8

Organic Chemistry–Some Basic Principles and Techniques

The cosmetics industry is a profitable branch of organic chemistry. Chemists study how the skin changes in response to metabolic and environmental factors, develop products to address skin problems and improve the beauty and investigate how cosmetics interact with the skin and other products.

Topic Notes

- *Some Basic Principles and Techniques*
- *IUPAC Nomenclature and Isomerism*
- *Reactions and their Mechanisms*
- *Methods of Purification*

SOME BASIC PRINCIPLES AND TECHNIQUES

1

TOPIC 1

INTRODUCTION TO ORGANIC CHEMISTRY

Organic compounds are important for the survival of life on the Earth and contain complex molecules such as genetic information-carrying deoxyribonucleic acid (DNA) and proteins, which are key components of our blood, muscles and skin. Organic compounds can be found in a variety of products, including clothes, fuels, polymers, dyes and pharmaceuticals. These are some of the most important applications for these chemicals.

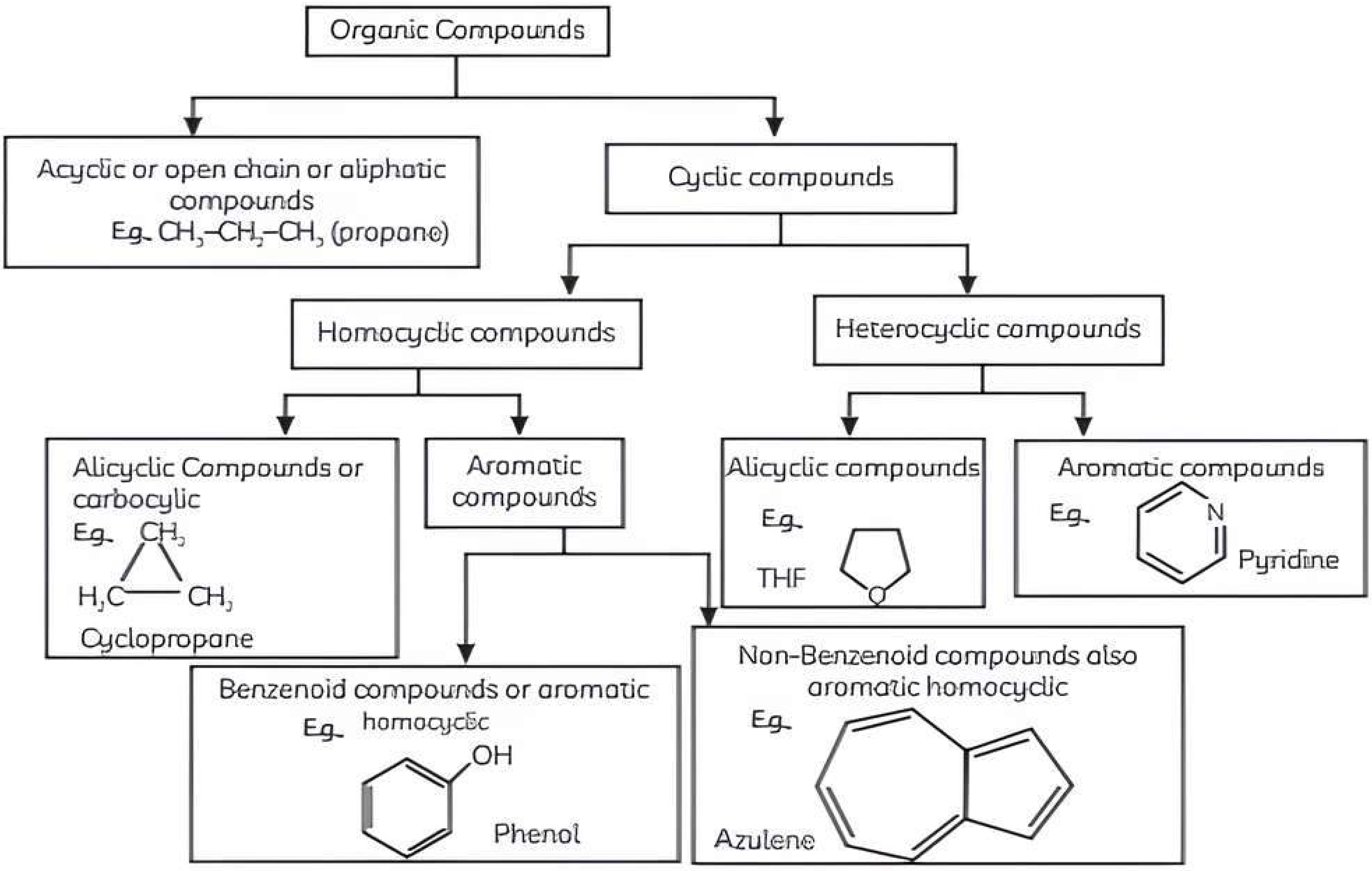
Organic chemistry is a nearly two-hundred-year-old science. Chemists began to distinguish between organic molecules derived from plants and animals and inorganic compounds derived from mineral sources around the year 1780. Berzelius, a Swedish chemist, believed that organic molecules were formed by a 'life force.' This theory was debunked in 1828, when F. Wohler synthesised an organic chemical, urea, from an inorganic substance ammonium cyanate.

$$NH_4CNO \xrightarrow{heat} NH_2CONH_2$$

The discovery of the electronic theory of covalent bonding ushered in the modern era of organic chemistry.

TOPIC 2

CLASSIFICATION OF ORGANIC COMPOUNDS



Classification of Organic Compounds

Acyclic or Open Chain Compounds

These compounds, also known as aliphatic compounds, are made up of straight or branched chain compounds. For example,

$$CH_3\text{-}CH_2\text{-}CH_3$$

propane

Alicyclic or Closed Chain or Ring Compounds

Alicyclic (aliphatic cyclic) compounds are made up of carbon atoms arranged in a ring (homocyclic). Other atoms besides carbon are known to occur in the ring (heterocyclic). Some of its characteristics are comparable to those of aliphatic compounds. For example, cyclobutane and furan.

Aromatic Compounds

Aromatic compounds are a group of compounds. Benzene and other similar ring compounds are examples of this (benzenoid). Aromatic compounds, like alicyclic compounds, may have a heteroatom in the ring. These are known as heterocyclic aromatic compounds.

Important

- *For aromatic compounds, three conditions should be followed:*

(1) *It should be cyclic and planar.*

(2) *The π-electrons should be delocalised over the ring.*

(3) *It should follow Huckel's Rule (4n + 2 π rule).*

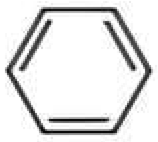
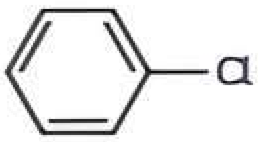
TOPIC 3

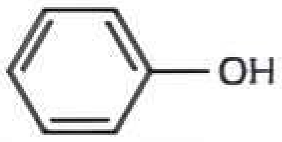
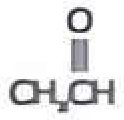
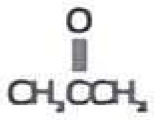
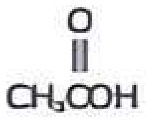
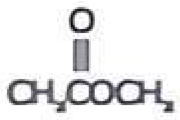
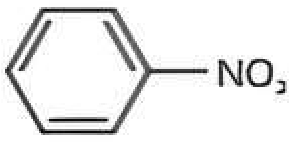
FUNCTIONAL GROUPS AND HOMOLOGOUS SERIES

Organic compounds can also be divided into families or homologous series based on their functional groups.

The functional group is an atom or group of atoms that are connected in a certain way and are responsible for the unique chemical properties of organic molecules. Examples include the hydroxyl group (–OH), aldehyde group (–CHO) and carboxylic acid group (–COOH), among others.

A homologous series is formed by a group or series of organic compounds, each of which contains a distinctive functional group. The members of the series are referred to as homologues. A homologous series' members can be represented by a general molecular formula, while the subsequent members differ in the molecular formula by a $-CH_2$ unit. Several homologous sequences of organic compounds exist. These include alkanes, alkenes, alkynes, haloalkanes, alkanols, alkanals and alkanones.

Class	General Formula	Example	Common Name (Systematic)	Common Suffix/Prefix (Systematic)
Hydrocarbons				
Alkanes	RH	CH_3CH_3	ethane	-ane
Alkenes	$RR'C = CR''R'''$	$H_2C = CH_2$	ethylene (ethene)	-ene
Alkynes	$CR = CR'$	$CH = CH$	acetylene (ethyne)	-yne
Arenes	ArH^{o}		benzene	-ene
Halogen-Containing Compounds				
Alkyl halides	RX	CH_3CH_2Cl	ethyl chloride (chloroethane)	halide (halo-)
Aryl halides	ArX^{o}		chlorobenzene	~~halo-~~

Oxygen-Containing Compounds				
Alcohols	ROH[a]	CH_3CH_2OH	ethyl alcohol (ethanol)	-ol
Phenols	$ArOH$[b]		phenol	phenol
Ethers	ROR'	$H_3CH_2COCH_2CH_3$	diethyl ether	ether
Aldehydes	$RCHO$	 $CH_3\overset{\overset{O}{\|}}{C}H$	acetaldehyde	-aldehyde (-al)
Ketones	$RR'C{=}O$	 $CH_3\overset{\overset{O}{\|}}{C}CH_3$	acetone (2-propanone)	-one
Carboxylic acids	RCO_2H	 $CH_3\overset{\overset{O}{\|}}{C}OH$	acetic acid (ethanoic acid)	-ic acid (-oic acid)
Carboxylic Acid Derivaties				
Esters	$RCOOR'$	 $CH_3\overset{\overset{O}{\|}}{C}OCH_3$	methyl acetate (methyl ethanoate)	-ate (-oate)
Amides	$RCONHR'$	 $CH_3\overset{\overset{O}{\|}}{C}NHCH_3$	*N*-methylacetamide	-amide
Nitrogen-Containing Compounds				
Amines	RNH_2, $RNHR'$.	$CH_3CH_2NH_2$	ethylamine	-amine
Nitriles	$RC\equiv N$	$H_3CC\equiv N$	acetonitrile	-nitrile
Nitro compounds	$ArNO_2$[a]		nitrobenzene	nitro-

[a] R indicates an alkyl group [b] Ar indicates an aryl group

Example 1.3: **Draw formulas for the first five members of each homologous series beginning with the following compounds:**

(A) $H{-}COOH$

(B) CH_3COCH_3

(C) $H{-}CH = CH_2$

Ans. The first five members of each homologous series beginning with the given compounds are

(A) $H{-}COOH$: Methanoic acid
$CH_3{-}COOH$: Ethanoic acid
$CH_3{-}CH_2{-}COOH$: Propanoic acid
$CH_3{-}CH_2{-}CH_2{-}COOH$: Butanoic acid
$CH_3{-}CH_2{-}CH_2{-}CH_2{-}COOH$: Pentanoic acid

(B) CH_3COCH_3: Propanone
$CH_3COCH_2CH_3$: Butanone
$CH_3COCH_2CH_2CH_3$: Pentan-2-one
$CH_3COCH_2CH_2CH_2CH_3$: Hexan-2-one
$CH_3COCH_2CH_2CH_2CH_2CH_3$: Heptan-2-one

(C) $H{-}CH{=}CH_2$: Ethene
$CH_3{-}CH{=}CH_2$: Propene
$CH_3{-}CH_2{-}CH{=}CH_2$: 1-Butene
$CH_3{-}CH_2{-}CH_2{-}CH{=}CH_2$: 1-Pentene
$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH{=}CH_2$: 1-Hexene

Example 1.4: **Case Based:**

Based on their functional groups, organic compounds can also be classified into families of homologous series. Among these are the hydroxyl group (–OH), aldehyde group (–CHO) and carboxylic acid group (–COOH). A homologous series is made up of a group or series of organic compounds, each with a distinct functional group. The series' members are referred to as homologues. Members of a homologous series can be represented by a general molecular formula, while subsequent members differ by a $-CH_2$ *unit in the molecular formula. There are several homologous sequences of organic compounds.*

(A) Which is not a condensed structural formula?

(a) CH_3CH_3 (b) $H_2C = CH_2$

(c) $H_3C - CH_3$ (d) CH_3OH

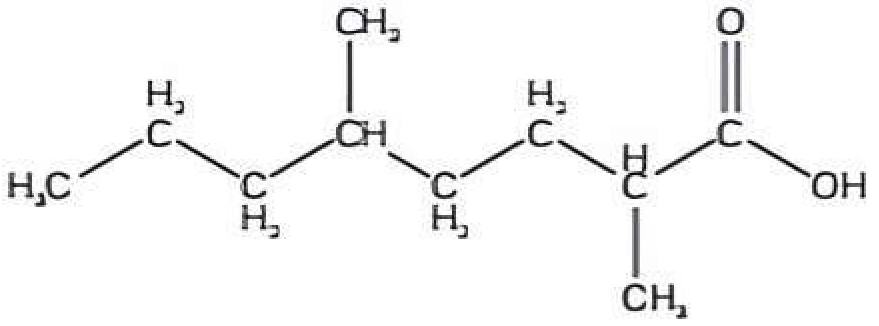
(B) The maximum number of carbon atoms arranged linearly in the molecule, $CH_3–C \equiv C–CH=CH_2$ is:

(a) 6 (b) 4

(c) 2 (d) 7

(C) What are functional groups?

(D) Classify the compound based on the presence of a functional group.



(E) Assertion (A): The members of a homologous series are as follows:
CH_3COOH, CH_3CH_2COOH,
$CH_3CH_2CH_2COOH$,
$CH_3CH_2CH_2CH_2COOH$

Reason (R): A homologous series is a group of compounds that share the same functional group but differ by $– CH_2$ unit.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

Ans. (A) *(c)* $H_3C – CH_3$

Explanation: In $H_3C–CH_3$, all the atoms are arranged and bonded together in a molecular formula of a chemical compound. But in the condensed formula, structural can be further simplified by eliminating some or all of the dashes signifying covalent bonds and by using a subscript to indicate the number of identical groups linked to an atom.

(B) *(c) 2*

Explanation: Triple (-) bonded carbons are arranged linearly.

(C) The functional group is an atom or group of atoms that are connected in a specific way and are responsible for organic molecules' unique chemical properties.

(D) Carboxylic Acid

Explanation: IUPAC name: 2, 5-dimethyl octanoic acid.

(E) *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

Explanation: All the compounds mentioned belong to a homologous series as they have the same functional group –COOH. and differ by $–CH_2$ unit. A homologous series is a group of compounds that have similar chemical properties and the same functional group but differ from one another by a $–CH_2$ unit.

OBJECTIVE Type Questions

[1 mark]

Multiple Choice Questions

1. The valency of carbon is:

(a) 1 (b) 2

(c) 3 (d) 4

Ans. *(d) 4*

Explanation: Carbon is tetravalent as it can form four bonds.

2. The general molecular formula, which represents the homologous series of alkanols is:

(a) $C_nH_{2n+2}O$ (b) $C_nH_{2n}O_2$

(c) $C_nH_{2n}O$ (d) $C_nH_{2n+1}O$

Ans. *(a)* $C_nH_{2n+2}O$

Explanation: In the IUPAC system, monohydric alcohols are referred to as alkanols and have the general formula $C_nH_{2n+2}O$.

3. Identify the condensed formula of ethane from the following.

(a) CH_3CH_3

(b) $H_3C–CH_2–CH_3$

(c) $CH_2 = CH_2$

(d) $CH_3–CH=CH_2$

Ans. *(a)* CH_3CH_3

Explanation: In the condensed formula, all the atoms are represented but single bonds are not shown. Only double and triple bonds will be represented. $CH_2 = CH_2$ is not ethane; it is ethene.

4. Which of the following is not an example of acyclic compound?

(a) Acetaldehyde (b) Ethane

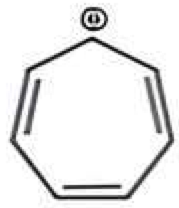
(c) Cyclobutane (d) Isobutane

Ans. *(c) Cyclobutane*

Explanation: Among the given options cyclobutane is not an open-chain compound rather it has a ring structure. Thus, it is not an acyclic compound.

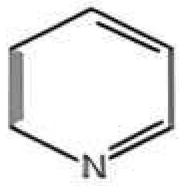
5. **Which of the following species has six π conjugated electrons?[Delhi Gov. QB 2022]**

(a)



(b) $CH_2 = CH - CH = CH - CH_2^-$

(c)



(d) All of the above

Ans. *(d) All of the above*

Explanation: All these contain (a) 6π-electron system.

Related Theory

- *Benzenoid and non-benzenoid compounds are that benzenoid compounds contain at least one benzene ring in the molecule whereas non-benzenoid compounds have no benzene rings. Both benzenoid and non-benzenoid compounds are aromatic compounds*

6. **Electronegativity of carbon atoms depends upon their state of hybridisation. In which of the following compounds, the carbon marked with an asterisk is most electronegative?**

(a) $CH_3 - CH_2 - {}^*CH_2 - CH_3$

(b) $CH_3 - {}^*CH = CH - CH_3$

(c) $CH_3 - CH_2 - C \equiv {}^*CH$

(d) $CH_3 - CH_2 - CH = {}^*CH_2$

[NCERT Exemplar]

Ans. *(c)* $CH_3 - CH_2 - C \equiv {}^*CH$

Explanation: s-character ∝ electronegativity

Hence the higher the s-character in the hybridisation of the C-atom, the higher will be the electronegativity.

In $CH_3 - CH_2 - {}^*CH_2 - CH_3$, *C is sp^3 hybridised, 25% s-character.

In $CH_3 - {}^*CH = CH - CH_3$, *C is sp^2 hybridised, 33.3% s-character.

In $CH_3 - CH_2 - C \equiv {}^*CH$, *C is sp hybridised, 50% s-character.

In $CH_3 - CH_2 - CH = {}^*CH_2$, *C is sp^2 hybridised, 33.3% s-character.

Thus, highest s-character and highest electronegativity is of $CH_3 - CH_2 - C \equiv {}^*CH$.

7. **Which of the following compounds contain all the carbon atoms in the same hybridisation state?**

(a) $H - C \equiv C - C \equiv C - H$

(b) $CH_3 - C \equiv C - CH_3$

(c) $CH_2 = C = CH_2$

(d) $CH_2 = CH - C \equiv CH$

Ans. *(a)* $H - C \equiv C - C \equiv C - H$

Explanation: In option (a), all 4-carbon atoms are sp-hybridised.

Assertion-Reason (A-R)

In the following question no. (8-9) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

8. **Assertion (A):** In $H_2C = C = CH_2$, all of the carbon atoms are sp^2 hybridised.

Reason (R): All of the carbon atoms in this molecule are linked together by double bonds.

Ans. *(d) (A) is false but (R) is true.*

Explanation: $CH_2 = C = CH_2$

All are bonded by double bonds.

9. **Assertion (A):** Butane and 2-methyl butane are homologous.

Reason (R): Butane is a straight-chain alkane while 2-methyl butane is a branched-chain alkane.

Ans. *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

Explanation: Butane and 2-methylbutane are homologous as they differ by a $-CH_2$ group.

Related Theory

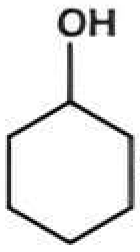
- *A homologous series is formed by a group or series of organic compounds, each of which contains a distinctive functional group. The members of the series are referred to as homologous. A homologous series' members can be represented by a general molecular formula, while the subsequent members differ in the molecular formula by a $-CH_2$ unit.*

CASE BASED Questions (CBQs)

[**4** & **5** marks]

Read the following passages and answer the questions that follow:

10. *Alicyclic compounds (aliphatic cyclic) are made up of carbon atoms arranged in a ring (homocyclic). Other atoms than carbon are known to exist in the ring (heterocyclic). A heterocyclic compound is an organic compound in which one or more of the carbon atoms in the backbone of the molecule has been replaced by an atom other than carbon. Some of its properties are similar to those of aliphatic compounds. Aromatic compounds are a class of chemicals. Examples include benzene and other similar ring compounds (benzenoid). Benzenoid compounds contain at least one benzene ring in the molecule whereas non benzenoid compounds have no benzene rings. Aromatic compounds can also have a heteroatom in the ring. This type of compound is known as a heterocyclic aromatic compound.*

(A) 

is an example of:

(a) Aliphatic cyclic compound
(b) Aromatic compound
(c) Straight chain compound
(d) Branched compound

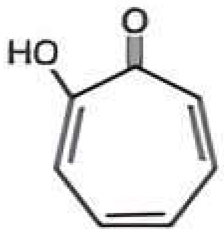
(B) Which of the following is a non-benzenoid aromatic compound?

(a) Anthracene
(b) Cyclohexane
(c) Naphthalene
(d) Tropolone

(C) Identify the pair of heterocyclic aromatic compounds.

(a) Benzene, Furan
(b) Furan, Pyridine
(c) Phenanthrene, Pyran
(d) Cyclohexane, Benzene

(D) The given structure can be classified as:



(a) Homocyclic aliphatic compound
(b) Heterocyclic aromatic compound
(c) Benzenoid aromatic compound
(d) Non- benzenoid aromatic compound

(E) What is the hybridisation of carbon in benzene?

(a) sp^2
(b) sp
(c) sp^3
(d) Not known

Ans. (A) *(a) Aliphatic cyclic compound*

Explanation: An alicyclic compound is a cyclic organic compound that is also aliphatic. They have one or more all-carbon rings that can be saturated or unsaturated but do not have aromatic properties. Alicyclic compounds may contain one or more aliphatic side chains.

(B) *(d) Tropolone*

Explanation: The primary distinction between benzenoid and non-benzenoid compounds is that benzenoid compounds have at least one benzene ring in the molecule, whereas non-benzenoid compounds do not.

(C) *(b) Furan, Pyridine*

Explanation: Examples of heterocyclic aromatic compounds are furan and pyridine Due to the presence of non-localised lone pair. Furan is an aromatic compound with the oxygen lone pair participating in the π-electron system to satisfy Huckel's rule. $4n + 2$ ($n = 1$) electrons. Pyridine is a cyclic conjugated compound with three π-bonds. The molecule has six π-electrons, which is a Huckel number and it is aromatic.

(D) *(d) Non-benzenoid aromatic compound*

Explanation: Non-benzenoid compounds have no benzene rings in their structure but they follow the Huckel rule.

(E) *(a) sp^2*

Explanation: The benzene hybridisation is said to be of the sp^2 type. Benzene is made up of six carbon and six hydrogen atoms. with the central atom usually hybridised. The central atom in this case is carbon.

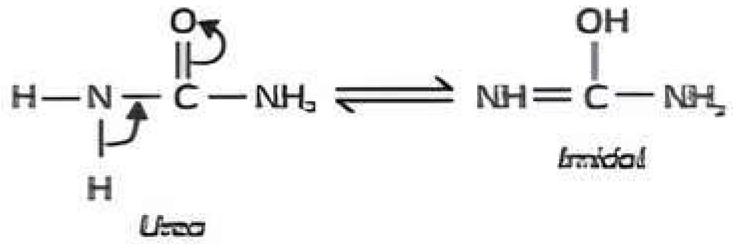
11. *Organic chemistry has a nearly two-hundred-year history. Around the year 1780, chemists began to distinguish between organic molecules derived from plants and animals and inorganic compounds derived from mineral sources. Swedish chemist Berzelius believed that organic molecules were formed by a 'life force.' This theory was debunked in 1828 when F. Wohler synthesised urea from ammonium cyanate, an inorganic substance. Urea is a carbonyl group with two C-bound amine groups. The commercially available fertilizer has an analysis of 46–0–0 (N – P_2O_5 – K_2O). It has a role as a flour treatment agent, a human metabolite, a Daphnia magna metabolite, a Saccharomyces cerevisiae metabolite, an Escherichia coli metabolite, a mouse metabolite and a fertilizer. It is a monocarboxylic acid amide and a one-carbon compound. It derives from carbonic acid.*

(A) Which was the first organic compound to be synthesised? Why does urea form tautomerism and not isomers?

(B) What is catenation?

(C) What is a benzenoid aromatic compound? Give the structure of naphthalene, phenanthrene and anthracene.

Ans. (A) F. Wohler created an organic chemical, urea, by converting an inorganic material, ammonium cyanate, into an organic compound. Urea ($H_2N–CO–NH_2$) has only one structure. There is no isomerism in Urea. Urea has a "keto-imine" tautomeric structure that exists in equilibrium. But these are not isomers, rather they are tautomers.



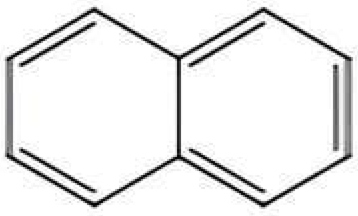
Urea
(Amido)

Imidol

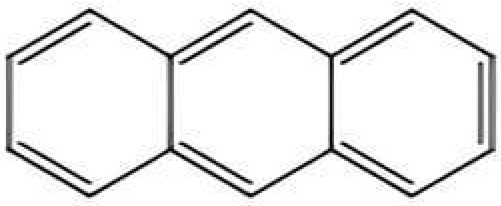
(B) Catenation is the property by which an element binds to itself via covalent bonds to create chain or ring molecules. Carbon is the most typical element that undergoes catenation. It can form lengthy hydrocarbon chains and rings.

(C) Benzenoid aromatic compound is an aromatic compound with only benzene rings in its structure. Examples include naphthalene, aniline and others.

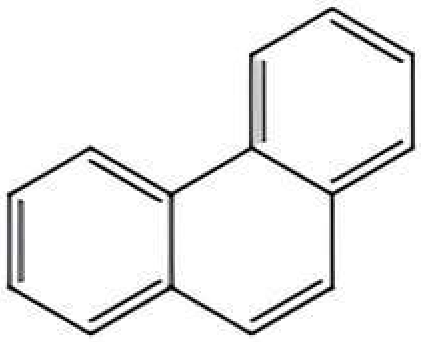
A molecular structures in which two carbon atoms are shared by two or more aromatic rings are fused aromatic rings.



Naphthalene



Anthracene



Phenanthrene

Related Theory

- *These are polycyclic aromatic compounds with fused rings between them. Anthracene and phenanthrene have same molecular formula and different structures.*

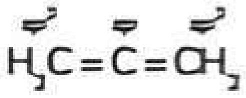
VERY SHORT ANSWER Type Questions (VSA)

[1 mark]

12. What is organic chemistry?

Ans. Organic chemistry is a discipline of chemistry that primarily studies the characteristics, structure and reactivity of organic molecules.

13. What is the hybridisation of each carbon in $H_2C = C = CH_2$? **[NCERT Exemplar]**

Ans. 
$H_2C=C=CH_2$

14. What exactly is a functional group?

Ans. The functional group is the atom or group of atoms in a molecule that determines its chemical properties.

SHORT ANSWER Type-I Questions (SA-I)

[2 marks]

15. How will you account for the presence of a large number of organic compounds?

[Delhi Gov. QB 2022]

Ans. The self-linking of atoms of an element to form chains and rings is responsible for the formation of a large number of compounds. This property is present only in certain elements such as carbon, sulphur, silicon and boron.

16. What type of hybridisation each carbon has in the following compounds?

CH_3Cl, CH_3CN

Ans. $\overset{sp^3}{C}H_3—Cl$ $\overset{sp^3}{C}H_3—\overset{sp}{C}\equiv N$

SHORT ANSWER Type-II Questions (SA-II)

[3 marks]

17. Define Heterocyclic compounds.

Ans. Cyclic compounds containing one or more heteroatoms in their rings are called heterocyclic compounds.

Heterocyclic compounds are classified into two categories:

(1) **Alicyclic heterocyclic compounds:** Alicyclic compounds containing one or more heteroatoms in their rings are called alicyclic compounds.

(2) **Aromatic heterocyclic compounds:** Aromatic cyclic compounds containing one or more heteroatoms in their molecules are called aromatic heterocyclic compounds.

18. Explain how the electronegativity of carbon atoms in an organic compound is related to their hybridisation state. [NCERT Exemplar]

Ans. Carbon's electronegativity is proportional to its 's' nature. When C is sp^3 hybridised, the s-character is 25%, when it is sp^2 hybridised, the s-character is 33% and when it is sp hybridised, the s-character is 50%. As a result, sp hybridised carbon possesses high electronegativity, s-electrons are more strongly attracted by the nucleus than p-electrons and carbon's electronegativity increases as the 's' character grow.

19. Define non-benzenoid aromatic compounds.

Ans. Aromatic compounds which do not contain a benzene ring but instead contain other highly unsaturated rings are called non-benzenoid aromatic compounds.

For example  Cyclopentadienyl anion.

LONG ANSWER Type Questions (LA)

[4 & 5 marks]

20. Which of the following represents the correct IUPAC name for the compounds concerned?

(A) 2, 2-Dimethyl pentane or 2-Dimethyl pentane

(B) 2, 4, 7-Trimethyl octane or 2, 5, 7-Trimethyl octane

(C) 2-Chloro-4-methyl pentane or 4-Chloro-2-methyl pentane

(D) But -3-yn-1-ol or But -4-ol-1-yne

[NCERT Exemplar]

Ans. (A) The prefix di indicates that the chain contains two methyl groups. As a result, the correct IUPAC name is 2, 2-Dimethyl pentane.

(B) In this case, 2, 4, 7, is less 2, 5, 7. As a result, the correct IUPAC name is 2, 4, 7-Trimethyl octane.

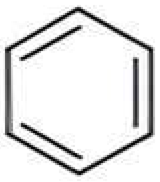
(C) If the substituents in the chain are in equivalent positions, the substituent group in alphabetical order receives the lower number. As a result, the correct IUPAC name is 2-Chloro-4-methyl pentane.

(D) The alcoholic functional group is the more important of the two functional groups present in the given compound. As a result, the parent chain will end in –ol. Because the alkyne group is in the C–3 position, the IUPAC name would be but –3-yn-1-ol.

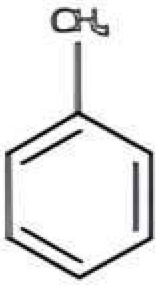
21. **Define benzenoid aromatic compounds with their example.**

Ans. The organic compounds containing one or more fused or isolated benzene rings have functionalised derivatives. Examples are:

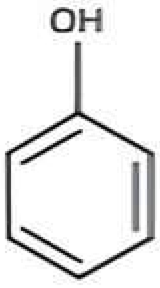
(1) Monocyclic aromatic compounds:



Benzene

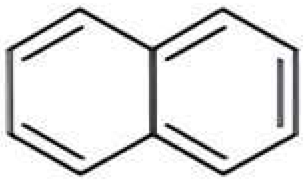


Toluene

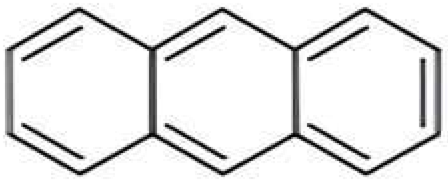


Phenol

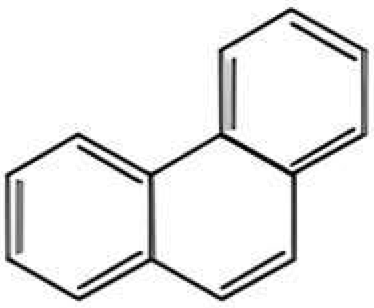
(2) Bicyclic aromatic compounds:



Naphthalene



Anthracene



Phenanthrene

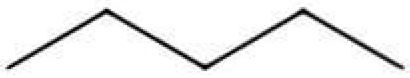
22. **Write the homologous series of ethane up to 5 homologous.**

Ans.

Ethane CH_3CH_3

Propane $CH_3CH_2CH_3$

Butane $CH_3CH_2CH_2CH_3$



Pentane $CH_3CH_2CH_2CH_2CH_3$

Hexane $CH_3CH_2CH_2CH_2CH_2CH_3$

Related Theory

- *Homologous series is formed by adding one CH_2 unit after each succeeding alkane.*

IUPAC NOMENCLATURE AND ISOMERISM

2

TOPIC 1

NOMENCLATURE OF ORGANIC COMPOUNDS

The system where we gave the name to the organic compounds is referred to as 'Nomenclature of Organic Compounds'. There are two nomenclature systems:

(1) The common or trivial system

(2) The IUPAC system of naming

Trivial or Common System

The names of organic compounds were assigned under this nomenclature depending on their source of origin or certain qualities. For example, formic acid was first derived from the Latin word, e.g., *Formica* which means ant. Similarly, Citric acid gets its name from the citrus fruits from which it was first extracted. Even today, certain common names are utilised. Although many common names are difficult to remember, they are frequently employed when the IUPAC name is too long.

Table: Common or Trivial Names of Some Organic Compounds

Compound	Common name
CH_4	Methane
$H_3CCH_2CH_2CH_3$	*n*-Butane
$(H_3C)_2CHCH_3$	Isobutane
$(H_3C)_4C$	Neopentane
$H_3CCH_2CH_2OH$	*n*-Propyl alcohol
$HCHO$	Formaldehyde
$(H_3C)_2CO$	Acetone
$CHCl_3$	Chloroform
CH_3COOH	Acetic acid
C_6H_6	Benzene
$C_6H_5OCH_3$	Anisole
$C_6H_5NH_2$	Aniline
$C_6H_5COCH_3$	Acetophenone

IUPAC system of nomenclature

Many organic compounds exist, which makes it tougher to remember all of the common names for chemical substances. As a result, the IUPAC (International Union of Pure and Applied Chemistry) nomenclature system was devised as a systematic means of identifying organic substances. The IUPAC NOMENCLATURE is done as

Secondary prefix + Primary prefix + Word root + Primary suffix + Secondary suffix

IUPAC Nomenclature of Alkanes

Straight chain hydrocarbons

Straight chain hydrocarbon names are made up of a word root and a primary suffix.

Table: The name of the number of carbon atoms

Chain Size	Nomenclature
1	Meth
2	Eth
3	Prop
4	But
5	Pent
6	Hex
7	Hept
8	Oct
9	Non
10	Dec

The suffix 'ane' is the main suffix for alkanes.

The following are the IUPAC names of certain unbranched saturated hydrocarbons (Carbon-Carbon single bond):

Table: IUPAC Names of Some Unbranched Saturated Hydrocarbons

Name	Molecular formula	Name	Molecular
Methane	CH_4	Heptane	C_7H_{16}
Ethane	C_2H_6	Octane	C_8H_{18}
Propane	C_3H_8	Nonane	C_9H_{20}
Butane	C_4H_{10}	Decane	$C_{10}H_{22}$
Pentane	C_5H_{12}	Icosane	$C_{20}H_{42}$
Hexane	C_6H_{14}	Triacontane	$C_{30}H_{62}$

Branched-chain hydrocarbons

Small carbon atom side chains are connected to the main carbon parent chain of branched-chain hydrocarbons. The side chains are referred to as alkyl groups, which are affixed to the name of a parent alkane. Alkyl groups are formed by removing one hydrogen atom from an alkane and they have the general formula C_nH_{2n+1} and are denoted by –R. By changing the alkane's 'ane' to 'yl'. It is called the alkyl group.

$$\text{Alkane} \xrightarrow[+\,yl]{-\,ane} \text{alkyl}$$

$$\underset{\text{Methane}}{CH_4} \xrightarrow[+\,yl]{-\,ane} \underset{\text{Methyl}}{CH_3}$$

Table: Some Alkyl Groups

Alkane		Alkyl group	
Molecular formula	Name of alkane	Structural formula	Name of alkyl group
CH_4	Methane	$-CH_3$	Methyl
C_2H_6	Ethane	$-CH_2CH_3$	Ethyl
C_3H_8	Propane	$-CH_2CH_2CH_3$	Propyl
C_4H_{10}	Butane	$-CH_2CH_2CH_2CH_3$	Butyl
$C_{10}H_{22}$	Decane	$-CH_2(CH_2)_8CH_3$	Decyl

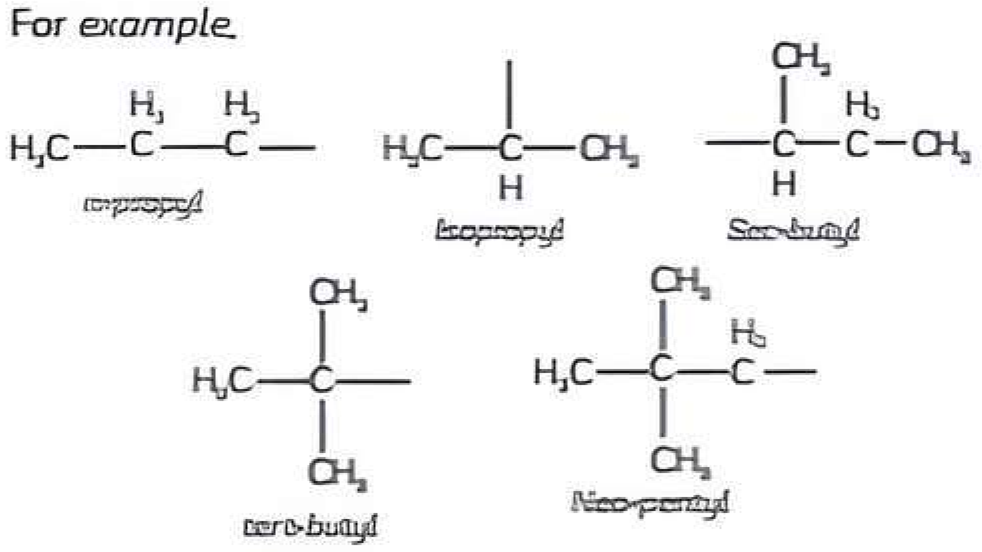
The alkyl groups aren't usually arranged in a straight line. They can also be branched.

Prefix, a word root and a major suffix are all required for naming branched-chain hydrocarbons.

Prefix + Word root + Primary suffix

For common names Prefixes such as *iso, sec, tert, neo* and others are added to an alkyl group when it is branched.

For *example*,



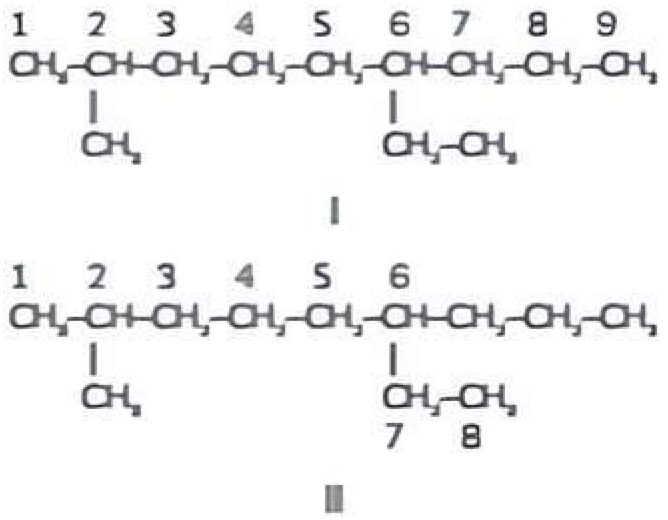
Some examples of branched alkyl groups.

Nomenclature of Branched-Chain Alkanes

Following principles are used while naming a branched-chain alkane:

(1) Longest chain rule

The first stage in nomenclature is to determine which carbon chain is the longest, which is then referred to as the parent chain.

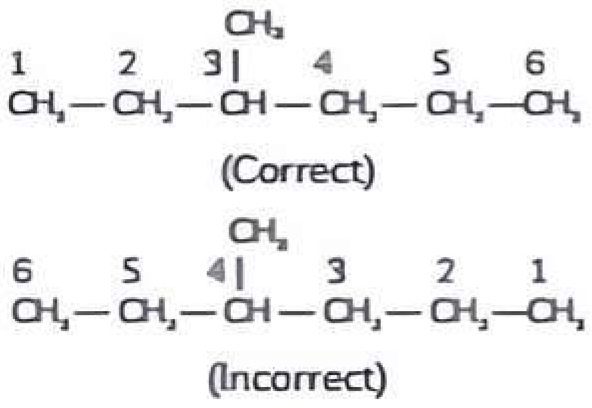


Longest Chain Rule

Way-I of the two methods for picking the parent chain is right because the parent chain has nine carbon atoms, but way-II contains just eight carbon atoms.

(2) Lowest number rule

The parent chain is numbered in such a way that the substituents attached to the parent chain get the lowest possible number.

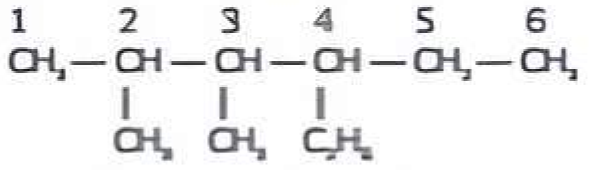


Lowest Number Rule

Way-I is correct because the substituents are assigned to the lowest locations 3, whereas the substituents are assigned to position 4 in way-II.

(3) Alphabetical order of the side chain

Before the name of the parent chain, the alkyl group's name is prefixed. The parent chain is precisely numbered to show the position of the alkyl group. When different alkyl groups are present as substituents, special attention is paid to naming the substituents in alphabetical order.

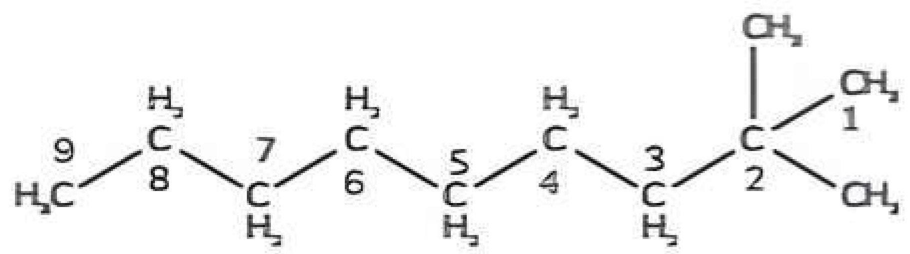


4-Ethyl-2, 3-dimethyl hexane

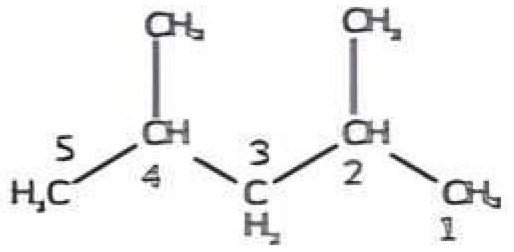
(4) Use of symbols

The numbers are separated by a comma in the IUPAC name of an organic compound, a dash or hyphen (–) is placed between a number and a letter which are merged into a single word.

When a branching hydrocarbon has more than one alkyl group, the names are not repeated; instead, the number of the same alkyl substituents is expressed as *di* for two, *tri* for three, *tetra* for four, *penta* for five, *hexa* for six and so on. The following instances demonstrate this rule:



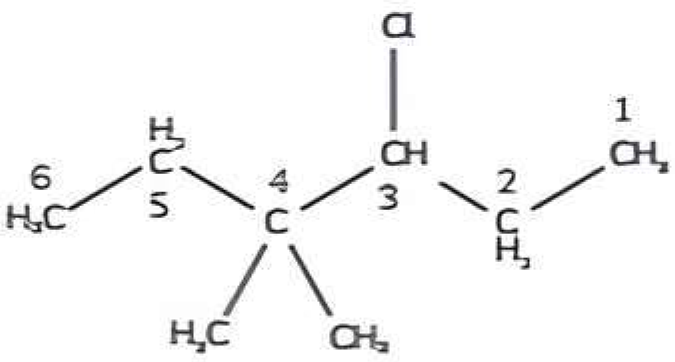
2, 2-Dimethyl nonane



2, 4-Dimethyl pentane

(5) Use of prefix

When an organic compound contains more than one alkyl group, its names are written in alphabetical order, but the prefixes *di*, *tri* and so on are not taken into account. As a result, the proper name for the following compound is 3-Chloro-4, 4-dimethyl hexane.



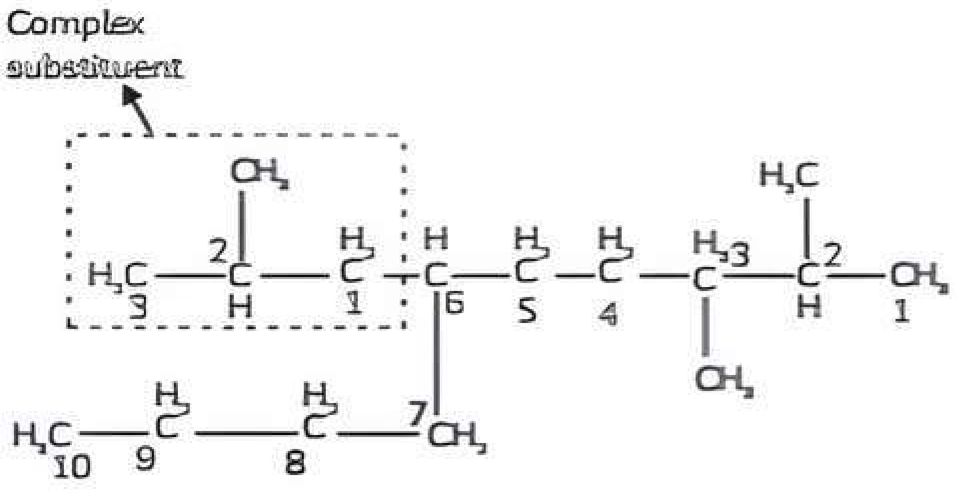
3-chloro-4, 4-dimethyl hexane

(6) Numbering of different alkyl groups at equivalent positions

When two different alkyl groups are present at the equivalent positions then the naming is done from that side which gives a lower number to alkyl group coming, first in alphabetical order.

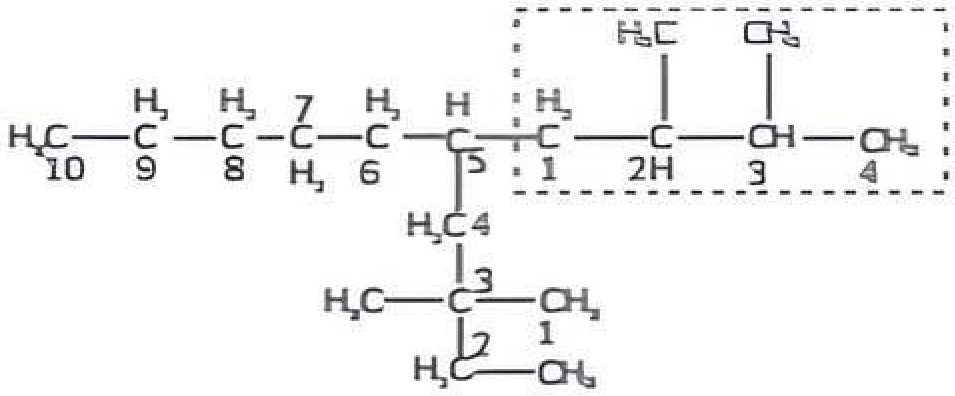
(7) Naming the hydrocarbon with complex substituent

(i) If the substituent is complex (i.e., further branched) then the carbon of the Substituent that is directly attached to a parent chain is numbered 1. When naming a compound, the name of a complex branched-chain alkyl group is placed in parenthesis.

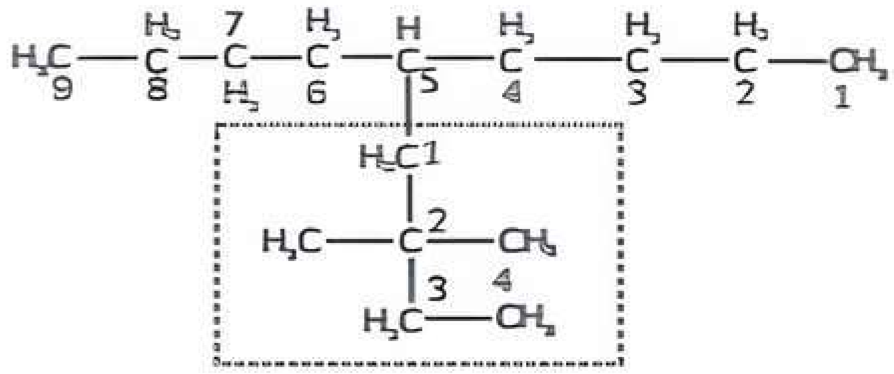


2, 3-Dimethyl-6-(2-methyl propyl) decane

(ii) When two substituted chains of comparable size exist, the parent chain with the most side chains is termed the parent chain. Furthermore, the numbering is done so that the substituent receives the lowest number.

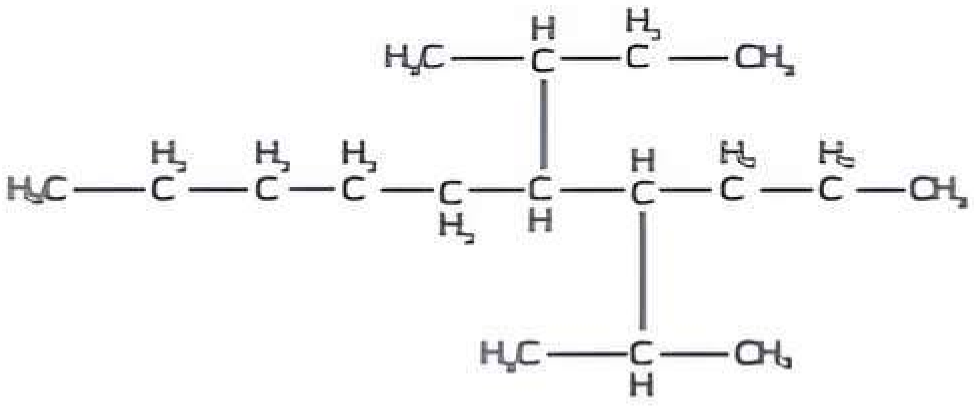


5-(2,3-Dimethyl butyl)-3, 3-dimethyl decane



5-(2, 2-Dimethyl butyl) nonane

The substituent having less branching is named in alphabetical order, then the prefixes *iso-* and *neo-* are considered part of the fundamental name of the alkyl group. *sec-* and *tert-* are the prefixes that do not appear in the fundamental name.

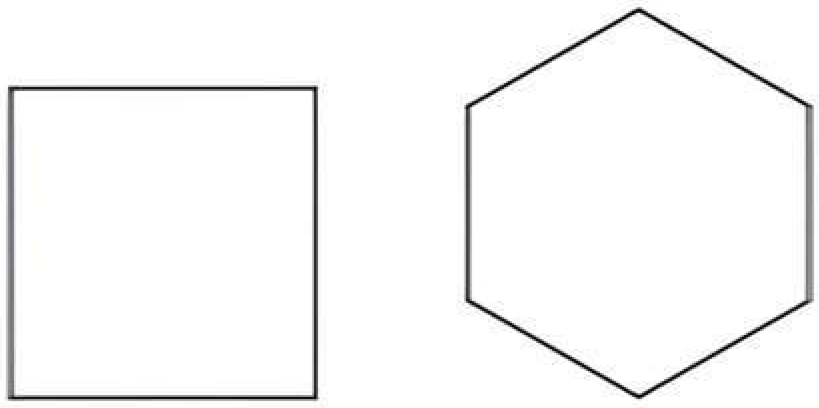


5-sec-butyl-4-isopropyl decane

Cyclic Compounds

The 'cyclo' prefix is used before the name of the parent chain for designating cyclic hydrocarbons and the other rules are the same as previously mentioned.

For example:



Cyclobutane Cyclohexane

Cyclic Compounds

Nomenclature of Organic Compounds having functional groups

Functional group

A functional group in a molecule is an atom or a group of atoms that are joined together in a specific way to determine the molecule's chemical characteristics. Organic molecules with the same functional group have similar chemical characteristics. When alcohols like CH_3OH, CH_3CH_2OH, $(CH_3)_2CHOH$ and others are exposed to sodium metal, they always create hydrogen.

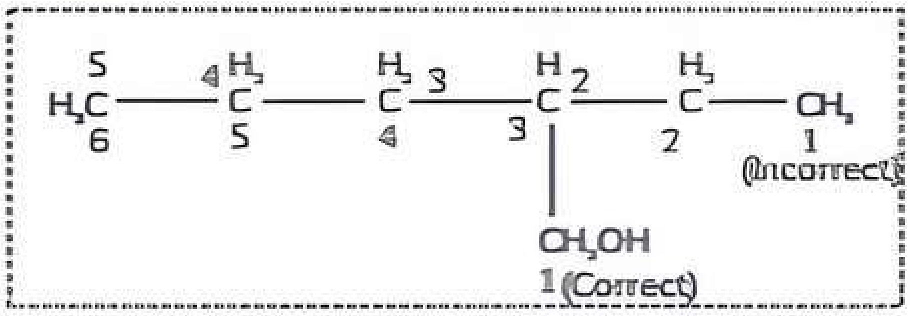
A functional group's presence is indicated by adding their suffixes or prefixes. The following table lists the prefixes and suffixes of similar functional groups.

Table: Some Functional Groups and Classes of Organic Compounds

Class of compounds	Functional group structure	IUPAC group prefix	IUPAC group suffix	Example
Alkanes	–	–	-ane	Butane, $CH_3(CH_2)_2CH_3$
Alkenes	$>C{=}C<$	–	-ene	But-1-ene, $CH_2{=}CHCH_2CH_3$
Alkynes	$-C{\equiv}C-$	–	-yne	But-1-yne $CH{\equiv}CCH_2CH_3$
Arenes	–	–	–	Benzene 
Halides	$-X$ $(X{=}F, Cl, Br, I)$	halo-	–	1-Bromobutane, $CH_3(CH_2)_2CH_2Br$
Alcohols	$-OH$	hydroxy-	-ol	Butan-2-ol, $CH_3CH_2CHOHCH_3$
Aldehydes	$-CHO$	formyl, or oxo	-al	Butanal, $CH_3(CH_2)_2CHO$
Ketones	$>C{=}O$	oxo-	-one	Butan-2-one, $CH_3CH_2COCH_3$
Nitriles	$-C{\equiv}N$	cyano	nitrile	Pentanenitrile, $CH_3CH_2CH_2CH_2CN$
Ethers	$-O-$	alkoxy-	–	Ethoxyethane, $CH_3CH_2OCH_2CH_3$
Carboxylic acids	$-COOH$	carboxy	-oic acid	Butanoic acid, $CH_3(CH_2)_2CO_2H$
Carboxylate ions	$-COO^-$	–	-oate	Sodium butanoate, $CH_3(CH_2)_2CO_2\ Na^+$
Esters	$-COOR$	alkoxycarbonyl	Alkyl-oate	Methyl propanoate, $CH_3CH_2COOCH_3$
Acyl halides	$-COX$ $(X{=}F, Cl, Br, I)$	halocarbonyl	-oyl halide	Butanoyl chloride, $CH_3(CH_2)_2COCl$
Amines	$-NH_2$, $>NH$, $>N-$	amino-	-amine	Butan -2-amine, $CH_3CHNH_2CH_2CH_3$
Amides	$-CONH_2$, $-CONHR$, $-CONR_2$	-carbamoyl	-amide	Butanamide, $CH_3(CH_2)_2CONH_2$
Nitro	$-NO_2$	nitro	–	1-Nitrobutane, $CH_3(CH_2)_3NO_2$
Sulphonic acids	$-SO_3H$	sulpho	-sulphonic acid	Methylsulphonic acid CH_3SO_3H

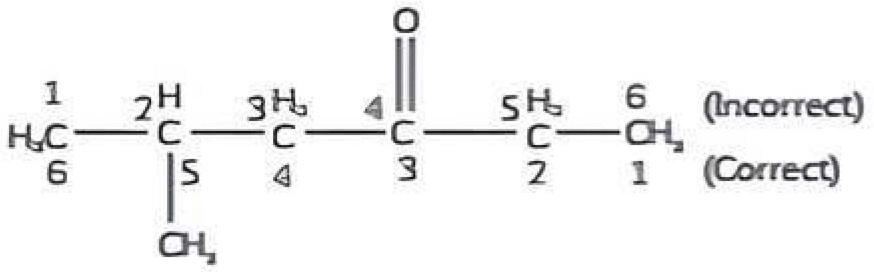
The rules that must be followed while naming an organic compound containing a functional group are as follows.

(1) **Parent Chain:** The parent chain is the carbon chain that includes the functional group, regardless of whether it will give the longest carbon chain or not.



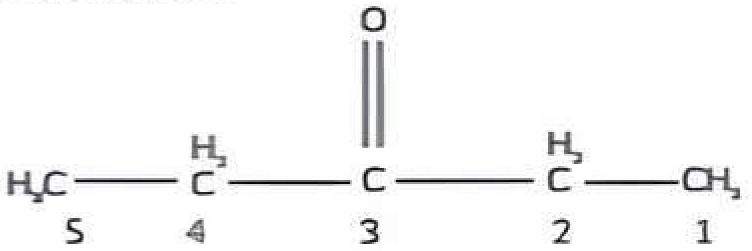
Parent Chain

(2) **Numbering of the parent chain:** The carbon associated with the functional group receives the lowest number in the chain possible when designating organic compounds containing functional groups.



Numbering of the Parent Chain

(3) To confirm the existence of a functional group, a secondary suffix is added after the primary suffix (one, ene, yne). If the secondary suffix begins with "a," I "o," "u," or "e," the main suffix's 'e' is dropped.



$H_3C-CH_2-CO-CH_2-CH_3$

Pentan-3-one

Naming of the Chain

(4) **More than one functional group:** When there are multiple functional groups in an organic compound, one of them is regarded as the primary functional group, while the others are treated as substituents. The major functional group is given a suffix, whereas the alternative functional groups are given a prefix. The order of preference is used to determine the primary functional group.

$-SO_3H > -COOH > -COOR > -COX >$

$-COCl > -CONH_2 > -CHO > -CN > \rangle C=O$

$> -OH > -SH > -NH_2 > \rangle C=C\langle > -C\equiv C- >$

$-NO_2 > -NO > -X$

Priority of functional groups

All other functional groups, such as halo (fluoro, chloro, bromo, iodo), nitroso (–NO), nitro (–NO_2), alkoxy (–OR), R(alkyl), C_6H_6 (phenyl) and so on, are always classified as substituents.

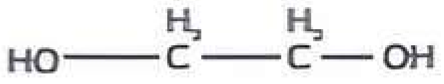
$H_2C=CH-CH_2-Br$

3-Bromoprop-1-ene (Correct)

1-Bromoprop-2-ene (Incorrect)

(5) **More than one functional group of the same type:** When there are many functional groups of the same type, the number of functional groups is specified by prefixing the class suffix with di, tri, etc.

For such organic compounds, the parent alkane's full name comes before the class suffix.



$HO-CH_2-CH_2-OH$

Ethane-1, 2-diol

Example 2.1: **Give condensed and bond-line structural formulas and identify the functional group(s) present, if any, for:**

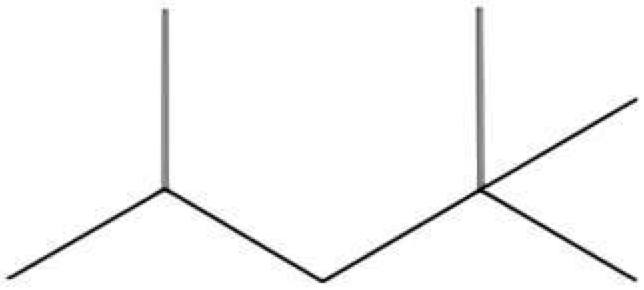
(A) 2, 2, 4-Trimethylpentane

(B) 2-Hydroxy 1, 2, 3-propane tricarboxylic acid

[NCERT]

Ans. (A) The condensed formula of 2, 2, 4 - trimethylpentane is. $(CH_3)_2\ CHCH_2C\ (CH_3)_3$

Bond-line formula of 2, 2, 4 - trimethylpentane is.

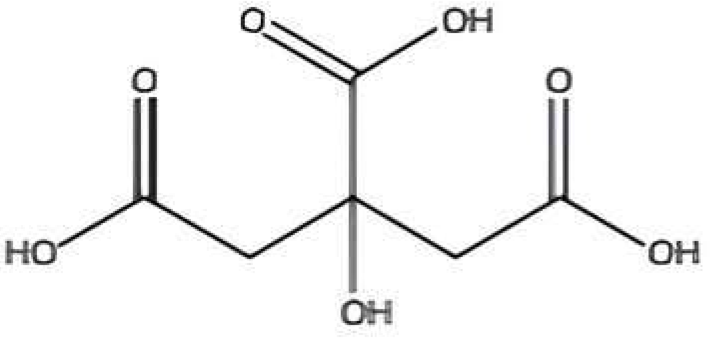


Bond-line formula

(B) The condensed formula of 2-hydroxy 1, 2, 3-propane tricarboxylic acid is.

$(COOH)\ CH_2C\ (OH)\ (COOH)\ CH_2\ (COOH)$

Bond-line formula of 2-Hydroxy 1, 2, 3-propane tricarboxylic acid is.



Bond-line formula

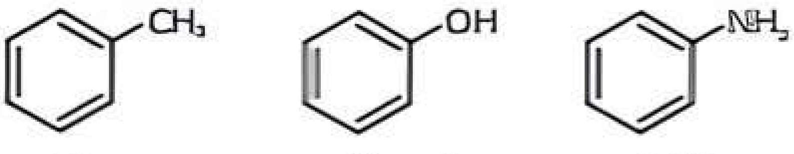
TOPIC 2

NOMENCLATURE OF SUBSTITUTED BENZENE COMPOUNDS

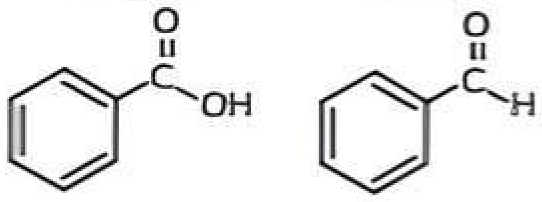
Monosubstituted Benzene Compounds

(1) The prefix used for the substituent is simply prefixed to the word 'benzene' for identifying the substituted benzene compounds.

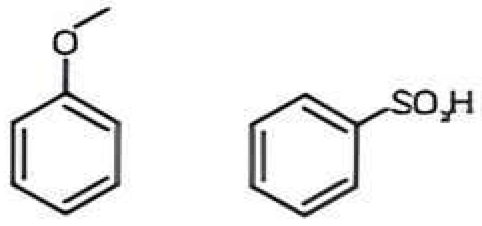
Common IUPAC names of monosubstituted aromatic compounds



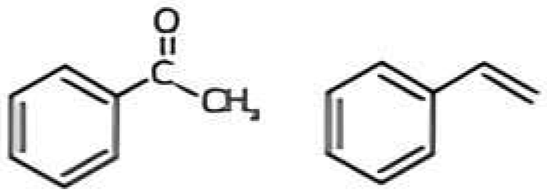
Toluene *Phenol* *Aniline*



Benzoic acid *Benzaldehyde*



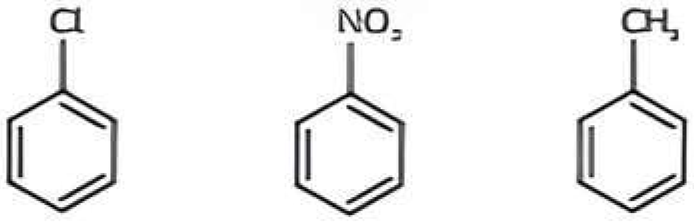
Anisole *Benzene sulphonic acid*



Acetophenone *Styrene*

Benzene Compounds.

(2) Many mono-substituted benzene compounds have well-known common names.



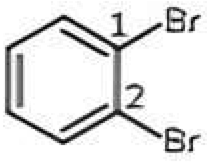
Chlorobenzene *Nitrobenzene* *Methylbenzene (Toluene)*

Benzene Compounds

Disubstituted Benzene Compounds

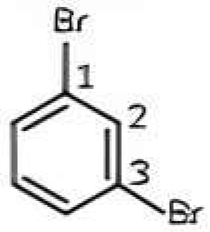
When two hydrogen atoms in benzene are replaced by two monovalent atoms or groups of atoms, a disubstituted benzene derivative is created. Counting up the carbon atoms of the ring in order to assign the lowest numbers to the substituents to determine the location of substituents in such compounds. There are three types of disubstituted benzene compounds.

(1) **1, 2 (ortho) – form:** When the 2 substituents are on carbon atoms that seem to be adjacent.



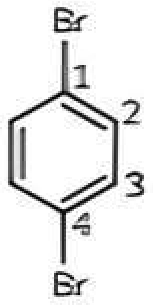
1, 2-dibromo benzene

(2) **1, 3 (meta) – form:** When the 2 substituents are on the carbon atoms in different directions.



1, 3-dibromo benzene

(3) **1, 4 (para) – form:** When the two substituents are on carbon atoms that are diagonally opposite to each other.

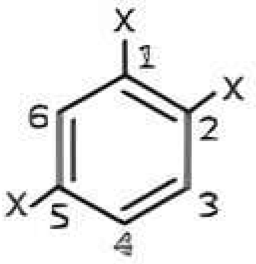


1, 4-dibromo benzene

Benzene Compounds.

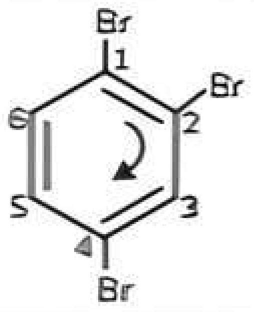
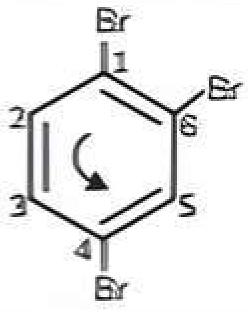
Tri- or higher substituted benzene derivatives

If more than two substituents are present, then the positions of the groups are indicated by numbering the carbon atoms according to the lowest locant rule.

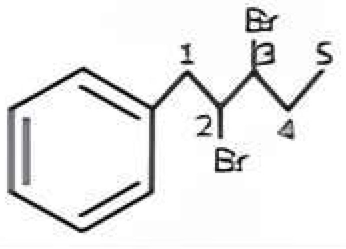
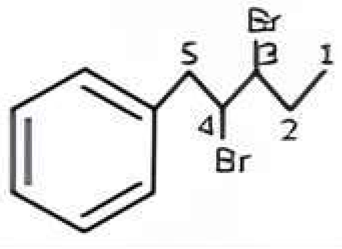


According to this rule, the sequence in which the numbering is done should have the lowest combination of numbers.

Example: Case I is preferred among the following.

Case I	Case II
	
1 + 2 + 4 = 7	1 + 4 + 6 = 11

Case I is preferred among the following.

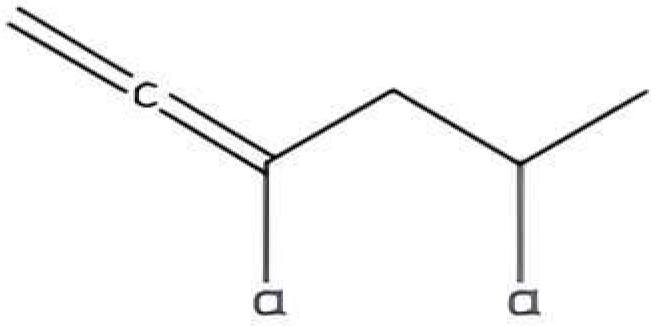
Case I	Case II
	
1 + 2 + 3 = 6	3 + 4 + 5 = 12

Example 2.2: Case Based:

The International Union of Pure and Applied Chemistry (IUPAC) nomenclature of organic chemistry is a system of naming organic distinct chemicals that are approved in chemical nomenclature. It's in the Journal of Organic Chemistry's Nomenclature (informally called the Blue Book). Every potential organic molecule should, in theory, have a name that can be translated into an unambiguous structural formula. Inorganic chemistry has its own IUPAC terminology.

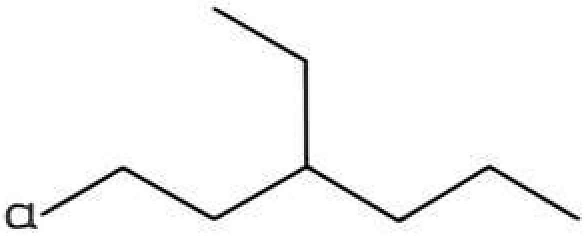
The official IUPAC naming rules are not often followed in practice, particularly where it is required to offer a clear and absolute description of a compound, to avoid long and laborious names in routine communication. In certain cases, such as ethanol instead of ethyl alcohol, IUPAC nomenclature is simpler than in earlier terms.

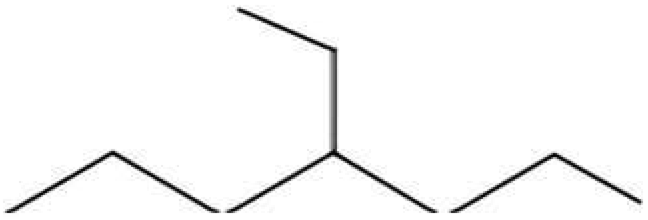
(A) The compound's IUPAC name is:



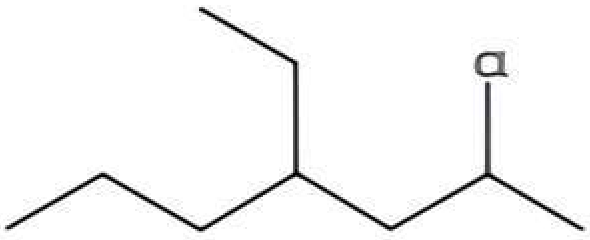
- (a) 2, 3 – Dichloro hex – 1, 4 – diene
- (b) 3, 5 – Dichloro hex – 1, 2 – diene
- (c) 4, 5 – Dichloro hex – 1, 2 – diene
- (d) None of the above

(B) Draw the structure of 1 – Chloro – 3 – ethyl hexane.

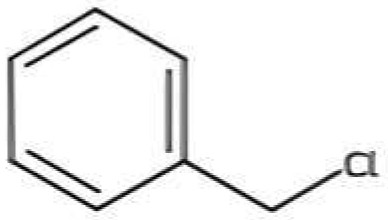
(a)


(b)


(c)

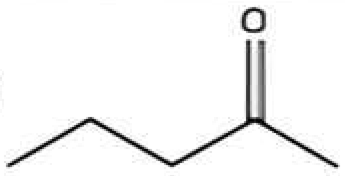
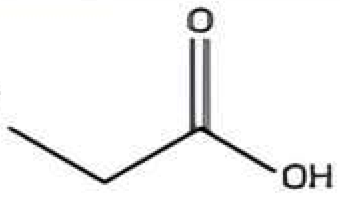

(d)


(C) Is the following structure being correct for given IUPAC name?



5-Chloromethyl benzene

(D) Match the following:

Column I	Column II
(a) 	(i) Propanoic acid
(b) 	(ii) Pentan – 2 – one
(c) 	(iii) Ethanol
(d) 	(iv) Butanal

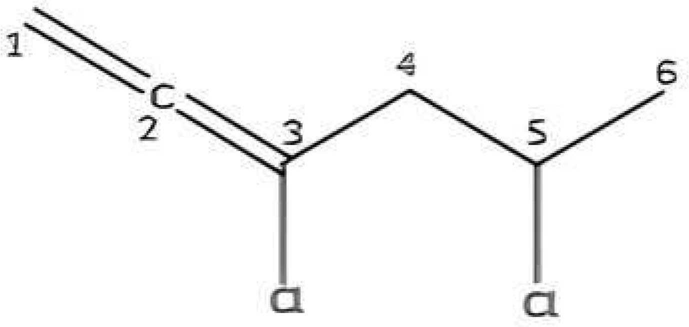
(E) Assertion (A): IUPAC naming is an easy way to learn the different structures of organic compounds.

Reason (R): Each compound does not have any other names except the IUPAC name.

- (a) Both (A) and (R) are true and (R) is the correct explanation of (A).
- (b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
- (c) (A) is true but (R) is false.
- (d) (A) is false but (R) is true.

Ans. (A) *(b) 3, 5 - Dichloro hex - 1, 2 - diene*

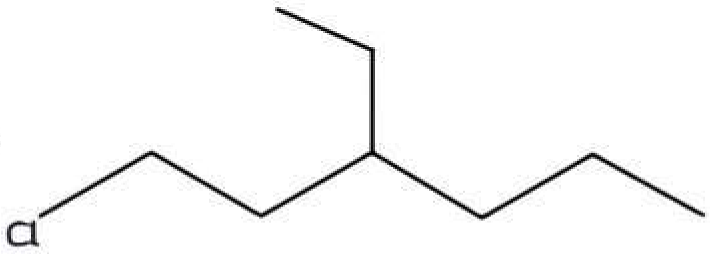
Explanation: The correct IUPAC nomenclature for the given compound is



3,5-Dichlorohex-1,2-diene

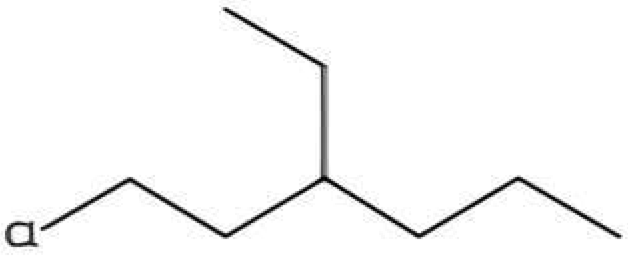
Here numbering will start from the left side and not from the right side as the double bond should get the lowest number.

(B) *(a)*



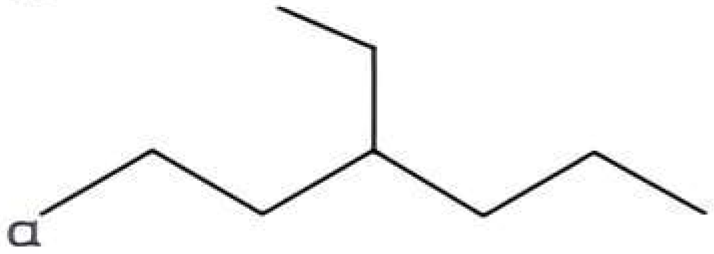
Explanation: the IUPAC nomenclature of given compounds are as follows:

(a)



1 - Chloro - 3 - ethyl hexane

(b)

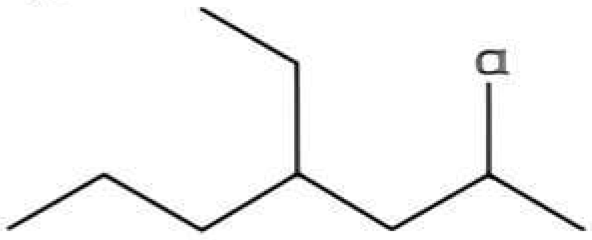


4 - Chloro heptane

(c)

1 - Chloro - 3 - methyl hexane

(d)

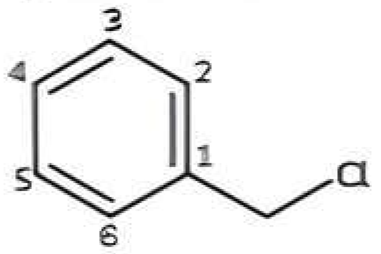


2 - Chloro - 4 - ethyl heptane

⚠ Caution

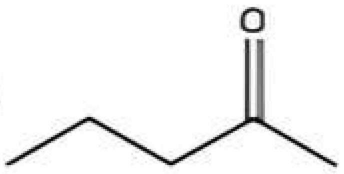
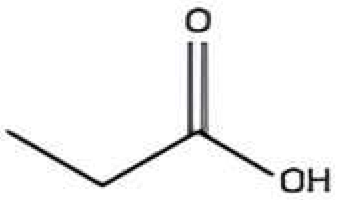
- *In all the given cases the substituents are numbered from that side where they get the lowest number. Also, chloro is named first because of the alphabetical order.*

(C) No, the given name is incorrect.



Chloromethyl benzene

(D) a→(iii), b→(iv), c→(ii), d→(i)

Column I	Column II
(a) 	(iii) Ethanol
(b) 	(iv) Butanal
(c) 	(v) Pentan – 2 – one
(d) 	(i) Propanoic acid

(E) *(c) (A) is true but (R) is false.*

Explanation: The International Union of Pure and Applied Chemistry (IUPAC) nomenclature is significant because it establishes a consistent system for naming chemical substances. So, the assertion is correct but some compounds also have their common names such as ethanoic acid also known as acetic acid. So, the reason is not correct.

OBJECTIVE Type Questions

[1 mark]

Multiple Choice Questions

1. IUPAC name of the given compound is:

$CH_2 = CH - CH_2 - OH$

(a) Propanal (b) Propanol

(c) Prop-2-enol (d) Prop-1-en-3-ol

Ans. *(c) Prop-2-enol*

Explanation: The correct IUPAC name for the given compound is prop-2-en-ol.

⚠ Caution

- *Students might get confused between options (c) and (d). The correct option is (c), as –OH functional group is given a priority over the double bond.*

2. Which one among the below matches is incorrect?

(a) $OHC - CH_2 - COOH$: 3 – Oxopropanoic acid

(b) $CH_3 - O - CH_3$: Methoxy methanal

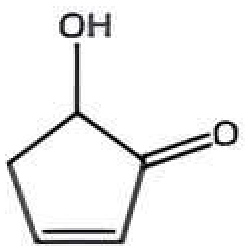
(c) $H_2N - CHO$: Methanamide

(d) CH_3CH_2CN : Propanenitrile

Ans. *(b) $CH_3 - O - CH_3$: Methoxy methanal*

Explanation: This is dimethyl ether or methoxy methanal.

3. The following molecule's IUPAC name is:



(a) 5 - Hydroxycyclopent - 2 - enone

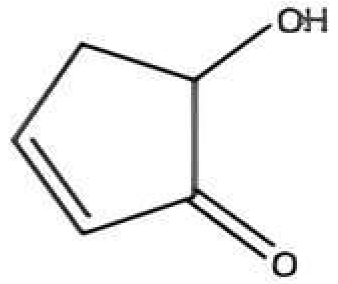
(b) 2 - Hydroxycyclopent - 4 - enone

(c) 5 - Hydroxycyclopent - 4 - enone

(d) 2 - Hydroxycyclopent - 2 - enone

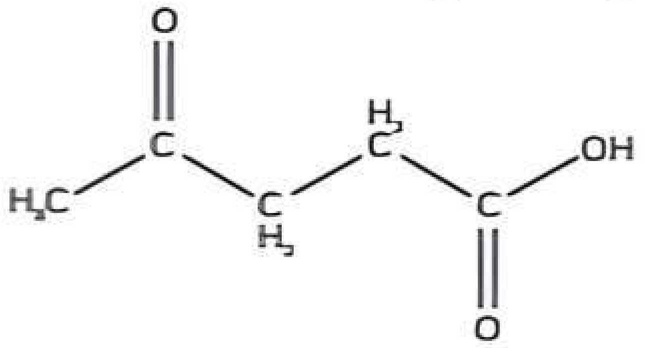
Ans. *(a) 5 - Hydroxycyclopent - 2 - enone*

Explanation: The structures of the compounds given in options are as follows:



5-Hydroxycyclopent-2-enone

4. The IUPAC name for the given compound is:



(a) 1 - hydroxy pentane - 1, 4 - dione

(b) 1, 4 - dioxopentanol

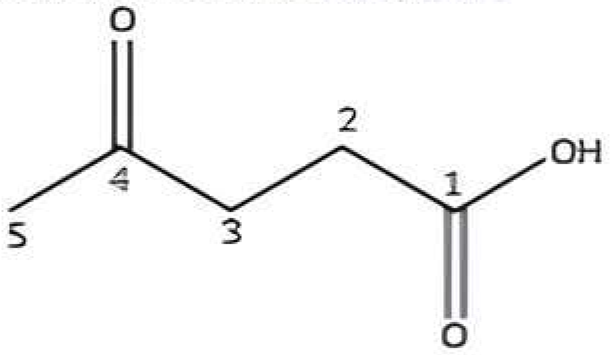
(c) 1 - carboxybutan - 3 - one

(d) 4 - oxopentanoic acid [NCERT Exemplar]

Ans. *(d) 4 – Oxopentanoic acid*

Explanation: The given compound is named as the substituent of carboxylic acid:

(d)



4-Oxopentanoic acid

Assertion-Reason (A-R)

In the following question no. (5-6) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

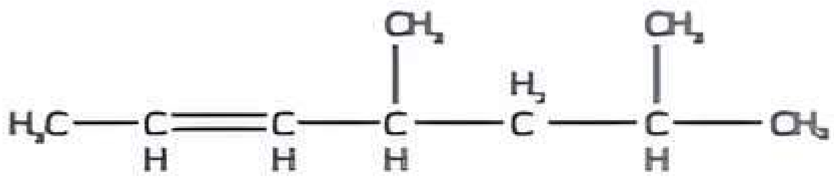
(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of A.

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

5. Assertion (A): 2, 3-Dimethylhept-5-ene is



$H_3C-\underset{H}{C}=\underset{H}{C}-\underset{H}{\overset{CH_3}{C}}-\overset{H_2}{C}-\underset{H}{\overset{CH_3}{C}}-CH_3$

Reason (R): The double-bond gets preference over the alkyl group.

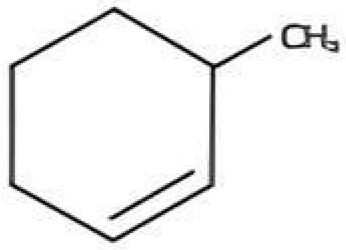
Ans. *(d) (A) is false but (R) is true.*

Explanation: The correct IUPAC name for the compound is 4,6-Dimethyl hept-2-ene.

⚠ Caution

➥ *Even though it defines saturated hydrocarbon rules, the parent carbon chain is numbered in such a manner that the carbon atom linked by a double or triple bond receives the lowest number.*

6. Assertion (A): The IUPAC name for the compound is 3-Methyl cyclohexene.



Reason (R): In cycloalkenes, double-bond carbon atoms take precedence over the alkyl group in numbering.

Ans. *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

Explanation: When naming cycloalkenes, number the ring to indicate the location of the double-bonded carbons and choose the numbering direction such that the substituents get the lowest number.

It is not defined because the location of the double bond is known to lie between C–1 and C–2.

VERY SHORT ANSWER Type Questions (VSA)

[1 mark]

7. Write the correct order of priority of the following functional groups:

$-C=N, >C=O, -OH, -COOH, -CONH_2$

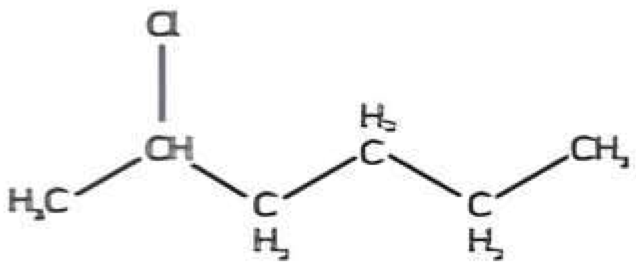
[Delhi Gov. QB 2022]

Ans. The decreasing order of priority of the given functional group is:

$-COOH > -CONH_2 > -CN > -C=O > -OH$

8. Draw the structure of 2-chloro hexane.

Ans.



2-Chloro hexane

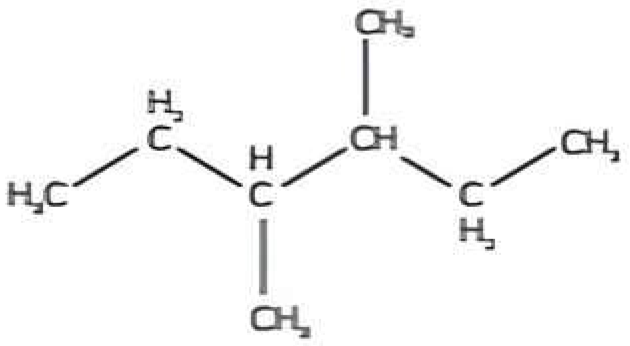
SHORT ANSWER Type-I Questions (SA-I)

[2 marks]

9. Write the IUPAC names of the substances listed below.

(A) $CH_3CH_2 - O - CH_2CH(CH_3)CH_3$

(B)



Ans. (A) 1-Ethoxy-2-methyl propane

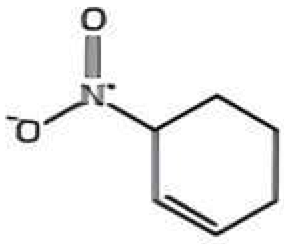
(B) 3, 4-Dimethyl hexane

10. Draw the structure of:

(A) 3-Nitro cyclohexene

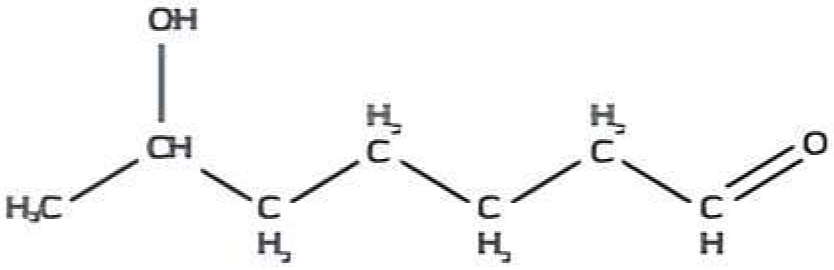
(B) 6-Hydroxy heptanal

Ans. (A)



3-Nitro cyclohexene

(B)



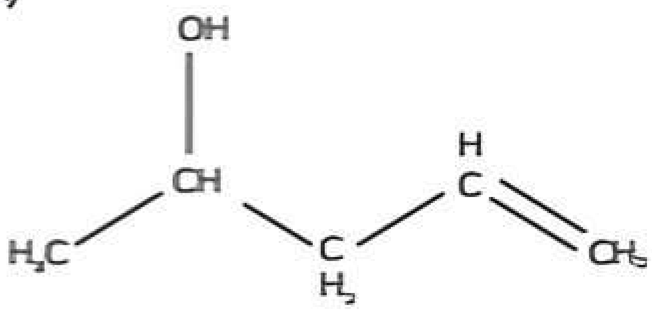
6-Hydroxy heptanal

11. Write the structure of:

(A) Pent-4-en-2-ol

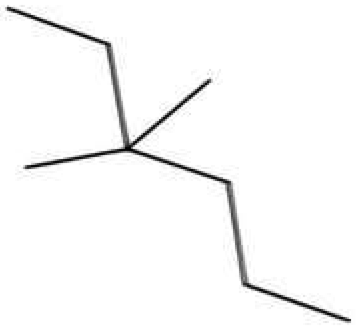
(B) 3, 3-Dimethyl hexane

Ans. (A)



Pent-4-en-2-ol

(B)



3,3-Di methyl hexane

12. How is alkyl group represented? Give the structure and the names of the alkyl groups which originate from:

(A) *n*-Butane (B) *iso*-butene

[Delhi Gov. QB 2022]

Ans. Alkyl group is generated when one of the hydrogens of alkane is removed and that one valency remains empty.

(A) From *n*-butane : $CH_3-CH_2-CH_2-CH_2-$ (butyl)

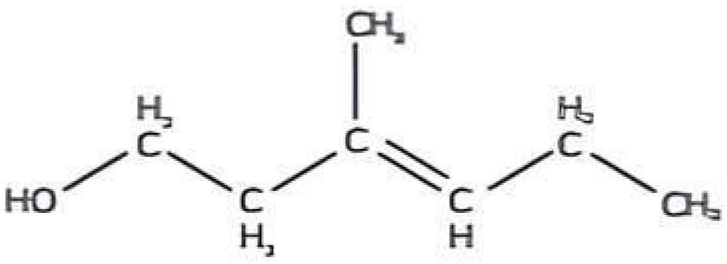
(B) From iso-butene : $CH_3-CH(CH_3) = CH-$ (iso-butyl)

SHORT ANSWER Type-II Questions (SA-II)

[3 marks]

13. Select the words root, 1° and 2° suffix and prefix to draw the structure of 3-Methyl hex-3-enol.

Ans: The structure of 3-Methyl hex-3-Enol is:



Here this compound's word root is hex. Its 1° and 2° suffix are 'en' and 'ol' whereas the prefix is methyl.

Related Theory

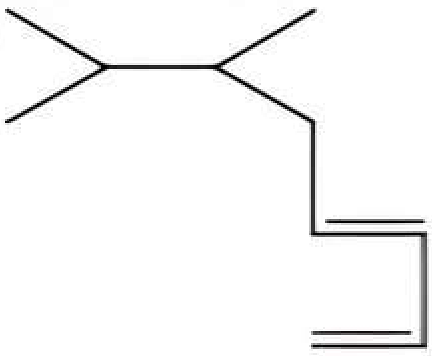
- *The number of carbon atoms in the parent chain is represented by the word root. Special word roots are used for chains with up to four carbon atoms, whereas Greek numerals are used for chains with more than four carbon atoms.*

LONG ANSWER Type Questions (LA)

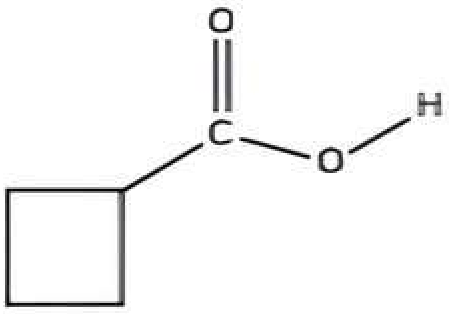
[4 & 5 marks]

14. Write the IUPAC name of the following.

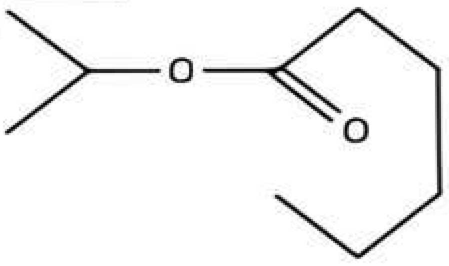
(A)



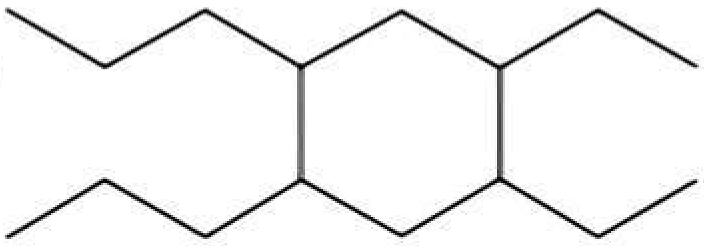
(B)



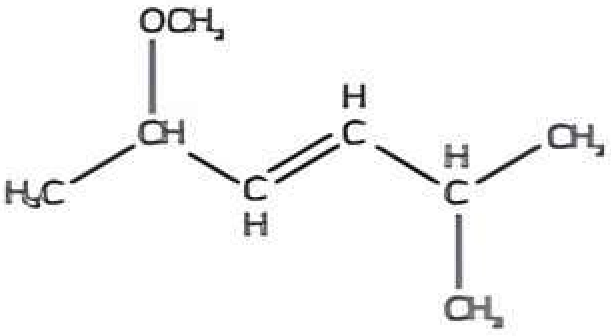
(C)



(D)



(E)



Ans. (A) 6,7 - Dimethyl oct-1, 3-diene

(B) Cyclo butanoic acid

(C) 2-Propyl hexanoate

(D) 3, 4-Diethyl-1, 6-dipropyl cyclohexane

(E) 5-Methyl-2-methoxy hex-3-ene

15. Write the structure of the given compounds.

(A) But-2-en-1-ol

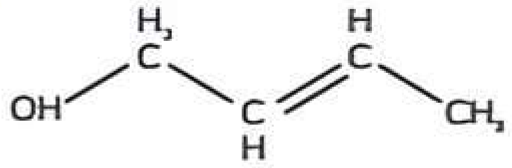
(B) 2-Amino ethan-1-ol

(C) 2, 4-Dimethyl hexan-3-one

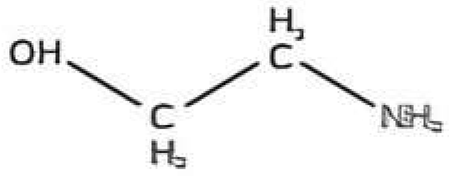
(D) 3-Hydroxy-5-methyl hexan-2-one

(E) 4-Ethyl-2, 4-dimethyl hexane

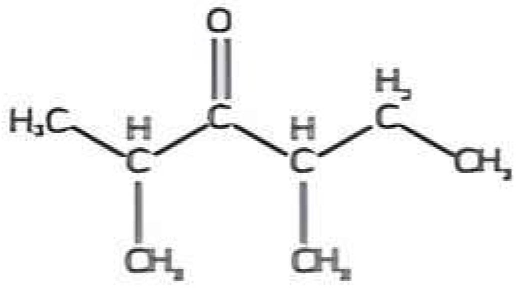
Ans. (A) But-2-en-1-ol



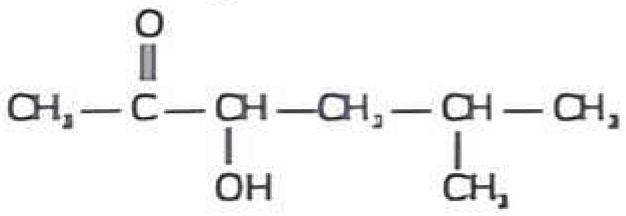
(B) 2-Amino ethan-1-ol



(C) 2, 4-Dimethyl hexan-3-one

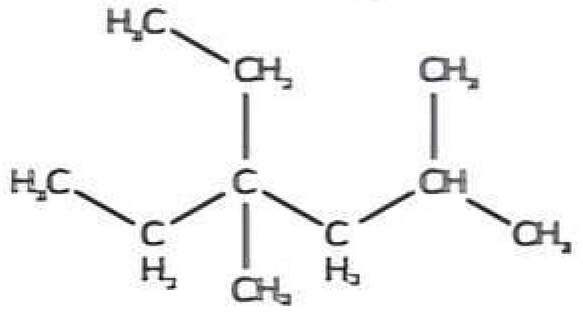


(D) 1, 3-Dimethyl hexan-3-one



$$CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{OH}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

(E) 4-Ethyl-2, 4-dimethyl hexane



REACTIONS AND THEIR MECHANISMS

3

TOPIC 1

CONCEPTS TO UNDERSTAND REACTION MECHANISM

(1) Fission of covalent bond / Bond cleavage
(2) Attacking reagent
(3) Reaction intermediate
(4) Electron displacement effects in covalent bonds

Fission of Covalent Bond

A covalent bond can be cleaved by two types:

(1) Heterolytic cleavage
(2) Homolytic cleavage

Heterolytic cleavage

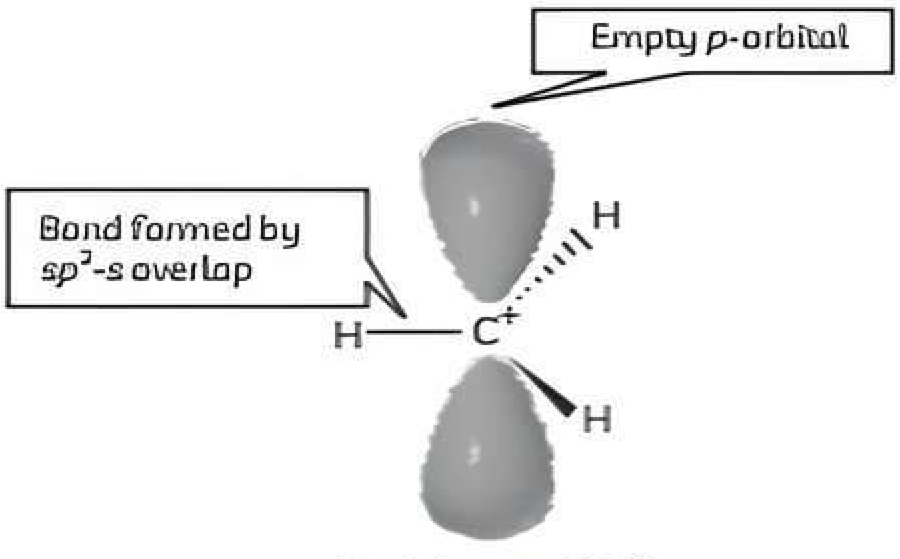
In heterolytic cleavage, unequal distribution of bonds takes place. Due to unequal distribution ions (cation and anion) are formed.

Example: Heterolytic cleavage is shown in the following figure:

Heterolytic cleavage of bonds

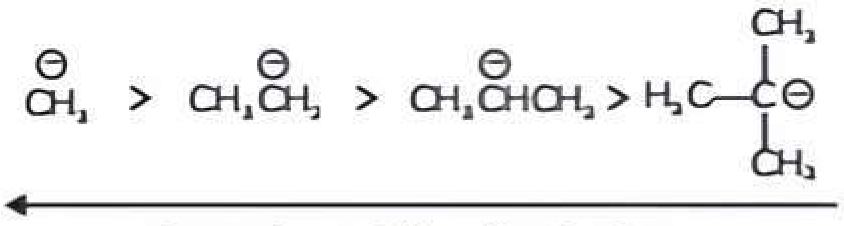
Heterolytic cleavage occurs in polar bonds. So, the organic reactions which proceed through heterolytic cleavage are called ionic or heterolytic or polar reactions. Heterolytic cleavage results in the formation of two types of species. They are:

(1) **Carbocations (carbonium ions):** These are the species with positively charged carbon atoms. Carbocations are highly unstable and reactive species. Six electrons are present in their valence shell. Alkyl group directly attach to positively charged carbon stabilises the carbocations due to effects like inductive, resonance and hyperconjugation(discussed later in this chapter). The three hybridised orbitals of carbocation are arranged in a trigonal planar shape. The remaining orbital is perpendicular to the molecular plane and is empty. The stability of carbocation is: $CH_3^+ < CH_3\,CH_2^+ < (CH_3)_3\,C^+$.



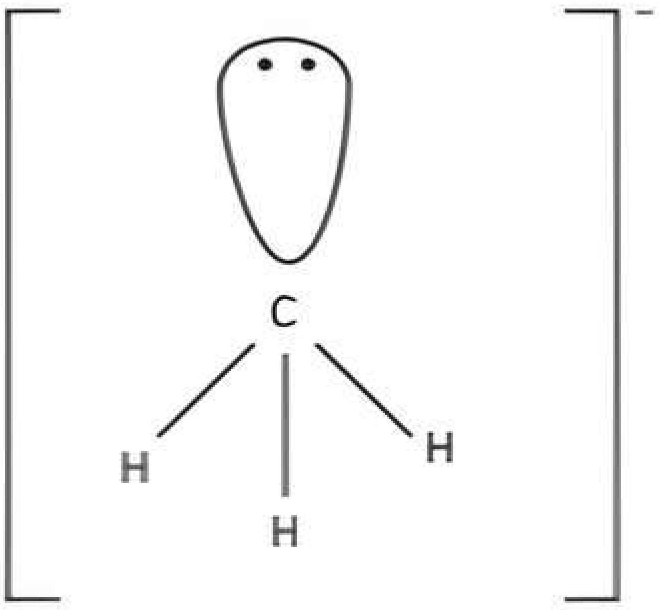
Trigonal planar shape of carbocation

(2) **Carbanions:** These are the species with negatively charged carbon atoms. These are unstable and reactive species. They have eight electrons in their valence shell. The hybridisation of carbon carrying a negative charge is sp^3 with pyramidal geometry. The order of stability of carbanions is:



$$\overset{\ominus}{C}H_3 > CH_3\overset{\ominus}{C}H_2 > CH_3\overset{\ominus}{C}HCH_3 > H_3C{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{}^{\ominus}$$

Increasing stability of carbanions



Methyl carbanion (CH_3^-)

Homolytic cleavage

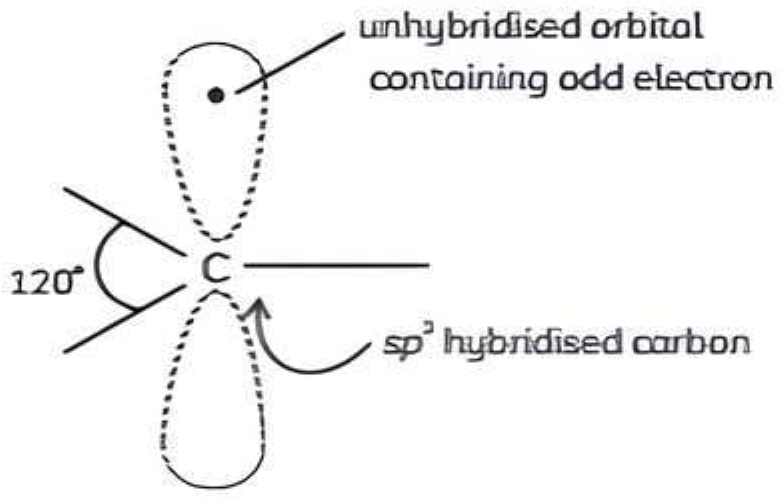
In homolytic cleavage, equal distribution of electrons takes place during the chemical reaction. Homolytic cleavage occurs in non-polar substrates. So, the organic reactions which proceed through homolytic cleavage are called free radical or homopolar. or non-polar reactions.

The single electron movement is represented by a 'half-headed curved arrow' as shown in the figure.

Homolytic cleavage of bond

Free radicals

The neutral chemical species formed by homolytic cleavage are called free radicals. They are highly reactive as they contain an odd electron. It has planar geometry with sp^2 hybridisation. The carbon atom lies at the centre of the triangle and the three sigma bonds are directed towards the three corners of planar trigonal geometry. The odd electron lies in the unhybridised *p*-orbital perpendicular to the plane.



Planar structure

The order of stability of alkyl free radicals is as follows.

$$\overset{R}{C}H_3 < CH_3\overset{R}{C}H_2 < (CH_3)_2\overset{R}{C}H < (CH_3)_3\overset{R}{C}$$

Types of Attacking Reagents (Nucleophiles and Electrophiles)

There are two types of attacking reagents:

(1) Electrophiles

(2) Nucleophiles

Electrophiles or electrophilic reagents

Those reagents which are electron deficient and attack the electron rich species are called electrophiles. Electrophiles are positively charged or neutral.

(Electro + philic)

↓

(electron + loving)

Example: **Positively charged electrophiles:**

$$\dot{N}O_2, \dot{H}, \dot{X}, R—\dot{C}=O$$

Neutral electrophiles: Central atom is electron deficient. All Lewis acids, functional groups like carbonyl group (> C = O), alkyl halides (R_3C –X), carbenes and nitrenes are neutral in nature.

Nucleophiles or nucleophilic reagents

(Nucleo + philes)

↓

(nucleus + loving)

Those reagents which are electron rich and attack the electron-deficient species are nucleophiles. Nucleophiles can be considered as Lewis bases.

Examples:

Negotively charged electrophiles:

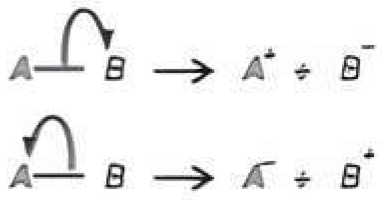
OH^-, OR^-, $R–COO^-$, SH

Neutral nucleophiles: $\bar{N}H_3$, $H_2\bar{O}$, $R—\bar{N}H_2$

Example 3.1: Case Based:

Bond cleavage or bond fission, is the splitting of chemical bonds. This can be generally referred to as Dissociation (chemistry) when a molecule is cleaved into two or more fragments. In general, there are two classifications for bond cleavage: homolytic and heterolytic, depending on the nature of the process. Due to the high bond-dissociation energy of the C – H, bond, around 100 kcal / mol (420 kJ / mol), a large amount of energy is required to cleave the hydrogen atom from the carbon and bond a different atom to the carbon. In biochemistry, the process of breaking down large molecules by splitting their internal bonds is catabolism. Enzymes that catalyse bond cleavage are known as lyases, unless they operate by hydrolysis or oxidoreduction, in that case, they are known as hydrolase and oxidoreductases respectively. In proteomics, cleaving agents are used in proteome analysis where proteins are cleaved into smaller peptide fragments. Examples of cleaving agents used are cyanogen bromide, pepsin and trypsin.

Homolytic cleavage



Heterolytic cleavage

(A) **When CH_3Cl undergoes homolytic bond fission:**
   - (a) **Carbon undergoes geometric change from tetrahedral to planar.**
   - (b) **Hybridisation changes from sp^3 to sp^2.**
   - (c) **Both (a) and (b)**
   - (d) **None of the above**

(B) **Which of the following statements is not correct for a nucleophile?**
   - (a) **Ammonia is a nucleophile.**
   - (b) **Nucleophiles attack low electron density sites.**
   - (c) **Nucleophiles are not electron-seeking.**
   - (d) **Nucleophile is a Lewis acid.**

(C) **State the order of stability of carbanion in ascending order in:**

$$\bar{C}H_3, C_6H_5\bar{C}H_2, (CH_3)_2-\bar{C}H\bar{C}H_2-CH-CH_3$$

(D) Among the benzyl carbocation ($C_6H_5\dot{C}H_2$) and alkyl carbocation $(CH_3)_3\dot{C}$, which one is more stable and why?

(E) **Assertion (A):** CN^- is an ambident nucleophile.

Reason (R): Nucleophiles are electron-rich species.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of A.

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

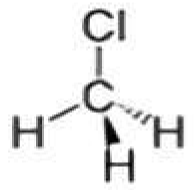
Ans. (A) *(c) Both (a) and (b)*

Explanation: CH_3Cl undergoes homolytic fission as:

$$CH_3:Cl \rightarrow \dot{C}H_3 + \dot{C}l$$

$\dot{C}H_3$ is a methyl free radical with sp^2 hybridisation (singly occupied orbital)

CH_3Cl have bond angle 109°28' with three co-planar C– H bonds and sp^3 hybridised carbon.



Structure of CH_3Cl

(B) *(d) Nucleophile is a Lewis acid.*

Explanation: Nucleophiles are electron-rich and negatively charged species. They attack on the positive site of the substrate or the low-density sites. Hence, they are considered as Lewis bases, not the Lewis acids. Ammonia is considered as nucleophile because nitrogen has lone pair of electrons and it is electron-rich species.

(C) The stability of carbanions is enhanced by the:

(1) Presence of conjugation

(2) Presence of group exerting

So, the correct order of stability will be:

$$C_6H_5\overset{-}{C}H_2 > \overset{-}{C}H_2-CH=CH_2 > \overset{-}{C}H_3 > (CH_3)_2-\overset{-}{C}H$$

(D) The stability of carbocations is influenced by the resonance and inductive effects. $(CH_3)_3\overset{+}{C}$ is stable due to the presence of +I effect in the three methyl groups but benzyl carbocation, $C_6H_5\overset{+}{C}H_2$ is still more stable than $(CH_3)_3\overset{+}{C}$ due to the dispersal of positive charge by the resonance.

(E) *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

Explanation: Nucleophiles are electron-rich species. They possess a lone pair of electrons or π e^-.

The nucleophiles which have more than one site of electron-rich centre or in which two or more atoms bear a lone pair of electrons are called as ambident nucleophiles.

Ambident nucleophile representation in CN^-

Important

➥ ***Reaction intermediate:*** *Reaction intermediate includes carbocation, carbanions, free radicals, carbenes* $(\bar{C}H_2)$, *nitrenes and* $(-\bar{N}:)$.

Let's say if the electrons were money, then a rich person who can donate some money is carbanions and the beggars who need money would be the carbocations. The carbocations and carbanions are the intermediates of the reaction and they carry positive and negative charges respectively.

Example 3.2: By giving proper justification categorize the following molecules/ions as nucleophile or electrophile:

$$HS^-, BF_3, C_2H_5O^-, (CH_3)_3N, Cl^+, CH_3-\overset{+}{C}=O, H_2\bar{N}^-, \overset{+}{N}O_2$$

[NCERT]

Ans. Nucleophiles are: HS^-, $C_2H_5O^-$, $(CH_3)_3N$, $H_2\bar{N}^-$

All these species have one or more lone pairs of electrons which can easily donate to an electrophile and hence behave as nucleophiles.

Electrophiles are: BF_3, Cl^+ $CH_3-\overset{+}{C}=O$, $\overset{+}{N}O_2$

The reagents which attack the negative part of the molecule are called electrophiles. Electrophiles are positively charged or neutral.

Example 3.3: Identify the electrophilic centre in the following: $CH_3CH=O$, CH_3-CN, CH_3-I. [NCERT]

Ans. The electrophilic centre is represented by (*) as follows :

(1) $CH_3\dot{C}H=O$

(2) $CH_3\dot{C}=N$

(3) $\dot{C}H_3-I$

The starred carbon atoms are electrophilic centres as they will have partial positive charge due to the polarity of the bond.

TOPIC 2

ELECTRON DISPLACEMENT EFFECTS IN COVALENT BONDS

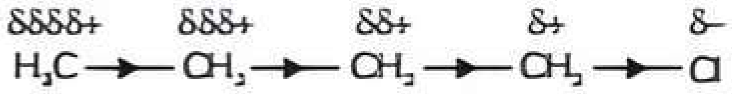
An atom or a substituent group can cause electron displacement in an organic molecule in the ground state or the presence of an appropriate attacking reagent. These electron displacements can be permanent or temporary displacement effects due to the influence of an atom or a substituent group present in the molecule. There are four electronic effects that affect the chemical reaction due to the transfer of electrons.

(1) Inductive effect
(2) Mesomeric effect
(3) Hyperconjugation
(4) Electronic effect

Inductive Effect

When a covalent bond is formed between the atoms, a polarity develops in the molecule. The electron density is higher towards the more electronegative atom of the bond. Hence, we can say that the polarity induced in a non-polar bond due to the presence of an adjacent polar bond is known as an inductive effect.

This is a permanent effect. The effect passes on to subsequent bonds, but it decreases rapidly as the number of intervening bonds increases.



$$\overset{\delta\delta\delta\delta+}{H_3C} \rightarrow\!\!- \overset{\delta\delta\delta+}{CH_2} \rightarrow\!\!- \overset{\delta\delta+}{CH_2} \rightarrow\!\!- \overset{\delta+}{CH_2} \rightarrow\!\!- \overset{\delta-}{Cl}$$

Based on the ability to withdraw and donate the electron density to the attached carbon atom, the substituents in the inductive effect can be classified as a positive or negative inductive effect.

Negative inductive effect (–*I* effect)

Electron withdrawing groups show –*I* effect. Examples: Nitro ($-NO_2$), halogens ($-X$), cyano ($-CN$), carboxy ($-COOH$), ester ($-COOR$), aryloxy ($-OAr$) etc.

Positive inductive effect (+*I* effect)

Electron donating groups show + *I* effect. Examples: Methyl ($-CH_3$), ethyl ($-CH_2-CH_3$), etc.

Example 3.4: In which C–C of $CH_3-CH_2-CH_2-Br$ the inductive effect is expected to be the least? **[NCERT]**

Ans. The magnitude of the inductive effect diminishes as the number of intervening bonds increases. Hence, the effect is the least on third carbon.

Resonance

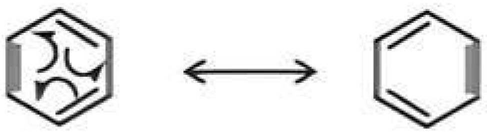
Resonance structures are hypothetical and individually do not represent any real molecule. They are the organic molecules whose behaviour cannot be explained by the single Lewis structure. They are also known as canonical structures. The energy of actual structures is always lower than that of any of the canonical forms . The difference in the energy between the hybrid and most stable canonical form is called as resonance energy.

The $\pi - e^-$ is delocalised from one atom to another, or we can say that resonance refers to the entire transfer of energy from one atom to another when they are in conjugation.

The number of unpaired electrons or the paired electrons in all the resonating structures should be the same.

All resonating and canonical structures must follow the Lewis structure and the resonating system should be in the same plane.

Example: Benzene has a cyclic structure with alternate C – C and C = C bonds.



Resonating structure of benzene

Resonance Effect

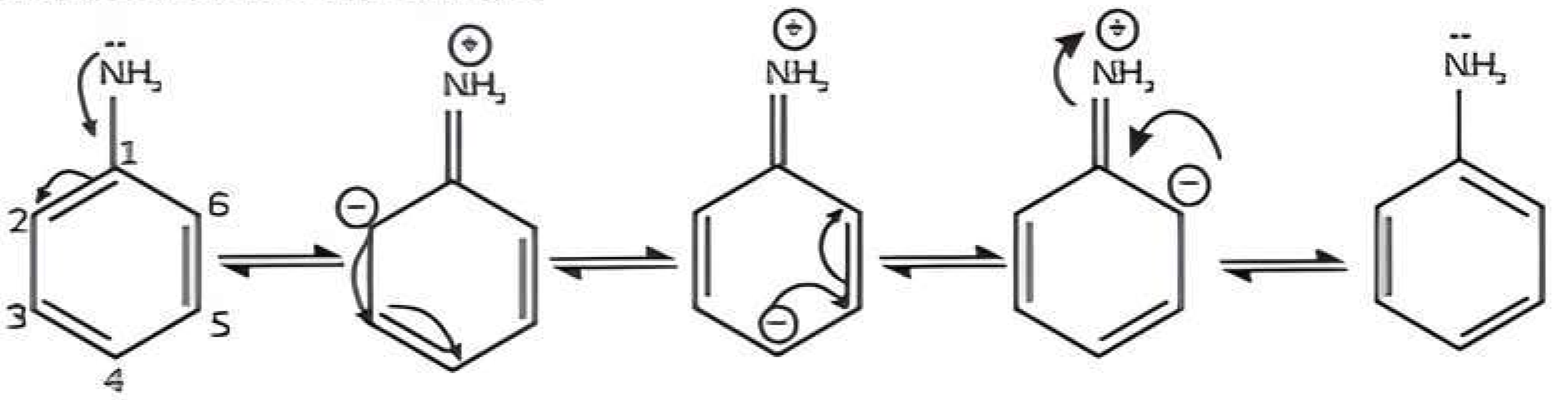
The polarity developed within a molecule due to the interaction of two π-bonds or a π-bond with lone pair of electrons present on the adjacent atom is called the resonance effect. It is produced when the polarity develops between the molecule by the interaction of conjugated systems. It is a permanent effect. There are two types of resonance or mesomeric effect.

Positive resonance effect (+ *R* effect)

In this effect, the transfer of electrons is away from an atom or substituent group due to the presence of an electron-donating group. + *R* effect is shown by groups like:

$-\bar{N}H_2, -\bar{O}H, -\bar{O}R, -\bar{N}R_2, -\underset{-}{\bar{S}}H, -\bar{N}HR, -\bar{X}, -\bar{N}HCOOCH_3$

A few rules for writing resonating structures are:
Example: This effect in aniline is shown as:

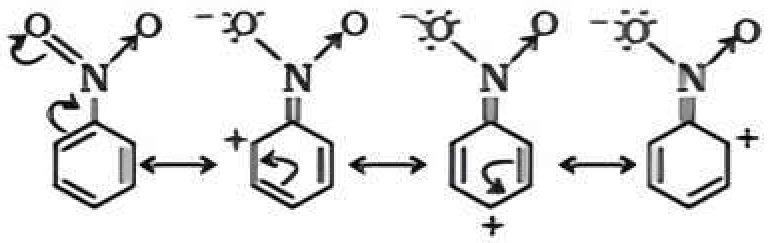


Resonating structure of aniline

Negative resonance effect (–R effect)

In this effect, the transfer of electrons is towards the substituent group attached to the conjugated system. –R effect is shown by groups like: –CHO, –COOH, –COOR, –COR, $-NO_2$, –CN, –COX, $-CONH_2$, $-SO_3H$.

Example: This effect in nitrobenzene is shown as:



Resonating structures of nitrobenzene

Important

- *π – π conjugation: If there are two π – bonds in conjugation then the electron of the one is π – bond transferred to the other.*
- *π – lone pair conjugation: If there is lone pair or a negative charge and π – bonds are in conjugation, then the lone pair of electrons or negative charge are transferred.*
- *π – vacant orbital conjugation: If there is a positive charge (vacant orbital) and π – bond are in conjugation then electron of π – bond are transferred towards the positive charge.*
- *π – unpaired electron configuration: If there is an unpaired electron and π – bond in conjugation.*
- *lone pair – vacant orbital conjugation: If there is a lone pair or negative charge and vacant orbital or positive charge are in conjugation then the electron of the negative charge is transferred towards the positive charge.*

Example 3.5: Write the resonance structures of CH_3COO^- and show the movement of electrons by curved arrows.

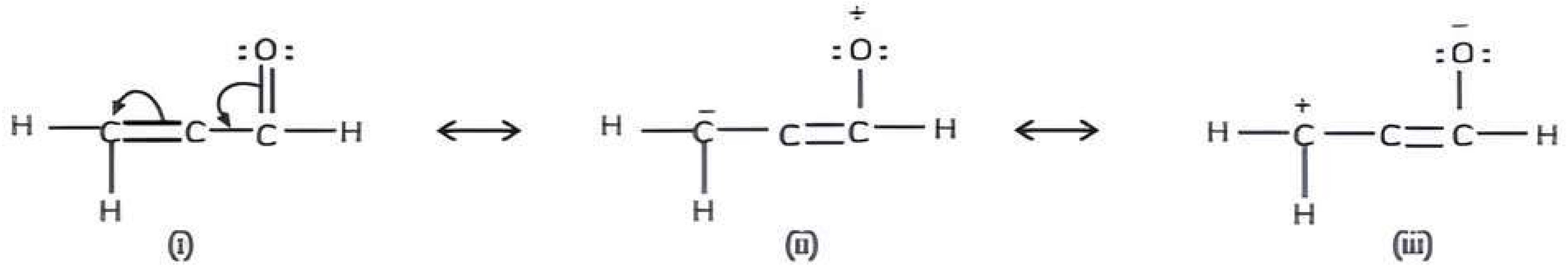
Ans.

$$CH_3COOH \longrightarrow CH_3COO^{\ominus} + H^{\oplus}$$

Resonating structures of carboxylate ion

Example 3.6: Write the resonating structures of $CH_2 = CH - CHO$. Indicate the relative stability of the contributing structures.

Ans.



Stability order: i > iii > ii

(i) is more stable because more covalent bonds are present and each carbon and oxygen atom has an octet and no separation of opposite charge. In (iii), negative charge is present on the more electronegative atom and positive charge on the more electropositive atom. Thus, it is more stable than (ii). In (ii), oxygen has a positive charge. So, it is the least stable structure.

Electromeric Effect

The complete transfer of shared pairs of e^- from one atom to another atom in the presence of an attacking reagent is known as the electromeric effect. It is a temporary effect. It is also known as E-effect. It is a strong effect because of the involvement of weak π bonds. There are two types of electromeric effects.

Positive electrometric effect (+E effect)

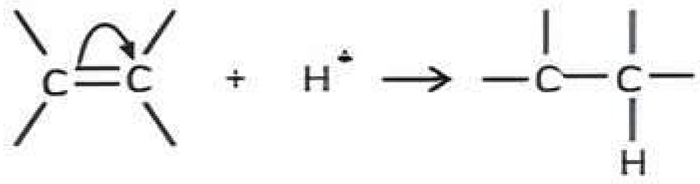
In this effect, the π-electrons of the multiple bonds are transferred to the atom to which the reagent gets attached.

Negative electrometric effect (–E effect)

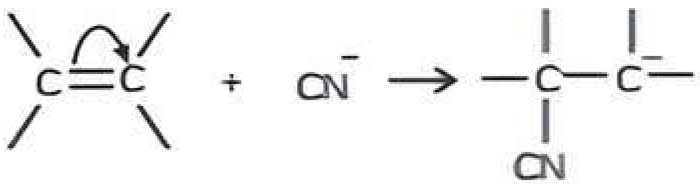
In this effect, the π-electrons of the multiple bonds are transferred to the atom to which the attacking reagent does not get attached.

Example:

Positive electromeric effect



Negative electromeric effect

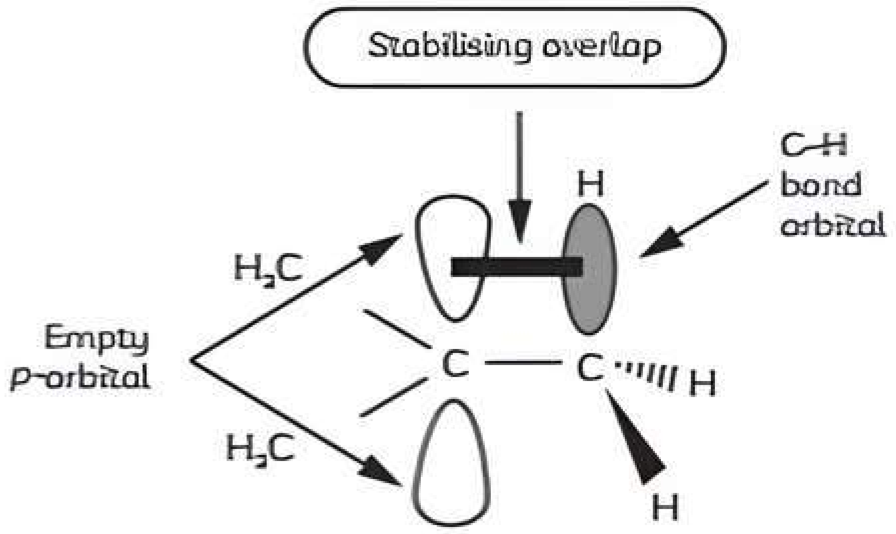


Electromeric effect

Electromeric effect predominates when both the inductive effect and electromeric effect operate.

Hyperconjugation

The complete transfer of $\sigma - e^-$ of C – H bond of an alkyl group towards π –bond or to an atom having an unshared *p*–orbital, is called as hyperconjugation effect. It is a permanent effect. It is also called the No-bond resonance or Baker and Nathan effect.



Hyperconjugation representation

Important

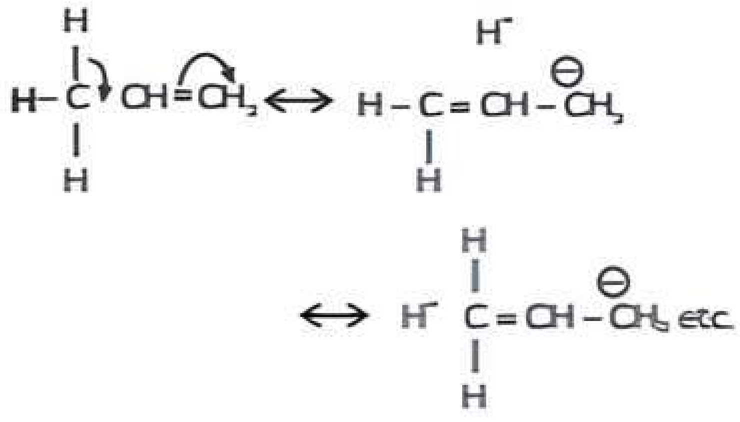
➥ *Conditions for hyperconjugation:*

(1) *If there is a C–H σ -bond and free electrons are in conjugation, then there will be H–effect.*

(2) *If there is a C–H σ -bond and positive charge is in conjugation, then there will be H–effect.*

(3) *If there is a C–H σ -bond and π – charge in conjugation, then there will be H–effect.*

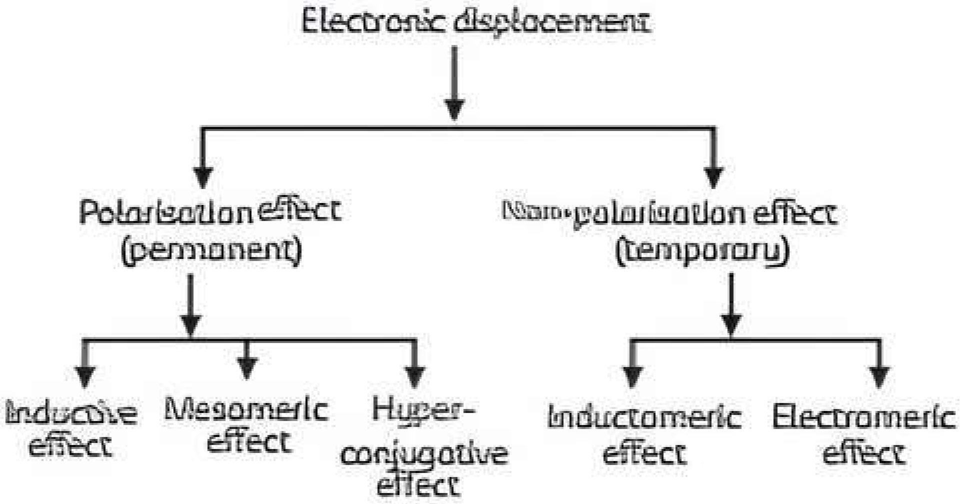
Example of hyperconjugation



Hyperconjugation effect in propene

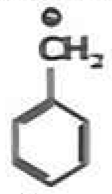
Example 3.7: Case Based:

An electronic effect influences the structure, reactivity, or properties of molecule but is neither a traditional bond nor a steric effect. In organic chemistry, the term stereo-electronic effect is also used to emphasize the relation between the electronic structure and the geometry (stereochemistry) of a molecule. Electronic factors that influence organic reactions include the inductive effect, electromeric effect, resonance effects and hyperconjugation. These electronic factors involve organic molecules, most of which are made from a combination of the following six elements: carbon, hydrogen, nitrogen, oxygen, phosphorus and sulphur. Yet, the limited number of building blocks does not prevent organic compounds from taking on diverse properties in their physical characteristics and chemical reactivity. The subtle differentiation of various compounds in organic chemistry is essential for the biological functions of the molecules and creates a wide variety of reactions. The different effects which influence the distribution of electrons in a covalent bond of an organic molecule are important for understanding the mechanism of the reactions the molecule undergoes.



(A) Compare the stability of free radicals

(i) $CH_3-\dot{C}H-CH_3$ (ii)



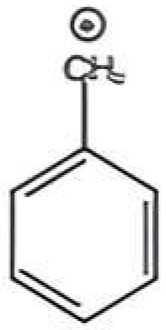
(iii) $\dot{C}H_2-CH(CH_3)_2$ (iv) $\dot{C}H_2-CH_3$

Options:

(a) (II) > (III) > (I) > (IV)
(b) (III) > (II) > (I) > (IV)
(c) (IV) > (III) > (I) > (II)
(d) (I) > (II) > (III) > (IV)

(B) Correct order of stability of carbocations is:

$H_2C=CH-\overset{\oplus}{C}H_2$; $H_3C-CH_2-\overset{\oplus}{C}H_2$;



(I) (II) (III)

Options:

(a) (II) > (III) > (I)
(b) (III) > (I) > (II)
(c) (I) > (III) > (II)
(d) (I) > (II) > (III)

(C) Which of the following is a permanent electron displacement effect?

(a) Inductive effect (b) Electromeric effect

(c) hyperconjugation (d) Both (a) and (c)

(D) Give the difference between hyperconjugation and resonance effect.

(E) Assertion (A): Cyclopentadienyl anion is much more stable than allyl anion.

Reason (R): Cyclopentadienyl anion is aromatic in character.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of A.

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

Ans. (A) *(a) (II) > (III) > (I) > (IV)*

Explanation: Among the given options, (II) is benzyl free-radical and it is most stable due to resonance. In the remaining free radicals, the more the alkyl group bounded to the electron-deficient carbon, the more is the stability of free radicals. Thus, the order of stability of free radicals is (II) > (III) > (I) > (IV).

(B) *(b) (III) > (I) > (II)*

Explanation: Benzyl carbocation (III) is most stable due to the presence of four resonating structures. In allylic carbocation (I), two resonating structures are possible and in (II) no resonating structures are present. The more is the resonating structure, the more is the stability of carbocation. So, the order of stability will be: (III) > (I) > (II).

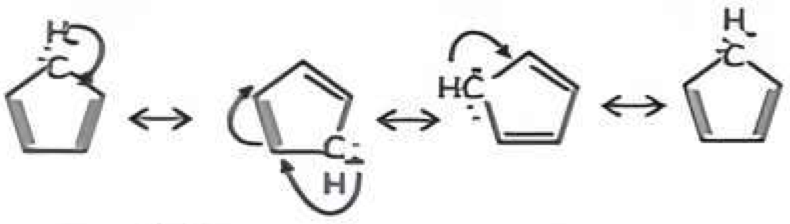
(C) *(d) Both (a) and (c)*

Explanation: Inductive and hyperconjugation effects are permanent effects whereas electromeric effect is a temporary effect.

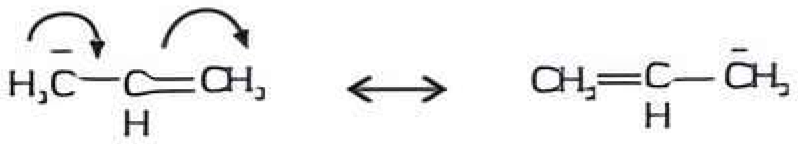
(D) The main difference between hyperconjugation and resonance is that hyperconjugation involves the interaction between a σ-bond and a p-orbital or a π-bond whereas resonance involves the interaction between two π-bonds.

(E) *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

Explanation: Cyclopentadienyl anion is more stable than allyl anion. In cyclopentadienyl anion, there are two π-bonds so there are a total four π-electrons. And there is one negative charge and lone pair. We should only consider negative charge because lone pair electrons are outside the ring and will not get included in the ring. So, there will be $6\pi e^-$. So, cyclopentadienyl anion will follow the Huckel rule (cyclic ring molecules follow the Huckel rule when the number of its π – electrons equal $4n$ ÷ 2 where n is a non-negative integer) and thus it is an aromatic compound.



In allyl ion also resonating structure is present. But it doesn't show aromatic nature, so, due to this it will be less stable.



$$H_2\bar{C}-\underset{H}{C}=CH_2 \longleftrightarrow CH_2=\underset{H}{C}-\bar{C}H_2$$

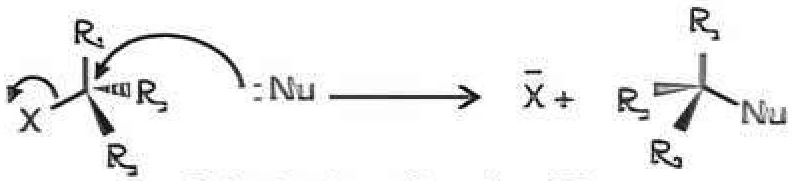
TOPIC 3

TYPES OF ORGANIC REACTIONS AND MECHANISMS

The organic reactions can be categorised into four categories:

Substitution Reactions

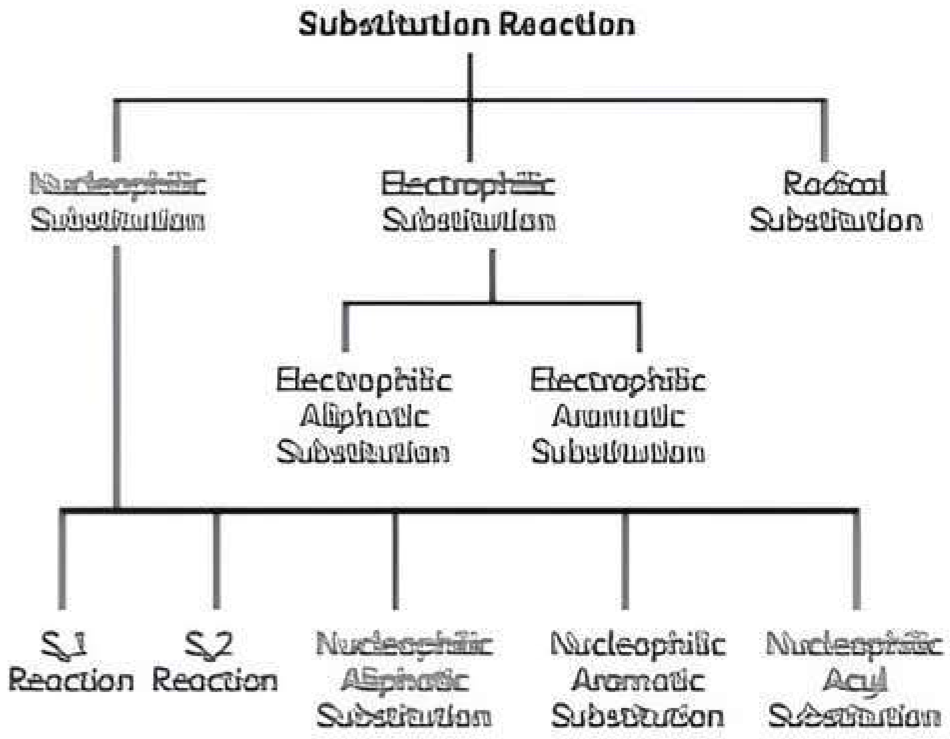
The reaction in which a functional group or atom of one compound is substituted by another group.



Substitution of nucleophile

Important

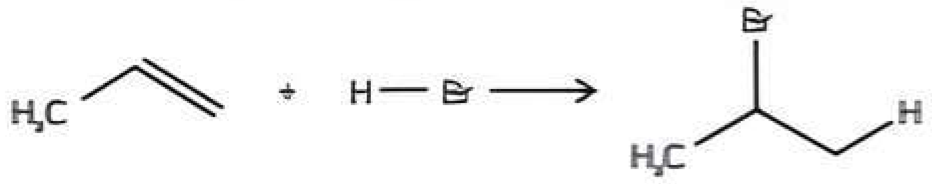
- *There are different types of substitution reactions:*
  - *(1) Free radical substitution*
  - *(2) Electrophilic substitution*
  - *(3) Nucleophilic substitution (S_N1 and S_N2)*



Types of substitution reaction

Addition Reactions

These reactions involve the combination between two molecules to give a single molecule of the product.

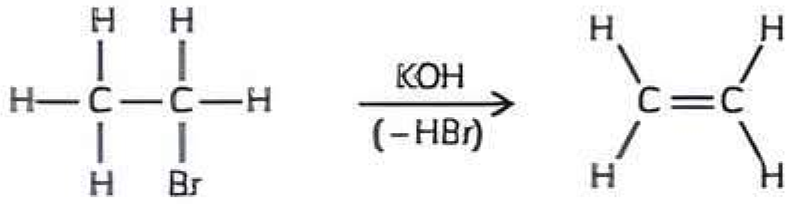


Addition of HBr in propene

Elimination Reactions

It involves the loss of two atoms or groups from the same or adjacent atoms of a substance leading to the formation of multiple bonds.

These are given by the molecules which have nucleophiles as a leaving group.



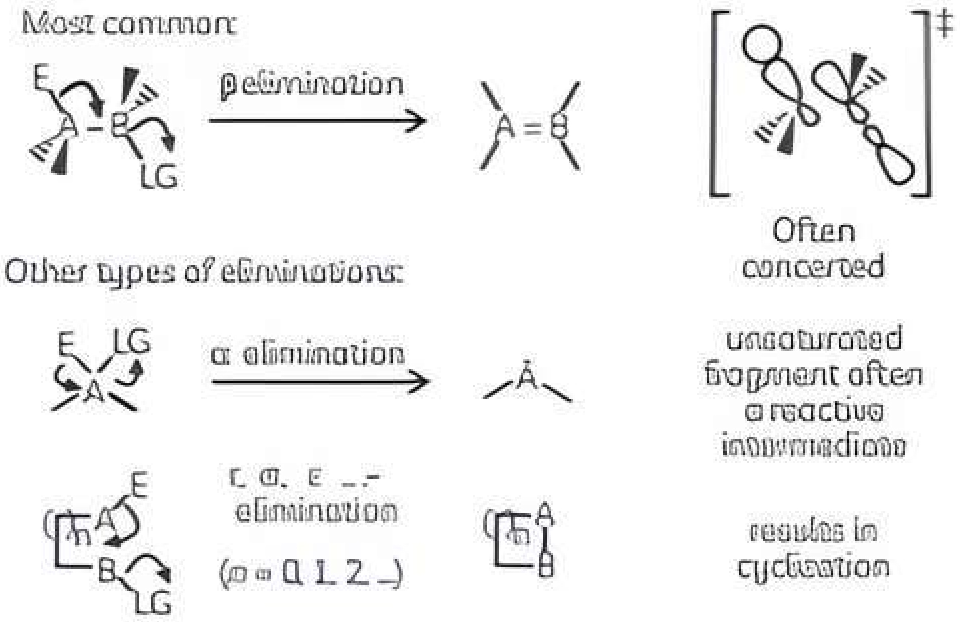
Elimination of H – Br in the given the reactant

Important

- *There are two types of elimination reaction:*

(1) α elimination reaction

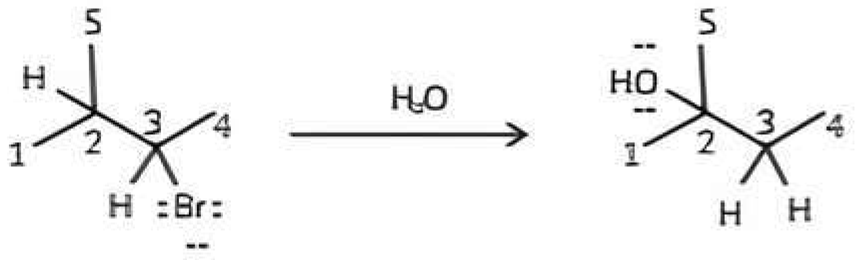
(2) β elimination reaction



Types of elimination reactions

Rearrangement Reactions

In this reaction, a carbon skeleton of a molecule is rearranged to give the different structural isomer of the original molecule.



Rearrangement reaction

OBJECTIVE Type Questions

[1 mark]

Multiple Choice Questions

1. What is the correct order of decreasing stability of the following cations?

(I) $CH_3-\overset{\bullet}{C}H-CH_3$

(II) $CH_3-\overset{\bullet}{C}H-OCH_3$

(III) $CH_3-\overset{\bullet}{C}H-CH_2-OCH_3$

Options:

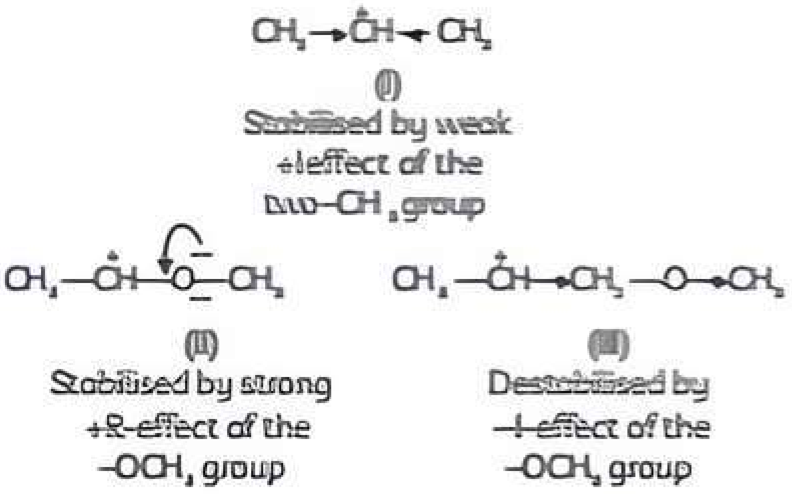
(a) (II) > (I) > (III) (b) (II) > (III) > (I)

(c) (III) > (I) > (II) (d) (I) > (II) > (III)

[NCERT Exemplar]

Ans. *(a) (II) > (I) > (III)*

Explanation:



Thus, the stability of carbocations decreases in the order (II) > (I) > (III).

2. In which of the following compounds is the carbon marked with an asterisk is expected to have the greatest positive charge?

(a) $\overset{\bullet}{C}H_3-CH_2Cl$

(b) $\overset{\bullet}{C}H_3-CH_2-Mg^{\bullet}Cl^{-}$

(c) $\overset{\bullet}{C}H_3-CH_2-Br$

(d) $\overset{\bullet}{C}H_3-CH_2-CH_3$ [NCERT Exemplar]

Ans. *(a) $\overset{\bullet}{C}H_3-CH_2Cl$*

Explanation: Electronegativity of Cl, Br, C and Mg is in the order Cl > Br > C > Mg. Cl and Br show (–I) effect and –I effect of Cl > Br. So, CH_3-CH_2-Cl has the greatest positive charge.

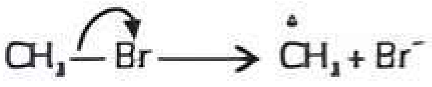
Related Theory

- *When a more electronegative atom is attached to the carbon then the shared pair of electrons move towards the more electronegative atom. Carbon has less electron density and it gains a partial positive charge.*

3. **Covalent bonds can undergo fission in two different ways. The correct representation involving the heterolytic fission of $CH_3 - Br$ is**

(a) 

$\overset{\curvearrowleft}{CH_3} - Br \longrightarrow \dot{C}H + Br_3^-$

(b) 

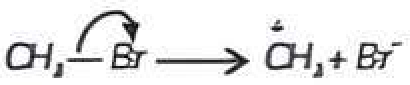
$CH_3 \overset{\curvearrowright}{-} Br \longrightarrow \overset{+}{C}H_3 + Br^-$

(c) 

$CH_3 \overset{\curvearrowright}{-} Br \longrightarrow \overset{-}{C}H_3 + Br^-$

(d) 

$CH_3 - Br \longrightarrow \dot{C}H_3 + \dot{B}r$

Ans. *(b)* 

$CH_3 \overset{\curvearrowright}{-} Br \longrightarrow \overset{+}{C}H_3 + Br^-$

Explanation: Here the arrows represent the direction of movement of electrons.

Br is more electronegative than carbon, that's why heterolytic fission occurs as

$CH_3 \overset{\curvearrowright}{-} Br \longrightarrow \overset{\oplus}{C}H_3 + \overset{\ominus}{Br}$

Caution

- *Homolytic fission gives free radical whereas heterolytic fission gives carbocation and carbanion intermediates.*

4. **Electrophiles are electron-seeking species. Which of the following groups contains only electrophiles?**
   (a) BF_3, NH_3, H_2O
   (b) $AlCl_3$, SO_3, NH_3
   (c) $NO_2^{\oplus}$, $CH_3^{\oplus}$, $CH_3 - C^{\oplus} = O$
   (d) C_2H_5, $\dot{C}_2H_5$, C_2H_6

Ans. *(c) NO_2, CH_3, $CH_3 - C^{\oplus}=O$*

Explanation: Electrophiles are electron-deficient species. Hence, they are Lewis acids or ions with a positive charge. Here, $AlCl_3$, SO_3, $NO_2^{\oplus}$, $CH_3^{\oplus}$, $CH_3 - C^{\oplus} = O$ are electron-deficient species.

5. **Hyperconjugation involves delocalisation of**
   (a) electrons of hydrogen of an alkyl group directly attached to an atom of an unsaturated system.
   (b) electrons of carbon-hydrogen σ-bond of alkyl group directly attached to the positively charged carbon atom.
   (c) π-electrons of the carbon-carbon bond.
   (d) lone pair of electrons.

Ans. *(b) electrons of carbon-hydrogen σ bond of alkyl group directly attached to the positively charged carbon atom.*

Explanation: Hyperconjugation is also known as conjugation. It is the delocalisation of sigma electrons. The presence of α-H with respect to a double bond, triple bond, or carbon-containing positive charge (carbonium ion) or unpaired electron (free radical) is a condition required for hyperconjugation.

6. **Which of the following does not show resonance effect?**
   (a) Buta -1, 3-diene
   (b) Acrylonitrile
   (c) Nitrobenzene
   (d) *Isopropyl Isothiocyanate*

[Delhi Gov. QB 2022]

Ans. *(d) Isopropyl isothiocyanate*

Explanation: Isopropyl isothiocyanate does not show resonance.

Resonance effect involves delocalisation of π-electrons of two or more conjugated double bonds or non-bonding electrons and π-electrons of a double bond. Hence, Isopropyl isothiocyanate $(CH_3)_2CH{-}SC{\equiv}N$ does not show resonance effect.

7. **The stabilisation due to resonance is maximum in:**
   (a) Cyclohexane
   (b) Cyclohexene
   (c) Cyclo1-4 diene
   (d) Benzene

Ans. *(d) Benzene*

Explanation: Benzene has three pi-bonds. It is a very stable molecule. Due to the presence of resonance in benzene $\pi - e^-$ charge over the benzene is distributed over a greater area. The density of charge decreases and hence the stability increases.

8. **Mesomeric effect is due to:**
   (a) Delocalisation of $\sigma - e^-$
   (b) Delocalisation of $\pi - e^-$
   (c) Migration of H – atom
   (d) Migration of proton

Ans. *(b) Delocalisation of $\pi - e^-$*

Explanation: Mesomeric or resonance effect is due to the delocalisation of $\pi - e^-$ or complete transfer of $\pi - e^-$ from one atom to another atom when they are in conjugation.

Assertion-Reason (A-R)

In the following question no. (9-12) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

(a) **Both (A) and (R) are true and (R) is the correct explanation of (A).**
(b) **Both (A) and (R) are true but (R) is not the correct explanation of A.**
(c) **(A) is true but (R) is false.**
(d) **(A) is false but (R) is true.**

9. Assertion (A): Energy of resonance hybrid is equal to the average of energies of all canonical forms.

Reason (R): Resonance hybrid cannot be presented by a single structure. [NCERT Exemplar]

Ans. *(d) (A) is true but (R) is false.*

Explanation: Resonance hybrid is more stable than the canonical structures. Canonical structures that are lower in energy make a greater contribution to resonance hybrid. Thus, the energy of the resonance hybrid is equal to the sum of energies of all canonical forms. So, here assertion is correct but the reason is not correct.

10. Assertion (A): Tertiary carbocations are generally formed more easily than primary carbocations.

Reason (R): Hyperconjugation as well as an inductive effect due to additional alkyl groups stabilise tertiary carbocations.

[Delhi Gov. QB 2022]

Ans. *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

Explanation: An alkyl group attached to the positively charged carbon of carbocation increases its stability by inductive effect (+I) as it release electrons toward that carbon. Thus, the positive charge get dispersed.

More the numbers of alkyl groups, greater is the dispersal of positive charge and therefore more easily it will formed.

11. Assertion (A): Alkyl carbanions like ammonia have a pyramidal shape.

Reason (R): The carbon atom carrying negative charge has an octet of electrons.

[Delhi Gov. QB 2022]

Ans. *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

Explanation: As both ammonia and alkyl carbanion have lone pairs of electrons on the central atom (3 bond pairs + 1 lone pair), thus they both have a pyramidal shape.

12. Assertion (A): Inductive effect is responsible for the dipole moment in the molecules.

Reason (R): All inductive effects are permanent polarisations in the ground state.

Ans. *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

Explanation: In the inductive effect, the bonded electrons are displaced towards the more electronegative atom. So, we can say that if the inductive effect increases, the polarity of the bond increases and hence the dipole moment increases. Also due to the displacement of electrons towards the more EN atom, a permanent state of bond polarisation occurs where the more EN atom has a negative charge and the less EN atom has a positive charge. So, both the assertion and reason are correct and the reason is the correct explanation of assertion.

CASE BASED Questions (CBQs)

[4 & 5 marks]

Read the following passages and answer the questions that follow:

13. *Hyperconjugation is the interaction of electrons in a sigma (σ) orbital (e.g., C–H or C–C) with an adjacent unoccupied non-bonding p or antibonding σ • or π • orbital to give a pair of extended molecular orbitals. Hyperconjugation affects several properties like dipole moment, bond length, stability of carbocations, etc. The stability of carbocations is in the order: $(CH_3)_3C^+ > (CH_3)_2\,CH^+ > (CH_3)\,CH_2^+ > CH_3^+$. Inductive effect can be used to determine the stability of a molecule depending on the charge present on the atom and the groups bonded to the atom. The inductive effect also plays a vital role in deciding the acidity and basicity of a molecule. As the number of groups with increases, the acidic character increases; as the number groups with +I effect increases the basic character increases.*

(A) What additional terminology is used to describe hyperconjugation? In hyperconjugation, which bonding orbitals are involved in the overlapping?

(B) How many hyperconjugation structures –I effect are possible for isopropyl radical?

(C) Answer the following questions:

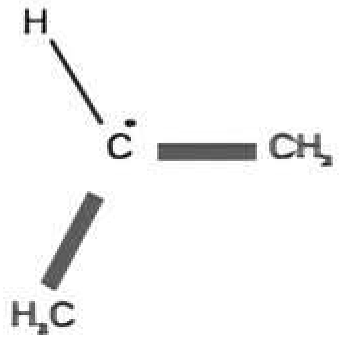
(i) Why ethene do not show hyperconjugation?

(ii) **Arrange phenol, *p*-methyl phenol, *m*-nitrophenol and *p*-nitrophenol in order of increasing acidity.**

Ans. (A) Hyperconjugation is also known as the Baker Nathan effect or no-bond resonance or $\sigma-\pi$ conjugation. The Delocalisation of electrons or lone pair of $\sigma-$ electrons into adjacent $\pi-$ orbital or p– orbital is called hyperconjugation. It occurs due to overlapping of $\sigma-$ bonding orbital or the orbital containing a lone pair with adjacent orbital $\pi-$ or p– orbital.

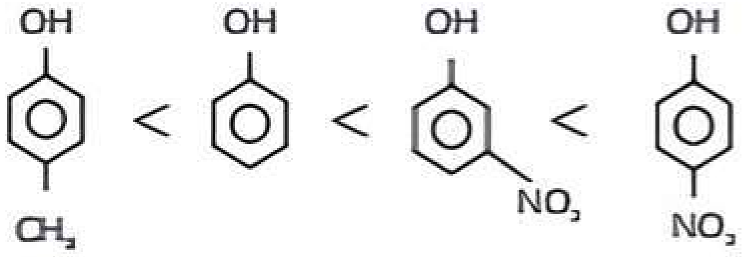
(B) The number of hyperconjugative structures for isopropyl radical C_3H_7 is 6.

The unpaired electron is shared by a total of seven atoms in the isopropyl carbocation, one carbon atom and six hydrogen atoms, due to hyperconjugation.



(C) (i) Ethene does not show hyperconjugation as it is devoid of alpha hydrogen. The presence of α-hydrogen is the characteristic feature of hyperconjugation.

(ii) The order of increasing acidity is as follows:



Related Theory

- *As the number of –I group increases, the acidity of the compound increases and here NO_2 shows –I effect while CH_3 show +I effect. So, it will show more acidity as compared to phenol and p-methyl phenol. At p-position $-NO_2$ group shows –M effect which is more effective than –I effect at m-position hence p-nitrophenol is more acidic than m-nitrophenol.*

14. *The reaction mechanism (or reaction path) is the process, or pathway, by which a reaction occurs. Reaction mechanism involves the bond cleavage, attacking reagent, reaction intermediate and the electronic effects. Bond cleavage can be heterolytic or homolytic cleavage. The attacking reagents involve the electrophiles and nucleophiles. The next is the intermediate which includes carbocation (positively charged carbon), carbanion (negatively charged carbon) and free radicals (electrically neutral species). Last comes to the effects which include inductive effect, mesomeric effect, hyperconjugation and electrometric effect. Mesomeric or resonance effect is defined as the polarity produced in the molecule by the interaction of two π-bonds or between a π-bond and lone pair of electrons present on an adjacent atom. The resonance energy, or resonance stabilisation energy, is the difference in energy between the real inductive structure and the (most stable contributing structures) worst kinetic structure. The mesomeric effect is completely different from the inductive effect.*

(A) I^-, Cl^-, OH^-, CN^- and NH_3 are referred as nucleophiles. Nucleophilic reagents behave as ....

(a) salts (b) Lewis's acid

(c) Lewis bases (d) water

(B) Which of the following is the correct statement regarding electrophile?

(a) Electrophiles are negatively charged species and can form a bond by accepting a pair of electrons from another electrophile.

(b) Electrophiles are generally neutral species and can form a bond by accepting a pair of electrons from another nucleophile.

(c) Electrophiles can be either neutral or positively charged species and can form a bond by accepting a pair of electrons from a nucleophile.

(d) Electrophiles are negatively charged species and can form a bond by accepting a pair of electrons from another electrophile.

(C) Among the following which one is most reactive towards the electrophilic nitration?

(a) Benzene (b) Benzoic acid

(c) Nitrobenzene (d) Toluene

(D) Select the correct statement from the following option.

(a) Benzene ring has two different types of bond lengths for single and double bonds.

(b) All the bond lengths in benzene are equal due to resonance.

(c) All the bond length in benzene is equal due to hyperconjugation.

(d) All of the above

(E) How does increasing the number of alpha hydrogens affect hyper-conjugation?

(a) It will increase.

(b) It will decrease.

(c) It will remain the same.

(d) Not defined.

Ans. (A) *(c) Lewis bases*

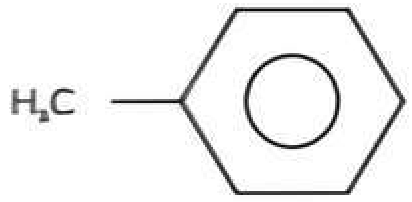
Explanation: Nucleophilic reagents are electron-rich species and thus they behave as Lewis bases. They attack on the electron-deficient area and in case of the same nucleophilic site, it parallels with the basicity. As the basicity increases the nucleophilicity also increases.

(B) *(c) Electrophiles can be either neutral or positively charged species and can form a bond by accepting a pair of electrons from a nucleophile.*

Explanation: A chemical species that accepts an electron pair and forms bonds with nucleophiles is known as an electrophile. Electrophiles carry a positive charge and some are neutral in nature. They have a partial positive charge on an atom or lack an octet of electrons. They receive electrons therefore, they are Lewis acids. Some examples of electrophiles are BF_3, H_3O^+, Cl_2, F_2, etc.

(C) *(d) Toluene*

Explanation: In toluene, the $-CH_3$ group is an electron-releasing group and the nitro group is an electron-withdrawing group. So, the electrophilic substitution of the $-NO_2$ group is possible here. In benzene, also nitration is possible. But its reactivity toward electrophilic nitration is less than toluene due to the absence of electron releasing group. Benzoic acid has a $-COOH$ group and it is an electron-withdrawing group. So, electrophilic nitration is less reactive. Similarly in nitrobenzene, $-NO_2$ group is electron-withdrawing group. So, it is less reactive towards electrophilic nitration.



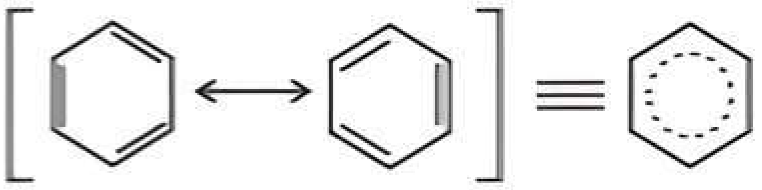
Structure of toluene

(D) *(b) All the bond length in benzene is equal due to resonance.*

Explanation: All the bond lengths in benzene are equal due to resonance.

Related Theory

Benzene is a cyclic structure containing alternate C–C and C=C as shown in the figure. Benzene should exhibit two different bond length, due to the C–C and C=C structures bonds. C–C have a bond length of 154pm and C=C have a bond length of 134pm. However, experimentally benzene has a uniform C–C bond length of 139pm, an intermediate value between both the bonds. According to the resonance theory, the actual structure of benzene is the resonance hybrid structure.



Resonating Structure *Resonance Hybrid*

(E) *(a) It will increase*

Explanation: On increasing the number of α–H, the number of hyperconjugation structures increases.

Hyperconjugation ∝ number of α-hydrogen.

VERY SHORT ANSWER Type Questions (VSA)

[1 mark]

15. Describe the term electrophile. Give an example of neutral electrophiles.

Ans. The reagents which attack the negative part of the molecule are called electrophiles. Electrophiles are positively charged or neutral. They are electron-loving groups. Example: NO_2^+

Examples of neutral electrophiles are: BF_3, $AlCl_3$, SO_3.

16. Classify the following into electrophiles and nucleophiles:

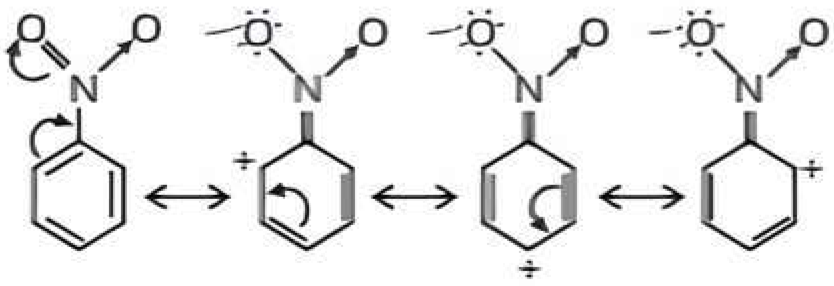
H^+, NH_3, $AlCl_3$, NO_2^+, CN^-, H_2O, ROH, RNH_2, Carbocation [Delhi Gov. QB 2022]

Ans. An electrophile is a chemical species that form bonds with nucleophiles by accepting an electron pair, these are generally positive ions or neutral atom with less number of electrons. Thus H^+, $AlCl_3$, NO_2^+ and carbocations are electrophiles.

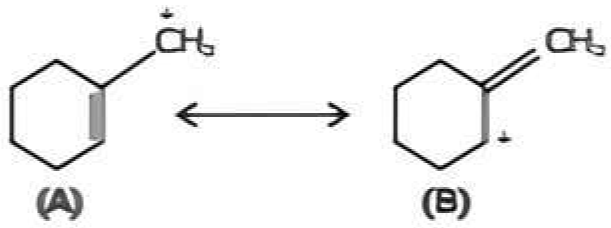
A nucleophile is a chemical species that form bonds with electrophiles by donating an electron pair. these are generally negative ions or neutral atoms with lone pair of electrons. Thus NH_3, CN^-, H_2O, ROH and RNH_2 are nucleophiles.

17. Draw the resonating structure of $C_6H_5NO_2$.

Ans.

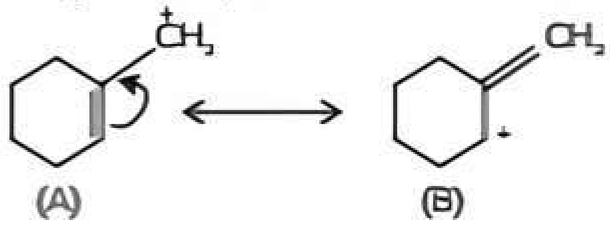


18. Which of the following ions is more stable? Use resonance to explain your answer.



[NCERT Exemplar]

Ans. Carbocation (A) is more stable than carbocation (B) because carbocation (A) is more polar than carbocation (B). It undergoes resonance. Further, the double bond is more stable within the ring in comparison to outside the ring.



SHORT ANSWER Type-I Questions (SA-I)

[**2** marks]

19. What is the effect of introducing an alkyl group on the stability of a free radical?

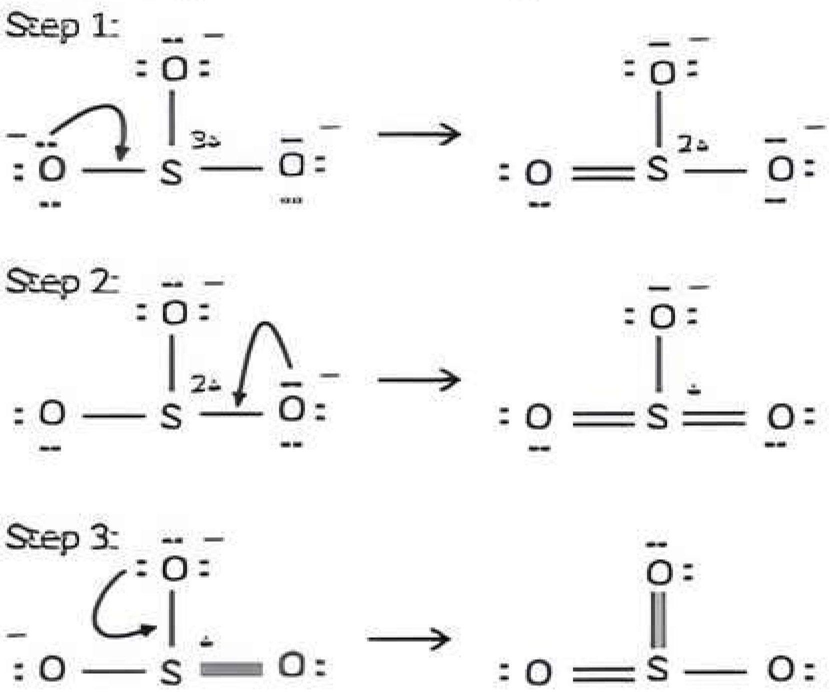
[Delhi Gov. QB 2022]

Ans. Alkyl group shows a positive inductive effect (+I). thus it will donate the electron to the free radical. The higher the electron density, the higher will be the stability. Hence, we can say that introducing an alkyl group will enhance the stability of free radicals.

20. Why does SO_3 act as an electrophile?

[NCERT Exemplar]

Ans. Due to the presence of three highly electronegative oxygen atoms the sulphur atom becomes electron-deficient. Further due to resonance, sulphur acquires a positive charge. Both these factors are responsible for the electrophilic nature of SO_3.



21. Identify the reagents shown in the following equations as nucleophiles or electrophiles.

(A) $CH_3COOH + HO^- \rightarrow CH_3COO^- + H_2O$

(B) $CH_3COCH_3 + \bar{C}N \rightarrow (CH_3)_2\,C(CN)(OH)$

(C) $C_6H_6 + CH_3\overset{+}{C}O \rightarrow C_6H_5\,COCH_3$

Ans. CN^- and OH^- are nucleophiles and CH_3CO^+ is an electrophile because the negatively charged ions or lone pair possessing atoms are nucleophiles while the positively charged or neutral ions or groups with fewer electrons are electrophiles. A nucleophile is a chemical species which in relation to a response, gives an electron pair to form a chemical bond while an electrophile is a positively charged or neutral species with an empty orbital attracted to a centre rich in electrons.

Caution

- *Don't get confused about nucleophiles and electrophiles. Nucleophiles are the electron donor species and the electrophiles are the electron acceptor species.*

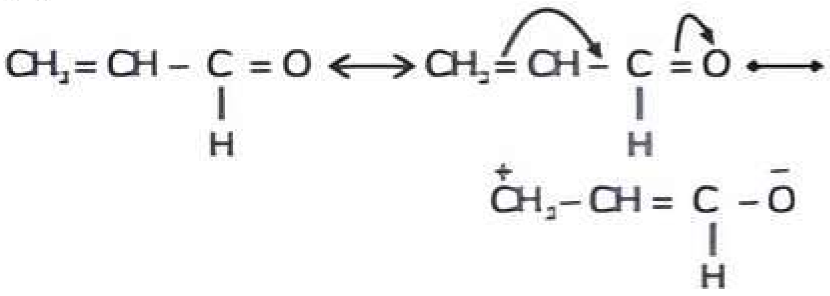
22. Draw the resonance structure of the following:

(A) $CH_2 = CH - \ddot{Cl}:$ (B) $CH_2 = CH - CH = O$

Ans. The resonance structure is as follows:

(A)

(B)



SHORT ANSWER Type-II Questions (SA-II)

[3 marks]

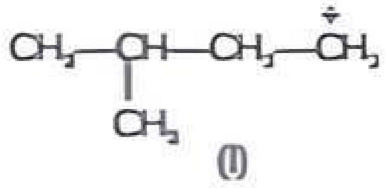
23. Give three points of differences between inductive and resonance effects.

Ans.

S. No.	Inductive effect	Resonance effect
(1)	The inductive effect involves displacement σ-e^- and occurs only in saturated compounds.	It involves π-e^- or lone pair of electrons and occurs only in unsaturated and conjugated system.
(2)	The inductive effect can move up to three carbons atoms	It is applicable all along the length of the conjugated system.
(3)	In the inductive effect, there is a slight displacement of electrons and thus only partial positive and partial negative charges appear.	In the resonance effect, there is a complete transfer of electrons so full positive and negative charges appear.

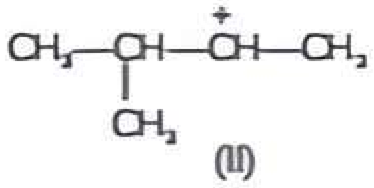
24. Write structures of various carbocations that can be obtained from 2-Methyl butane. Arrange these carbocations in order of increasing stability. [NCERT Exemplar]

Ans. Carbocation is formed when a hydrogen ion leaves with the electron of the bond from an alkane. Following four carbocations are possible for 2-Methyl butane:



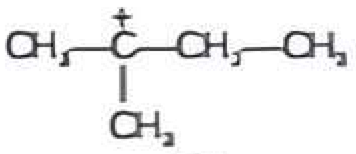
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-\overset{+}{C}H_2$

(I)



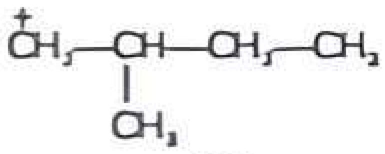
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\overset{+}{C}H-CH_3$

(II)



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{+}{C}}}-CH_2-CH_3$

(III)



$\overset{+}{C}H_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$

(IV)

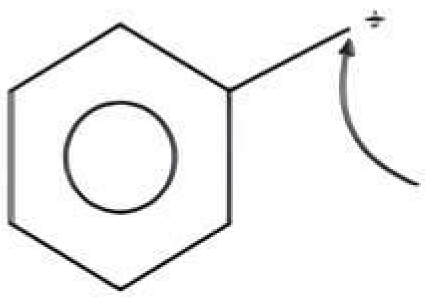
Tertiary carbocations are most stable due to +I effect of three alkyl groups, hence (III) is most stable, followed by secondary carbocations (II) in this case and primary carbocations (I) and (IV) are least stable. Out of (I) and (IV), (I) is less stable.

Hence, the order of stability is: (I) < (IV) < (II) < (III)

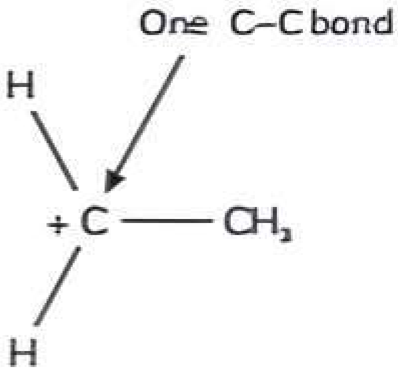
25. Benzyl carbocation is more stable than ethyl carbocation. Justify.

Ans. Benzyl carbocation is more stable than ethyl carbocation because, in ethyl carbocation, hyperconjugation of three α–H is present while in benzyl carbocation, resonance is present.

In comparison to hyperconjugation, resonance is the stronger effect due to the delocalisation of π-bond. Thus, benzyl is more stable than ethyl carbocation.



Benzyl Carbocation



Ethyl Carbocation

⚠ Caution

- *Students might get confused between benzyl carbocation and phenyl carbocation stability. Remember that benzyl carbocation is a more stable one due to its resonance in it. Phenyl carbocation ($C_6H_5^+$) does not have resonance.*

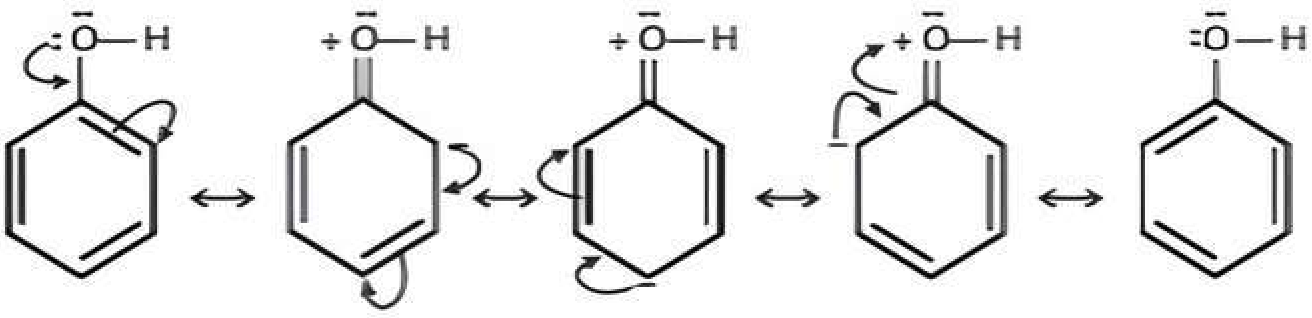
LONG ANSWER Type Questions (LA)

[**4** & **5** marks]

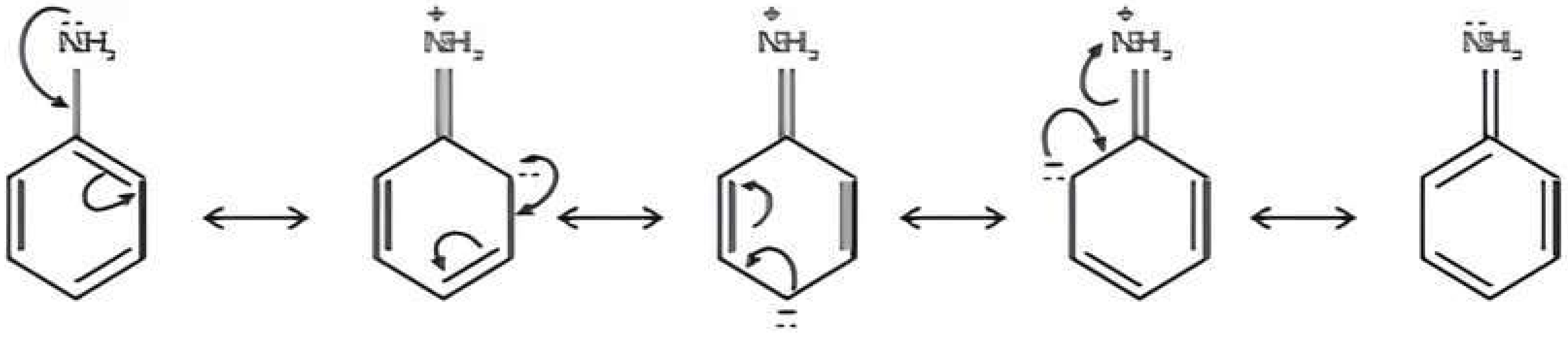
26. Draw the resonating structure of the following compounds. Show the electron shift using curved arrow notation.

(A) C_6H_5OH
(B) $C_6H_5NH_2$
(C) CH_3COO^-

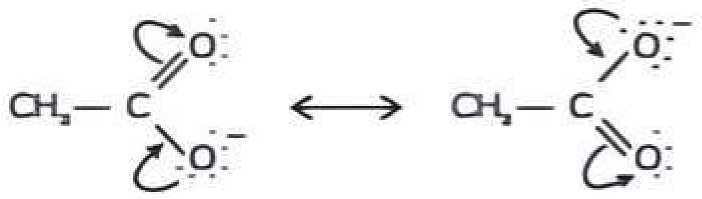
Ans. (A) C_6H_5OH



(B) $C_6H_5NH_2$



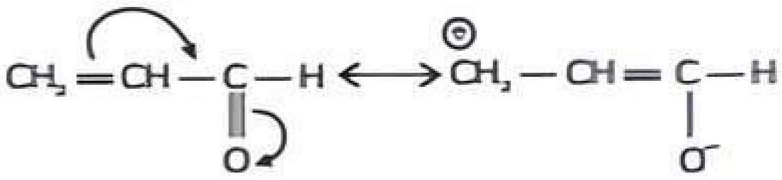
(C) CH_3COO^-



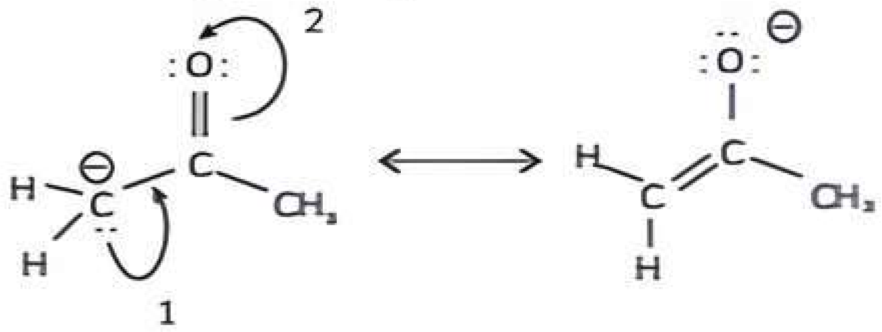
27. **What are the different types of conjugation in resonance?**

Ans. Different types of conjugation in resonance are:

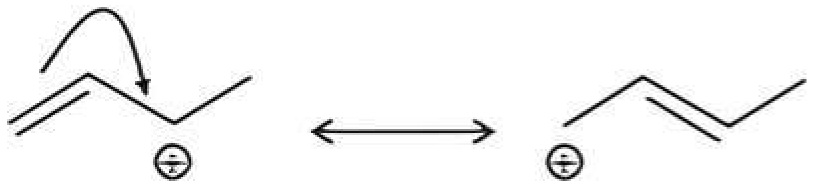
(1) π–π conjugation: If there are two π– bonds in conjugation then the electron of the one π– bond is transferred to the other.



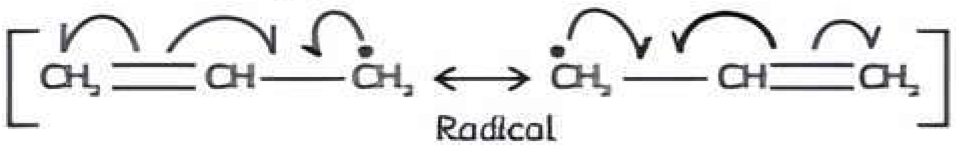
(2) π– lone pair conjugation: If there is lone pair or a negative charge and π–e⁻ are in conjugation then the lone pair of electrons or negative charge are transferred towards.



(3) π– vacant orbital conjugation: If there is a positive charge (vacant orbital) and π–*bond* are in conjugation then electron of π–*bond* are transferred towards the positive charge.

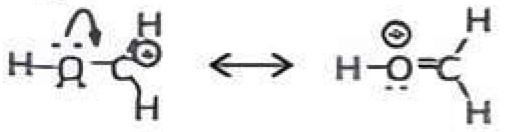


(4) π– unpaired electron configuration: If *there is an unpaired electron and π–bond in conjugation.*

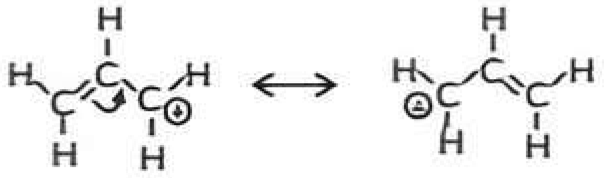


(5) *lone pair – vacant orbital conjugation:* If there is a lone pair or negative charge and vacant orbital or positive charge are in conjugation then the electron of the negative charge is transferred towards the positive charge.

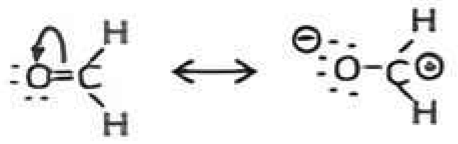
Lone pair to bond



Bond to bond



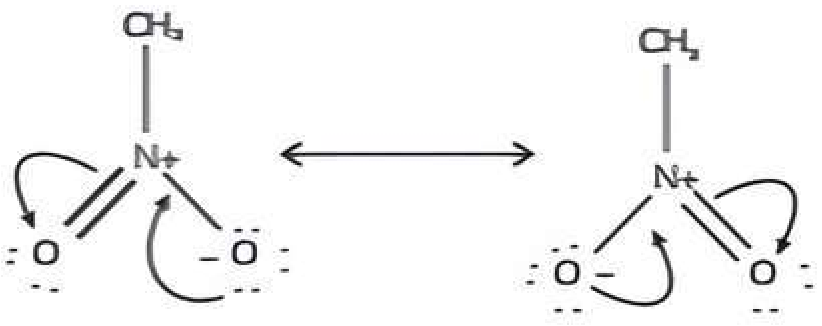
Bond to lone pair



28. Define resonance stabilisation energy. Draw the resonating structure of CH_3NO_2 and also describe its bond length details.

Ans. The difference in energy between the actual and the lowest resonance structure is called the resonance stabilisation energy or the resonance energy.

Nitromethane CH_3NO_2 is the simplest organic compound having nitro as the functional group. Nitromethane is widely known as the nitro-booster used in the drag-racing engine. It is a colourless liquid with a strong pungent smell that produces fumes of nitrogen oxides when decomposing violently when overheated. The resonance in nitromethane can be represented by two resonating structures. Two types of bonds are present in these structures.



Resonating structure of CH_3NO_2

The two bonds of nitromethane are of the same length (i.e. intermediate between $N-O$ and $N=O$) due to resonance. Thus, the actual structure of nitromethane is a resonance hybrid structure of two canonical structures.

◆◆◆

METHODS OF PURIFICATION 4

TOPIC 1

METHODS OF PURIFICATION OF ORGANIC COMPOUNDS

The most common techniques employed for the purification of organic compounds are

(1) Sublimation
(2) Crystallisation
(3) Distillation
(4) Differential extraction and
(5) Chromatography

After using any of the techniques, the purity of the compound is done by determining the melting or its boiling point. The pure compounds mostly show sharp melting and boiling points. Nowadays chromatographic and spectroscopic techniques are used for determining its purity.

Sublimation

It is a purification technique, in which on heating some solid substances it directly changes to vapour phase without the involvement of liquid phase. This principle is known as sublimation. This method is used for purifying sublimable compounds from non-sublimable impurities. Example, impure samples of naphthalene, camphor, dry ice and salicylic acid can be purified by this method.

Camphor (Solid) *Used in diyas* *Gas*

Example of sublimation process where the camphor is directly passing from solid to the vapour phase no existence of liquid phase.

Crystallisation

This method is commonly employed for the purification of solid organic compounds. Also, it is suitable for the mixtures of the compound that have a higher solubility in one solvent and have a lower solubility in another solvent. The principle behind this is the solubility difference between the compounds and the impurities that are present in the suitable solvent. The compounds that are impure are dissolved in a suitable solvent where it is partially soluble at normal room temperature and completely dissolvable at higher temperatures. The solution is kept a concentrated one to make it a saturated solution. On cooling this, the pure substance crystallises out and can be separated by means of filtration and the remaining solution contains impurities and scarce amount of compound which is called mother liquor. The activated charcoal is used to remove the colour imparted by impurities by means of adsorption. The process had to be repeatedly done for the substances having impurities of comparable solubility.

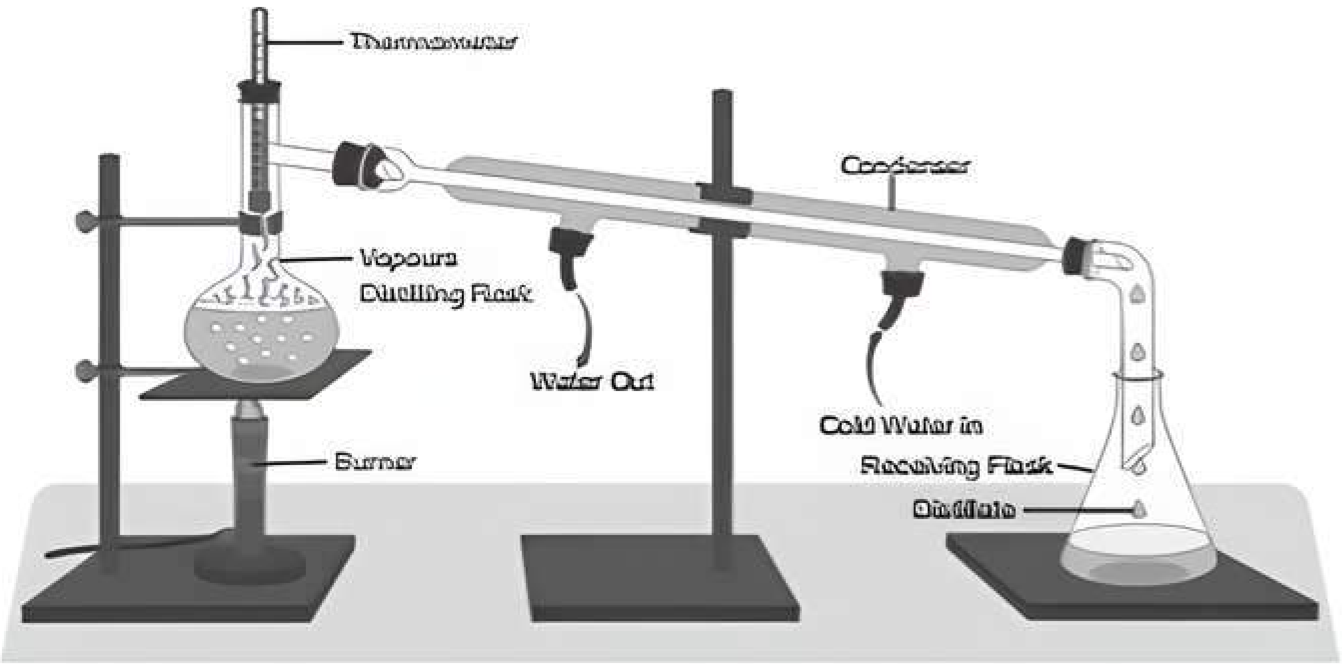
A real-life example of crystallisation of salt from seawater.

Distillation

The method can be used to separate :

(1) Volatile liquids from the non-volatile impurities
(2) Liquids that have good differences in their boiling points.
(3) Chloroform (*b.p.*334 K) and aniline (*b.p.*457 K) can be easily separated by this technique.

The principle behind this is different organic compounds show different boiling points that can vaporise at different temperatures. These vapours are cooled and the liquid formed are separately collected. The impure liquid mixture is heated in a round bottom flask. On boiling this, the compounds having lower boiling points are obtained first and this is condensed by the condenser and the condensed liquid is collected in a receiver. The condensed vapour of a higher boiling liquid is collected separately. Example chloroform and aniline, benzene and aniline.

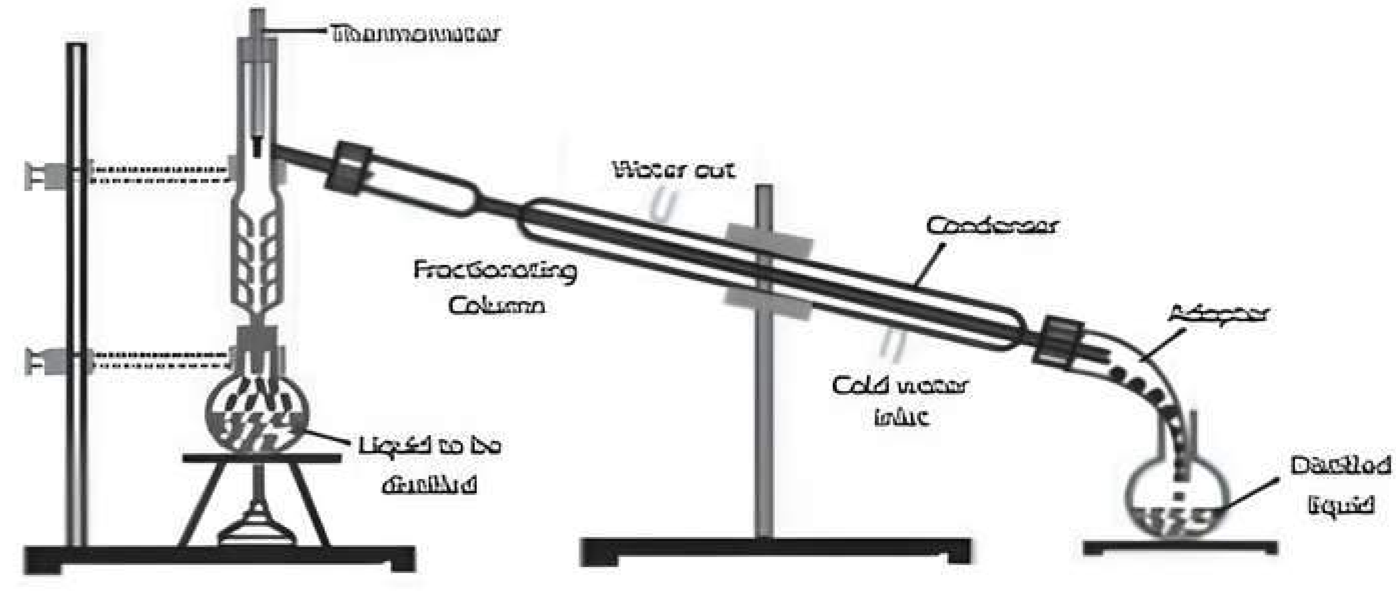


Simple distillation. The substance vapours get condensed and collected as a liquid in a conical flask.

Fractional Distillation

If the mixtures of a compound have a small difference in boiling point, then, simple distillation cannot be used. Due to this, the compound vaporises and gets condensed simultaneously at the same temperature. For this fractional distillation method is used. The vapours that are formed are allowed to pass through a fractionating column before the vapours enter for condensation. The vapours with a higher boiling point get condensed first and then the vapours of a lower boiling point condense. The fractionating column gets attached to the mouth of the round bottom flask. The vapours which reach the top of the column first are rich in the more volatile components. The fractionating columns are available in various sizes and designs, it provides more surface for the heat exchange between ascending and descending vapours and gets revaporises. The vapours are rich in low boiling liquid which ascends to the top of the column and vapours become pure which passes through the condenser and the pure liquid is collected in a receiver. After repeating the same process, now the remaining liquid mostly contains the high boiling component which on condensation can be collected. Each vaporisation and condensation unit present in the column is called **a theoretical plate** which is available with hundreds of plates.

Application: Fractional distillation technique is used to separate different components of crude oil from petroleum.

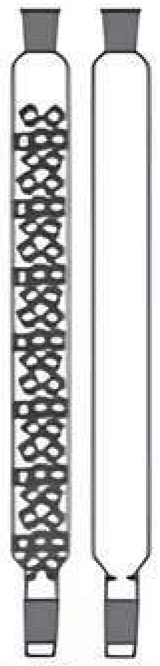


Fractional distillation. The vapours of low boiling liquid reach the column top first and then are followed by high boiling liquid.

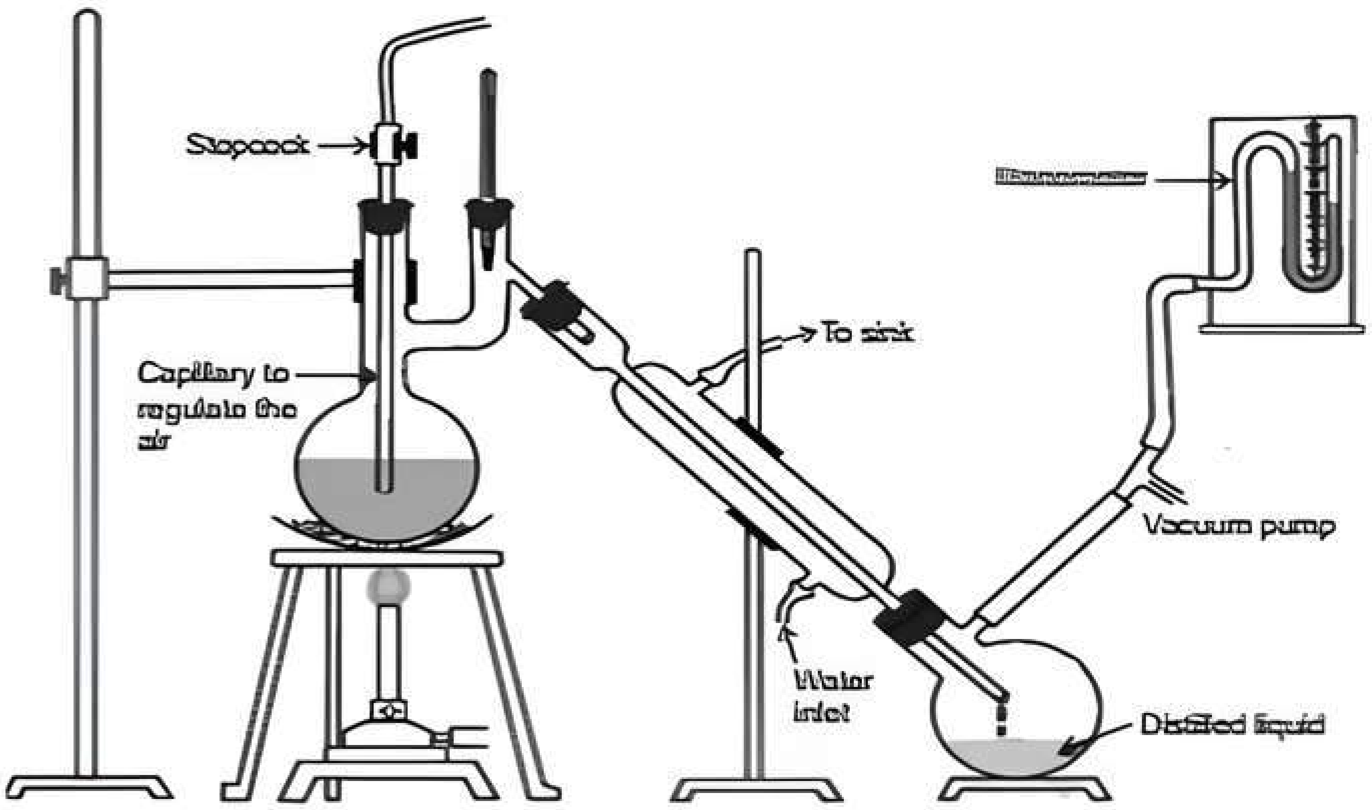
Distillation under reduced pressure

Distillation under reduced pressure purify liquids having a higher boiling point and the compounds which decompose below their boiling point. Such liquids are boiled at a temperature below their actual boiling points by reducing pressure on their surface. The boiling of the liquids under reduced pressure makes their vapour pressure be equal to the pressure outside or external pressure. The pressure of the set-up can be reduced with the help of a vacuum pump or water pump.

Application: By using this technique, the glycerol present in the spent-lye can be separated, which is employed in the soap industry.



Different types of fractionating columns

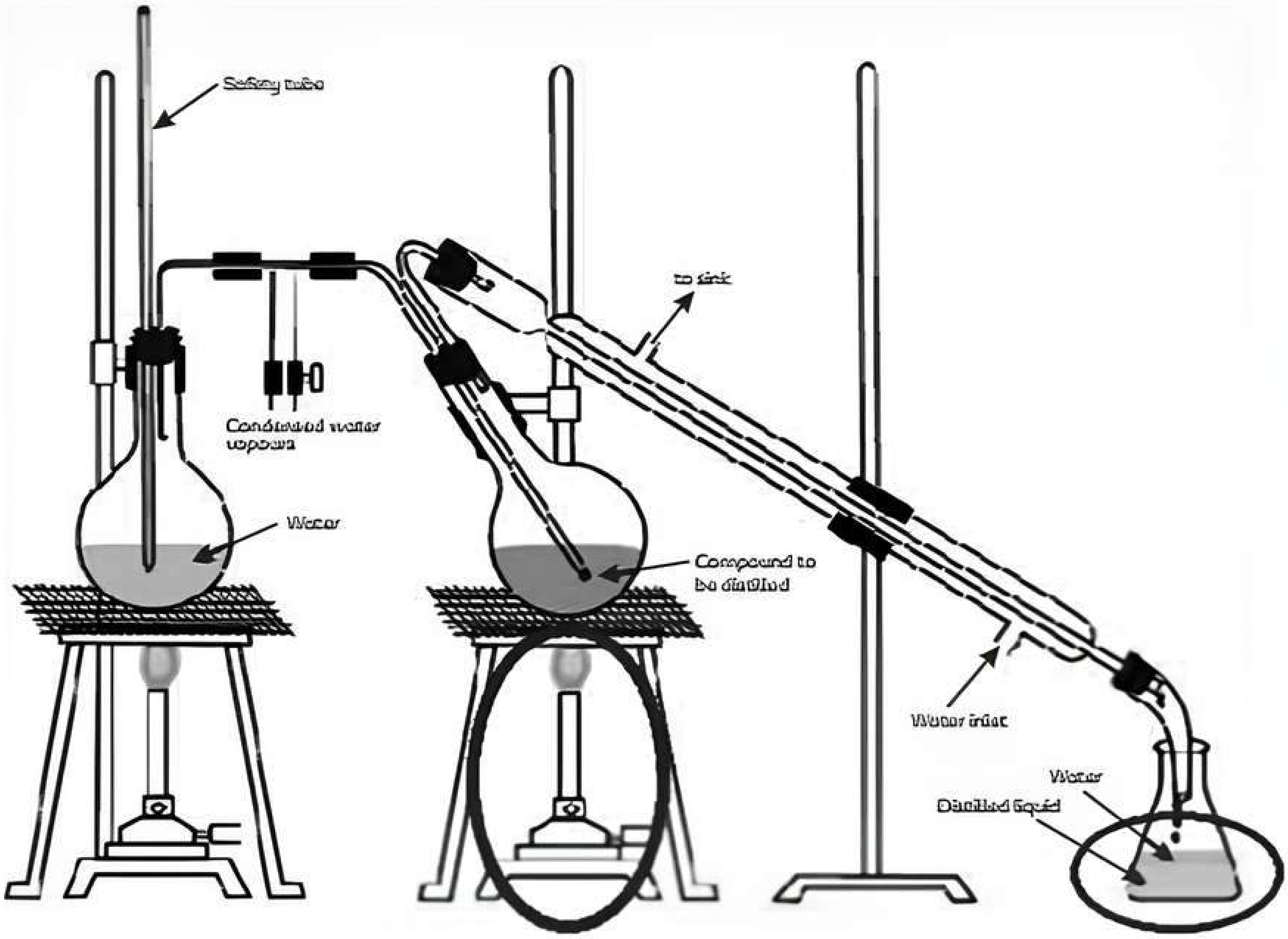


The set-up for Distillation under reduced pressure method

Steam Distillation

Steam distillation method is employed to separate substances that exist as steam which are volatile and these vapours are immiscible in water. In this steam method, the boiling of liquid starts when the sum of the vapour pressure due to organic liquid (p_1) and the sum of the vapour pressure due to water (p_2) will be equal to the atmospheric pressure (p), i.e., $p = p_1 + p_2$. Since the vapour pressure of the liquid is lower than the atmospheric pressure, the organic liquid gets vaporised at a lower temperature below its boiling point. The steam is generated from the steam generator which is passed through the heated flask containing a liquid that has to be distilled. A mixture of the steam mixture and volatile organic compound is allowed to condense and then collected. Then, the organic compound can be separated by a separating funnel from the water. In a mixture, one of the substances is water and the other substance is water-insoluble one then both of them will closely boil below 373 K. Then the mixture containing water and the other substance can be separated using a separating funnel.

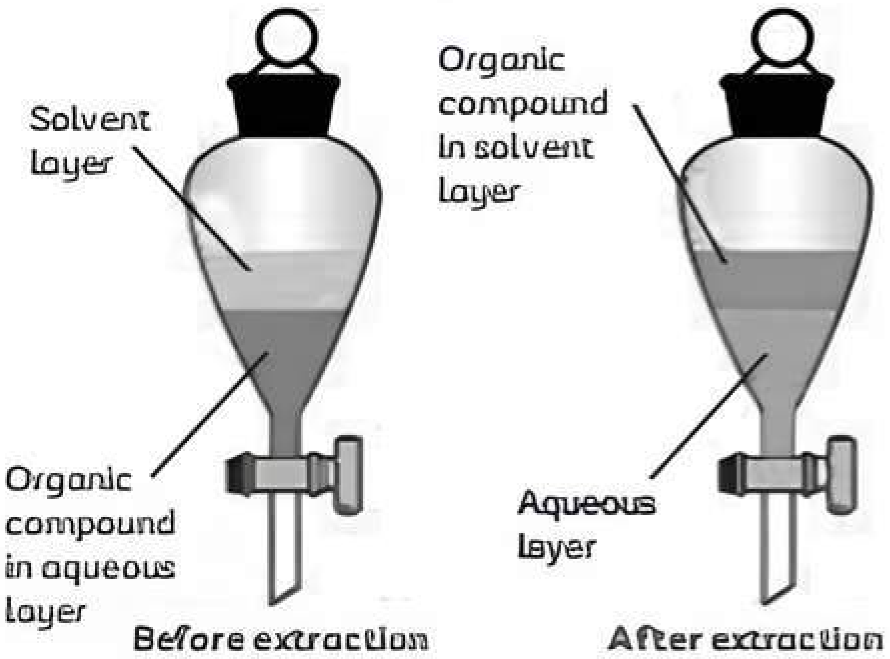
Application: Aniline is separated from the water by this technique in an aniline-water mixture system.



Steam distillation apparatus

Differential Extraction

If the organic compounds have lesser solubility in an organic solvent. A large quantity of solvent will be required to extract the small amount of the compound present in it. In such cases, differential extraction is used. The extraction of compound is done with the same solvent every time. The organic compound in the aqueous medium can be separated by shaking them which forms two immiscible distinct layers, these layers are separated using a separating funnel. The organic solvent can be removed by evaporation or distillation to get the compound back. This is also called **continuous extraction**.



Differential extraction takes place on the basis of difference in their solubility.

Chromatography

Chromatography technique is mostly employed to separate, a mixture of compounds into individual components, purify the compounds and test their purity of the compound. The word chroma (from chromatography) is derived from the Greek word meaning colour. This method is employed for separating the coloured substances found in plants. There are two phases involved in this.

Stationary phase: The substance is applied on a stationary phase it may be a solid one or liquid. The pure solvent or mixture of solvents or gas is allowed to flow slowly over a stationary phase. During this process, the individual components get separated into one another.

Mobile phase: The phase which is moving is called a mobile phase. It may be a liquid or gas.

The chromatography is classified into two different categories based on the different principles they are used

(1) Adsorption chromatography

(2) Partition chromatography.

Adsorption Chromatography

Principle: It is based on the principle that different compounds get adsorbed at different degrees in an absorbent. The adsorbent mostly employed is silica gel or alumina.

When a mobile phase passes through a stationary phase, the components in the mixture move over the stationary phase at different distances.

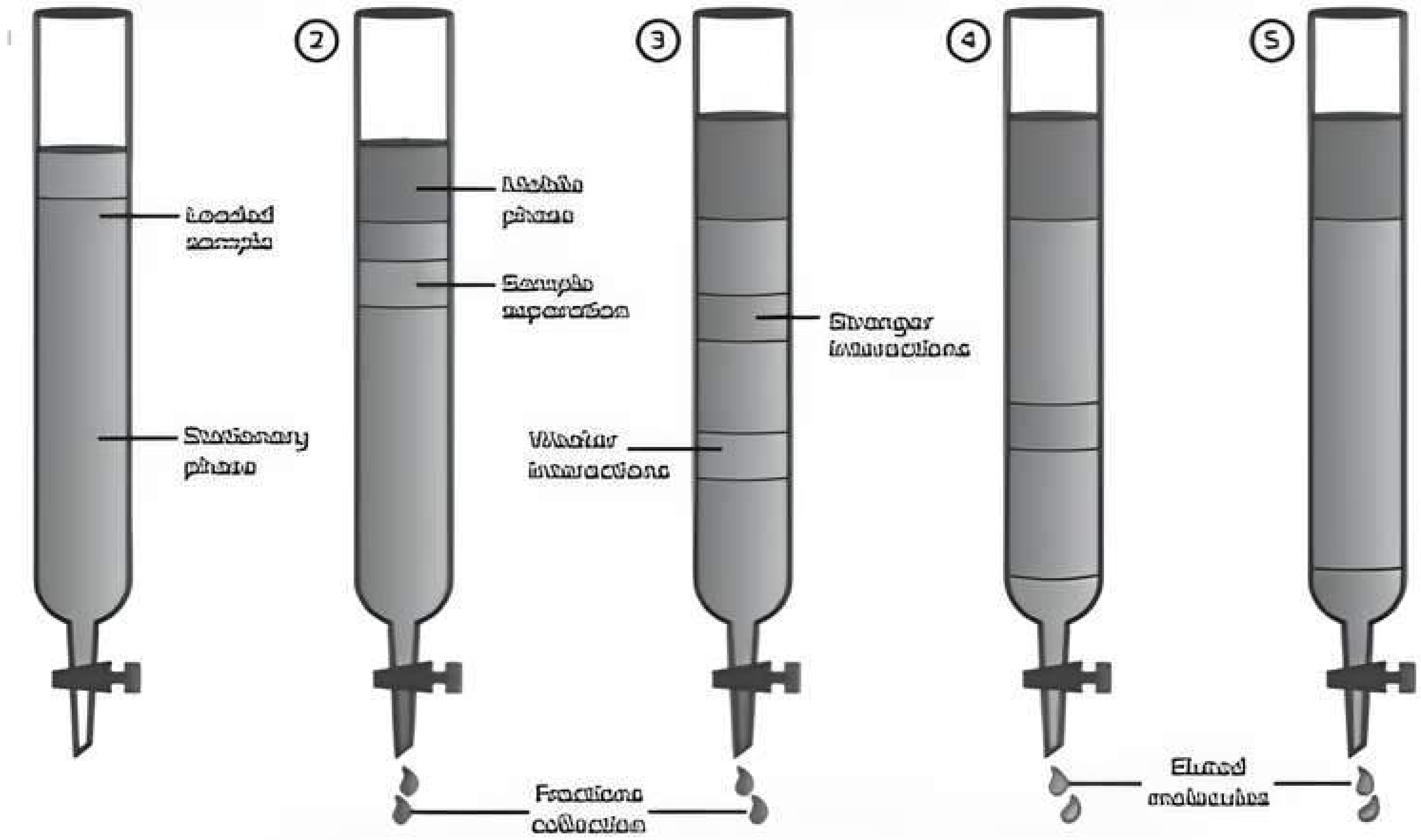
The two important techniques based on the differential adsorption principle is

(1) Column chromatography

(2) Thin-layer chromatography.

Column Chromatography

Column chromatographic technique involves separating the mixture of components using a column of adsorbent which acts as a stationary phase. The column is packed inside a glass tube and a stopcock is fitted with the lower end of the column. The mixture that is adsorbed on an adsorbent is placed on the column's top. An eluent (a mixture of liquid) will flow down through the column. Based on the degree of adsorption of compounds the complete separation will be done. The most adsorbed compound will be at the top and other compounds are adsorbed at different distances in the column.



Different stages of separation in Column chromatography.

Thin-Layer Chromatography (TLC)

Thin-layer chromatography separates the mixture of components using a thin layer coated on a glass plate that acts as an adsorbent. (Stationary phase).

The adsorbent (Silica gel or alumina) is applied as a thin layer (0.2 mm thick) over a glass plate. This plate is known as a thin-layer chromatographic plate or chrome plate. The mixture to be separated is applied as a small spot of about 2 cm at one end of the TLC plate. The plate is then placed in a closed jar that contains the eluant. As the eluant rises to the plate, the mixture's components rise at varying distances depending on their degree of adsorption, resulting in component separation. The relative adsorption of the individual components in a mixture can be expressed by the retardation factor R_f value

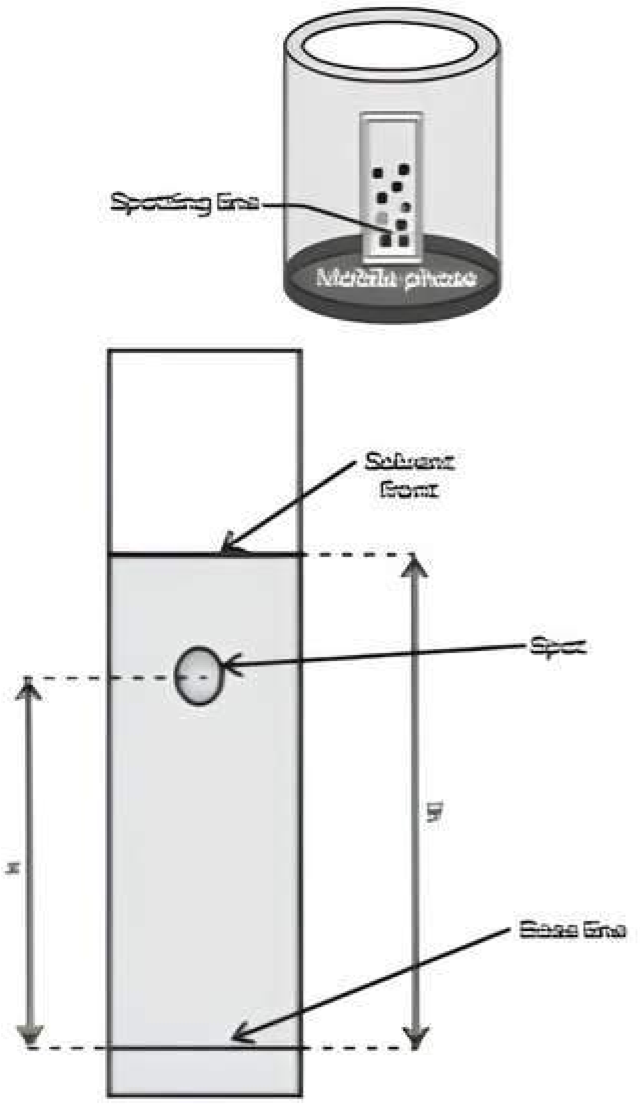
$$R_f = \frac{\text{Distance moved by the substance from baseline } (x)}{\text{Distance moved by the solvent from baseline } (y)}$$

Characterisation: The TLC plate show spots of coloured compounds due to their original colour. Some compounds are colourless, these can be visualised by placing the plate under fluorescence & ultraviolet light. Another method is placing the plate in a container that contains a few iodine crystals, the components which absorb iodine will show brown spots or some reagents can be sprayed according to the specific compounds.

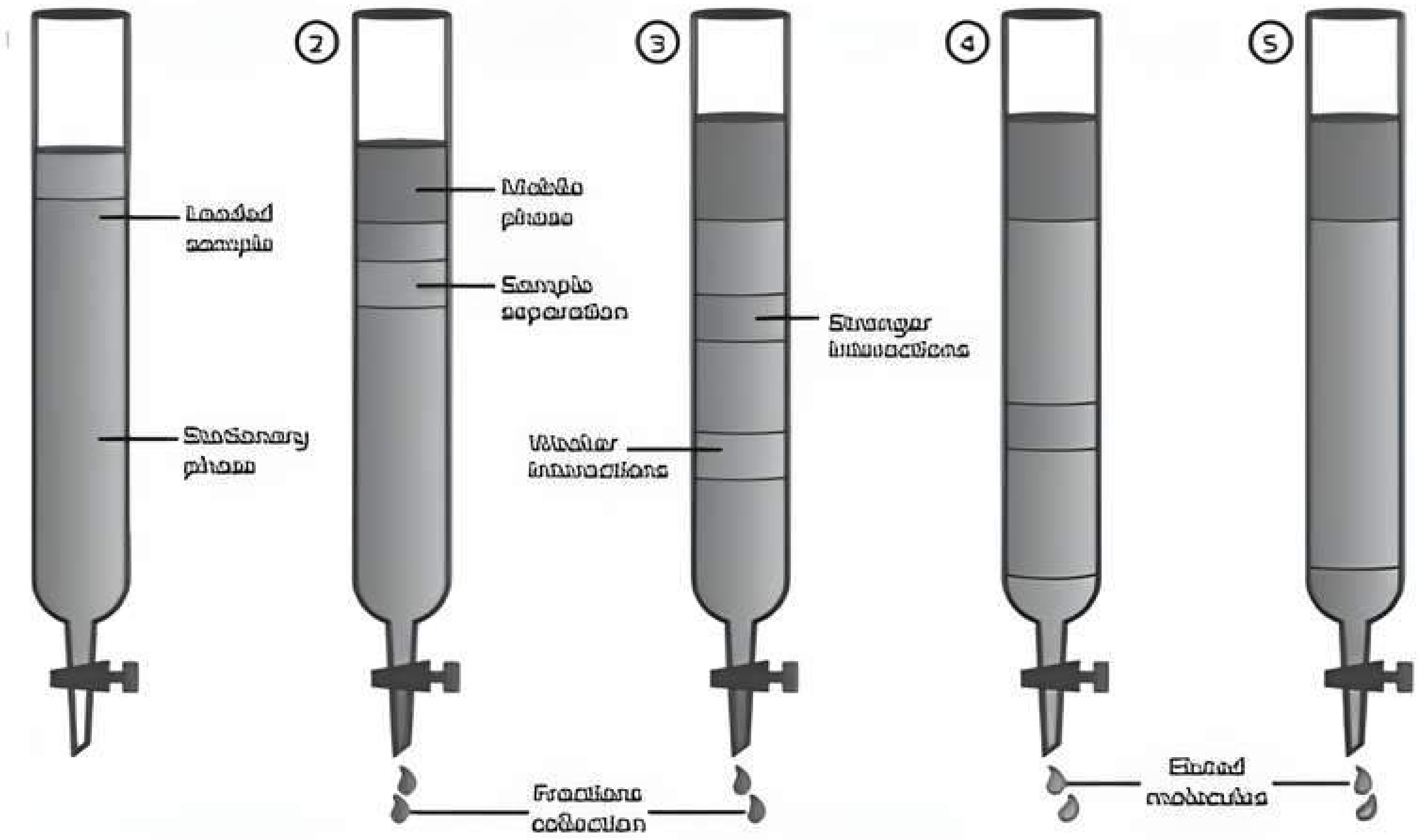
E.g., Ninhydrin solution is sprayed over the plate to detect amino acids.

Example 4.1: Case Based:

Chromatography is a separation process in which the components to be separated are distributed between two phases: a stationary phase and a mobile phase that flows through it in a specific direction. Column chromatographic technique involves separating the mixture of components using a column of adsorbent which acts as a stationary phase. The column is packed inside a glass tube and a stopcock is fitted with the lower end of the column. The mixture that is adsorbed on an adsorbent is placed on the column's top. An eluent (a mixture of liquid) will flow down through the column. Based on the degree of adsorption of compounds the complete separation will be done. The most adsorbed compound will be at the top and other compounds are adsorbed at different distances in the column.



(A)



(B)

(A) What type of chromatography is given in diagrams (A) and (B)?

- (a) Adsorption chromatography and gas chromatography
- (b) Thin-layer chromatography and column chromatography
- (c) Partition and thin-layer chromatography
- (d) Partition and paper chromatography.

(B) What is the mobile phase and stationary phase used in diagram (A)?

- (a) Thin layer of alumina or silica gel and liquid.
- (b) A plastic-supported plate and gas.
- (c) Thin layer of alumina or silica gel and gas.
- (d) Liquid column and solid.

(C) What is the principle used in the diagram (A) and suggest which type of molecules will have a smaller retention factor value?

(D) What Is meant by the retention factor?

(E) Assertion (A): TLC is a type of adsorption chromatography.

Reason (R): TLC separates compounds based on their differential adsorption.

- (a) Both (A) and (R) are true and (R) is the correct explanation of (A).
- (b) Both (A) and (R) are true but (R) is not the correct explanation of A.
- (c) (A) is true but (R) is false.
- (d) (A) is false but (R) is true.

Ans. (A) *(b) Thin-layer chromatography and column chromatography.*

Explanation: The given diagram comes under the separation technique of thin-layer chromatography and column chromatography.

(B) *(a) Thin layer of alumina or silica gel and liquid.*

Explanation: Thin-layer chromatography is employed for the separation of a mixture of components using a thin-layer coated on a glass plate that acts as an adsorbent (stationary phase) and the mobile phase is a liquid. The adsorbent (Silica gel or alumina) is spread over a glass plate as a thin layer (0.2 mm thick). This plate is known as thin layer chromatography plate or chrome plate.

(C) The principle used in the diagram A is to separate the compounds based on their polarity. The more polar the compound, the more will be the adsorbent and the smaller the distance it will travel and have a small R_f value.

(D) Retention factor R_f: The retention factor is the value of the ratio between the distance travelled by the analyte to the solvent front on a chromatogram.

$$R_f = \frac{\text{Distance moved by the substance from baseline } (x)}{\text{Distance moved by the solvent from baseline } (y)}$$

(E) *(c) (A) is true but (R) is false.*

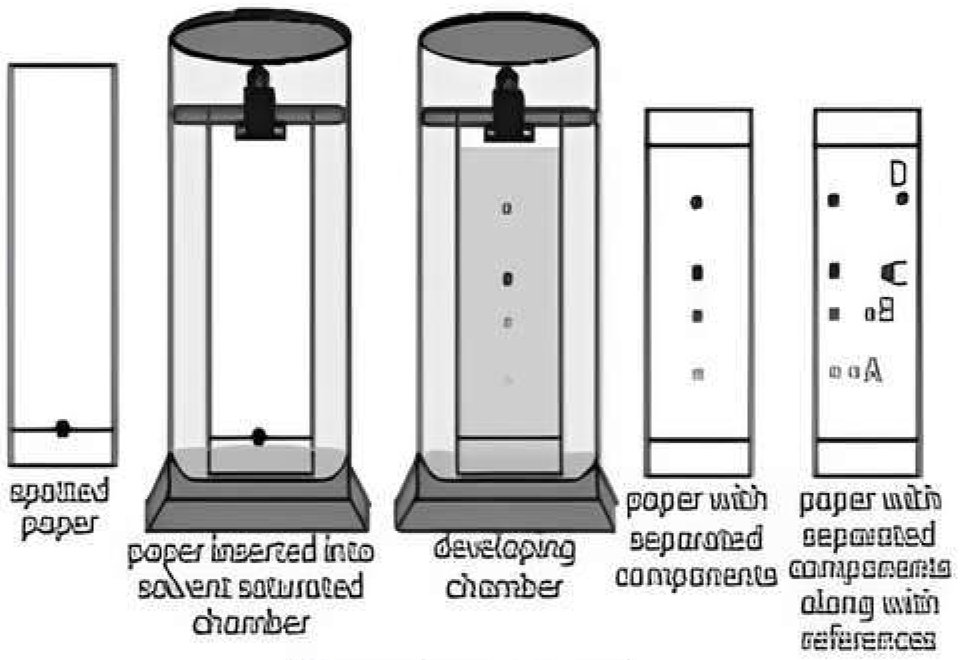
Explanation: Thin layer chromatography is used to separate compounds in a mixture based on the polarity. Not on the differential adsorption type. It is meant for column chromatography. So (A) is true and (R) is false.

Partition Chromatography

The compounds in a mixture are separated by continuous differential partitioning between stationary & mobile phases. Paper chromatography comes under partition chromatography, in which a special quality chromatography paper is used. The chromatography paper contains water that serves as a stationary phase.

Process: A spotted chromatography paper strip is suspended in a suitable solvent or a combination of solvents that serves as the mobile phase. The solvent rises and runs over the spots due to capillary action. According to their partitioning, the paper preferentially retains distinct components at different phases.

Development: The developed paper strip is called chromatogram. The component spots on the chromatogram are visible at various heights from the beginning spot on the chromatogram. Under UV light or by spraying a suitable reagent, the dots of colourless substances can be seen.



Paper chromatography

TOPIC 2

QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

The organic compounds chiefly contain carbon and hydrogen, in addition to this oxygen, nitrogen, sulphur, halogens and phosphorus are also present in smaller concentrations.

Detection of Carbon and Hydrogen

Carbon and hydrogen present in the compound are detected by heating the compound with copper (II) oxide which acts as an oxidising agent. It oxidises carbon to carbon dioxide (tested using lime water which develops turbidity) and oxidises hydrogen to water (tested with anhydrous copper sulphate which turns the solution to blue coloured).

$$C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$$

$$2H + CuO \xrightarrow{\Delta} Cu + H_2O$$

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + H_2O$$

$$5H_2O + CuSO_4\text{ (white)} \rightarrow CuSO_4.5H_2O\text{ (blue)}$$

Detection of other Elements

Nitrogen, sulphur, halogens and phosphorus in a compound can be detected by Lassaigne's test. Sodium metal fused with elements to convert from the covalent form into ionic form. The following reactions take place:

$$Na + C + N \xrightarrow{\Delta} NaCN$$

$$2Na + S \xrightarrow{\Delta} Na_2S$$

$$Na + X \xrightarrow{\Delta} NaX$$

$$(X = Cl, Br, I)$$

C, N, S and X come from an organic compound. By boiling the fussed material with distilled water, the cyanide, sulphide and halide of sodium are extracted. The above extracted liquid is called sodium fusion extract.

(1) Test for Nitrogen:

A small amount of sodium fusion extract is boiled with iron sulphate, which is acidified with sulphuric acid. The presence of nitrogen is confirmed by the formation of Prussian blue colour.

Sodium cyanide reacts with iron (II) sulphate and forms sodium hexacyanidoferrate (II). Which is then heated with sulphuric acid and oxidises some iron (II) ions to iron (III) ions which then reacts with sodium hexacyanoferrate to form iron (III) hexacyanoferrate (II) (ferric ferrocyanide--Prussion blue).

$$6CN^- + Fe^{2+} \rightarrow [Fe(CN)_6]^{4-}$$

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow[xH_2O]{xH_2O} Fe_4[Fe(CN)_6]_3$$

Prussian blue

(2) Test for Sulphur:

On acidification of sodium fusion extract with nitric acid using acetic acid and lead acetate. A black precipitate of lead sulphide formed indicates the presence of Sulphur.

$$S^{2-} + Pb^{2+} \rightarrow PbS\text{(black)}$$

A small amount of sodium fusion extract is treated with sodium nitroprusside and the appearance of violet colour indicates the sulphur present in the compound.

$$S^{2-} + [Fe(CN)_5NO]^{2-} \rightarrow [Fe(CN)_5NOS]^{4-}\text{ (Violet)}$$

If both Nitrogen and Sulphur are present in an organic compound, instead of violet colour, a blood red -coloured sodium thiosulphate is formed. There are no free cyanide ions so Prussion blue can't be formed.

$$Na + C + N + S \rightarrow NaSCN$$

$$Fe^{3+} + SCN^- \rightarrow [Fe(SCN)]^{2+}$$

(Blood red)

The sodium fusion extract is treated with an excess sodium and then the thiocyanate decomposes to form cyanide and sulphide.

$$2Na + NaSCN \rightarrow NaCN + Na_2S$$

(3) Test for Halogens:

(i) On acidification of sodium fusion extract with nitric acid, which is then treated with silver nitrate forms a white precipitate which is insoluble in ammonium hydroxide indicates the chlorine present in the compound.

(ii) Yellow precipitate that is partially soluble in ammonium hydroxide indicates the bromine presence in an organic compound.

(iii) Yellow precipitate insoluble in ammonium hydroxide indicates the iodine presence.

$$X^- + Ag^+ \rightarrow AgX$$

[X represents halogen - chlorine, bromine or iodine]

(iv) If they also include nitrogen or sulphur, the sodium fusion extract is first boiled with strong nitric acid, which decomposes to generate sodium cyanide or sulphide in Lassaigne's test. Silver nitrate reacts with these ions.

(4) Test For Phosphorus:

The compound is treated with an oxidising agent (sodium peroxide). It oxidises the phosphorous to phosphate. The solution is boiled with nitric acid and ammonium molybdate is added. A yellow colour precipitate indicates the presence of phosphorous.

$$Na_3PO_4 + 3HNO_3 \rightarrow H_3PO_4 + 3NaNO_3$$

$$\underset{\text{(Ammonium molybdate)}}{H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3} \rightarrow \underset{\text{(Ammonium phosphomolybdate)}}{(NH_4)_3PO_4.12MoO_3} + 21NH_4NO_3 + 12H_2O$$

Example 4.2: Case Based:

Raju and Meena are doing the qualitative analysis based in the laboratory. They are detecting different components in a mixture. Based on the observation identify the compounds.

(A) On acidification of sodium fusion extract with nitric acid, which is then treated with silver nitrate. Forms a white precipitate that is insoluble in ammonium hydroxide. Which of the given element is present in it?

(a) Bromine (b) Phosphorous
(c) Chlorine (d) Sulphur

(B) On treating the sodium extract with sodium nitroprusside, appearance of violet colour indicates the presence of:

(a) sulphur (b) oxygen
(c) nitrogen (d) chlorine

(C) Which forms a black precipitate on acidification with nitric acid?

(D) Write the test for phosphorous.

(E) Assertion (A): A small amount of sodium fusion extract is reacted with sodium nitroprusside, the violet colour of the mixture indicates presence of sulphur.

Reason (R): The violet colour is due to the formation of sodium thionitroprusside.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).
(b) Both (A) and (R) are true but (R) is not the correct explanation of A.
(c) (A) is true but (R) is false.
(d) (A) is false but (R) is true.

Ans. (A) *(c) Chlorine*

Explanation: On acidification of sodium fusion extract with nitric acid, which is treated with silver nitrate solution forms a white precipitate which is insoluble in ammonium hydroxide indicating the presence of chlorine.

$$Cl^- + Ag^+ \rightarrow \underset{\text{(white ppt.)}}{AgCl}$$

(B) *(a) Sulphur*

Explanation: The sodium fusion extract is treated with sodium nitroprusside; the appearance of violet colour indicates the sulphur present in the compound.

$$S^{2-} + [Fe(CN)_5NO]^{2-} \rightarrow \underset{\text{(Violet)}}{[Fe(CN)_5NOS]^{4-}}$$

(C) On acidification of sodium fusion extract with nitric acid by acetic acid and lead acetate. Lead sulphide is formed (black precipitate) indicating the presence of sulphur in the compound.

$$S^{2-} + Pb^{2+} \rightarrow \underset{\text{(black)}}{PbS}$$

(D) The compound is treated with an oxidising agent (sodium peroxide). It oxidises the phosphorous to phosphate. The oxidised solution is then boiled with nitric acid followed by the addition of ammonium molybdate. A yellow colour precipitate indicates the presence of phosphorous in the compound.

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3$$

(Ammonium phosphomolybdate)

$$\rightarrow (NH_4)_3PO_4.12MoO_3 + 21NH_4NO_3 + 12H_2O$$

(Ammonium phosphomolybdate)

(E) *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

Explanation: The sodium fusion extract is treated with sodium nitroprusside; the appearance of violet colour indicates the sulphur presence. The violet colour is due to the formation of sodium thionitroprusside.

$$S^{2-} + [Fe(CN)_5NO]^{2-} \rightarrow \underset{\text{(Violet)}}{[Fe(CN)_5NOS]^{4-}}$$

TOPIC 3

QUANTITATIVE ANALYSIS

Quantitative analysis is a technique which determines the percentage composition of components present in an organic substance. This can be determined by the following methods:

Carbon and Hydrogen

Carbon and hydrogen can be estimated by burning the organic compound in the presence of excess oxygen and copper (II) oxide which acts as an oxidising agent. It oxidises carbon and hydrogen to carbon dioxide and water.

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \left(\frac{y}{2}\right)H_2O$$

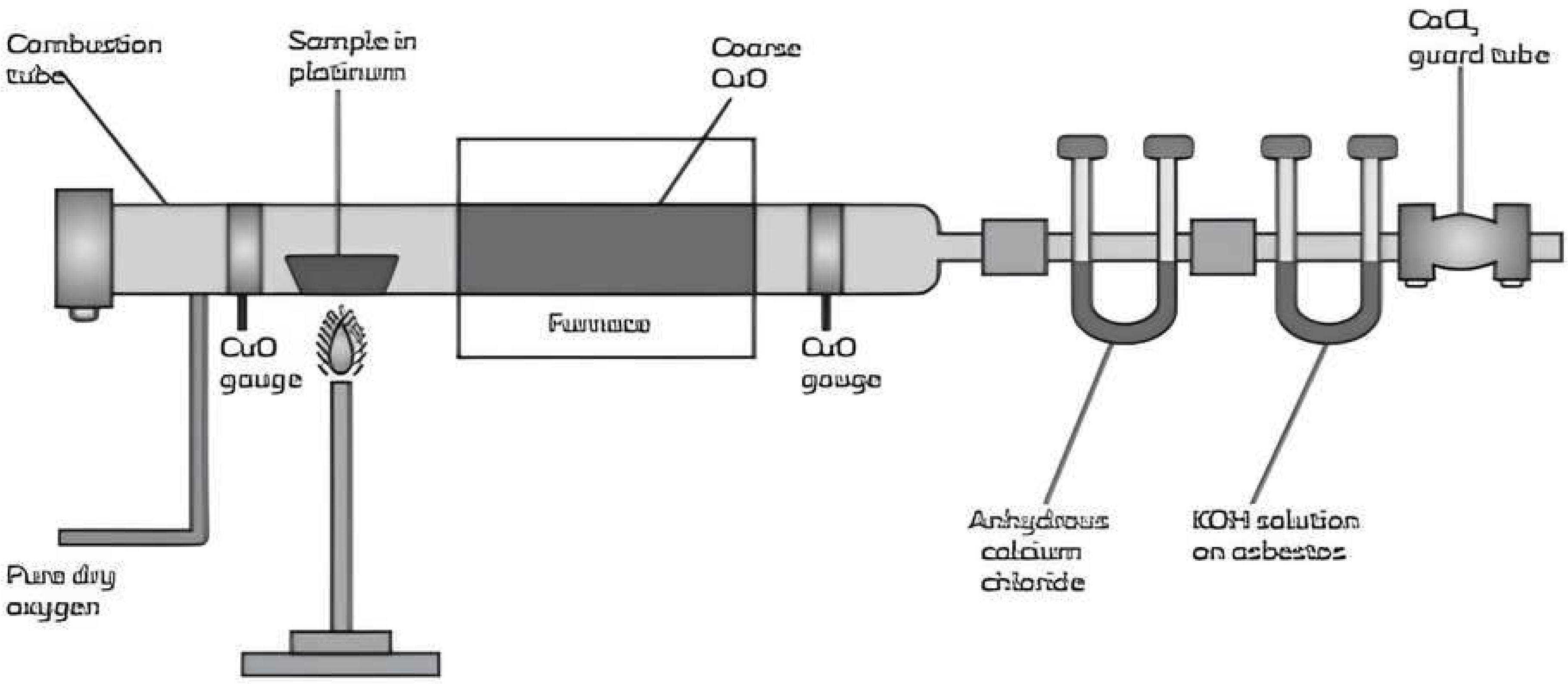
The U tube containing anhydrous calcium chloride which is weighed is used for the determination of mass of the water produced. the mixture is allowed to pass through the U tube. The carbon dioxide is absorbed by the concentrated solution of potassium hydroxide in another U tube. These U tubes are connected in a linear or series manner.

The potassium hydroxide and calcium chloride mass will be increased due to the absorption of carbon dioxide and water using this percentage of mass of the carbon and hydrogen can be estimated.

Let the mass of organic compounds be m(g). m_1 be the mass of water and m_2g be mass of carbon dioxide.

$$\text{Percentage of carbon} = \frac{12 \times m_2 \times 100}{44 \times m}$$

$$\text{Percentage of hydrogen} = \frac{2 \times m_1 \times 100}{18 \times m}$$



Apparatus used for the estimation of carbon and hydrogen which on oxidation forms carbon dioxide and water.

Example 4.3: On complete combustion of 0.246 g of an organic compound, it gives a 0.198 g of carbon dioxide and 0.1014 g water. Determine the percentage composition of carbon and hydrogen in the compound.

Ans. $$\text{Percentage of carbon} = \frac{12 \times 0.198 \times 100}{44 \times 0.246}$$

$$= 21.95\%$$

$$\text{Percentage of hydrogen} = \frac{2 \times 0.1014 \times 100}{18 \times 0.246}$$

$$= 4.58\%$$

Nitrogen

Two methods are used for the estimation of nitrogen:

(1) Dumas method

(2) Kjeldahl's method.

Dumas method

The organic compounds that contain nitrogen is heated with copper oxide in the carbon dioxide atmosphere giving free nitrogen with carbon dioxide and water.

$$C_xH_yN_z + \left(\frac{2x+y}{2}\right)CuO \rightarrow xCO_2 + \frac{y}{2}H_2O + \frac{z}{2}N_2 + \left(\frac{2x+y}{2}\right)Cu$$

By passing the gaseous mixture over a heated copper gauze. a large amount of nitrogen oxide is generated. which is reduced to nitrogen. The mixture is allowed to pass through an aqueous potassium hydroxide solution. which absorbs the carbon dioxide. The nitrogen is collected in the graduated tube's upper section.

Let the mass of organic compounds = m(g)

Volume of nitrogen collected = V_1mL

Room temperature = T_1K

$$\text{Volume of nitrogen at STP}(v) = \frac{P_1V_1 \times 273}{760 \times T_1}$$

Where P_1 and V_1 are the pressure and volume of nitrogen. P_1 will be different from the atmospheric pressure.

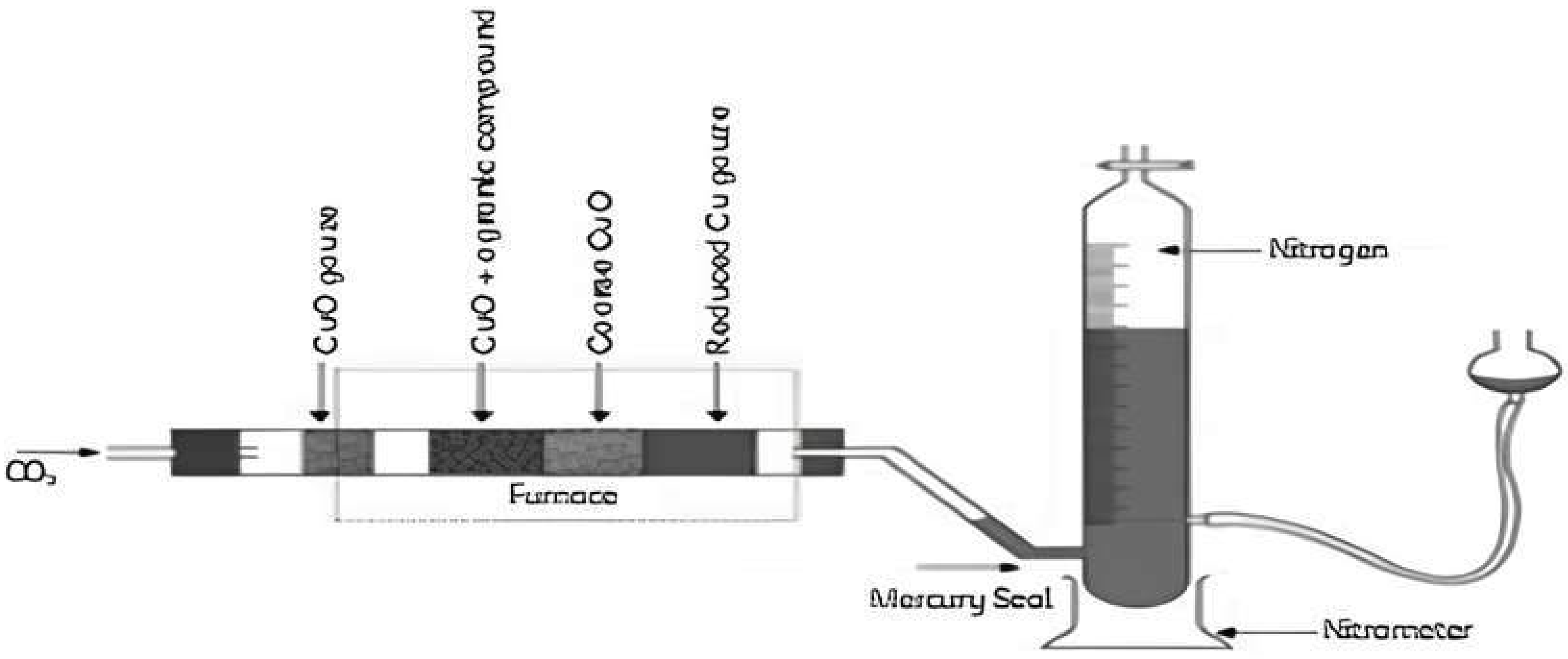
The value of P_1 can be calculated by the relation:

P_1 = Atmospheric pressure -aqueous tension

24000 mL N_2 at STP weighs 28g

$$\text{V mL } N_2 \text{ at STP weighs} = \frac{28 \times V}{22400} \text{ g}$$

$$\text{Percentage of nitrogen} = \frac{28 \times V \times 100}{22400} \%$$



Dumas Method

Example 4.4: **In Duma's method, when 0.3 g of an organic compound gave 50 mL of nitrogen collected at 300 K temperature and 715 mm pressure. Calculate the percentage composition of nitrogen in the compound (Aqueous tension at 300 K = 15 mm).**

Ans. Volume of nitrogen collected at 300 K and 715 mm pressure is 50 mL

Actual pressure = pressure – pressure due to aqueous tension

$$= 715 - 15$$

$$= 700 \text{ mm}$$

Volume of nitrogen at STP (V_2) = $\frac{P_1 \times V_1 \times T_2}{T_1 \times P_2}$

(T_2 and P_2 are the standard pressure and temperature values)

$$= \frac{273 \times 700 \times 50}{300 \times 760}$$

$$= 41.9 \text{ mL}$$

22.400 mL of N_2 At STP weighs = 28 g

41.9 mL of nitrogen weighs = $\frac{28 \times 41.9}{22400}$ g

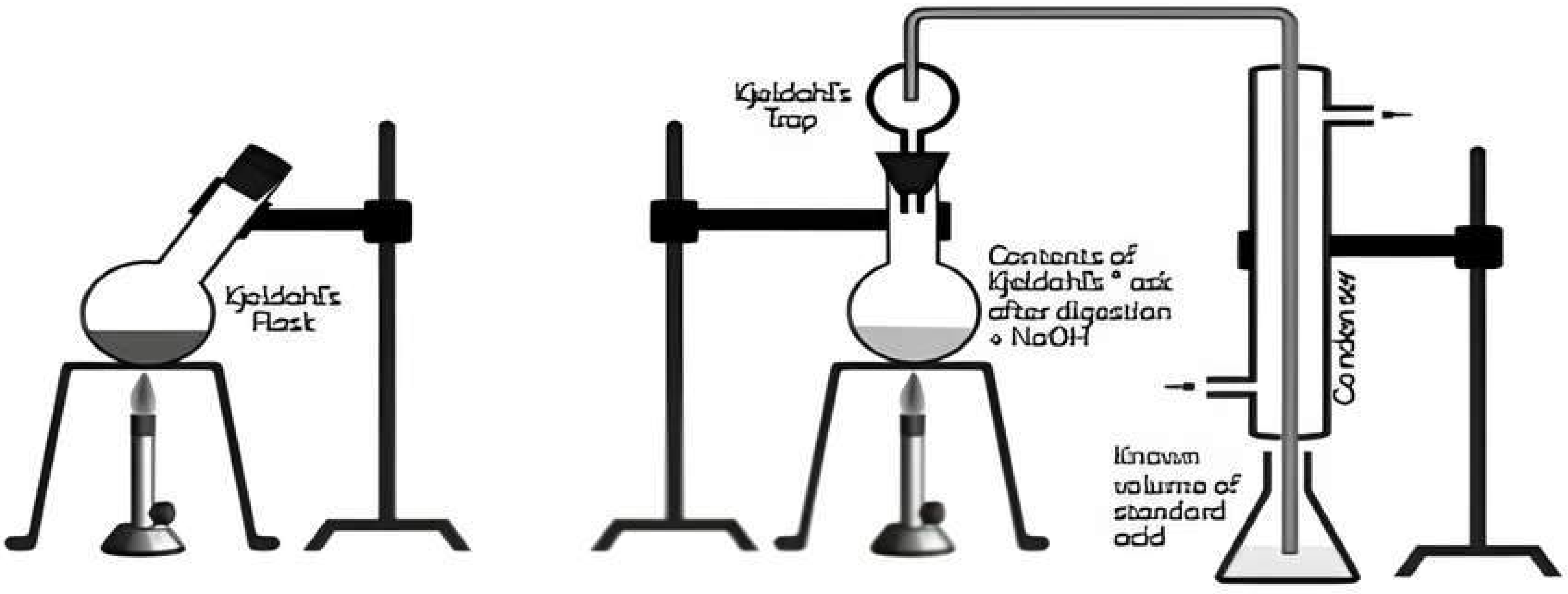
Percentage of Nitrogen

$$= \frac{28 \times 41.9 \times 100}{22400}$$

$$= 5.24\%$$

Kjeldahl's method

When a nitrogen-containing compound is heated with conc. sulphuric acid, nitrogen is converted to ammonium sulphate. The resulting mixture is then heated with sodium hydroxide in excess. An excess of sulphuric acid solution absorbs the ammonia gas. The amount of ammonia produced is equal to the amount of sulphuric acid consumed. The unreacted sulphuric acid (which does not absorb ammonia) is titrated with a normal alkali solution. The difference between the initial and final amounts of acid consumed and remaining after the reaction can be used to estimate the amount of acid that remains unreacted.



Kjeldahl method for detecting the nitrogen.

Organic compound + $H_2SO_4 \rightarrow (NH_4)_2SO_4$

$$\xrightarrow{2NaOH} Na_2SO_4 + 2NH_3 + 2H_2O$$

Let the mass for organic compound taken = mg

Volume of = $(NH_4)_2SO_4$ taken = V mL

Volume of NaOH molarity M used for the titration of excess of $H_2SO_4 = V_1$ mL

V_1 mL Of NaOH of molarity M = $\frac{V_1}{2}$ mL of H_2SO_4 of molarity M

Volume of H_2SO_4 of molarity M unused = $\left(V - \frac{V_1}{2}\right)$mL

$\left(V - \frac{V_1}{2}\right)$ mL of H_2SO_4 of molarity M = $2\left(V - \frac{V_1}{2}\right)$ mL of NH_3 solution of molarity M.

1000 mL of 1 M NH_3 solution contains 17g of NH_3 or 14g of N_2

$\left(V - \frac{V_1}{2}\right)$ mL of NH_3 solution of molarity

Contains: $\dfrac{14 \times M \times 2\left(V - \frac{V_1}{2}\right)}{1000}$N

$$\text{Percentage of nitrogen} = \frac{14 \times M \times 2\left(V - \frac{V_1}{2}\right)}{1000} \times \frac{100}{m}$$

$$= \frac{1.4 \times M \times 2\left(V - \frac{V_1}{2}\right)}{m}$$

Non-suitability: This method is not applicable for compounds even they contain nitrogen like azo, nitro and nitrogen in ring systems (eg: Pyridine). Because these compounds do not convert to ammonium sulphate.

Example 4.5: During the estimation of nitrogen present in an organic compound by Kjeldahl's method, the ammonia evolved from 0.5 g of the compound in Kjeldahl's estimation of nitrogen, neutralised 10 mL of 1M H_2SO_4. Find out the percentage of nitrogen in the compound.

Ans. 1M of 10 mL of H_2SO_4 = 1M of 20 mL of NH_3

1000 mL of 1M ammonia contains 14 g nitrogen.

20 mL of 1M of ammonia contains $\frac{14 \times 20}{1000}$ g of nitrogen.

Percentage of nitrogen

$$= \frac{14 \times 20 \times 100}{1000 \times 0.5}$$

= 56.0%

Halogens

Carius method: In a furnace, an organic compound of known mass is heated in a hard glass tube known as a carius tube with conc. nitric acid in the presence of silver nitrate. Carbon dioxide and water are produced as the carbon and hydrogen present are oxidised. The halogen in the compound, on the other hand, generates silver halide. After that, it's rinsed, filtered and dried.

Let the mass of organic compound take = mg

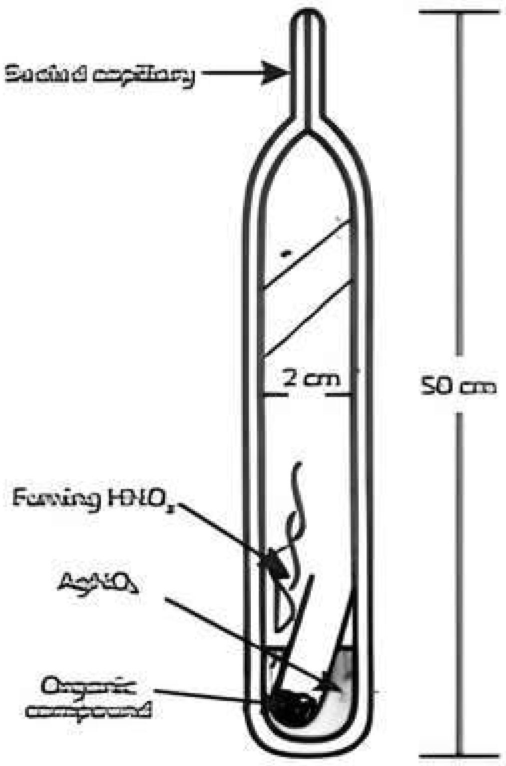
mass of AgX formed = m_1g

1 mol of AgX contains 1 mol of X

$$\text{Mass of halogen in of AgX} = \frac{\text{Atomic mass of X} \times m_1 g}{\text{Molecular mass of AgX}}$$

Percentage of halogen

$$= \frac{\text{Atomic mass of X} \times m_1 g \times 100}{\text{Molecular mass of AgX} \times m}$$



Carius method for detection of halogens

Example 4.6: In carius method of estimation of halogen, 0.15 g of an organic compound gave 0.12g of AgBr. Find out the percentage of bromine in the compound.

Ans. Molar mass of AgBr = 108 + 80

= 188 $g mol^{-1}$

188g of AgBr contains 80g of bromine.

0.12g of AgBr contains = $\frac{80 \times 0.12}{188}$ g bromine

$$= \frac{80 \times 0.12 \times 100}{188 \times 0.15}$$

Percentage of bromine = 34.04%

Sulphur

An organic compound of known mass is heated with sodium peroxide or con. nitric acid in a carius tube. When sulphur is present in that compound, it is oxidised to sulphuric acid. When an excess barium chloride in water is added barium sulphate gets precipitated. The precipitate is then filtered, washed, dried and weighed. By calculating barium sulphate's mass, the percentage of sulphur can be estimated.

Let the mass of organic compound taken = mg

The mass of barium sulphate formed = m_1g

$$1 \text{ mol of } BaSO_4 = 233\text{g of } BaSO_4 = 32\text{g sulphur}$$

$$m_1\text{g of } BaSO_4 \text{ contains} = \frac{32 \times m_1}{233} \text{ sulphur}$$

$$\text{Percentage of sulphur} = \frac{32 \times m_1 \times 100}{233 \times m}$$

Example 4.7: In sulphur estimation, 0.157g of an organic compound gave 0.4813g of barium sulphate. What is the percentage of sulphur in the compound?

Ans. Molecular mass of $BaSO_4 = 137 + 32 + 64 = 233$ g

233 g of $BaSO_4$ contains 32g of sulphur

$$0.4813\text{g of } BaSO_4 \text{ contains } \frac{32 \times 0.4813}{233} \text{g sulphur}$$

$$\text{Percentage of sulphur} = \frac{32 \times 0.4813 \times 100}{233 \times 0.157} = 42.10\%$$

Phosphorous

An organic compound of known mass is heated with con. nitric acid that oxidises the phosphorous present in the compound to phosphoric acid. When ammonia and ammonium molybdate is added ammonium phosphomolybdate $(NH_4)_3PO_4.12MoO_3$ is precipitated. When magnesia mixture is added alternatively phosphoric acid precipitated as $MgNH_4PO_4$ which on ignition yields $Mg_2P_2O_7$.

Let the mass of organic compound taken = mg

Mass of ammonium phosphomolybdate = m_1g

Molar mass of $(NH_4)_3PO_4.12MoO_3$ = 1877g

$$\text{Percentage of phosphorous} = \frac{31 \times m_1 \times 100}{1877 \times m}$$

If phosphorous present is estimated as $Mg_2P_2O_7$

$$\text{Percentage of phosphorous} = \frac{62 \times m_1 \times 100}{222 \times m}$$

Where, 222u is the molar mass of $Mg_2P_2O_7$, m, the mass of organic compound taken, m_1, the mass of $Mg_2P_2O_7$ formed and 62, the mass of two phosphorous atoms present in the compound $Mg_2P_2O_7$.

Oxygen

Typically, oxygen is estimated, by calculating the overall percentage composition from the sum of the percentages of the other elements. There is also a direct method for estimating oxygen, which is as follows:

When an organic substance with a known mass is heated in nitrogen gas, it decomposes. The oxygen is transformed to carbon monoxide when a gaseous mixture containing oxygen is passed over red-hot coke. The carbon monoxide is oxidised to carbon dioxide and iodine is produced when the mixture is passed through warm iodine pentoxide I_2O_5.

$$\text{Compound} \xrightarrow{heat} O_2 + \text{Other gaseous products}$$

$$2C + O_2 \xrightarrow{1373K} 2CO] \times 5 \qquad \text{—(A)}$$

$$I_2O_5 + 5CO \rightarrow I_2 + 5CO_2] \times 2 \qquad \text{—(B)}$$

When the amount of carbon monoxide produced in A equal to the amount of carbon monoxide used in B, by multiplying both the equations. It is observed that each mole of oxygen liberated from the compound generates two moles of carbon dioxide.

Thus 88g of CO_2 of is obtained if 32g oxygen is liberated

Let the mass of organic compound taken being mg

Mass of carbon dioxide produced be (m_1g)

$$m_1\text{g Carbon dioxide so obtained from } \frac{32 \times m_1}{88} \text{g} O_2$$

$$\text{Percentage of oxygen} = \frac{32 \times m_1 \times 100}{88 \times m}$$

The percentage of oxygen calculated using the amount of iodine produced. To determine the elements present in an organic compound, micro amounts of chemicals are now utilised. An apparatus known as CHN an elemental analyser can be used to determine the elements carbon, hydrogen and nitrogen. It just requires a minimal number of chemicals and produces results in a short time.

OBJECTIVE Type Questions

[1 mark]

Multiple Choice Questions

1. **What is the composition of the magnesia mixture used in the estimation of phosphorous?**
   - **(a) Ammonium hydroxide + magnesium chloride + ammonia.**
   - **(b) Ammonium sulphate + magnesium oxide + nitric oxide.**
   - **(c) Ammonium chloride + magnesium sulphate + ammonia.**
   - **(d) Ammonium chloride + magnesium sulphate + nitric oxide.**

Ans. *(c) Ammonium chloride + magnesium sulphate + ammonia.*

Explanation: The magnesia mixture is a reagent used in the estimation of phosphorous which contains an aqueous mixture of ammonium chloride, magnesium sulphate and ammonia. It is used for the precipitation of phosphorus compounds.

2. **What is the role of Iodine pentoxide in the estimation of oxygen:**
   - **(a) Reducing agent (b) Catalyst**
   - **(c) Oxidising agent (d) Buffer.**

Ans. *(c) Oxidising agent*

Explanation: Iodine pentoxide acts as an oxidising agent in the estimation of oxygen. it converts the carbon monoxide into carbon dioxide.

3. **In steam distillation, the substance boils when the sum of the vapour pressure due to organic liquid and water is:**
   - **(a) lower than atmospheric pressure**
   - **(b) higher than atmospheric pressure**
   - **(c) equal to the atmospheric pressure**
   - **(d) greater than or equal to atmospheric pressure.**

Ans. *(c) equal to the atmospheric pressure*

Explanation: When the substances have to be boiled they should have a vapour pressure of water and organic liquids equal to the atmospheric pressure. This state of equalised pressure is called boiling point at that point only the boiling starts.

4. **Which one is the application of distillation under reduced pressure?**
   - **(a) Crude oil in the Petroleum industry**
   - **(b) Glycerol in the soap industry**
   - **(c) Aniline**
   - **(d) None of the above**

Ans. *(b) Glycerol in the soap industry*

Explanation: Glycerol can be separated from spent-lye in the soap industry using the distillation under reduced pressure technique. The technique separates compounds of higher boiling point likewise glycerol also has a higher boiling point. Crude oil is separated by fractional distillation method and aniline is separated by steam distillation.

5. **The judge in the court suspected that the document has some changes. To check that, the judge asked the forensic department to check the ink used at two different places. Which technique is suitable to detect?**
   - **(a) Distillation**
   - **(b) Solvent extraction**
   - **(c) Column chromatography**
   - **(d) Thin-layer chromatography**

[NCERT Exemplar]

Ans. *(d) Thin-layer chromatography*

Explanation: TLC involves the separation of substances of the mixture over a thin layer of absorbent coated on a glass plate. The different inks get adsorbed at different degrees and move at different distances.

Distillation is used to separate volatile liquids. Solvent extraction is used to separate two immiscible liquids. Column chromatography uses a column to separate the compounds.

6. **The principle used in the paper chromatography is:**
   - **(a) Adsorption (b) Volatility**
   - **(c) Partition (d) Solubility**

[NCERT Exemplar]

Ans. *(c) Partition*

Explanation: Partition chromatography is based on the continuous differential partitioning of components of a mixture between stationary and mobile phases. Paper chromatography is a type of partition chromatography.

Related Theory

- *The compounds in a mixture are separated by continuous differential partitioning between stationary and mobile phases. Paper chromatography comes under partition chromatography, in which a special quality chromatography paper is used. The chromatography paper contains water which acts as a stationary phase.*

7. **For which of the following compounds will Lassaigne's test for nitrogen fail.**

(a) NH_2CONH_2 (b) CH_3CONH_2

(c) NH_2NH_2 (d) $C_6H_5NH_2$

[Delhi Gov. QB 2022]

Ans. *(c) NH_2NH_2*

Explanation: Lassaigne's test is not given by compounds, which do not contain C atoms but contains N-atoms like Hydrazine (NH_2–NH_2), NH_2OH. As NH_2NH_2 does not contain C. Hence, on fusion with Na metal, it cannot form NaCN.

8. **In the test for sulphur, when sodium fusion extract is treated with sodium nitroprusside gives violet colour it is due to the formation of**

(a) $[Fe(CN)_4]^{2-}$ (b) $[Fe(CN)_5 NOS]^{4-}$

(c) $[Fe(CN)_6]^{4-}$ (d) $[Fe(CN)_5 NOS]^{2-}$

Ans. *(b) $[Fe(CN)_5 NOS]^{4-}$*

Explanation: The sodium fusion extract is treated with sodium nitroprusside; the appearance of violet colour is due to the formation of Penta cyano nitrosyl which indicates the presence of sulphur.

$$S^{2-} + [Fe(CN)_5 NO]^{2-} \rightarrow \underset{\text{Violet}}{[Fe(CN)_5 NOS]^{4-}}$$

9. **When distillation is done under reduced pressure, the temperature at which the liquid vaporises will be:**

(a) increased

(b) decreased

(c) remains the same

(d) first increased then decreased [Diksha]

Ans. *(b) decreased*

Explanation: The distillation under reduced pressure is generally used for those liquids having high boiling points or which decompose below their boiling point. So, the liquids are boiled lower than their boiling point otherwise the compound will be decomposed. So, the temperature for liquid vaporisation will be decreased.

10. **A mixture of acetone and methanol can be separated by:**

(a) Simple distillation

(b) Fractional distillation

(c) Steam distillation

(d) Distillation under reduced pressure

Ans. *(b) Fractional distillation*

Explanation: Acetone and methanol can be separated by fractional distillation. This method is based on the purification of compounds which are having a low boiling point difference. The acetone which is having low boiling point will condense first and when temperature increases the methanol can be separated.

Related Theory

- *If the mixtures of a compound have small differences in their boiling point, then, simple distillation cannot be used. Due to this, the compound vaporises and gets condensed simultaneously at the same temperature. For this fractional distillation method is used. Fractional distillation involves passing the vapours through a fractionating column before the vapours enter for condensation. The vapours with a higher boiling point get condensed first and then the vapours of a lower boiling point condense.*

Assertion-Reason (A-R)

In the following question no. (11-14) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of A.

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

11. **Assertion (A): Simple distillation is used to separate ethanol from water.**

Reason (R): **Liquids with higher boiling point differences can be separated.**

Ans. *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

Explanation: Simple distillation is the method used to separate ethanol from water. This method can separate the liquids having a big boiling point difference (more than 20°C).

12. **Assertion (A): Adsorption Chromatography is a technique where the compounds get adsorbed at different distances based on the degree of adsorption.**

Reason (R): **The thin layer chromatography and column chromatography are also classified based on this principle.**

Ans. *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

Explanation: TLC works on the concept that different compounds are absorbed at varying degrees in an absorbent. When a mobile phase passes through a stationary phase, the components in the mixture move over the stationary phase at different distances. The two important techniques based on the differential adsorption principle are

(1) Column chromatography

(2) Thin-layer chromatography.

13. **Assertion (A):** Quantitative analysis is used to estimate the percentage mass of the compound present.

Reason (R): Lassaigne's test is one of the qualitative tests for nitrogen, sulphur and halogen in the compounds.

Ans. *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

Explanation: The Lassaigne's test is for the qualitative study it doesn't give an explanation for the quantitative analysis. The quantitative analysis methods are Kjeldahl's, Carius and Dumas which are not mentioned here.

14. **Assertion (A):** An organic compound that contains halogen can be quantitatively estimated by the carius method.

Reason (R): Halogens are precipitated as a yellow solid.

[NCERT Exemplar]

Ans. *(c) (A) is true but (R) is false.*

Explanation: In the carius method, the halogen is treated with fuming nitric acid and silver nitrate, the halogen gets precipitated as a silver halide.

⚠ Caution

➥ *The student may get confused between quantitative & qualitative analysis. Qualitative analysis involves what are the different types of elements present in a given mixture of samples and quantitative is how much amount of a particular element is present in a mixture, this is estimated by the percentage composition.*

CASE BASED Questions (CBQs)

[**4 & 5** marks]

Read the following passages and answer the questions that follow:

15. *Essential oils are used in a wide variety of consumer goods such as detergents, soaps, toilet products, cosmetics, pharmaceuticals, perfumes, confectionery food products, soft drinks, distilled alcoholic beverages (hard drinks) and insecticides. The world's production and consumption of essential oils and perfumes are increasing very fast. Production technology is an essential element to improve the overall yield and quality of essential oil. The traditional technologies pertaining to essential oil processing are of great significance and are still being used in many parts of the globe. Water distillation, water and steam distillation, steam distillation, cohobation, maceration and enfleurage are the most traditional and commonly used methods. Maceration is adaptable when oil yield from distillation is poor. Distillation methods are good for powdered almonds, rose petals and rose blossoms, whereas solvent extraction is suitable for expensive, delicate and thermally unstable materials like jasmine, tuberose and hyacinth. Water distillation is the most favoured method of production of citronella oil from plant material.*

(A) The method used for the extraction of oils from the flower is:

(a) Simple distillation

(b) Steam distillation

(c) Chromatography

(d) Distillation under reduced pressure.

(B) In steam distillation the substance starts to boil at:

(a) $p = p_1 + p_2$ (b) $p = p_1 - p_2$

(c) $p = 2p_1 + p_2$ (d) $p = p_1 + 2p_2$

(C) Choose the correct statement about the steam distillation.

(a) Separates the organic compounds have lesser solubility in an organic solvent.

(b) Separates the mixtures of a compound having a small boiling point difference.

(c) Separates the mixtures of the compound that have a higher solubility in one solvent and have a lower solubility in another solvent.

(d) Separate substances that exist as steam which are volatile and these vapours are immiscible in water

(D) In steam distillation, intramolecular hydrogen-bonded molecules are .... than intermolecular hydrogen-bonded molecules

(a) more flammable

(b) non-flammable

(c) less volatile

(d) more volatile

(E) Limonene can be isolated by which of the given methods?

(a) Fractional distillation

(b) Steam distillation

(c) Distillation under reduced pressure

(d) Simple distillation

Ans. (A) *(b) Steam distillation*

Explanation: The Steam distillation method can be used to separate oils from the flowers. These essential oils are immiscible in water and soluble at the vapour phase which is the principle of steam distillation. It is employed to remove aromatic compounds from a plant.

(B) *(a)* $p = p_1 + p_2$

Explanation: In steam distillation, the boiling of liquid will start when the sum of the vapour pressure due to organic liquid (p_1) and the sum of the vapour pressure due to water (p_1) will be equal to the atmospheric pressure (p). i.e. $p = p_1 + p_2$

(C) *(d) Separate substances that exist as steam which are volatile and these vapours are immiscible in water*

Explanation: It is used to separate substances that exist as steam which are volatile and these vapours are immiscible in water. In steam distillation, the liquid starts to boil when the sum of the vapour pressure due to organic liquid (p_1) & the sum of the vapour pressure due to water (p_2) will be equal to the atmospheric pressure (p). i.e. $p = p_1 + p_2$. Since the vapour pressure of liquid is lower than the atmospheric pressure, the organic liquid vaporises at a low temperature below its boiling point.

(D) *(d) More volatile.*

Explanation: During boiling in the steam distillation, the strong intermolecular hydrogen bonding increases the boiling point but intramolecular hydrogen bonding does not increase the boiling point. So, the intramolecular hydrogen-bonded molecules are more volatile than intermolecular-bonded molecules.

(E) *(b) Steam distillation*

Explanation: Limonene is a high-boiling liquid which decomposes under the high temperature, therefore steam distillation is used to obtain their oils, as distillation of co-mixture of oil and water at a lower boiling point.

16. *The Carius halogen method in analytical chemistry is a method for the quantitative determination of halogens in chemical substances. A known mass of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass tube known as carius tube, in a furnace.*

(A) What is the resulting salt formed at the end of the reaction?

(B) The carbon and hydrogen will be converted to X and Y? What are the X and Y? What is the reaction that takes place during the reaction?

(C) What is the formula for estimating the percentage of the compound by the carius method?

Ans. (A) When silver nitrate reacts with halogen present in an organic compound a simple displacement reaction takes place which converts silver nitrate to insoluble precipitate of silver halide.

(B) The compounds X and Y are carbon dioxide and water. Which are obtained by the oxidation of carbon and hydrogen. So, the reaction that takes place here is oxidation. Nitric acid is used as an oxidising agent.

$$C + H \xrightarrow{HNO_3} CO_2 + H_2O$$

(C) Percentage of halogen

$$= \frac{\text{Atomic mass of } X \times m_1 g \times 100}{\text{Molecular mass of } AgX \times m}$$

VERY SHORT ANSWER Type Questions (VSA)

[**1** mark]

17. What are the different methods for the development of TLC plate techniques used for the separation of the compound? [Diksha]

Ans. The spots that are coloured can be seen by our human eye and colourless spots on TLC can be developed by keeping the plate in Iodine chamber or irradiation of ultraviolet rays on the plate.

18. What type of mobile and stationary phase is used in chromatography?

Ans. The mobile phase may be a gas or liquid that can be used. The stationary phase may be a solid

19. **For testing halogens in an organic compound with silver nitrate solution, sodium extract (Lassaigne test) is acidified with dilute nitric acid. What will happen when it is treated with sulphuric acid is used instead of nitric acid? [NCERT Exemplar]**

Ans. A white precipitate of silver sulphate Ag_2SO_4 will be formed instead of silver nitrate. This will interface with the test of chlorine.

20. **Give an example from daily life, of a substance that can sublime**

Ans. Naphthalene and camphor are the two substances that can sublime directly from solid to the gaseous state.

SHORT ANSWER Type-I Questions (SA-I)

[**2** marks]

21. **What precautions are necessary while purifying an organic solid with the help of crystallisation process? [Delhi Gov. QB 2022]**

Ans. Crystallisation method is used to purify the impure substances. The precautions which used to take care of during crystallisation method are

(1) Washed the crystals well.

(2) Avoid overheating of the solution.

(3) The solution should be heated gently.

(4) Any rapid cooling of solution should be avoided. that means the solution must be cooled slowly.

22. **Why Kjeldahl's method is not suitable for some nitrogen-containing compounds? What are they?**

Ans. The Kjeldahl's method is not suitable for compounds containing nitro, diazo groups or nitrogen atom present in the aromatic ring system. Because these compounds cannot be converted to ammonium sulphate when treated with concentrated sulphuric acid.

23. **What type of solvent should be chosen for the differential extraction of an organic compound? [Diksha]**

Ans. A good extraction solvent should meet the following two requirements:

(1) The substance to be extracted should be highly soluble in the solvent.

(2) The solvent should be easily separable from the compound after extraction.

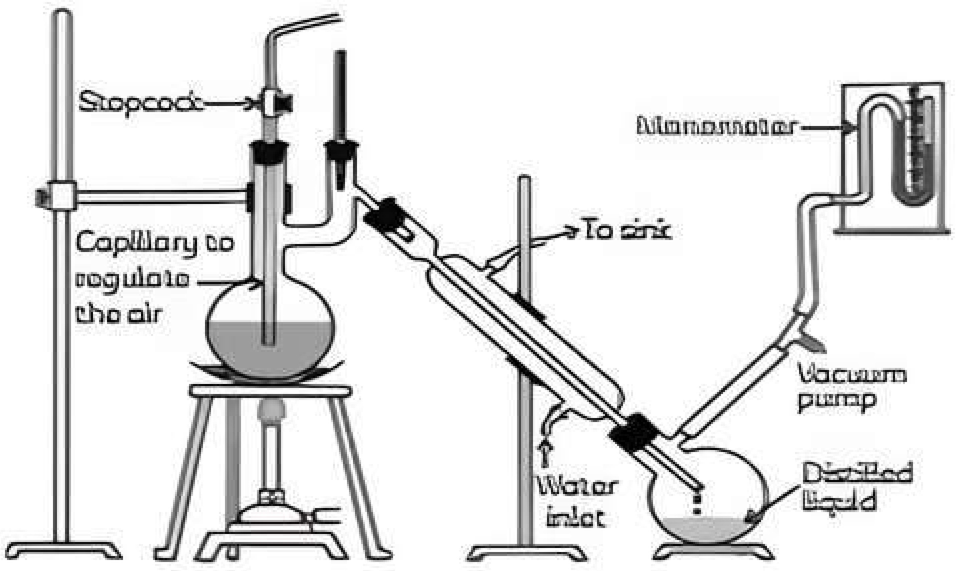
24. **If a liquid compound decomposes at its boiling point, which method is suitable for the purification? It is known that the compound is stable at low pressure, steam volatile and insoluble in water. [NCERT Exemplar]**

Ans. Steam distillation can be used for the purification of such compounds. As this method is based on the separation of compounds having a property of steam volatile and insoluble in water.

SHORT ANSWER Type-II Questions (SA-II)

[**3** marks]

25. **Which of the separation technique is shown in the figure below? Write its principle.**



Ans. The given figure is showing distillation under reduced pressure technique. It is based on the principle of a liquid boiling at a temperature where its vapour pressure becomes equal to the atmospheric pressure by decreasing the outer pressure.

26. **In DNA and RNA, nitrogen atom is present in the ring system. Can the Kjeldahl method be used for the estimation of nitrogen present in these? Give reasons. [NCERT Exemplar]**

Ans. In Kjeheldal method. the nitrogen present in organic compound is first converted to ammonia and then this ammonia is then estimated.

This method is not suitable for compounds containing nitrogen in azo and nitro groups or in rings (quinoline, pyridine, etc.). Beacuose in these cases, the nitrogen cannot be converted to ammonia.

In DNA and RNA, the nitrogen atom is present in the ring system. So, Nitrogen present in DNA and RNA cannot be converted to ammonia by following the Kjeldahl method. Therefore, the Kjeldahl method cannot be used for the estimation of nitrogen present in DNA and RNA.

27. **You are given a mixture of methanol and acetone. Discuss the process which you will employ to separate them.**

[Delhi Gov. QB 2022]

Ans. B.P. of methanol and acetone are 338K and 330K which have boiling points very close to each other. Thus these cannot be separated by using simple distillation. Thus fractional distillation method is employed.

This process involves repeated distillations and condensations and the mixture is usually separated into component parts. The separation happens when the mixture is heated at a certain temperature where fractions of the mixture start to vaporise.

Throughout the process, vaporisation and condensation take place repeatedly until the two mixtures are separated completely.

LONG ANSWER Type Questions (LA)

[**4** & **5** marks]

28. **There are three students, Manish, Ramesh and Rajni were tasked with identifying the additional elements in an organic complex provided by their teacher. They made Lassaigne's extract by fusing the chemical with sodium metal on their own. They next mixed a pat of the extract with solid iron sulphate and dilute sulphuric acid. Manish and Rajni received Prussian blue, but Ramesh received only red. Ramesh tried the test again with the same extract, but this time also he only obtained red colour. They were taken aback and went to their teacher to inform him of their discovery. The teacher asked them to consider why this observation was made. Write the chemical equations to explain the formation of different colours.**

[NCERT Exemplar]

Ans. A small amount of sodium fusion extract is boiled with Iron sulphate which on acidification with con. sulphuric acid. The Prussian blue formation confirms the presence of Nitrogen. So, Manish and Rajni have the mixture that contains nitrogen.

Sodium cyanide first reacts with iron (II) sulphate and forms sodium hexacyanidoferrate (II). Which is then heated with sulphuric acid and oxidises some iron (II) ion to iron (III) ions which then reacts with sodium hexa cyanidoferrate to form iron (III) hexacyanidoferrate (II) (ferriferrocyanide – Prussian blue).

$$6CN^- + Fe^{2+} \rightarrow [Fe(CN)_6]^{4-}$$

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} \underset{\textit{Prussian blue}}{Fe_4[Fe(CN)_6]_3 \cdot xH_2O}$$

The compound they were analysing have both N and S. Thus, in Lassaigne's test SCN^- ions are formed due to the presence of sulphur and nitrogen both. These give red colour with Fe^{3+} ions.

$$Na + C + N + S \rightarrow NaSCN$$

$$Fe^{3+} + SCN^- \rightarrow \underset{\textit{Blood red}}{[Fe(SCN)]^{2+}}$$

This happens when fusion is not carried out in the excess of sodium. With an excess of sodium the thiocyanate ion, if formed, is decomposed as follows:

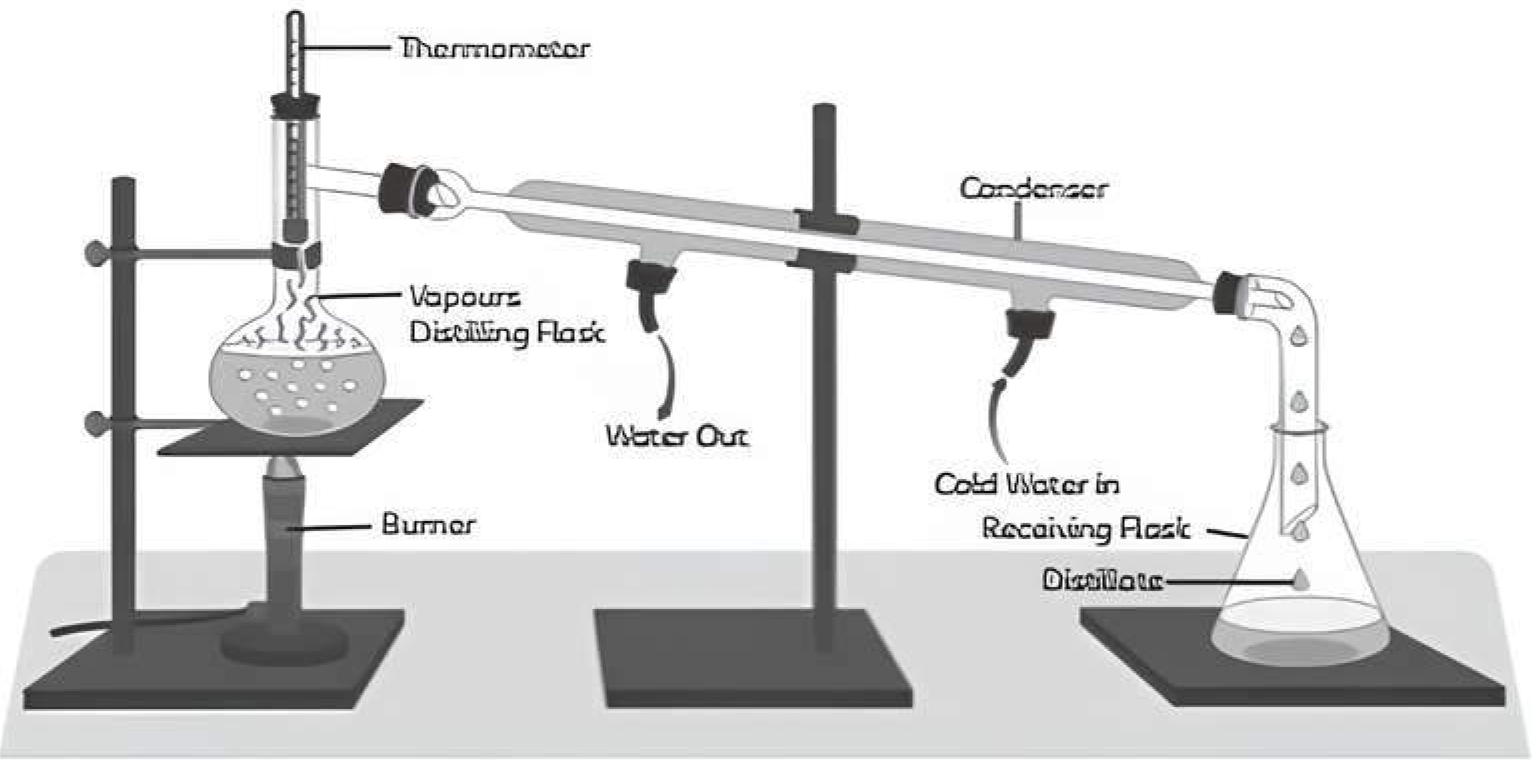
$$NaSCN + 2Na \rightarrow NaCN + Na_2S$$

So, we can conclude that Manish and Rajni used an excess of sodium and thus got Prussian blue colour while Ramesh didn't use an excess of sodium, hence got red colour.

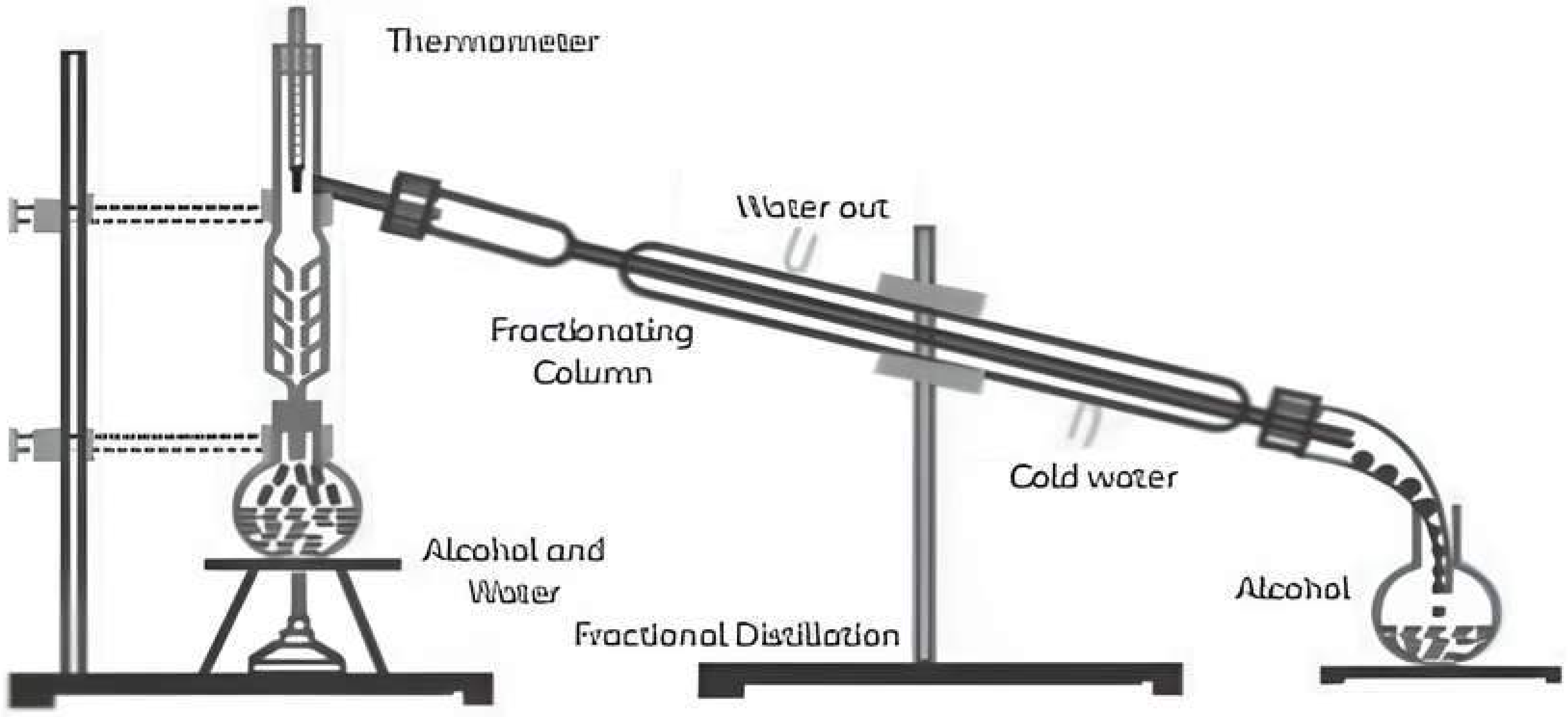
29. **Raman has three liquids L, M and N. The liquid L possessed by Raman is having a large difference between the boiling points and than rest of the liquids. The liquid M and N are having a quiet closer boiling points. Liquid L boils at a higher temperature than M and N then M boils at a higher**

temperature than N. How will you separate the components of the mixture? Draw a diagram showing the setup of the apparatus for the process.

Ans. For L compound which is having a high boiling point can be separated by simple distillation. It is based on the principle of liquids having different boiling points vaporise at different temperatures. These vapours are cooled separately. The impure liquid mixture is heated in a round bottom flask. On boiling this, the compounds having lower boiling points are obtained first and this is condensed by the condenser and the condensed liquid is collected in a receiver. The condensed vapour of a higher boiling liquid is collected separately. In this way, we can separate L from M and N. Because simple distillation separates mixtures that boil at a very high temperature.



Liquids M and N which are having boiling points very close to each other which cannot be separated by a simple distillation method as higher boiling liquids only can be separated by that. The remaining mixture can be separated by using the fractional distillation method. Fractional distillation involves passing the vapours through a fractionating column before the vapours enter for condensation. The vapours with a higher boiling point (M) gets condensed first and then the vapours of lower boiling point condense (N). The fractionating column gets attached to the mouth of the round bottom flask. The vapours reaching the top of the fractionating column are rich in the more volatile components. The fractionating column is available in various sizes and designs, it provides more surface for the heat exchange between ascending and descending vapours and gets revaporises. The vapours are rich in low boiling liquid which ascends to the top of the column and vapours become pure which passes through the condenser and the pure liquid is collected in a receiver. After repeating the same process, now the remaining liquid in the flask is enriched with a high boiling component which on condensation it can be collected. Thus the order of boiling point of liquids is L > M > N



30. **What is the difference between column chromatography, thin layer chromatography and paper chromatography?**

Ans.

Column chromatography	Thin-layer chromatography	Paper chromatography
It is based on the principle of adsorption chromatography.	It is based on the principle of adsorption chromatography.	It is based on the principle of partition chromatography.
It is a descending type of chromatography.	It is an ascending type of chromatography.	It is an ascending type of chromatography.
It uses a packed column with a silica gel or alumina that is used to separate molecules based on the size and affinity towards adsorbent.	It involves the separation of substances over a thin layer of adsorbent (stationary phase) coated on a glass plate and is based on solid-liquid adsorption of molecules.	Paper chromatography is a technique that is used to separate compounds based on the liquid-liquid adsorption and solubility of the compound.
Stationary phase: Adsorbent (silica gel or alumina)	Stationary phase: Adsorbent (silica gel or alumina)	Stationary phase: Paper made of nitrocellulose.
Mobile phase: Solvent or a mixture of solvents.	Mobile phase: Solvent or a mixture of solvents.	Mobile phase: Solvent or a mixture of solvent.

NUMERICAL Type Questions

31. **An organic compound of 0.356g on complete combustion was given of 0.187g carbon dioxide and 0.1034g water. Determine the percentage composition of carbon and hydrogen present in the given organic compound.** **(2m)**

Ans. CO_2 – molecular weight = 44

Mass of carbon = 12

$$\text{Percentage of carbon} = \frac{12 \times 0.187 \times 100}{44 \times 0.356}$$

$$= 14.325\%$$

Mass of hydrogen = 2(as water molecule contains two hydrogen atoms Molecular weight of water = 18

$$\text{Percentage of hydrogen} = \frac{2 \times 0.1034 \times 100}{18 \times 0.356}$$

$$= 3.227\%$$

32. **The nitrogen is estimated by Dumas method, where 0.5g of an organic compound gave 100 mL of nitrogen collected at 300K temperature and 750mm pressure. Calculate the percentage composition of nitrogen in the compound.**

(Aqueous tension at 300K = 15mm) **(3m)**

Ans. Volume of nitrogen collected at the pressure is

Actual pressure = pressure-pressure due to aqueous tension

$$= 750 - 15$$

$$= 735 \text{ mm}$$

$$\text{Volume of nitrogen at STP } (V_2) = \frac{P_1 \times V_1 \times T_2}{T_1 \times P_2}$$

T_2 and P_2 – are standard temperature and pressure values.

$$= \frac{273 \times 735 \times 100}{300 \times 760}$$

$$= 88\text{mL}$$

22400mL of N_2 at STP weighs = 28g

$$\text{88mL of nitrogen weighs} = \frac{28 \times 88}{22400}\text{g}$$

$$\text{Percentage of nitrogen} = \frac{28 \times 88 \times 100}{22400 \times 0.5}\%$$

$$= 22\%$$