COURSE CODE: CHM 123
COURSE TITLE: INTRODUCTORY CHEMISTRY II
NUMBER OF UNITS:3 Units
COURSE DURATION: Three hours per week

COURSE LECTURER: **KELANI TAWAKALIT**

INTENDED LEARNING OUTCOMES

At the completion of this course, students are expected to:

1. Understand the basic concepts of Organic Chemistry.
2. Draw structures and identify the general classes of organic compounds
3. Understand the principles of separating organic mixtures.
4. Apply the principle of separating techniques in real life synthesis
5. Carry out project on identification of organic compounds.

COURSE DETAILS:

- *Week 1: INTRODUCTION TO ORGANIC CHEMISTRY*

- *Week 2:IDENTIFICATION OF ORGANIC COMPOUNDS*

- *Week 3: ELECTRONIC THEORY IN ORGANIC CHEMISTRY*

- *Week 4-5 ORGANIC REACTIONS &CHEMISTRY OF HYDROCARBONS: ALKANES, ALKENES, ALKYNES AND PETROLEUM CHEMISTRY.*

- *Week 6: CHEMISTRY OF AROMATIC COMPOUNDS.*

- *Week 8 CHEMISTRY OF ALCOHOLS AND PHENOLS*

- *Week 7 KETONES AND ALDEHYDES*

- *Week 8 CARBOXYLIC ACID,.*

- *Week 9 AMINES, AMINO ACIDS AND PROTEINS.*

- *Week 10 CHEMISTRY OF CARBOHYDRATES*

- *Week11: FATS AND OILS*

- *Week 12: INTRODUCTION TO POLYMERS*

❖ **Lecturer's Office Hours:**
• Dr. Onyeachu B.I.   2-4m.
• Kelani T.O.   2-4pm,

• **RECOMMENDED TEXTBOOKS:**

  ❖ Organic chemistry by L.G. Wade. 8th edition, (2013). Published by Prentice hall, USA,.ISBN-10: 0-321-76841-8; ISBN-13: 978-0-321-76841-4
  ❖ Organic Chemistry by Paula Y. Bruice , 6th edition, (2011). Published by Prentice hall, USA. ISBN-13:978-0-321-66313-9
  ❖ Organic Chemistry by Janice Gorzynski Smith. 3rd edition, (2011). Published by McGraw-Hill companies, New York. ISBN 978–0–07–337562–5

ASSESSMENT

Continuous Assessment (30%) includes:
Attendance, term paper, assignment, presentation and/or mid-semester test

• **Exams:**
• Final, comprehensive (according to university schedule): ~ 70% of final grade

Assignments & Grading

• **Academic Honesty:** All classwork should be done independently, unless explicitly stated otherwise on the assignment handout.
• You may discuss general solution strategies, but must write up the solutions yourself.
• If you discuss any problem with anyone else, you must write their name at the top of your assignment, labeling them "collaborators".
• **NO LATE HOMEWORKS ACCEPTED**
• Turn in what you have at the time it's due.
• All homeworks are due at the start of class.
• If you will be away, turn in the homework early.
• Late assignments (projects) will not be accepted, but penalized according to the percentages given on the syllabus.

PREAMBLE:

Organic Chemistry is the chemistry of natural and synthetic compounds of carbons except simple

ones such as CO, CO_2, carbides, carbonates. The term organic compound was originally believed

to be from living organisms only (organic origin). But in 1828, a German chemist, Fredrich Wohler, synthesized urea in the laboratory and many other organic compounds. Hence, the idea of organic force behind the synthesis of organic compounds is now discarded.

$$NH4CNO \xrightarrow{\text{heat}} \underset{H_2N}{\overset{H_2N}{>}}C=O$$

ammoniumcyanate   **Urea**
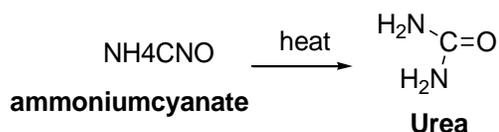
There are so many materials containing carbon compounds including hormones and enzymes in living organisms, the foods you eat, the clothes (cotton, silk, wool) you wear, fossil fuel used to power automobiles, plastics, dyes, paints, drugs, pesticides, fertilizers are all organic chemicals.

➢ Features of organic compounds

1. All organic compounds contain carbon and hydrogen atoms e.g. C_6H_{14}(n-hexane)

2. Heteroatoms such as N, O, S, P, halogens e.t.c may also be present e.g. $C_4H_9NH_2$ (butylamine)

➢ Why do we have so much carbon compounds? Why is carbon atom unique?

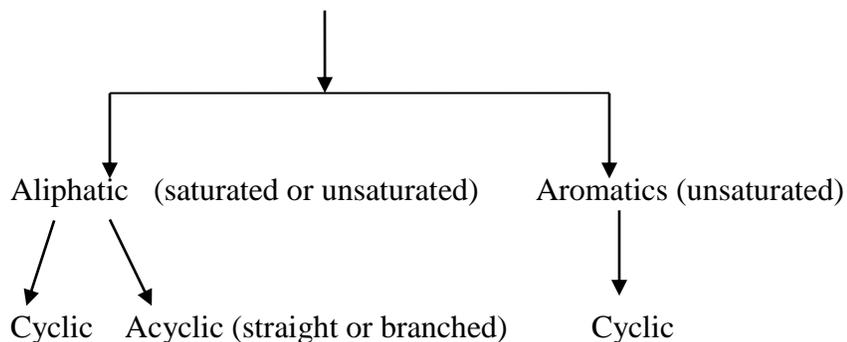Carbon compounds are numerous due to the following reasons:

1. Abilty of cabon atom to catenate. i.e. ability of carbon atom to form very strong covalent bonds with one another resulting to long chains or rings.

2. C-C bond is stronger than X-X bonds; where X= non metal.

3. Carbon form strong covalent bond with other elements e.e: C-H, C-N, C-S, C=O, C=N e.t.c.

NOTE : a carbon atom is tetravalent. i.e.: surrounded by four bonds $-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-$

➢ **Classification of Organic Compounds**

A. Classification based on structure:

Aliphatic   (saturated or unsaturated)   Aromatics (unsaturated)

Cyclic   Acyclic (straight or branched)   Cyclic

B. Classification based on solubility:

Polar organic compounds and non-polar organic compounds.

Polar organic compounds are those that can dissolve in water and polar organic solvents.

Non polar organic compounds do not dissolve in water and polar organic solvents. They dissolve in non-polar organic solvents such as benzene, n-hexane
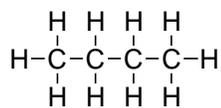
Examples of polar organic compounds are alkanols (alcohols), phenols, carboxylic acid, ether, aldehydes e.t.c.

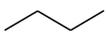Examples of non-polar organic compounds are: alkanes, alkenes e.t.c.

➢ Structural formula

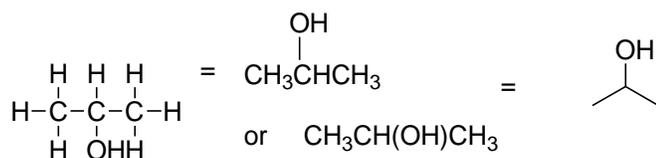This formula shows how one atom is linked to another in a compound. i.e. bonding sequence.

e.g: butane has a molecular formula C_4H_{10} has a structural formula:

H H H H
H−C−C−C−C−H
H H H H

Condensed structural formula of butane is $CH_3CH_2CH_2CH_3$

Bond lines structural formula of butane

Other examples are

H H H   = $CH_3\overset{\underset{|}{OH}}{C}HCH_3$
H−C−C−C−H
H OHH   or $CH_3CH(OH)CH_3$

= (structure with OH)

Assignment 1:

Redraw the following bond-line structural formula to condensed structures:

1. (bond-line structure with OH)

2. (bond-line structure)
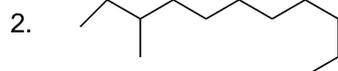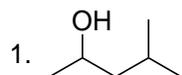
STRUCTURE ELUCIDATION

Techniques used in determining structures of organic compounds include:

- X-ray crystallography

- Infra-red spectroscopy

- Mass spectroscopy

- UV spectroscopy

- Nuclear magnetic resonance (NMR) spectroscopy

HOMOLOGOUS SERIES AND FUNCTIONAL GROUP

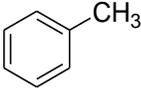Homologous series is a group of organic compounds whose successive members usually differ by CH_2 unit in the main carbon chain.

Homologous series	general formula	examples
Alkanes	C_nH_{2n+2}	CH_4 (n=1)
Alkenes	C_nH_{2n}	C_6H_{12}
Alkynes	C_nH_{2n-2}	
Alkyl	C_nH_{2n+1}	
Alkanols	$C_nH_{2n+1}OH$	
Aldehydes/ alkanals	$C_nH_{2n}O$	

Functional group

A functional group is an atom or a group of atoms that determines the chemical and physical properties of a molecule or compound. In addition, a functional group also determines the bonding and shape, the types and strength of intermolecular forces.

Homologous series	General structure	Examples	Functional group
Alkanes	**R-H (R= alkyl group)**	CH_3CH_3	-------
alkenes	$\begin{smallmatrix} R \\ R \end{smallmatrix} C=C \begin{smallmatrix} R \\ R \end{smallmatrix}$ **(R=alkyl or H)**	$H_2C=CHCH_3$	$C=C$
alkynes	$R-C\equiv C-R$ **(R=alkyl or H)**	$HC\equiv CH$	$C\equiv C$
aromatic compound	R	CH_3	

	(R=alkyl or H)		
alkyl halide	R-X X= halogens	CH_3Br	C-X
Alcohols	R-OH	CH_3CH_2OH	-OH (hydroxyl group)
Ether	R-O-R	H_3C-O-C_2H_5	-OR (alkoxy)
Amines	$R-NH_2$, R_2NH, R_3N	CH_3NH_2	$-NH_2$ (amino group)
Thiols	R-SH		-SH (mercapto group)
Sulphide	R-S-R		-S-R (alkylthiol group)
Aldehydes	$\overset{\displaystyle O}{\underset{\displaystyle \parallel}{R-CH}}$	$\overset{\displaystyle O}{\underset{\displaystyle \parallel}{H_3C-CH}}$	C=O
Ketones	$\overset{\displaystyle O}{\underset{\displaystyle \parallel}{R-C-R}}$	$\overset{\displaystyle O}{\underset{\displaystyle \parallel}{H_3C-C-CH_3}}$	C=O
Carboxylic acid	$\overset{\displaystyle O}{\underset{\displaystyle \parallel}{R-C-OH}}$	$\overset{\displaystyle O}{\underset{\displaystyle \parallel}{H_3C-C-OH}}$	-COOH
Ester	$\overset{\displaystyle O}{\underset{\displaystyle \parallel}{R-C-OR_1}}$	$\overset{\displaystyle O}{\underset{\displaystyle \parallel}{H_3C-C-OC_2H_5}}$	$\overset{\displaystyle O}{\underset{\displaystyle \parallel}{-C-OR}}$
Amide	$\overset{\displaystyle O}{\underset{\displaystyle \parallel}{R-C-NH_2}}$	$CH_3CH_2NH_2$	$\overset{\displaystyle O}{\underset{\displaystyle \parallel}{-C-NH}}$
Acid chloride	$\overset{\displaystyle O}{\underset{\displaystyle \parallel}{R-C-Cl}}$	$\overset{\displaystyle O}{\underset{\displaystyle \parallel}{H_3C-C-Cl}}$	$\overset{\displaystyle O}{\underset{\displaystyle \parallel}{-C-Cl}}$

EXERCISE

write out all the functional groups in the structure given below:
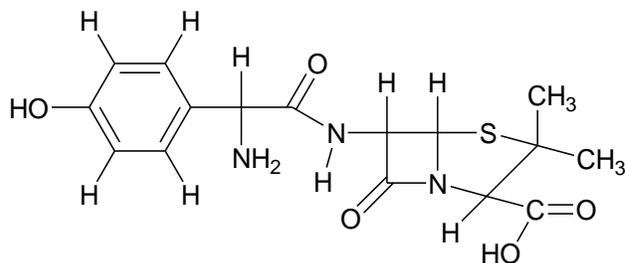
Amoxicillin (an antibiotic)

WEEK 2: *IDENTIFICATION OF ORGANIC COMPOUNDS*

Sub-topics:

- Isolation and purification of organic compounds

- Qualitative test (Elemental analysis)

- Quantitative analysis (Percentage composition, Molecular and Empirical formula)

Isolation and purification of organic compounds.

- Purification of organic compounds is important because most synthetic reactions give mixture of products. Also, most compounds of biochemical interest occur naturally in plants as components of complex mixture from which they can be separated.

- A pure compound is a homogeneous sample consisting of molecules of the same structure. A pure solid has a sharp and constant melting point or constant boiling point (if liquid).

- A mixture is a substance which consists of two or more components that are not chemically combined together.Separation of mixture into individual components can be achieved by differences in physical properties such as differences in boiling point, solubility, volatility, size, density e.t.c.

❖ Techniques used in separating organic mixture include

- Filtration

- Simple distillation

- Fractional distillation

- Decantation

- Evaporation

- Steam distillation

- Chromatography

- Solvent extraction (liquid-liquid extraction)

- Recrystallization

Isolation of products from reaction mixture is accomplished by series of laboratory procedures called **work-ups**. The choice of choosing a technique depend on a large extent the physical and chemical properties of the desired product.

In a one phase solid system, if the organic product is neutral and water insoluble, the product can be *washed with water* to remove water-soluble inorganic impurities. Alternatively, the crude solid may be *extracted with suitable organic solvent*, filtered and then washed with water. Further washing with dilute aqueous acid and dilute alkaline removes basic and acidic impurities. Continuous extraction of the solid may be necessary if the required solid is sparingly soluble in organic solvent. However, if the crude product is inform of a salt and water soluble, acidification (or basification in case of amine salts) will liberate the free acidic compound (or base) which can be recovered by filtration or solvent extraction as the case may be.

One-phase liquid system is often encountered in organic synthesis, since many of the reactions are carried in solution. Direct fractional distillation or distillation may separate the product, if it is a liquid, from the solvent cooling may lead to direct crystallization of the product if this is a solid.

A crude reaction mixture involving two phases is very common. The case of solid/ liquid, the organic product can be isolated by filtration (when the product have crystallized out of solution). Liquid-liquid phase systems, often results from the use of steam distillation as a preliminary isolation process or procedure.

Filtration technique:

This is used to remove insoluble solid from solutions. The solid is washed with appropriate solvent and dried. The filtered solid is then subjected to further purification using suitable crystallization procedure

Recrystallization technique:

Solid organic compounds are seldom pure after isolation from reaction mixture; they are usually contaminated with small impurities which are produced along with the desired product. The purification of impure crystalline compound is effected by crystallization from a suitable solvent or mixture of solvents.

The most desirable characteristics of a solvent for recrystallization are as follows:

1. It should not dissolve the solid (desired product) when cold but it should dissolve it when hot.

2. It should dissolve the impurities readily or to only to a small extent

3. It should yield well-formed crystals of the purified compound.

4. It should be capable of easy removal from the crystals of the purified compound, i.e. possess a relatively low boiling point.

FREEZE DRYING

This is a process called lyophilisation. This is process is used when water is to be removed from heat-labile materials e.g. polysaccharides, enzymes and peptides.

*STEAM DISTILLATION***:**

This is the used to extract steam volatile natural product (e.g. those occurring in oil),such as phenol, benzaldehyde, aniline and simpler aromatic system.
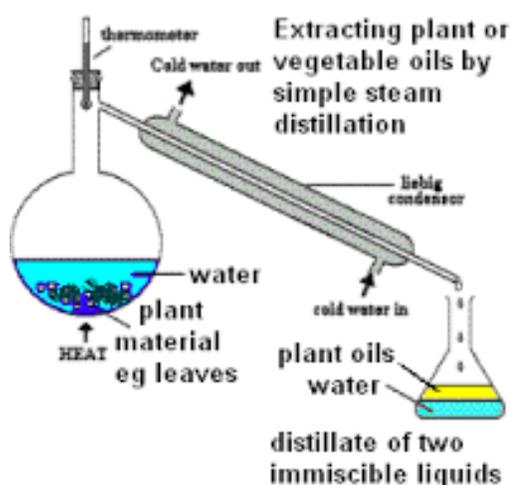
When an impure sample of such compounds is boiled with water, the distillate contains both the steam and the vapour of the pure organic compound, even though its boiling point is higher than that of water. Steam distillation takes place below the boiling point of water. This renders possible the purification of many substances of high boiling point by low temperature distillation. The purpose of steam distillation is to get rid of non- steam organic matter (high will remain undistilled in the flask). An organic compound to be suitable for steam distillation, it must possess the following characteristics:

1. It should have considerable vapour pressure (25-40 mmHg) at the boiling point of water

2. It should have a fairly high molecular weight (90-140)

3. It should only be slightly soluble in water but readily soluble in ether to facilitate its extraction with ether after steam distillation.

This method can be used to estimate the vapour pressure or the molar mass of the unknown steam volatile organic compound using the following expression:

$$\frac{m_A}{m_{H2O}} = \frac{P_A M_A}{P_{H2O} M_{H2O}}$$

where m_A= mass of A in the distillate; m_{H2O} = mass of H_2O in the distillate

P_A= vapour pressure of A; P_{H2O}= vapour pressure of H_2O

M_A = molecular weight of A; M_{H2O}= molecular weight of H_2O

N.B: $P_A + P_{H2O}$= 760mmHg

Example 1:

An insoluble compound A was steam distilled, the atmospheric pressure being 760mmHg. Of the 69cm^3 distillate obtained, 60cm^3 was water. The mixture boiled at 99.3°C at which the vapour pressure of water is 740mmHg. If the density of A is 1.22g/cm3, calculate the molar mass of A.

Solution:

Density = 1.22g/cm^3; V_A= 9cm3 ; mass of A= 1.22g/cm^3 X 9cm^3 = 10.98g

P_{H2O} = 740mmHg; P_A= 20mmHg; mass of H2O= 1g/cm^3 X 60cm^3 = 60g

M_{H2O}= 18g/mol

M_A =?

Using $\frac{m_A}{m_{H2O}} = \frac{P_A M_A}{P_{H2O} M_{H2O}}$

$$\frac{10.98\ g}{60\ g} = \frac{20X\ M_A}{740X18}$$

M_A= 122. 88 g/mol

Solvent extraction (liquid- liquid extraction):

This technique is used to isolate organic compound from aqueous solution of the compound. The solution of the compound in water transfers to the organic solvent (e.g. ether), because organic compounds are more soluble in organic solvents than water.

Differential Extraction
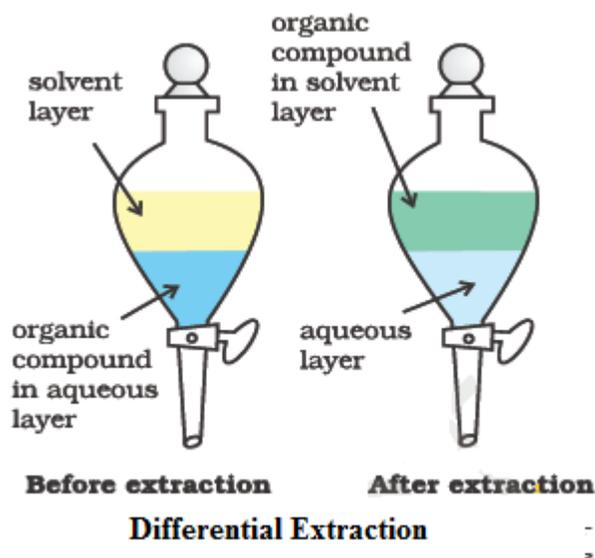
The procedure is

1. Saturate the liquid to be extracted with common salt: this is to reduce the solubility of the compound in water (salting out) and to further enhance its transfer to the organic layer

2. Place the aqueos solution in a separatory funnel and shake vigorously in the desired volume

   Of the ethereal layer in one batch , 2 or more batches.

3. Separate the aqueous layer from the ether layer using the tap

4. Dry the ethereal layer over desiccant (drying agents) such as anhydrous $MgSO_4$, $CaCl_2$, anhydrous Na_2SO_4etc

Solvent extraction is concerned with the distribution law or partition law which states that when a solute X distributes itself between 2 immiscible liquids, the ratio of the concentration of X in solvent A and the concentration of X in solvent B is constant (at constant temperature).

i.e: $[X]_A$ organic layer/$[X]_B$ aqueous layer = K_{AB}

it is assumed that the solute X is in the same molecular state in the 2 solvents

$[X]$ether layer = <u>mass of X extracted into ether layer (g)</u>

Volume of ether used

$[X]$ aqueous layer = <u>mass of X left into aqueus layer (g)</u>

Volume of water used

Example 2

$50cm^3$ of water containing 2g of caffeine was extracted with $20cm^3$ of ether. Given that the partition coefficient between ether and water is 8, calculate the mass of caffeine extracted.

Solution:

$$\frac{\left[mass\ of\frac{caffeine}{volume}of\ ether\ used\right]}{\left[mass\ of\ caffeine\ left\ in\frac{aqueous}{volume}\right]} = k_{ether/water}$$

Let the mass of caffeine extracted into ether layer be y

$\frac{yg/\ 20cm^3}{2\text{-}y\ /\ 50cm^3}$ = 8

(y X 50)/ (20X 2-y) = 8
50y/(40-20y) = 8
50y = 320 -160y
210y = 320
    y= 320/210 = 1.524g

CHROMATOGRAPHY

Chromatography is a separation technique which depends on the distribution of the components of a mixture between a mobile phase and a stationary phase. The stationary phase may be inform

of a packed column (column chromatography) through which a mobile phase can flow, or in the form of a thin layer adhering to a suitable form of packing material (thin layer chromatography) over which the mobile phase is allowed to ascend by capillary action.

The stationary phase may be a liquid or solid (silica or alumina) and the mobile phase can be liquid or an inert gas

Based on the arrangement of the stationary phase and the mobile phase , chromatography can be classified as follows:

1. Paper chromatography (PC)

2. Thin layer chromatography (TLC)

3. Column chromatography (CC)

4. Gas –liquid chromatography(GLC)

5. High performance liquid chromatography (HPLC)

PC/TLC

The stationary phase is paper or glass plate coated with layers of solid stationary phase, which adhere to the plate generally by virtue of a binding agent such as CaSO4, whuch is incorporated. The most common stationary phases are silica gel, alumina, sepahadex, cellulose powder. Many of those are available with a fluorescent compound (e.gZnS) incorporated in order to facilitate the detection of the resolved component of the mixture which is then achieved by viewing the plates under UV light.

This technique is used to identify the number of components in complex organic mixture e.g. extract from plants, dyes. It involves ascending of organic solvent (mobile phase) over the mixture (spotted on the stationary phase) in the bid to separating the mixture into its components.
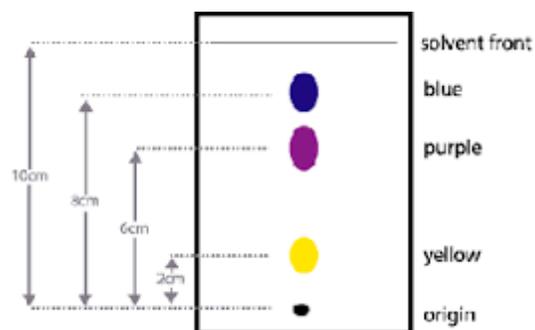
The movement of mobile phase over the stationary phase in a bid to separate the mixture is called development or elution. The eluted paper or plate gives a chromatogram. Each spot is characterized by a property called retention factor (RF). RF of each component depends on its rate of adsorption on the stationary phase; this in turn depends on the polarity of the compound

RF= distance moved by the solute from origin/ distance moved by the solvent front from origin

Note that 0<RF<1.

RF can be used for identify a compound when compared with the existing literature. It can also be used to monitor the progress of an organic reaction.

TLC can be used to establish the purity of an organic compound.

COLUMN CHROMATOGRAPHY

This is used for separation of the constituents of organic mixture. The stationary phase is a column packed with an adsorbent. The mobile phase is an organic solvent (known as eluant). This technique involves using the eluent to elute each component of the mixture (after being adsorbed to the stationary phase). Each component of the mixture is adsorbed to the stationary phase at different rates and hence they move at different speed down the column. Aliquots (equal volumes) of the eluates are then collected into test tubes or beakers. Components with the same RF values are then bulked together.

layer of solvent on top of column

column packed with silica gel or alumina completely saturated with solvent

glass wool to prevent stationary phase being washed out of column
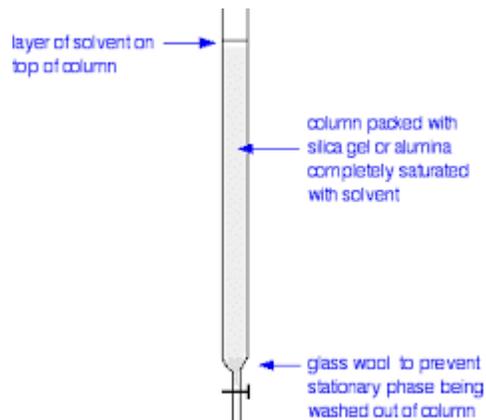
The purity of a sample can also be ascertained by melting point determination or spectroscopic analysis.

Practice questions:

A solution of a substance was spotted at the distance 0.5cm from the base of a 20cm high plate. Upon elution the solvent front got to a place of 0.5cm from the top of the plate. If the compound moves half way up the 20cm long plate. Whai is the RF value of this compound?

2. arrange the following compounds in the order of increasing RF

(A) PhCH2CH2Ph (B) PhCH(OH)CH2Ph (c) PhCH(OH)CH(OH)Ph (D) PhCOCH2Ph

3. 100cm3 of water containing 12g of an organic compound X is extracted by 50cm3 of ether in

   (a) One batch (b)2 batches each of 25cm3 of ether. Assuming that ether and water are immiscible and that the partition coefficient of X between ether and water is 8 at the temperature in question, calculate the mass of X extracted in the 2 cases.

QUALITATIVE ANALYSIS (ELEMENTAL ANALYSIS)

This method deals with detection of various elements present in an organic sample. Most organic compound contains C,H O, and other element (such as N,S,P,halogensands metals).

1. DETECTION OF C AND H

This is achieved by combustion method. The organic sample is burnt in excess O_2 in the presence of CUO in a combustion tube.

Sample+ $O_{2(g)}$ $\longrightarrow$ $CO2_{(g)}$ + $H2O_{(g)}$
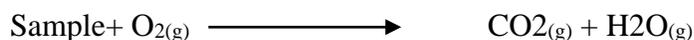
CO_2 turns lime water milky and H_2O turns anhydrous $CUSO_4$ from white to blue or anhydrous $CoCl_2$fom blue to pink.

2. Detection Of N,S and halogens (Lassaigne's sodium fusion test)

Lassaigne's sodium fusion test is used to convert elements into soluble sodium compound or to ionisable inorganic material by fusion of sodium metal with the organic compound.

The organic compound is heated with excess sodium metal to redness and then pluged into water in a mortar. After cooling, the content is then ground and filtered. The filtrate is then divided into 3 portions

[C,H,N,X,P, S] $\underrightarrow{\text{Na (excess)}}$ $NaCN + Na_2S + NaX$

[C,H,N,X,P, S] $\underrightarrow{\text{Na (limited)}}$ $NaSCN$ +NaX

$\downarrow$ Na

$NaCN + Na_2S$

1. Test for Nitrogen

First portion of filtrate

Lassaignesfitrate + $FeSO_4$ + $FeCl_3$ $\longrightarrow$ prussian blue solution

Prussian blue solution indicates the presence of CN-, which in turn indicates the presence of N in the organic sample.

Equations:

$NaCN + FeSO_4$ $\longrightarrow$ $Na_4Fe(CN)_{6\,(aq)} + Na_2SO_{4(aq)}$

$3Na_4Fe(CN)_{6\,(aq)} + 4FeCl_3$ $\longrightarrow$ $Fe_4[Fe(CN)_6]_3 + 12NaCl$

prussian blue solution

Test for S

To the second filtrate, add dilute lead ethanoate and dilute nitric acid.

Na_2S + dil. $Pb[CH3COO]_2$ $\xrightarrow{\text{dilute } CH_3COOH}$ $PbS + 2CH3COONa$

Filtrate black ppt

Test for halogens

To test for halogens, the third portion of the lassaignesfitrate is first acidified with few drops of dilute H2SO4 and boiled to remove S And CN in the form of HCN g and H2S g. these S2- and CN- ions can also interfere with the precipaitating agents such as $AgNO_3$

$NaX + AgNO_3$ $\xrightarrow{\text{dil HNO3}}$ $NaNO3 + AgX$

White ppt soluble in excess aqueous NH3, it indicates the presence of Cl- present

Pale yellow ppt sparingly soluble in excess aqueous NH_3, it indicates the presence of Br- present

yellowppt insoluble in excess aqueous NH3, it indicates the presence of I- present.

ELECTRONIC THEORY IN ORGANIC CHEMISTRY: BONDING, LEWIS STRUCTURES, VSEPR THEORY, CONCEPT OF HYBRIDIZATION, VALENCE BOND THEORY AND SHAPES OF MOLECULES.

Bonding is the joining of two atoms in a stable arrangement. It is a favourable process because it leads to lowered energy and increased stability. Bonding may occur between atoms of the same or different elements. In an atom, valence electrons (outermost electrons) participate in bonding, leading to a stable configuration of electrons (octet rule). First row element hydrogen ($1s^1$) will attain the electronic configuration of a noble gas He ($1S^2$), after bonding.

There are 2 types of bonding: ionic and covalent

Ionic bonding is the transfer of an electron from an atom (a metal) to another atom (a non metal) to give ions. So, ionic bond is an electrostatic attraction between oppositely charge ions.

Covalent bonding involves sharing of electrons between 2 participating atoms. Compounds that results from covalent bonding are called molecules. E.g CH_4, H_2, NH_3, O_2, N_2e.t.c. the major type of bonding that exist between organic molecules is a covalent bond. There are two types of covalent bonding: ordinary and coordinate covalent bonding. Covalent bond could be single bond, double bond or triple bond. i.e: C-C, C=O, C=C etc.

LEWIS STRUCTURES

This is the representation of covalent bonds with electron dots. It is used to show shared electron pairs(bonding electrons) and lone pairs (non bonding electrons) in form of a dot. A covalent bond is a two electron bond e.g CH4 is represented as :

In the lewis structure, most atoms attain the electronic configuration of a noble gas (octet rule)

Rules for drawing Lewis structure:

Arrange the atoms

Count the electrons

The number of covalent bonds can be predicted by 8-valenc e electrons. E.g the no of covalent bond around N is 8-5=3 covalent bonds.

N.B:

Atoms   no of covalent bonds

H	1
Halogens	1
N (with one lone pair)	3
N(with a + charge)	4
C	4
C(with a + charge)	3
O	2
O (with a + charge)	3
O (with a -ve charge)	1
S	6 (or less with lone pairs)
P	5 (or 3 with a lone pair).

Example: draw the Lewis structure of CH_4

$$
\begin{array}{c}
H \\
H : C : H \\
H
\end{array}
$$
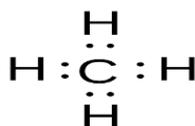
Exceptions to octet rule:

Incomplete octet: e.g. BF3, BeCl2, .they are stable and yet they do not possess the octet configuration.

Odd electron species: e.g. NO. in odd electron species, one of the atoms lack an octet configuration and there is always an unpaired electron. All odd electron species are paramagnetic due to the presence of a unpaired electron

Expanded octet: this is due to availability of a 3d orbital for expansion. E.g phosphorus has an expanded octet, hence it has valency of 3 or 5.

Exercise

Draw the Lewis structures for the following compunds:

N_2, HCHO, NH_3, H_3O^+, CH_3NO_2

Limitations of the Lewis structure

This model could not give the bond angles and shapes of molecules.

VALENCE SHELL ELECTRON PAIR REPULSION THEORY (VSEPR)

This theory gives the shape of molecules by predicting the bond angles between two bonded atoms.The VSEPR model is based on the fact that electron pairs repel each other. The most stable arrangement keeps the groups (atoms or lone pairs) as far away from each other as possible.

Lone pair- Lone pair repulsion > Lone pair-bond pair repulsion> bond pair- bond pair repulsion.

This order can be explained do the basis that the lone pair is under the influence of only one nucleus, hence its electron cloud will spread out in space to aa greater extent a a bond pair which is under the influence of two nuclei. This greater spread over of electron cloud in space results to a greater repulsion between a lone pair and another lone pair than a bond pair and a lone pair.

Predicting shapes of molecules using VSEPR model:

1. Draw possible lewis structure

2. Determine the number of electron pair around the central atoms i.e. add the valence electrons of the central atom to the bonding electrons of the surrounding atoms, Add +1 for negative charges and -1 for positive charges and determine the number bond pair and lone pairs around the central atom

3. Establish the geometrical orientations of the electron pairs around the central atom

Case 1 : when the central atom is surrounded by two groups:

e.g BeCl$_2$

valence electrons of central atom(Be) = 2es

bonding electrons from chlorine = 2es

totales =4

electron pair = total electrons/2 =2e pair.

any atom surrounded by 2 groups is linear and has a bond angle of 180°

Cl-Be-Cl is linear and the bond angle between each Be-Cl is 180

Case 2: three groups surrounding an atom.

An atom surrounded by 3 groups is trigonal planar and the bond angle is 120°

e.g BF$_3$ (Boron trifluoride),

valencees of B= 3

bonding electrons from F= 1X 3= 3es

total electrons = 6es

electron pairs = 6/2 =3

It implies that the shape of BF3 is trigonal planar and the bond angle is between each B-F is 120°

All the B-F bonds lie in one plane (symmetrical)

Case 3: when an atom is surrounded by 4 groups.

Any atom surrounded by 4 groups is a tetrahedral and has a bond angle of 109.5o

e.g CH4

ep = 4es

so CH4 (has a central carbon with 4 bonds to hydrogen atoms, each pointing towards a corner of tetrahedron)

In methane, there are four bonds of equal repulsive forces and which completetly balance each other, resulting to a tetrahedral shape.
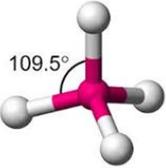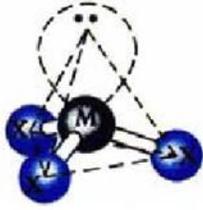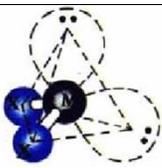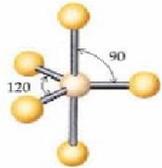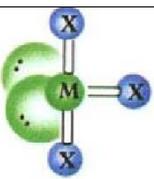
But in ammonia NH3, there are 3 bond pairs and 1 lone pair of electrons. There is a greater repulsion between the lone pair and the 3 bond pairs than the bond pair- bond pair repulsion. Hence the three bond pairs are forced closer together resulting to a bond angle of 107

Similarly, water has 2 lone pairs and 2 bond pairs, and hence there is a greater repulsion between the 2 lone pairs and also forcing the two bond pairs still closer together resulting in H-O-H bond angle of 104.5
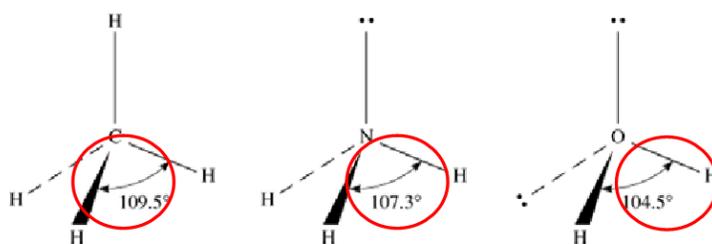
bonding-pair vs. bonding pair repulsion < **lone-pair vs. bonding pair repulsion** < **lone-pair vs. lone pair repulsion**

Molecules	Electron pairs	Bond pairs	Lone pairs	VSEPR notation	Molecular geometry	Predicted bond angles	Shape
$BeCl_2$	2	2	0	MX_2	Linear	180º	
BF_3	3	3	0	MX_3	Trigonar planar	120º	

CH_4	4	4	0	MX_4	tetrahedral	109.5°	
NH_3	4	3	1	MX_2L	Trigonal pyramid	107°	
H_2O	4	2	2	MX_2L_2	Angular or v-shape	104.5°	
PCl_5	5	5	0	MX_5	Trigonalbipyramid	120°&90°	
ClF_3	5	3	2	MX_3L_2	T-shaped	120°&90°	
SF_6	6	6	0	MX_6	octahedral	90°	
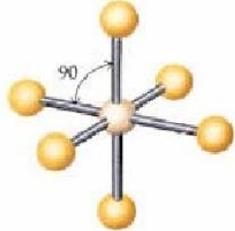
BrF$_5$	6	5	1	MX$_5$L		90º	
XeF$_4$	6	4	2	MX$_4$L$_2$		90º	
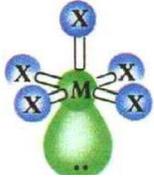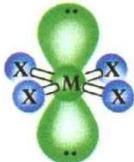
Where M= central atom, X = bond pairs and L = lone pairs of electrons

EXERCISE:

Using the VSEPR model, predict the structure of the following compounds:

ICl$_4$-, ClO$_3^-$, SCl$_2$, XeF$_2$, I$_3^-$
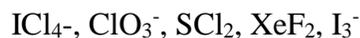
VALENCE BOND THEORY

According to this theory, a covalent bond is formed by overlapping of two half-filled atomic orbitals containing electron of opposite spins. The greater the overlapping, the stronger the covalent bond. All atoms are made up of nucleus surrounded by electrons in concentric shells. Each shell surrounding the nucleus corresponds to a principal quantum no n. n=1, 2, 3 , 4, 5,6. etc. each shell has sub shells known as orbitals. An atomic orbital is a region in space around the nucleus where there is probability of finding an electron. Types of subshell or orbitals include: s, p, d, f..

So in n=1 level has subshell l s or s orbital.

n=2 level has s, p or orbitals

n=3 has s,p,d.

Each orbital has its own characteristic energy and shape.

An s orbital has spherical shape. The orbital is spherically symmetrical around the nucleus.

A p orbital has two lobes forming a dumb-bell shape. The p orbital has 3 sub-orbitals of equal energy (degenerate orbitals). They are directed perpendicular to each other just as Cartesian coordinate and are designated as px, py and pz. Corresponding to their axes orientation

Based on this, there are 2 types covlant bonds based on the type of overlapping:

Sigma and pi bond.

Types of overlapping

s-s overlapping e.g

s-p

p-p linear overlapping

p-p parallel overlapping

summarily, sigma bond results from

    a. Hybrid –hybrid overlap

    b. Hybrid –s overlap

    c. Hybrid-p overlap

    d. S-s overlap

    Π bond results fromp-p orbital overlap that are parallel to each other. E.g

Cl_2

Sigma bond is stronger than a pi bond.

QUESTION

Despite that a sigma bond is stronger than a pi bond, why is than C=C bond stronger C-C ?