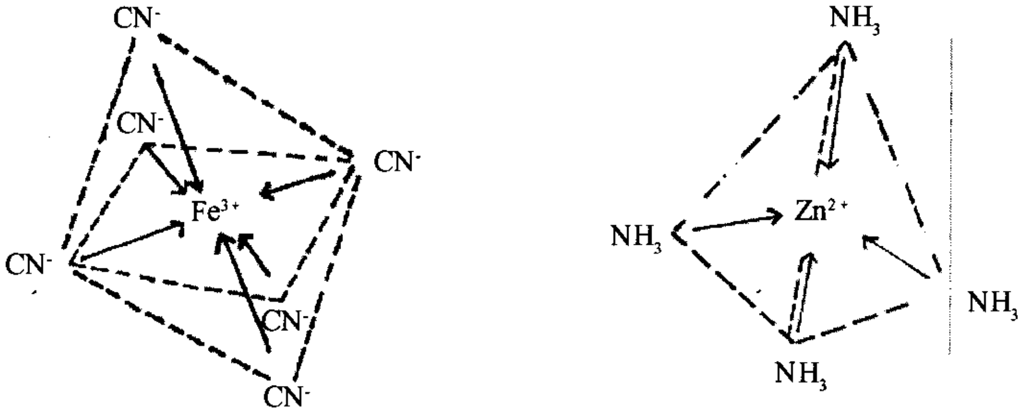


Fig. 14.1
Tetraamine copper (II) ion

Transition metals are usually coordinated or linked to four or six ligands. When the complex ion has six ligands e.g. $[Fe(CN)_6]^{3-}$, the ligands are arranged octahedrally (see Fig. 14.2) around the central metal ion. When four ligands are present, they may be arranged tetrahedrally e.g. in $[Zn(NH_3)_4]^{2+}$, see Fig.14.2; or at the corners of a square e.g. $[Cu(NH_3)_4]^{2+}$ see Fig. 14.1

Fig 14.2



Octahedral
$[Fe(CN)_6]^{3-}$

tetrahedral
$[Zn(NH_3)_4]^{2+}$

The ligands are electron donors and the electrons usually fill up the incomplete d-orbitals and the 4s and 4p orbitals in the central transition metal ion.

14.7 Colour of Transition Metal Ions

Ionic and covalent compounds of transition metals are usually markedly coloured, in contrast to compounds of the s-and p- block elements which are almost always colourless. Colour formation is associated with the ability to promote an electron from one energy level to another on absorption of energy. The colour of transition metal ions usually serve as a useful guide in identifying a compound.

For the first transition series metals, the colours are associated with partially filled 3d orbitals (i.e. $3d^1$ to $3d^9$). Scandium and zinc ions are colourless because they do not have partially filled 3d orbitals. Table 14.5 shows the characteristic colours of transition metal ions.

Table 14.5: Colour of the 1st transition series metal ions in water.

Ion	d-electrons	colour
Sc^{3+}	$3d^0$	colourless
Ti^{3+}	$3d^1$	purple
V^{3+}	$3d^2$	green
Cr^{3+}	$3d^3$	violet
Mn^{3+}	$3d^4$	violet
Mn^{2+}	$3d^5$	pink
Fe^{3+}	$3d^5$	yellow
Fe^{2+}	$3d^6$	green
Co^{2+}	$3d^7$	pink
Ni^{2+}	$3d^8$	green
Cu^{2+}	$3d^9$	blue
Zn^{2+}	$3d^{10}$	colourless

14.8 Catalytic Activity

Catalytic ability is one of the pronounced characteristics of transition metals. The ease with which ions of transition metals change their oxidation states enable them to act as catalysts. The most common catalyst and their uses is given in Table 14.6

Table 14.6: Common Catalyst and their uses

Catalyst	Use
$TiCl_4$ (Ziegle-Natta catalyst)	polymerisation of ethene to polyethene
Ni	hydrogenation of vegetable oil to margarine
MnO_2	decomposition of H_2O_2 to water and oxygen
V_2O_5	contact process for H_2SO_4 manufacture
Fe	Haber process for NH_3 manufacture

14.9 Industrial Uses of Transition Metals

(a) Iron is used in the manufacture of steel, which are used in the making of tin-plates, corrugated sheets, car bodies, nails, screws, pipes, etc.

(b) Copper is widely used for making electric wires, metal-work because of its attractive appearance, and in alloys such as bronze, brass.

(c) Zinc is used widely for galvanizing iron and steel, in alloys such as bronze, brass and in making dry cells and package foils.

(d) Several of them are used as catayst for important industrial process (see 14.8) and to impact colour to objects e.g. ceramics, paints etc

14.10 Alloys

The characteristics of metals can be improved by mixing them with other elements to form alloys. **An alloy is a substance prepared by adding one or more elements to a base or parent metal to obtain desired properties.** The added elements are usually metals or carbon.

Alloys are economically important because most of the metallic things we use are made of alloys and not the pure metals. Table14.7 gives some common alloys, their compositions and uses.

Table14.7: Some alloys, their compositions and uses

Alloy	Composition	Advantages	Uses
Brass	60-80% Cu 20-40% Zn	Stronger and more malleable than copper, greater workability because of lower melting point; more attractive appearance, does not corrode easily.	For making moving parts of clocks and watches, nuts, bolts rods, tubes, musical instruments ornaments and for general metalwork.
Bronze	90% Cu 10% Sn	Stronger than copper; greater resistance to chemical attack; more attractivve appearance.	For making coins and medals sculptures and for general metalwork.
Duralumin	95% Al 3% Cu 1% Mg 1% Mn	Very light but stronger than aluminium	Construction of aircraft, ships cars and machinery.
Steel	99.8% Fe 0.2% C	More malleable and ductile than iron; harder and stronger; can withstand great stress and strain.	Construction of bridges, ships, cars and machinery.
Stainless	60-80% Fe 10-20% Cr 8-20% Ni	Hard; resistant to corrosion; very attractive in appearance	For making cutlery, tools and surgical instruments

- Tracing movement of a substance in a process.
- Source of energy as in fission.
- Radioactive dating e.g. carbon dating.

3.5 Hazards of Radioactivity

Gamma radiation is used to destroy cancerous cells. This is one use gamma radiaiton is put into. F-radiation also destroys healthy cells as well and too much exposure to it can do more harm than good. The extent of damage depends on the energy and type of radiation. The effect of radiation is also cumulative and small doses over a long period of time will also cause serious damage to biological systems.

Radioactive waste is very dangerous and must be disposed properly to avoid unnecessary exposure to its hazards.

3.6 Conclusion

The nucleus is sterilised in part by the presence of neutrons. Nuclear reactions unlike chemical reactions which involve valence electrons, nuclear reactions involve protons and neutrons. Nuclear reactions are much more exothermic than chemical reactions.

Many atomic nuclei are unstable. Some occur naturally and some are man-made. Unstable nuclei emit radiations with characteristic properties. The emitted radiations find application in various fields of human endeavour but also pose danger to users and non users alike. Radioactive waste must be properly disposed to avoid unwanted effects. Radioactive materials must always be handled with care.

3.7 Summary

This unit discusses the properties and applications of the nucleus.

- When nuclei react they are transformed in the reactions.
- Unstable nuclei decay to give out three major types of radiations with characteristic properties. The radiations have properties that make them detectable.
- Reactions of atomic nuclei in fission and fusion processes are important because of the high energies involved.
- Fission reactors are used to generate electricity.
- Radioactivity is used in medicine, agriculture, industry, engineering and chemical research laboratories.
- The emitted radiations can lead to unwanted efects in biological systems.
- The environment must be protected by proper disposal of radioactive waste.

3.8 Tutor-Marked Assignments

1 (a) List the three types of radiations emitted by radioisotopes and show how they are differentiated in an electric field.

(b) Fill in the missing nuclei in the following nuclear equations.

(i) $^{70}_{30}Zn \rightarrow {}^{0}_{-1}e + ?$

(ii) $^{137}_{57}La + {}^{4}_{2}He \rightarrow {}^{1}_{1}P + ?$

2 (a) List four uses of radioactivity

(b) Give some empirical observations suggesting that neutrons are partly responsible for nuclear stability.

(c) How many protons, neutrons and electrons are present in the following

$$^{60}_{27}C_o \ , ^{43}_{19}K \quad \text{and} \quad ^{55}_{26}Fe$$

3.9 References

Bajah, S. T., Teibo, B. O., Onwu, G. and Obikwere A., (2002). *Senior Secondary Chemistry Textbook 2* Lagos Longman Publishers.

Osei Yaw Ababio, (2002). *New School Chemistry.* Onitsha. Africana-FEP Publishers.

Unit 4

Chemical Bonding 1: Electrovalent, Covalent and Co-ordinate Covalent

4.0 Introduction

When elements combine, compounds are formed. The forces that hold atoms together in compounds are called chemical bonds. The combination of chemical elements to give a compound is a chemical reaction. Some elements are very reactive and exist in nature only in combined states, e.g. sodium in sodium chloride (common salt) and calcium in calcium trioxocarbonate (marble). Few elements are relatively unreactive and exit rarely as free elements. They are called noble or rare elements, e.g. no compound of helium, argon and neon exists. Most elements have intermediate reactivity and exist as free elements as well as in chemical compounds e.g. carbon occurs as graphile and diamond as well as in petroleum and many organic compounds. There are some non metallic elements that exist only as diatomic molecules in the free state. These elements also occur in combined states.

In the previous unit, you were shown that arrangement of electrons in atoms showed some correlation between electron arrangement and properties.

Li (2, 1), Na (2,8,1), K (2,8,8,1) all have similar configuration with one electron each in their outermost shell. They are metals. F (2,7) and Cl(2,8,7) all need one electron to complete their outermost electron shell. They are non-metals. The inert or noble elements He (2), Ne (2,8), Ar (2,8,8) all have complete shell arrangement of electrons. The electron arrangement in stable ions of metals and non metals also show that complete shell of electrons is a stable configuration e.g. Na^+ (2,8), F^- (2,8) and O^{2-} (2,8).

In chemical bonding therefore elements tend to attain the noble or inert gas configuration. There are many types of bonds but in this unit, you will focus on three types:

- electrovalent
- co-valent
- co-ordinate covalent.

4.1 Objectives

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

- Explain electrovalent and covalent bonding.
- Write electron dot formulae for compounds.
- List properties of electrovalent and covalent compounds.
- State the octet rule.

- Explain the importance of noble gas configuration on chemical bonding.
- Predict the type of bonds between atoms.
- Explain the difference between covalent and co-ordinate covalent bonding.

4.2 Electrovalent (Ionic) Bonding

When atoms interact for bond formation only the outermost parts of the atoms are in contact and so only the outer electrons in the outermost shell (valence electrons) are involved. The outermost shell electron arrangement is therefore very important in determining the type of bond. Electrovalent bonding involves electron transfer from the valence shell of one atom to the valence shell of the other.

One atom loses electrons to become positively charged and the other gains electrons to become negatively charged. **The positively and negatively charged ions are called cations and anions respectively.** The ionic bond results from the attraction between these oppositely charged ions. This type of bonding is usually between metals and non-metals.

e.g. Li and F

$Li \longrightarrow 2,1$

$F \longrightarrow 2,7$

$Li \longrightarrow Li^+ (2) + e$

$F, +e \longrightarrow F^- (2,8)$

$Li^+ + F^- \longrightarrow Li^+ [:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:]^-$

The formula of LiF written as above is the electron dot formula (Lewis structure). The brackets around the fluorine are intended to show that all eight electrons are the exclusive property of the fluoride ion (F). Another example is the bond between sodium and chlorine.

$Na\ (2, 8, 1) \longrightarrow Na^+ (2, 8) + e$

$Cl\ (2, 8, 7) +e \longrightarrow Cl^- (2, 8, 8)$

$Na^+ + Cl^- \longrightarrow Na^+[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:]$

As can be seen from the examples, the loss and gain of electrons result in inert gas configurations for the cation and anion. Except for helium, He (2) the inert gas configuration corresponds to eight electrons in the outershell.The electronic theory of valency as postulated by Kossel and Lewis 1716 was prompted by the remarkable stability of the rare gas elements. This stability is associated with the presence in the atoms of a group of eight electrons in the outer shell. This completeness appears to be the source of stability in rare gases.

The tendency for atoms to have eight electrons in their outermost shell (is explained by the octet rule). The octet rule states that:

- atoms tend to gain or lose electrons until there are eight electrons in their valence shell.

Note that the rule does not always hold. In cases like these, other stable configurations explain ion stability. The number of bonds to a particular atom depends on the number of electrons gained or lost to attain stable configurations for example.

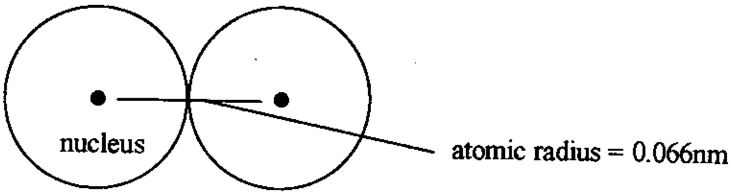
$Ca\ (2, 8, 8, 2) \longrightarrow Ca^{2+}\ (2, 8, 8) + 2e$

8.4 The Periodic Table and Atomic Properties

We learned that physical and chemical properties of the elements vary periodically with the atomic number. The periodic table therefore provides an organized structure to the knowledge and understanding the chemistry of the elements. Apart from this, there is also a variation of atomic properties of elements in the periodic table. Some of these properties are atomic and ionic sizes, ionization energy, electron affinity and electronegativity.

8.4.1 Atomic size

The atom is a very small entity and so it is difficult to determine its size i.e. distance from the center of the nucleus to the outermost orbital. However with the aid of modern techniques such as X-ray and electron diffraction, it is possible to determine the distance between covalently bonded atoms. For example, the distance between the nuclei of oxygen atoms in an oxygen molecule is 0.132nm, so the atomic radius of an oxygen atom is approximately 0.066nm. **The atomic radius or sizes of any atom is taken to be one-half the distance of closest approach between the nuclei of atoms in the elemental substance.**



oxygen atom + oxygen atom = oxygen molecule

Fig 8.1 Atomic radius of oxygen

Atomic size decreases from left to right across a period in the periodic table. In other words, as the atomic number increases across any period, the size of the atom decreases. Recall that as we move across a period one electron is added increasingly from one element to the next and the electrons are being added to the same shell at about the same distance from the nucleus. At the same time, protons are also being added to the nucleus. Increase in the number of proton, increases the nuclear charge which progressively exert a stronger attraction upon the electrons around it and would pull them towards the nuclei. As the nuclear charge increases with atomic number across a period, the attractive force exerted by the nucleus on the outermost electrons of the atom increases hence the atomic radius or size decreases across a period. For example, on moving from Lithium to beryllium, the number of charges on the nucleus is increased by one, so that all the orbital electrons are pulled in closer to the nucleus. In a given period, the alkali, metal is the largest atom and the halogen the smallest. Table 8.2 shows the atomic radii (in nm) of the first twenty elements of the Periodic Table.

Table 8.2: Atomic radii of the first twenty elements

Group / Period	1	2	(nm)	3	4	5	6	7	0
1	H ● 0.037							H ● 0.039	He ● 0.049
2	Li ● 0.152	Be ● 0.111		B ● 0.088	C ● 0.077	N ● 0.070	O ● 0.066	F ● 0.064	Ne ● 0.070
3	Na ● 0.186	Mg ● 0.160		Al ● 0.143	Si ● 0.117	P ● 0.110	S ● 0.104	Cl ● 0.099	Ar ● 0.094
4	K ● 0.231	Ca ● 0.197							

On descending a group in the periodic table such as lithium, sodium, potassium etc, the atomic size increases due to the effect of extra shells of electrons being added; this outweighs the effect of increased nuclear charge. Recall the lithium in period 2 has two shells; sodium in period 3 has three shells while potassium in period 4 has four shells. In general, as we go down the group, atomic size increases with atomic number (see Table 8.2).

8.4.2 Ionic radius

Ions of elements are formed when atoms lose or gain electron. The size of an ion called ionic radii is different from atomic sizes. Ionic sizes are measured in electrovalent compounds.

The ionic radius of a given compound is the distance between the centre of one ion and the centre of its nearest neighbour of opposite charge.

A positive ion is formed by removing one or more electrons from an atom. When this happens, the number of positive nuclear charge is more than the number of negative electronic charge, hence the electrons are pulled in. *A positive ion is therefore smaller than the corresponding atom and the more electrons removed (that is, the greater the charge on the ion), the smaller it becomes* e.g.

Atomic radius Na = 0.186nm
Ionic radius Na^+ = 0.116nm

Atomic radius Fe = 0.139nm
Ionic radius Fe^{2+} = 0.090nm
Ionic radius Fe^{3+} = 0.076nm

When a negative ion is formed, one or more electrons are added to an atom. The number of positive nuclear charge is now less than the number of negative electronic charge hence the pull on the electrons is reduced. In general, ionic radii of negative ions are greater than the corresponding atomic radii i.e. negative ions are bigger than the corresponding atom e.g.

Atomic radius Cl = 0.099
ionic radius Cl^- = 0.128

8.4.3. Ionization energy

If energy is supplied to an atom, electrons may be promoted to a higher energy level. If sufficient energy is supplied, the electron may be completely removed, giving a positive ion. The energy required to remove the most loosely bound electron from each atom in a mole of gaseous atom, producing one mole of gaseous ion is called **ionization energy** (KJ mol^{-1}). Since it is possible to remove one, two or three.... electrons from most atoms there is a first second or third... ionization energy (I.E.).

$$M \xrightarrow{1^{st}\,I.E} M^{+} \xrightarrow{2^{nd}\,I.E} M^{2+} \xrightarrow{3^{rd}\,I.E} M^{3+} \xrightarrow{\quad}$$

The factors influencing the ionization energy are the

(a) size of the atom which is a measure of the outermost electron from the nucleus.

(b) charge on the nucleus - as nuclear charge increases, the attraction for outermost electron increases, and so more energy is required to ionise .

(c) screening effect of inner electron shells - the outermost electrons are repelled by all the other inner shell electrons and prevented from experiencing the full attraction of the positively charged nucleus.

Across a period, the first ionization energy increases as atomic number increases since the atomic radius decreases. As the distance decreases, the attraction of the positive nucleus for the electron will increase, hence more energy is required to remove the outermost electron hence the ionization energy will increase. Note that the screening effect remain almost the same across a period since electrons are added to the same shell. Table 3 shows the first ionization energies of the first twenty elements.

Table 8.3 First Ionization Energies of the Elements (KJ mol^{-1})

Table 8.2: Atomic radii of the first twenty elements

Group / Period	1	2		3	4	5	6	7	0
1	H • 1311								He ● 2372
2	Li ● 520	Be • 899		B • 801	C • 1086	N • 1403	O • 1410	F • 1681	Ne ● 2080
3	Na ● 496	Mg • 737		Al ● 577	Si ● 786	P ● 1012	S ● 999	Cl • 1255	Ar ● 1521
4	K ● 419	Ca ● 590							

The first ionization energies of the elements in the first two short periods are shown in Fig. 8.2. These show a general upward trend from Li to Ne and from Na to Ar. The values for Ne and Ar are the highest in their periods because it requires a great deal of energy to break a stable filled shell of electrons. There are several irregularities. The high values for Be and Mg are attributed to the stability of a filled *s* level. The high values for N and P indicate that a half-filled *p* level is also particularly stable. The values for B and /*Al*/ are lower because removal of one electron leaves a stable filled *s* shell, and similarly with O and S a stable half-filled *p* shell is left.

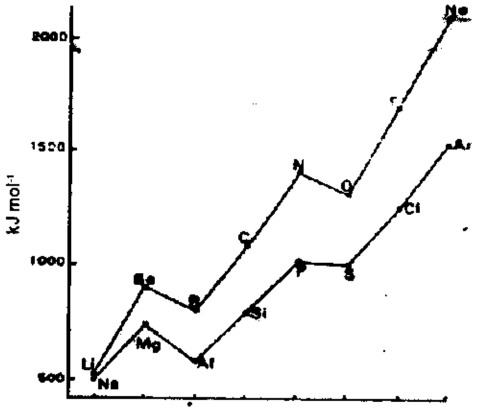
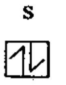
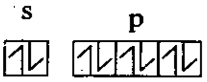


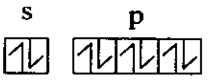
Fig 8.2. First ionization energies of the elements in the first two short periods.



Filled s level e.g. Be $1s^2\ 2s^2$
Mg $1s^2\ 2s^2\ 2p^6\ 3s^2$



Half-filled p level e.g. N $1s^2\ 2s^2\ 2p^3$
P $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$



Completely full - inert gas structure
è.g.Ne $1s^2\ 2s^2\ 2p^6$
Ar $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

In general, the ionization energy decreases on descending a group because an extra shell of electron is added which also help to screen the outer electron from the nucleus. This trend is shown with the alkali, metals from Li(520) to Na(496) to K(419).

8.4.4 Electron affinity

Electron affinity has to do with the gain of electrons to form negative ions while ionization deals with loss of electrons to form positive ions. *The energy released when an extra electron is added to a neutral gasesous atom to form a univalent negative ion is termed the electron affinity.* Since energy is given off in the process, electron affinity has a negative value. Electron affinities depend on the size and effective nuclear charge of the atom. Moving from left to right across a period, electron affinities decreases (i.e. increase in negative value), expect for the noble gases which have positive values. Down a group of the periodic table, electron affinities increase (i.e. decrease in negative value). The reason for the observed trend is that atoms with smaller atomic radii tend to have a stronger attraction for electrons and thus form negative ions more readily.

Unit 1

Introduction to Organic Chemistry and Classification of Organic Molecules

1.0 Introduction

You should have read through the Course Guide on Organic Chemistry. If so, you will have noticed that organic chemistry is essentially the chemistry of carbon compounds. However, if this was not apparent from the Course Guide, we can define organic chemistry as the study of carbon compounds. Organic chemistry owes its name to the fact that the original compounds studied came from living things plants or animals. The term "organic" means things formed from living things. Over time, the study of organic chemistry has expanded to include other compounds other than the so-called organic compounds e.g. plastics, which have no direct relation to living matter. Nevertheless, organic chemistry is retained as the umbrella name for the study of compounds of carbon, irrespective of its origin, but excluding the oxides of carbon. Apart from carbon, organic compounds, may contain one or more other elements e.g hydrogen, oxygen, nitrogen, sulphur and the halogens.

The scope of organic chemistry is very large, millions of organic compounds have been isolated or prepared, yet the number of guiding principles is relatively small. The continuing interest and importance of organic chemistry stems from the fact that organic compounds are essential for the sustainance of life e.g carbohydrates, proteins, fats and oils etc. Modern civilization consumes vast quantities of organic compound. Coal, petroleum, and natural gas are primary sources of carbon compounds for use in production of energy and as starting materials for the preparation of plastics, synthetic fibers, dyes, pesticides, fertilizers, detergents, rubbers, paints, medicines and drugs, perfumes and flavours.

I hope you now appreciate the importance of the subject organic chemistry and the relevance of organic compounds to us.

1.1 Objectives

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

- State the distinct nature of organic chemistry.
- Define organic chemistry.
- Explain the uniqueness of carbon as a building block for organic compounds.
- Enumerate the broad classifications of organic compounds.

1.2 Definition and Scope of Organic Chemistry

Organic Chemistry is the study of the chemistry of carbon compound, which apart from carbon, m contain one or more of hydrogen, oxygen, nitrogen, sulphur and any of the halogens. Carbon compounds are ,undant in nature all well over 50% of all known compounds. All living organisms comprised of, manufacre and consumes organic or carbon compounds. Millions of organic compounds are known and the poteial to identify or prepare millions of such compounds is real. Organic compounds are found in and essential, all aspects of our lives.

Recall the impact of organic compounds in our day-to-day living as enumerated in the introductory sectn to this unit.

1.3 Uniqueness of Carbon Atom

We had earlier defined organic chemistry as the study of the compounds of carbon. Why is so much chemistry centred on a single element, carbon? Carbon is so unique amongst the elements, in that its known compounds are much more numerous than the known compounds of all the other 105 elements put together. Carbon atom is an element which has six electrons with four in the outermost orbit; and is placed in period 2 and Group 4 of the Periodic Table. The uniqueness of carbon atom stems from its ability to form:

(i) a variety of strong covalent carbon-carbons bond
(ii) long chains or rings of carbon atoms bonded to one another called CATENATION.
(iii) strong covalent bonds with other elements
(iv) multiple bonds (double and triple) with another carbon atom or other elements.

Examples of such bond forming ability are. (Fig. 1.1)

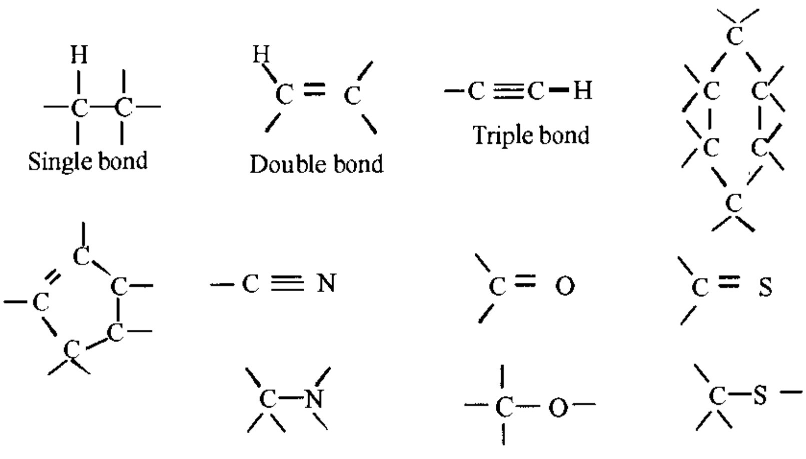


Fig. 1:1 Types of covalent bonds formed by carbon

In all these bonds, carbon shows a valency of four. The special properties of carbon can be attributed to its being a relatively small atom with four valence electrons. The energy changes involved in gaining or losing four electrons, to form a stable configuration, are very high so that simple C^{4+} and C^{4-} ions do not exist, but customarily, carbon completes its valence-shell octet by sharing electrons (covalent bond formation) with other atoms (carbon or other elements).

Exercise :1

(a) Define catenation.

(b) List the four features that make carbon unique in its bond forming ability.

(c) Why does carbon form covalent bonds and not ionic bonds?

1.4 Representation of Organic Molecules

From our discussion so far, it should be clear that carbon forms three types of covalent bonds – single - double and triple bonds with either itself or with other elements. Covalent bonds are directed in space (spatial arrangement) so that molecules containing them may be three-dimensional; as for CH_4(methane). It is not easy to represent such spatial arrangement on paper but look at the model below.

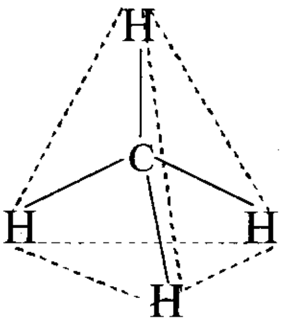
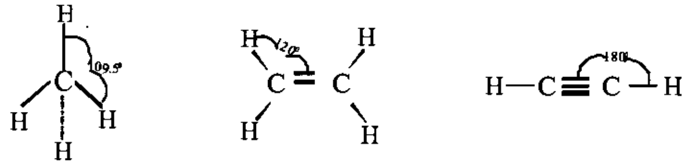


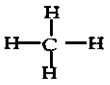
Fig. 1:2 Three-dimensional structure of the molecule CH_4

The four single covalent bonds around carbon if equivalent, are arranged at the corners of a tetrahedron (Fig. 1.3(i)) with the H–C–H bond angles of 109°. In molecules, e.g ethene, C_2H_4, in which the carbon atom is surrounded by two single and one double bond, such a molecule is planar (Fig. 1.3(ii)) with bond angle of 120⁰. For molecules e.g ethyne, C_2H_2, in which the carbon atom is surrounded by one single and one triple bond, such molecule is collinear (Fig. 1.3(iii)) with bond angles of 180⁰.



(i) tetrahedron (ii) planar (iii) collinear

Fig.1.3: Directional nature of bonds formed in simple molecules

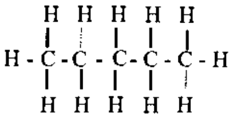
On paper, either the molecular formula e.g CH_4 or planar structural formula  $H-\overset{H}{\underset{H}{C}}-H$ can be used for representing molecule. It is easy when reading a book to come to regard all organic molecules as being flat; it is important to remember that most of them are not.

1.5 Classification of Organic Compounds

You will recall that in this unit, it was mentioned that organic compounds are numerous. However, the number of guiding principles is relatively small; one of such principles is the classification of organic compounds as shown in Fig.1.4.

1.5.1 Open-chain or aliphatic compounds

These are compounds that contain chains of interlinked carbon atoms(may involve other elements). The chains length varies over a wide range of carbon atoms e.g. Pentane, C_5H_{12}



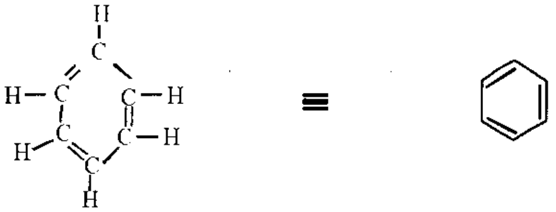
$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$$

1.5.2 Saturated and unsaturated compounds

When all the bonds between the carbon atoms (may involve other elements) are single, the compound is said to be saturated e.g Pentane. If, however, multiple bonds e.g the double bond in alkenes $>C=C<$ and triple bond in alkynes $-C\equiv C-$ is present in the molecule, the compound is said to be unsaturated.

1.5.3 Aromatic compound

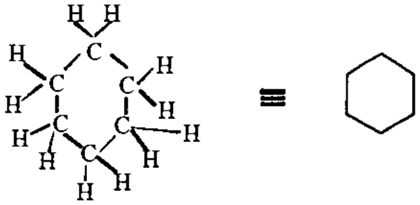
These are carbocyclic compounds endowed with what is referred to as aromatic character i.e. they contain rings of carbon atoms, based on benzene C_6H_6; (Unit 7) which can be represented as shown below



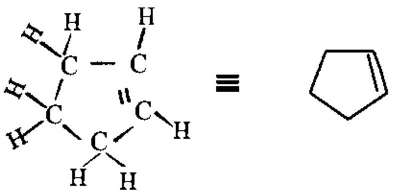
There are important differences in properties between aliphatic and aromatic compounds, e.g between hexane C_6H_{12} and benzene, C_6H_6.

1.5.4 Alicyclic compound

These are carbocyclic compounds with C–C and/or C = C bonds between the carbon atoms in the ring. Benzene is not normally classified as alicyclic even though it is carbocyclic. The reasons for this will be explained in Unit 7. Compounds in this group have some properties similar to those of aliphatic compounds; hence the name alicyclic.



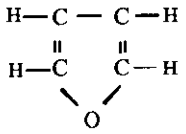
cyclohexane



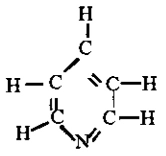
cyclopentene

1.5.5 Heterocyclic compounds

These are cyclic compounds containing elements other than carbon, particularly oxygen, nitrogen or sulphur in the ring e.g.



Furan



Pyridine

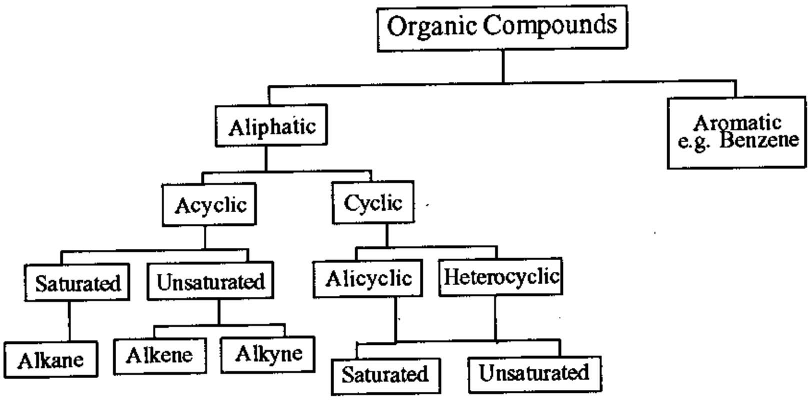


Fig. 1.4: Classification of organic compounds

1.6 Conclusion

In this unit you have learned about organic chemistry as the study of carbon compounds. These compounds are abundant in nature and they play important roles in our life. Carbon is able to form such vast amount of compounds because of its ability to covalently bond with carbon atoms and other elements in chains or ring forms. The vast numbers of carbon compounds makes it necessary to classify them into groups of compounds with similar characteristic for easy comprehension.

1.7 Summary

You have learnt in this unit the definition of organic chemistry and about organic compounds. This has served to introduce you to the nature and scope of organic chemistry, as well as the special position of carbon atom in organic compounds. The classification of these compounds shall form the frame work for our discussion in subsequent unit.

1.8 Tutor-Marked Assignment

Briefly explain the features that enable carbon atoms to form vast amount of organic compounds.

1.9 Reference

Brown, G. I. (1978). *An Introduction to Organic Chemistry.* Lagos: Longman Publishers.

Unit 2

The Homologous Series, Functional Groups and Isomerism

2.0 Introduction

You have been introduced to organic chemistry in Unit 1 and now that you are aware of the scope of this section of chemistry; you will learn in this unit some important concepts or terminologies commonly used in organic chemistry. The terms homologous series and functional groups explain some of the umbrella principles that help in the understanding of organic compounds despite their large number. Isomerism explains the existence of organic compounds having the same number and kind of atoms but showing differing characteristics due to the differences in the way the atoms are arranged within the molecules.

2.1 Objectives

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

- Define the terms homologous series, functional groups and isomerism.
- List the characteristics of a homologous series.
- Identify the structural representation of simple organic functional groups.
- Draw and name the structural isomers of hydrocarbon compounds having a maximum of five carbon atoms.
- Distinguish between structural and geometrical isomerism.

2.2 The Homologous Series

In unit 1 you learned that organic compounds are numerous in number, in fact, they are in millions. In dealing with such large number of compounds, some form of classification is essential as was exemplified in unit 1. It was observed that certain set of compounds show structural, physical and chemical similarities and are said to constitute a homologous series. A homologous series can be defined as a collection of a small number of series of organic compounds with unique structural pattern and properties; each member differs by a constant $-CH_2-$ unit. The term homologous is used to describe a group of compounds with the following characteristics:

(i) they can be prepared by similar methods;
(ii) they have similar chemical properties;
(iii) there is a regular gradation of physical properties (melting or boiling points, solubility);
(iv) they can be represented by a general formula e.g. C_nH_{2n+2} for alkanes; C_nH_{2n} for alkenes, C_nH_{2n-2} for alkynes, $C_nH_{2n+1}OH$ for alkanols, $C_nH_{2n+1}COOH$ for alkanoic acids;
(v) each member differs in molecular formula from the preceeding compound by $-CH_2-$ (mass unit of 14) e.g. in alkanes, CH_4, C_2H_6, C_3H_8, C_4H_{10}, etc.

(vi) each member contains at least one functional group e.g. C=C for alkene, C≡C for alkynes, –OH for alkanols, –COOH for alkanoic acid.

These characteristics are very essential for the understanding of organic chemistry and will be encountered throughout your study of organic chemistry.

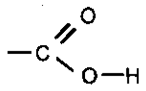
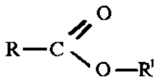
Exercise 1

Write the structure of the first 10 members of the alkane homologous series.

2.3 Functional Groups

One of the characteristics of a homologous series you learned in Section 2.2 of this unit, is that each member of a series contains at least one functional group. In fact, the functional group determines the properties of a homologous series. A functional group is a structural feature consisting of atoms or bonds found in organic compounds that control the classification and reactivity of the molecules. The study of organic chemistry becomes simplified when examined according to their functional groups. One of the main reasons for classifying compounds by their functional groups is that it also classifies their chemical behaviour and, to some extent, their physical properties. Table 2.1 summarizes some of the commonest functional groups.

Table 2.1 Classification of Simple Organic Compounds by Functional Groups

Class of Compounds	Functional Group	Suffix	General Representation	Example
Alkanes	–C–C– bond	-ane	RH or R—R	ethane
Alkenes	–C=C– bond	-ene		ethene
Alkynes	–C≡C– bond	-yne		ethyne
Alkanols (alcohols)	–O–H	-ol	R–OH	ethanol
Alkanoic acids (carboxylic acids)	 or –COOH or $-CO_2H$	-oic acid	R–COOH	ethanoic acid
Alkanoates (esters)		-oates	$R-CO_2R'$	ethyl ethanoate
Alkanamine (Amine)	$-NH_2$	-amine	$R-NH_2$	ethanamine

Note: 'R' in organic chemistry represents an alkyl group or radical which is an alkane less one hydrogen atom.

The number of common functional groups is small in comparison with the total number of organic compounds. The contents of organic chemistry are, therefore, arranged together if the emphasis is put on the characteristics of individual functional groups. Once these properties e.g. method of preparation, chemical reactivity, etc. have been illustrated it is possible, with reasonable accuracy, to predict the properties of any compound containing such functional groups. This is what makes the study of organic chemistry simple despite the large number of compounds involved.

2.4 Isomerism

This is the term used to describe the existence of two or more organic compounds with the same molecular formula, but different structural formulae. The different forms of the compounds are called isomers and have different chemical and physical properties.

structural formula of isomers

molecular formula $C_2H_6O \Longrightarrow CH_3-O-CH_3 \qquad CH_3-CH_2-OH$

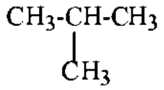
Stated in another way, compounds having the same number and kind of atoms but the atoms are arranged differently are called isomers. Your left and right hands contain the same features but arranged differently; they are isomers of one another. What about your pair of shoes?

Activity: Look around you and see how many pairs of isomers you can recognise. There are two types of isomerism that are known to exist in organic compounds - structural isomerism and stereoisomerism is also known as Geometric isomerism.

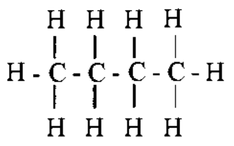
2.4.1 Structural isomerism

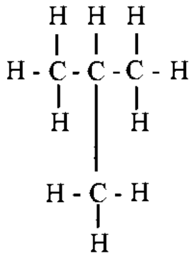
In structural isomers the molecules contain the same number of each kind of atom but differ in regard to which atom is linked to which. In structural isomerism the difference arise simply from the arrangement of atoms within the molecule, resulting in two or more different structural formulae.

$CH_3-CH_2-CH_2-CH_3$



$CH_3-CH(CH_3)-CH_3$

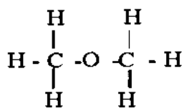




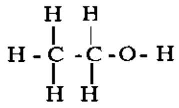
butane C_4H_{10} 2-methylpropane

- Consider the words Ronald, Roland, Arnold, they contain the same numbers of the same letters written in such a way to give different words - structural isomers.

The isomers are all separate, distinct compounds and even the names may be different. If they contain the same functional group and are members of the same homologous series e.g. C_4H_{10}. They have many chemical properties in common but have different physical properties. If they contain different functional groups and belong to different homologous series they differ in both chemical and physical properties, e.g. C_2H_6O



methoxymethane



ethanol

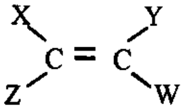
Exercise 2

(a) The first three members of the alkane series, methane (CH_4), ethane (C_2H_6) and propane (C_3H_8) do not exhibit structural isomerism; confirm this by drawing their structural formula yourself.

(b) C_4H_{10} has two structural isomers as shown above. The next member of the alkane series C_5H_{12} has three structural isomers.

2.4.2 Geometric isomerism

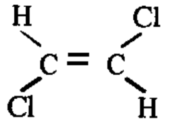
This is a type of isomerism existing in compounds containing double bonds because there is no free rotation of the carbons about double bonds so that these bonds lock the two groups they link in permanent positions.



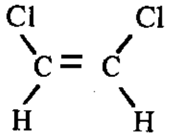
Generally, all alkenes that have two different groups attached to each carbon atom containing the double bond may show geometric isomerism. Two arrangements are possible; an isomer in which similar groups are on the same side of the double bond (it is called cis-isomer from the latin word 'same') and the other isomer in which the similar groups are on the opposite sides of the double bond (it is called trans-isomer from the latin word meaning 'across'). Geometric isomerism is sometimes called cis-trans isomerism.

Examples of Geometric Isomers are shown below:

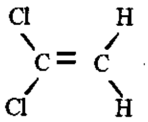
1. $C_2H_2Cl_2$



trans-isomer

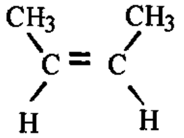


cis-isomer

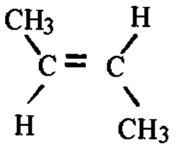


No geometric isomerism. Can you explain this?

2. C_4H_8

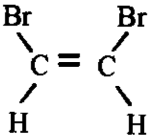


cis-2-butene

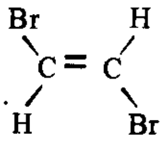


trans-2-butene

3. $C_2H_2Br_2$



cis-1,2-dibromoethene



trans-1,2-dibromoethene

2.5 Conclusion

In this unit you have learned about the homologous series and functional groups, two important terms used in organic chemistry to explain the arrangement of organic compounds into a number of chemically similar groups or families. These terms should help you to view organic chemistry as a collection of a set of compounds with similar characteristics rather than the study of all individual compounds. The aim of these classifications therefore is to make the study of the subject matter easy. You have also learned about isomerism which explains the importance of the mode of arrangement of atoms in a molecule and how it could influence the characteristics of the molecules.

2.6 Summary

- What you have learned in this unit concerns the terms homologous series, functional groups and isomerism as they relate to the study of organic compounds.
- The homologous series is used to describe set of compounds with similar characteristics grouped to ease our understanding of organic chemistry.
- The functional group is the common structural feature in organic compounds that is used for their classification and determines their properties. Isomerism deals with organic compounds having the same number and kind of atoms but structurally different and hence show different characteristics.

2.7 Tutor-Marked Assignments

(a) Draw all the structural isomers of the compound C_5H_{12}.
(b) Draw the cis-trans isomers of C_4H_7Cl (chlorobutene).

2.8 References

Bajah, S. T., Teibo, B. O., Onwu G and Obikwere, A. (2002). *Senior Secondary Chemistry - Textbook 2.* Lagos. Longman Publishers.

Tewari, K. S., Mehrotra V. and Vishnoi, N. K. *Textbook of Organic Chemistry.*

Unit 3

IUPAC Nomenclature of Organic Compounds

3.0 Introduction

In unit 1 you learned about organic chemistry and the abundance and relevance of organic compounds in nature. You will also recall that the number of known organic compounds are in millions, and continue to increase as more naturally occurring compounds are discovered and many more are prepared. Can you imagine what it takes to remember over a million names? There are so many organic compounds that it is a real problem to provide them all with different, yet sensible, names. It is rather like trying to find different, yet related, surnames for everyone in the world. At the onset of organic chemistry, the names of organic compounds is based on the source from which the compound was obtained or on the structure or properties of the compound. This is known as *trivial system* and the names are called *trivial names* or *common names* e.g.

Trivial Name	***Source***
Urea	Urine
Citric acid	Citrus fruit

This naming system could not be sustained because of the enormous increase in the number of known organic compounds. The new system (or rule) for naming organic compounds, which is now widely accepted, is in accordance with the rules formulated by the International Union of Pure and Applied Chemistry (IUPAC) and is known as *IUPAC System of Nomenclature*. The full set of rules to cover every known compound is complicated. A brief outline is therefore given in this unit and extended throughout the subsequent units.

3.1 Objectives

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

- Recall the IUPAC rules for systematic naming of simple organic compounds.
- Name the first ten members of each homologous series
- Identify the structure of simple organic functional groups and name them using the IUPAC nomenclature

3.2 Nomenclature of Organic Compounds

3.2.1 The hydrocarbons

These are organic compounds consisting of carbon and hydrogen atoms only. There are three most important homologous series of hydrocarbons namely alkanes, alkenes and alkynes. Recall the classification of organic compounds as illustrated in Fig. 1.4 of Unit 1; alkanes are saturated hydrocarbons while alkenes and alkynes are unsaturated hydrocarbons. Examples of these classes organic compounds are illustrated in Fig. 3.1 below.

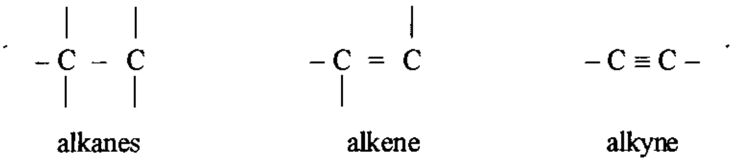


Fig. 3.1: Examples of three classes of hydrocarbons

(a) Alkanes

The general formula of alkanes is C_nH_{2n+2} (where n = whole number). Alkanes are considered to be the parent compound and have the basic formula for writing the structure and name of organc compounds as illustrated in Table 3.1. The alkanes have an *-ane* ending (suffix) and the prefix for members of the series is based on the carbon atoms involved. (Table 3.1) *Meth-*, *eth-*, *Prop-* and but – prefixes for the first four members

The hydrocarbon group formed by the removal of one hydrogen atom from an alkane is called an alkyl group, and is named by dropping 'ane' from the name of the corresponding alkane and adding the suffix 'yl' as shown in Table 3.1

Table 3:1 IUPAC nomenclature of simple alkanes

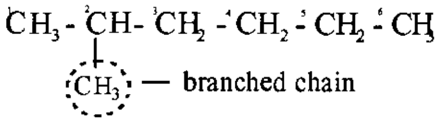
IUPAC NAME	*Formula* C_nH_{2n+2}	*Alkyl group*	*Formula* C_nH_{2n+2}
Methane	CH_4	Methyl	CH_3
Ethane	C_2H_6	Ethyl	C_2H_5
Propane	C_3H_8	Propyl	C_3H_7
Butane	C_4H_{10}	Butyl	C_4H_9
Pentane	C_5H_{12}	Pentyl	C_5H_{11}
Hexane	C_6H_{14}		
Heptane	C_7H_{16}		
Octane	C_8H_{18}		
Nonane	C_9H_{20}		
Decane	$C_{10}H_{22}$		

Exercise 1

Complete the blank spaces in Table 3.1 following the trend shown for the first five members of the alkane series.

In alkanes with branched (groups not part of the longest chain of carbon) chains the IUPAC name is based on the number of carbon atoms in the longest chain. This longest chain is then numbered from one end so that the position of the branched chains can be indicated.

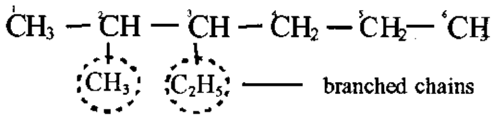
The longest chain of carbon atoms can be numbered from either end; the direction chosen is that which enables the lowest numbers to be used. For example:


$$\overset{1}{C}H_3-\underset{\displaystyle CH_3}{\overset{2}{C}H}-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H_3$$

— branched chain

2-methylhexane

When two or more branched chains are present they are listed alphabetically.


$$\overset{1}{C}H_3-\underset{\displaystyle CH_3}{\overset{2}{C}H}-\underset{\displaystyle C_2H_5}{\overset{3}{C}H}-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H_3$$

branched chains

3-ethyl-2-methylhexane

(b) Alkenes

The general formula for alkenes is C_nH_{2n} showing that they have two hydrogen atoms less than the corresponding alkanes. Recall the prefixes for the alkanes; which depend on the number of carbon atoms in the organic compound; the same prefixes are retained for the alkenes. However, organic compounds which have double bonds (alkenes) have the suffixes –ene (compare this with the suffixes for alkanes –ane). I guess it is easy to remember. CH_3-CH_3 $CH_2=CH_2$

ethane, an alkane ethene, an alkene

Table 3.2: IUPAC nomenclature of simple alkenes

IUPAC Name	*Formula C_nH_{2n}*	*Alkenyl Group*	*Formula C_nH_{2n-1}*
Ethene	C_2H_4	Ethenyl	C_2H_3-
Propene	C_3H_6	Propenyl	C_3H_5-
Butene	C_4H_8	Butenyl	C_4H_7-
Pentene	C_5H_{10}	Pentenyl	C_5H_9-

Exercise 2

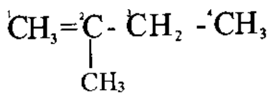
Complete the bank spaces in Table 3.2 using the guide from Table 3.1. The positions of the double bond and of any branched chains are shown by numbering the longest straight chain of carbon atoms. Thus,

$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H_2-\overset{4}{C}H_3$

but-1-ene
(not but-3-ene)

$\overset{1}{C}H_3-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}H_3$

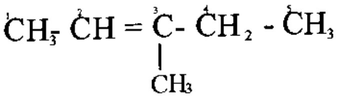
but-2-ene



$\overset{1}{C}H_3=\underset{\underset{CH_3}{|}}{\overset{2}{C}}-\overset{3}{C}H_2-\overset{4}{C}H_3$

2-methylbut-1-ene

(not 3-methylbut-3-ene)
(not 2-ethylprop-1-ene)



$\overset{1}{C}H_3-\overset{2}{C}H=\underset{\underset{CH_3}{|}}{\overset{3}{C}}-\overset{4}{C}H_2-\overset{5}{C}H_3$

3-methylpent-2-ene

(not 3-methylpent-3-ene)
(not 2-ethylbut-2-ene)

The hydrocarbon residue formed by the removal of one hydrogen atom from an alkene is called an *alkenyl*. e.g. $CH_2=CH_2 \xrightarrow{-H} -CH=CH_2$ ethenyl; $CH_3CH=CH_2 \xrightarrow{-H} -CH_2CH=CH_2$

ethene propene propenyl

Exercise 3

Can you explain why the names in bracket for the structures above are incorrect?

(c) Alkynes

The general formula for alkynes is C_nH_{2n-2}. The pattern you learnt for alkanes and alkenes is also used for alkynes except that the suffix 'ane' for the alkanes is replaced by 'yne' for the alkynes series.

e.g. CH_3-CH_3	$CH_2=CH_2$	$CH\equiv CH$
ethane an alkane	ethene an alkene	ethyne an alkyne

3.2.2 Rules for IUPAC Nomenclature

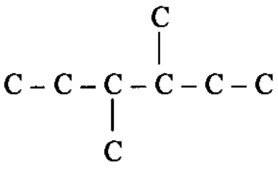
(a) Introduction

You have been introduced in Section 3.2.1 to the nomenclature of hydrocarbons before been introduced to the rules for the IUPAC nomenclature. This is not an oversight, it is because most organic compounds are considered as derivatives (derived from) of the alkanes formed when the hydrogen(s) of alkanes are replaced by various groups or substituents. Thus, the name of any organic compound depends on the correct selection of the parent hydrocarbon or the basic carbon skeleton.

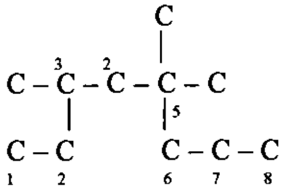
(b) The rules of IUPAC nomenclature

(i) The first step is to select the longest possible continuous chain of carbon atoms which is called the parent chain.

The parent chain is determined by the number of carbon atoms. All other carbon chains attached to the parents chain are referred to as side chains or substituents. Thus, if the parent chain contains six carbon atoms, the parent hydrocarbon is hexane (structure 1)



(I)



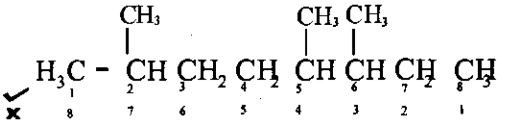
(II)

In structure (II), the straight chain contains only five carbon atoms whereas the longest continuous chain of carbon atoms contains eight carbon atoms and hence it is an octane chain. Straight chain is not the same as continuous chain so what is important is the longest continuous carbon atoms and not the straightness or zig-zag nature of the chain.

It is possible that sometimes there may be two carbon chain having the same number of carbon atoms in the molecule. In such a case, the next rule will teach you how to select the longest continuous chain.

(ii) The second step is to number (Arabic numericals 1,2,3,...etc) the longest continuous chain from one end to the other in such a manner that the carbon atom carrying substituents get the lowest numbers.

The positions of the side chains or substituents are indicated by the numbers assigned to the carbon atoms to which they are attached. If there are more than one substituent then the numbering of carbon atoms is done in such a way that the sum of the numbers used to locate the subsituents is minimum. This is also known as the lowest sum rules. The number that locates the position of a substituent is known as **Locant**. (Structure III).



$$\underset{\overset{1}{8}}{H_3C} - \overset{CH_3}{\underset{\overset{2}{7}}{CH}}\ \underset{\overset{3}{6}}{CH_2}\ \underset{\overset{4}{5}}{CH_2}\ \overset{CH_3}{\underset{\overset{5}{4}}{CH}}\ \overset{CH_3}{\underset{\overset{6}{3}}{CH}}\ \underset{\overset{7}{2}}{CH_2}\ \underset{\overset{8}{1}}{CH_3}$$

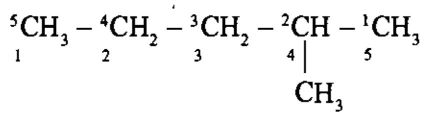
Sum of Locant

(2 + 5 + 6) = 13 ✓

(3 + 4 + 7) = 14 ×

So Structure (III) is 2,5,6, trimethyloctane and not 3,4,7, trimethyloctane

(iii) The name of the substituents is prefixed, preceded by the locant, to the name of the parent chain. A hyphen separates the locant from the name of the substituents e.g 2-methylpentane. (structure iv).

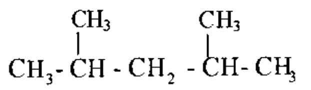


$$\underset{1}{{}^5CH_3} - \underset{2}{{}^4CH_2} - \underset{3}{{}^3CH_2} - \underset{4}{\underset{CH_3}{{}^2CH}} - \underset{5}{{}^1CH_3}$$

- longest chain contains 5 carbon atom, so parent is pentane
- a $-CH_3$ (methyl) group located at 2 or 4; however is 2 smaller than 4, so 2-methylpentane

(IV)

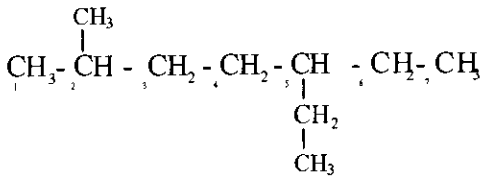
(iv) When there are more than one substitutent, each substituent is prefixed by its locant and arranged in alphabetical order preceeding the name of the parents chain. The prefix di–, tri– or tetra– (for two, three or four substituents), is attached to the substituents name when more than one of a kind of substituents is present and the locants are written in increasing order separated by commas amongst themselves. (see Structure (III). However the prefixes di–, tri– or tetra–, etc are not considered while deciding the alphabetical order of the substituents. Although this rule seems complicated the following examples will illustrate the rule and improve your understanding (Structure (v) – (vii)).



$$\begin{array}{ccccc} CH_3 & & & CH_3 & \\ | & & & | & \\ CH_3-CH & - & CH_2 & -CH- & CH_3 \end{array}$$

2,4-dimethylpentane

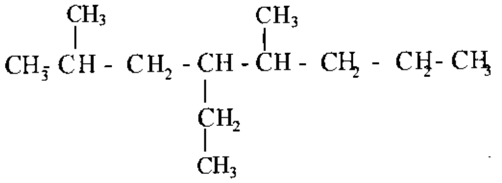
(V)



$$\begin{array}{ccccccc} CH_3 & & & & & & \\ | & & & & & & \\ \overset{}{\underset{1}{CH_3}}-\underset{2}{CH} & - & \underset{3}{CH_2} & - & \underset{4}{CH_2} & -\underset{5}{CH}- & \underset{6}{CH_2}-\underset{7}{CH_3} \\ & & & & & | & \\ & & & & & CH_2 & \\ & & & & & | & \\ & & & & & CH_3 & \end{array}$$

5-ethyl-2-methylheptane
(not 2-methyl-5-ethylheptane)

(VI)



$$\begin{array}{cccccccc} CH_3 & & & CH_3 & & & \\ | & & & | & & & \\ CH_3-CH & - CH_2 & -CH & -CH & - CH_2 & - CH_2 & - CH_3 \\ & & | & & & & \\ & & CH_2 & & & & \\ & & | & & & & \\ & & CH_3 & & & & \end{array}$$

4 - ethyl - 2,5 - dimethyloctane
(not 2,5 - dimethyl - 4 - ethyloctane)

(VII)

- I am sure you feel a lot better now. Can you then explain why the names in bracket for structures vi and vii are incorrect?

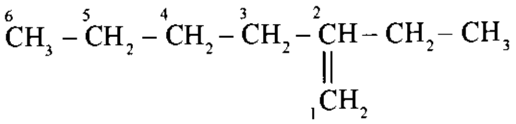
Did your answer corresponds to this?

- For Structure VI, the name 2 methly-5- ethylheptane is incorrect because it violates the aliphabetical rule
- For structure VII, the name 2,3 dimethyl-4-ethyloctane is incorrect because the prefix 'di-' was used in determination of the alphabetical order of substituents which should be based only of the names of the substituents - ethyl and dimethyl.

Congratulations !!!

If however your explanation was wrong, use the explanation given to improve your understanding of the subject matter.

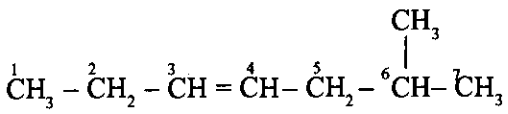
(v) When a double or triple bond is present in the molecule then the longest chain of carbon atoms is chosen as to include the multiple bond even if it is not longest continuous chain of carbon atoms. This rule is illustrated for you in structure VIII.



$$\overset{6}{C}H_3-\overset{5}{C}H_2-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{2}{C}H-CH_2-CH_3 \qquad \overset{\|}{{}_1CH_2}$$

2-ethyl-1-hexene (VIII)

Although the longest continuous chain is of 7 atoms but since it does not include the double bond, it is rejected as the parent chain and the carbon chain of 6 atoms (which is shorter) including the double is selected as the parent chain for naming the compound. The position of double or triple bond is indicated by prefixing the number of the carbon atom preceding the multiple bond.



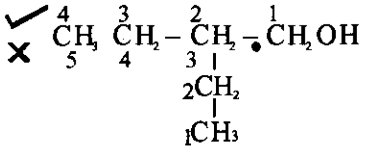
$\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}H=\overset{4}{C}H-\overset{5}{C}H_2-\overset{6}{C}H(CH_3)-\overset{7}{C}H_3$

(IX) = 6-methyl-3-heptene

The selected parent carbon chain is numbered in a manner that gives the lowest number to the multiple bond. For example structure (IX) is named 6 – methyl-3-heptene and not 2-methyl-4-heptane.

3.2.3 Naming non-hydrocarbon compounds: Compounds with functional groups

You can still remember what functional groups are as learnt in unit 2. If an organic compound contains a functional group, the longest carbon chain must be chosen as to include the functional group. The parent chain selected is numbered in a way to give the lowest number to the functional group even if it violates the lowest sum rule.



$\overset{4}{C}H_3\overset{3}{C}H_2-\overset{2}{C}H(CH_2CH_3)-\overset{1}{C}H_2OH$

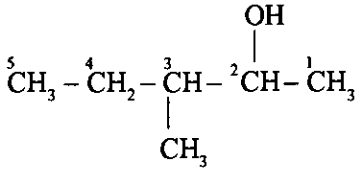
2-ethyl-1-butanol ✓

(C_4 not C_5 because only the C_4 contain the functional group)

The name of the substituents are prefixed to the parent hydrocarbon according to the IUPAC rules discussed in section 3.2.2. of this unit and the 'e' of the parent hydrocarbon name is replaced with the suffix of the functional group e.g.

- butane to butanol for alkanol
- hexane to hexaoic acid for alkanoic acid
- butane to butanoate for alkanoate

This rule is illustrated in structures (X) and (XI) and will be applied in subsequent units this will improve your understanding of the concept.



$\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H(CH_3)-\overset{2}{C}H(OH)-\overset{1}{C}H_3$

3-methyl-2-pentanol (X)

CH_3-CH_2-COOH

propanoic acid (XI)

3.3 Conclusion

This is the end of the unit in which you have learned the basic IUPAC rules for naming organic compounds. The rules followed a systematic way of naming groups of compounds using the alkane parent compounds as the building block. The rules may appear difficult to apply at first but with practice you will get to understand it better and find it easy to use. Opportunity for more practice will be provided in subsequent units.

3.4 Summary

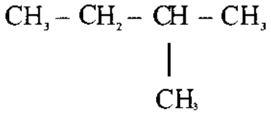
The IUPAC nomenclature for systemic naming of organic compounds involves the following rules.

- The longest continuous chain of carbon atoms containing the functional group is selected and named according to the parent alkane
- The selected parent chain is numbered to indicate the postitions of any substituent in the chain and such numbering should give the lowest possible number to the carbon atom to which a substituent is attached.
- The name of substituents prefix the names of the parent alkane alphabetically and the positions of substituents preceed the names.
- The position of functional groups are given preference over those assigned to other substituents even if the lowest sum rule is violated.

3.5 Tutor-Marked Assignments

1. Give the IUPAC names of the following compounds

(a)

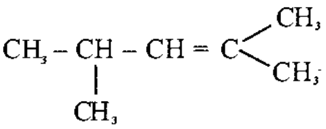


$CH_3 - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_3$

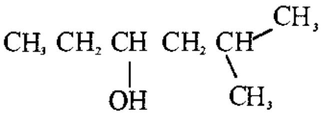
(b)

$CH_3 - CH = CH - CH_2 - CH_3$

(c)



(d)



2. Draw the structures for the following IUPAC named compounds
   (a) 2 - ethylpentanol
   (b) 2, 3-dimethyl -2- octene
   (c) 3 –ethyl -2- methylheptane

3.6 References

Norman R.O.C. and Waddington D. J. "Modern Organic Chemistry".
Teweri K. S. Mehrotra V and Vishnoi, N. K. "Textbook of Organic Chemistry".

Unit 4

Purification Methods and the Determination of Empirical, Molecular and Structural Formula of Organic Compounds

4.0 Introduction

Organic compounds are usually represented in organic chemistry with formula, which is a shorthand method of showing the constituent atoms. The formula of a compound consist of chemical symbols of the constituent atoms and numerical subscript to indicate the ratio of the atoms. Recall that chemical bonds hold atoms together in the molecule and for organic compounds, the bond is essentially covalent. In the molecular orbital theory of covalent bonding, a bond is thought of in terms of the overlapping of two atomic orbitals each containing one electron. Covalent bonding formed by overlap of atomic orbitals are of two types, the sigma (σ) bond and the pie (π)bond. All single bonds in organic compounds are of the σ-type; double bonds consist of one σ-bond and one π bond types; while triple bonds consist of one σ bond and two π-bond types. Although when bonds between atoms are drawn, they are all represented with a straight line (–), it is important to note that these two types of bonds exist because they determine the reactivity of organic compounds.

Once an organic compound is prepared in the laboratory or isolated from some natural source, the procedure for the determination of its nature consists of the following steps.

(i) state of purity and purification,
(ii) determination of elemental composition-qualitative analysis,
(iii) determination of relative numbers of each atom present in one molecule of the compound-quantitative analysis,
(iv) determination of empirical and molecular formula,
(v) determination of the structure of the molecule.

In this unit, our primary concerns are the methods for purification; determination of empirical, molecular and structural formula of organic compounds.

4.1 Objectives

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

- Explain the methods for the purification of organic compounds.
- Derive the empirical and molecular formula of organic compounds.
- Draw the structural formula of organic compounds.

4.2 Purification Methods

Investigation of any compound must be preceded by careful purification to separate the pure substance from the impurities. In order to separate any two substances it is necessary to find some differences between them and the generally used ones are differences in solubility or vapour pressure (boiling point). **The greater the differences between the two compounds the easier it is to separate them.**

4.2.1 Distillation

This is a process used in separating two or more volatile, miscible liquids with different boiling points. For example a mixture of two liquids A (b.p. = 50^{0}C) and B (b.p. 100^{0}C). Distillation is of two types, simple distillation and fractional distillation. Simple distillation is used when the difference in boiling points, of the compounds to be separated is high; while fractional distillation is required when the boiling points are close and several compounds are to be separated.

The process of distillation involves boiling the mixture in a flask and the vapour from it is passed through a condenser. Pure liquid collects in a receiver and is referred to as the distillate; the impurities remain in the distillation flask. A simple arrangement is shown in Fig. 4.1

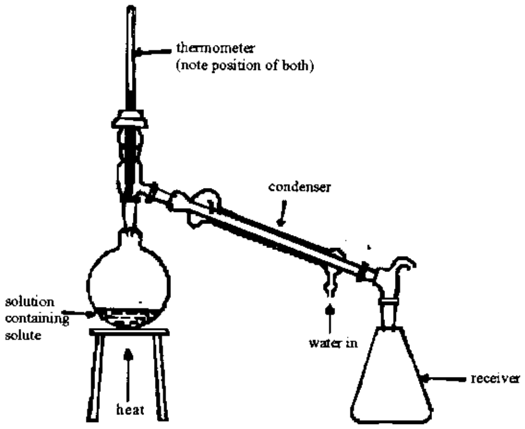


Fig 4.1 Simple distillation

The process of fractional distillation is not, however, always simple and straightforward as described above. It involves the use of fractionating column for good separation of liquids with very similar boiling points. Fractional distillation will be discussed in details in Unit 8 as it relates to the fractional distillation of crude oil or petroleum.

4.2.2 Crystallization

This is the commonest method for purifying a solid. The process of crystallization involves finding a solvent, by experimental trial, in which the solid is more soluble when the solvent is hot than when it is cold. The impure solid is then dissolved in the minimum amount of hot solvent, the aim is to get a solution which is nearly saturated at the boiling point of the solvent. The hot solution is then filtered, through a filter paper or funnel, so that any insoluble impurities can be removed. The filtration must be rapid to avoid crystallization during the process. A Buchner flask and funnel is the most suitable. (Fig. 4.2)

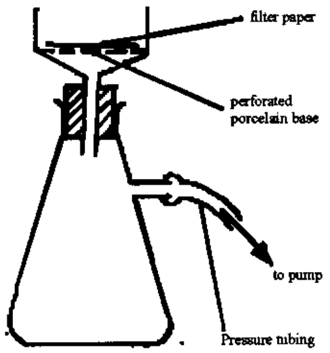


Fig. 4.2 Buchner Flask and Funnel

Soluble impurities remain, together with the solid required, in the filtrate. This is cooled for crystallization and the crystals formed are filtered off through a Buchner funnel. The crystals are then washed in the funnel with a little of the cold solvent and allowed to dry by pressing between filter papers or in a desiccator or oven.

Crystallisation is used in the manufacture of drugs and sugar.

4.2.3 Chromatography

Many natural products, for example extracts from plants and animals, are particularly difficult to purify. They may only be available in small quantities, they tend to decompose on heating, and the impurities are generally chemically similar to the product of interest. Chromatography is a useful separation technique in situations where traditional methods of separation is not successful.

Chromatography involves moving a solvent over a porous, adsorbent medium (e.g. paper or powdered material such as silica and alumina) to separate a mixture of solute. There are many types of chromatographic techniques but our main concern in this unit is paper chromatography and column chromatography

(a) Paper chromatography

This uses one strip of chromatographic or filter paper as an adsorbent medium. A solution containing the mixture of solutes to be separated is spotted near one end of the paper. The paper is then suspended in a closed air-tight jar with the spotted end (but not the spot) dipped into a suitable solvent e.g. hexane, water. As the solvent front rises up the paper by ascending capillary action the various solutes present are carried forward at different speed. When the solvent front reaches almost to the top of the paper, the paper is removed and dried. If the solutes are coloured their positions on the paper can be seen. For colourless solutes the paper can be treated with appropriate chemical reagent to convert the solutes into coloured compounds. Each solute can then be identified by the distance travelled and separated by cutting up each spot on the paper and each solute extracted separately. Fig. 4.3 shows a typical ascending paper chromatography set up.

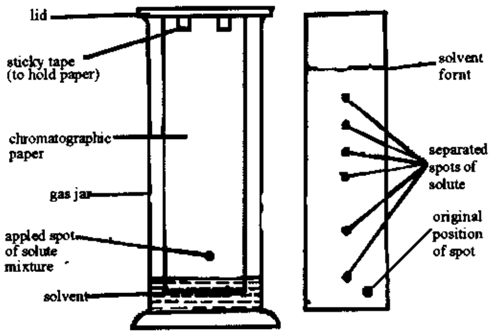


Fig. 4.3 Ascending paper chromatography

(b) Column chromatography

In column chromatography the solution containing the solutes is passed through a glass tube or column packed with solid adsorbent such as alumina or silica. The mixture is then washed or moved through the column using an appropriate solvent. The solutes move through the column at different speed and are collected as separate component or fractions as the solvent elutes the column. The solvent is then evaporated to obtain each component of the mixture.

Many different packing materials e.g. alumina, silica, charcoal, starch, calcium carbonate, can be used. Typical solvents, which may be mixed together, include water, propanone, benzene, ethanol, trichloromethane and hexane. Chromatographic technique has been successfully used in the petroleum industry, hospitals, food industry and research organisation to effect the separation of mixtures of compounds.

4.3 Empirical and Molecular Formula

Qualitative and quantitative elemental analysis is used to know the various elements present and their relative composition respectively. Since a detailed study of these processes is beyond the scope of this programme, we shall discuss the next stage involved in the identification of an unknown organic compound, which is structural formula determination. The stages involve the determination of the empirical formula and molecular formula of the compound first; and then the structure, which shows the way the atoms are attached to one another, is then determined.

4.3.1 Empirical formula

This provides information about the simplest ratio of the different atoms in a molecule of a compound, it does not give the actual number of atoms in the molecule. For example, the empirical formula of ethane, CH_3CH_3 is CH_3 which is the same for all members of the alkane series (Unit 5). For ethanoic acid, CH_3CO_2H, the empirical formula is $CH_2 0$ which is the same for glucose, $C_6H_{12}0_6$. **The empirical formula, therefore, gives the simple relative ratio of atoms of each element present in the molecule of the compound.**

The basic steps involved in the determination of the empirical formula of an organic compound are:

(a) Write the percentage by mass of each element in the compound and the sum must add up to 100% (neglect experimental error). **As a rule, if the sum is less than 100%, then the difference is allocated to oxygen atom.**

(b) The percentage composition of each element is divided by the relative atomic mass of the elements in order to obtain the ratio of the moles of atoms present.

(c) Then divide each ratio by the smallest ratio value to obtain the simplest whole number ratio (empirical ratio).

The following examples will help to illustrate these steps.

Example 1

Experimental determination of the elemental composition of an organic compound gave 79.9% carbon and 20.1% hydrogen by mass. Determine the empirical formula of the compound.

Solution 1

Since the percenta and H added up to 100%, then the compound contains C and H only.

Step 1	Element	C	H
	%	79.9	20.1
Step 2:	% Ratio/Relative Atomic Mass	$^{79.9}/_{12}$	$^{20.1}/_{1}$
	Ratio of atoms	6.67	20.1
Step 3:	Smallest ratio	$^{6.67}/_{6.67}$	$^{20.1}/_{6.67}$
	whole number ratio	1	3

Therefore empirical formula = $C_1H_3 = CH_3$

Example 2

An organic compound contains 26.7% carbon and 2.2% hydrogen. Derive the empirical formula of the compound.

Solution 2

The % sum is 26.7 + 2.2 = 28.9% which is less than 100%; so the compound contains oxygen

Step 1:	Element	C	H	O
	%	26.7	2.2	100 - 28.9 = 71.1
Step 2:	% ratio/RAM	$^{26.7}/_{12}$	$^{2.2}/_{1}$	$^{71.1}/_{16}$
	Ratio of atoms	2.22	2.2	4.44
Step 3:	Smallest ratio	$^{2.22}/_{2..2}$	$^{2.2}/_{2.2}$	$^{4.44}/_{2.2}$
		1 :	1 :	2

The empirical formula = $C_1H_1O_2 = CHO_2$

4.3.2 Molecular Formula

The molecular formula of a compound gives the exact number of moles of atoms of the component elements in one mole of the compound. In some compounds, the empirical formula and the molecular formula are the same. In other cases, the molecular formula is a simple multiple, n, of the empirical formula. For instance, ethanol, C_2H_6O has the same empirical formula and molecular formula; while both ethyne, C_2H_2 and benzene, C_6H_6 have the same empirical formula, CH.

A simple relationship is: molecular formula = n x (empirical formula)

$$\text{or} \qquad n = \frac{\textit{molecular formula}}{\textit{empirical formula}}$$

(where n = 1, 2, 3, 4, 5 etc.)

To calculate the molecular formula of a compound it is necessary to experimentally determine the relative molecular mass of the compound. Details of the experimental procedure for molecular mass determination is beyond the scope of this programme. For gases and volatile liquids, once the relative vapour density is known, the relative molecular mass can be calculated using the relation

Relative molecular mass = 2 x Relative vapour density

The following examples will illustrate how the molecular formula of compounds are estimated from empirical formula.

Example 3

The empirical formula for the compound in example 2 is $CH0_2$. Given that the relative molecular mass of the compound is 90, calculate its molecular formula.

Solution 3

Sum of relative atomic masses of the elements in the empirical formula

$CH0_2 = (12 \times 1) + (1 \times 1) + (16 \times 2) = 45$

$$n = \frac{\textit{molecular formula}}{\textit{empirical formula}} = \frac{90}{45}$$

n = 2

.: Molecular formula = 2 x $(CH0_2) = C_2H_20_4$.

Example 4

An organic compound with a vapour density of 45 was found to contain 54.5% carbon and 9.1% hydrogen. Calculate the molecular formula of the compound.

Solution 4:

	C	H	O
	54.5%	9.1%	100 – 63.6 = 36.4%
% / Ram	$^{54.5}/_{12}$	$^{9.1}/_{1}$	$^{36.4}/_{16}$
	4.54	9.1	2.27
Dividing by smallest ratio	$^{4.54}/_{2.27}$	$^{9.1}/_{2.27}$	$^{2.27}/_{2.27}$
Whole number ratio	2 :	4 :	1
Empirical formula	$C_2H_4 0$		

Relative molecular mass = 2 x vapour density

RAM = 2 x 45 = 90

∴ Empirical formula mass = (12 x 2) + (1 x 4) + (16 x 1) = 44

$$\therefore\ n = \frac{molecular\,formula}{empirical\,formula\ mass} = \frac{90}{44} = 2.05 \approx 2$$

Molecular formula = 2 x $(C_2H_4 0)$ = $C_4H_8 0_2$.

4.4 Structural Formula

The structural formula of an organic compound gives information on the kind, number, arrangement and the nature of bonds of the atoms in the molecule. The structural formula therefore fully describes a compound. The molecular formula as determined in section 4.3.2 does not have complete information about a compound, since it is possible for two or more compounds to have the same molecular formula but different structural formula – a phenomenon called isomerism (Unit 2).

The additional information required to move from molecular formula to structural formula of a compound can be obtained through:

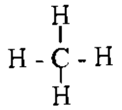
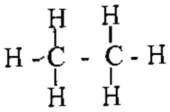
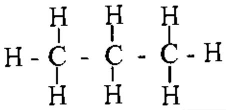
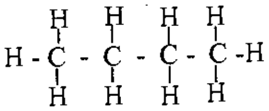
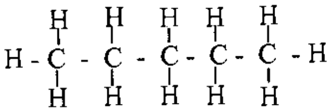
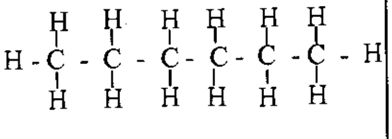
(a) physical properties determination e.g. colour, boiling point;

(b) the use of modem physical instrumentation e.g. mass spectroscopy, nuclear magnetic resonance, x-ray crystallography, etc. to establish structure.

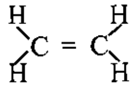
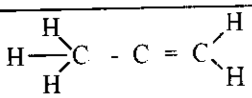
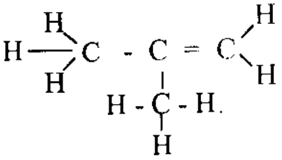
(c) chemical reactions to determine the functionality (Unit 2) present in the structure.

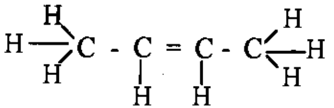
Once these information have been determined then the structural formula is drawn based on the information obtained and the molecular formula. Examples of the structural formula of several organic compounds based on their various functionality (Unit 2), are illustrated. You will learn more about the structure of these classes of compounds in subsequent units.

(i) **Alkanes**

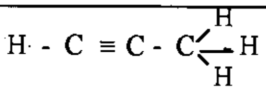
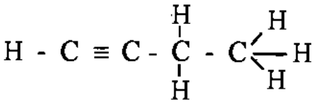
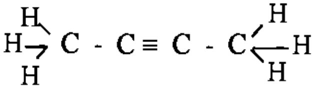
Name	*Molecular Formula*	*Structural Formula*	*Condensed Structural Formula*
Methane	CH_4	 $H-\underset{H}{\overset{H}{C}}-H$	CH_4
Ethane	C_2H_6	 $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$	$H_3C–CH_3$
Propane	C_3H_8	 $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$	$H_3C–CH_2–CH_3$
Butane	C_4H_{10}	 $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$	$H_3C–CH_2–CH_2–CH_3$ or $H_3C(CH_2)_2CH_3$
Pentane	C_5H_{12}	 $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$	$H_3C–CH_2–CH_2–CH_2–CH_3$ or $H_3C(CH_2)_3CH_3$
Hexane	C_6H_{14}	 $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$	$H_3C-CH_2-CH_2-CH_2-CH_2-CH_3$ or $H_3C(CH_2)_4CH_3$

(ii) **Alkenes**

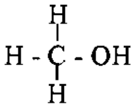
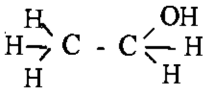
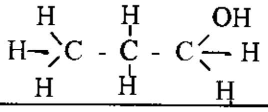
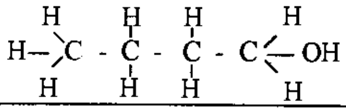
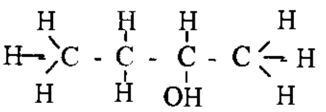
Name	*Molecular Formula*	*Structural Formula*	*Condensed Structural Formula*
Ethene	C_2H_4		$H_2C=CH_2$
Propene	C_3H_6		$CH_3CH=CH_2$
2-methyl prop-1-ene	C_4H_8		$(CH_3)_2\,C=CH_2$

Name	***Molecular Formula***	***Structural Formula***	***Condensed Structural Formula***
But-2-ene	C_4H_8		$CH_3CH=CHCH_3$

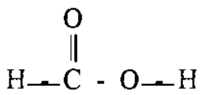
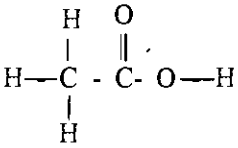
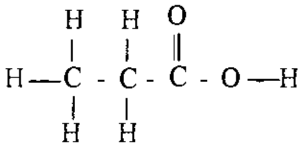
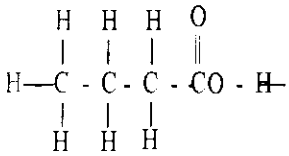
(iii) **Alkynes**

Name	***Molecular Formula***	***Structural Formula***	***Condensed Structural Formula***
Ethyne	C_2H_2	$H—C \equiv C—H$	$HC \equiv CH$
Propyne	C_3H_4		$HC \equiv C\text{-}CH_3$
1-Butyne	C_4H_6		$HC \equiv CCH_2CH_3$
2-Butyne	C_4H_6		$H_3CC \equiv CCH_3$

(iv) **Alkanols**

Name	***Molecular Formula***	***Structural Formula***	***Condensed Structural Formula***
Methanol	CH_4O		CH_3OH
Ethanol	C_2H_60		H_3CCH_2OH
1-Propanol or Propan-l-ol	C_3H_8O		$H_3CCH_2CH_2OH$
1-Butanol or Butan-1-ol	$C_4H_{10}O$		$H_3C(CH_2)_2CH_2OH$
2-Butanol or Butan-2-ol	$C_4H_{10}O$		$H_3CCH_2CH(OH)CH_3$

(v) Alkianoic Acids

Name	*Molecular Formula*	*Structural Formula*	*Condensed Structural Formula*
Methanoic acid	CH_2O_2	 $H-\overset{\overset{O}{\|}}{C}-O-H$	HCOOH or HCO_2H
Ethanoic acid	$C_2H_4O_2$	 $H-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-\overset{\overset{O}{\|}}{C}-O-H$	CH_3COOH or CH_3CO_2H
Propanoic acid	$C_3H_6O_2$	 $H-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-\overset{\overset{O}{\|}}{C}-O-H$	CH_3CH_2COOH or $CH_3CH_2CO_2H$
Butanoic acid	$C_4H_8O_2$	 $H-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-\overset{\overset{O}{\|}}{C}O-H$	$CH_3CH_2CH_2COOH$ or $CH_3(CH_2)_2CO_2H$

4.5 Conclusion

In this unit you have learned about the methods for purification of organic compounds. You should also have learned about how to determine the empirical formula, molecular formula and structural formula of organic compounds. You should be aware of the stages involved and the calculation required to fully determine the chemical nature of organic molecules.

4.6 Summary

What you have learned in this unit concerns distillation, crystallization and chromatography as purification methods in organic chemistry. In addition, you learned about method of estimating the molecular formula and hence structure of organic compounds. The unit that follows shall build up this foundation.

4.7 Tutor-Marked Assignments

1. (a) Describe, using adequate illustrations,
   (i) simple distillation
   (ii) paper chromatography
(b) An organic compound contains 62.1% carbon and 10.3% hydrogen by mass. The vapour density of the compound is 29. Calculate its empirical and molecular formula.
(c) Write the structural formula of
   (i) But-l-ene
   (ii) propan-2-ol

4.8 References

Tewari, K.S., Mehrotra V. and Vishnoi, N.K. *'Textbook of Organic Chemistry'*.

Unit 5

The Chemistry of Alkanes

5.0 Introduction

In unit 3 you learned about hydrocarbons as organic compounds consisting of carbon and hydrogen only. You were also informed that hydrocarbons can simply be subdivided into alkanes, alkenes, alkynes and aromatic (specifically benzene) compounds. The nomenclature of these classes of hydrocarbon was also explained.

The alkanes, with a general formula C_nH_{2n+2} or RH is the simplest homologous series and consist of saturated hydrocarbons. Can you recall the structures and names of the first ten members of the series? Check your note in unit 2 for a quick revision. The first three members of the series (methane, ethane and propane) only exist in the straight chain form but for the higher alkanes branched-chain isomers exist (refer to section on isomerism in Unit 2).

Alkanes, being saturated hydrocarbons are moderately inert and do not undergo any reaction other than combustion and substitution. They play an important part in petroleum chemistry (Unit 8). Alkanes are also referred to as paraffins from the Latin words meaning a little affinity. Because alkanes contain atoms which are linked by only single bonds (saturation), the few chemical reactions they undergo are mainly substitution type reactions-one atom being replaced by another.

5.1 Objectives

At the end of this unit you should be able to:

- Recall the names and structures of the first ten members of the alkanes.
- List the natural sources and synthetic methods for alkanes.
- State the types of reactions alkanes undergo in terms of starting material, reaction conditions and products
- Enumerate the uses of alkanes

5.2 Natural Sources of Alkanes

5.2.1 Natural Gas

This is one of the major source of alkanes. Natural gas is found in the strata of the earth in different parts of the universe e.g. Nigeria, USA, Kuwait, Saudi Arabia, Iraq etc, and it is sometimes found associated with petroleum. Natural gas is the main source of methane together with smaller quantities of C_2– C_6 alkanes (ethane, propane, butane, pentane and hexane). The alkanes are separated by fractional distillation. If sulphur is present, it is oxidised to sulphur (VI) oxide, the precusor to H_2SO_4.

5.2.2 Petroleum or crude oil

Fractional distillation of petroleum provides a wide range of alkanes. The $C_1 - C_5$ alkanes are also obtained like in natural gas and the fractions of higher boiling points contain mainly higher alkanes. Petroleum as a major source of alkanes will be discussed in more detail.

5.2.3 Vegetable Origin

Methane is obtained as product of anaerobic action on organic matter found buried in the earth or in sewages or in march gas and fire damp. Coal gas obtained from the destructive distillation of natural coal contains about 30% methane.

5.3 Laboratory preparation of alkanes

(a) Heating anhydrous salts of alkanoic (organic) acids. The $-CO_2-$ group of alkanoic acid can be removed by heating the sodium salts of the alkanoic acid with soda lime (a mixture of sodium and calcium hydroxides). For example

$$RCOONa^{+} + NaOH \longrightarrow RH + Na_2CO_3$$

$$\underset{\text{sodium ethanoate}}{CH_3CO_2Na} + \underset{\text{(from soda lime)}}{NaOH} \longrightarrow \underset{\text{methane}}{CH_4} + Na_2CO_3$$

The methane gas is collected over water.

(b) Wurtz coupling - alkyl halides e.g. iodoalkanes can be coupled in the presence of sodium metal to produce alkanes e.g.

$$2RI + 2Na \longrightarrow R{-}R + 2NaI$$

$$2CH_3I + 2Na \longrightarrow \underset{\text{ethane}}{CH_3 - CH_3} + 2NaI$$

5.4. Properties of Alkanes

5.4.1 Physical properties

(a) The boiling and melting points of simple alkanes rise steadily as the number of carbon atoms increases due to the increasing strength of the van der waals'forces and increase in molecular mass. There is a gradation in state from gas to liquid to solid as you move from lower to higher members. e.g. methane, CH_4, is a gas, hexane C_6H_{12} is a liquid dodecane $C_{12}H_{24}$ is a waxy solid.

(b) All alkanes are practically insoluble in water, and being less dense, the liquid and solid alkanes float on the surface of water. e.g. hexane, dodecane. That is why water cannot be used for putting out petrol and oil fires. The lower members of the alkane series are soluble in organic solvents.

5.4.2 Chemical Properties

(a) Combustion

Alkanes burn in an adequate supply of oxygen to form carbon (IV) oxide and water. This is also characteristic of other hydrocarbons - ethene, ethyne, benzene. In limited supply of oxygen, carbon (II) oxide and water is formed instead.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

$$2CH_4 + 3O2 \longrightarrow 2CO + 4H2O \text{ (limited supply of oxygen)}$$

$$2C_2H_6 + 7O_2 \longrightarrow 4CO_2 + 4CO_2 + 6H_2O$$

The ease of burning accounts for the use of many alkanes as fuels.

(b) Substitution Reactions

One or more of the hydrogen atoms in an alkane can be replaced by the halogens (Cl, Br or I). The alkane reacts with chlorine, bromine or iodine in the presence of ultra-violet light or a temperature of about 400°C. The reaction is halogenation (addition of halogens) reaction and it is a substitution (replacing the hydrogen atom with another element) process.

$$CH_4 + Cl_2 \xrightarrow[\text{or 400C}]{\text{uv}} CH_3-Cl + HCl$$

$$CH_4 \xrightarrow{Cl_2} \underset{\text{chloro-methane}}{CH_3-Cl} \xrightarrow{Cl_2} \underset{\text{dichloro-methane}}{CH_2Cl_2} \xrightarrow{Cl_2} \underset{\text{trichloro-methane (chloroform)}}{CHCl_3} \xrightarrow{Cl_2} \underset{\text{tetrachloromethane (carbon tetrachloride)}}{CCl_4}$$

(c) Cracking

Is an important industrial process used for breaking large hydrocarbon molecules to smaller ones. Alkanes undergo industrially important elimination reactions in which they lose hydrogen. The reaction require a high temperature and, possibly, a catalyst. The products are usually unsaturated hydrocarbons (alkenes and alkynes) and sometimes soot (carbon black) is formed.

$$C_2H_6 \xrightarrow{850^\circ C} \underset{\text{ethene}}{H_2C=CH_2} + H_2$$

$$C_3H_8 \xrightarrow{Cr_2O_3/Al_2O_3 \text{ catalyst}} \underset{\text{propene}}{H_3C-CH=CH_2} + H_2$$

$$2CH_4 \xrightarrow{1500^\circ C} HC \equiv CH + 3H_2$$

5.5. Uses of Alkanes

(i) They are widely used as fuels - butane gas, petrol

(ii) Higher alkanes such as paraffin wax is used for candle manufacture, lubricants etc

(iii) Alkanes react with chlorine in the presence of light to give chloroalkanes e.g. chloroform, used in hospitals as an 'Anaesthetic'; carbontetrachloride used as solvent for grease in dry cleaning and also in fire extinguishers.

5.6 Conclusion

You have learned the chemistry of the simplest homologous series consisting of the saturated hydrocarbon called alkanes. Alkanes constitute an important class of compounds because they are the major constituent of natural gas and petroleum which gives us our cooking gas, petrol, kerosene and several other useful products. With the study of the first homologous series of organic chemistry, you must begin to appreciate the relevance of organic compounds to us all.

5.7 Summary

In this unit you have learned about alkanes as a class of saturated hydrocarbons. The primary sources of alkanes are crude oil and natural gas although they can be prepared on a small scale in the laboratory. Alkanes being saturated are moderately inert. However they undergo combustion, substitution and cracking reactions. Alkanes on their own are widely used as fuels and also in the manufacture of useful products like candles, lubricants and haloalkanes.

5.8 Tutor-Marked Assignments

(a) List three natural sources of alkanes
(b) Use equations only to illustrate the combustion and substition reactions of a simple alkane
(c) Enumerate four (4) uses of alkanes.

5.9 References

Bajah, S.T., Teibo, B.O., Onwu, G and Obikwere A. (2002) *Senior Secondary Chemistry Textbook 2* Lagos: Longman Publishers.

Osei Yaw Ababio (2002). *New School Chemistry.* Onitsha: Africana-Fep Publishers.

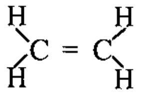
Unit 6

The Chemistry of Alkenes and Alkynes

6.0 Introduction

You have learned in units 1 and 3 that hydrocarbons can be subdivided into saturated and unsaturated compounds. In unit 5 the learning centered on the saturated hydrocarbon called alkanes, which is the parent homologous series from which others are derived. In this unit the focus will be on the unsaturated hydrocarbons, alkenes and alkynes.

Alkenes and alkynes are classified as unsaturated hydrocarbons with general formula C_nH_{2n} and C_nH_{2n-2} respectively. They are characterised by the $C = C$ and $C^{\circ} C$ bonds respectively. Recall the systems of IUPAC nomenclature for these classes of homologous ending with the suffix –ene for alkene and –yne for alkynes.



ethene

$H{-}C\ {}^{\circ}C{-}H$

ethyne

Ethene and ethyne are the first members of the alkenes and alkynes series respectively.

You also learned in Unit 2, the concept of isomerism and that cis-trans isomerism exist in alkenes. Isomerism does not exist in alkynes because the molecules are collinear as learned in unit 1. The main feature of the chemistry of alkenes and alkynes is their addition reactions in which the C=C and C° C are converted into C–C bond. For the alkenes, the products formed of such addition reactions with chlorine and bromine are oily liquids; hence the older name of 'olefines' for the series.

6.1 Objectives

At the end of this unit you should be able to:

- Identify the feature that differentiate unsaturated (alkanes) and unsaturated (alkenes and alkynes) hydrocarbons
- State the names and structures of all members of alkene and alkyne series up to $C_{10}H_{20}$ and $C_{10}H_{18}$ respectively.
- Discuss the sources and basic reactions of unsaturated hydrocarbons (alkenes and alkynes).
- Describe the laboratory method for detection of unsaturation.
- State why alkenes are important starting material for several industrial processes.

6.2 Sources of Alkenes and Alkynes

6.2.1 Natural sources of alkenes

(a) Cracking of alkanes

Natural gas contains large amounts of ethane, propane and butane; and these alkanes can be cracked either thermally or catalytically. The alkenes formed are then separated from the resulting gas mixture.

$$C_2H_6 \longrightarrow \underset{\text{ethene}}{C_2H_4} + H_2$$

$$\underset{\text{propene}}{C_3H_6} + H_2 \longleftarrow C_3H_8 \longrightarrow \underset{\text{ethene}}{C_2H_4} + CH_4$$

(b) Cracking of naphtha

A mixture of naphtha and steam are heated to about 800°C. The cracked mixture obtained is then separated into a liquid fraction (provides fuel-oil and petrol) and a gas fraction which contains hydrogen, C_1–C_4 alkanes and C_1–C_4 alkanes. These gases can be separated by distillation under pressure.

6.2.2. Manufacture of ethyne

Ethyne is the most common member of the alkyne series and will therefore be used as the representative member for alkynes throughout this unit.

Modem processes produce ethyne, on a large scale, from methane or naphtha by applying a temperature of about 1500°C for a fraction of a second. Hydrogen is obtained as a useful by-product.

$$2CH_4 \xrightarrow{1500^\circ C} C_2H_2 + 3H_2$$

This process has replaced the older method of obtaining ethyne by reaction between calcium dicarbide and water. The reaction still serves as a satisfactory source of ethyne on a small scale particularly for welding purposes.

$$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + C_2H_2.$$

6.3 Laboratory Preparation of Ethene and Ethyne

(a) Ethene by dehydration of Ethanol

Ethene is produced by dehydration (removal of water) of ethanol. This can be achieved in two ways, either by passing the vapour of ethanol over finely divided aluminium oxide heated to 300C; or heating the ethanol with excess concentrated tetraoxosulphate (vi) acid at 180°C. Both reagents act as dehydrating agents.

$$C_2H_4 + H_20 \xleftarrow[300^\circ C]{Al_2O_3} \underset{\text{ethanol}}{C_2H_5OH} \xrightarrow[180^\circ C]{\text{Excess conc. } H_2SO_4} C_2H_4 + H_20$$

(b) Ethyne from calcium dicarbide

The reaction of calcium dicarbide with water, as discussed in section 6.2.2 of this unit, is the method used to obtain ethyne in laboratory.

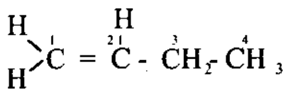
6.4 Isomerism in Alkenes

You will recall that in Unit 2, the concept of isomerism was discussed and alkenes are said to exhibit cis-trans isomerism. All akenes above C_3H_6 show isomerism. For C_4H_8, recall the structure of cis-but-2-ene and trans-but-2-ene.

Exercise 1

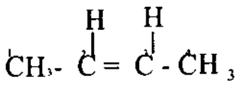
Can you explain why 1- butene does not exhibit cis-trans isomerism?

Apart from cis-trans isomerism, alkenes also show a type of structural isomerism known as positional isomerism. This type of isomerism is dependent on the position of the double bond as well as the way atoms are arranged in the molecule. For C_4H_8, three structural isomers are known.



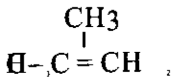
$H_2\overset{1}{C} = \overset{H}{\overset{2}{C}} - \overset{3}{C}H_2 - \overset{4}{C}H_3$

but -1- ene



$CH_3 - \overset{H}{C} = \overset{H}{C} - CH_3$

but -2- ene



$H - \overset{CH3}{C} = CH$

2–methylpropene

6.5 Chemical Properties

6.5.1 Alkenes

(a) Addition reactions

Alkenes are unsaturated due to the presence of C = C and therefore atoms can add across the double bond to give addition products and in the process convert C = C to C – C bond. Four types of molecules, H_2, halogens (Cl_2, Br_2, I_2), hydrogen halides (HCl, HBr_2, HI) and H_2O; can add on to the C = C.

— $H_2C = CH_2 + H_2 \xrightarrow[200^\circ C]{\text{Ni or Pt}} H_3C - CH_3$ hydrogenation (useful for the hardening of oil to margarine)

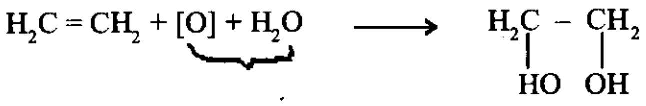
— $H_2C = CH_2 + Cl_2 \xrightarrow[\text{temp.}]{\text{room}} ClCH_2 - CH_2Cl$ halogenation (e.g chlorination)

— $H_2C = CH_2 + HI \xrightarrow[\text{temp.}]{\text{room}} H_3C - CH_2I$ Hydrohalogenation (e.g hydroiodination)

— $H_2C = CH_2 + H_2O \xrightarrow[80^\circ C]{H_2SO_4} H_3C - CH_2OH$ Hydration

(b) Oxidation reaction

Aqueous solution of potassium tetraoxomaganate (VII) acting as an oxidizing agent can add two –OH groups onto C = C of alkenes.



$$H_2C = CH_2 + \underbrace{[O] + H_2O}_{\text{from KMnO}_4\text{ Solution}} \longrightarrow \underset{HO}{H_2C} - \underset{OH}{CH_2}$$

from
$KMnO_4$
Solution

Ethane-1, 2-diol
(Ethylene glycol)

(c) Polymerisation Reaction

This is an industrially important reaction of alkenes. Polymerisation is the process by which many simple molecules (called monomers) join together to form very giant molecules (called polymers). Alkenes, particularly ethene, is an important monomer and undergo addition polymerisation. For ethene.

$$2nCH_2 = CH_2 \longrightarrow \ldots(-CH_2 - CH_2 - CH_2 - CH_2-)-_n-$$

ethene

Poly (ethene)
(Polythene)

Polythene is widely used for making buckets, pipes, bottles, cups, spoons, toys, packing materials and cable insulating materials.

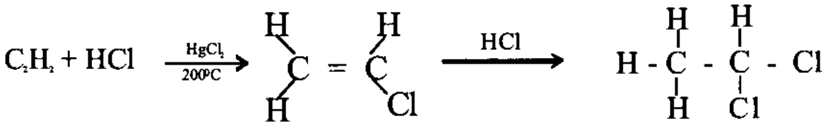
6.5.2 Alkynes

(a) Addition Reactions

Alkynes, like alkenes, are unsaturated and so undergo addition reaction. For alkynes the reaction occurs in two stages, the first addition converts the C ° C to C = C and the second addition converts C = C to C – C. For example:

$$HC \circ CH \xrightarrow[150^{0}C]{H_2/Ni} H_2C = CH_2 \xrightarrow[150^{0}C]{H_2/Ni} H_3C - CH_3$$

$$C_2H_2 + 2Cl_2 \xrightarrow{FeCl_2} Cl_2CH - CHCl_2$$



Chloro ethene
(vinyl chloride)

1,1–dichloroethane

The chloroethene product is important in making polyvinyl chloride (PVC), an inert polymer used as insulating materials for electrical cables, boots.

(b) Polymerisation

Ethyne does not polymerise so reaily as ethene. On heating, however, ethyne is polymerised to benzene, and important hydrocarbon that will be studied in Unit 7.

6.6 Test for Unsaturation

The presence of multiple bonds (unsaturation) as found in alkenes and alkynes can be detected in the laboratory using two common reaction studies in Section 6.5

(a) Bromine in carbon tetrachloride (Br_2 / CCl_4)

When an alkene or alkyne is passed through Br_2/CCl_4 or bromine water (brown) there is decolourisation because the bromine which is responsible for the brown colour adds across the multiple bond.

(b) Aqueous potassium permanganate [$KMnO_{4(aq)}$]

The purple colour of $KMnO_{4(aq)}$ disappears (decolorised) when any unsaturated hydrocarbon (alkenes and alkynes) is passaed through. This is an oxidation process in which the purple Mn(VII) is converted to colourless Mn(V).

The two tests are used to distinguish saturated alkanes from unsaturated alkenes and alkynes.

6.7 Conclusion

You have learned the chemistry of the aliphatic unsaturated hydrocarbons, alkenes and alkynes. The principal source of alkenes and alkynes is from the parents hydrocarbon, alkanes, obtained from natural gas and petroleum. However, the reactivity of alkenes and alkynes are different from those of alkanes because of the presence of multiple bonds. Their reactions are essentially addition to the multiple bonds hence they are far more reactive than alkanes. Several of these reactions are industrial processes that lead to useful end products.

6.8 Summary

What you have learned in this unit is about unsaturated hydrocarbons – alkenes and alkynes. Their chemistry is essentially centered on the multiple bond which are converted to saturated bonds by several reagents like hydrogen, halogens, hydrogen halides and water. In addition, alkenes undergo polymerization reaction to give useful polymer materials.

6.9 Tutor-Marked Assignments

(a) Draw the structure and name all the two geometric and five structural isomers of C_5H_{10}.
(b) Explain, with varied illustrative examples, the meaning of the term addition reaction.

6.10 Reference

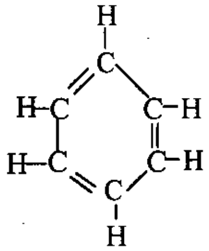
Osei Yaw Ababio (2002) *New School Chemistry*. Onitsha. Africana-FEP Publishers.

Unit 7

Introduction to the Chemistry of Benzene

7.0 Introduction

In units 5 and 6 you learned about the aliphatic hydrocarbons-alkanes, alkenes and alkynes as distinct homologous series. There are a number of homologous series of aromatic hydrocarbons or arenes. The simplest, based on benzene, C_6H_6, and containing one ring of six carbon atoms have a general formula C_nH_{2n-6} ($n \geq 6$). The chemistry of benzene, the simplest aromatic hydrocarbon, is the subject of this unit. Aromatic compounds were originally so named because many of them were **fragrants** and the term aromatic is derived from the Greek word aroma, meaning pleasant smell. The structure of benzene is represented simply as a **conjugated** (alternating single and double bonds) system of three double bonds forming an hexagonal ring with the carbon atoms.



The benzene ring as represented above is not strictly on alternating single and double bonds in cyclic form but an acceptable and convenient way of drawing the structure of benzene. The true nature of the bonds is explained in this unit.

Other members of the benzene homologous series are formed by successive replacement of hydrogen atoms by-CH_3 groups. Only benzene, as representative of the series, will be discussed in this unit as the chemistry of the other members are beyond the scope of this programme.

7.1 Objectives

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

- Explain the concept of resonance in terms of delocalisation of electrons.
- Explain the unusual stability of the benzene nucleus in terms of resonance.
- Compare the reactions of benzene with those of the other unsaturated hydrocarbons, (alkenes and alkynes).
- Discuss the types of reactions benzene undergo.

7.2 Structure and Bonding in Benzene

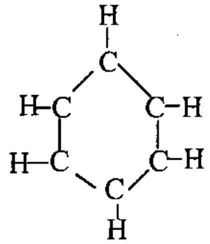
Benzene is normally drawn as a six-membered carbocyclic ring with alternating single and double carbon-to-carbon bonds. Each carbon is connected to a single hydrogen. Is benzene simply a cyclic alkene? On the account of the structure, the C=C should behave like those found in alkenes, but benzene does not behave like alkenes i.e. it does not give addition products across the C=C like alkenes.

Studies have shown that benzene is a regular planar hexagon, with the carbon-carbon bond length of 1.39nm. This bond length is **shorter** than the C–C bond length of alkanes **(1.54nm)** and longer than C=C of alkanes **(1.34nm)**. For benzene, however, the carbon-to-carbon bonds for all the six carbon atoms in the ring is **1.39nm**; an intermediate value between the single and double carbon-to-carbon bond. How can this observation be explained? The solution lies in the concept of a phenomenon known as resonance.

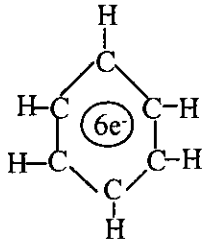
7.2.1 Resonance in Benzene

To explain the unusual observation in respect of the benzene structure, we have to recall that we have discussed bonding only in terms of electron pairs associated with two nuclei. These we may call **localised electron** i.e. shared bonding electrons located between the two bonded atoms. The fact, however, is that bonding electrons can be associated with more than two nuclei, and there is a measure of stability to be gained by this because the degree of bonding increases when the electrons can distribute themselves over a greater volume. This effect is called electron delocalization or resonance.

Let us now see how this concept can be used to explain the benzene ring structure i.e. all the carbon-to-carbon bonds in the ring are usual. You will recall (unit 1) that carbon has four electrons available for bonding. Let us look at a typical six carbon ring system similar to



that proposed for benzene but with only the single bonds shown. Focus your attention on the asterisk carbon atom. It has four valence electrons, one is used for bonding with hydrogen atom and one used each to bond with one carbon to the right and one to the left, making a total of three electrons used for bonding and one electron unused. This statement is true for all the six carbon atoms in the ring, giving a total of six unused electrons. Rather than localising any of these six electrons, as pairs of electrons between two adjacent carbon atoms, to form three bonds usually shown as the three double bonds (π bonds) in the benzene; the six electrons are delocalised (resonance) between all six carbon atoms. In other words, the six unused electrons are pooled together as electron cluster from which any of the six carbon atoms can pool from. Study the representation below



The structure above gives a better picture of the benzene molecule although the earlier shown in the introduction is still acceptable once it is clear that the bonds are not actually alternating single and double bonds. The true structure of benzene is a resonating hybrid of various resonance structure in which there is movement of electrons; most of the time delocalised but sometimes localised in a dynamic equilibrium

[The ↔ is used as symbol to represent resonance]

This suggestion is in agreement with the fact that all the carbon-to-carbon bonds in benzene are of the same length, and intermediate between the C-C single bond of alkanes and the C=C double bond of alkenes. This concept of resonance confer stability on the benzene, hence any attempt to change (e.g. addition reaction), this arrangement can lead to instability and it is normally resisted.

It is the lack of simple C-C and C=C bonds which make the properties of benzene different from those of the alkanes and alkenes, and the delocalisation in the benzene molecule is the cause of aromatic character. Therefore, benzene though unsaturated like alkenes and alkynes does not decolourise bromine water and aqueous potassium tetraoxomanganate (VII) since it does not undergo substitution reaction.

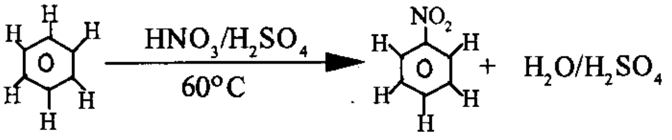
7.3 Chemical Properties of Benzene

The stability of the aromatic nucleus in benzene due to resonance means that it does not undergo similar reactions like alkenes; even though it is also unsaturated. Benzene reacts mainly by substitution in which the hydrogen atoms are replaced with other groups while still retaining its aromatic stabilisation. In some reactions, however, this aromatic stabilisation is lost and benzene undergoes addition reactions such as catalytic hydrogenation.

7.3.1 Substitution reactions of benzene

(a) Nitration

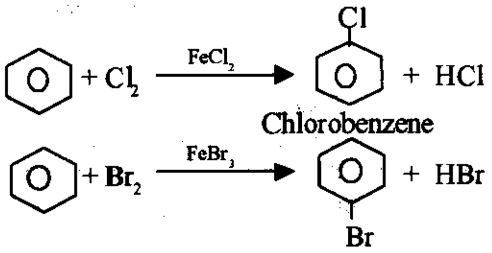
A mixture of concentrated trioxonitrate (V) HNO_3 and tetraoxosulphate (VI), H_2SO_4; acids reacts with benzene, at 60°C, to form nitrobenzene



Nitrobenzene

(b) Halogenation

Benzene reacts with chlorine or bromine in the presence of a reagent called Lewis acid ($FeCl_3$ or $FeBr_3$) to form chloro-or bromo-benzene. Light must be excluded from the reaction mixture.

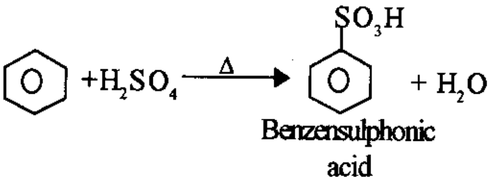


Chlorobenzene

Bromobenzene

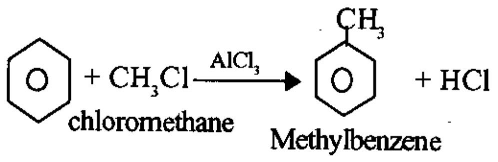
(c) Sulphonation

Benzene reacts on heating with concentrated tetraoxosulphate (VI) acid, H_2SO_4, to form, benzenesulphonic acid.



(d) Alkylation

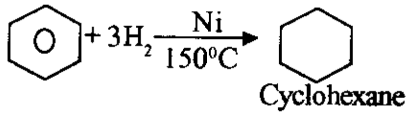
Benzene and halogenoalkanes e.g. chloromethane react, in the presence of Lewis acids, $AlCl_3$, as catalyst, to form alkyl benzenes e.g. methylbenzene. The reaction is known as the Friedel-Crafts reaction.



7.3.2 Addition reactions of benzene

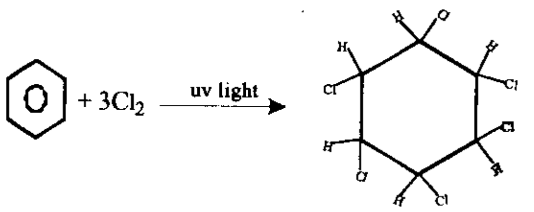
(a) Hydrogenation

If a mixture of hydrogen gas and benzene vapour is passed over finely-divided nickel at 150°C, the benzene is reduced to cyclohexane.



(b) Halogenation

Chlorine and bromine add on to benzene in the presence of sunlight or ultra-violet light producing, for example 1,2,3,4,5,6, - hexachlorocyclohexane.



hexachlorocyclohexane

7.4 Conclusion

You have been introduced to the chemistry of benzene, the simplest of the aromatic hydrocarbon series. You should have also realised the importance of resonance in the understanding of the study of aromatic compounds in general and specifically benzene. The effect of aromatic stabilisation is that aromatic compounds e.g. benzene do not react like alkenes despite the fact that they are also unsaturated.

7.5 Summary

- In this unit, you were introduced to benzene as an unusually stable unsaturated hydrocarbon. The nature of the structure and bonding in benzene was explained using the resonance concept.
- The reactivity of benzene towards organic reagents shows that it reacts mainly by substitution reactions as opposed to addition reactions observed with the unsaturated hydrocarbon, alkenes. This shows that the bonds in benzene are different from those of alkenes.

7.6 Tutor-Marked Assignments

(a) Use the concept of resonance to account for the structure of benzene.
(b) Use equations only to illustrate four substitution reactions of benzene.

7.7 References

Bajah, S. T., Teibo, B. O., Onwu, G. and Obikwere, A. (2002) *Senior Secondary Chemistry - Text book 2.* Lagos. Longman Publishers.

Holtzclaw, A. and Robinson, W. R. General Chemistry.

Unit 8

Introduction to Petroleum Chemistry

8.0 Introduction

Petroleum also known as crude oil is a viscous liquid mixture of organic compounds deposited in the strata of the earth. Crude oil is found in Nigeria, U.S.A., Kuwait, Saudi Arabia, Iraq, etc. It varies widely in composition but consists mainly of alkanes (C_1 to C_{40} per molecule), cycloalkanes and aromatic hydrocarbons. It may also contain some proportions of sulphur, nitrogen, oxygen, etc.

Crude oil is believed to have been formed by the bacterial decomposition, under pressure, of animal and plant remains. Petroleum is an extremely important raw material. It is required both to provide fuels for energy generation and as source of many organic and inorganic chemicals.

Petroleum is extracted from the earth crust essentially through drilling. This is then followed by a difficult process of separating the individual component through the refining process. The process of petroleum refining is basically that of converting crude oil into a range of high quality economically important products.

The complex mixtures of hydrocarbons present in the crude exist in gaseous, liquid or solid forms. Also present with the crude are a number of 'inorganic impurities' that are detrimental (dangerous) to the refining process; and solid impurities such as sand. Petroleum is sometimes found associated with 'Natural Gas'.

8.1 Objectives

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

- Describe the fractional distillation of petroleum process.
- List the essential fractions obtained from the distillation process.
- Define the term cracking and reforming; and their relevance in the petroleum industry.
- List the uses of the factions of the refining process.
- Explain the importance of octane number in petrol quality.
- Discuss how petroleum has affected the economy of Nigeria.

8.2 Crude Oil Reserves

About 60% of the world's oil reserves are found in Asia, with the Middle East (Saudi Arabia, Iraq, Iran, Kuwait, Bahrain, Oman) having the lion share. China and Indonesia are other Asian countries with large oil reserves. Russia as a country has the largest reserve in the world. Large deposits of crude oil is also found in United States, Venezuala, Canada, Australia and in some West African countries e.g. Nigeria.

The Nigerian crude oil reserve was discovered in 1956 at Oloibiri. Since then crude oil has become the principal source of revenue for Nigeria. Large deposits of crude oil has been found in the Niger Delta region – Afam, Abata, Bomu, Owaza, Egbema, and the Ughelli-Kokori – Oleh zone. Offshore, crude oil has been found around Calabar and in the Burutu – Forcados – Escravas zone of Delta State. From all these oil fields, the crude is pumped through pipes to the oil terminals at Bonny or Forcados for export or to our refineries located at Warri, Port-Harcourt and Kaduna.

8.3 The Refining Process

There are two main stages, desalting and distillation processes. The desalting is simply a process of removing salt compounds; and is more of a mechanical process than chemical which is beyond the scope of this programme.

8.3.1 Fractional Distillation

This process facilitates the separation of the petroleum into 'fractions' or 'cuts' hence the name fractional distillation, which is the principal method for the purification of petroleum. Crude oil is heated to about 400°C by passing it through coils of pipes in a gas-heated pipe-still furnace.

The resulting hot oil, which is at 400°C is a mixture of vapours and liquids, is passed into a tall cylinder known as a fractionating tower or column. The column is divided into a number of compartments by means of trays, which contain holes covered by 'bubble-cap' and overflow pipes.

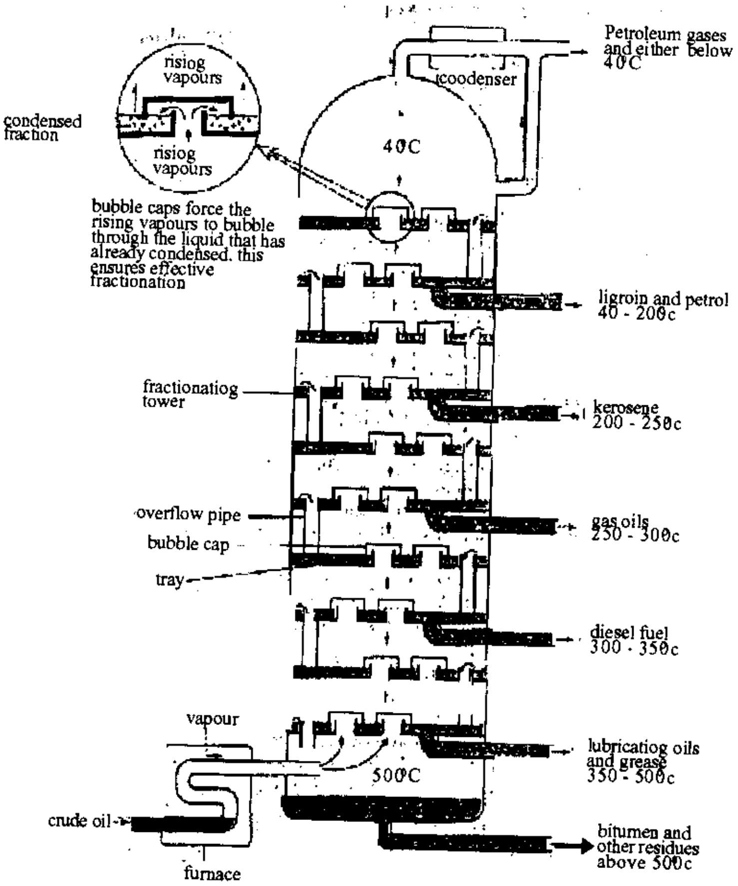


Fig 8.1: Fractionating column for fractional distillation of crude oil

The temperature of the fractionating column ranges from about 400°C at the bottom to about 40°C at the top, and each tray is at a controlled temperature. As the mixture passes into the column, the liquids fall to the bottom whilst the vapours pass up through the trays. As each tray is at a different temperature, different mixtures of vapour condense to give different petroleum fractions in each tray.

The main fractions collected and their uses are tabulated in Table 8.1

Fraction	***Boiling Range °C***	***Approximate carbon chain***	***Use***
Gas fraction	< 40	1–5	gaseous fuel for cooking and heating; source of alkanes
Petroleum ether	40–66 60–80		solvent
Petrol or gasoline	70–180	5–10	fuel
Naphtha	100–200		solvent; source of alkanes and alkenes
Kerosine or Paraffin oil	200–300	11–14	Fuel oil lanterns, tractor and jet engines
Light gas-oil or fuel oil	250–400	13–17	Fuel oil for diesel engines
Heavy gas oil, light lubricating oil	300–400	18–25	Fuel, lubricants, paraffin wax, medicinal paraffin.
Residue	> 400	> 25	Bitumen for surfacing road and roofing materials.

Nigeria has three refineries located at Kaduna, Port-Harchourt and Warri. They refine the crude oil to meet the domestic needs of petroleum products, e.g. petrol, kerosene, diesel, butane gas etc., and some of the products are exported to neighouring countries e.g. Niger, Chad.

8.3.2 Quality of petrol — octane number

Most of the gasoline fraction obtained from the column, requires further treatment as it knocks easily if used directly. This means that the petrol-air mixture in the cylinders, when it is being used as fuel in engines, explodes prematurely and incompletely causing a metallic rattle known as knocking.

The knock properties of a petrol is measured by its octane number, 2, 2, 4-Trimethylpentane (iso-octane) cause almost no knocking (octane number 100) and heptane, which knocks very readily (octane number O), have been chosen as standards against which the performance of any petrol can be measured. The octane number of any fuel is the percentage of iso-octane in a mixture of iso-octane and heptane that will knock to the same extent as the fuel under the same conditions. The difference in the grades of petrol is the difference in their octane number.

The octane rating of a fuel can be improved by adding anti-knock agents such as tetraethyl lead. Also, straight-chain alkanes (e.g. heptane) cause knocking far more readily than branched-chain alkanes (e.g. iso-octane). Alkenes and aromatic hydrocarbons have better known qualities than straight-chain alkanes. So delicate conversion processes has been developed that balances all these characteristics to change the composition of the original gasoline fraction.

Exercise 1

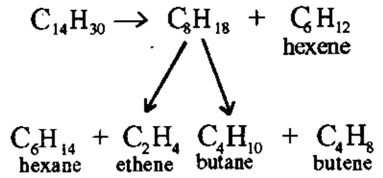
Draw the structural formula of iso-octane and heptane.

8.4 The Conversion Processes

The distillation process merely separates the crude oil into various fractions but it cannot change the proportion of the constituent hydrocarbons in the fractions. These proportions vary with the source of crude oil and in most cases do not meet the standard for their desired use. Both the yield and quality of the fractions can be improved upon by various conversion processes.

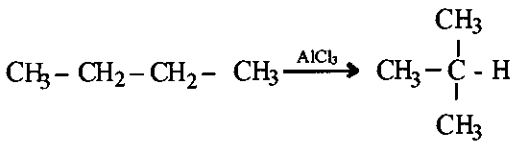
8.4.1 Cracking

In the cracking process larger hydrocarbons in fuel oil fractions are broken down into smaller hydrocarbons needed in petrol. This same process also converts some of the straight-chain alkanes (which knock easily) into branched-chain alkanes. Cracking can be achieved at high temperature and pressure (thermal) but cracking using catalyst is more common. Alkanes (saturated) with lower relative molecular mass are produced, together with a mixture of gaseous alkenes e.g., C_2H_4, C_3H_6, C_4H_8.



8.4.2 Isomerisation

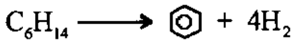
In this process, straight-chain alkanes are converted into branched-chain isomers at about 100° C and under pressure; with $AlCl_3$ as catalyst



$$CH_3-CH_2-CH_2-CH_3 \xrightarrow{AlCl_3} CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-H$$

8.4.3 Reforming

This process involves the conversion of straight-chain alkanes into aromatic hydrocarbon. The process involves a simultaneous cyclisation (forming ring compound), catalyst by Al_2O_3; and dehydrogenation, catalyst by platinum.



In these conversion processes, more useful alkanes and alkenes are produced and straight-chain alkanes are transformed to branched alkanes and aromatic hydrocarbon; all of which improves the octane number or quality of petrol.

8.5 Petrochemicals

The term petrochemicals is used to describe the chemicals obtained from petroleum which are useful raw materials for the chemical industries.

The gas and naphtha fractions from the fractional distillation of petroleum, together with gases obtained from cracking process, and natural gas, provide the major starting materials. They serve as a source of these petrochemicals – methane, ethane, propane, butane, ethene, propene, butenes and aromatic hydrocarbons such as benzene, toluene and xylenes; which are starting materials for a very wide range of important products, e.g. plastics, cosmetics, pharmaceutics, detergents and synthetic fibres such as nylon. The petrochemicals are often referred to as value-added products.

There are three petrochemical factories in Nigeria located in Lagos, Port Harcourt and Kaduna. When fully functional, they will produce important petrochemicals such as synthesis gas, alkenes and aromatic compounds. From the synthesis gas, we can produce ammonia, methanol, gasoline, fertilizers, refrigerant, explosives, urea, polymers, etc. From the alkenes, we can produce several types of polymers e.g. polythene, nylon; ethanol, cosmetics, synthetic rubber. From the aromatic compounds, we can produce insecticides, detergents, solvents, nylon. These products will increase our export earnings and reduce our dependence on importation of finished products.

8.6 Oil Production and the Nigerian Economy and Environment

The production of oil in Nigeria has increased steadily since 1956, when oil was first discovered. Nigeria now ranks among the top ten oil producers in the world. By 1975, petroleum accounted for about 90% of all export earning of Nigeria and is still the major source of foreign exchange earnings. The earnings form petroleum exports have been used for development projects in agriculture and industry, as well as to construct many roads, buildings and set up several public utilities services.

The extraction, transport and refining of crude oil has provided employment opportunities for Nigerians. The proposed petrochemical industry become fully functional, Nigeria's earnings will increase and more jobs will be provided. Petroleum products such as plastics, detergents, insecticides, etc. have become part of our lifes and has greatly improved our standard of living.

The availability of petrol has lead to a tremendous increase in the number of motor vehicles on roads of Nigerian cities. The distribution of population within the country has changed since the discovery of petroleum because of job-related mobilities and the need for better living.

The benefits of petroleum are enormous however it also brought along some serious environmental pollution problems. The emissions of pollutants such as hydrocarbon gases, tetraethyl lead, carbon (II) oxide, nitrogen oxides, sulphur (IV) oxides etc. have made our environment less safe. Besides air pollution, there is also the problem of oil spills which destroy marine life.

8.7 Conclusion

In this unit you have been introduced to the chemistry of petroleum, which is an extremely important raw material. Although the composition of petroleum vary with source, the principal component still remained alkanes which are separated into various fractions by fractional distillation. The end products of this process have varied applications in the world and no fraction is useless. More useful fractions can be obtained from the less useful ones by various conversion processes. Some products of the conversion process are useful petrochemicals which are important starting materials for the chemical industry.

8.8 Summary

In this unit, you learned about the source and composition of crude oil. Crude oil as obtained from the earth crust is converted to more useful products through the refining process, principal of which is fractional distillation.

Fractional distillation separates petroleum into fractions based on boiling ranges and these fractions are used mainly as fuels. Several conversion processes are known which improves the quality of the fractions e.g. petrol and provide useful petrochemicals for the chemical industries.

8.9 Tutor-Marked Assignments

(a) Describe the fractional distillation of petroleum and list the fractions obtained with their uses.
(b) Explain the term octane number and its importance in determining the quality of petrol.
(c) Describe cracking and reforming as conversion processes in the petroleum industry.

8.10 References

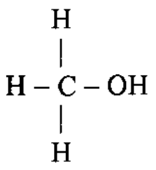
Bajah, S.T., Teibo, B.O., Onwu, G. and Obikwere, A. (2002) *Secondary Secondary Chemistry Textbook 1*. Lagos. Longman Publishers.

Unit 9

Alkanols I: Classification, Sources and Uses of Alkanols

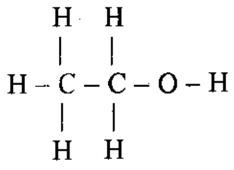
9.0 Introduction

In unit 2 you learned about organic functional groups. Alkanol are a group of compounds in which the hydrogen atom(s) of alkanes have been replaced with the hydroxyl (-OH) functional group. Alkanols are generally referred to as 'alcohols'. You will also recall that the general formula of alkanols is $C_nH_{2n+1}OH$ and are named by replacing the 'e' of the alkane name by 'ol.' For example methanol and ethanol from methane and ethane.



$$H-\overset{H}{\underset{H}{C}}-OH$$

methanol



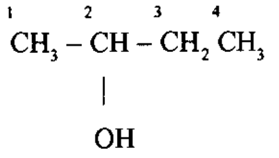
$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-O-H$$

ethanol

A simple general representation for alkanols is R–OH, where 'R' represents an alkyl group. When necessary, the position of the –OH group is shown numerically, e.g propanol. The carbon atoms are numbered in the longest chain. The position of the OH group determines the numbers. Study the structures below.

$$\overset{3}{CH_3}-\overset{2}{CH_2}-\overset{1}{CH_2}-OH$$

propan-1-ol or 1-propanol



$$\overset{1}{CH_3}-\underset{OH}{\overset{2}{CH}}-\overset{3}{CH_2}\,\overset{4}{CH_3}$$

propan-2-ol or 2-propanol

This is postional isomerism, a form of structural isomerism which you learned in units 2 and 6.

The hydroxyl group is one of the most important functional groups of naturally occurring molecules such as carbohydrates and nucleic acids. These are complex alkanols but our concern in this unit are simple alkanols which are made from petroleum-derived hydrocarbons.

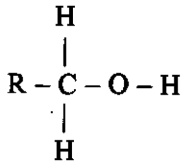
9.1 Objectives

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

- Classify alkanols into primary, secondary or tertiary groups.
- Enumerate the sources of simple alkanols.
- Describe the process involved in the local production of ethanol.
- List the uses of ethanol.

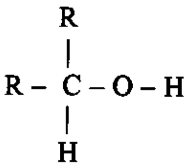
9.2 Classification of Alkanols

Alkanols are classified as primary, secondary or tertiary depending on whether the OH functional group is attached to a primary, secondary or tertiary carbon atom e.g



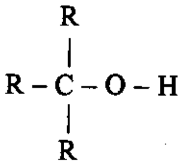
$$R-\underset{\displaystyle H}{\overset{\displaystyle H}{C}}-O-H$$

primary (1°)



$$R-\underset{\displaystyle H}{\overset{\displaystyle R}{C}}-O-H$$

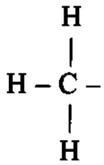
secondary (2°)



$$R-\underset{\displaystyle R}{\overset{\displaystyle R}{C}}-O-H$$

tertiary (3°)

Where R = alkyl group

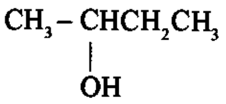


$$H-\underset{\displaystyle H}{\overset{\displaystyle H}{C}}-$$

or CH_3- or H_3C-

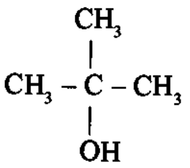
$CH_3\,CH_2\,CH_2\,CH_2OH$

butan-1-ol (1°)



$$CH_3-\underset{\displaystyle OH}{CH}CH_2CH_3$$

butan-2- ol (2°)



$$CH_3-\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{C}}-CH_3$$

2-methylpropan-2-ol (3°)

Exercise

Three structural isomers of $C_4H_{10}O$ are represented above. There is one more isomers alkanol not shown, can you draw and name it? (Hint: it is a 1° alkanol).

In general, the characteristic of primary alkanols is)CH_2OH; secondary alkanols is –;CHOH and tertiary alkanol –;COH.

9.3 Sources of Alkanols

9.3.1 General methods of preparation

(a) Hydrolysis of halogenoalkanes or alkyl halides: Alkyl halides are compounds formed by replacing one of the hydrogen of an alkane with a halogen (Cl or Br or I). When alkylhalides are treated with dilute aqueous sodium hydroxide, the halogen is replaced by - OH groups thus forming an alkanol.

$$R-Cl + Na^+ + OH^- \longrightarrow R-OH + NaCl$$

e.g. $$\underset{\text{ethyl chloride}}{CH_3CH_2Cl} + NaOH \longrightarrow \underset{\text{ethanol}}{CH_3CH_2-OH} + NaCl$$

(b) Hydration of alkenes: Alkenes react with steam when passed over phosphoric (v) acid catalyst at 300°C and 70 atmosphere. For example.

$$CH_2 = CH_2 + H_2O \xrightarrow[300^0C\ +\ 70\ atms]{H_3PO_4} CH_3-CH_2-OH$$

The process, as shown in the equation, is used industrially for the production of ethanol and some higher alkanols.

9.3.2 Manufacture of alkanols

(a) Methanol: Methanol is manufactured from mixture of carbon (II) oxide and hydrogen (obtained from either water gas or synthesis gas) in the presence of a catalyst.

$$C_{(coke)} + H_2O_{(g)} \longrightarrow CO + H_2\ \text{(water gas)}$$

$$CH_4\ \text{(natural gas)} + H_2O_{(g)} \longrightarrow CO + 3H_2\ \text{(synthesis gas)}$$

$$CO + 2H_2 \xrightarrow[400^oC\ and\ 300\ atm]{ZnO\ +\ Cr_2O_3} CH_3OH$$

(b) Ethanol

(i) **From ethene:** The major source of ethanol industrially is by hydration of alkenes, as described in section 9.3.1(b)

(ii) **By fermentation**: The fermentation process of obtaining ethanol from starch materials is still popular.

Fermentation is the decomposition of complex organic compounds e.g. carbohydrates, into simpler compounds through the action of enzymes.

Materials such as, sugar, rice, guinea-corn, cassava, maize, potatoes, wheat, barley, etc. can be used as the source of glucose from which the ethanol is derived.

- From starchy materials: The material is crushed and treated with steam to extract the starch from them. Malt, made from partially germinated barley, is added and then kept at about 50°C for one hour. The enzyme diastase, present in the malt, catalyses the conversion of starch into maltose.

$$\underset{\text{starch}}{2(C_6H_{10}O_5)n + nH_2O} \xrightarrow{\text{diastase}} \underset{\text{maltose}}{n\,C_{12}H_{22}O_{11}}$$

Yeast is then added at room temperature. This causes fermentation, the enzyme maltase in the yeast, converts the maltose to glucose and another enzyme zymase in yeast, then decomposes the glucose into ethanol and carbon (iv) oxide.

$$C_{12}H_{22}O_{11(aq)} + H_2O \xrightarrow{\text{maltase}} \underset{\text{glucose}}{2C_6H_{12}O_{6(aq)}}$$

$$C_6H_{12}O_6 \xrightarrow{\text{zymase}} \underset{\text{ethanol}}{2C_2H_5OH} + 2CO_2$$

- From molasses: In countries like Brazil, U.S.A; where the production of sugar cane is high, the main raw material for ethanol production is molasses, a syrupy liquid that remains after the crystallization of sugar. It contains sucrose, a type of sugar. When molasses is mixed with yeast, the enzyme **invertase** in yeast, converts the sucrose to two simple isomeric sugars, glucose and fructose, which are both fermented into ethanol by zymase.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6} \xrightarrow{\text{zymase}} 4C_2H_5OH + 4CO_2$$

- From palm wine: In some parts of Africa e.g. Nigeria, Ghana, South Africa, local gin is obtained by fermenting palm wine which is rich in sugar. Fresh palm wine contains sugar and yeast, which on storage in large earthenware pots or drums for 3–4 days, is fermented to ethanol. The resulting solution is then distilled to obtain the clear ethanol usually called gin. (*ogogoro* in Nigeria).

(c) Purification of ethanol

The ethanol obtained from the fermentation process can only give a maximum concentration of 18%, since the yeast cells die above this concentration. For commercial use, ethanol is required in various compositions and to achieve further concentration and purification, fractional distillation is employed.

For alcoholic beverages, different concentrations of ethanol is used and their flavour varies with raw material fermented. Table 9.1 shows the percentage of ethanol and the method of preparation.

Table 9: 1 Kinds of alcoholic beverages

Raw material	*Alcohol beverage*	*% Ethanol* $(^{v}/_{u})$	*Method of preparation*
Barley, wheat	Beer e.g. star	3 – 8	Fermentation
Grapes/ Rice	Wines	8 – 18	Fermentation
Barley, wheat, Grapes	Whisky /spirit/brandy	30 – 60	Fermentation and distillation

Commercial ethanol is sold as pure spirit or rectified spirit or methylated spirit containing 95% ethanol. When sold to the public, 5% methanol, which is toxic, is added to prevent it being consumed as a drink.

9.4 Uses of ethanol

(a) It is used as solvent for resins, varnishes, polishes, liquid soaps, perfumes, drugs and paints
(b) It is used as a fuel, either by itself or mixed with petrol, in racing cars and rockets
(c) It is used as an anti-freeze in automobile radiator
(d) It is present in many alcoholic beverages
(e) It is used for sterilization and preservation of specimens and food
(f) It is used as raw material in the manufacture of chemical e.g. ethanal, trichloromethane, ethoxyethane.

9.5 Conclusion

In this unit you have learned about the group of compounds known as alkanols. You should also have learned about the classification and the principal sources of alkanols. You need to be aware of the fermentation process for the conversion of various raw materials to alcoholic beverages. In addition you should be able to enumerate the various uses of ethanol as the most important compound of the alkanol series.

9.6 Summary

- What you have learned in this unit concerned an important homologous series, the alkanols which are characterized by the presence of the OH functional group.
- Alkanols are classified into primary, secondary and tertiary alkanols depending on the position of the –OH group.
- The main source of alkanols is by hydration of alkenes; however the most important compound of the series, ethanol, can also be obtained by the fermentation process. Alkanols, particularly ethanol plays an important role in our lives owing to its numerous uses.

9.7 Tutor-Marked Assignments

(a) Write and name all the structural isomers of $C_5H_{12}O$ which are alkanols. Indicate whether they are primary, secondary and tertiary alkanols.
(b) Describe the fermentation process for the production of ethanol.

9.8 References

Bajah, S.T., Teibo, B.O., Onwu, G. and Obikwere, A. (2002) *Secondary Secondary Chemistry Textbook 3*. Lagos. Longman Publishers.

Unit 10

Alkanol II - Characteristics of Alkanols

10.0 Introduction

In unit 9 you were introduced to the Chemistry of alkanols, a homologous series characterised by the –OH functional group. You learned about the classification of alkanols into primary, secondary or tertiary based on the position of the –OH group in the molecule. The sources of alkanols were discussed. However of principal interest is the methods used for the production of the most important member of the series, ethanol. Ethanol is produced mainly by hydration of ethene and the fermentation of glucose.

In this unit you will learn about the characteristics of alkanols. Like all organic compounds, the behaviour of alkanols is controlled by the-OH functional group. The -OH is polar in nature.

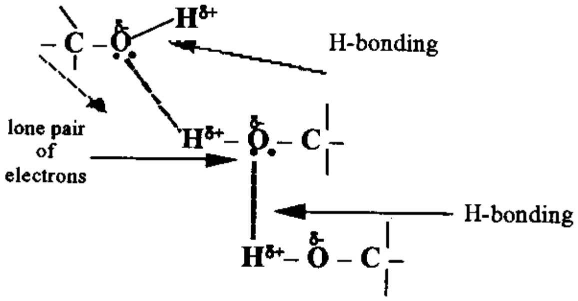
10.1 Objectives

At the end of this unit you should be able to:

- Use hydrogen bonding to explain the variation in physical properties of alkanols
- Discuss the basic reactions of alkanols
- Describe the laboratory test for alkanols

10.2 Intermolecular Hydrogen Bonding in Alkanols

In unit 5, volume I you learned about the secondary types of bonding to exist in organic molecules, one of these is hydrogen bonding. Recall that hydrogen bonding exist only in compounds with groups that have highly electronegative atoms, like O, N(with lone pair of electrons) attached to hydrogen. The -OH of alkanols lead to intermolecular hydrogen bonding between alkanol molecules



H-bonding is a stronger bond than the Vander Waal's forces, which are known to hold molecules together. Hence, alkanols exist as aggregates of molceules and not as individual molecules existing in isolation.

10.3 Physical Properties of Alkanols

(a) The physical properties of alkanols show the normal gradation associated with any homologous series. They are, however, considerably affected by hydrogen bonding between alkanol molecules. This causes some degree of intermolecular association in alkanols, as it does in water, so that boiling points of alkanols are higher than those of other classes of compounds with similar molecular mass in which there is no H- bonding. For example:

Table 10.1

Compound	**Molecular Mass**	**B.p°C**
benzene (C_6H_6)	78	80
pentane (C_5H_{12})	72	36
chloropropane (C_3H_7Cl)	79	47
Ethoxyethane ($C_4H_{10}O$)	74	35
butanal (C_4H_8O)	72	76
*butan-l-ol ($C_4H_{10}O$)	74	118
*water (H_2O)	18	100

Note: * hydrogen bonding exists in these molecules, hence their high boiling point.

(b) The –OH group is polar and as expected alkanols are soluble in water. Lower members of the series are very soluble in water, however, solubility decreases as the alkyl group or molecular mass increase within the series. This is because the organic character (determined by the alkyl group, R) increases with molecular mass down the series when compared to the relative polar character (determined by the –OH group).

10.4 Chemical Properties of Alkanols

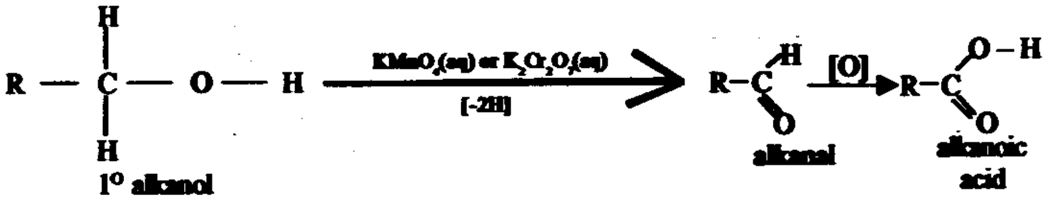
Primary and secondary, but not tertiary alkanols can be easily oxidised, and most alkanols also undergo elimination (dehydration) and substitution reactions. The substitution reaction can be of two kinds. The hydrogen atom of the hydroxyl group can be substituted with the O–H bond being split. In these reactions the alkanols act as an acid and the R–O⁻ ion is formed as intermediate i.e. $ROH \rightleftharpoons RO^- + H^+$

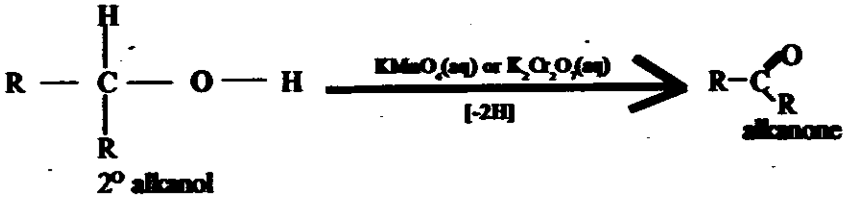
Alternatively, the whole hydroxyl group may be substituted with the C-O bond splitting. Direct substitution of the hydroxyl groups is not easy but it is facilitated in acid solution.

10.4.1 Oxidation Reactions

Primary and secondary alkanols are oxidised, by dehydrogenation, to form alkanals and alkanones respectively. Alkanals and alkanones are two important homologous series of organic compounds. However, discussions on them is beyond the scope of this programme. The oxidation can be achieved using oxidising agents such as $KMnO_4$ or $K_2Cr_2O_7$.

The reactions involve the loss of the -OH hydrogen together with a hydrogen atom from the adjacent alkyl group. With primary alkanols, the initial alkanal product may be oxidised further to an alkanoic acid, if excess oxidising agent is used, but alkanones cannot be readily oxidised.





Tertiary alkanols have no hydrogen atom on the alkyl group adjacent to the hydroxyl group and they are, therefore, not readily oxidised.

10.4.2. Elimination (dehydration) Reactions

Alkanols are readily dehydrated (removal of H_2O) on heating with conc. tetraoxosulphate (VI) acid to give alkenes. The best yields of alkenes are obtained at 170°C and by using excess concentrated H_2SO_4. This dehydration is only possible in molecules containing at least one hydrogen atom on the carbon atom next but one to the –OH group.

When the alkanol is present in excess, however, the dehydration occurs between two molecules to form another class of compounds called alkoxyalkanes.

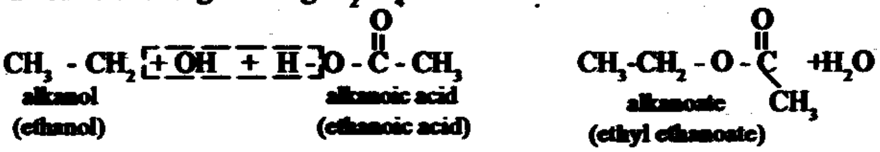
$$\underset{\text{alkanol}}{2R-CH_2OH} + H_2SO_4 \xrightarrow{140°C} \underset{\text{alkoxyalkane}}{R-CH_2OCH_2R} + H_2O$$

10.4.3 Substitution Reactions

(a) Reaction with sodium : the acidic nature of the -OH group shows up in their reaction with reactive metals, such as sodium, to liberate hydrogen gas.

$$2R-O-H + 2Na \longrightarrow 2R-O^-Na^+ + H_2$$

(b) Esterification: alkanols react with alkanoic acids to form alkanoates a series of compounds to be studied in Unit 12. Alkanoates are commonly called esters (hence the term esterification for this reaction) and are usually sweet-smelling liquids. The reaction involves the replacement of the –OH group of alkanols, thus showing a basic character. The reactions are both slow and reversible; and is therefore catalysed using small amounts of strong acids e.g. H_2SO_4.



10.4.4 Iodoform test

Ethanol and methanol react with a mixture of iodine and sodium hydroxide to form a yellow precipitate of triodomethane, CHI_3, (iodoform).

$$CH_3CH_2OH + 4I_2 + 6NaOH \xrightarrow{\Delta} CHI_3 + HCOONa + 5NaI + 5H_2O$$

This reaction is used to confirm the presence of certain types of alkanols namely, methanol, ethanol and other alkanols with the -OH group on a carbon atom adjacent to a methyl ($-CH_3$) group.

10.5 Laboratory Test for Alkanols

The presence of alkanols is confirmed based on the differences in the rate of reaction of primary, secondary and tertiary alkanols with Lucas reagent (mixture of conc.HCl and $ZnCl_2$).

$$R-OH \xrightarrow[ZnCl_2]{conc.\ HCl} R-Cl$$

At room temperature, a tertiary alkanol reacts with Lucas reagent to give immediately turbidity (cloudy) of the chloride. Secondary alkanols also react at room temperature, however, the reaction is a lot slower and the turbidity only appears after about 5minutes. Primary alkanols does not react with Lucas reagent at room temperature at all, however, the turbidity can be observed when the reaction mixture is heated.

10.6 Conclusion

In this unit you have learned about the properties of alkanols. You have learned about the influence of hydrogen bonding on the physical properties of alkanols. Furthermore, you should have learned that the reactivity of the alkanols is centered around the –OH functional group. The hydroxyl group, though essentially neutral, but in the presence of certain reagents can undergo a series of reactions such as its action with sodium or potassium which is an important reduction reaction, it also gives an important reaction with phosphorous pentachloride and forms esters with organic acids.

10.7 Summary

In this unit you have learnt about the important characteristics of alkanols and how the functional group –OH plays an important role in the chemical reactivity of alkanols. You will in the next unit, study the chemistry of alkanoic acids which will focus fundamentally, on such aspects as its sources, methods of preparation, physical/ chemical properties etc.

10.8 Tutor-Marked Assignments

1. Explain why alkanols exist as agggegate of molecules and not as isolated or individual molecules.
2. Why are alkanols soluble in water, why does the solubility in water decrease as you go up the series.
3. Given a mixture of primary, secondary and tertiary alcohols, how can you proceed to distinguish between the various classes.

10.9 References

Bajah, S.T., Teibo, B.O., Onwu G., and Obikwere, A. (2002). *Senior Secondary Chemistry-Textbook 3.* Lagos. Longman Publishers.

Osei Yaw Ababio (2002) *New School Chemistry*. Onitsha. Africanan Fep Publishers.

Unit 11

Alkanoic Acids

11.0 Introduction

Alkanoic acids are groups of organic compounds which contain the –COOH group linked to a hydrogen atom or to an alkyl group. The old name for members of this homologous series is carboxylic acids. The names of members of the series are obtained by replacing the '–e' of the corresponding alkane by '–oic' and add the word 'acid'. Members of the series can be represented by the general molecular formula of C_nH_{2n+1} COOH where n ≥ O. They are sometimes called fatty acids because some of them are found in natural fats and oils.

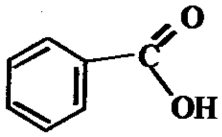
The first five members of the alkanoic acid series are shown in Table 11.1 below:

Table 11.1

Molecular Formula	*Structural formula*	*IUPAC name*
CH_2O_2	HCOOH	methanoic acid
$C_2H_4O_2$	CH_3COOH	ethanoic acid
$C_3H_6O_2$	CH_3CH_2COOH	propanoic acid
$C_4H_8O_2$	$CH_3CH_2CH_2COOH$	butanoic acid
$C_5H_{10}O_2$	$CH_3CH_2CH_2CH_2COOH$	pentanoic acid

Alkanoic acids are sometimes represented as R-COOH, where R = alkyl group. Older names of specific alkanoic acids refer to the origin or use of the acid, e.g. methanoic acid was first made from ants (Formica = ant) and is called formic acid; ethanoic acid occurs in vinegar (acetus = sour) and is called acetic acid.

Apart from the aliphatic acids, aromatic acids such as benzoic acid are also important members of this series.



benzoic acid, an aromatic acid

11.1 Objectives

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

- Name using the IUPAC nomenclature of simple alkanoic acid.
- Explain how hydrogen bonding affects the properties of alkanoic acids.
- Explain the methods of preparation and properties of alkanoic acids

11.2 Sources of Alkanoic Acids

11.2.1 Natural Sources

Several members of the alkanoic acid series are widely distributed in nature and found in living organisms. For example, methanoic acid was first obtained from ants; ethanoic acid is present in vinegar and is responsible for its sour taste; butanoic acid has been isolated from human sweat. Higher alkanoic acids, such as citric acid, tartaric acid, are known to be present in several types of fruits and vegetables.

11.2.2 General Methods of Preparation

(a) Oxidation of primary alkanols

Primary alkanols are oxidised by oxidising agents, such as potassium tetraoxomanganate (VII), potassium heptaoxochromate (VI) to alkanoic acids. The reaction is usually carried out by refluxing excess of the oxidising agent with the alkanol.

$$R-CH_2OH \xrightarrow[\text{heat}]{[O]} R-COOH + H_2O$$

Note: [o] represents the oxidising agent.

(b) Hydrolysis of nitrile

The acid catalysed hydrolysis of nitrile with water, yield alkanoic acid. For example ethanonitrile can be hydrolysed to ethanoic acid in the presence of small amount of tetraoxosulphate (VI) acid.

$$\underset{\text{ethanonitrile}}{CH_3CN} + 2H_20 \xrightarrow{H^+} CH_3COOH + NH_3$$

Exercise 1

(a) Find out the names of the alkanoic acids present in lemons, grapes and sour milk.

(b) Write equation to show the preparation of butanoic acid from butanol

11.3 Characteristics of Alkanoic Acids

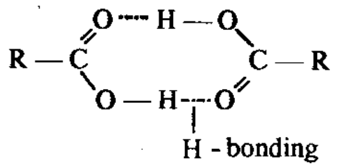
11.3.1 Physical properties

(a) Lower members of the alkanoic acid series, such as methanoic acid and ethanoic acid, are completely miscible in water. Solubility, however, decreases with higher members of the series. In general, alkanoic acids are more soluble in water, (a polar solvent) than the corresponding alkanols with the same number of carbon atoms. This is partly due to the high polarity of the $C^{\delta+}-O^{\delta-}$ and $O^{\delta-}-H^{\delta+}$ bonds, which makes it easier for the alkanoic acid molecules to bond readily with water molecules hence increased solubility. With higher members of the series, however, the hydrocarbon component (R groups which are organic) becomes larger than the polar component in the molecules, hence the decrease in solubility.

(b) Alkanoic acids have usually higher boiling points than other compounds with comparable relative molecular mass e.g.

	Relative Molecular Mass	*Boiling point*
ethanoic acid	60	118°C
propan-1-ol	60	97°C
butane	58	-1°C

The high boiling points of alkanoic acids is as a result of strong intermolecular hydrogen bonding that exist between the molecules. In fact, lower members of the series do not exist as single molecules but as dimers (as shown below), giving them an unusually higher molecular mass than expected.



The hydrogen bonding between alkanoic acid molecules and water molecules, also partly explains their high solubility in water.

11.3.2 Chemical properties

(a) **Acidity:** Due to the polar nature of the bonds in alkanoic acids they ionise in water as follows:

$$R-C(=O)-O-H + H_2O \rightleftharpoons R-C(=O)-O^- + H_3O^+$$

However, alkanoic acids are weaker acids than mineral acids, such as hydrochloric acids, but they are very much stronger than alkanols. The strength of any alkanoic acid depends on the equilibrium position of the equation above. The stronger the acid the further to the right will be the equilibrium position so that the acid strength will depend on the readiness with which the –O–H bond will split in the presence of water.

Exercise 2

Can you explain why alkanols, R–OH are weaker acids than alkanoic acids, R–COOH.

(b) **Formation of salts:** Alkanoic acids react with bases and trioxocarbonate(iv) to form salts. Thus, it

(i) reacts with trioxocarbonate(iv) and hydrogen trioxocarbonate(iv) to give salts of the acid with liberation of carbon(iv) oxide.

$$2RCOOH + Na_2CO_3 \longrightarrow 2RCOONa + H_2O + CO_2\uparrow$$

(ii) reacts with bases or alkalis to form salts of the acids and water. This is an acid-base neutralisation.

$$RCOOH + NaOH \longrightarrow RCOO^-Na^+ + H_2O$$

In the reactions above, alkanoic acids behave like mineral acids, exhibiting their acidic property. Alkanols do not undergo these reactions because they are weaker acids.

(c) **Formation of esters (esterification):** Alkanoic acids react with alkanols to form alkanoates (esters); the H-atom of the carboxyl group is replaced by an alkyl group e.g.

$$\underset{\text{alkanoic acid}}{R\text{–}COOH} + \underset{\text{alkanol}}{R^1\text{–}OH} \rightleftharpoons \underset{\text{alkanoate}}{R\text{–}COOR'} + \underset{\text{water}}{H_2O}$$

The reaction is usually catalysed with mineral acids e.g. HCl or H_2SO_4. **This reaction is commonly referred to as esterification** Alkanoates or esters is an important homologous series and is the subject of our discussion in the next unit.

(d) **Reduction:** Alkanoic acids can be reduced to primary alkanols using a special reducing agent called lithium aluminium hydride, $LiAlH_4$.

$$R\text{–}COOH \xrightarrow{LiAlH_4,\ HCl} R\text{–}CH_2OH$$

This reduction reaction is the reverse process of the oxidation of primary alkanols, used for producing alkanoic acids (see section 11.2.2 of this unit).

11.4 Laboratory Test for Alkanoic Acids

The presence of the alkanoic acid functionality is usually confirmed in the laboratory by utilising its acidic properties. As stated in Section 11.3 of this unit, alkanoic acids react with trioxocarbonate(iv) or hydrocarbonates to liberate carbon(iv) oxide. This is the laboratory test for the –COOH group present in all alkanoic acids. The evolution of the CO_2 gas is used as evidence of the presence of alkanoic acids.

$$R - COOH + NaHCO_3 \longrightarrow R - COONa + H_2O + CO_2\uparrow$$

11.5 Uses of Alkanoic Acids

(a) Methanoic acid is used in dyeing, electroplating, tanning and in coagulating rubber.
(b) Ethanoic acid is used as a raw material in the
- manufacture of cellulose ethanoate (used for packing, in varnishes, in the filter tips of cigarettes and in synthetic fibres).
- manufacture ethanoic anhydride which is used in aspirin.

(c) Ethanoic acid is an important organic solvent.
(d) Higher alkanoic acids are used for making soaps and detergents.

11.6 Conclusion

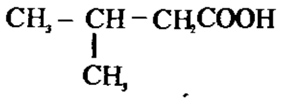
In this unit you have learned about an important class of organic compounds called alkanoic acids. You have learned about their presence in living organisms and how they are made in the laboratory. You should also have learned about the polarity of the functional group and the influence of H-bonding on the physical properties of alkanoic acids. You should be aware of the acidic nature of the —OH bond of the acids and how it influences its characteristic reactions.

11.7 Summary

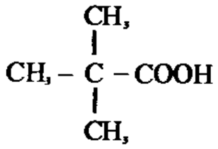
What you have learned in this unit concerns the chemistry of the —COOH functional group as present in the alkanoic acid series. It has served to underscore the importance of functional groups in understanding organic chemistry in general, as specific characteristics of the classes of organic compounds.

11.8 Tutor-Marked Assignments

(a) Give the IUPAC name of the following compound.



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2COOH$$



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-COOH$$

(b) Write the equations for the following reactions
- (i) ethanoic acid with calcium trioxocarbonate (iv)
- (ii) ethanoic acid with calcium hydroxide
- (iii) ethanoic acid with ethanol.

11.9 References

Bajah, S.T., Teibo, B.O., Onwu, G., and Obikwere, A. (2002). *Senior Secondary Chemistry-Textbook 3.* Lagos. Longman Publishers.

Osei Yaw Ababio (2002) *New School Chemistry.* Onitsha. Africana–Fep Publishers.

Unit 12

Alkanoates

12.0 Introduction

Alkanoic acids form a variety of important derivatives one of which is the alkanoates. The common name for alkanoates is esters. Alkanoates are formed from alkanoic acids by replacing the – OH of alkanoic acids with –OR group (where R = alkyl group). They are represented by the general formula, $RCOOR'$ or $C_nH_{2n+1}COOC_nH_{2n-1}$ (where $n \geq O$).

The IUPAC nomenclature for members of the series are derived from the alkanols ($R'OH$) and the alkanoic acid ($RCOOH$) from which the alkanoates are formed. The alkanol portion, R', is named first as alkyl and a space is left, which is followed by the alkanoic acid portion R' COO, named as alkanoate. For example,

(a) CH_3CCOCH_3 = methylethanoate indicating that it is formed from methanol (as the alkanol) and ethanoic acid (as the alkanoic acid).

(b) $CH_3CH_2COOCH_2CH_3$ = ethyl propanoate indicating that it is formed from ethanol (as the alkanol) and propanoic acid (as the alkanoic acid).

Naturally occurring esters are called fats and oils, formed from long-chain alkanoic acids. If the esters are liquids at room temperature, they are called oils, whereas if they are solids at room temperature they are called fats. Examples of these are the fats (tallow from cows, cocoa butter from cocoa) and oils (palm oil from oil palm, groundnut oil from groundnut, castor oil from castor plants) which are used for cooking, as source of energy and in the manufacture of soaps.

Lower alkanoates are known for their characteristic sweet strong aroma and are found in many flowers and fruits e.g. methyl butanoate in pineapple, pentyl ethanoate in banana. The aroma of alkanoate is sometimes used to confirm their presence.

12.1 Objectives

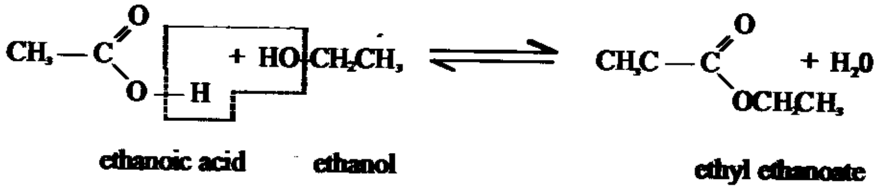
At the end of this unit, you should be able to:

- Identify and name alkanoates based on their formula.
- Identify some of the natural sources of alkanoates.
- Explain esterification as the preparatory route to alkanoate.
- Explain the characteristics of alkanoates.

12.2 Preparation of Alkanoates: Esterification

Racall from unit 11, the esterification process. This process is the principal route for making alkanoates. The direct reaction of alkanoic acid and alkanols in the presence of catalytic amounts of a mineral acid is known as esterification.

For example, ethyl ethanoate is prepared by heating ethanoic acid and ethanol with concentrated tetraoxo sulphate (vi) acid as catalyst.



$$CH_3-C(=O)-O-H + HO-CH_2CH_3 \rightleftharpoons CH_3C-C(=O)OCH_2CH_3 + H_2O$$

Esterification is an equilibrium process, and for the production of ethyl ethanoate, the forward and backward reaction occur at about the same rate. A convenient procedure for making ethylethanoate in good yield, is to run a mixture of ethanoic acid and ethanol into a hot mixture of ethanol (excess) and concentrated tetraoxosulphate (vi) acid at the same rate as the alkanoate distills off. The solution obtained from the distillation is shaken with concentrated trioxocarbonate (iv) to remove acids, and with concentrated calcium chloride solution to remove ethanol. The resultant solution is then dried over anhydrous calcium chloride, and the ethyl ethanoate is obtained pure by redistillation.

12.3 General Characteristics of alkanoates

12.3.1 Physical properties

Alkanoates are colourless liquids or solids, sparingly soluble in water. Most of them have a characteristic fragrant odour or sweet smell and many of them occur naturally. The fragrances in flowers and fruits attracts the insects and animals which are responsible for the pollination of flowers and dispersal of seeds.

12.3.2 Chemical properties

Alkanoates are generally not very reactive but can be hydrolysed to their precursor alkanoic acids and alkanols; and reduced to primary alkanols.

(a) Hydrolysis of alkanoates: Alkanoates are hydrolysed very slowly by boiling with water to give the component alkanoic acids and alkanols. The reaction can be made faster by catalyzing the hydrolysis with acids or bases.

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$$

The acid – catalyzed process is the revese of esterification and, as it is reversible, an excess of acidic solution is required to give a good yield of alkanoates.

The base-catalysed hydroysis is a more efficient process for the alkanoate ion formed, does not react appreciably with alkanols so that the reaction goes almost to completion e.g.

$$\underset{\text{alkanoate}}{R-COOR'} + \underset{\substack{\text{from}\\ \text{base}}}{OH^-} \longrightarrow \underset{\substack{\text{alkanoate}\\ \text{ion}}}{R-COO^-} + R'-OH$$

This alkaline hydrolysis process commonly called **saponification** is used for the conversion of naturally occurring esters (alkanoates) into soaps. The process of soap making by saponification will be discussed in details in the next unit.

(b) Reduction of alkanoates: Alkanoates can be reduced to primary alkanols more easily than alkanoic acid. Lithium aluminum hydride and catalytic hydrogenation are both effective catalysts for reduction.

$$R-COOR' \xrightarrow[H_2/Ni]{LiAlH_4\ or} R-CH_2OH + R'-OH$$

alkanoate primary alkanol

$$CH_3COOC_2H_5 + 4[H] \longrightarrow 2C_2H_5OH$$

from
reducing agent

12.4 Uses of Alkanoates

(a) A large number of alkanoates are used as perfumes and flavourings. For example ethyl methanoate obtained from rum; 3-methylbutyl ethanoate obtained from pear; and ethyl butanoate obtained from pineapple are all used in this way for perfumes and for flavouring

(b) Ethyl ethanoate is a good solvent

(c) Certain useful waxes are composed mainly of alkanoates e.g beeswax, $C_{15}H_{31}COOC_{31}H_{63}$.

(d) Alkanoates of trihydric alkanols and akanoic acids are of great, importance in making soap and propane 1,2,3-triol (glycerol).

12.5 Conclusion

In this unit you have learned about alkanoates a class of organic compounds known for their sweet smelling fragrants. You should have also realized that the odour of flowers and fruits are largely due to the alkanoates present in them. In addition, you should be familiar with the processes of esterification and saponification. You need to be aware of the numerous uses and importance of alkanoates.

12.6 Summary

What you have learned in this unit concerns the chemistry of alkanoates and the importance of this class of compounds as fragrants and flavouring. Alkanoates are the basic raw material for the manufacture of soaps which will be discussed in detail in the next unit.

12.7 Tutor-Marked Assignments

(a) Write the structure and name four alkanoates with the general formula. $C_4H_8O_2$

(b) Describe the esterification process for the preparation of ethyl ethanoate.

(c) Write the equation for the alkaline hydrolysis of methyl ethanoate

12.8 References

Bajah, S.T., Teibo, B.O., Onwu, G., and Obikwere, A. (2002). *Senior Secondary Chemistry-Textbook 2*. Lagos. Longman Publishers.

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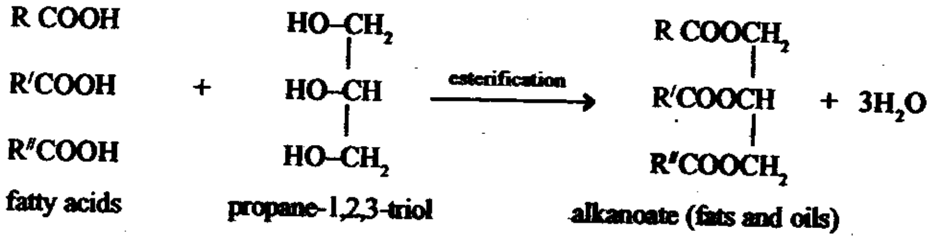
Unit 13

Fats, Oils and Amino acids

13.0 Introduction

Fats and oils are naturally occurring alkanoates formed from the trihydric alkanol, propane – 1,2,3- triol (commonly known as glycerol) and long-chain alkanoic acids (commonly known as fatty acids) with C_{12} to C_{24} carbon atoms. A trihydric alkanol is one with three hydroxyl group (–OH) in the molecule; hence during esterification, each molecule of the trihydric alkanol reacts with three molecules of fatty acids to give the fats and oils as follows



$$\begin{array}{lcccll} R\,COOH & & HO{-}CH_2 & & R\,COOCH_2 & \\ & & | & & | & \\ R'COOH & + & HO{-}CH & \xrightarrow{\text{esterification}} & R'COOCH & +\ 3H_2O \\ & & | & & | & \\ R''COOH & & HO{-}CH_2 & & R''COOCH_2 & \\ \text{fatty acids} & & \text{propane-1,2,3-triol} & & \text{alkanoate (fats and oils)} & \end{array}$$

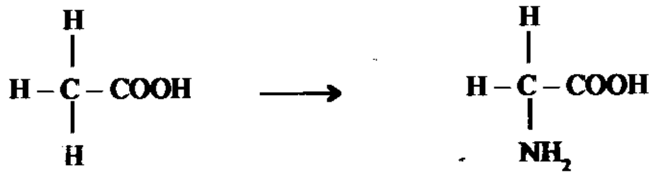
This esterification process occurs naturally in plants and animals to give fats and oils, which are generally referred to as lipids. Fats are solids, at room temperature, usually of animal origin while oils are liquids, at room temperature, mainly of plant origin. The fatty acids commonly found in lipids can be subdivided into saturated fatty acids (have no double bond in their hydrocarbon chain) and unsaturated fatty acids (have one or more double bond in their hydrocarbon chain). Examples of these fatty acids are given below (Table 13.1):

Table 13.1

Common Name	*Source*	*Formula*	*IUPA nomenclature*
Palmitic acid	Oil Palm	$CH_3(CH_2)_{14}COOH$	hexadecanoic acid
Stearic acid	Tallow (animal fat)	$CH_3(CH_2)_{16}COOH$	octadecanoic acid
Oleic acid	Olive or Peanut Oil	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	Octadec-9-enoic acid
Linoleic acid	Vegetable oil	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	Octadeca-9,12-dienoic acid

Amino acids are substituted alkanoic acids in which the hydrogen atom(s) in the alkyl groups have been replaced by amino group (-NH_2 group).

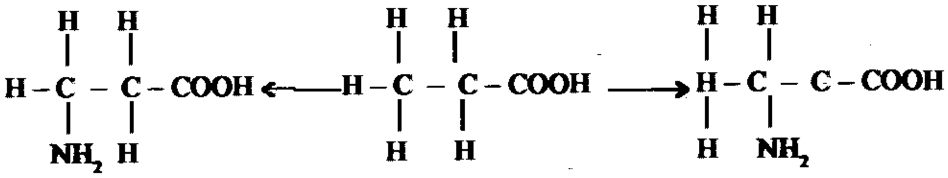
For example:



$$CH_3COOH \longrightarrow CH_2(NH_2)COOH$$

Ethanoic acid

2-amino ethanoic acid
an amino acid commonly called glycine



$$CH_2(NH_2)CH_2COOH \longleftarrow CH_3CH_2COOH \longrightarrow CH_3CH(NH_2)COOH$$

3-aminopropanoic acid propanoic acid 2- amino propanoic acid

Amino acids are important substituted alkanoic acids for they are the components parts of proteins, which occur widely in all plants and animals. Proteins will be part of our discussion in Unit 14.

13.1 Objectives

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

- Identify fats and oils as alkanoates.
- Recall some of the natural sources of fats and oils.
- Describe the saponification process for the manufacture of soap.
- Describe the process of hardening of oils.
- Compare properties of soap and detergent.
- Identify the functional groups in amino acids.

13.2 Sources of Fats and Oils

Fats and oils are widely distributed in nature. They are used by man for cooking, as source of energy and for the manufacture of soap. Animal fats and oils are usually obtained by treating the animal tissues with hot water. This breaks down the cell walls and allows the molten fat or oil to rise to the surface of water. Tallow is obtained in this way from beef or mutton (remember the sauce obtained when meat is boiled in water); pure lard from pigs. Vegetable oils are usually obtained by pressing the plant to squeeze out the oil or both extraction with organic solvents.

Table 13.2 shows some common fats and oils; their natural sources and producer countries.

Table 13:2

	Fats or Oils	*Natural Source*	*Producer Countries*
1.	Groundnut oil	Groundnut	Nigeria, Gambia
2.	Palm oil	Oil Palm	Nigeria, Malaysia
3.	Coconut oil	Coconut tree	Nigeria, Malaysia
4.	Cotton seed oil	Cotton	Nigeria, USA, Egypt
5.	Soya bean oil	Soya tree	Nigeria, USA
6.	Castor oil	Castor seed	Nigeria, Malaysia
7.	Palm kernel oil	Oil Palm	Nigeria, Malaysia
8.	Sunflower oil	Sunflower	Nigeria, Kenya
9.	Tallow fat	Sheep and Cow	Argentina, USA, Australia
10.	Lard fat	Pigs	USA, China
11.	Coca butter	Cocoa	Brazil, Nigeria, Ghana
12.	Wool grease	Sheep	Argentina, Australia

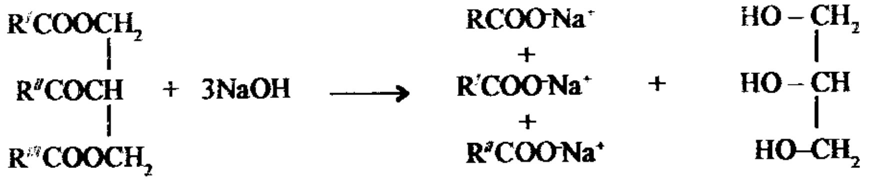
13.3 Hardening of Oils

Vegetable oils can be changed to fats by catalytic hydrogenation (addition of hydrogen to the double bond present in the hydrocarbon chain of the oil). Margarine (e.g. Blue Band) is made by this process. The oils, usually from plants such as oil palm, groundnut and soya-been oil, are heated to about 180°C in the presence of finely divided nickel, as catalyst, and hydrogen gas is bubbled in at 2–5 atmosphere. The hydrogen is added across the double bonds present in the unsaturated hydrocarbon chains of the oil. The product is a fat, which is then mixed with salt, vitamins, milk and other additives to form margarine.

13.4 Soap Manufacture: Saponification

Recall from Unit 12 that saponification is the alkaline hydrolysis of alkanoates. Fats and oils, which are alkanoates of fatty acids, can be hydrolysed with caustic alkali to give propane-1,2,3-triol and the corresponding sodium and potassium salts of the component fatty acid. These salts are the main constituents of soap. Sodium chloride is used to remove (salt out) the soap from the mother liquor, which is denser than the soap. After washing the soap free of excess alkali, different additives (dyes, perfumes) are then added to give varieties of soaps. The nature of the starting oil also determines the types of soap obtained.

$$\text{Fat or oil + caustic alkali} \xrightarrow{\text{saponification}} \text{soaps + propane-1,2,3-triol}$$



$$\begin{array}{l} R'COOCH_2 \\ \quad | \\ R''COCH \\ \quad | \\ R'''COOCH_2 \end{array} + 3NaOH \longrightarrow \begin{array}{c} RCOO^-Na^+ \\ + \\ R'COO^-Na^+ \\ + \\ R''COO^-Na^+ \end{array} + \begin{array}{l} HO-CH_2 \\ \qquad | \\ HO-CH \\ \qquad | \\ HO-CH_2 \end{array}$$

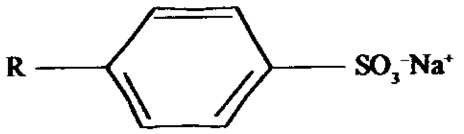
soaps propane-1,2,3-triol (glycerol)

13.5 Detergents

These are substances which have the ability to clean an object such as soaps. Detergents are usually classified into two main types – soapy detergents and soapless detergents. The soapy detergents e.g. soaps are the sodium or potassium salts of fatty acids produced by the saponification of fats and oils, as described in Section 13.4

Soapless detergents are the alkyl benzene sulphonates, abbreviated as ABS.

A soapless detergent molecule is



R = long hydrocarbon chain

[ABS]

Like soap, soapless detergents are sodium salts of sulphonic acid to which an aromatic – alkyl chain is attached. Soapless detergents are the more favoured cleaning agents nowadays than the soapy detergents. They are available as liquids or solids and the raw materials for their manufacture are petrochemicals obtained from refining crude oil.

Soapless detergents, are preferred because:

(a) they do not form scum with hard water and therefore retain their cleansing properties irrespective of the type of water used.

(b) they are neutral in water, whereas soapy detergents are slightly alkaline in water and therefore not suitable for washing acid-sensitive fabrics

(c) they have wider applications, in terms of removing various types of stains, than soapy detergent.

13.6 Uses of Fats and Oils

(a) As foodstuffs: most fats are consumed as food; together with carbohydrates, they provide source of energy for animals.

(b) In making soaps: the fats and oils commonly used for making soaps are tallow, coconut oil, bleached palm oil, soya bean oil and olive oil.

(c) In making candles: when tallow is hydrolysed under pressure it gives products used in making candles.

(d) In making glycerol: glycerol is the by-product obtained in the manufacture of soap. It is used in the manufature of creams, medicine.

(e) In making paints: linseed oil is used for making oil paints.

(f) In making margarine: margarine is made by hadening oils and is a good substitute for butter.

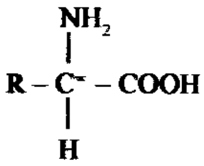
13.7 Tests for Fats and Oils

(a) Paper test: a drop of oil or melted fat on a piece of paper forms a translucent (allow light to pass through) grease spot.

(b) Sudan III test: to a mixture of oil and water add 4 to 5 drops of sudan III stain, a red stain confirms fats and oils.

13.8 Amino Acids

Amino acids are derivatives of alkanoic acids in which the hydrogen of the alkyl chain is replaced by the amino group ($-NH_2$). Each amino acid contains two functional groups, the carboxyl group ($-COOH$) and the amino group ($-NH_2$). It therefore has a general structure as follows.



$$R-\overset{NH_2}{\underset{H}{C^*}}-COOH$$

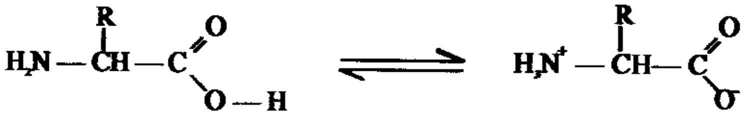
Amino acids are the basic structural units of proteins. All the amino acids obtained by hydrolysis of animal and plant proteins have the amino group attached to the carbon adjacent the carboxyl group. They are called ∝ - amino acids and twenty (20) of such amino acids have been isolated in nature. All proteins found in living organisms are combinations of these amino acids. You will learn more about proteins in the next unit.

In aqueous solution, amino acids are neutral to litmus, but they can act as an acid, on account of the $-COOH$ group, or as a base, on account of the $-NH_2$ group. Amino acids can therefore react with acids or bases to form salts.

Let us consider the following reactions:

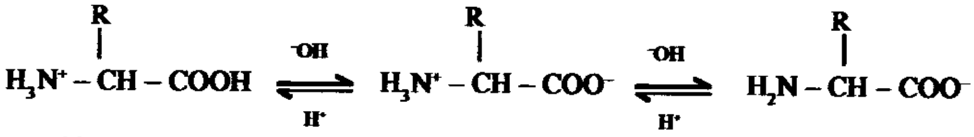
$$NH_2CH_2COOH + HCl \longrightarrow Cl^-\,{}^+NH_3CH_2COOH$$
$$NH_2CH_2COOH + NaOH \longrightarrow NH_2CH_2COO^-Na^+ + H_2O$$

In neutral solution, amino acids exist as dipolar ions (zwitterion) and this polar structure accounts for their high melting point (e.g amino-ethanoic acid melts at 235°C), solubility in water and insolubility in organic solvent.



dipolar ion

Amino acids exist in three different forms depending on the pH of the medium



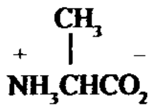
$$H_3N^+-\overset{R}{CH}-COOH \underset{H^+}{\overset{^-OH}{\rightleftharpoons}} H_3N^+-\overset{R}{CH}-COO^- \underset{H^+}{\overset{^-OH}{\rightleftharpoons}} H_2N-\overset{R}{CH}-COO^-$$

acid condition | neutral condition | basic condition

Examples of simple amino acids, with their common and IUPAC names, are given below.

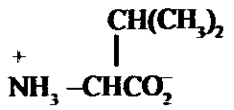
$\overset{+}{N}H_3CH_2\overset{-}{CO_2}$

2-amino ethanoic acid
(glycine)



$\overset{+}{N}H_3\overset{\overset{CH_3}{|}}{C}H\overset{-}{CO_2}$

2 – aminopropanoic acid
(alanine)



$\overset{+}{N}H_3-\overset{\overset{CH(CH_3)_2}{|}}{C}HCO_2^-$

2-amino-3-methylbutanoic acid
(valine)

13.9 Conclusion

In this unit you have learned about fats and oils as naturally occurring alkanoates obtained from fatty acids and trihydric alkanols. You should have learned the varied sources of these classes of compounds also known as lipids. Furthermore, you should have learned how fats and oils can be converted into margarine and soap. You need to be aware of the various types of detergents and the advantages of soapless detergent over soapy detergents. You were introduced to amino acids and the polar nature of their structure.

13.10 Summary

What you have learned in this unit concerns the sources and uses of fats and oils. The unit also introduced you to the dipolar nature of amino acids and that they are the basic units of proteins. The unit that follows shall explain more about the chemistry of proteins.

13.11 Tutor-Marked Assignments

(a) Explain the following
  (i) soap formation by saponification
  (ii) influence of pH on the structure of amino acids

(b) Write briefly on detergents and their advantages over soap.
(c) Give the IUPAC name of the following
  (i) $(CH_3)_2CHCH_2-CH(NH_2)-COOH$
  (ii) $CH_3CH_2CH(CH_3)-CH(NH_2)-COOH$
  (iii) State the relationship between the two structures

13.12 References

Bajah, S.T., Teibo, B.O., Onwu G., and Obikwere, A. (2002). *Senior Secondary Chemistry-Textbook 3.* Lagos. Longman Publishers.

Osei Yaw Ababio (2002). *New School Chemistry*. Onitsha. Africana Fep Publishers.

Unit 14

An Introduction to Polymer Chemistry

14.0 Introduction

Polymers are very large molecules which are made up of repeating (recurring) structural units. Polymers are formed by the linking together of many smaller units (molecules) known as monomers, the overall process being known as polymerisation.

$$\underset{\text{monomer}}{nA} \longrightarrow \underset{\text{polymer}}{An} \equiv -A-A-A-A-A-A-A-$$

Polymerisation is defined as the process (reaction) by which many simple molecules (monomers) join together to form giant molecules (polymers) of high molar mass (>200,000). There are two types of polymerisation, addition polymerisation and condensation polymerisation.

Some typical monomers and the corresponding polymer are listed below:

Monomer	*polymer*
ethene	polythene
vinyl chloride	polyvinyl chloride
amino acids	proteins
glucose	starch

Polymers can be naturally-occuring e.g. protein, rubber, starch and cellulose, or synthetised in the laboratory e.g. polythene, nylon 66, polyvinyl chloride and terylene. The naturally occuring polymers are called natural polymers while the man-made polymers are called synthetic polymers.

14.1 Objectives

At the end of this unit, you should be about to:

- Define polymerisation.
- Distinguish between natural and synthetic polymers.
- Recall the different processes involved in polymerisation and the types of polymers obtains.
- Recall different types of monomers and their corresponding polymers.

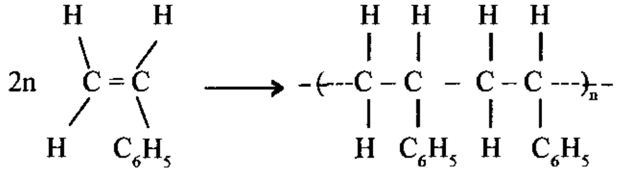
- List the uses of different types of polymers.

14.2 Polymerisation Processes

14.2.1 Addition polymerisation

Monomers which are unsaturated (having multiple bond) can react with each other to **form addition compounds**, a polymer with the same empirical formula as the monomer. Ethene and substituted ethenes, for example, form addition polymer.

$$\underset{\text{ethene}}{2n\ CH_2 = CH_2} \xrightarrow[\text{high temp and pressure}]{\text{catalyst}} \underset{\text{polythene}}{-(CH_2-CH_2-CH_2-CH_2)-_n}$$



phenylethene (styrene) poly(phenylethene) or polystyrene

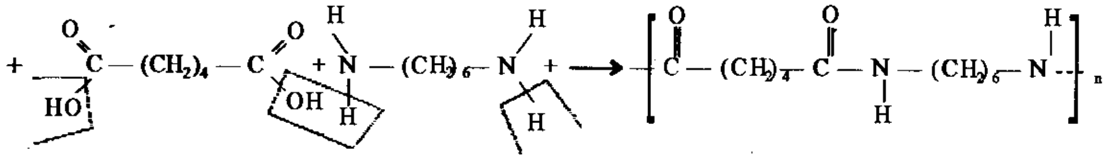
Several types of this polymer and their uses are listed in Table 14.1

Table 14.1

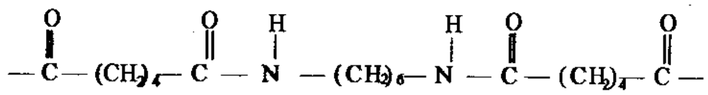
	Monomer	*Polymer*	*Common name*	*Uses*
1.	$CH_2= CH_2$ (ethene)	$-[CH_2-CH_2]-_n$	Polyethene	Plastic bottles, pipes, toys and packaging material
2.	$CH_2= CHCl$ (vinyl chloride)	$-[CH_2-CHCl]-_n$	Polyvinyl chloride (PVC)	insulating material, pipe film, coatings and automobile parts
3.	$CF_2= CF_2$ (tetrafluoro-ethene)	$-[CF_2-CF_2]-_n$	Poly(tetrafluoro-ethene) (Teflon)	high-temperature resistant rubber stopcocks, gaskets
4.	$CH_2= CH(OCOCH_3)$ (vinyl acetate)	$-[CH_2-\underset{\substack{\vert \\ OCOCH_3}}{CH}]-_n$	Polyvinyl acetate (PVA)	adhesives, emulsion paints.
5.	$CH_2 = CHC_6H_5$ (styrene)	$-[CH_2-\underset{\substack{\vert \\ C_6H_5}}{CH}]-_n$	Polystyrene	Utensils,foam toys and packaging

14.2.2 Condensation polymerisation

Condensation polymerisation occur between monomers that have at least two functional groups that can react or repeated with one another. The polymerisation process occur by the elimination of small molecules such as H_2O or NH_3 between two different monomer molecules each of which has at least two functional groups which can participate in the condensation. Nylon-6,6, for example, is a condensation polymer formed by the elimination of H_2O molecules from hexadioic (adipic) acid and hexane -1,6-diamine.



Nylon-6,6

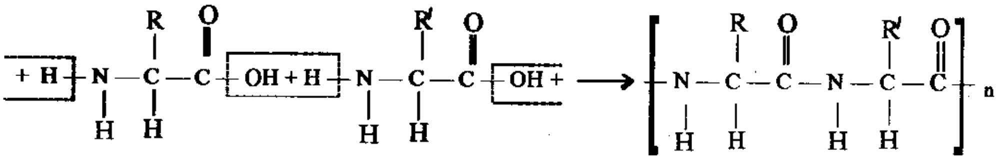


$$-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-$$

Nylon-6,6

Nylon-6,6 is an example of a **copolymer**. When two different monomers, e.g. ethene and propene, hexadioic acid and hexane -1,6-diamine, react to give a polymer the product is called a co-polymer.

Another example of condensation polymerisation is the repeated condensation of amino acids with one another to give a protein molecule.



amino acids

protein molecule

When the R and R' are different then the protein molecule is a co-polymer.

Table 14.2 shows some condensation polymers and their uses.

Table 14.2

Monomer	*Polymer*	*Uses*
1. hexanedioic acid + hexane-1,6-diamine	Nylon-6,6	Fabric, tiles, tyre cord
2. benzene-1,4-dialkanoic acid +1,2-ethanediol	Terylene (polyester)	cloths, recording tapes, tyre cord,
3. amino acids	proteins	structural materials and biochemical functions for living organisms

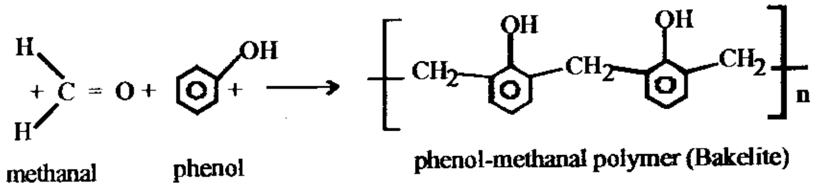
Monomer	Polymer	Uses
4. glucose	starch (carbohydrate)	source of energy for living organisms

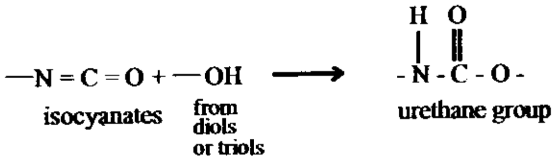
14.3 Plastics and Resins

Plastics are high molar mass synthetic (man-made) polymers that can be deformed and moulded into various shapes, at high temperatures. Linear polymers or copolymers have only weak van der waal's forces between their long chains. These polymers and those with only a few, weak cross links between the chains are called **thermoplastics** because on heating they soften and on cooling harden again. Thermoplastics can be re-softened and re-hardened over and over again; and this hardly affects the property of the plastics. They are usually soluble in organic solvents.

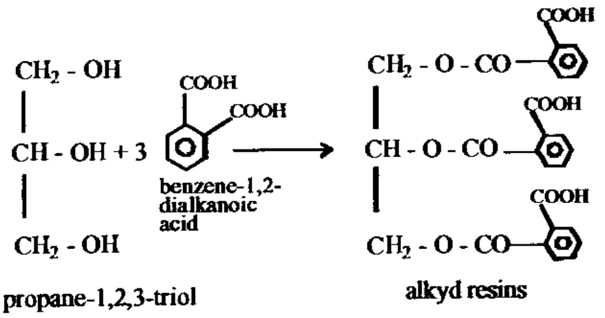
Examples of thermoplastics are cellulose acetate, polythene, polyvinyl chloride. Thermoplastics are generally used in the form of moulded shapes, fibres, pipe, sheets or films. They are generally very good insulators and are resistant to many chemicals. If the original thermoplastic is too brittle its properties can be changed by adding plasticisers e.g. esters of benzene dialkanoic acids.

Polymers that contain highly crosslinked structure cannot be softened once they have hardened, that is they can only be heat-treated once. They are called **thermosetting plastics** and are insoluble in any kind of solvent. The rigidity in structure on cooling is as a result of chemical reactions leading to extensive cross-linking. Examples of thermosetting plastics are phenol-methanal polymer, polyurethanes and alkyd resins.





$$—N=C=O + —OH \longrightarrow -\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-$$



Thermosetting plastics are used to make articles such as electric plugs and switches, telephones, wireless and television cabinets, lavatory seats, ash trays and plastic tableware. Bakelite is a good insulator; polyurethanes are used in floor finishes and hard-wearing paints, in the form of foams; and alkyd resins are used as binding resins and in alkyd paints.

Naturally occurring resins are sticky substances, insoluble in water, that flows out from most plants when cut or secreted by plants and animals. Shellac is a natural resin oozes out by insects living on trees.

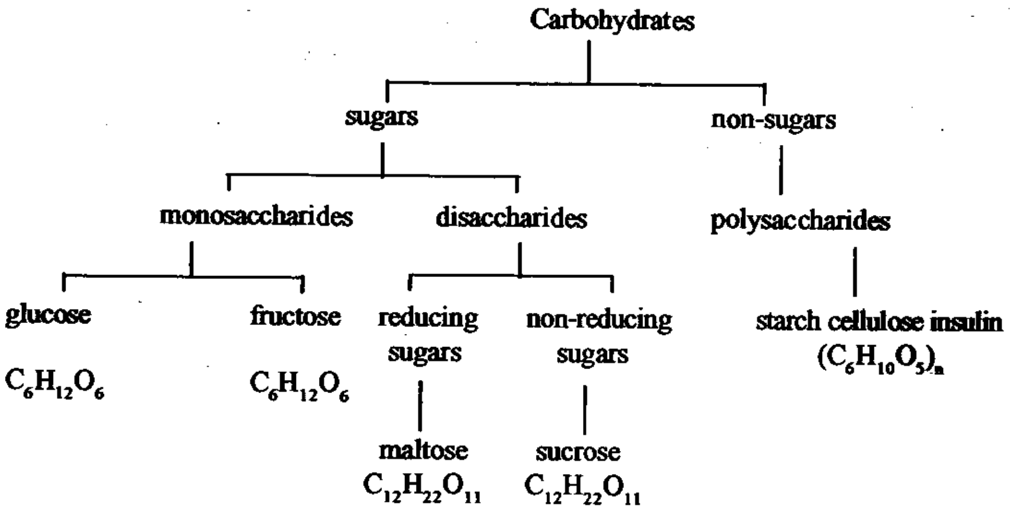
14.4 Natural Polymers

Polymer materials are widely found in living organisms where they play important structural and physiological roles. Carbohydrates and proteins belong to this class of natural polymers.

14.4.1 Carbohydrates

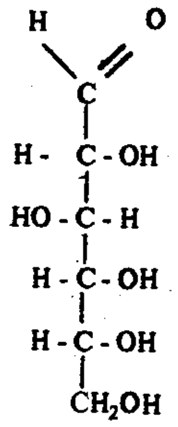
Carbohydrates are large groups of compounds with the molecular formula which can be written as $(C_x(H_2O)y$; such a formula does not, however, indicate the correct structural arrangement. All carbohydrates are composed of carbon, hydrogen and oxygen; among which includes sugars, starches and celluloses.

Carbohydrates can be classified as shown below

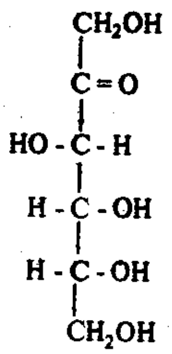


Sugars are crystalline substances with sweet taste and are soluble in water. They are generally classified into the monosaccharides and the disaccharides. Non-sugars are complex molecules with relatively larger molar mass than the simple sugars.

(i) **Monosaccharides:** These are carbohydrates containing six or less carbon atoms per molecule. Monosaccharide sugars cannot be hydrolysed into smaller sugar molecules, they are the simplest unit of carbohydrates. The two most important monosaccharide are glucose, which in an **aldose** (because it contains an aldehyde, -CHO group) and fructose, which is a **ketoses** (because it contains a keto, >C=O, group). They both have a molecular formula of $C_6H_{12}O_6$, but this represents many isomers.



glucose



fructose

(ii) **Disaccharides:** These are carbohydrates containing twelve carbon atoms per molecule and having the molecular formula $C_{12}H_{22}O_{11}$. They are formed by the elimination of water molecule from two C_6 monosaccharide molecules i.e. $2C_6H_{12}O_6 - H_2O = C_{12}H_{22}O_{11}$. When hydrolysed, disaccharides split into two C_6 monosaccharides. There are two classes of disaccharides, the reducing sugars and the non-reducing sugars. A reducing sugar is a disaccharide, which turns Fehling's solution from blue to red; while a non-reducing sugar has no effect on Fehling's solution. Sucrose (a non-reducing sugar) and maltose (a reducing sugar) are the most important disaccharide.

Sucrose, which is obtained from sugar cane, is a colourless crystalline solid with a sweet taste. The sugar which we use for our tea is sucrose. On hydrolysis with dilute acids, sucrose gives equal amounts of glucose and fructose.

$$\underset{\text{sucrose}}{C_6H_{11}O_5 - O - C_6H_{11}O_5} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

(iii) **Polysaccharides:** These are high molar mass polymers of monosaccharides. They are built up from many C_6 monosaccharides linked together in long-chains, with water molecule being eliminated between each pair of the C_6 molecules. Polysaccharides have a general formula

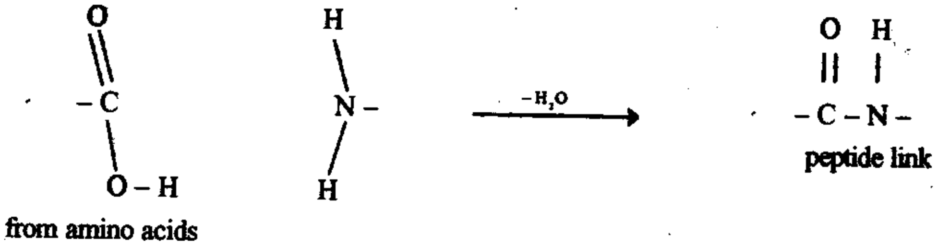
$$(C_6H_{10}O_5)_n \quad \text{i.e. } {}_nC_6H_{12}O_6 - {}_nH_2O$$

where n=very large number

Important polysaccharides include starch (n ≈ 330) and cellulose (n ≈ 600). On hydrolysis, the polysaccharides split up into disaccharides and/or monosaccharides. Starch occurs as white granules in almost all plants e.g. rice, maize, barley, wheat and potatoes. It is used hy plants as a reserve food supply and it provides a very important component of animal's diet as source of energy. Cellulose is the main constituent of the cell-walls of plants e.g. cotton, flax, jute, and is very widely distributed.

14.4.2 Proteins

Protein is a group of complex polymers which occurs very widely in all plants and animals. Typical examples of proteins are collagen (found in tissue and skin); keratin (found in hair, nails) and haemoglobin (oxygen carrier in blood). **Proteins are made up of amino acids joined by what are known as peptide links.** These are formed by the elimination of water molecule between the - COOH group of one acid and the -NH_2 group of an adjacent acid i.e.



Proteins are therefore polymers whose monomer is amino acids joined together by the peptide links.

(a) **Hydrolysis of proteins:** Although different proteins vary widely in physical properties and functions they can all be hydrolysed into a mixture of amino acids. The hydrolysis can be brought about by acids, alkalis or enzymes. About twenty different amino-acids have so far been isolated as products of protein hydrolysis. The protein, insulin, for example, yields sixteen different amino-acids on hydrolysis.

(b) **Uses of proteins in living systems:** Simple proteins like collagen, is the structural material in connective tissue, skin and cartilage; keratin as a structural material in skin, hair and nails; insulin as a hormone governing sugar metabolism; and haemoglobin as the oxygen carrier in blood. Some other proteins act as enzymes and as plant viruses.

14.5 Synthetic Polymers

Synthetic polymers are the man-made polymers, several of which has been mentioned in this unit. All the addition polymers listed in Table 14.1 are synthetic polymers. Several condensation polymers are also man-made, among which include polyesters (terylene) and polyamides (Nylon -6,6) - Table 14.2; synthetic rubber.

14.6 Conclusion

In this unit you have learned about polymers, as molecules made up of repeating structural units of monomers. You should have also learned that polymers can be natural or synthetic (man-made), all of which are made by either addition or condensation polymerisation process. You need to be aware of the importance of polymers to living organism and the device applications of polymers.

14.7 Summary

What you have learned in this unit concerns the sources, method of production, types and uses of natural and synthetic polymers. It has served to introduce you to this class of important compounds that is essential to us all.

14.8 Tutor–Marked Assignments

(a) Which of the following compounds can undergo addition polymerisation?
  (i) Propene
  (ii) Hexane
  (iii) Benzene
  (iv) Butadiene

(b) List ten different polymers and give the name and structures of the monomers.

(c) Define the following terms with suitable structural representation:
  (i) Polymerisation
  (ii) Disaccharide
  (iii) Peptide link

14.9 References

Bajah, S.T., Teibo, B.O., Onwu, G. and Obikwere, A. (2002). *Senior Secondary Chemistry - Textbook 3.* Lagos: Longman Publishers.

Unit 15

Environmental Impact of the Chemical Industry: Air and Water Pollution

15.0 Introduction

You must have learned a lot about chemical facts and their relevance to living organisms. Chemistry has affected our life so much that we do not want to imagine life without it. The story of chemistry is not entirely a happy one mainly because people have of recent became aware of the effects of chemical processes in our environment. Of particular concern is the pollution of the environment caused by human activity and specifically those arising from the chemical industry.

Water and air are two essential elements of our physical environment because they sustain life. Similarly water and air are sources of essential raw materials for the chemical industry. Water as a universal solvent for numerous chemical process; for cooling and cleaning purposes; as well as for hydroelectric power generation. Some industrial raw materials such as salt, magnesium, calcium etc. are obtained from sea water. Air on the other hand, is the main source of oxygen and nitrogen. Oxygen is used as combustion fuel while nitrogen is used in the manufacture of ammonia, trioxonitrate(v) acid fertilizers, etc.

Ironically, the same water and air are the recipient of all industrial wastes. Most of our wastes end up in the air or water. The chemical industry generates and discharges so much waste into the air and water that unless special care is taken the environment may be so polluted to the extent that our own lives could be in great danger. The quality of our air and water can deteriorate to the level that these essential elements of the environment may be sources of poison. This is the challenge currently facing our world in general and the chemical industry in particular.

15.1 Objectives

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

- Show the inter-relation between chemistry and the environment.
- Identify sources and effects of pollutants.
- Identify control measures for reducing the level of pollution.
- Explain the greenhouse effect and depletion of the ozone layer.
- Explain and identify biodegradable and non-biodegradable pollutants.

15.2 Water Pollution

Pure and drinkable water is normally an odourless, tasteless and colourless liquid. Water is used as a universal solvent for several purposes and discharged back into the environment.

- Can you imagine life without water?

The water used for any human activity is never returned the same, to its source. Used water contained dissolved or suspended foreign materials which are responsible for water pollution. The sources and nature of water pollutants are numerous but we shall discuss a few of them.

15.2.1 Phosphates

The detergent industry responsible for producing various cleaning agent is a large and essential industry. Everybody and all industries do one form of cleaning or the other, and only detergents have the characteristics for removing all types of stains. Phosphates are widely incorporated into detergents and hence are released in large quantities through water into rivers and lakes. Most fertilizers contain phosphates which are washed into rivers, lakes and underground water, when not utilised by plants.

Phosphates in rivers and lakes act as nutrients for the growth of algae and other water weeds. This reduces the oxygen level in the waters and prevent other living organisms in water e.g. fish from getting adequate supply of oxygen. The weeds also cover the surface of waters and hinder sufficient light, required for plant photosynthesis, from getting down the waters, and hence reduced food production.

15.2.2 Industrial discharges

Several industries dump their liquid and solid chemical wastes into rivers and streams. Depending on the type of industry; the chemical wastes may contain benzene, acetone, trichloromethane, tetra-chloromethane, phenols, acids, alkalis etc. These chemicals constitute pollutants to water bodies and are hazardous to organisms that live in water and other living things that get in contact with such waters.

15.2.3 Pesticides

Increased food production has been achieved by the use of pesticides, which help control the damaging effects of pests to crops. Several of these pesticides e.g. DDT, which are toxic, end up in rivers and lakes. Mercury containing pesticides have been used over the years, and mercury which is toxic, easily concentrates in fish. When such fish is consumed, they can lead to mercury-poisoning.

15.2.4 Hot Water

Water is used as a coolant for machineries in several industries and the discharge of the hot water, which may seem harmless, can be source of pollution. Hot water raise the temperature of river water which may harm fish and also increase the growth of algae and other water weeds. The consequences of increased microbial growth in river water is as stated in Section 15.2.1

15.3 Air Pollution

Industrialization has caused an increase in the level of pollutants into the air and may be present in concentrations that can harm the environment and its inhabitants. The main cause of air pollution is the combustion of fossil fuels such as coal, petrol and gases, by power plants and vehicles to obtain energy. The main air pollutants are discussed below.

15.3.1 Solid particles

Industrial processes such as coal burning, can lead to the emission of smoke, soot and dust which are discharged into the atmosphere. These pollutants when inhaled can damage the respiratory system particularly the lungs. Sometimes, the pollutants became trapped just above the earth's surface leading to the formation of smog, particularly over cities with high industrial emissions. Another toxic solid pollutant found in the atmosphere is lead emitted from the exhaust of motor vehicles using leaded petrol. Lead dust can cause lead poisoning and injury to the nervous system.

15.3.2 Oxides of carbon

Incomplete combustion of fuel lead to the formation of carbon (II) oxide (CO) which is a poisonous gas. With modernization and increase wealth, the use of motor vehicles has increased. Motor vehicles are the largest single source of carbon (II) oxide emission. When inhaled, carbon (II) oxide competes with oxygen for the haemoglobin in blood. This can lead to reduction in blood oxygen. Carbon (II) oxide gas causes dizziness, headaches, fatigue and can course death at high concentrations.

Carbon(iv) oxide (CO_2) is the principal product of the combustion of fossil fuel. The increase in the use of fossil fuels as source of energy has given rise to the excessive production of the gas. Plants use carbon(iv) oxide for photosynthesis. The combined effect of deforestation and excessive combustion of fossil fuels has led to the increase in the level of atmospheric carbon (iv) oxide. The consequence of an increase in the level of carbon(iv) oxide is a greater retention of infrared ray in the earth, giving rise to the **green house effect** - a gradual warming of our planet. This occurrence will lead to the melting of the ice in the polar regions of the earth and many costal regions and islands on earth will then be submerged by the increase in ocean water level.

15.3.3 Oxides of nitrogen and sulphur

When sulphur-containing coal is burnt in electric power stations and industrial plants, sulphur(iv) oxide is produced. This oxide of sulphur is acidic, corrosive and poisonous. Similarly, in the combustion of fuels at high temperatures, oxides of nitrogen e.g. NO and NO_2, are produced.

The oxides of sulphur and nitrogen released into the atmosphere combine with rain-water to produce acids — the so-called acid rain. When acid rain falls it harms plant and animal life, building and metal structures. In addition, oxides of sulphur and nitrogen cause irritation of the eyes, nose, throat and respiratory tissues.

15.3.4 Hydrocarbons

Hydrocarbons such as methane, ethane, propane, butane, etc., which are constituents of fuels are released into the air through evaporation from storage tanks. These hydrocarbons are believed to cause cancer i.e. they are carcinogenic. The hydrocarbons are also known to react with oxides of nitrogen in the presence of light to produce smog or heavily stagnant air. Hydrocarbons are known to retard the growth of plants and cause abnormal leaf and bud development.

15.3.5 Chlorofluorocarbons

Chlorofluorocarbons or CFCs are man-made chemicals e.g. freon, which are used as propellants for spray cans like sheltox, coolants in refrigerators and air-conditioners, and for making plastic forms. When these chemicals are released into the atmosphere, ultra-violet light breaks off free chlorine atoms, Cl, from the CFC molecule. The free chlorine atom which is very reactive, attacks a molecule of ozone, O_3, to produce an ordinary oxygen molecule and other reactive species. The reaction is a chain reaction and the process is repeated numerous times. This causes a depletion or reduction in the ozone layer, which protects us on earth from harmful radiations released in the atmosphere.

The ozone layer is found in the stratosphere. Studies from satellites show a definite reduction in the ozone levels and revealed an 'ozone hole' (area without ozone protection) over the Antartic. The effect of diminished ozone layer protection means an increase in the level of ultra-violet radiation that reaches earth. These radiations are known to cause cataracts (eye disease), skin cancer and sunburns.

15.4 Biodegradable and Non-biodegradable Pollutants

The discharge of pollutants in the environment is an undesirable effect of industrial revolution. Many harmful chemical wastes from detergents, crude oil spill, insecticides and mercury compounds are non-biodegradable, i.e. they cannot be broken down into harmless compounds by living organisms. They remain in the environment and harm its inhabitant. For example, mercury accumulates in the body of aquatic organisms e.g. fish, which when eaten can eventually lead to mercury poisoning.

Some chemical pollutants are however biodegradable and are converted into harmless substances e.g. fertilizers by living organisms in the environment. Sometimes harmful effluents are treated in sewage plants to convert them to useful chemicals utilizable for other purposes or before discharge into the environment.

15.5 Pollution Control

(a) Legislations have been enacted in several countries to control the level of pollutant discharged into the air and water bodies. Agencies like FEPA have been established to monitor compliance with the legislations.
(b) The use of unleaded petrol is encouraged to reduce emission of lead compounds.
(c) Industrial effluents and emissions are treated to convert them to harmless biodegradable substances before being discharged.
(d) The combustion of fuels are now more efficiently done, to reduce carbon(II) oxide emission, by proper tuning of and the use of catalytic converters in engines.
(e) The emission of oxides of sulphur can be reduced by using sulphur-free crude oil or low-sulphur coal as fuel.
(f) Aforestation programmes are now seriously encouraged in several countries.
(g) The ban on the use of CFCs as refrigerants and propellants has been ratified by several countries.
(h) Education is an important anti-pollution measure, so that each of us is aware of the consequences of polluting our environment.

15.6 Conclusion

In this unit you have learned a number of important issues that relate to the effects of the chemical industries in the environment. You should have learned about the sources and nature of chemicals that lead to pollution in water bodies and the air. Furthermore, you should have learned about the control measures aimed at reducing the level of pollution and saving our environment from danger.

15.7 Summary

What you have learned in this unit concerns the effect of water and air pollution on our environment. The pollution which is as a result of harmful substances, discharged from our chemical industries and combustion of fossil fuels, can cause serious harm to human, animal and plant life, and property. It has served to expose you to the hazards of industrialization and the control measures necessary to avert damage to our precious environment.

15.8 Tutor-Marked Assignments

(a) What are the main pollutants in
  (i) air;
  (ii) water?
(b) Explain the green house effect and the depletion of the ozone layer.
(c) Enumerate six control measures aimed at reducing the level of pollution.

15.9 References

Bajah, S.T., Teibo, B.O., Onwu, G. and Obikwere, A. (2002). *Senior Secondary Chemistry Textbook 3.* Lagos: Longman Publishers.

Osei Yaw Ababio.(2002). *New School Chemistry.* Onitsha: African-Fep Publishers.

NATIONAL OPEN UNIVERSITY OF NIGERIA

Form QST1

Questionnaire

Dear Student,

While studying the units of this course, you may have found certain portions of the text difficult to comprehend. We wish to know your difficulties and suggestions, in order to improve the course. Therefore, we request you to fill out and send us the following questionnaire, which pertains to this course. If you find the space provided insufficient, kindly use additional sheet.

Course Code: ____________ Course Title: ______________________________

1. How many hours did you need for studying each of these units?

Unit	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
No. of hours															
Unit	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
No. of hours															

2. Which of these units do you find most difficult to understand?

3. Please give specific problem you find difficult with the unit.

____

____

____

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4. How would you like the unit improved?

____

____

____

Please Mail to
The Course Coordinator...............THROUGH the Study Centre Manager
National Open University of Nigeria
Victoria Island,
Lagos.

NATIONAL OPEN UNIVERSITY OF NIGERIA

Form QST2
Questionnaire

In the questions below, we ask you to reflect on your experience of the course as a whole.

1 Course Code and Title..

2 Mother tongue ....

3 I am registered for a .... **Degree/Programme**

4 Why did I choose to take this course? ....

5 Which study unit did I enjoy the most and why?...

6 Which study unit did I enjoy the least and why?...

7 Was the course material easy to understand or difficult?......................................

8 Which particular topic do I understand better than before and how?.........................
....

9 Does the course have any practical applications in the real world, e.g. for the work I currently do?...YES/NO? EXPLAIN..
....

10 What aspects would I like to know more about or study further?...........................

11 How could the course be improved?...

12 Other comments about the course (*Please Tick*)..

Items	**Excellent**	**Very Good**	**Good**	**Poor**	Give specific examples, if poor
Presentation Quality					
Language and Style					
Illustrations Used (diagrams, tables, etc.)					
Conceptual Clarity					
Self Assessment Questions					
Facilitators response to TMA Questions					

In the questions below, we ask you to reflect on your experience of the course as a whole