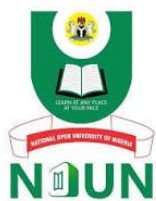


COURSE GUIDE

SED222 GENERAL CHEMISTRY FOR INTEGRATED SCIENCE II

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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 "General Chemistry for Integrated Science II" 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.

Learning Outcomes-Aims and Objectives

The broad aims of this foundation chemistry course can be summarized thus. The course aims to provide you with chemistry content that will be sufficient for you in the integrated science program. 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 everyday living.
- 3) Apply the language of chemistry in describing the world around you.
- 4) Carry out simple chemical calculations.

**MAIN
COURSE**

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MODULE 1

- Unit 1 Introduction to Organic Chemistry and Classification of Organic Molecules
- Unit 2 The Homologous Series, Functional Groups and Isomerism
- Unit 3 IUPAC Nomenclature of Organic Compounds
- Unit 4 Purification Methods and the Determination of Empirical, Molecular and Structural Formula of Organic Compounds
- Unit 5 The Chemistry of Alkanes

UNIT 1 INTRODUCTION TO ORGANIC CHEMISTRY AND CLASSIFICATION OF ORGANIC MOLECULES

Unit Structure

- 1.1 Introduction
- 1.2 Learning Outcomes
- 1.3 Introduction to Organic Chemistry
 - 1.3.1 Meaning and scope of organic chemistry
 - 1.3.2 Uniqueness of carbon atom
 - 1.3.3 Representation of organic molecules
- 1.4 Classification of organic compounds
 - 1.4.1 Open-chain or aliphatic compounds
 - 1.4.2 Saturated and unsaturated compounds
 - 1.4.3 Aromatic compounds
 - 1.4.4 Alicyclic compounds
 - 1.4.5 Heterocyclic compound
- 1.5 Summary
- 1.6 References/Further Reading/Web Resources
- 1.7 Possible Answers to Self- Assessment Exercise(s) within the Contents



1.1 Introduction

You are welcome to Unit 1 of this module. You should have read through the Course Guide on Organic Chemistry and acquainted yourself with expectations from the course. Can you recall the **elements that make up organic chemistry**? If you have read through the Course Guide, you will have noticed that organic chemistry is essentially the chemistry of carbon and its compounds. However, if this was not apparent from the Course Guide, this unit focuses on the meaning and scope of organic chemistry. It also discusses the representation and classification of organic

compounds. Other elements that may be contained in organic compounds are highlighted in the unit. I enjoin you to pay rapt attention to the sub-topics discussed in the unit and endeavour to make maximum benefit from the subject- matter.



1.2 Learning Outcomes

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

- define organic chemistry
- state the distinct nature of organic chemistry.
- discuss the uniqueness of carbon as a building block for organic compounds.



1.3 Introduction to Organic Chemistry

In this section, we shall be concerned with the meaning and scope of organic chemistry. The major families of organic compounds, their characteristics, properties and uses. You shall as well appreciate the vastness of the compounds that make up organic chemistry.

1.3.1 Meaning and Scope of Organic Chemistry

Organic chemistry is a very important discipline. It entails the study of carbon and its 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. Can you recall the meaning of organic manure? They are those manures that are derived from plant and animal materials. Over time, the study of organic chemistry has expanded to include other compounds other than the ones derived from plants and animals which have no direct relation to living matter. They however, excludes the oxides, hydroxides, trioxo-carbonate (IV), hydrogen trioxo-carbonate (IV) salts of carbon and the carbides. Which of these is not an organic compound: CH_4 , CO_2 , C_5H_{12} ? Oxides are excluded from organic compounds, therefore, CO_2 is the answer. Organic compounds are essential for the sustenance of life e.g. carbohydrates, proteins, fats and oils etc. Modern civilization consumes vast quantities of organic compounds. Coal, petroleum, and natural gas are primary sources of carbon compounds for use in production of energy. They are the starting materials for the preparation of plastics, synthetic fibers, dyes, pesticides, fertilizers, detergents, rubbers, paints, medicines and drugs, perfumes and flavours.

1.3.2 Uniqueness of Carbon Atom

At this point, our concern should be why a vast number of compounds owe their origin to carbon? In other words, why is it that the known compounds of carbon are much more numerous than the known compounds of all the other 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 bonds
- 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. I .1)

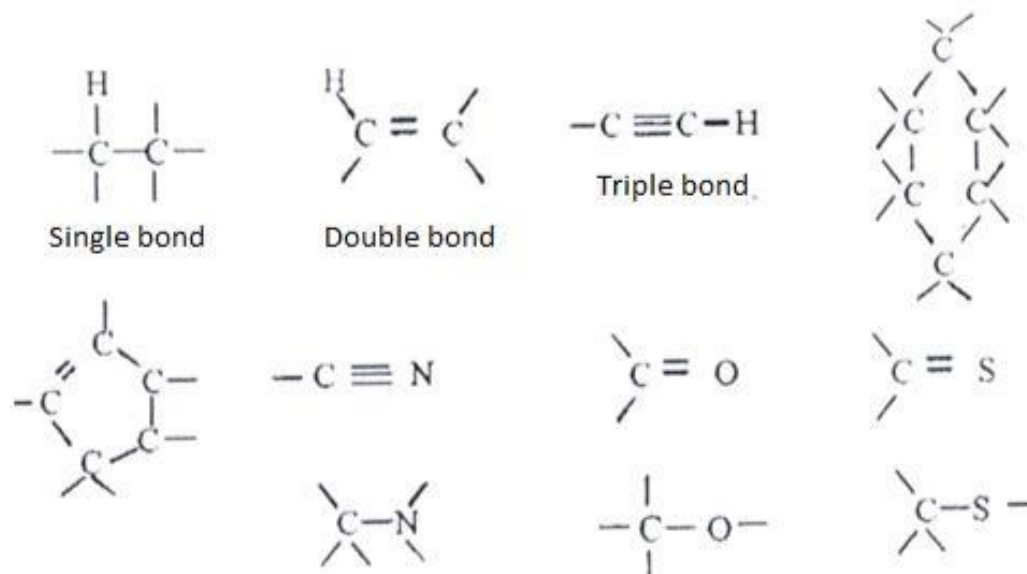


Fig. 1:1 Types of covalent bonds formed by carbon

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).

Self-Assessment Exercise 1

- 1) Define catenation.
- 2) List the four features that make carbon unique in its bond forming ability.

1.3.3 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. How do we represent double or triple bond? This occurs whenever such bond exists between two carbon atoms, not at the end or beginning of a carbon atom. See figures 1.3 ii and iii, below. 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.

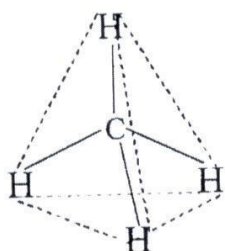
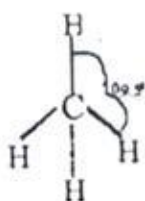
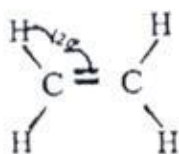


Fig. 1.2 Three-dimensional structure of the molecule CH_4

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 120° . 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 180° .



(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

formular $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{H} \\ | \\ \text{H} \end{array}$ 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.

1.4 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.

1.4.1 Open-Chain or Aliphatic Compounds

Open chains are linear. They are not closed or cyclic. Aliphatic compounds contain chains of interlinked carbon atoms (may involve other elements). The chains length varies over a wide range of carbon atoms starting from simplest with one carbon atom C to infinity, all of them being carbon to carbon chains e.g. -C-C-C-C-C- Pentane, C_5H_{12} Propane is an open chain hydrocarbon containing 3 carbon atoms. Can you sketch the structure ?

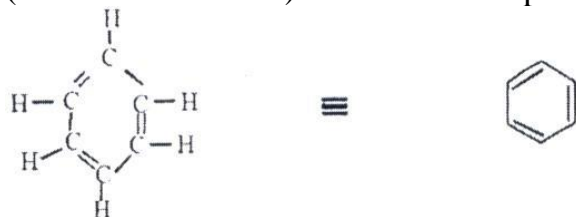
1.4.2 Saturated and unsaturated compounds

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. From structure of alkyne above, how many bonds are represented around each carbon atom? Four of course, since carbon atom shows valency of four (tetravalent).

1.4.3 Aromatic Compound

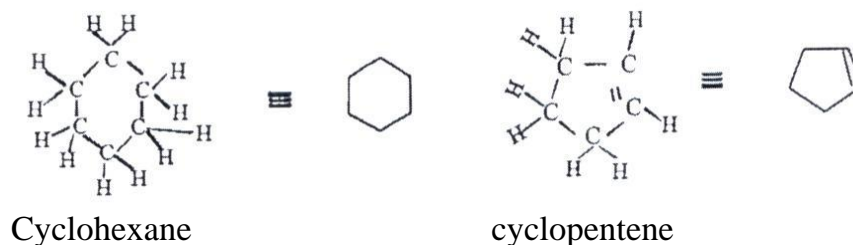
Recall that the opposite of open is closed. Aliphatic compounds have open structure while aromatic compounds have closed or cyclic structure. Aromatic compounds have cyclic structure as opposed to linear. They are carbocyclic compounds endowed with what is referred to as aromatic character i.e. they contain rings of carbon atoms, based on benzene C_6H_6 ; (Unit 2 of Module 2) 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 . In aromatic compounds such as benzene, there are alternating single and double bonds.

1.4.4 Alicyclic Compound

Refer to structure of benzene in 1.4.3, compare it with cyclohexane in 1.4.4. which has alternating double and single bonds?. Alicyclic compounds 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.



1.4.5 Heterocyclic compounds

These are cyclic compounds containing elements other than carbon and hydrogen, particularly oxygen, nitrogen or sulphur in the ring e.g.

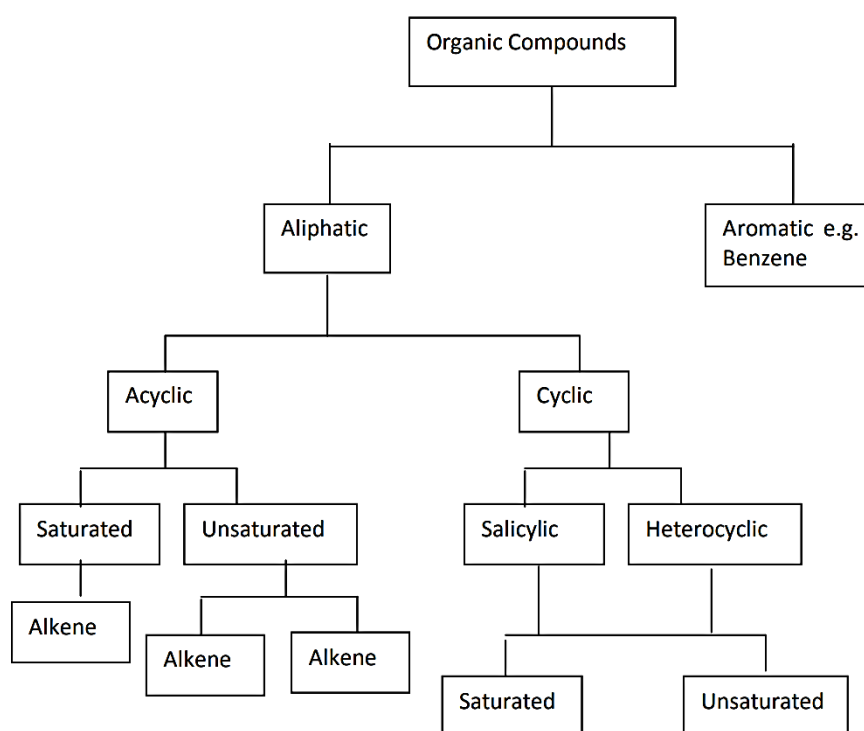
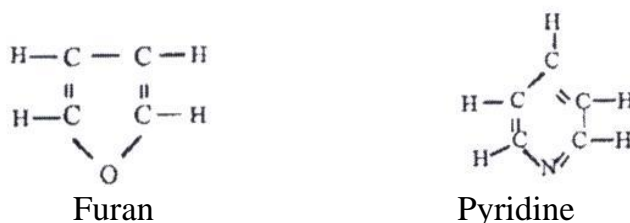


Fig. 1.4: Classification of organic compounds

Self-Assessment Exercise 2

Briefly explain the feature that enables carbon atoms to form vast amount of organic compounds.

**1.5 Summary**

In this unit, organic chemistry is described as the study of carbon compounds. These compounds are abundant in nature and they play important roles in our life. 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. 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 of ring forms. The vast numbers of carbon compounds makes it necessary to classify them into groups of compounds with similar characteristic for easy comprehension. The classification of these compounds shall form the frame work for our discussion in subsequent unit.

**1.6 References/Further Reading/Web Resources**

Ababio, O.Y. (2013). *New School Chemistry for Senior Secondary Schools*. Onitsha: Africana First Publishers Limited

Brown, G.A. (1978). *An Introduction to Organic Chemistry*. Lagos: Longman Publishers.



1.7 Possible Answers to Self- Assessment Exercise(s) within the Contents

Self-Assessment Exercise 1

Answers

- 1) Catenation is the ability of carbon to form long chains or rings of carbon atoms bonded to one another.
- 2) Four Features that make carbon unique in its bond forming ability:
 - i. A variety of strong covalent carbon – carbon bond
 - ii. Ability to exhibit catenation
 - iii. Ability to form strong covalent bond with other elements
 - iv. Ability to form multiple bonds (ie double and triple) with another carbon atom or other elements

Self-Assessment Exercise 2

Answers

The feature that enable carbon atoms to form vast amount of organic compounds:

1. The ability of carbon atoms to covalently bond with other carbon atoms and other elements in chains or ring forms enables the formation of vast amount of organic compounds (catenation),
2. Formation of multiple bonds,
3. Formation of infinite open and branched chains of carbon compounds.
4. Formation of cyclic and heterocyclic compounds.

UNIT 2 THE HOMOLOGOUS SERIES, FUNCTIONAL GROUPS AND ISOMERISM

Unit Structure

- 2.1 Introduction
- 2.2 Learning Outcomes
- 2.3 The Homologous Series
- 2.4 Functional Groups
- 2.5 Isomerism
 - 2.5.1 Structural isomerism
 - 2.5.2 Geometric isomerism
- 2.6 Summary
- 2.7 References/Further Reading/Web Resources
- 2.8 Possible Answers to Self- Assessment Exercise(s) within the Contents



2.1 INTRODUCTION

You have been introduced to organic chemistry in Unit 1. You have also learnt that organic compounds are numerous. To simplify its study, organic compounds are studied in families, not as individual compounds. This brings about the terms homologous series, functional groups and isomerism. These are umbrella terms (like surnames), that help in the understanding of families of organic compounds despite their vast nature. For instance, in every human family, the SURNAME runs through every member of the family while FIRST names are unique but takes bearing from the surname. Can you recall how many members of your family and even extended family that share the same surname with you?



2.2 LEARNING OUTCOMES

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

- explain the terms homologous series, functional groups and isomerism.
- list the characteristics of a homologous series,
- draw the structural representation of simple organic compounds indicating functional groups.
- draw and name the structural isomers of hydrocarbon compounds having a maximum of five carbon atoms.
- distinguish between structural and geometrical isomerism.



2.3 The Homologous Series

You may liken homologous series to the surname shared by all members of your family. It reflects certain peculiarities shared by members of a family. In organic chemistry, it was observed that certain set of compounds show structural, physical and chemical similarities and are thus, 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. All members of homologous series have the following characteristics:

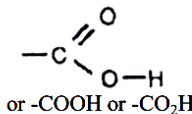
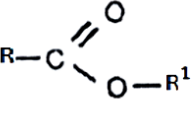
- (i) they can be prepared by similar methods;
- (ii) they have similar chemical properties;
- (iii) there is a regular gradation of physical properties (melting or boiling points, solubility);
- (iv) they can be represented by a general formula e.g. $\text{C}_n\text{H}_{2n+2}$ for alkanes; C_nH_{2n} for alkenes, $\text{C}_n\text{H}_{2n-2}$ for alkynes, $\text{C}_n\text{H}_{2n+1}\text{OH}$ for alkanols, $\text{C}_n\text{H}_{2n+1}\text{COOH}$ for alkanolic acids;
- (v) each member differs in molecular formula from the preceding compound by $-\text{CH}_2-$ (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. $\text{C}=\text{C}$ for alkene, $\text{C}\equiv\text{C}$ for alkynes, $-\text{OH}$ for alkanols, $-\text{COOH}$ for alkanolic acid.

These characteristics are very essential for the understanding of organic chemistry and will be encountered throughout your study of organic chemistry. Can you distinguish between general molecular formulae of alkanes and alkynes? You may refer to item (iv), above.

2.4 Functional Groups

Recall that one of the characteristics of a homologous series you learned in Section 2.3 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 an atom, group of atoms (radical) or a bond common to a homologous series in an organic compound which controls the classification and reactivity of the molecules (Ababio, 2013). The study of organic chemistry becomes simplified when examined according to their functional groups. Can you recall the functional group of alkenes, alkynes and alkanols? You may wish to refer to item (vi) in section 2.3 above. 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	-aie		ethene
Alkynes	-C≡ bond	-yne		ethyne
Alkanols (alcohols)	-O-H	-al	R-OH	ethanol
Alkanoic acids (carboxylic acids)	 or -COOH or -CO ₂ H	-oic acid	R-COOH	ethanoic acid
Alkanoates (esters)		-oates	R-OO ₃ H ¹	ethyl ethanoate
Alkanamine (Amine)	-NH ₂	-amine	R-NH ₂	ethanamine

Note: An 'R' in organic chemistry represents an alkyl group or radical which is an alkane less one hydrogen atom. For instance: from methane CH₄, we get methyl -CH₃

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 with emphasis put on the characteristics of individual functional groups. Once these characteristics 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 and interesting despite its vast nature.

Self-Assessment Exercise 1

1. Write the structure of the first 10 members of the alkane homologous series
2. Draw the structural formula of 2-methylbut-2-ene

2.5 Isomerism

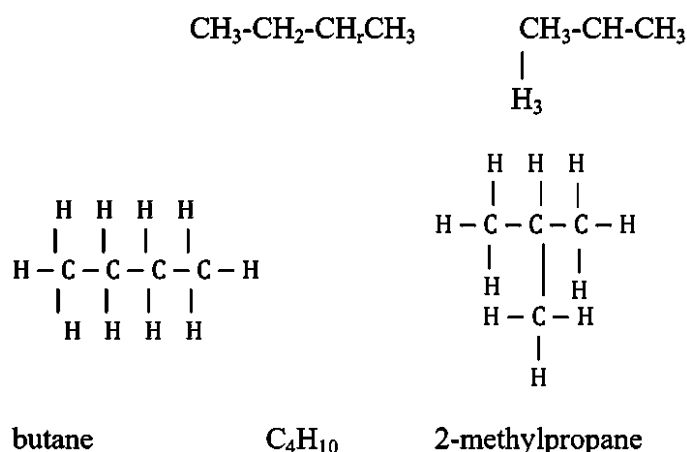
This is the term used to describe the existence of two or more organic compounds with the same molecular formula, but different structural formulae. Isomerism is the existence of organic compounds having the same number and kind of atoms but showing differing characteristics due to the differences in the way the atoms are arranged within the molecules. The different forms of the compounds are called isomers and have different chemical and physical properties.

Look at the palms of your hands. Your left and right palms contain the same features but arranged differently; they are isomers of one each other. Look closely at the toes on your right and left feet. Are they arranged similarly or differently? Are their numbers the same or different? 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. Stereoisomerism is also known as Geometric isomerism.

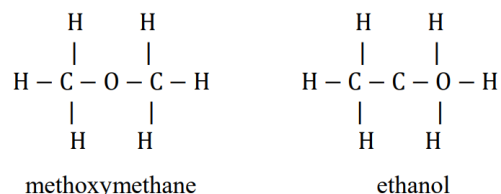
2.5.1 Structural Isomerism

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.



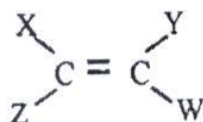
Consider the words Ronald, Roland, Arnold, they contain the same numbers of the same letters written in such a way to give different words - structural isomers. Can you identify similar words depicting structural isomers? Once you can do that successfully well, you may have no problem identifying structural isomers from given organic compounds.

The isomers are all separate, distinct compounds and even the names may be different. They contain the same functional group and are members of the same homologous series e.g. C₄H₁₀. 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. CH₃-O-CH₃ and C₂H₅OH named, methoxymethane or dimethyl ether and ethanol respectively.



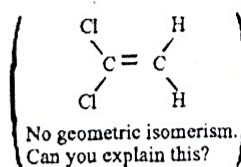
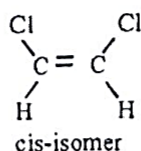
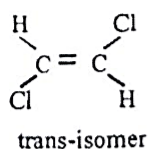
2.5.2 Geometric isomerism

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 that link in permanent positions.

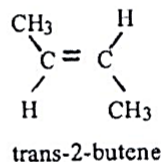
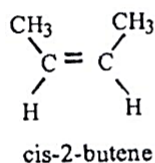


Generally, all alkenes that have two different groups attached to each carbon atom containing the double bond may show geometric isomerism. Two arrangements are possible; an isomer in which similar groups are on the same side of the double bond (it is called cis-isomer from the latin word 'same') and 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.

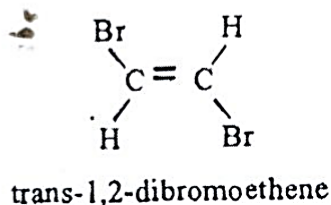
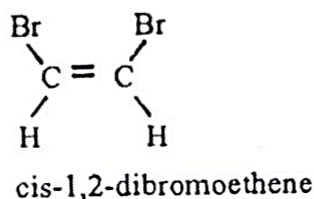
1. $\text{C}_2\text{H}_2\text{Cl}_2$



2. C_4H_8



3. $\text{C}_2\text{H}_2\text{Br}_2$



SELF-ASSESSMENT EXERCISE 2

- 1) Write the molecular formulae of all structural isomers of the compound C_5H_{12}
- 2) Draw the structural formulae of the following compounds: methane, ethane and propane.

**2.6 Summary**

This unit discussed the terms homologous series, functional groups and isomerism as they relate to the study of organic compounds. Homologous series and functional groups are described as two important terms used in organic chemistry to explain the arrangement of organic compounds into a number of chemically similar groups or families. The homologous series is highlighted as a 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. You have also learnt 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. Isomerism deals with organic compounds having the same number and kind of atoms but structurally different and hence show different characteristics.

**2.7 References/Further Reading/Web Resources**

- Ababio, O.Y. (2013). *New School Chemistry for Senior Secondary Schools*. Onitsha: Africana First Publishers Limited
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2.8 Possible Answers to Self- Assessment Exercise(s) within the Contents

Self- Assessment Exercise 1

Answers			
1) The structure of the first 10 members of the alkane homologous series:			
Name	Molecular Formula	Structural Formula	Condensed Structural Formula
Methane	CH ₄	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	CH ₄
Ethane	C ₂ H ₆	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	H ₃ C-CH ₃
Propane	C ₃ H ₈	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	H ₃ C-CH ₂ -CH ₃
Butane	C ₄ H ₁₀	$\begin{array}{c} \text{HHHH} \\ \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	H ₃ C-CH ₂ -CH ₂ -CH ₃ or H ₃ C(CH ₂) ₂ CH ₃
Pentane	C ₅ H ₁₂	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	H ₃ C-CH ₂ -CH ₂ -CH ₂ -CH ₃ Or H ₃ C(CH ₂) ₃ CH ₃
Hexane	C ₆ H ₁₄	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	H ₃ C-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃ or H ₃ C(CH ₂) ₄ CH ₃

Heptane	C_7H_{16}	$ \begin{array}{cccccccc} & H & H & H & H & H & H & H \\ H & C & C & C & C & C & C & C & H \\ & H & H & H & H & H & H & H \end{array} $	$CH_3(CH_2)_5CH_3$
Octane	C_8H_{18}	$ \begin{array}{ccccccccccc} & H & H & H & H & H & H & H & H & H \\ H & C & C & C & C & C & C & C & C & H \\ & H & H & H & H & H & H & H & H \end{array} $	$CH_3(CH_2)_6CH_3$
Nonane	C_9H_{20}	$ \begin{array}{ccccccccccc} & H & H & H & H & H & H & H & H & H & H \\ H & C & C & C & C & C & C & C & C & C & H \\ & H & H & H & H & H & H & H & H & H \end{array} $	$CH_3(CH_2)_7CH_3$
Decane	$C_{10}H_{22}$	$ \begin{array}{ccccccccccc} & H & H & H & H & H & H & H & H & H & H \\ H & C & C & C & C & C & C & C & C & C & H \\ & H & H & H & H & H & H & H & H & H \end{array} $	$CH_3(CH_2)_8CH_3$

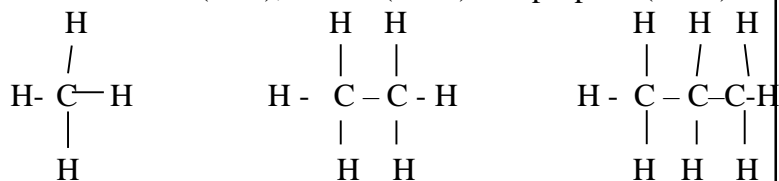
(2). 2-methylbut-2-ene: $Me-CHMe=CHMe$ where $Me = CH_3$

Self-Assessment Exercise 2

Possible structural isomers of pentane C_5H_{12} are:

- 2- methylbutane
- 2,2-dimethylpropane

2) Structural formula of methane (CH_4), ethane (C_2H_6) and propane (C_3H_8)



UNIT 3 IUPAC NOMECLATURE OF ORGANIC COMPOUNDS

Unit Structure

- 3.1 Introduction
- 3.2 Learning Outcomes
- 3.3 Nomenclature of organic compounds
 - 3.3.1 The hydrocarbons -
 - 3.3.2 Rules for IUPAC nomenclature
- 3.4 Naming non-hydrocarbon compounds
- 3.5 Summary
- 3.6 References/ Further Reading
- 3.7 Possible Answers to Self- Assessment Exercise(s) within the Contents (SAEs)



3.1 Introduction

Remember that Unit 1 focused on organic chemistry and the abundance and relevance of organic compounds in nature. Recall that the numbers 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. A brief outline is therefore given in this unit and extended throughout the subsequent units of the new system (or rule) for naming organic compounds which is now widely accepted and in accordance with the IUPAC system of nomenclature. (IUPAC = International Union of Pure and Applied Chemistry).



3.2 Learning Outcomes

By 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
- deduce the IUPAC names of given organic compounds.



3.3 Nomenclature of Organic Compounds

Different classes of hydrocarbons, namely alkanes, alkenes and alkynes are discussed. Rules for IUPAC nomenclature are highlighted. At the onset of organic chemistry, the trivial names of organic compounds are based on the source from which the compound was derived, for instance we have:

<i>Trivial Name</i>	<i>Source</i>
Urea	Urine
Citric acid	Citrus fruit

The full set of rules as applied in naming simple organic compounds are discussed hereunder.

3.3.1 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. Can you classify these families based on their level of saturation? Alkanes are saturated hydrocarbons while alkenes and alkynes are unsaturated hydrocarbons. Examples of these classes of 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 organic 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 number of carbon atoms involved. (Table 3.1) *Meth-*, *Eth-*, *Prop-* and *But-* prefixes are for the first four members having 1, 2, 3 and 4 carbon atoms respectively.

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

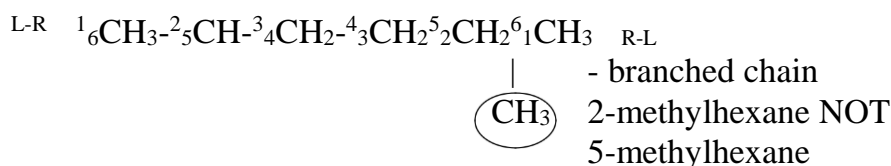
IUPAC NAME	Formula C.H _{2n3}	Alkyl group	Formula
Methane	CH ₄	Methyl	CH ₃
Ethane	C ₂ H ₆	Ethyl	C ₂ H ₅
Propane	C ₃ H ₈	Propyl	C ₃ H ₇
Butane	C ₄ H ₁₀	Butyl	C ₄ H ₉
Pentane	C ₅ H ₁₂	Pentyl	C ₅ H ₁₁
Hexane	C ₆ H ₁₄		
Heptane	C ₇ H ₁₆		
Octane	C ₈ H ₁₈		
Nonane	C ₉ H ₂₀		
Decane	C ₁₀ H ₂₂		

Self-Assessment Exercise 1

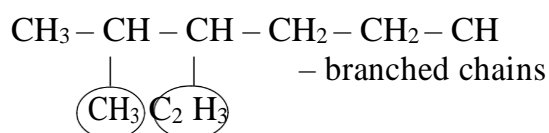
Complete the blank spaces in Table 3.1 following the trend shown for the first five members of the alkane series.

In alkanes with branched (groups not one of the longest chain of carbon) chains the IUPAC name is based on the number of carbon atoms in the longest chain. This longest carbon chain is then numbered from left to right and right to left. The preferred direction of numbering is that one that assigns the least set of number(s) to the carbon atom(s) bearing the branch (substituent group) or functional group as the case may be. In this way, the position of the branched chains can be indicated.

In other words, 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:



When two or more branched chains are present they are listed alphabetically. For example:



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.



Table 3.2- IUPAC nomenclature of simple alkenes

<i>IUPAC Name</i>	<i>Formula C,H</i>	<i>Alkenyl Group</i>	<i>Formula C/I</i>
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-

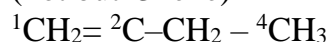
Self-Assessment Exercise 2

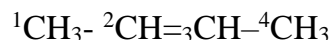
Complete the blank spaces in Table 3.2 using the guide from Table 3.1.

The positions of the double bond and of any branched chains are shown by numbering the longest straight chain of carbon atoms, as we did in alkanes. Thus,



but-1-ene
(not but-3-ene)



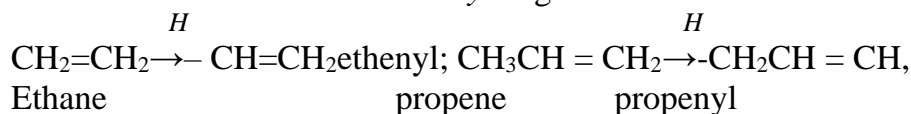
$$\begin{array}{c} | \\ CH_3 \\ \text{2-methylbut-1-ene} \\ \text{(not 3-methylpent-3-ene)} \\ \text{(not 2-ethylbut-2-ene)} \end{array}$$


but-2-ene



$$\begin{array}{c} | \\ CH_3 \\ \text{3-methylpent-2-ene} \\ \text{(not 3-methylpent-3-ene)} \\ \text{(not 2-ethylbut-2-ene)} \end{array}$$

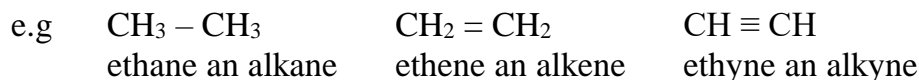
The hydrocarbon residue formed by the removal of one hydrogen atom from an alkene is called an *alkenyl*. e.g.

**SELF-ASSESSMENT EXERCISE 3**

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.

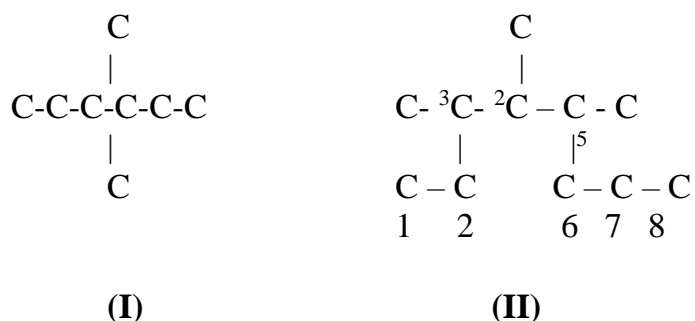
**3.3.2 Rules for IUPAC Nomenclature****(a) Introduction**

You have been introduced in Section 3.3.1 to the nomenclature of hydrocarbons before being 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 parent chain are referred to as side chains or substituents or branch chain. Thus, if the parent chain contains six carbon atoms, the parent hydrocarbon is hexane (structure I)

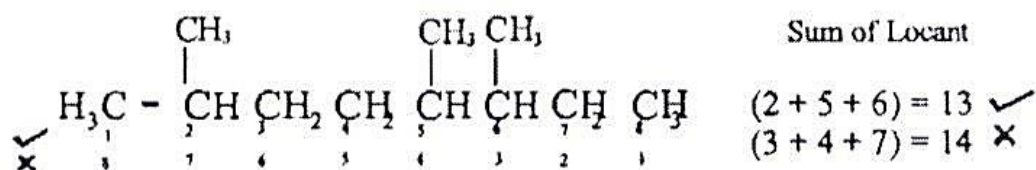


In structure (II), the straight chain contains only five carbon atoms whereas the longest continuous chain of carbon atoms contains eight carbon atoms and hence it is an octane chain. Straight chain is not the same as continuous chain so what is important is the longest continuous carbon atoms and not the straightness or zig-zag nature of the chain.

It is possible that sometimes there may be two carbon chains 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.

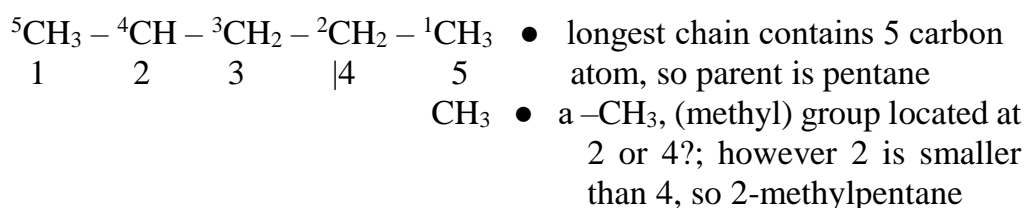
- (ii) The second step is to number (Arabic numerals 1,2,3,, ..etc) the longest continuous chain from one end to the other in such a manner that the carbon atom carrying substituents get the lowest numbers.

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 substituents 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).



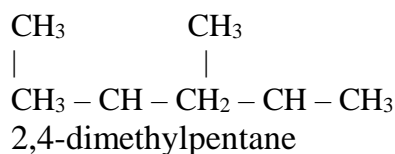
So Structure (III) is 2,5,6, trimethyloctane and not 3,4,7, trimethyloctane

- (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)

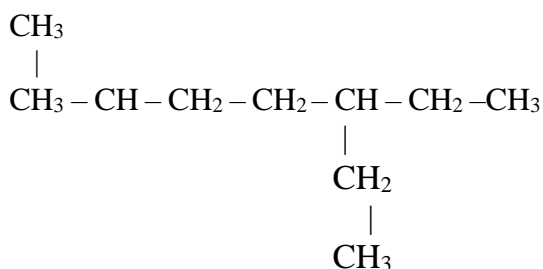


(iv)

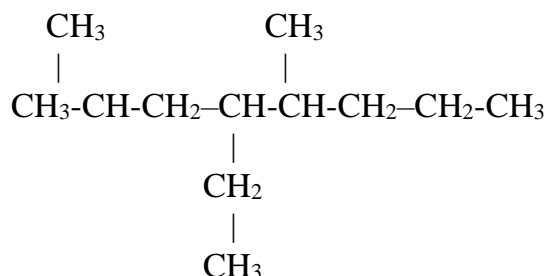
(iv) When there are more than one substituent, each substituent is prefixed by its locant and arranged in alphabetical order proceeding the name of the parent chain. The prefix di-, tri- or tetra- (for two, three or four substituents), is attached to the substituent name when more than one of a kind of substituent 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)).



(v)



5-ethyl-2-methylheptane
(not 2-methyl-5-ethylheptane)
(VI)



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 correspond to this?

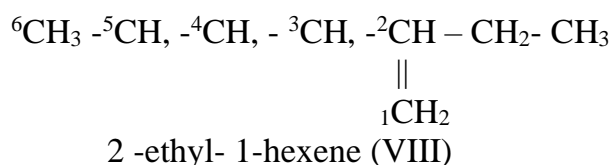
- For Structure VI, the name 2-methyl-5-ethylheptane is incorrect because it violates the alphabetical rule
- For structure VII, the name 2,3-dimethyl-4-ethyloctane is incorrect because the prefix 'di-' was used in determination of the alphabetical order of substituents which should be based only on the names of the substituents - ethyl and methyl.

Congratulations !!!

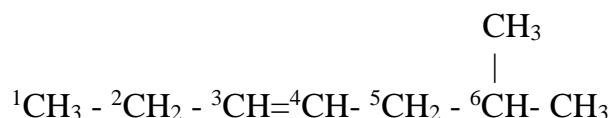
Can you draw the structure of : 5-ethyl-2-methylheptane?

If however your explanation is 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 the longest continuous chain of carbon atoms. This rule is illustrated for you in structure 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. The C=C double bond indicates the functional group of the molecule, which is more reactive than the C-C single bond.

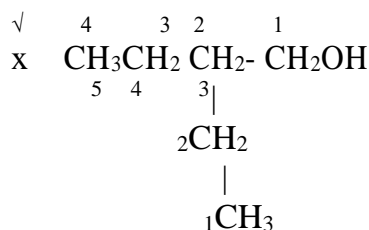


(IX) = 6-methyl-3-heptene

The selected parent carbon chain is numbered in a manner that gives the lowest number to the multiple bond (functional group) rather than the substituent group. For example structure (IX) is named 6 - methyl-3-heptene and not 2-methyl-4-heptane.

3.4 Naming non-hydrocarbon compounds: Compounds with functional groups

You can still remember what functional groups are as learnt in unit 2.11 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.



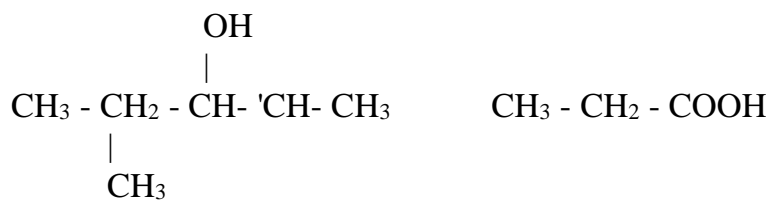
2-ethyl- 1-butanol

(C₄ not C₅ because only the C₄ 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 alcohol
- hexane to hexanoic 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.

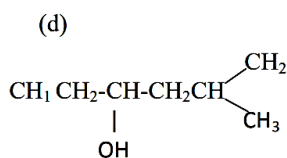
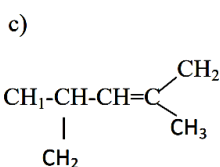
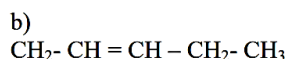
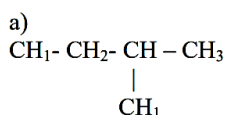


3-methyl-2-pentanol (X)

propanoic acid (XI)

Self-Assessment Exercise 4

i. Give the IUPAC names of the following compounds



3.5 Summary

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. The IUPAC nomenclature for systemic naming of organic compounds as discussed in the unit 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 positions 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 substituent prefix the names of the parent alkane alphabetically and the positions of substituents precede the names.

The positions of functional groups are given preference over those assigned to other substituents even if the lowest sum rule is violated.



3.6 References/Further Reading/Web Resources

Ababio, O.Y. (2013). *New School Chemistry for Senior Secondary Schools*. Onitsha: Africana First Publishers Limited

Norman R.O.C. and Waddington D. J. "Modern Organic Chemistry"
Tewari IC S. Mehrotra V and Vishnoi, N. K. "Textbook of organic Chemistry".



3.7 Possible Answers to Self-Assessment Exercise(s) within the Contents

Self-Assessment Exercise 1

Answer

Complete the blank spaces in Table 3.1 following the trend shown for the first five members of the alkane series.

IUPAC NAME	Formula C_nH_{2n+2}	Alkyl group	Formula
Hexane	C_6H_{14}	Hexyl	C_6H_{13}
Heptane	C_7H_{16}	Heptyl	C_7H_{15}
Octane	C_8H_{18}	Octyl	C_8H_{17}
Nonane	C_9H_{20}	Nonyl	C_9H_{19}
Decane	$C_{10}H_{22}$	Decyl	$C_{10}H_{21}$

Self-Assessment Exercise 2

Answer

Complete the blank spaces in Table 3.2 using the guide from Table 3.1.

IUPAC Name	Formula	Alkenyl Group	Formula
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-
Hexene	C_6H_{12}	Hexenyl	C_6H_{11}
Heptene	C_7H_{14}	Heptenyl	C_7H_{13}
Octene	C_8H_{16}	Octenyl	C_8H_{15}
Nonene	C_9H_{18}	Nonenyl	C_9H_{17}
Decene	$C_{10}H_{20}$	Decenyl	$C_{10}H_{19}$

Self- Assessment Exercise 3**Answer**

- (a) $\text{CH}_3\text{CH}_2\text{-}\underset{\text{CH}_3}{\text{CH}}\text{-CH}_3$ 2 – Methylbutane
- (b) $\text{CH}_3\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$ Pent – 2 – ene
- (c) $\text{CH}_3\text{CH}_2-\text{CH}=\underset{\text{CH}_3}{\text{CH}}\overset{\text{CH}_3}{/}$ 1, | – dimethylbut-| -ene
- (d) $\text{CH}_3\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_2\underset{\text{CH}_3}{\text{CH}}\overset{\text{CH}_3}{/}$ 1, | – dimethylbut | -3-pentanol
- (ii) (a) $\text{H}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\underset{\text{CH}_2}{\overset{\text{H}}{\text{C}}}-\underset{\text{CH}_3}{\overset{\text{H}}{\text{C}}}-\text{OH}$ 2 – ethyl - | -pentanol
- (b) $\text{H}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\underset{\text{CH}_3}{\overset{\text{H}}{\text{C}}}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\text{H}$
2, 3, - dimethyl – 2 - Octanol
- (c) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_2}{\text{CH}}-\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}-\text{CH}_3$
3 – ethyl, 2 – methyl heptane
- (d) $\text{CH}_3-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}_2}-\underset{\text{OH}}{\text{CH}_2}-\text{CH}_3$
3 – methyl pentan – 2 – Ol

Explain why the names in bracket for the structures above are incorrect?

Answer:

The names in the bracket for the structures are incorrect because the numbering on the parent hydrocarbon did not give the double bond (which is the functional group) the lowest numbering possible and in naming, you adopt the numbering which gives the functional group or substituent a lower set of number.

Self-Assessment Exercise 4**Answer**

- a. 2-methylbutane
- b. Pent-2-ene
- c. 2,4-dimethylpent-2-ene
- d. 5-methylhexan-3-ol

UNIT 4 PURIFICATION METHODS AND THE DETERMINATION OF EMPIRICAL, MOLECULAR AND STRUCTURAL FORMULA OF ORGANIC COMPOUNDS

Unit Structure

- 4.1 Introduction
- 4.2 Learning Outcomes
- 4.3 Purification Methods
 - 4.3.1 Distillation
 - 4.3.2 Crystallization
 - 4.3.3 Chromatography
- 4.4 Empirical and Molecular Formula
 - 4.4.1 Empirical Formula
 - 4.4.2 Molecular Formula
 - 4.4.3 Structural Formula
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- 4.7 Possible Answers to Self – Assessment Exercise(s) within the Content



4.1 Introduction

Based on the residual knowledge you have in Chemistry and the discussions from the previous units of this module, remember that organic compounds are usually represented in organic chemistry with formula, which is a shorthand method of showing the constituent atoms. Can you recall the molecular formula of ethene? Did you write C_2H_4 ? That is correct. The formulae of a compound consist of chemical symbols of the constituent atoms and numerical subscript to indicate the ratio of the atoms. Chemical bonds hold atoms together in the molecule and for organic compounds, the bond is essentially covalent. **True or False?** The answer is true. In this unit, our primary concerns are the methods for purification; determination of empirical, molecular and structural formula of organic compounds. Endeavour to make maximum benefit from the content of the unit.



4.2 Learning Outcomes

By 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.



4.3 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 difference between the two compounds the easier it is to separate them.

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.

4.3.1 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.

5°C) and B (b.p. 100°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. Can you recall the change of state that takes place in the condenser?. Yes, it is change of state from vapour/gas to liquid. A simple arrangement is shown in Fig. 4.1

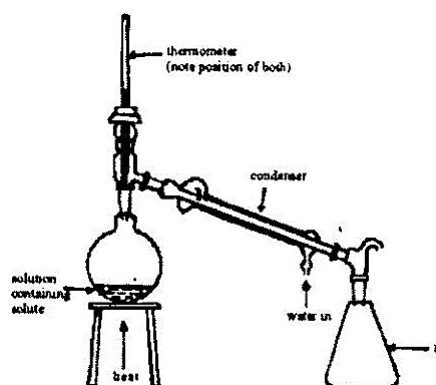


Fig 4.1 Simple distillation

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. Can you draw and label correctly the simple distillation set-up? Refer to Figure 4.1 above.

4.3.2 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. What is the role of the filter paper? Similar to filtration process. Can you recall? The filtration must be rapid to avoid crystallization during the process. A Buchner flask and funnel is the most suitable. (Fig. 4.2)

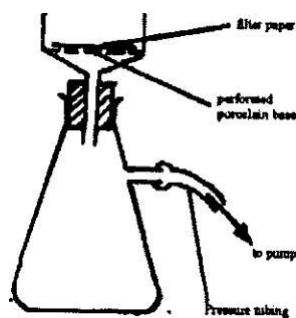


Fig. 4.2 Buchner *Flask* and Funnel

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.

4.3.3 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 suspended in a closed airtight 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.

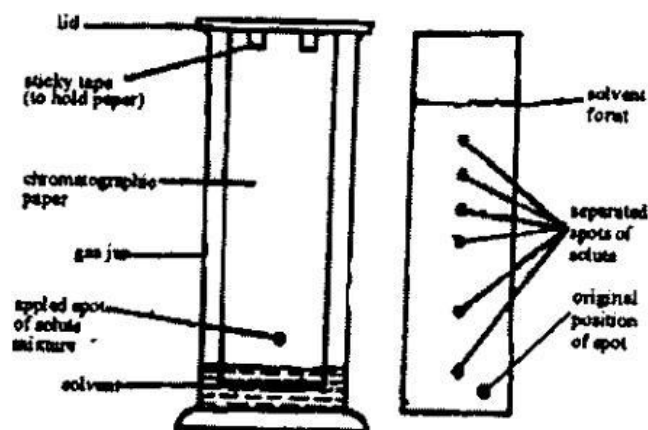


Fig. 4.3 Ascending paper chromatography

(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, hospital; food industry and research organization to effect the separation of mixtures of compounds.

Self- Assessment Exercises 1

Describe, using adequate illustrations,

- (i) simple distillation
- (ii) crystallization
- (iii) paper chromatography

4.4 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 course, 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 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.

4.4.1 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, $\text{CH}_2\text{CO}_2\text{H}$, the empirical formula is CH_2O which is the same for glucose. 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:

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- 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.
- 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
- 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 percentages of C and H added up to 100%, then the compound contains C and H only.

<i>Step 1</i>	Element	C	H
	%	79.9	20.1
<i>Step 2:</i>	%Ratio/Relative Atomic Mass	$79.9/12$	$20.1/1$
	Ratio of atoms	6.67	20.1
<i>Step 3:</i>	Smallest ratio	$6.67/6.67$	$20.1/6.62$
	whole number ratio	1	3

Therefore empirical formula - CH_3

Example 2

An organic compound contains 26.7% carbon and 12% 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

<i>Step 1:</i>	<i>Element</i>	<i>C</i>	<i>H</i>	<i>O</i>
	%	26.7	2.2	$100 - 28.9 = 71.1$
<i>Step 2:</i>	% ratio/RAM	$26.7/12$	$12/1$	$71.1/16$
	Ratio of atoms	2.22	2.2	4.44
<i>Step 3:</i>	Smallest ratio	$2.22/2.2$	$12/2.2$	$4.44/2.2$
		1	1	2

The empirical formula $C_1 H_1 O_2 = CHO_2$

4.4.2 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, $C_2 H_2$ and benzene, C_6H_6 , have the same empirical formula, CH.

A simple relationship is: molecular formula = $n \times$ (empirical formula)

$$\text{or } n = \frac{\text{molecular formula}}{\text{empirical formula}}$$

(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 course. For gases and volatile liquids, once the relative vapour density is known, the relative molecular mass can be calculated using the relation

$$\text{Relative molecular mass} = 2 \times \text{Relative vapour density}$$

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 CHO₂. Given that the relative molecular mass of the compound is 90, calculate its molecular formula. (C = 12, H = 1, O = 16)

Solution 3

Sum of relative atomic masses of the elements in the empirical formula

$$\text{CHO}_2 = (12 \times 1) + (1 \times 1) + (16 \times 2) = 45$$

$$n = \frac{\text{molecular formula}}{\text{empirical formula}} = \frac{90}{45}$$

$$n = 2$$

$$\therefore \text{Molecular formula} = 2 \times (\text{CHO}_2) = \text{C}_2\text{H}_2\text{O}_4.$$

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.

	C	H	O
% / Ram	54.5%	9.1%	100-63.6=36.4%
	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 member ratio	2	4	1

Empirical formula C₂H₄O

Relative molecular mass = 2 x vapour density

$$\text{RAM} = 2 \times 45 = 90$$

$$\text{Empirical formula mass} = (12 \times 2) + (1 \times 4) + (16 \times 1) = 44$$

$$\therefore n = \frac{\text{molecular formula}}{\text{empirical formula}} = \frac{90}{44} = 2.05 = 2$$

$$\text{Molecular formula} = [\text{C}_2\text{H}_4\text{O}]_n = 90$$

$$= [12 \times 2 + 1 \times 4 + 16 \times 1]_n = 90$$

$$44n = 90$$

$$n = 90/44 = 2.02 = 2$$

Therefore, molecular formula = $2 \times (\text{C}_2\text{H}_4\text{O}) = \text{C}_4\text{H}_8\text{O}_2$

Molecular formula = $2 \times (\text{C}_2\text{H}_4\text{O}) = \text{C}_4\text{H}_8\text{O}_2$

Self-Assessment Exercise 2

An organic compound contains 62.1% carbon and 1.02% hydrogen by mass. The vapour density of the compound is 49. Calculate its empirical and molecular formula.

4.4.3 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 modern 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 this information has 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	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	CH ₄
Ethane	C ₂ H ₆	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	H ₃ C-CH ₃
Propane	C ₃ H ₈	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	H ₃ C-CH ₂ -CH ₃
Butane	C ₄ H ₁₀	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	H ₃ C-CH ₂ -CH ₂ -CH ₃ or H ₃ C(CH ₂) ₂ CH ₃
Pentane	C ₅ H ₁₂	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	H ₃ CCH ₂ -CH ₂ -CH ₂ -CH ₃ or H ₃ C(CH ₂) ₃ CH ₃
Hexane	C ₆ H ₁₄	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	H ₃ C-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃ or H ₃ C(CH ₂) ₄ CH ₃

ii) Alkenes

Name	Molec	Structural Formula	Condensed
Ethene	C_2H_4	$\begin{array}{c} H & & H \\ & \diagdown & / \\ & C=C & \\ & / & \diagdown \\ H & & H \end{array}$	$H_2C=CH_2$
Propene	C_3H_6	$\begin{array}{c} H & & H \\ & \diagdown & / \\ H-C & - & C=C \\ & / & \diagdown \\ H & & H \end{array}$	$CH_3CH=CH_2$
2-methyl prop-1-ene	C_4H_8	$\begin{array}{c} H & & H \\ & \diagdown & / \\ H-C & - & C=C \\ & / & \diagdown \\ H & & H \\ & & \\ & & H-C-H \\ & & \\ & & H \end{array}$	$(CH_3)_2C=CH_2$

Name	Molecular Formula	Structural Formula	Condensed Structural Formula
But-2-ene	C_4H_8	$\begin{array}{c} H & & H & & H \\ & \diagdown & / & & \diagdown & / \\ H-C & - & C=C & - & C \\ & / & \diagdown & & \diagdown & / \\ H & & H & & H & & H \end{array}$	$CH_3CH=CHCH_3$

iii) Alkynes

Name	Molecular	Structural Formula	Condensed Structural
Ethyne	C_2H_2	$H-C\equiv C-H$	$HC\equiv CH$
Propyne	C_3H_4	$H-C\equiv C-\begin{array}{c} H \\ \\ C-H \\ \\ H \end{array}$	$HC\equiv C-CH_3$
1-Butyne	C_4H_6	$H-C\equiv C-\begin{array}{c} H \\ \\ C \\ \\ H \end{array}-\begin{array}{c} H \\ \\ C-H \\ \\ H \end{array}$	$HC\equiv CCH_2CH_3$
2-Butyne	C_4H_6	$\begin{array}{c} H \\ \\ H-C \\ \\ H \end{array}\equiv C-C-\begin{array}{c} H \\ \\ C-H \\ \\ H \end{array}$	$H_3CC\equiv CCH_3$

iv) Alkanols

Name	Molecular Formula	Structural Formula	Condensed Structural Formula
Methanol	CH ₄ O	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C} \\ \\ \text{-OH} \\ \end{array}$	CH ₂ OH
Ethanol	C ₂ H ₆ O	$\begin{array}{c} \text{H} \quad \text{OH} \\ \quad / \\ \text{H} \rightarrow \text{C} - \text{C} \leftarrow \text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	H ₃ CCH ₂ OH
I-Propanol or Propan-1-ol	C ₃ H ₈ O	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{OH} \\ \quad \quad / \\ \text{H} \rightarrow \text{C} - \text{C} - \text{C} \leftarrow \text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	H ₃ CCH ₂ CH ₂ OH
I-Butanol or Butan-1-ol	C ₄ H ₁₀ O	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{OH} \\ \quad \quad \quad / \\ \text{H} \rightarrow \text{C} - \text{C} - \text{C} - \text{C} \leftarrow \text{H} \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	H ₃ C(CH ₂) ₂ CH ₂ OH
2-Butanol or Butan-2-ol	C ₄ H ₁₀ O	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{OH} \\ \quad \quad \quad / \\ \text{H} \rightarrow \text{C} - \text{C} - \text{C} - \text{C} \leftarrow \text{H} \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{OH} \quad \text{H} \end{array}$	H ₃ CCH ₂ CH(OH)CH ₃

v) Alkanoic Acids

Name	Molecular Formula	Structural Formula	Condensed Structural Formula
Methanoic acid	CH ₂ O ₂	$\begin{array}{c} \text{O} \\ \\ \text{H}-\text{C}-\text{O}-\text{H} \end{array}$	HCOOH or HCO ₂ H
Ethanoic acid	C ₂ H ₄ O ₂	$\begin{array}{c} \text{H} \quad \text{O} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{O}-\text{H} \\ \\ \text{H} \end{array}$	CH ₃ COOH or CH ₃ CO ₂ H
Propanoic acid	C ₃ H ₆ O ₂	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{O} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{O}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	CH ₃ CH ₂ COOH or CH ₃ CH ₂ CO ₂ H
Butanoic acid	C ₄ H ₈ O ₂	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{O} \\ \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{CO}-\text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	CH ₃ CH ₂ CH ₂ COOH or CH ₃ (CH ₂) ₂ CO ₂ H

Self- Assessment Exercise 3

Write the structural formula of

- (i) But-1-ene
- (ii) propan-2-ol
- (iv) 2-chlorohexan-1-ol

**4.5 Summary**

This unit focused on the methods for purification of organic compounds. Also, you are acquainted with how to determine the empirical formula, molecular formula and structural formula of organic compounds. You should be able to outline the stages involved and the calculation required to fully determine the chemical nature of organic molecules.

Distillation, crystallization and chromatography are discussed as purification methods in organic chemistry. In addition, the unit addressed the method of estimating the molecular formula and hence structure of organic compounds. The unit that follows shall build up on this foundation.

**4.6 References/Further Reading/Web Resources**

Ababio, O.Y. (2013). New School Chemistry for Senior Secondary Schools. Onitsha: Africana First Publishers Limited

Ojokuku, G.O. (2012). Textbook of Practical Chemistry for Schools and Colleges. Zaria: Press-on Chemresources

Tewari, K. S., Mehrotra V. and Vishnoi, N.K. *Textbook of Organic Chemistry*.



4.6 Possible Answers to Self-Assessment Exercise(s) within the Contents

Self – Assessment Exercises

Answers to SAEs 1

- 1) Simple distillation is a separation technique used to separate two or more miscible liquids with differences in boiling points. For example ethanol (b.p 78°) and water (b.p 100c) can be separated by this method
- 2) Paper chromatography uses a filter paper as an adsorbent medium and a variety of solvents such as ethanol, methanol, chloroform or even water can also be used. A solution containing the mixture of solute to be separated is spotted near one end of the paper with a faint pencil line across the breach of the filter paper through the spotted mixture.

The paper is then suspended vertically in a closed air tight jar with the spotted end dipped in the solvent but the spot will clear of the solvent level. As the solvent moves up, the different solutes in the mixture move along the paper strip together with the solvent at different speed, thus separated. Dyes in coloured ink can be separated by this method.

Answer to SAE 2

Divide by RAM

C : H O

$$\text{But O} = 100 - [62.1 + 1.02]$$

$$100 - 63.12 = 36.88$$

$$\frac{62.11.02}{12} \quad \frac{36.88}{1} \quad 16$$

$$5.1751.02 \quad 2.305$$

$$\text{Divide by the smallest} \quad \frac{5.175}{1.02} : \frac{1.02}{1.02} : \frac{2.305}{1.02}$$

$$= \quad 5.02 : 1 : 2$$

$$= \quad 5 : 1 : 2$$

Therefore, empirical formular = C_5HO_2

$$\text{Relative molecular mass} = 2 \times \text{vapour density} = 2 \times 49 = 98$$

$$(C_5HO_2)_n = 58 \quad = (12 \times 5 + 1 \times 1 + 16 \times 2)n = 93n = 98$$

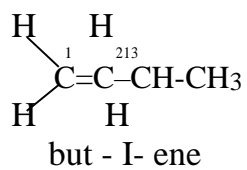
$$n = \frac{98}{93} = 1.05 = 1$$

Therefore, molecular formula = $(C_5HO_2)_1 = C_5HO_2$

Answer to AE3

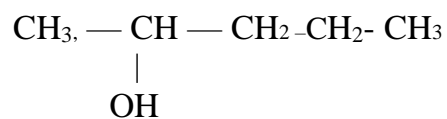
The structural formula for

i) But - 1 - ene



OR $\text{CH}_3\text{CH}=\text{CH}_2$

ii) Propan - 2- ol



propan-2-ol

iii) 2-chlorohexan- 1 - ol



UNIT 5 THE CHEMISTRY OF ALKANES

Unit Structure

- 5.1 Introduction
- 5.2 Learning Outcomes
- 5.3 Natural Sources of Alkanes
 - 5.3.1 Natural gas
 - 5.3.2 Petroleum or crude oil
 - 5.3.3 Vegetable origin
- 5.4 Laboratory preparation of alkanes
- 5.5 Properties of alkanes
 - 5.5.1 Physical properties
 - 5.5.2 Chemical properties
- 5.6 Uses of alkanes
- 5.7 Summary
- 5.8 References/Further Reading/Web Resources
- 5.9 Possible Answers to Self- Assessment Exercise(s) within the Contents



5.1 Introduction

Welcome to the last unit of Module 1. In the previous units particularly Unit 3, hydrocarbons were described 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. This unit focuses on the names, structures and natural sources of alkanes. The synthetic methods for alkanes and the types of reactions alkanes undergo, alongside the uses are discussed in this unit.



5.2 Learning Outcomes

By 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.



5.3 Natural Sources of Alkanes

Some of the natural sources of alkanes highlighted include natural gas, petroleum or crude oil, buried organic matter and natural coal. Before delving into the sources of alkanes, let's have a short review on the chemistry of alkanes.

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 backwards 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.

5.3.1 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 anti hexane). The alkanes are separated by fractional distillation. If sulphur is present, it is oxidised to sulphur (VI) oxide, the precursor to H_2SO_4 .

5.3.2 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.

5.3.3 Buried Organic Matter and Natural Coal

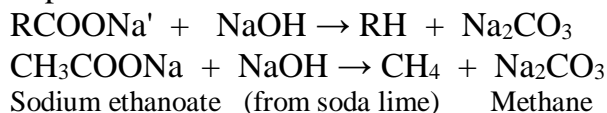
Methane is obtained as product of anaerobic action on organic matter found buried in the earth or in sewages or in marsh gas and fire damp. Coal gas obtained from the destructive distillation of natural coal contains about 30% methane.

5.3.4 Vegetable Origin

5.4 Laboratory Preparation of Alkanes

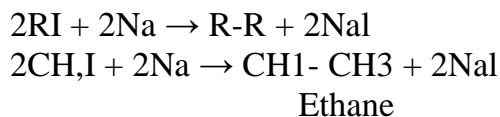
- (a) Heating anhydrous salts of alkanolic (organic) acids. The $-\text{CO}_2$ - group of alkanolic acid can be removed by heating the sodium salts of the alkanolic acid with soda lime (a mixture of sodium and calcium hydroxides).

For example



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.



Self-Assessment Exercise 1

- i. List three natural sources of alkanes
- ii. Describe the ways of preparing alkanes in the laboratory.

5.5 Properties of Alkanes

This can be sub-divided into physical and chemical properties which are discussed in the following sub-sections.

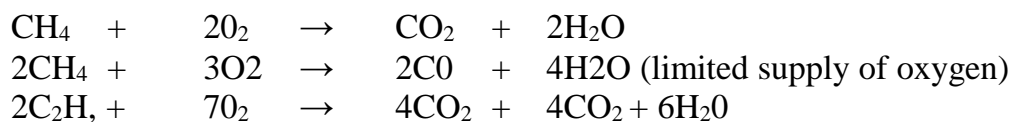
5.5.1 Physical properties

- (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 $\text{C}_{12}\text{H}_{24}$ 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.

5.5.2 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.



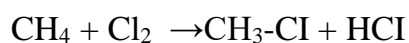
The ease of burning accounts for the use of many alkanes as fuels.

(b) Substitution Reactions

One or more 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. By successively substituting the four hydrogen atoms in methane, four halogenated alkanes are produced, one after the other at each stage of the substitution process. The four products are named monochloromethane, dichloromethane, trichloromethane and tetrachloromethane

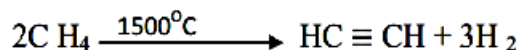
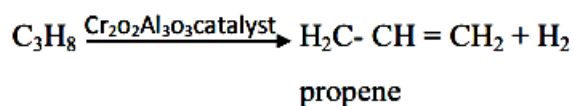
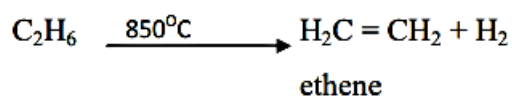
Below is equation for formation of monochloromethane.

Can you attempt equation for the formation of the other three products?



(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.



Self- Assessment Exercise 2

Use equations only to illustrate the combustion and substitution reactions of a simple alkane

5.6 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.

Self- Assessment Exercise 3

Enumerate four (4) uses of alkanes.

**5.7 summary**

In this unit, the focus is on alkanes, the simplest homologous series consisting of 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. It is gathered from the discussion that 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. 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. With the study of the first homologous series of organic chemistry, you must begin to appreciate the relevance of organic compounds to us all.

**5.8 References/Further Reading/Web Resources**

Bah, ST., Tube, RD., 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.



5.9 Possible Answers to Self- Assessment Exercise(s) within the Contents

Self- Assessment Exercise

Answers to SAE 1

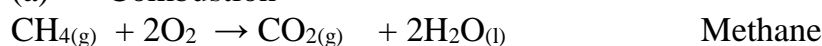
Natural sources of alkanes

- Natural gas
- Petroleum (crude oil)
- Vegetable origin
- Coal

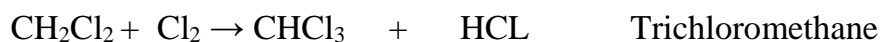
Answer to SAE 2

Illustrating the combustion and substitution reactions of a simple alkane

(a) Combustion



(b) Substitution reaction with chlorine



Answer to SAE 3

Four uses of alkanes

- (i) Alkanes are widely used as fuels as methane, butane, propane gases
- (ii) Higher alkanes such as paraffin wax is used for candle production and for lubrication purpose
- (iii) Methane is used in the production of water gas
- (iv) It is used for making hydrogen, carbon black, carbon (iv) sulphide, alkyne etc
- (v) Chloro alkanes are used in hospitals e.g chloroform as anesthetics

MODULE 2

Unit 1	The Chemistry of Alkenes and Alkynes
Unit 2	Introduction to the Chemistry of Benzene
Unit 3	Introduction to Petroleum Chemistry
Unit 4	Alkanols I Uses Alkanols
Unit 5	Alkanols II Characteristics of Alkanols

UNIT 1 THE CHEMISTRY OF ALKENES AND ALKYNES

Unit Structure

- 1.1 Introduction
- 1.2 Learning Outcomes
- 1.3 Chemistry of Alkenes and Alkynes
 - 1.3.1 Sources of alkenes
 - 1.3.2 Manufacture of ethyne
 - 1.3.3 Laboratory preparation of ethene and ethyne
 - 1.3.4 Isomerism in alkenes
- 1.4 Chemical Properties
 - 1.4.1 Alkenes
 - 1.4.2 Alkynes
- 1.5 Test for unsaturation
- 1.6 Summary
- 1.7 References/Further Reading/Web Resources
- 1.8 Possible Answers to Self- Assessment Exercise(s) within the Contents



1.1 Introduction

You are welcome to Unit 1 of Module 2. Recall that hydrocarbons can be subdivided into saturated and unsaturated compounds as pointed out in units 1 and 3 of Module 1. In unit 5 of Module 1, 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 is on the unsaturated hydrocarbons, namely **alkenes** and **alkynes**. Sources of alkenes and alkynes, their preparations and chemical properties are discussed in the unit.



1.2 learning Outcomes

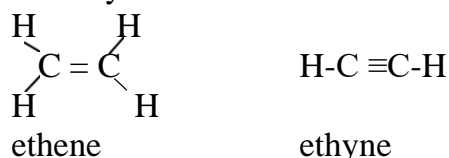
By the end of this unit, you should be able to:

- Identify the feature that differentiate saturated (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
- Examine the reason for alkenes being important starting material for several industrial processes.



1.3 Chemistry of 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 $C\equiv C$ bonds respectively. Recall the systems of IUPAC nomenclature for these classes of homologous ending with the suffix -ene for an alkene and -yne for alkynes.



Ethene and ethyne are the first members of the alkenes and alkynes series respectively.

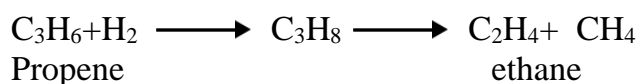
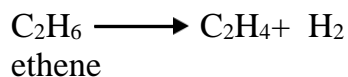
You also learned in Unit 2, the concept of isomerism *and* that cis-trans isomerism exist in alkenes. Isomerism does not exist in alkynes because the molecules are collinear as learned in unit I The main feature of the chemistry of alkenes and alkynes is their addition reactions in which the $C=C$ and $C\equiv$

Care 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.

1.3.1 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.



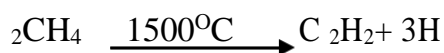
(b) Cracking of naphtha

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, C₁-C₄ alkanes and C₁-C₄ alkenes. These gases can be separated by distillation under pressure.

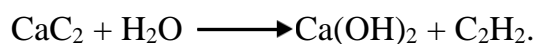
1.3.2 Manufacture of ethyne

Ethyne is the most common member of the alkyne series and will therefore be used as the representative member for alkynes throughout this unit.

Modern 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.



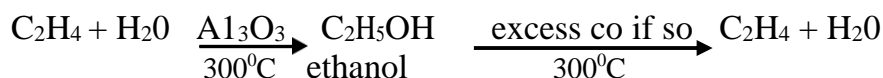
This process has replaced the older method of obtaining ethyne by reaction between calcium dicarbide and water. The reaction still serves as a satisfactory source of ethyne on a small scale particularly for welding purposes.



1.3.3 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 300°C; or heating the ethanol with excess concentrated tetraoxosulphate (vi) acid at 180°C. Both reagents act as dehydrating agents.



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.

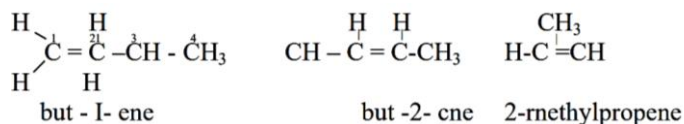
1.3.4 Isomerism in Alkenes

You will recall that in Unit 2, the concept of isomerism was discussed and alkenes are said to exhibit cis-trans isomerism. All alkenes above C_3H_6 show isomerism. For C_4H_8 , recall the structure of cis-but-2-ene and trans-but-2-ene.

Can you explain why 1-butene does not exhibit cis-trans isomerism?

Answer: 1-butene does not exhibit a cis-trans isomerism due to position isomerism existing in the structure.

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.



Self-Assessment Exercise 1

Describe the modern process of producing ethyne.

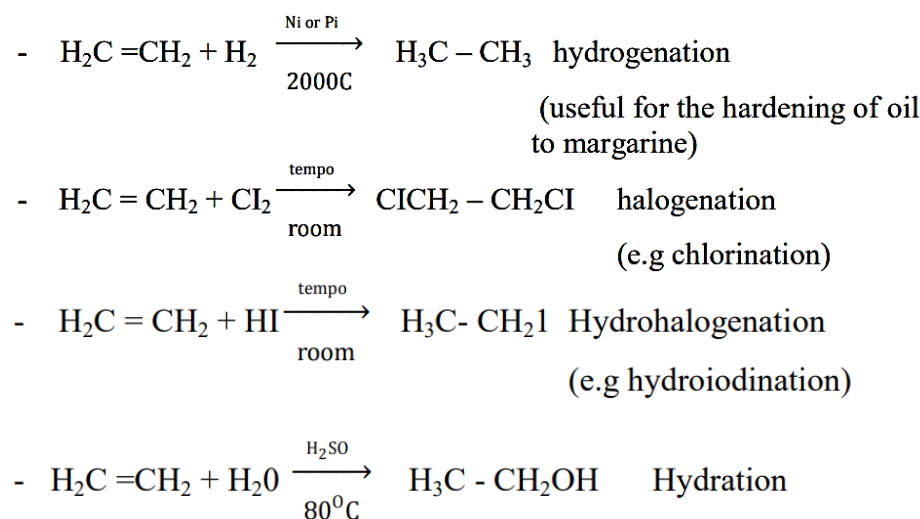
1.4 Chemical Properties

The chemical properties of alkenes and alkynes are explored. The various reactions such as addition reactions, oxidation reaction and polymerization reactions involving alkenes and alkynes are discussed.

1.4.1 Alkenes

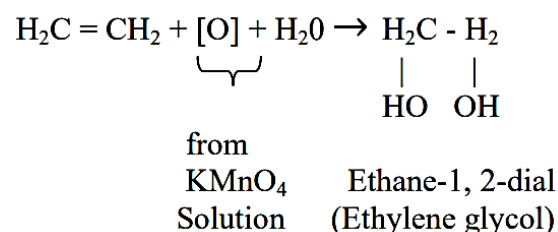
(a) Addition reactions

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, halogens (Cl₂, Br₂, I₂), hydrogen halides (HCl, HBr, HI) and H₂O; can add on to the C = C.



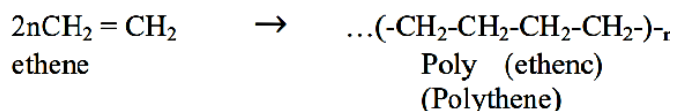
(b) Oxidation reaction

Aqueous solution of potassium tetraoxomanganate (VII) acting as an oxidizing agent can add two -OH groups onto C = C of alkenes.



(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.

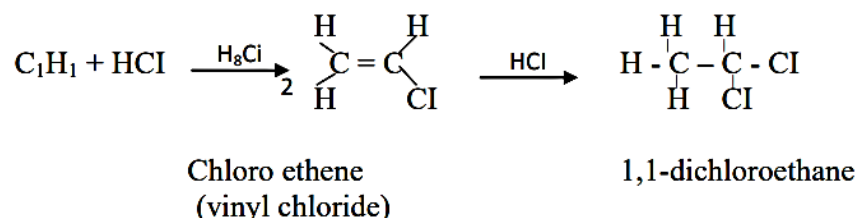
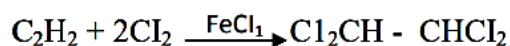
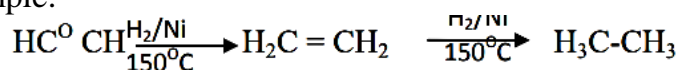


Polythene is widely used for making buckets, pipes, bottles, cups, spoons, toys, packing materials and cable insulating materials.

1.4.2 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 $\text{C} \equiv \text{C}$ to $\text{C} = \text{C}$ and the second addition converts $\text{C} = \text{C}$ to $\text{C} - \text{C}$. For example:



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 readily as ethene. On heating, however, ethyne is polymerised to benzene, and important hydrocarbon that will be studied in Unit 7.

Self –Assessment Exercise 2

- 1) Explain, with varied illustrative examples, the meaning of the term addition reaction.
- 2) Describe polymerisation reaction

1.5 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 passed 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.



1.6 Summary

This unit focused on the chemistry of the aliphatic unsaturated hydrocarbons, alkenes and alkynes. As described in the unit, 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 are said to undergo polymerization reaction to give useful polymer materials. The principal source of alkenes and alkynes is the parent 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.



1.7 References/Further Reading/Web Resources

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

Ababio, O.Y. (2013). *New School Chemistry for Senior Secondary Schools*. Onitsha: Africana First Publishers Limited

Norman R.O.C. and Waddington D. J. "Modern Organic Chemistry"
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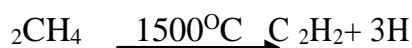


1.8 Possible Answers to Self-Assessment Exercises within the content

Self-Assessment Exercises

Answer to SAE1

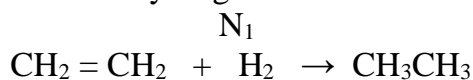
Modern Process of producing ethyne: This involves the application of temperature of about 1500°C for a fraction of a second on methane or naphtha. This involves a large scale production. Hydrogen is obtained as a useful by- product as shown in the reaction.



Answer to SAE 2

1) Addition reaction involves the direct addition of an attacking reagent across the double or triple bond of an unsaturated hydrocarbon to yield a saturated product. Ethene and ethyne undergo addition reaction. The following are some examples.

(i) With hydrogen

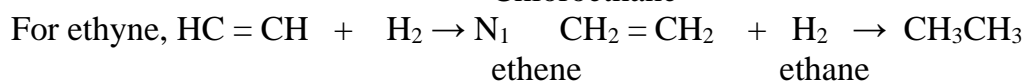


(ii) With hydrogen halide

- Hydrogen chloride



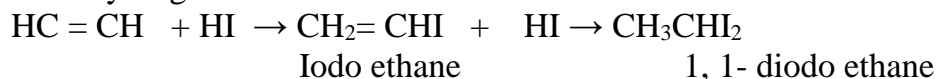
Chloroethane



ethene

ethane

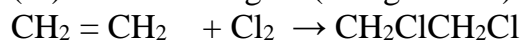
With hydrogen Iodide



Iodo ethane

1, 1- diodo ethane

(iii) With halogen (halogenation)



1, 2 -dichloromethane

UNIT 2 INTRODUCTION TO THE CHEMISTRY OF BENZENE

Unit Structure

- 2.1 Introduction
- 2.2 Learning Outcomes
- 2.3 The Chemistry of Benzene
 - 2.3.1 Structure and bonding in benzene
 - 2.3.2 Resonance in benzene
 - 2.3.3 Chemical properties of benzene
 - 2.3.4 Substitution reactions of benzene
 - 2.3.5 Addition reactions of benzene
- 2.4 Summary
- 2.5 References/Further Reading/Web Resources
- 2.6 Possible Answers to Self- Assessment Exercise(s) within the Contents



2.1 Introduction

Previous units of this course introduced to you and taught you the aliphatic hydrocarbons-alkanes, alkenes and alkynes as distinct homologous series. There are a number of homologous series of aromatic hydrocarbons. The simplest, based on benzene, C_6H_6 and containing one ring of six carbon atoms have a general formula C_nH_{2n-6} , ($n = 6$). The chemistry of benzene, the simplest aromatic hydrocarbon, is the subject-matter of this unit. Aromatic compounds were originally so named because many of them were fragrances and the term aromatic is derived from the Greek word aroma, meaning pleasant smell. 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.



2.2 Learning Outcomes

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

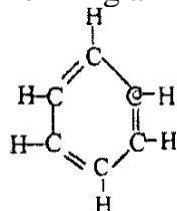
- explain the concept of resonance in terms of delocalisation of electrons
- discuss the unusual stability of the benzene nucleus in terms of resonance

- compare the reactions of benzene with those of the other unsaturated hydrocarbons, (alkenes and alkynes)
- examine the types of reactions benzene undergo.



2.3 Chemistry of Benzene

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.

2.3.1 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.

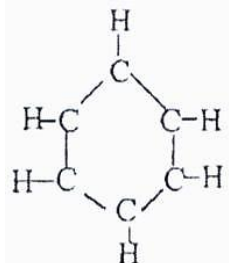
Studies have shown that benzene is a regular planar hexagon, with the carbon-carbon bond length of 1.39nm. This bond length is shorter than the C-C bond length of alkanes (1.540nm) and longer than C=C of alkenes (1.34nm). For *benzene*, however, the carbon-to-carbon bonds for all the six carbon atoms 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.

2.3.2 Resonance in Benzene

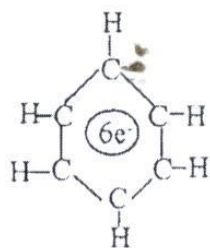
To explain the unusual observation in respect of the benzene structure, we have to recall that we have discussed bonding only in terms of electron pairs associated with two nuclei. These we may call localised electron i.e. shared bonding electrons located between the two bonded atoms. The

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.

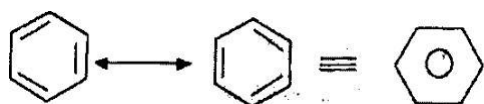
Let us now see how this concept can be used to explain the benzene ring structure i.e. all the carbon-to-carbon bonds in the ring are usual. You will recall (unit I) that carbon has four electrons available for bonding. Let us look at a typical six carbon ring system similar to



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 (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 \leftrightarrow 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 since it does not undergo substitution reaction.

Self-Assessment Exercise 1

- 1) Benzene is a regular planar hexagon with carbon-carbon bond. Discuss.
- 2) Use the concept of resonance to account for the structure of benzene.

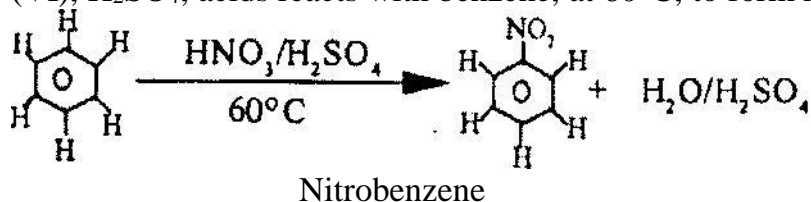
2.3.3 Chemical Properties of Benzene

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 stabilization. In some reactions, however, this aromatic stabilization is lost and benzene undergoes addition reactions such as catalytic hydrogenation.

2.3.4 Substitution Reactions of Benzene

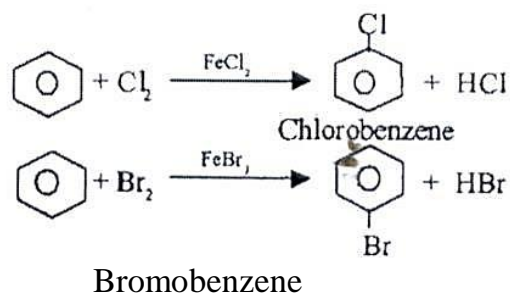
(a) Nitration

A mixture of concentrated trioxonitrate (V) HNO_3 , and tetraoxosulphate (VI), H_2SO_4 ; acids reacts with benzene, at 60°C , to form nitrobenzene

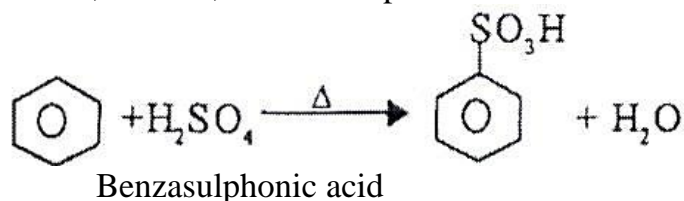


(b) Halogenation

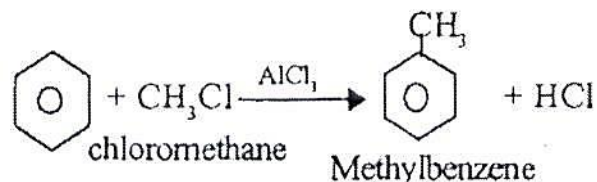
Benzene reacts with chlorine or bromine in the presence of a reagent called Lewis acid (FeCl_3 or FeBr_3) to form chloro- or bromo-benzene. Light must be excluded from the reaction mixture.

**(c) Sulphonation**

Benzene reacts on heating with concentrated tetraoxosulphate (VI) acid, H_2SO_4 , to form, benzenesulphonic acid.

**(d) Alkylation**

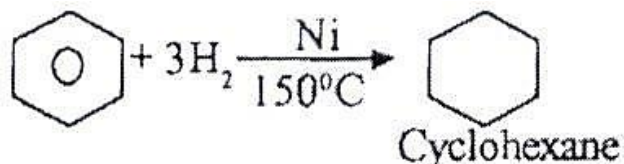
Benzene and halogenoalkanes e.g. chloromethane react, in the presence of Lewis acids, AlCl_3 , as catalyst, to form alkyl benzenes e.g. methylbenzene. The reaction is known as the Friedel-Crafts reaction,

**Self-Assessment Exercise 2**

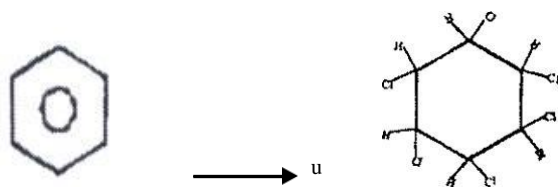
Use equations only to illustrate four substitution reactions of benzene.

2.3.5 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

Self- Assessment Exercise 3

Use equations only to describe hydrogenation and halogenation as addition reactions of benzene.

**2.4 Summary**

You have been introduced to the chemistry of benzene, the simplest of the aromatic hydrocarbon series and an unusually stable unsaturated hydrocarbon. The nature of the structure and bonding in benzene was explained using the resonance concept, a concept that is important in the study of aromatic compounds in general and benzene in specific. 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.

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.

**2.5 References/Further Reading/Web Resources**

Bajah, S. T., Teibo, B. O., Onwu, G. and Obilwere, A. (2002) *Senior Secondary Chemistry - Text book 2*. Lagos. Longman Publishers.

Holtzclaw, A. and Robinson, W. *It General Chemistry*.

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Norman R.O.C. and Waddington D. J. "Modern Organic Chemistry"
Tewari IC S. Mehrotra V and Vishnoi, N. K. "Textbook of organic Chemistry".

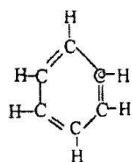


2.6 Possible Answers to Self-Assessment Exercise(s) within the Contents

Self-Assessment Exercise

Answer

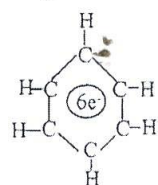
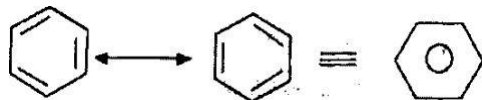
- 1) Benzene is a regular planar hexagon with carbon – carbon bond, the length of which is 1.39nm, an intermediate value between the single and double carbon-to-carbon bond. This can be explained by the concept of a phenomenon known as resonance. The bond length is shorter than the C- C bond length of alkanes (1.54nm) and longer C- C of alkenes (1.34nm). Benzene does not give addition products across the C= C like those found in alkenes. It 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. Benzene ring is represented in a cyclic form thus:



- 2) Concept of Resonance to account for the structure of benzene:

The concept of resonance delocalizes the six electrons in a benzene ring, such that the unused six electrons pooled together as electron cluster from which any of the six carbon atoms can pool from. The concept gives the benzene ring a stability, because the degree of bonding increases when the electrons can distribute themselves over a greater volume.

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



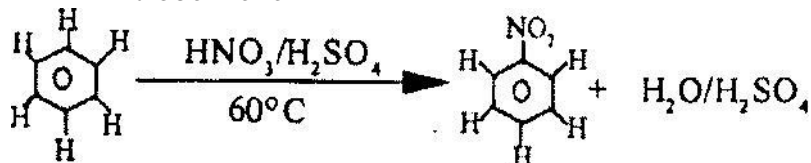
This suggestion is in agreement with the fact that all the carbon-to-carbon bonds in benzene are of the same length, and intermediate between the C- C single bond of alkanes and the C=C double bond of alkenes. This

concept of resonance confer stability on the benzene, hence any attempt to change (e.g. addition reaction), this arrangement

Answer to SAE 2

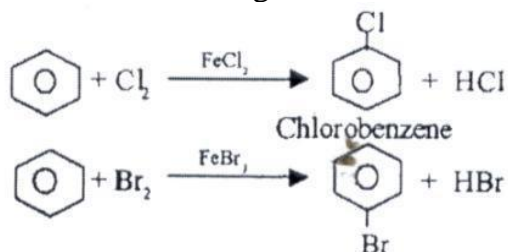
(1) Equations to illustrate substitution reactions of benzene:

i) Nitration with a mixture of concentrated trioxonitrate (V) HNO_3 , and tetraoxosulphate (VI), H_2SO_4 ; acid at 60°C , to form nitrobenzene



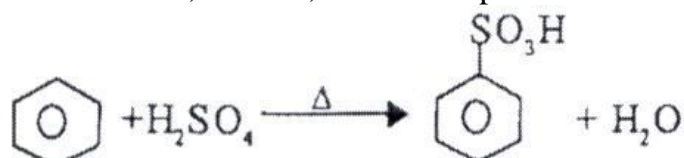
Nitrobenzene

ii) Halogenation 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.



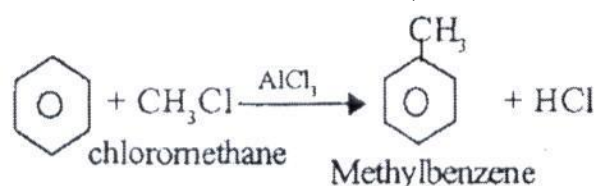
Bromobenzene

iii) Sulphonation with concentrated tetraoxosulphate (VI) acid, H_2SO_4 , to form, benzenesulphonic acid.



Benzenesulphonic acid

iv) Alkylation with chloromethane. The reaction is known as the Friedel-Crafts reaction,



(2) Equations to describe hydrogenation and halogenations as addition reactions of benzene

UNIT 3 INTRODUCTION TO PETROLEUM CHEMISTRY

UNIT STRUCTURE

- 3.1 Introduction
- 3.2 Learning Outcomes
- 3.3 Chemistry of Petroleum
 - 3.3.1 Crude oil reserves
 - 3.3.2 The refining process
 - 3.3.1.1 Fractional distillation
 - 3.3.1.2 Quality of petrol - octane number
 - 3.3.3 The conversion processes
 - 3.3.3.1 Cracking
 - 3.3.3.2 Isomerisation
 - 3.3.3.3 Reforming
- 3.4 Petrochemicals
- 3.5 Oil Production and the Nigerian Economy and Environment
- 3.6 Summary
- 3.7 References/Further Reading/Web Resources
- 3.8 Possible Answers to Self-Assessment Exercise(s) within the Content



3.1 Introduction

In this unit, the focus is on the chemistry of petroleum. Its meaning, refining process and conversion process are discussed. Also highlighted in the unit are petrochemicals, oil production and the Nigerian economy and environment. **Petroleum** (also referred to as **crude oil**) varies widely in composition but consists mainly of alkanes (C_1 to C_{40} per molecule), cycloalkanes and aromatic hydrocarbons; may also contain some proportions of sulphur, nitrogen, oxygen, etc. 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'. Pay rapt attention to the content of the unit and make optimum use of the lesson.



3.2 Learning Outcomes

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
- write short on the term cracking and reforming; also pointing out their relevance in the petroleum industry
- outline the uses of the fractions of the refining process
- explain the importance of octane number in petrol quality
- discuss the effect of petroleum to the economy of Nigeria.



3.3 Chemistry Of Petroleum

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. 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.

As earlier stated in the introduction, petroleum is made up of mainly alkanes (C_1 to C_{40} per molecule), cycloalkanes and aromatic hydrocarbons; and may contain some proportions of sulphur, nitrogen, oxygen, etc. The composition of petroleum varies. **It is a viscous liquid mixture of organic compounds deposited in the strata of the earth crust.**

3.3.1 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, Venezuela, 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 Want Port-Harcourt and Kaduna.

3.3.2 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.

3.3.2.1 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.

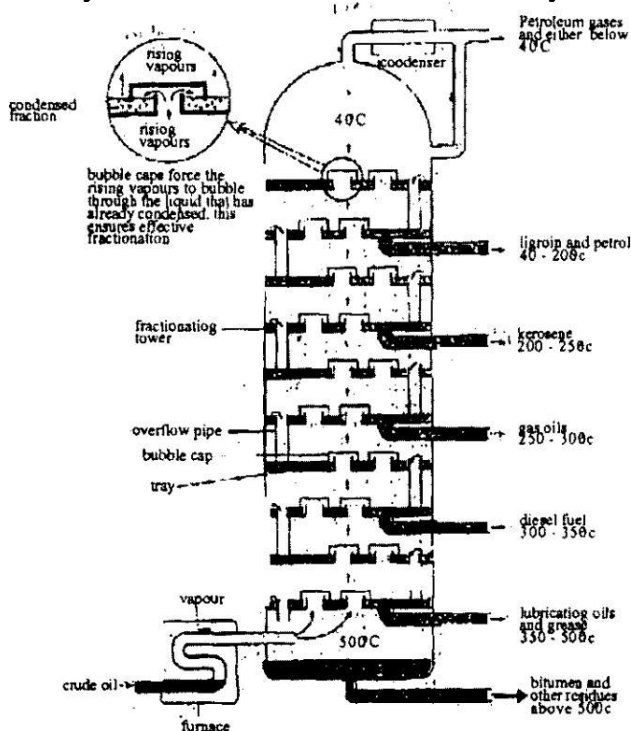


Fig 8.1: Fractionating column for fractional distillation of crude oil

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 oC	Approximate	Use
Gas fraction	< 40	1-5	gaseous fuel for cooking and heating; source of alkanes ,
Petroleum ether	40-66	5-10	Solvent
Petrol or gasoline	60-80		Fuel
Naphtha	70-180 100-200		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-Harcourt 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 neighbouring countries e.g. Niger, Chad. However, the extent these refineries are meeting the demands of Nigerian petroleum needs today, is below expectation. Hence, the incessant crises in the petroleum sector in Nigeria.

Self-Assessment Exercise 1

Describe the fractional distillation of petroleum and list the fractions obtained with their uses.

3.3.2.2 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 0), 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. isooctane). 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.

Self-Assessment Exercise 2

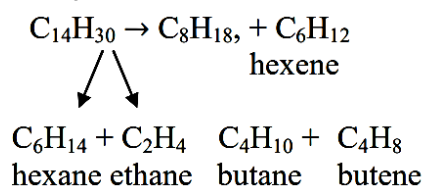
- 1) Explain the term octane number and its importance in determining the quality of petrol.
- 2) Draw the structural formula of iso-octane and heptane.

3.3.3 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.

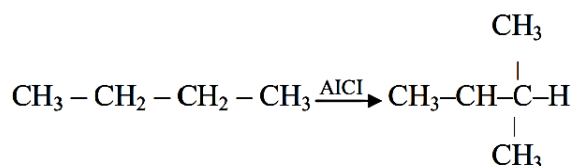
3.3.3.1 Cracking

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 .



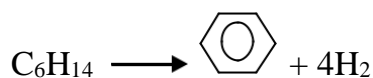
3.3.3.2 Isomerisation

In this process, straight-chain alkanes are converted into branched-chain isomers at about 100° C and under pressure; with AlCl₃ as catalyst



3.3.3.3 Reforming

This process involves the conversion of straight-chain alkanes into aromatic hydrocarbon. The process involves a simultaneous cyclisation (forming ring compound), catalyst by Al₂O₃; 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.

3.4 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, pharmaceuticals, 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 eg. 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.

3.5 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 earnings of Nigeria and is still the major source of foreign exchange earnings. The earnings from 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 lives and has greatly improved our standard of living.

The availability of petrol has led 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.

Self-Assessment Exercise 3

- 1) Describe cracking and reforming as conversion processes in the petroleum industry.
- 2) Discuss the effect of petroleum to the Nigerian economy with emphasis on its availability and benefits.



3.6 Summary

In this unit you have been introduced to the chemistry of petroleum, which is an extremely important raw material and obtained from the earth's crust. Although the composition of petroleum varies with the source, the principal component still remains alkanes which are separated into various fractions based on boiling ranges 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 as outlined in the unit. Some products of the conversion process are useful petrochemicals which are important starting materials for the chemical industry.



3.7 References/Further Reading/Web Resources

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



3.8 Possible Answers to Self- Assessment Exercise(s) within the Contents

Self- Assessment Exercise

Answer to SAE 1

1. Fractional distillation is the separation of petroleum into fractions based on boiling points.

During the process, the oil (crude) is heated to a temperature of about 400°C in a full cylinder which has a fractionating column which is divided into compartments. As the mixture passes through the column, the liquids falls to the bottom of the cylinder while the vapour goes up the cylinder while the vapour goes up the cylinder. The separation is done based on the boiling points of each fraction.

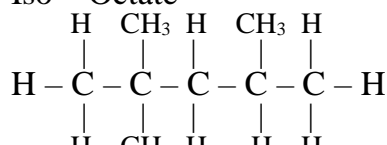
Fractions obtained with their uses

FRACTIONS	USES
Gas fractions	Used as gaseous fuels for cooking and lighting
Petroleum ether	Used as solvents
Petrol or gasoline	Used as fuel for automobiles
Naphtha	Used as solvents and source of alkane and alkene
Kerosene	Used as fuel for lantern, tractors and jets engine
Light gas oil	Used as fuel for diesel engine
Heavy oil, light lubricating Oil	Used as lubricant, paraffin wax, medicinal paraffin
Residue	Bitumen for surface road and roofing materials

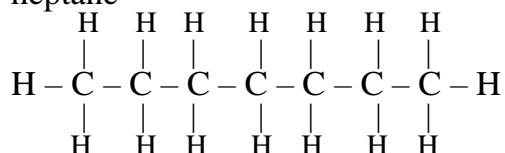
Answers to SAE 2

1) Octane number of any fuel is the percentage of iso- octane in a mixture of iso- octane and heptanes that will knock to the same extent as the fuel under the same condition. It accounts for the differences in the grade of petrol.

Iso – Octate



2, 2, 4 – trimethyl pentane
heptane

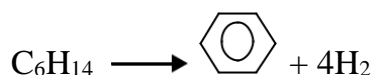


2) See the structural formular of iso- octane and heptane sketched below:

Answers to SAE 3

1) **Cracking** is a process in which larger molecular hydrocarbons are broken down into smaller hydrocarbons needed in petrol. There are two types of cracking: thermal cracking and catalytic cracking.

Reforming process involves the conversion of straight- chained hydrocarbons into aromatic hydrocarbons. The process involves a simultaneous cyclisation (forming ring compounds) by a catalyst such as Al_2O_3 and dehydrogenation using platinum catalyst. This is shown below:



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.

2) Petroleum accounted for about 90% of all export earning of Nigeria and is still the major source of foreign exchange earnings. The earnings from 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 lives and has greatly improved our standard of living.

The availability of petrol has led 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.

UNIT 4 ALKANOLS I (CLASSIFICATION, SOURCES AND USES)

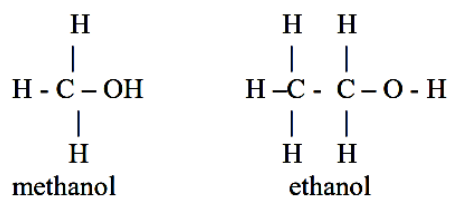
Unit Structure

- 4.1 Introduction
- 4.2 Learning Outcomes
- 4.3 Alkanols I
 - 4.3.1 Classification of alkanols
 - 4.3.2 Sources of alkanols
 - 4.3.2.1 General methods of preparation
 - 4.3.2.2 Manufacture of alkanols
 - 4.3.3 Uses of ethanol
- 4.4 Summary
- 4.5 References/Further Reading/Web Resources
- 4.6 Possible Answers to Self-Assessment Exercise(s) within the Content



4.1 Introduction

Recall that unit 2 of Module 1 discussed organic functional groups and their properties. You will also remember that the general formula of alkanols is $C_nH_{2n+1}OH$ as pointed out in that unit, and that alkanols are named by replacing the 'e' of the alkane name by 'ol.' For example methanol and ethanol from methane and ethane.



In this unit, chemistry of alkanols are discussed with emphasis on the classification and sources of alkanols. Also, the uses of ethanols are highlighted.



4.2 Learning Outcomes

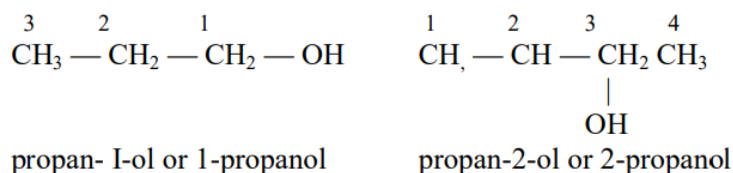
By the end of this unit, you should be able to:

- classify alkanols into primary, secondary or tertiary groups
- enumerate the sources of simple alkanols
- describe the process involved in the local production of ethanol.
- outline the uses of ethanol.



4.3 Alkanols

Alkanols 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'. 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.

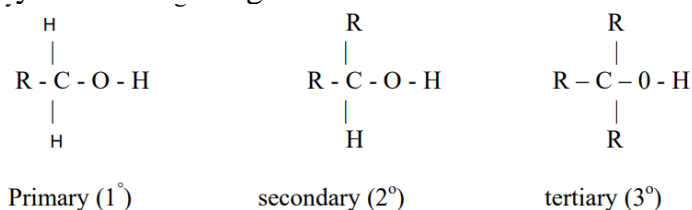


This is positional isomerism, a form of structural isomerism which you learned in unit 2 of Module 1 and unit 1 of Module 2.

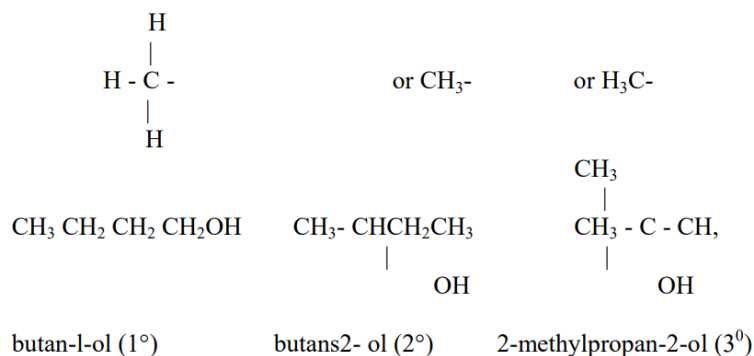
The hydroxyl group is one of the most important functional groups of naturally occurring molecules such as carbohydrates and nucleic acids. These are complex alkanols but our concern in this unit is the simple alkanols which are made from petroleum-derived hydrocarbons.

4.3.1 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



Where R = alkyl group



Self-Assessment Exercise 1

- 1) Write and name all the structural isomers of C_3H_7OH which are alkanols. Indicate whether they are primary, secondary and tertiary alkanols.
- 2) Three structural isomers of C_4H_9OH are represented above. There is one more isomer of alkanol not shown, can you draw and name it? (Hint: it is a 1° alkanol).

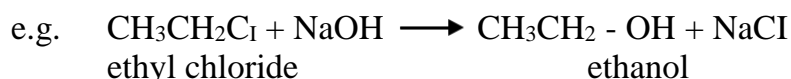
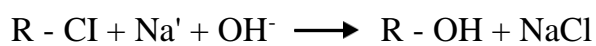
In-general, the characteristic of primary alkanols is CH_2OH ; secondary alkanols is $CHOH$ and tertiary alkanol COH .

4.3.2 Sources of Alkanols

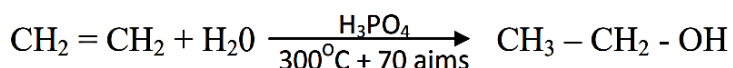
Main sources of alkanols are discussed here including the general methods of preparation and manufacture.

4.3.2.1 General methods of preparation

- (a) Hydrolysis of halogenoalkanes or alkyl halides: Alkyl halides are compounds formed by replacing one of the hydrogen of an al/cane 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.



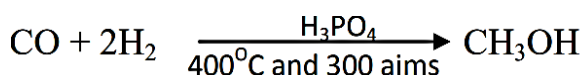
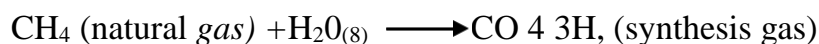
- (b) Hydration of alkenes: Alkenes react with steam when passed over phosphoric (v) acid catalyst at $300^\circ C$ and 70 atmosphere. For example.



The process, as shown in the equation, is used industrially for the production of ethanol and some higher alkanols.

4.3.2.2 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.



(b) Ethanol

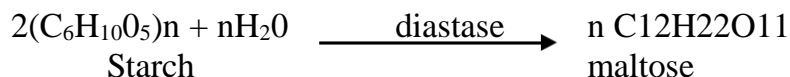
(i) From ethene: The major source of ethanol industrially is by hydration of alkenes as described in section 9.3.1(b)

(ii) By fermentation: The fermentation process of obtaining ethanol from starch materials is still popular

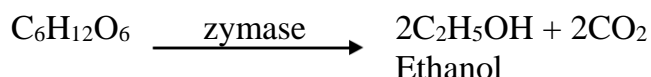
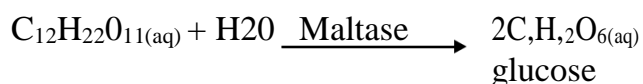
Fermentation is the decomposition of complex organic compounds e.g. carbohydrates, into simpler compounds through the action of enzymes.

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.

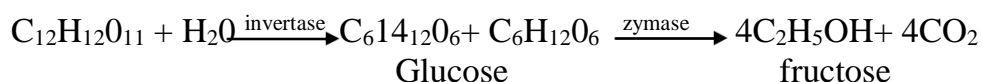
- From starchy materials: The material is crushed and treated with steam to extract the starch from them. Malt, made from partially germinated barley, is added and then kept at about 50°C for one hour. The enzyme diastase, present in the malt, catalyses the conversion of starch into maltose.



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.



- From molasses: In countries like Brazil, USA; 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.



- From palm wine: In some parts of Africa e.g. Nigeria, Ghana, South Mica, 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: I 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.

4.3.3 Uses of Ethanol

- It is used as solvent for resins, varnishes, polishes, liquid soaps, perfumes, drugs and paints
- It is used as a fuel, either by itself or mixed with petrol, in racing cars and rockets
- It is used as an anti-freeze in automobile radiator
- It is present in many alcoholic beverages
- It is used for sterilization and preservation of specimens and food
- It is used as raw material in the manufacture of chemical e.g. ethanal, trichloromethane, ethoxyethane

SELF- ASSESSMENT EXERCISE 2

- | |
|---|
| 1) Describe the fermentation process for the production of ethanol. |
| 2) Outline four uses of ethanol. |

**4.4 SUMMARY**

This unit discussed a group of compounds, an important homologous series known as alkanols and characterized by the presence of OH functional group. You should also have been acquainted with the classification and the principal sources of alkanols. Based on the units' content, alkanols are classified into primary, secondary and tertiary alkanols depending on the -OH group. The fermentation process for the conversion of various raw materials to alcoholic beverages was highlighted, though the main source of alkanols is by hydration. In addition you should be able to enumerate the various uses of ethanol as the most important compound of the alkanol series.

**4.5 References/Further Reading/Web Resources**

Bajah, ST., Teibo, B.O., Onwu, G. and Obikwere, A. (2002) *Secondary Secondary Chemistry Textbook 3*. Lagos. Longman Publishers.

Ababio, O.Y. (2013). *New School Chemistry for Senior Secondary Schools*. Onitsha: Africana First Publishers Limited

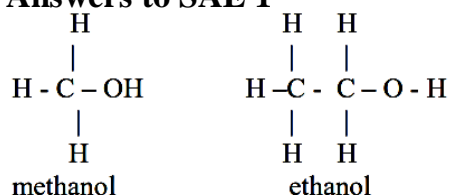
Norman R.O.C. and Waddington D. J. "Modern Organic Chemistry"
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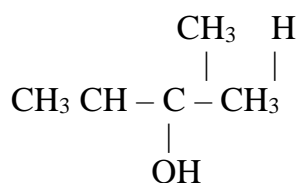
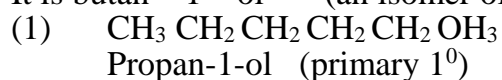
4.6 Possible Answers to Self- Assessment Exercise(s) within the Contents Within the content

Self- Assessment Exercise

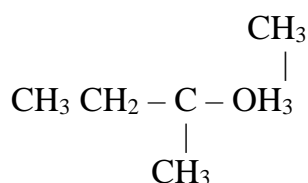
Answers to SAE 1



It is butan – 1 – ol (an isomer of alkanol)



3 – methyl butan-2-ol (Secondary 2^0)

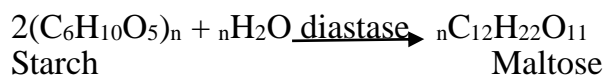


0, 2 – methyl butan – 2-ol (Tertiary 3^0)

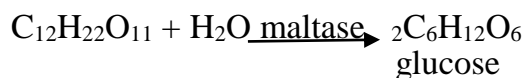
Answers to SAE 1

- ii. Fermentation is the decomposition of complex organic compound eg carbohydrate into simpler compounds through the actions of enzymes.

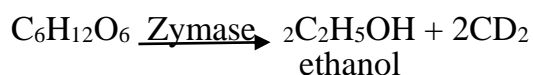
From starch



The maltose is converted to glucose by the enzyme maltase from yeast



The glucose is then converted to ethanol by the enzyme zymase



2) Some 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
It is used as an anti-freeze in automobile radiator
- c) It is present in many alcoholic beverages
- d) It is used for sterilization and preservation of specimens and food
- e) It is used as raw material in the manufacture of chemical e.g. ethanal, trichloromethane, ethoxyethane

UNIT 5 ALKANOLS II (CHARACTERISTICS OF ALKANOLS)

- 5.1 Introduction
- 5.2 Learning Outcomes
- 5.3 Alkanols II
 - 5.3.1 Intermolecular hydrogen bonding in alkanols
 - 5.3.2 Physical properties of alkanols
 - 5.3.3 Chemical properties of alkanols
 - 5.3.3.1 Oxidation reactions
 - 5.3.3.2 Elimination (dehydration) reactions
 - 5.3.3.3 Substitution reactions
 - 5.3.3.4 Iodoform test
 - 5.3.4 Laboratory test for alkanols
- 5.4 Summary
- 5.5 References/Further Reading/Web Resources
- 5.6 Possible Answers to Self-Assessment Exercise(s) within the Content



5.1 Introduction

In unit 4 of this Module 2, you were introduced to the Chemistry of alkanols, a homologous series characterised by the -OH functional group. Highlight centred on the classification of alkanols into primary, secondary or tertiary based on the position of the -OH group in the molecule. Also, 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 as pointed out in the previous unit.

In this unit, you will focus on the characteristics of alkanols and highlight the bonding, physical and chemical properties as well as the laboratory test for alkanols. Like all organic compounds, the behaviour of alkanols is controlled by the-OH functional group. The -OH is polar in nature.



5.2 Learning Outcomes

By 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

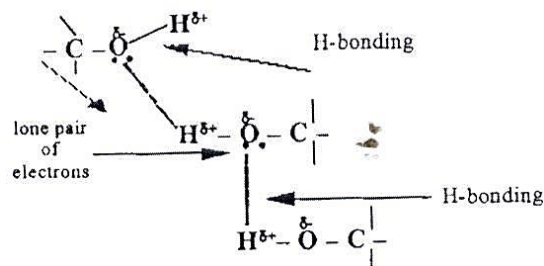


5.3 Characteristics Of Alkanols

Such characteristics of alkanols discussed here include the intermolecular hydrogen bonding, the physical properties, chemical properties and the laboratory test.

5.3.1 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. Remember that hydrogen bonding exists 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 leads 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 molecules and not as individual molecules existing in isolation.

5.3.2 Physical Properties of Alkanols

- (a) The physical properties of Drano's 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:

Compound	Molecular Mass	B. p °C
benzene (end	78	80
pentane tel112)	72	36
chloropropane (efi,C1)	79	47
Ethoxyethane (C41-1100)	74	35
*butanal (C4110)	72	76
*butm4-ol (C411,30)	74	118
*water (Hp)	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).

5.3.3 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

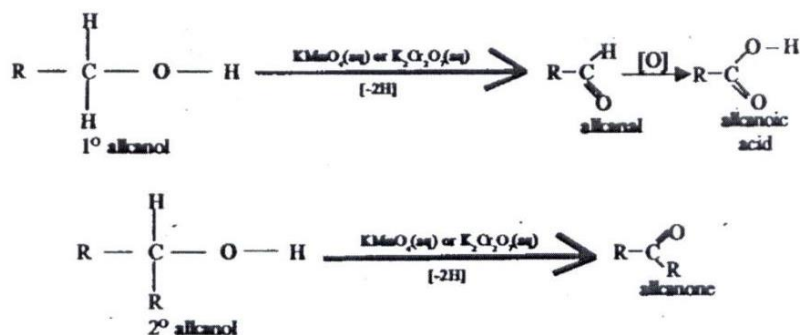
R-O⁻ ion is formed as intermediate i.e. $\text{ROH} \rightleftharpoons \text{RO}^- + \text{H}^+$

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.

5.3.3.1 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, discussion on them is beyond the scope of this programme. The oxidation can be achieved using oxidising agents such as KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$.

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 alkanonic 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 oxidized.

5.3.3.2 Elimination (dehydration) Reactions

Alkanols are readily dehydrated (removal of H₂O) on heating with conc, tetraoxaolphate (IV) acid to give alkenes. The best yields of alkenes are obtained at 170°C and by using excess concentrated H₂SO₄. This dehydration is only possible in molecules containing at least one hydrogen atom on the carbon atom next but one to the –OH group.

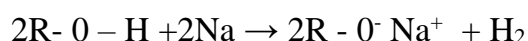


When the alkanol is present in excess, however, the dehydration occurs between two molecules to form another class of compounds called alkoxy alkanes.



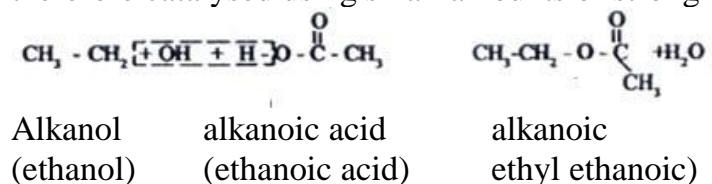
5.3.3.3 Substitution Reactions

- (a) Reaction with sodium: the acidic at of die -OH group shows up in their reaction with reactive metals, such as sodium, to liberate hydrogen gas.



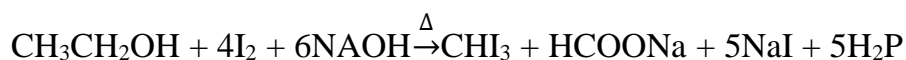
- (b) Esterification: alkanols react with alkanolic acids to form alkanooance a series of compounds to be studied in Unit 2 of Module 3.

Alkanoates are commonly called ester (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. H₂SO₄.



5.3.3.4 Iodoform Test

Ethanol and methanol react with a mixture of iodine and sodium hydroxide to form a yellow precipitate of triiodomethane CHI_3 (Iodoform).



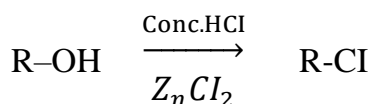
This reaction is used to confirm the presence of certain types of alkanols namely, methanol, ethanol and other alkanols with the $-\text{OH}$ group on a carbon atom adjacent to a methyl ($-\text{CH}_3$) group.

Self –Assessment Exercise 1

- i. Explain why alkanols exist as aggregate of molecules and not as isolated or individual molecules.
- ii. Give reason for alkanols being soluble in water. Why does the solubility in water decrease as you go up the series.

5.4 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).



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 'tertiary 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.

Self- Assessment Exercise 2

Given a mixture of primary, secondary and tertiary alcohols, how can you proceed to distinguish between the-various classes.



5.5 Summary

This unit examined the properties of alkanols and how the functional group $-\text{OH}$ plays an important role in the chemical reactivity. You have learned about the influence of hydrogen bonding on the physical

properties of alkanols. The hydroxyl group, though essentially neutral, can undergo a series of reactions in the presence of certain reagents. Example of such reaction is 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.

You will in the next unit, study the chemistry of alkanolic acids which will focus fundamentally, on such aspects as its sources, methods of preparation, physical/ chemical properties etc.



5.6 References/Further Reading/Web Resources

Baja, S. T. Teibo, B.O, Onwu G., and Obikwere, A. (2002). *Senior Secondary Chemistry-Textbook 3*. Lagos. Longman Publishers.

Osei Yaw Abaltio (2002) *4tew School, Chemistry*. Onitsha. Africanan Tap Publishers.

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Norman R.O.C. and Waddington D. J. "Modern Organic Chemistry"
Teweri IC S. Mehrotra V and Vishnoi, N. K. "Textbook of organic Chemistry".



5.6 Possible Answers to Self-Assessment Exercise(s) within the Contents

Self-Assessment Exercise

Answers to SAE 1

- 1) Alkanols exist as aggregate of molecules and not as isolated or individual molecules. This is because of the presence of hydrogen bonding which is considered to be a more stronger bond compared to the Vander Waal's forces even when both are known to hold molecules together.
- 2) Alkanols are soluble in water, but the solubility in water decrease as you go up the series. The reason for this is that the -OH group is polar in nature. The solubility decreases due to the addition of alkyl group which increases the molecular mass as you go down the series.

Answer to SAE 2

Ina order to distinguish between the various classes in a mixture of primary, secondary and tertiary alcohols, oxidation reaction is applied. Primary alkanols are oxidized in the presence of an oxidizing agent, such as KMnO_4 first to alkanal. Further oxidation converts the alkanal to alkanolic acid. Secondary alkanols are oxidized to alkanones and do not oxidize further. The tertiary alkanols are resistant to oxidization.

MODULE 3

Unit 1	Alkanoic Acids
Unit 2	Alkanoates
Unit 3	Fats, Oils and Amino Acids
Unit 4	An Introduction to Polymer Chemistry
Unit 5	Environmental Impact of the Chemical Industry Air and Water Pollution

UNIT 1 ALKANOIC ACIDS**Unit Structure**

- 1.1 Introduction
- 1.2 Learning Outcomes
- 1.3 Alkanoic Acids
 - 1.3.1 Sources of alkanoic Acids
 - 1.3.1.1 Natural sources
 - 1.3.1.2 General methods of preparation
 - 1.3.2 Characteristics of alkanoic acids
 - 1.3.2.1 Physical properties
 - 1.3.2.2 Chemical properties
 - 1.3.3 laboratory test for alkanoic acids
 - 1.3.4 Uses of alkanoic acids
- 1.4 Summary
- 1.5 References/Further Reading/Web Resources
- 1.6 Possible Answers to Self-Assessment Exercise(s) within the Content

**1.1 Introduction**

Welcome to Unit 1 of Module 3 in this course. In this unit, the search-light is beamed on alkanoic acids. 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 $n \geq 0$. They are sometimes called fatty acids because some of them are found in natural Fats oils.



1.2 Learning Outcomes

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

- name *using* the IUPAC nomenclature of simple alkanolic acid
- explain how hydrogen bonding affects the properties of alkanolic acids
- explain the methods of preparation and properties of alkanolic acids.



1.3 Alkanolic Acids

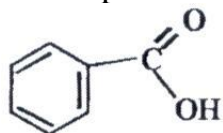
Alkanolic acids are groups of organic compounds which contain the -COOH group fixed to a hydrogen atom or to an alkyl group. The first five members of the alkanolic acid series are shown in Table 11.1 below:

Table 11.1

<i>Molecular Formula</i>	<i>Structural formula</i>	<i>IUPAC name</i>
CH ₂ O ₂	HCOOH	methanoic acid
C ₂ H ₄ O ₂	CH ₃ COOH	ethanoic acid
C ₃ H ₆ O ₃	CH ₃ CH ₂ COOH	propanoic acid
C ₄ H ₈ O ₂	CH ₃ CH ₂ CH ₂ COOH	butanoic acid
C ₅ H ₁₀ O ₂	CH ₃ CH ₂ CH ₂ CH ₂ COOH	pentanoic acid

Alkanolic acids are sometimes represented as R-COOH, where R = alkyl group. Older names specific to alkanolic 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 (aces 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

1.3.1 Sources of Alkanoic Acids

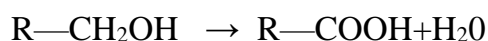
1.3.1.1 Natural Sources

Several members of the alkanolic 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 alkanolic acids, such as citric acid, tartaric acid, are known to be present in several types of fruits and vegetables.

3.1.1.2 General Methods of Preparation

(a) oxidation of primary alkanols

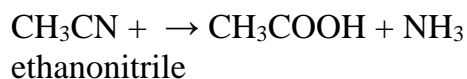
Primary alkanols are oxidised by oxidising agents, such as potassium tetraoxomanganate (VII), potassium heptaoxochromate (VI) to alkanolic acids. The reaction is usually carried out by refluxing excess of the oxidising agent with the Alkanol.



Note: [O] represents the oxidising agent

b) Hydrolysis of nitrile

The acid catalysed hydrolysis of nitrile with water, yields organic acid. For example ethanenitrile can be hydrolysed to ethanoic acid in the presence of small amount of tetraoxosulphate (VI) acid.



SELF-ASSESSMENT EXERCISE 1

- (a) Find out the names of the alkanolic acids present in lemons, grapes and Sour milk.
- (b) Write equation to show the preparation of butanoic acid from butanol.

3.1.2 Characteristics of Alkanolic Acids

3.1.2.1 Physical Properties

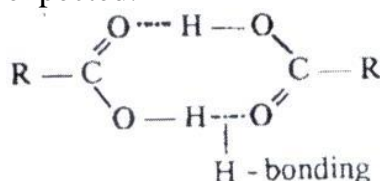
(a) Lower members of the alkanolic acid series, such as methanoic acid and ethanoic acid, are completely miscible in water. Solubility,

however, decreases with higher members of the series. In general, alkanolic 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 alkanolic acid molecule 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) Alkanolic acids have many 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 alkanolic 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 then an usually higher molecular mass than expected.



The hydrogen bonding between alkanolic acid molecules and water molecules, also partly explains their high solubility in water.

3.1.2.2 Chemical Properties

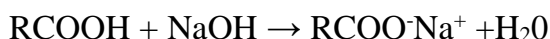
- (a) Acidity: Due to the polar nature of the bonds in alkanolic acids they ionise in water as follows:

However, alkanolic acids *are weaker* acids than mineral acids, such as hydrochloric acids, but they are very much stronger than alkanols. The strength of any alkanolic 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. **Alkanols, R- OH are weaker acids than alkanolic acids, R- COOH due to the following reasons:**

- (i) Formation of salts: Alkanoic acids react with bases and trioxocarbonate (iv) to form salts. Thus it
- (ii) reacts with trioxocarbonate (iv) and hydrogen trioxocarbonate(iv) to give salts of the acid with liberation of carbon(iv) oxide.

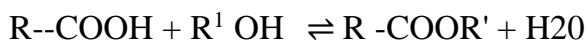


- (iii) reacts with bases or alkalis to form salts of the acids and water. This is an acid-base neutralization.



In the reaction above, alkanolic acids behave like mineral acids, exhibiting their acidic property. Alkanols do not undergo these reactions because they are weaker acids.

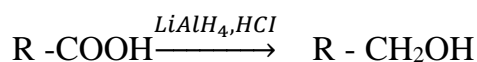
- (c) Formation of esters (esterification): Alkanoic acids react with alkanols to form alkanoates (esters), the H-atom of the carboxyl group is replaced by an alkyl group e.g.



alkanoic acid alkanol alkanoate water

The reaction is usually catalysed with mineral acids e.g. HCl or H₂SO₄. 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, LiAlH₄.



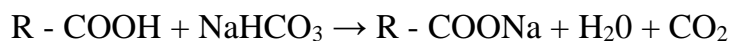
This reduction reaction is the reverse process of the oxidation of primary alkanols, used for producing alkanolic acids (see section 11.2.2 of this unit).

Self-Assessment Exercise

- 1) Can you explain why alkanols, R-OH are weaker acids than alkanolic acids, R-COOH?
- 2) Give the IUPAC name of the following compound

1.3.3 Laboratory Test for Alkanoic Acids

The presence of the alkanolic acid functionality is usually confirmed in the laboratory by utilizing its acidic properties. As stated in Section 3.2 of this unit, alkanolic acids react with trioxocarbonate(iv) or hydrocarbonates to liberate carbon(iv) oxide. This is the laboratory test for the COOH group present in all alkanolic acids. The evolution of the CO₂ gas is used as evidence of the presence of alkanolic acids



1.3.4 Uses of Alkanolic 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 alkanolic acids are used for making soaps and detergents.

Self- Assessment Exercise 3

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.



1.5 Summary

This unit focused on the chemistry of the - COOH functional group as present in the alkanolic 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. Their presence in living organisms and how they are made in the laboratory were highlighted. The polarity of the functional group and the influence of H-bonding on the physical properties of alkanolic acids were exploid. You should be acquainted with the acidic nature of the -OH bond of the *acids* and how it influences its characteristic reactions.



1.6 References/Further Reading/Web Resources

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.



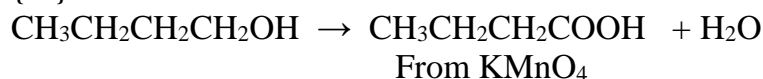
1.7 Possible Answers to Self- Assessment Exercise(s) within the Contents

Self- Assessment Exercise

Answers to SAE 1

- (a) Names of alkanolic acids present in lemons, grapes and sour milk:
 Alkanolic acid in lemon is **citric acid**
 Alkanolic acid in grape is **tartaric acid**
 Alkanolic acid in sour milk is **lactic acid**

- (b) Equation showing the preparation of butanoic acid from butanol:
 {O}

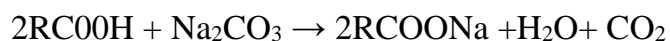


Answer to SAE 2

Why alkanols, R-OH are weaker acids than alkanolic acids, R- COOH?

1.

- (i) formation of salts: Alkanolic acids react with bases and trioxocarbonate
- (ii) to form salts. Thus it
- (iii) reacts with trioxocarbonate
- (iv) and hydrogen trioxocarbonate
- (v) to give salts of the acid with liberation of carbon oxide.



- (i) reacts with bases or alkalis to form salts of the acids and water. This is an acid-base neutralization.

2. The IUPAC names of the compounds drawn in Self Assessment Exercise 2

- (i) 2 – methyl butanoic acid
- (ii) 2, 2 – dimethyl propanoic acid

Answer to SAE 3

Equations for the reactions

- (i) ethanoic acid with calcium trioxocarbonate (iv)
 $2\text{CH}_3\text{COOH} + \text{CaCO}_3 \rightarrow (\text{CH}_3\text{COO})_2\text{Ca} + \text{H}_2\text{O} + \text{CO}_2$
- (ii) ethanoic acid with calcium hydroxide
 $2\text{CH}_3\text{COOH} + \text{Ca}(\text{OH})_2 \rightarrow (\text{CH}_3\text{COO})_2\text{Ca} + 2\text{H}_2\text{O}$
- (iii) ethanoic acid with ethanol
 $\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$

UNIT 2 ALKANOATES

Unit Structure

- 2.1 Introduction
- 2.2 Learning Outcomes
- 2.3 Alkanoates
 - 2.3.1 Preparation of Alkanoates - Esterification
 - 2.3.2 General Characteristics of Alkanoates
 - 2.3.2.1 Physical Properties
 - 2.3.2.2 Chemical Properties
 - 2.3.3 Uses of Alkanoates
- 2.4 Summary
- 2.5 References/Further Reading/Web Resources
- 2.6 Possible Answers to Self-Assessment Exercise(s) within the Content



2.1 Introduction

In the last unit, the chemistry of the COOH functional group as present in the alkanoic acid series was discussed. Alkanoic acids form a variety of important derivatives one of which is the alkanoates. The common name for alkanoates is esters. 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 fat from cocoa butter, palm oil from oil palm tree, groundnut oil from groundnut, castor oil from castor plant etc. Alkanoates are used for cooking and ready source of energy and useful in the manufacture of soaps. Lower alkanoates are known for their characteristic sweet strong aroma and are found in many flower, and fruits e.g. methyl butanoate in pineapple, pentyl ethanoate in banana. The aroma of alkanoate is sometimes used to confirm their presence. Also examined in the unit is the preparation of alkanoates, properties and uses of alkanoates.



2.2 Learning Outcomes

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

- identify and name 3 alkanoates based on their formula
- mention some of the natural sources of alkanoates
- explain esterification as the preparatory route to alkanoate
- discuss the characteristics of alkanoates
- Examine some of the uses of alkanoates.



2.3 Chemistry of Alkanoates

Alkanoates are formed from alkanolic acids by replacing the - OH of alkanolic acids with -OR group (where R = alkyl group). They are represented by the general formula, $RCOOR^1$ or $C_nH_{2n-1}COOC_nH_{2n-1}$ (where $n \geq 0$).

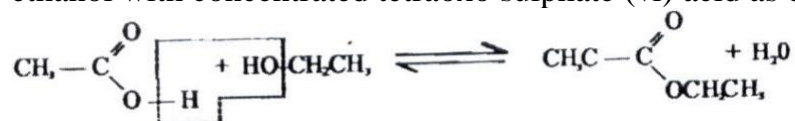
The IUPAC nomenclature for members of the series are derived from the alkanols (ROH) and the alkanolic acid (RCOOH) from which the alkanoates are formed. The alkanolic portion, R^1 is named first as alkyl and a space is left, which is followed by the alkanolic acid portion R^1 COO. named as alkanoate. For example.

- (a) CH_3COOCH_3 , = methylethanoate indicating that it is formed from methanol as the alkanol and ethanoic acid (as the alkanolic acid)
- (b) $CH_3CH_2COOCH_2CH_3$ = ethyl propanoate indicating that it is formed from ethanol (as the alkanol and propanoic acid (as the alkanolic acid).

2.3.1 Preparation of Alkanoates: Esterification

Recall from unit 1, the esterification process. This process is the principal route for making alkanoates. The direct reaction of alkanolic acid and alkanols in the presence of catalytic 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.



Ethanoic acid

ethanol

ethyl ethanoate

Esterification is an equilibrium process, and for 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.

SELF- ASSESSMENT EXERCISE 1

- i) Write the structure and name of the alkanoates with the general formula $C_4H_8O_2$
- ii) describe the esterification process for the preparation of ethyl ethanoate

2.3.2 General Characteristics of Alkanoates

The physical and chemical properties of alkanoates are examined here.

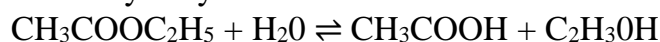
2.3.2.1 Physical Properties

Alkanoates are cold lipids or solids, sparingly soluble in water. Most of them have a characteristic fragrant odour or sweet smell and many of them occur naturally. The fragrance in flowers and fruits attracts the insects and animals which are responsible for the pollination of flowers and dispersal of seeds.

2.3.2.2 Chemical Properties

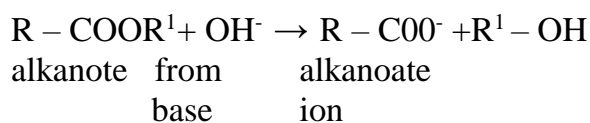
Alkanoates are generally not very reactive but can be hydrolysed to their precursor alkanolic acids and alkanols; and reduced to primary alkanols.

- a) Hydrolysis of alkanoates: Alkanoates are hydrolysed very slowly by boiling with water to give the component alkanolic acids and alkanols. The reaction can be made faster by catalyzing the hydrolysis with acids or bases.



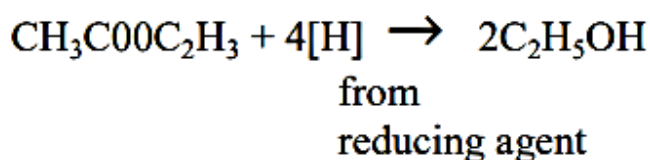
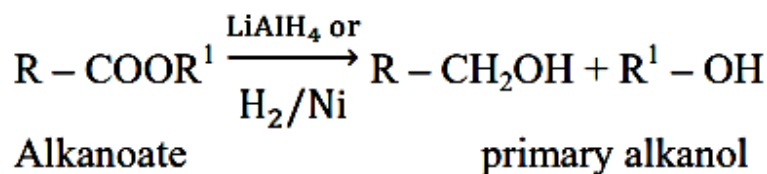
The acid – catalyzed process is the reverse of esterification and, as it is reversible, an excess of acidic solution is required to give a good yield of alkanoates.

The base–catalysed hydrolysis 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.



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 alkanolic acid. Lithium aluminum hydride and catalytic hydrogenation are both effective catalysts for reduction



2.3.3 Uses of Alkanoate

- (a) A large number of alkanoates are used as perfume and flavourings. For example ethyl methanoate obtained from rose; 3-methylbutyl ethanoate obtained from pear, and ethyl butanoate obtained from pineapple are all used in this way for perfumes and few flavouring
- (b) Ethyl ethanoate is a good solvent
- (c) Certain useful *waxes* are composed mainly of alkanoates e.g. beeswax, $\text{C}_{15}\text{H}_{31}\text{COOC}_2\text{H}_5$
- (d) Alkanoates of trilydric alkanols and alkanolic acids are of great importance in making soap and propane 1,2,3-triol (glycerol).

SELF- ASSESSMENT EXERCISE 2

- 1) write the equation for the hydrolysis of methyl ethanoate
- 2) Outline any 3 uses of alkanoates



2.4 Summary

This unit focused on the chemistry of alkanoates and the importance of this class of compound as fragrant; and flavouring agent. The odour of flowers and fruits are largely due to the alkanoates present in them as discussed in the unit. In addition, you should be familiar with the processes of esterification and saponification. You should be able to outline the numerous uses and importance of alkanoates. Alkanoates are

the basic raw material for the manufacture of soaps which will be discussed elaborately in the next unit.



2.5 References/ Further Readings/Web Resources

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.

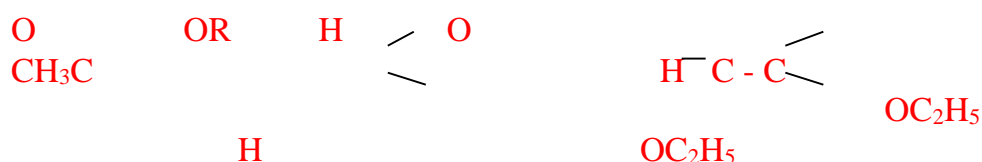


2.6 Possible Answers to Self – Assessment Exercises within the content

Self- Assessment Exercises

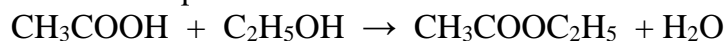
Answers to SAE 1

- 1) The name and structure of the alkanoate with the formula $C_4H_8O_2$



The name is **ethyl methanoate**

- 2) Ethyl ethanoate is obtained when ethanol is passed through ethanoic acid in the presence of H_2SO_4 as catalyst. The chemical reaction's equation is shown below:



Answer to SAE 2

- 1) Equation for the hydrolysis of methyl ethanoate:
 $CH_3COOCH_3 + H_2O \rightarrow CH_3COOH + CH_3OH$
- 2) Uses of alkanoates
- (a) A large number of alkanoates are used as perfume and flavourings. For example ethyl methanoate obtained from room; 3-methylbutyl ethanoate obtained from pear, and ethyl butanoate obtained from pineapple are all used in this way for perfumes and few flavouring
- (b) Ethyl ethanoate is a good solvent
- (c) Certain useful *waxes* are composed mainly of alkanoates e.g. beeswax, $C_{15}H_{31}COOC_{16}H_{33}$
- (d) Alkanoates of trilydric alkanols and alkanolic acids are of great importance in making soap and propane 1,2,3-triol (glycerol).

UNIT 3 FATS, OILS AND AMINO ACIDS

Unit Structure

- 3.1 Introduction
- 3.2 Learning Outcomes
- 3.3 Fats, Oils and Amino acids
 - 3.3.1 Sources of Fats and Oils
 - 3.3.2 Hardening of Oils
 - 3.3.3 Soap Manufacture - Saponification
 - 3.3.4 Detergents
 - 3.3.5 Uses of Fats and Oils
 - 3.3.6 Tests for Fats and Oils
- 3.4 Amino Acids
- 3.5 Summary
- 3.6 References/Further Reading/Web Resources
- 3.7 Possible Answers to Self- Assessment Exercise(s) within the Contents



3.1 Introduction

Welcome to this unit which focuses on Fats, Oils and Amino acids. Recall that the last unit dwelt on alkanooates of which fats and oils are mentioned as good examples. Fats and oil are spotlighted as naturally occurring alkanooates formed from the trihydric alkanol, propane – 1,2,3- triol (commonly known as glycerol) and long-chain alkanooic acids (commonly known as fatty acids) with C_{12} to C_{24} carbon atoms. Apart from discussing the sources and uses of fats and oils, searchlight was beamed on the chemistry of amino acids. Pay rapt attention and make maximum benefit from the unit's content.



3.2 Learning Outcomes

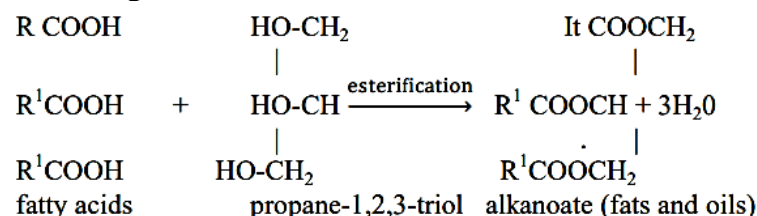
By the end of this unit, you should be able to:

- identify fats and oils as alkonooates.
- 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 oil
- compare properties of soap and detergent.
- explain the functional groups in amino acids.



3.3 Chemistry of Fats, Oils and Amino acids

Fats and oil have been earlier described as naturally occurring alkanooates formed from the trihydric alkanol, propane – 1,2,3- triol (commonly known as glycerol) and long-chain alkanooic acids (commonly known as fatty acids) with C₁₂ to C₂₄ 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



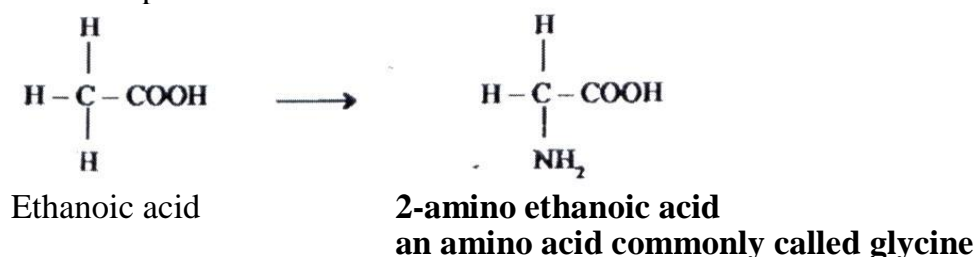
This esterification process occurs naturally in plants and animals to give fats and oils, which are generally referred to as lipids. Fats are solids, at room temperature, usually of animal origin while oil are liquids, at room temperature, mainly of plant origin. The fatty acids commonly found in their lipids can be subdivided into saturated fatty acids (have no double bond in 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):

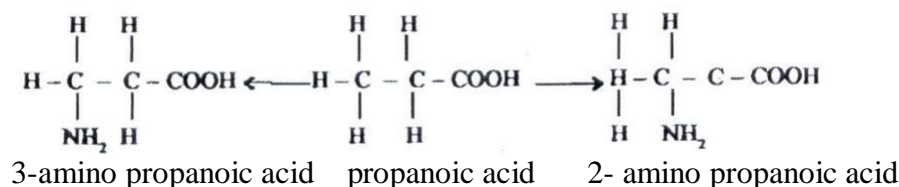
Table 13.1

Common Name	Source	Formula	IUPA nomenclature
Palmitic acid	oil palm	CH ₂ (CH ₂) ₁₄ COOH	hexadecanoic acid
Stearic acid	tallow (animal fat)	CH ₂ (CH ₂) ₁₆ COOH	octadecanoic acid
Oleic acid	olive or peanut oil	CH ₂ (CH ₂) ₇ CH=CH(CH ₂) ₇ COOH	Ociadec-9-enoic acid
Linolic acid	vegetable oil	CH ₂ (CH ₂) ₄ CH=CHCH ₂ CH=CH(CH ₂) ₇ COOH	Octadeca-9,12-dienoic acid

Amino acids are substituted organic acids in which hydrogen atom(s) in the alkyl group has been replaced by amino group (-NH₂ group).

For example





Amino acids are important substituted alkanolic acids for they are the component parts of proteins, which occur widely in all plants and animals. Proteins will be part of our discussion in Unit 14.

3.3.1 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 fats or oil to rise to the surface of water. Tallow is obtained in this way from beef or mutton (remember the substance 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.

	Fats or oils	Natural source	Producer countries
1.	Groundnut oil	Groundnut	Nigeria, Gambia
2.	Palm oil	Oil palm	Nigeria, Malaysia
3.	Coconut oil	Cocnut tree	Nigeria, Malaysia
4.	Cotton seed oil	Cotton	Nigeria, USA, Egypt
5.	Soya been oil	Soya tree	Nigeria, USA
6.	Castor oil	Castor seed	Nigeria, Malaysia
7.	Palm kenel 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

3.3.2 Hardening of Oils

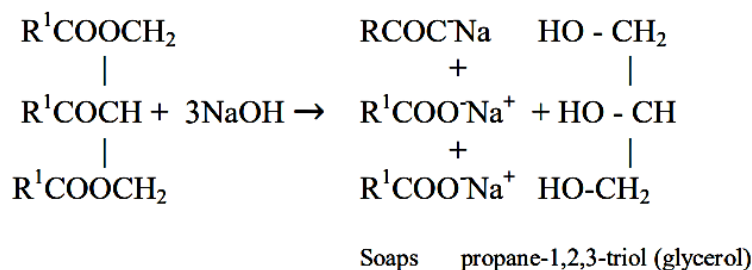
Vegetable oils can be changed to fats by catalytic hydrogenation (addition of hydrogen to the double bond present in the hydrocarbon chain of the oil). Margarine (e.g. Blue Band) is made by this process. The oils, usually from plants such as oil palm, groundnut and soya-been are heated to about

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.

3.3.3 Soap Manufacture: Saponification

Recall from unit 2 of module 3, 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 is used to determine the type of soap obtained.

Fat or + caustic alkali $\xrightarrow{\text{saponification}}$ soaps + propane-1,2,3-triol

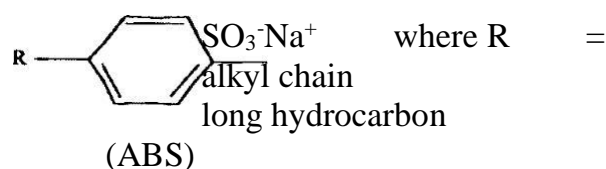


3.3.4 Detergents

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 3.3.3

Soapless detergents *are* the alkyl benzene sulphonates, abbreviated as ABS.

A soapless detergent molecule is



Like soap, soapless detergents are sodium salts of sulphonic acid to which an aromatic - alkyl chain is attached. Soapless detergents are the more flavoured cleansing agents nowadays than the soapy detergents. They are available as liquids or solids and the raw materials for their manufacture are petrochemicals obtained from refined 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 stable for washing acid-sensitive fabrics
- (c) they have wider application, in terms of removing various types of stains, than soapy detergent.

SELF- ASSESSMENT EXERCISE 1

- i. explain the following:
 - a. soap manufacture by saponification
 - b. influence of pH on the structure of amino acids
- ii. Write briefly on detergents and their advantages over soap.

3.3.5 Use of Fats and Oils

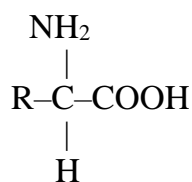
- (a) As foodstuffs: most fats are consumed as food; together with carbohydrates, they provide source of energy for animals.
- (b) In making soaps the fats and oils commonly used for making soaps are tallow, coconut oil, bleached palm oil, soya bean oil and olive oil.
- (c) In making candles: when tallow 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 manufacture of creams, medicine.
- (e) In making paints: linseed oil is used for making oil paints.
- (f) in making margarine: margarine is made by hardening oils and is a good substitute for butter.

3.3.6 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.

3.4 Amino Acids

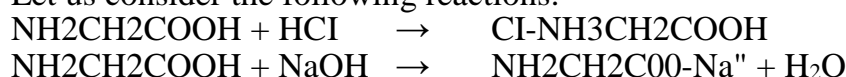
Amino acids are derivatives of alkanolic acids in which the hydrogen of the alkyl group is replaced by the amino group (-NH₂). Each amino acid contains two functional groups, the carboxylic acid group (-COOH) and the amino group (-NH₂). It therefore has a general structure as follows:



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 α -amino acids, more than 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 -NH₂ group. Amino acids can therefore react with acids or bases to form salts.

Let us consider the following reactions:

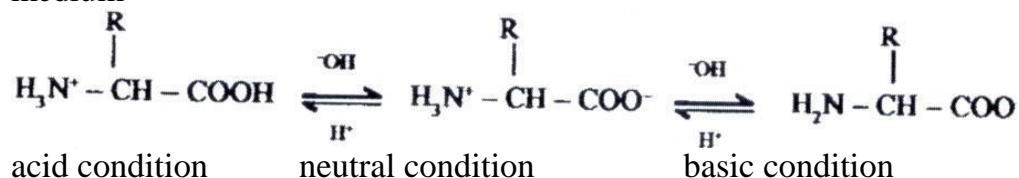


In neutral solution, amino acids exist as dipolar ions (zwitterion) and this polar structure accounts for their high melting point (e.g. amino-ethanoic acid melts at 235°C) solubility in water and insolubility in organic solvent.

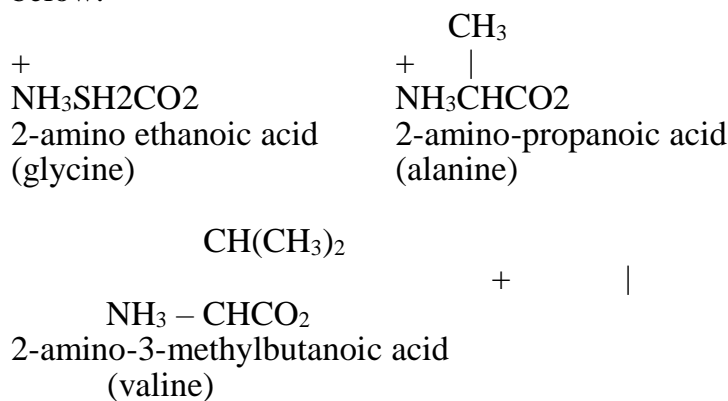


dipolar ion

Amino acids exists in three different ways depending as the pH of the medium



Examples of these acids, with their anion and IUPAC names; are given below.



SELF ASSESSMENT EXERCISE 2

Give the IUPAC name of the following

- | | |
|------|---|
| i) | $(\text{CH}_3)_2\text{CHCH}_2 - \text{CH}(\text{NH}_2) - \text{COOH}$ |
| ii) | $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3) - \text{CH}(\text{NH}_2) - \text{COOH}$ |
| iii) | State the relationship between the two structures |



3.5 Summary

This unit discussed fats and oils as naturally occurring alkalinites obtained from fatty acids and trihydric alkanols. The various sources of these classes of alkanoates also known as lipids were highlighted. Furthermore, also focused on was how fats and oils can be converted into margarine and soap. You need to be acquainted with the various types of detergents and the advantages of soapless detergent and soapy detergents. You were introduced to amino acids and the polar nature of their structure, also described as the basic unit of protein. The unit that follows shall explain more about the chemistry of proteins.



3.6 References/Further Reading/Web Resources

Bajah, S.T Teibo B.O, Onwu G., aid Obikwere, A. (2002). *SeniorSecondary Chemistry-Textbook 3*. Lagos. Longman Publishers.

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



3.7 Possible Answers to Self- Assessment Exercise(s) within the Contents

Self- Assessment Exercise

Answers to SAE 1

(a) Explain

(i) Soap Manufacture by Saponification:

Saponification is the alkaline hydrolysis of alkanoates to give sodium and potassium salt of the component fatty acid and propan 1, 2, 3 – triol. The component salt formed is referred to as soap. Sodium chloride is added to separate the salt from the mother liquor. Other additives such as perfumes, dyes are added to give the variety of soaps.

(ii) Influence of pH on the structure of amino acids:

In aqueous solution, amino acids are neutral to litmus paper but the presence of $-\text{COOH}$ group make them act as acid, as well as bases with the presence of $-\text{NH}_2$.

(b) Brief note on detergents and their advantages over soap:

Detergents are alkyl benzene sulphonates abbreviated as ABS. Their advantages over soap include the following:

- i) They are not affected by hard water and so, do not form scum with hard water. It can be used for all types of water.
- ii) They are neutral in water where as soapy detergents are slightly alkaline in water.
- iii) They have wider applications in terms of removing various types of stains compared to soapy detergents.

Answers to SAE 2

1. The IUPAC name of the following:

i) $(\text{CH}_3)_2\text{CH}_2\text{CH}_2 - \text{CH}(\text{NH}_2) - \text{COOH}$
2 amino – hexanoic acid

ii) $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3) - \text{CH}(\text{NH}_2) - \text{COOH}$
3 – methyl, 2 – amino pentanoic acid

2. The relationship between the two structures:

The structures are dipolar in nature comprising an amino group and the carboxyl group.

UNIT 4 AN INTRODUCTION TO POLYMER CHEMISTRY

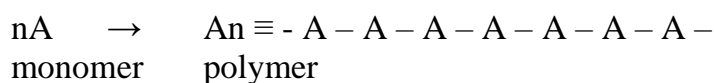
Unit Structure

- 4.1 Introduction
- 4.2 Learning Outcomes
- 4.3 Chemistry of Polymer
 - 4.3.1 Polymerisation Processes
 - 4.3.1.1 Addition Polymerisation
 - 4.3.1.2 Condensation Polymerisation
 - 4.3.2 Plastics and Resins
 - 4.3.3 Natural Polymers
 - 4.3.3.1 Carbohydrates
 - 4.3.3.2 Proteins
 - 4.3.4 Synthetic Polymers
- 4.5 Summary
- 4.6 References/Further Reading/Web Resources
- 4.7 Possible Answers to Self-Assessment Exercise(s) within the Content



4.1 Introduction

Welcome to Unit 4 of Module 3 which focuses on Polymer chemistry. From the discussion in the last unit, protein, a polymer has amino acids as the basic units. 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.



The Unit also focuses on polymerization processes, plastics and resins, natural polymers and synthetic polymers alongside their uses.



4.2 Learning Outcomes

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

- define polymerisation
- distinguish between natural and synthetic polymers.
 - outline the different processes involved in polymerisation and the types of polymers obtained.
 - recall different types of monomers and their corresponding polymers.
 - mention the uses of different types of polymers.



4.3 Chemistry of Polymer

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

Polymerization: **addition polymerisation** and **condensation polymerisation**.

Some typical monomers and the corresponding polymers are listed below:

<i>Monomer</i>	<i>polymer</i>
ethene	polythene
vinyl chloride	polyvinyl chloride
amino acids	proteins
glucose	starch

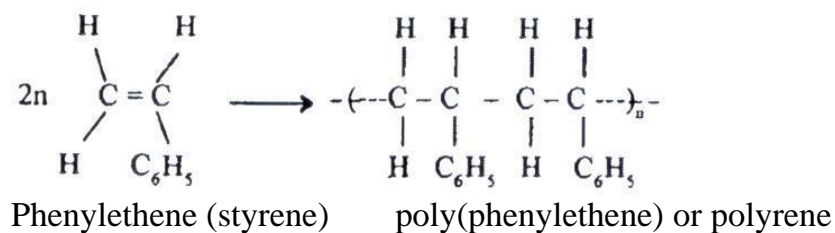
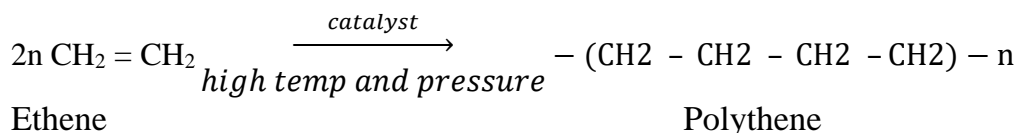
Polymers can be naturally-occurring e.g. protein, rubber, starch and cellulose, or synthesized in the laboratory e.g. polythene, nylon 66, polyvinyl chloride and terylene. The naturally occurring polymers are called natural polymers while the man-made polymers are called synthetic polymers.

4.3.1 Polymerisation Processes

The polymerisation processes for discussion include addition, polymerisation and condensation polymerisation

4.3.1.1 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, for example, reacts to form addition polymer.



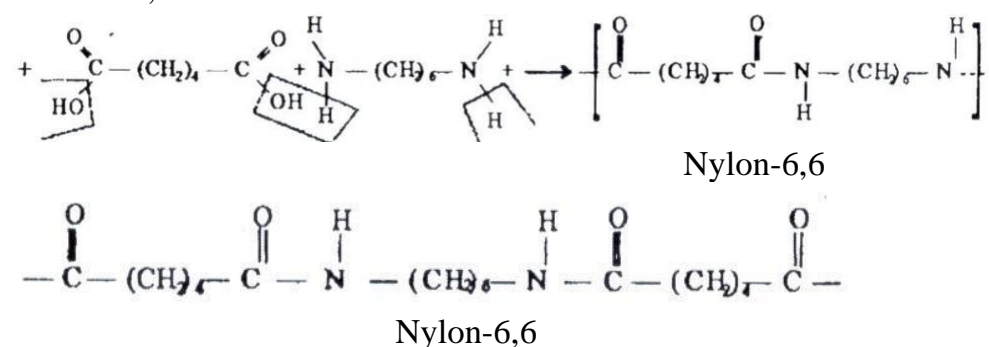
Several types of this polymer *and* their uses are listed in Table 14.1

Table 4.1

1.	Manager $\text{CH}_2 = \text{CH}_2$ (ethane)	Polymer $[\text{CH}_2 - \text{CH}_2]_n$	Common name Polyethene	Uses Plastic bottles, pipes, toys and packaging material
2.	$\text{CH}_2 = \text{CHCl}$ (VINYL CHLORIDE)	$[\text{CH}_2 - \text{CH}_2]_n$	Polyvinyl Chloride (PVC)	Insulating material, pipe film, coatings and automobile parts
3.	$\text{CF}_2 = \text{CF}_2$ (tetrafluoro-ethene)	$[\text{CH}_2 - \text{CH}_2]_n$	Poly (tetrafluoro- ethene) (Teflon)	High-temperature resistant rubber stopcocks, gaskets
4.	$\text{CH}_2 = \text{CH}(\text{OCOCH}_3)$ (vinyl acetate)	$[\text{CH}_2 - \text{CH}_2]_n$ OCOCH_3	Polyvinyl Acetate (PVA)	adhesives, emulsion pairs
5.	$\text{CH}_2 = \text{CHC}_6\text{H}_5$ (styrene)	$[\text{CH}_2 - \text{CH}]_n$ C_6H_5	Polystyrene	Utensils, foam Toys and packaging

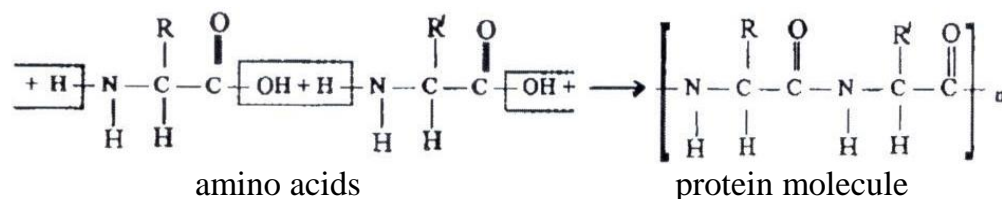
4.3.1.2 Condensation polymerisation

Condensation polymerization occurs 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 hexadecanoic (adipic) acid and hexane -1,6-diamine.



Nylon-6,6 is an example of a copolymer. When two different monomers, e.g. ethene and propene, hexadecanoic 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.



When the R and R' are different then the protein molecule is a co-polymer. Table 4.1 shows some condensation polymers and their uses.

Table 4.1

	<i>Monomer</i>	<i>polymer</i>	<i>Uses</i>
1.	hexanedioic acid + hexamethylenediamine	Nylon-6,6	Fabric, tiles, tyre cord
2.	Benzene-1,4 dicarboxylic acid + 1,2-ethanediol	Terylene (polyester)	cloths, recording tapes. tyre cord.
3.	amino acids	proteins	structural materials and biochemical functions for living organisms
4.	Glucose	starch (carbohydrate)	source of energy for living organisms

SELF- ASSESSMENT EXERCISE (SAE) 1

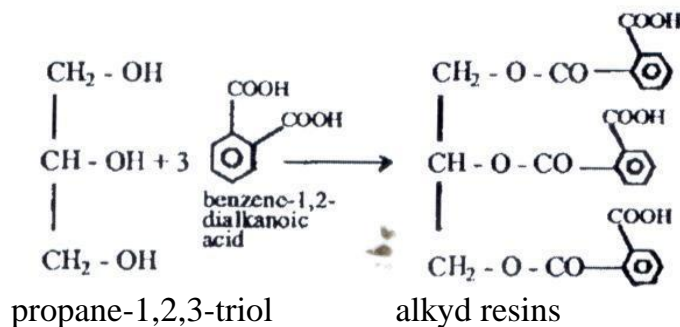
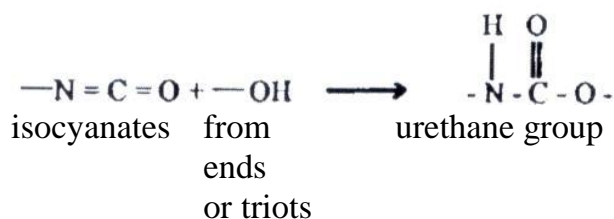
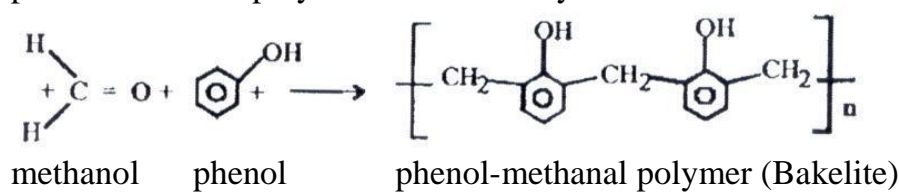
1)	Which of the following compounds can undergo addition polymerisation?
	a) Propene b) Hexane c) Benzene
d)	Butadiene
2)	List ten different polymers and give the name and structures of the monomers.

4.3.2 Plastics and Resins

Plastics are high molar mass synthetic (*man-made*) polymers that can be deformed and molded into various shapes, at high temperatures. Linear polymers or copolymers have only weak van der Waals 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 molded 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 cross-linked 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. Example of thermosetting plastics are phenol-methanal polyurethanes and alkyd resins.



Thermosetting plastics are used to make articles such as electric plugs and switches, telephones, wireless and television cabinets, lavatory seats, at pays 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 rains 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.

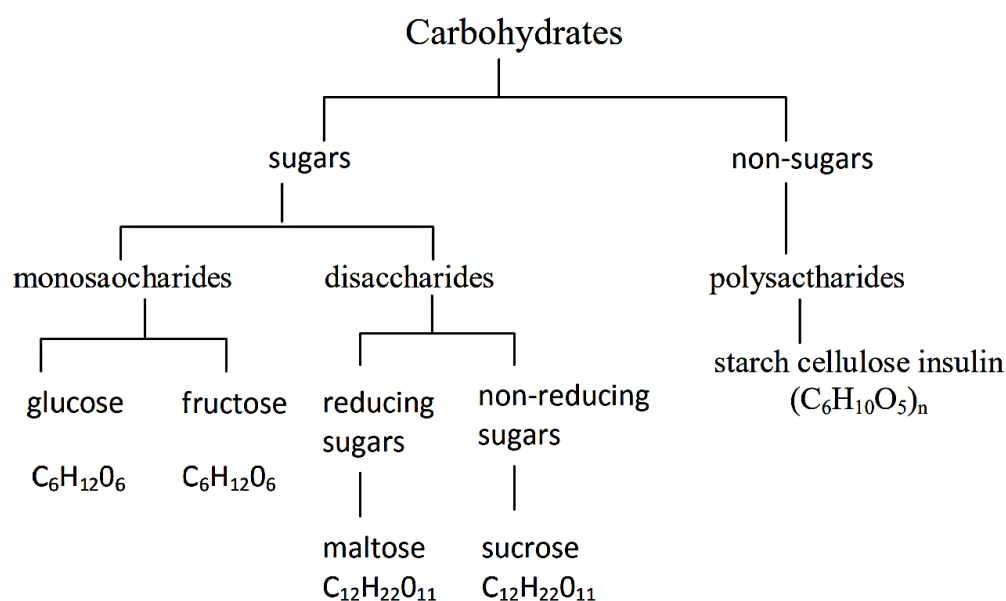
4.3.3 Natural Polymers

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.

4.3.3.1 Carbohydrates

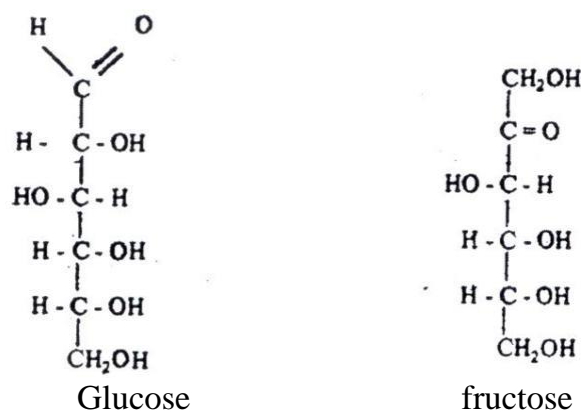
Carbohydrates *are* large groups °compounds with the molecular formula which can be written as $(C_x(H_2O)_y)$; such a formula does at, however, indicate the correct structural arrangement. All carbohydrates are composed of carbon, hydrogen and oxygen; among which includes sugars, starches and celluloses.

Carbohydrates can be classified as shown below



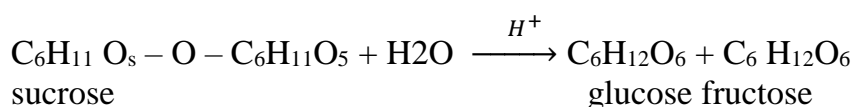
Sugars are crystalline substances with sweet taste and are soluble in water. They are generally classified into the monosaccharides and the disaccharides. Non-sugars are complex molecules with relatively larger molar mass than the simple sugars.

(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 monosaccharides are glucose, which is an aldose (because it contains an aldehyde, -CHO group) and fructose, which is a ketose (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.

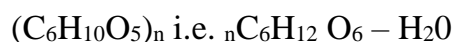


(ii) Disaccharides: These are carbohydrates containing twelve carbon atoms per molecule and having the molecular formula $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. They are formed by the elimination of water molecule from two C_6 monosaccharide molecules i.e. $2\text{C}_6\text{H}_{12}\text{O}_6 - \text{H}_2\text{O} = \text{C}_{12}\text{H}_{22}\text{O}_{11}$. 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.



(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



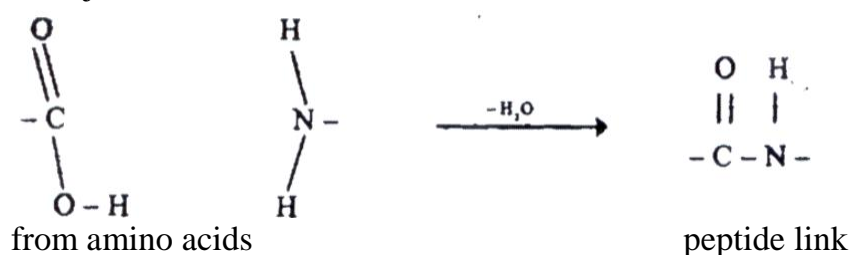
where $n = \text{very large number}$

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 by 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.

4.3.3.2 Protein

Protein is a group of complex polymers which occurs very widely in all planet-and inns. 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 -NH₂ group of an adjacent acid i.e.



Proteins we therefore polymers whose monomer is amino acids joined together by the peptide link.

(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 product of protein hydrolysis. The protein, insulin, for example, yields sixteen different amino-acids. on hydrolysis

(b) Uses of proteins in living systems: Simple mains 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.

4.3.4 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 4.1 are synthetic polymers. Several condensation polymers are also man-made, among which include polyesters (terylene) and polyamides (Nylon -6,6) - Table 4.2; synthetic rubber.

Self-Assessment Exercise 2

Define the following terms with suitable 'statue' representation:

- a) Polymerisation
- b) Disaccharide
- c) Peptide link

**4.4 Summary**

This unit focuses on polymers, as molecules made up of repeating structural units of Monomers. The unit discussed the sources, method of production, types and uses of polymers which can be natural or synthetic (man-made), all of which are made by either addition or condensation polymerisation process. You are also acquainted with the importance of polymers to living organisms and the diverse applications of polymers.

**4.5 References/Further Reading/Web Resources**

Bajah, S.T., Teibo, B.O., Onwu, G. and Obikwere, A. (2002). *Senior Secondary Chemistry - Textbook 3*. Lagos: Longman Publishers.



4.6 Possible Answers to Self-Assessment Exercises within the content.

Self-Assessment Exercises

Answers to SAE 1

- The compound that can undergo addition polymerization among the listed options is **propane**.
- Ten different polymers and the names and structures of the corresponding monomers:**

Monomer	Polymer
Ethene $\text{CH}_2 = \text{CH}_2$	Polyethene
Vinyl chloride $\text{CH}_2 = \text{CHCl}$	Polyvinyl chloride
Tetrafluoro-ethene $\text{CF}_2 = \text{CF}_2$	Polytetrafluoroethene (Teflon)
Vinyl acetate $[\text{CH}=\text{CH}(\text{OCOCH}_3)]$	Polyvinyl acetate PVA
Styrene $\text{CH}_2 = \text{CHC}_6\text{H}_5$	Polystyrene
Methyl – 2 – methyl	Polymethyl – 2 – methyl
Propenoate $\text{CH}_2 = \text{CCH}_3\text{COOCH}_3$	Propenoate or Perspex
Natural rubber (2-methylbuta-1,3 diene)	Poly 2-methylbuta -1, 3 diene
Benzene -1, 4 dialkanoic acid +1,2-ethandiol	Polyester (Terylene)
Amino acids	Proteins
Glucose	Starch

Answers to Self-Assessment Exercise 2

Definition of terms listed with suitable representation:

- Polymerisation is the process by which many simple molecules (monomers) join together to form giant molecules (polymer) of a higher molar mass.
- Disaccharides are carbohydrates containing twelve carbon atoms per molecule and having the molecular formula $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. They are formed by the elimination of water molecule from two six carbon monosaccharides.
- Peptide link is the process by which amino acids join together to form proteins

UNIT 5 ENVIRONMENTAL IMPACT OF THE CHEMICAL INDUSTRY (AIR AND WATER POLLUTION)

Unit Structure

- 5.1 Introduction
- 5.2 Learning Out
- 5.3 Air and Water
 - 5.3.1 Water pollution
 - 5.3.1.1 Phosphates
 - 5.3.1.2 Industrial discharges
 - 5.3.1.3 Pesticides
 - 5.3.1.4 Hot water
 - 5.3.2 Air pollution
 - 5.3.2.1 Solid particles
 - 5.3.2.2 Oxides of carbon
 - 5.3.2.3 Oxides of nitrogen and sulphur
 - 5.3.2.4 Hydrocarbons
 - 5.3.2.5 Chlorofluorocarbons
 - 5.3.3 Biodegradable and non-biodegradable pollutants
 - 5.3.4 Pollution control
- 5.4 Summary
- 5.5 References/Further Reading/Web Resources
- 5.6 Possible Answers to Self-Assessment Exercise(s) within the Content



5.1 Introduction

You are welcome to the last unit of this course which subject-matter all along centred on Organic chemistry and carbon compounds. You must have been acquainted with chemical facts and their relevance to living organisms. Chemistry has affected our lives 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 become 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? In this unit, the environmental impact of the chemical industry is discussed with particular emphasis on air and water pollution.



5.2 Learning Outcomes

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

- show the inter-relation between chemistry and the environment
- identify sources and effects of pollutants
- discuss control measures for reducing the level of pollution
- explain the greenhouse effect and depletion of the ozone layer
- examine biodegradable and non-biodegradable pollutants.

5.3 Water and air pollution- environmental impact of 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 purpose; 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 too 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.

5.3.1 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.

5.3.1.1 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 utilized 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.

5.3.1.2 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, retra-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.

5.3.1.3 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.

5.3.1.4 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 5.3.1.1

SELF ASSESSMENT EXERCISES 1

- 1) List and discuss briefly any 3 sources and nature of air pollution.
- 2) In one sentence, outline the basic attribute of pure and drinkable water.

5.3.2 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.

5.3.2.1 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 become 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.

5.3.2.2 Oxides of carbon

Incomplete combustion of fuel leads to the formation of carbon (II) oxide (CO) which is a poisonous *gas*. With modernization and increase in 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 a reduction in blood oxygen. Carbon (II) oxide gas causes dizziness, headaches, fatigue and can cause death at high concentrations.

Carbon(IV) oxide (CO₂) is the principal product of the combustion of fossil fuel. The increase in the *use* of fossil fuels as a 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 rays 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 coastal regions and islands on earth will then be submerged by the increase in ocean water level.

5.3.2.3 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 NO₂, 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.

5.3.2.4 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.

5.3.2.5 Chlorofluorocarbons

Chlorofluorocarbons or CFCs are man-made chemicals e.g. freon, which are used as propellants for spray cans like Shalton, 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, O₃, 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 Antarctic. 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.

SELF ASSESSMENT EXERCISE 2

- 1) Outline any 4 main sources of water pollution.
- 2) Write short note on the depletion of ozone layer.
- 3) Explain the cause and consequence of green house effect.

5.3.3 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.

5.3 4Pollution 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) Afforestation 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

SELF- ASSESSMENT EXERCISE 3

- 1) Explain succinctly biodegradable and non-biodegradable pollutants mentioning at least two examples of each.
- 2) Enumerate 5 control measures aimed at reducing the level of pollution.



5.4 Summary

This unit discussed the effect of water and air pollution on our environment. It has shed light on the sources and nature of chemicals that lead to pollution in water bodies and the air. 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, animals 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.



5.5 References/Further Reading/Web Resources

Bajah, S.T., Teibo, B.O., Onwu, G. and Obikwere, A. (2002). *Senior Secondary Chemistry Textbook 3*. Lagos: Longman Publishers.

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5.6 Possible Answers to Self- Assessment Exercise(S) Within The Contents

Self- Assessment Exercise

Answers to SAE 1

1) Sources of air pollution

- (i) Solid particles
- (ii) Oxides of carbon
- (iii) Oxides of nitrogen
- (iv) Oxides of sulphur
- (v) Hydrocarbons
- (vi) Chlorofluorocarbons

- 2) Pure and drinkable water is normally an odourless, tasteless and colourless liquid and used as a universal solvent for several purposes and discharged back into the environment.

Answers to SAE 2

1) Main sources of water pollution:

- (i) Phosphates
- (ii) Industrial discharges
- (iii) Pesticides
- (iv) Hot water

2) Short note on the depletion of ozone layer:

Ozone layer depletion is the reduction in the ozone level by creating a hole in the ozone layer which is found in the stratosphere. This hole is a result of man- made activities which releases chlorofluorocarbon, CFCs into the atmosphere. The ozone layer was to serve as shield or protection from ultra- violet light reaching the earth. The effect of these damage on the ozone layer is that the earth is unprotected from dangerous UV light. As a result, inhabitants of the earth feel various effects such as cataracts, (eye disease), skin burns and skin cancers etc.

3) Explanation on cause and consequence of green house effect

Evidence exists based on experiment to show that carbon dioxide in the atmosphere acts to direct heat back to the earth. As radiations from the solar system and sunlight escape into space, the heat released is trapped by air pollutants causing the planet to become hotter. A green house can be compared with a glass house where plants grow. Glass lets light in and keeps heat from escaping. The

trapped heat in turn keeps the plants warm even when it is cold outside. In a similar way, the earth's atmospheric gases (carbon dioxide and other gases) referred to as green house gases in the air trap heat energy from the sun. Without these gases, too much heat can go back to the atmosphere, and living things can be endangered for survival. As more greenhouse gases get into the air, they trap more heat, thereby leading to global warming. Excess greenhouse gases in the atmosphere are capable of causing ozone layer depletion.

Answers to SAE 3

1) **Biodegradable and Non-biodegradable Pollutants**

Biodegradable pollutants are chemical wastes that can be converted into harmless or useful substances by living organisms. Sometimes, harmful effluents are treated in sewage plants and broken down (converted) to useful chemicals usable for other purposes before discharge into the environment, for example, fertilizers, pulp, used/old papers and toilet tissues. Non – biodegradable pollutants are harmful chemical wastes that cannot be broken down into harmless compounds by living organisms. They remain in the environment and harm its inhabitants. For example is mercury compounds and insecticides.

2) **Control measures to reduce the level of pollution: (Any 5 answered correctly are acceptable and be awarded the full mark)**

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) Afforestation 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