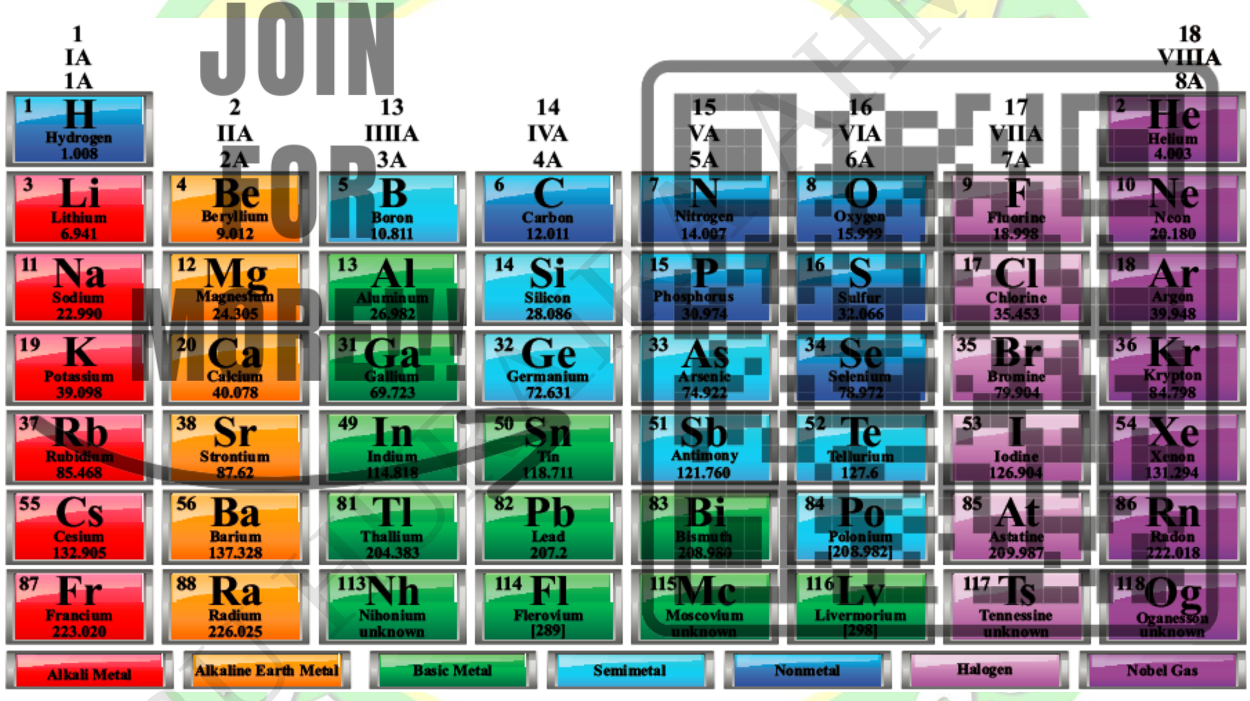
DUA-E-ILM COACHING CENTER

XII-CHEMISTRY NOTES

Written by: *Sir Nasim Zulfiqar*

CHAPTER 1

CHEMISTRY OF REPRESENTATIVE ELEMENTS



1 IA 1A	2 IIA 2A	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 H Hydrogen 1.008							2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012	5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.972	35 Br Bromine 79.904	36 Kr Krypton 84.798
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294
55 Cs Cesium 132.905	56 Ba Barium 137.328	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	113 Nh Nihonium unknown	114 Fl Flerovium [289]	115 Mc Moscovium unknown	116 Lv Livermorium [298]	117 Ts Tennessine unknown	118 Og Oganesson unknown

Alkali Metal	Alkaline Earth Metal	Basic Metal	Semimetal	Nonmetal	Halogen	Nobel Gas

Representative Elements:

Elements in the periodic table from group I-A to VIII-A are called representative elements. They are found in excess amount in nature that's why they're called as representative elements.

Representative Elements are further divided into s-block elements and p-block elements.

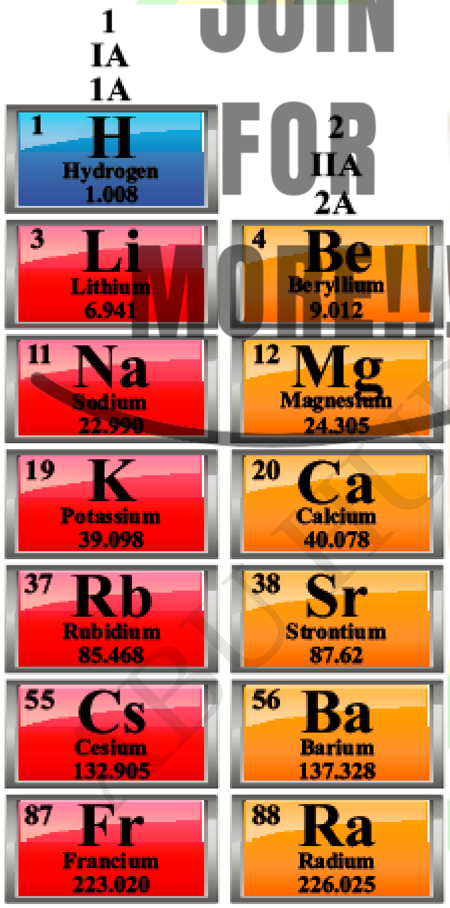
s-block Elements:

The elements in which the valence electron enters in s-orbital is called s-block elements. Elements of group I-A and II-A are included in s-block elements.

The general valence shell electronic configuration of s-block elements can be given by $ns^{1\text{-}2}$.

Elements of group I-A are also called “Alkali Metals” and the general valence shell electronic configuration of this group is ns^1.

Elements of group II-A are also called “Alkaline Earth Metals” and the general valence shell electronic configuration of this group is ns^2.



p-block Elements:

The elements in which the valence electron enters in p-orbital is called s-block elements. Elements of group III-A to VIII-A are included in s-block elements.

The general valence shell electronic configuration of p-block elements can be given by ns^2, np^{1-6}.

Elements of group III-A are also called "Boron Family" and the general valence shell electronic configuration of this group is ns^2, np^1.

Elements of group IV-A are also called "Carbon Family" and the general valence shell electronic configuration of this group is ns^2, np^2.

Elements of group V-A are also called "Nitrogen Family or Pnictogens" and the general valence shell electronic configuration of this group is ns^2, np^3.

Elements of group VI-A are also called "Oxygen Family or Chalcogens" and the general valence shell electronic configuration of this group is ns^2, np^4.

Elements of group VII-A are also called "Halogens" because they are salt formers and the general valence shell electronic configuration of this group is ns^2, np^5.

Elements of group VIII-A are also called "Noble gases or Inert gases" and the general valence shell electronic configuration of this group is ns^2, np^6.

13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
					2 He Helium 4.003
5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.972	35 Br Bromine 79.904	36 Kr Krypton 84.798
49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294
81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
113 Nh Nihonium unknown	114 Fl Flerovium [289]	115 Mc Moscovium unknown	116 Lv Livermorium [298]	117 Ts Tennessine unknown	118 Og Oganesson unknown

GENERAL GROUP TRENDS OF REPRESENTATIVE ELEMENTS

The regular variations in the properties of elements in a group is called group trends.

The regular variations in the properties of elements in a period is called periodic trends.

1) Atomic Radii

2) Ionization Energy

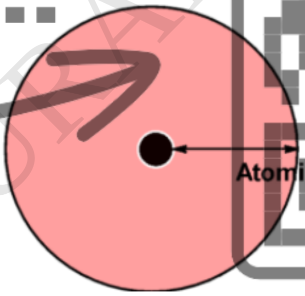
3) Electronegativity

4) Electrical conductivity

5) Melting Point and Boiling Point

Atomic Radii

"Atomic radius is the distance between the nucleus of an atom to its outermost electron shell".



The unit of atomic radius is Angstrom (Å)

Atomic radius is directly proportional to the number of shells and inversely proportional to the magnitude of nuclear charge.

Down the group in periodic table, atomic radius increases due to increase in number of shells.

From left to right along a period in the periodic table, atomic radius decreases due to increase in magnitude of nuclear charge. The increasing nuclear charge shrinks the orbits due to electrostatic attraction between proton and electron.

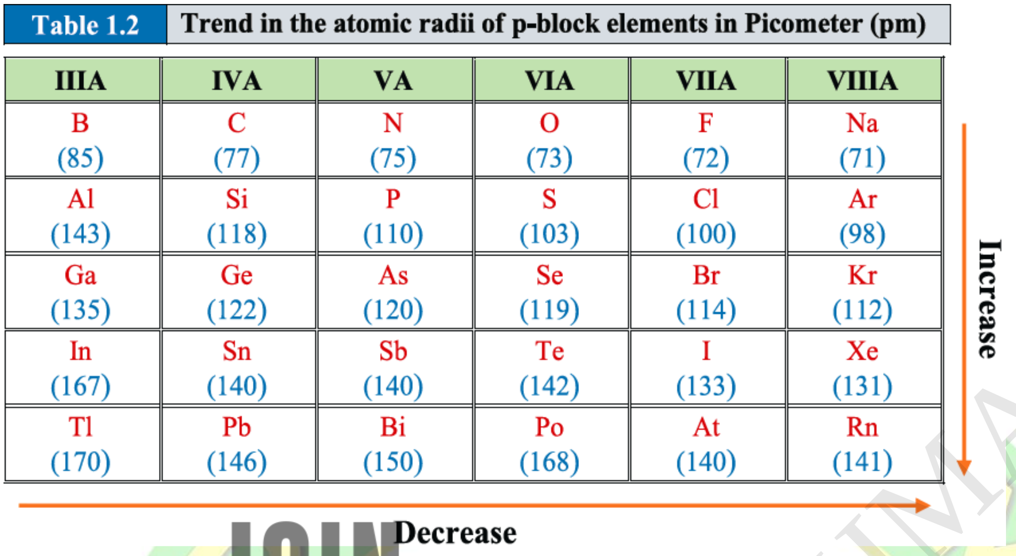


Table 1.2 Trend in the atomic radii of p-block elements in Picometer (pm)

IIIA	IVA	VA	VIA	VIIA	VIIIA
B (85)	C (77)	N (75)	O (73)	F (72)	Na (71)
Al (143)	Si (118)	P (110)	S (103)	Cl (100)	Ar (98)
Ga (135)	Ge (122)	As (120)	Se (119)	Br (114)	Kr (112)
In (167)	Sn (140)	Sb (140)	Te (142)	I (133)	Xe (131)
Tl (170)	Pb (146)	Bi (150)	Po (168)	At (140)	Rn (141)

MCQ's:

1. Which element has the largest atomic radius?

A	Li	B	Na	C	K	D	Rb

2. Which elements has the smallest atomic radius?

A	Be	B	Mg	C	Ca	D	Sr

3. Which elements has the largest atomic radius?

A	Li	B	Be	C	B	D	C

4. Which group has the biggest atoms?

A	I-A	B	II-A	C	III-A	D	IV-A

Give reasons for the following:

1. Cs atom is bigger than Li atom.

Ans. Cs contains more number of shells than Lithium, that's why it has a larger atomic radius.

2. Na atom is bigger than Mg atom.

Ans. Magnesium atoms have more nuclear charge, so there will be more shrinking effect in orbits. Due to this face, sodium is bigger is size.

Ionization Energy

"It is the energy needed to remove an electron from a neutral atom in the gas phase".

Ionization energy is also called Ionization Potential and it's denoted by IP.

The unit of ionization energy is KJ/mol, Kcal/mol or eV/atom.

For Example: $Na_{2,8,1} + \text{heat} \rightarrow Na^{+}_{2,8} + 1e^{-}$ Δ_{IE}= +ve KJ/mol

Ionization energy is inversely proportional to number of shells. As the number of shell increases, it will be easier to remove electron by providing a little amount of energy.

Ionization energy is directly proportional to the magnitude of nuclear charge. As the nuclear charges increases, the valence shell comes close to the nucleus due to strong electrostatic attraction, hence the removal of electron requires more energy.

Down the group in periodic table, Ionization energy decreases due to increase in number of shells.

From left to right along a period, ionization energy increases due to increase in magnitude of nuclear charge.

Table 1.3 First ionization energies of representative elements in KJ/mol

Group IA	Group IIA	Group IIIA	Group IVA	Group VA	Group VIA	Group VIIA	Group VIIIA
Li (520)	Be (900)	B (800)	C (1090)	N (1400)	O (1310)	F (1680)	Ne (2080)
Ne (490)	Mg (730)	Al (577)	Si (780)	P (1060)	S (1001)	Cl (1250)	Ar (1520)
K (420)	Ca (590)	Ga (580)	Ge (762)	As (960)	Se (950)	Br (1140)	Kr (1350)
Rb (400)	Sr (550)	In (560)	Sn (700)	Sb (830)	Te (870)	I (1010)	Xe (1170)
Cs (380)	Ba (500)	Tl (590)	Pb (710)	Bi (800)	Po (810)	At (920)	Rn (1030)

Decrease

Increase

MCQ’s:

1. Which element has the highest ionization energy?

A	Li	B	Na	C	K	D	Rb

2. Which elements has the lowest ionization energy?

A	Be	B	Mg	C	Ca	D	Sr

3. Which elements has the highest ionization energy?

A	Li	B	Be	C	B	D	C

4. Which group has the highest ionization energy?

A	I-A	B	II-A	C	III-A	D	IV-A

Give reasons for the following:

1. The ionization energy of Na is more than K.

Ans. Sodium contains a smaller number of shells so that it is difficult to remove its electron due to strong electrostatic attraction. Hence, sodium has more ionization energy than potassium.

2. The ionization energy of Nitrogen is more than oxygen.

Ans. Nitrogen is a stable element due to its half-filled p-sub shell. Due to this reason, it has more ionization energy than oxygen.

Electronegativity (EN)

“It is the measure of the tendency of an atom to attract the shared pair of electrons towards itself when it is involved in a covalent bond”.

Electron gaining tendency of an element is also called electronegativity.

Non-metals are electronegative because they have a tendency to accept electron.

There is no unit of electronegativity. Its values were determined by Linus Pauling.

The most electronegative element is Fluorine (F) having EN value 4.0

The least electronegative element in Cesium (Cs) having EN value 0.7

Electronegativity is inversely proportional to the number of shells and directly proportional to the magnitude of nuclear charge.

Down the group in periodic table, EN decreases due to increase in number of shells. From left to right along a period in periodic table, EN increases due to increase in magnitude of nuclear charge.

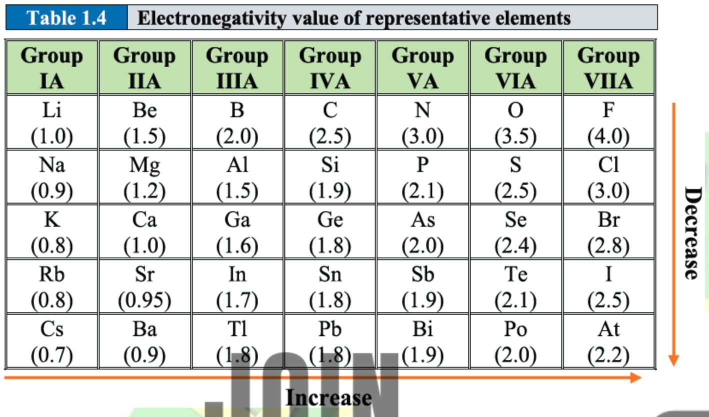


Table 1.4 Electronegativity value of representative elements

Group IA	Group IIA	Group IIIA	Group IVA	Group VA	Group VIA	Group VIIA
Li (1.0)	Be (1.5)	B (2.0)	C (2.5)	N (3.0)	O (3.5)	F (4.0)
Na (0.9)	Mg (1.2)	Al (1.5)	Si (1.9)	P (2.1)	S (2.5)	Cl (3.0)
K (0.8)	Ca (1.0)	Ga (1.6)	Ge (1.8)	As (2.0)	Se (2.4)	Br (2.8)
Rb (0.8)	Sr (0.95)	In (1.7)	Sn (1.8)	Sb (1.9)	Te (2.1)	I (2.5)
Cs (0.7)	Ba (0.9)	Tl (1.8)	Pb (1.8)	Bi (1.9)	Po (2.0)	At (2.2)

MCQ's:

1. Which element has the highest electronegativity?

A	Li	B	Na	C	K	D	Rb

2. Which elements has the lowest electronegativity?

A	Be	B	Mg	C	Ca	D	Sr

3. Which elements has the highest electronegativity?

A	Li	B	Be	C	B	D	C

4. Which group has the highest electronegativity?

A	I-A	B	II-A	C	III-A	D	IV-A

Give reasons for the following:

1. The electronegativity of Na is more than K.

Ans. Sodium contains a smaller number of shells so that its shared pair will be nearer to nucleus and nucleus can attract it with a stronger force.

Electrical Conductivity

The ability of an element to conduct electric current is called electrical conductivity.

Table 1.5 **Electrical conductivity trends of representative elements**

Group Number	Trend of Electrical Conductivity
Group I and IIA	High electrical conductivity
Group IIIA	Moderate electrical conductivity
Group IVA	Variable electrical conductivity (Carbon: poor, Silicon: moderate, Germanium: moderate, Tin: moderate, Lead: poor)
Group VA	Moderate electrical conductivity
Group VIA	Poor electrical conductivity
Group VIIA (Halogens)	Poor electrical conductivity
Group VIIIA (Noble gases)	Extremely low electrical conductivity

Oxidation State

"An oxidation number is a value assigned to an element in a chemical compound or combined state.

Table 1.6 **Oxidation states of representative elements**

Group	Elements	Oxidation States
IA (Alkali Metals)	Li, Na, K, Rb, Cs	+1
IIA (Alkaline Earth Metals)	Be, Mg, Ca, Sr, Ba	+2
IIIA	B, Al, Ga, In, Tl	+3
IVA	C, Si, Ge, Sn, Pb	-4, -2, +2, +4
VA	N, P, As, Sb, Bi	-3, -2, +3, +5
VIA	O, S, Se, Te, Po	-2, +2, +4, +6
VIIA (Halogens)	F, Cl, Br, I, At	-1, +1, +3, +5, +7
VIIIA (Noble Gases)	He, Ne, Ar, Kr, Xe, Rn	0

Melting and Boiling Point

The temperature at which a solid start converting into liquid is called melting point.

The temperature at which a liquid starts boiling is called boiling point.

Boiling point and melting point are measured in °C or K.

The trend of Melting Point and Boiling Point is irregular in the periodic table.

In group I-A and II-A, MP and BP decrease down the group due to increase in atomic volume which makes the element less dense.

There is no regular pattern of MP and BP in group III-A

From group IV-A to VII-A MP and BP increases down the group due to stronger intermolecular forces.

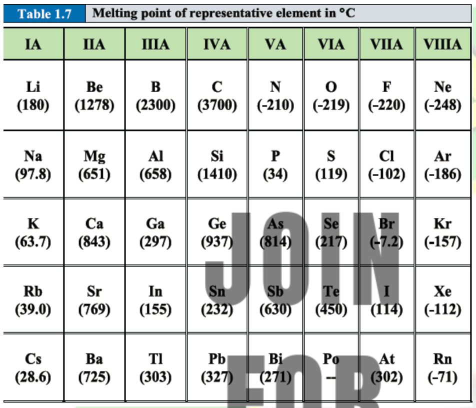


Table 1.7 Melting point of representative element in °C

IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
Li (180)	Be (1278)	B (2300)	C (3700)	N (-210)	O (-219)	F (-220)	Ne (-248)
Na (97.8)	Mg (651)	Al (658)	Si (1410)	P (34)	S (119)	Cl (-102)	Ar (-186)
K (63.7)	Ca (843)	Ga (297)	Ge (937)	As (814)	Se (217)	Br (-7.2)	Kr (-157)
Rb (39.0)	Sr (769)	In (155)	Sn (232)	Sb (630)	Te (450)	I (114)	Xe (-112)
Cs (28.6)	Ba (725)	Tl (303)	Pb (327)	Bi (271)	Po --	At (302)	Rn (-71)

MCQ's:

1. Which element has the highest melting point?

A	Li	B	Na	C	K	D	Rb

2. Which elements has the highest melting point?

A	F	B	Cl	C	Br	D	I

REACTIONS OF REPRESENTATIVE ELEMENTS

s-block elements

1) Reaction with Oxygen:

$$4Li_{(s)} + O_{2(g)} \longrightarrow 2Li_2O_{(s)} \quad \text{(Normal oxide)}$$

$$2Na_{(s)} + O_{2(g)} \xrightarrow{\text{(Excess)}} Na_2O_{2(s)} \quad \text{(Per oxide)}$$

$$K_{(s)} + O_{2(g)} \longrightarrow KO_{2(s)} \quad \text{(Super oxide)}$$

$$Rb_{(s)} + O_{2(g)} \longrightarrow RbO_{2(s)} \quad \text{(Super oxide)}$$

$$Cs_{(s)} + O_{2(g)} \longrightarrow CsO_{2(s)} \quad \text{(Super oxide)}$$

$$2M + O_2 \longrightarrow 2MO \text{ (Where M = Be, Mg, Ca)}$$

$$M + O_2 \longrightarrow MO_2 \text{ (Where M = Sr, Ba)}$$

2) Reaction with Water:

$$2M_{(s)} + 2H_2O_{(\ell)} \longrightarrow 2MOH_{(aq)} + H_{2(g)}\uparrow$$

(Where M = Li, Na, K, Rb, Cs).

$$M_{(s)} + 2H_2O_{(\ell)} \longrightarrow M(OH)_{2(aq)} + H_2\uparrow$$

(Where M = Mg, Ca, Sr and Ba).

3) Reaction with Halogens:

$$2M_{(s)} + X_{2(g)} \longrightarrow 2MX_{(s)}$$

(Where M = Li, Na, K, Rb, Cs)

$$M_{(s)} + X_{2(g)} \longrightarrow MX_{2(s)}$$

(Where M = Be, Mg, Ca, Sr, Ba)

4) Reaction with Nitrogen:

$$6M_{(s)} + N_{2(g)} \longrightarrow 2M_3N_{(s)} \text{ (M = Li, Na, K, Rb, Cs)}$$

$$3M_{(s)} + N_{2(g)} \longrightarrow M_3N_{2(s)} \text{ (M = Be, Mg, Ca, Sr, Ba)}$$

5) Reaction with Hydrogen:

$$2M_{(s)} + H_{2(g)} \longrightarrow 2MH_{(s)} \text{ (M = Li, Na, K, Rb, Cs)}$$

$$M_{(s)} + H_{2(g)} \longrightarrow MH_{2(s)} \text{ (M = Ca, Sr, Ba)}$$

5) Reaction with Alcohols:

$$2M_{(s)} + 2C_2H_5OH_{(aq)} \longrightarrow 2C_2H_5OM_{(aq)} + H_{2(g)} \text{ (M = Li, Na, K, Rb, Cs)}$$

Alkaline earth metals have a very limited reactivity with alcohols.

6) Reaction with Acids:

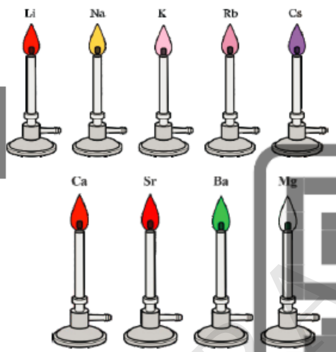
$$2M_{(s)} + 2HCl_{(aq)} \longrightarrow 2MCl_{(s)} + H_{2(g)} \text{ (Where M = Li, Na, K, Rb, Cs)}$$

Alkaline earth metals can react with acids but their reactivity is generally lower compared to alkali metals.

FLAME TEST FOR S-BLOCK ELEMENTS

"Flame test is a qualitative method used to identify the presence of alkali metals based on their characteristic flame colours".

Elements	Flame Colour
Lithium	Red
Sodium	Yellow
Potassium	Violet
Rubidium	Red Violet
Cesium	Blue Violet
Beryllium	No characteristic flame colour
Magnesium	Silver white
Calcium	Orange red
Strontium	Deep Red
Barium	Pale Green



INDUSTRIAL PREPARATION OF SODIUM HYDROXIDE (NaOH)

Castener-Kellner's Cell

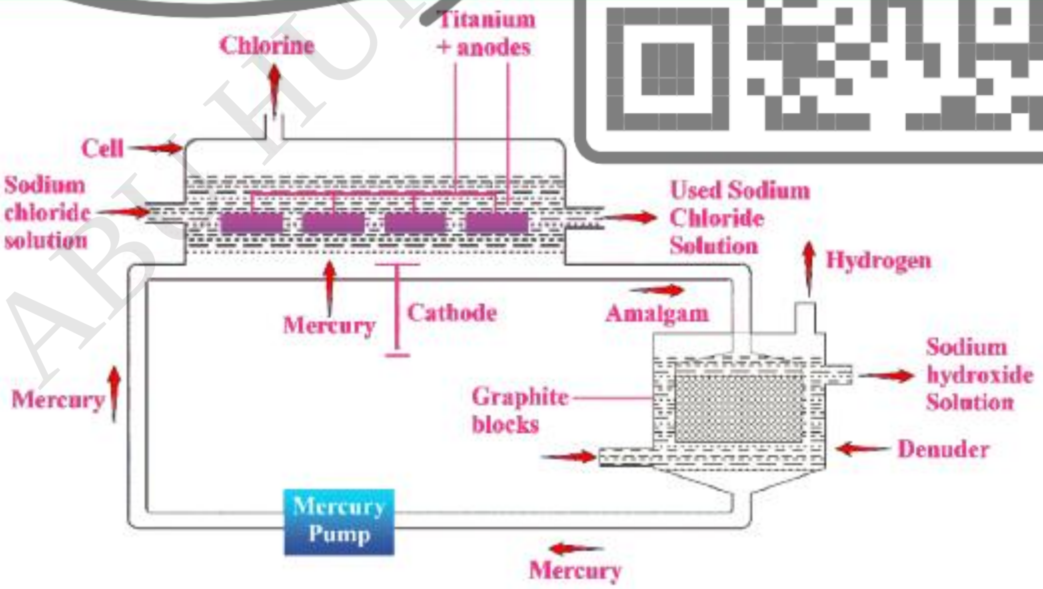


Fig 1.1: Structure of Castner Kellner cell

Introduction

Sodium hydroxide is also known as caustic soda having chemical formula NaOH. It is prepared in industries by the electrolysis of brine in Castener-Kellner's electrolytic cell.

Construction of the Cell:

Castner-Kellner's cell consist of two compartments. The upper compartment contains a tank in which brine is filled. Brine is the saturated solution of sodium chloride and water. Brine is the electrolyte in this process. Titanium (Ti) blocks are dipped in the electrolyte. These blocks are connected to the positive terminal of battery so they are anode.

The lower compartment contains a circular steel pipe in which mercury is circulated by means of a mercury pump. The moving mercury is connected to the negative terminal of battery so it is anode. A denuder is also present in the lower compartment. A graphite block is present in the denuder and water is filled inside the denuder. Sodium hydroxide is produced in the denuder.

Working of the Cell:

When electric current is passed through the cell then chloride ions (Cl$^-$ ions) move towards titanium anode and oxidize into chlorine gas by the loss of two electrons. Chlorine gas is ejected at the top of upper compartment.

Sodium ions (Na$^+$ ions) move towards moving mercury cathode and reduce into sodium metal by the gain of an electron. Sodium metal mixes with mercury to form sodium amalgam. sodium amalgam is then transferred into the denuder where it reacts with water to produce sodium hydroxide and hydrogen gas. The unreacted mercury metal is separated at denuder for further electrolysis of brine.

Cell Reactions:

1. Ionization: $NaCl \rightarrow Na^+ + Cl^-$

2. Reaction at Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$

3. Reaction at Cathode: $Na^+ + 1e^- \rightarrow Na/Hg$ (Amalgam)

4. Reaction at Denuder: $2Na/Hg + 2H_2O \rightarrow 2NaOH + H_2 + 2Hg$

Advantage of the process:

Sodium hydroxide and chlorine gas are produced in different compartments so that the reaction between them is avoided. Otherwise, both the products can react together.

Disadvantage of the process:

This process is not recommended due to the usage of mercury which is toxic in nature. When mercury is discarded into rivers or oceans then it harms fresh water as well as marine life.

Physical Properties

- **State**: It is a solid at room temperature, typically appearing as white pellets, flakes, or granules.
- **Odor**: It is odorless.
- **Melting Point**: Its melting point is approximately 318 °C (604 °F). At this temperature, it melts and forms a liquid.
- **Solubility**: It is highly soluble in water.

- **Corrosiveness**: It is highly corrosive and can cause burns and irritation to the skin, eyes, and respiratory system.

Chemical Properties of NaOH:

Reaction with acids

Being a strong base, it reacts with all acids to produce sodium salt and water.

$$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(\ell)}$$

$$2NaOH_{(aq)} + H_2SO_{4(aq)} \longrightarrow Na_2SO_{4(aq)} + 2H_2O_{(\ell)}$$

Reaction with Ferric Chloride

On reaction with aqueous ferric chloride, it gives brown ppt of ferric hydroxide.

$$3NaOH_{(aq)} + FeCl_{3(aq)} \longrightarrow Fe(OH)_{3(s)} + 3NaCl_{(aq)}$$

Reaction with Aluminum and Zinc

Caustic soda can react with aluminum and zinc to form aluminate and zincate salts.

$$2NaOH_{(aq)} + 2Al_{(s)} + 2H_2O_{(\ell)} \longrightarrow 2NaAlO_{2(s)} + 3H_{2(g)}$$

$$2NaOH_{(aq)} + Zn_{(s)} \longrightarrow Na_2ZnO_{2(s)} + H_{2(g)}$$

Reaction with Chlorine

The reaction of hot aqueous sodium hydroxide with chlorine gas gives sodium chloride and sodium chlorate.

$$6NaOH_{(aq)} + 3Cl_{2\,(g)} \longrightarrow NaClO_{3(aq)} + 5NaCl_{(aq)} + 3H_2O_{(l)}$$

Uses of Sodium Hydroxide

- It is a key ingredient in the production of detergents and soaps.
- It is utilized in the production of bleach, such as chlorine bleach, which is commonly used as a disinfectant and stain remover.
- Its strong alkaline nature makes it effective for unclogging drains and pipes by breaking down organic matter.
- It is used to remove heavy metals and adjust pH levels in water, ensuring safe and clean drinking water.
- It is used as a food preservative to prevent bacterial and mold growth, enhancing the shelf life of certain food products.

Bleaching Powder($CaOCl_2$)

Bleaching powder is also known as calcium chloro hypochlorite having chemical formula $CaOCl_2$ or Ca(OCl)Cl. It is a white crystalline powder having chlorine like smell. It is called bleaching powder because it can remove color from any surface. The formula of bleaching powder was suggested by Professor Odling.

Bleaching powder can be prepared in industries by Hasen-Clever's plant. It contains four cast iron pipes fitted with rotating blades. Slaked lime or calcium hydroxide is introduced at the top while chlorine gas is introduced from the bottom. Both the reactants react together to produce bleaching powder.

$$Ca(OH)_{2(aq)} + Cl_{2(aq)} \longrightarrow CaOCl_{2(s)} + H_2O_{(l)}$$

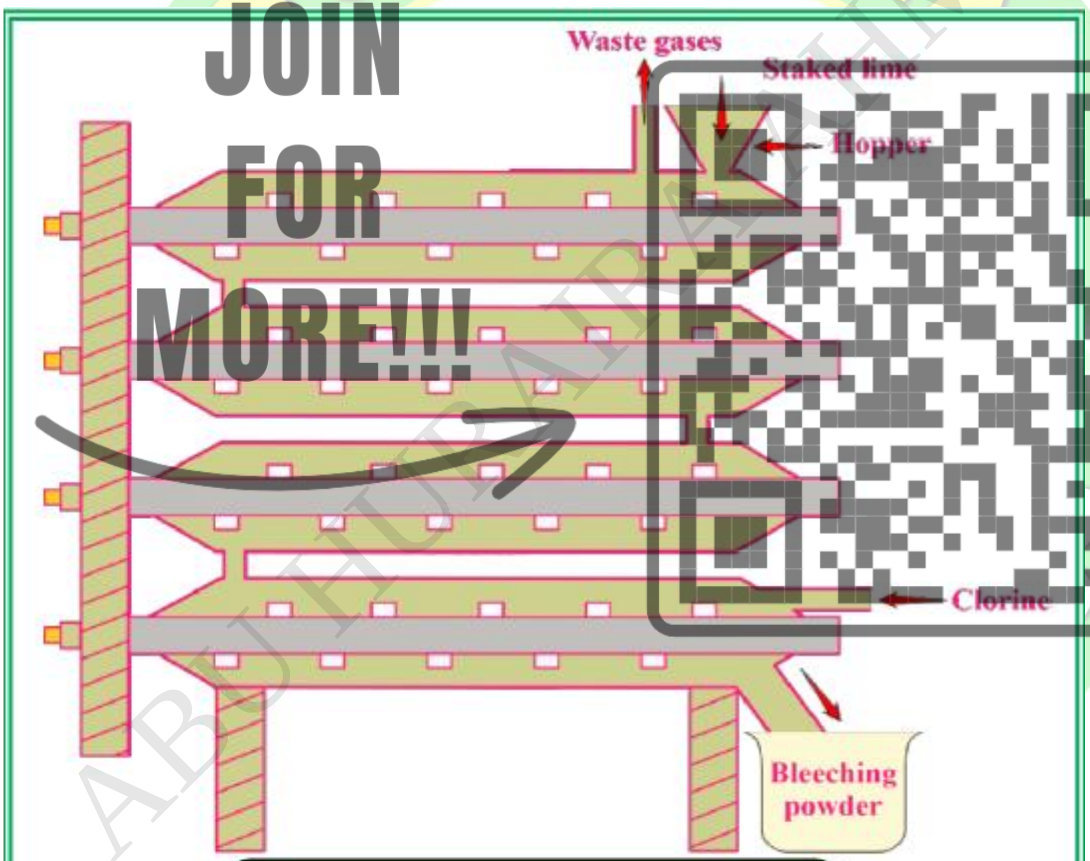


Fig 1.2: Structure of Hasenclever process

Physical Properties of Bleaching Powder

- Bleaching powder has a dirty white appearance.
- It has a distinct chlorine odour.
- It is soluble in water.

Chemical Properties of Bleaching Powder

(i) Reaction with Water

$$CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2$$

(ii) Reaction with Acids

$$CaOCl_{2(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2(s)} + 2H_2O_{(l)} + Cl_{2(g)}$$

Uses of Bleaching Powder

- It is used for sterilization of water.
- It is used for bleaching of cotton, linen and paper.
- It is used for the preparation of chlorine gas and chloroform.

Selected s-block elements and their compounds	**Significant Uses**
Sodium (Na)	It helps to regulate the balance of fluids inside and outside our tissues and facilitates the absorption of various nutrients.
Potassium (K)	It helps to balance the pH level in the body.
Calcium (Ca)	It is essential for the growth of bones and teeth.
Common Salt ($NaCl$)	It is a raw material for the synthesis of various chemicals such as soda ash, caustic soda and chlorine gas etc. It plays a vital role in maintaining electrolyte balance in the body.
Washing Soda ($Na_2CO_3.10H_2O$)	It is used in the manufacturing of glass, soap and borax. It is also used for laundry purpose.
Backing Soda ($NaHCO_3$)	It is used in bakeries to prepare various food items.
Potassium Nitrate (KNO_3)	It is used in fireworks and fertilizer.

REACTIONS OF p-BLOCK ELEMENTS

1) Reaction with Oxygen:

$$4B_{(s)} + 3O_{2(g)} \longrightarrow 2B_2O_{3(s)}$$

$$4Al_{(s)} + 3O_{2(g)} \longrightarrow 2Al_2O_{3(s)}$$

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$$

$$N_{2(g)} + O_{2(g)} \xrightarrow{\text{High temp.}} 2NO_{(g)}$$

$$2N_{2(g)} + O_{2(g)} \xrightarrow{\text{Catalyst}} 2N_2O_{(g)}$$

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$$

$$2F_{2(g)} + O_{2(g)} \longrightarrow 2OF_{2(g)}$$

2) Reaction with Halogens:

$$2Al_{(s)} + 3Cl_{2(g)} \xrightarrow{\Delta} 2AlCl_{3(s)}$$

$$C_{(s)} + 2Cl_{2(g)} \longrightarrow CCl_{4(l)}$$

$$N_{2(g)} + 3Cl_{2(g)} \longrightarrow 2NCl_{3(g)}$$

$$O_{2(g)} + 2F_{2(g)} \longrightarrow 2OF_{2(g)}$$

3) Reaction with Nitrogen:

$$2B_{(s)} + N_{2(g)} \xrightarrow{\Delta} 2BN_{(s)}$$

$$2Al_{(s)} + N_{2(g)} \xrightarrow{\Delta} 2AlN_{(s)}$$

$$3C_{(s)} + 2N_{2(g)} \xrightarrow{\Delta} C_3N_{4(s)}$$

$$3Si_{(s)} + N_{2(g)} \xrightarrow{\Delta} Si_3N_{4(s)}$$

$$3Cl_{2(g)} + N_{2(g)} \longrightarrow 2NCl_{3(s)}$$

4) Reaction with Hydrogen:

$$Si_{(s)} + 2H_{2(g)} \xrightarrow{\text{High Temperature}} SiH_{4(s)}$$

$$N_{2(g)} + 3H_{2(g)} \xrightarrow{400 - 450°C} 2NH_{3(g)}$$

$$S_{(s)} + H_{2(g)} \xrightarrow{850°C} H_2S_{(g)}$$

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

CHEMICAL BEHAVIOR OF HALOGENS

Bond enthalpies in halogens

Bond energy in halogens increase down the group due to increasing strength of London dispersion forces but bond energy of fluorine is lesser than chlorine due to the repulsion between electrons of fluorine.

Halogens	Atomic radii (pm)	Bond length (in gaseous phase) (pm)	Bond enthalpies (KJ/mole)
F – F	72	143	159
Cl – Cl	100	199	242
Br – Br	114	228	193
I – I	133	266	151

Acidity of Hydrogen Halides

Hydrogen halides or halogen acids are denoted by HX. Those acids which can loss H^+ ions easily are termed as strong acids. H-I has the weakest bond that's why it is the strongest acid while H-F has the strongest bond that's why it is the weakest acid.

The decreasing order of acidic strength can be given by:

$(HF < HCl < HBr < HI)$

Strength of Halogens as oxidizing agent

Halogens are good oxidizing agents due to their high electronegativities and ability to readily accept electrons. The strength of halogens as oxidizing agent decreases from top to bottom in group VIIA.

$$F_2 > Cl_2 > Br_2 > I_2$$

Halide ions as a reducing agent

Halide ions $(\bar{Cl},\ B\bar{r}, \bar{I})$ can serve as reducing agents in chemical reactions due to their ability to readily donate electron to an oxidizing species thereby undergoing oxidation.

The decreasing strength of reducing strength of halide ions can be given by:

$$I^- > Br^- > Cl^- > F^-$$

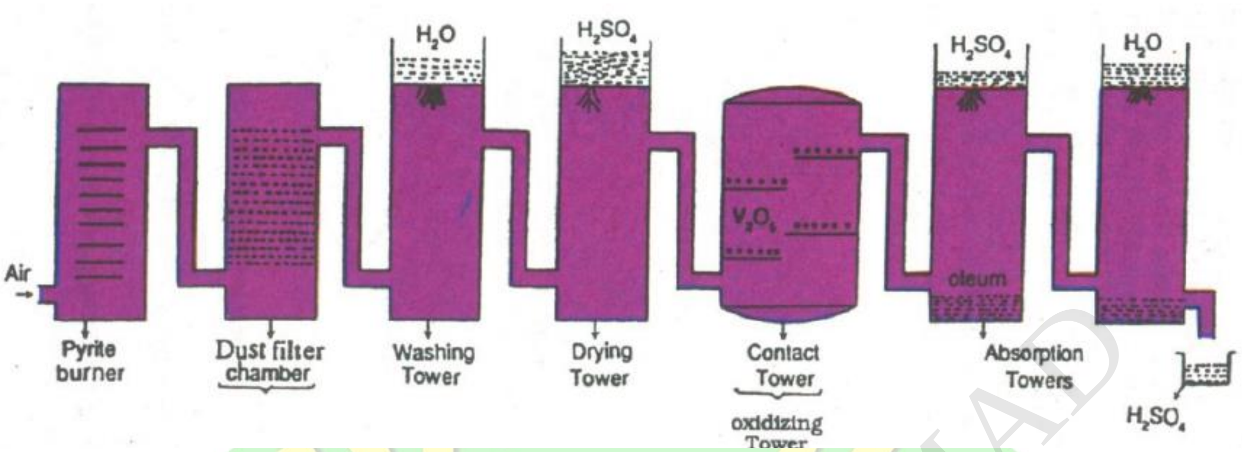
Chlorine as an auto oxidizing and reducing agent

Chlorine reacts with water to form hydrochloric acid and hypochlorous acid. In this reaction chlorine itself reduces into hydrochloric acid and oxidizes into hypochlorous acid and hence serves as auto oxidizing and reducing agent.

$$\underset{\textbf{(Chlorine)}}{Cl_{2(g)}} + H_2O_{(l)} \longrightarrow \underset{\textbf{(Hydrochloric acid)}}{HCl_{(aq)}} + \underset{\textbf{(Hypochlorous acid)}}{HOCl_{(aq)}}$$

INDUSTRIAL PREPARATION OF SULPHURIC ACID (H_2SO_4)

Contact Process



Sulfuric acid is a strong mineral acid having chemical formula H_2SO_4. It is also called oil of vitriol because it was first obtained by green vitriol ($FeSO_4$). Sulfuric acid is known as king of compounds due to its vast industrial usages. Sulfuric acid is prepared in industries in large scale through contact process. This process involves the following five steps:

Step 1: Oxidation of Sulfur to Sulfur Dioxide

First of all, sulfur is burned in the presence of oxygen at high temperature to produce sulfur dioxide gas in sulfur burner.

$$S_{(s)} + O_{2(g)} \xrightarrow{400\text{-}500°C} SO_{2(g)}$$

SO_2 gas produced in sulfur burner is impure. It contains impurities of dust and arsenic oxide (As_2O_3). These impurities must be removed otherwise it could poison the catalyst inside contact tower.

Step 2: Purification of Sulfur Dioxide gas:

The impurities in SO_2 gas are removed in purification chambers. Dust is removed in dust filter. Arsenic oxide is removed in washing chamber by the spray of water. The moisture of SO_2 gas is then removed in dryer. Dryer contains concentrated sulfuric acid which is the dehydrating agent. Pure and dry SO_2 gas is then transferred into contact tower.

Step 3: Oxidation of SO_2 gas:

Contact tower is the most important and biggest tower in this process. Here, SO_2 gas is oxidized into SO_3 gas through a reversible reaction. To obtain the maximum yield of SO_3 gas, Le-Chatelier's principle is applied.

a) Continuous supply of reactants (SO_2 and O_2) is provided

b) Since the reaction is exothermic so maximum yield of SO_3 gas is obtained at low temperature i.e, 500°C.

c) Since the number of moles of reactant are more than the number of moles of product so maximum yield of SO_3 gas is obtained at high pressure i.e, 1-2 atm.

d) A catalyst Vanadium pentoxide (V_2O_5) is used to increase the speed of reaction

$$2SO_{2(g)} + O_{2(g)} \underset{\text{1-2 atm}}{\overset{V_2O_5\ \ 400\text{-}500^\circ C}{\rightleftharpoons}} 2SO_{3(g)} \quad (\Delta H = -45\ \text{Kcal/mol})$$

Step 4: Formation of Oleum ($H_2S_2O_7$)

In the absorption tower, SO_3 gas is absorbed in sulfuric acid to produce oleum. Water cannot be directly added to SO_3 gas for the formation of sulfuric acid because this reaction would be highly exothermic.

$$SO_{3(g)} + H_2SO_{4(l)} \longrightarrow H_2S_2O_{7(l)}$$

Step 5: Formation of Sulfuric Acid (H_2SO_4)

In the dilution tower, water is added to oleum to produce 98% concentrated sulfuric acid.

$$H_2S_2O_{7(l)} + H_2O_{(l)} \longrightarrow 2H_2SO_{4(l)}$$

Physical Properties

- **Boiling Point:** Commercial sulphuric acid has a boiling point of 290ºC. However, the boiling point increases with increasing concentration.
- **Solubility:** Sulphuric acid is highly soluble in water.
- **Corrosive Nature:** Sulphuric acid is a highly corrosive substance and can react with metals and organic compounds etc.

Chemical Properties

An oxidizing agent

In sulphuric acid, sulphur exists in its highest oxidation state of +6. This highest oxidation state of sulphur makes the sulphuric acid to serve as an oxidizing agent when reacts with metals and non metals.

$$C_{(s)} + 2H_2SO_{4(aq)} \longrightarrow CO_{2(g)} + 2SO_{2(g)} + 2H_2O_{(\ell)}$$

$$S_{(s)} + 2H_2SO_{4(aq)} \longrightarrow 3SO_{2(g)} + 2H_2O_{(\ell)}$$

$$Cu_{(s)} + 2H_2SO_{4(aq)} \xrightarrow{\text{(conc.)}} CuSO_{4(aq)} + SO_{2(g)} + 2H_2O_{(\ell)}$$

$$2Al_{(s)} + 6H_2SO_{4(aq)} \xrightarrow{\text{(conc.)}} Al_2(SO_4)_3 + 3SO_{2(g)} + 6H_2O_{(\ell)}$$

A dehydrating agent

The dehydrating ability of sulphuric acid can be attributed to its capability to extract water molecules from other substances.

$$\underset{\text{(glucose)}}{C_6H_{12}O_{6\,(s)}} \xrightarrow{H_2SO_{4(conc.)}} 6C_{(s)} + 6H_2O_{(l)}$$

$$\underset{\text{(sugar)}}{C_{12}H_{22}O_{11(S)}} \xrightarrow{H_2SO_{4(conc.)}} 12C_{(s)} + 11H_2O_{(\ell)}$$

$$\underset{\text{(wood)}}{(C_6H_{12}O_5)_n} \xrightarrow{H_2SO_{4(conc.)}} 6nC_{(s)} + 5nH_2O_{(\ell)}$$

A sulphonating agent

$$\underset{\text{(Benzene)}}{C_6H_{6(l)}} + H_2SO_{4(aq)(conc.)} \longrightarrow \underset{\text{(Benzene sulphonic acid)}}{C_6H_5SO_3H_{(l)}} + H_2O_{(l)}$$

$$\underset{\text{(Toluene)}}{C_7H_{8(l)}} + H_2SO_{4(conc.)} \longrightarrow \underset{\text{(p-toluene sulphonic acid)}}{C_6H_4(CH_3)SO_3H_{(l)}} + H_2O_{(l)}$$

A dibasic acid

Sulphuric acid has the ability to donate two protons in water in two dissociation steps and serves as dibasic acid.

$$H_2SO_{4(aq)} \rightleftharpoons H_3O^+ + HSO^-_{4(aq)}$$

$$HSO^-_{4(aq)} \rightleftharpoons H_3O^+ + SO^{-2}_{4(aq)}$$

Uses of Sulphuric acid

Sulphuric acid is used in various industries for:

- Producing fertilizers, dyes, pigments, detergents, pharmaceuticals, and synthetic fibers.
- Refining petroleum to make high-octane gasoline additives.
- Processing and purifying metals, including removing rust and scale.
- Etching and electroplating processes.
- Manufacturing lead-acid batteries.
- Cleaning and descaling due to its strong acidic properties.

DIAGONAL RELATIONSHIP OF REPRESENTATIVE ELEMENTS

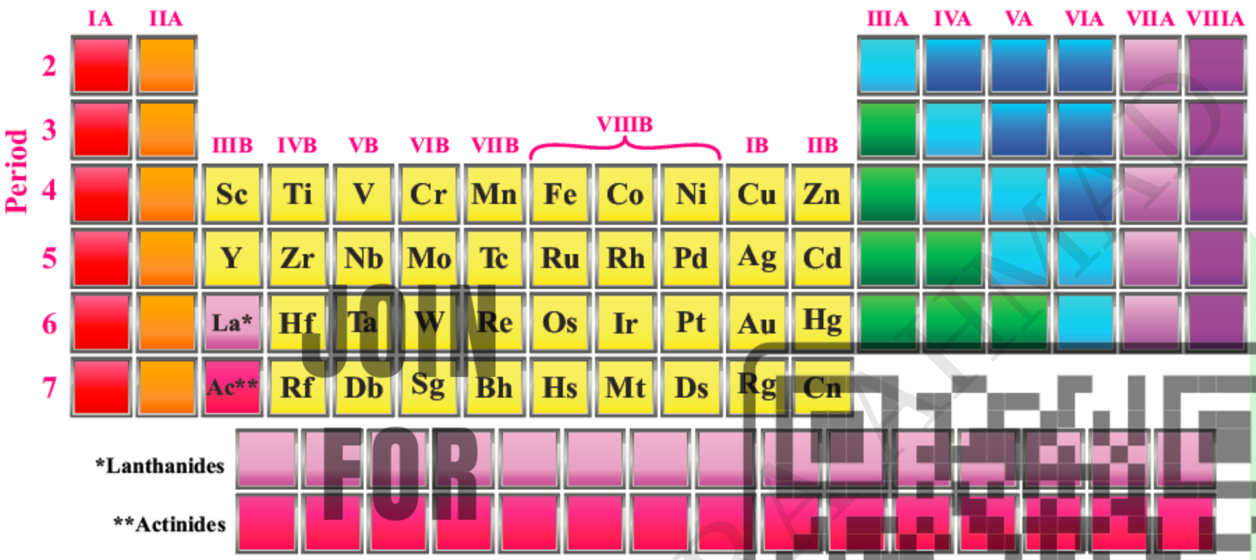
The diagonal relationship refers to the resemblance in the properties exhibited by certain pairs of elements that are located diagonally to each other within the periodic table.

Periods	Groups			
	IA	IIA	IIIA	IVA
Second	Li	Be	B	C
Third	Na	Mg	Al	Si

Important functions of selected elements and compounds of representative elements

Element/Compound	Significant Uses
Aluminum	It is used in making coils, alloys, kitchen utensils, window frames, chocolate foils etc.
Sulphur	It is used in the manufacturing of sulphuric acid, hydrogen sulphide and pesticides.
Chlorine	It is used in the manufacturing of plastic, bleaching powder and in the purification of drinking water.
Borax ($Na_2B_4O_7.10H_2O$)	It is used in cleaning, laundry, cosmetics and as flux in welding.
Alum ($K_2SO_4.Al_2SO_4.24H_2O$)	It is used for the purification of water, tanning of leather, fire extinguishers and as an antiseptic for minor cuts and wounds.
Ammonia (NH_3)	It is used in the manufacturing of fertilizers, nitric acid and refrigeration.

CHAPTER 2 CHEMISTRY OF OUTER TRANSITION ELEMENTS



Period	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB	VIIIB	VIIIB	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
2																		
3																		
4			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn						
5			Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd						
6			La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg						
7			Ac**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn						

*Lanthanides

**Actinides

Transition Elements:

The elements in periodic table from group I-B to VIII-B are called transition elements. They are also known as transition metals.

Transition elements can be further classified into two blocks.

(i) d-block elements (Outer Transition Elements)

(ii) f-block elements (Inner Transition Elements)

Outer Transition Elements:

d-block elements are also known as outer transition elements. Their valence electron enters in d-orbital that's why they are known as d-block elements.

The general valence shell electronic configuration of d-block elements is ns^{1-2}, $(n-1)\ d^{1-10}$

The general valence shell electronic configuration of all the groups are given below:

GVSEC of group III-B → **ns^2, $(n-1)\ d^1$**

GVSEC of group IV-B → **ns^2, $(n-1)\ d^2$**

GVSEC of group V-B → **ns^2, $(n-1)\ d^3$**

GVSEC of group VI-B → $ns^1, (n-1)\ d^5$ (Stable Configuration)

GVSEC of group VII-B → $ns^2, (n-1)\ d^5$

GVSEC of group VIII-B → $ns^2, (n-1)\ d^6$ $ns^2, (n-1)\ d^7$ $ns^2, (n-1)\ d^8$

GVSEC of group I-B → $ns^1, (n-1)\ d^{10}$ (Stable Configuration)

GVSEC of group II-B → $ns^2, (n-1)\ d^{10}$

There are total four series of d-block elements found in the 4th, 5th, 6th and 7th periods.

3d – series:

This ten element series is located in the 4th period. It includes elements from scandium (Sc) to zinc (Zn).

4d – series:

This series is placed in 5th period and consists of elements from yttrium (Y) to cadmium (Cd).

5d – series:

This series is situated in the sixth period and consists of elements from lanthanum (La) to mercury (Hg).

6d – series:

This series consists of elements from actinium (Ac) to copernicium (Cn).

GENERAL FEATURES OF OUTER TRANSITION ELEMENTS

Variable Oxidation States

The number of electrons lost or gained by an atom to acquire stability is called oxidation number. Transition elements exhibits variable oxidation states or variable valency because they can make bond with ns orbital as well as (n-1)d orbital.

Elements of group I-B such as Zn/Cd/Hg/Cn only have +2 oxidation state. Due to this reason, they are also known as pseudo transition elements.

Elements	Outer Electronic Configuration	Oxidation States
Scandium (Sc)	$[Ar]3d^1\ 4s^2$	+2, +3
Titanium (Ti)	$[Ar]3d^3\ 4s^2$	+2, +3, +4
Vanadium (V)	$[Ar]3d^3\ 4s^2$	+2, +3, +4, +5
Chromium (Cr)	$[Ar]3d^5\ 4s^1$	+1, +2, +3, +4, +5, +6
Manganese (Mn)	$[Ar]3d^5\ 4s^2$	+2, +3, +4, +5, +6, +7
Iron (Fe)	$[Ar]3d^6\ 4s^2$	+2, +3, +4, +5, +6
Cobalt (Co)	$[Ar]3d^7\ 4s^2$	+2, +3, +4
Nickel (Ni)	$[Ar]3d^8\ 4s^2$	+2, +3, +4
Copper (Cu)	$[Ar]3d^{10}\ 4s^1$	+1, +2
Zinc (Zn)	$[Ar]3d^{10}\ 4s^2$	+2

Catalytic Activity

Transition elements and their compounds can be used as catalyst to increase the rate of reaction.

For example:

In contact process, V_2O_5 is used as catalyst.

In Haber's process Fe is used as catalyst.

In Ostwald's process Pt is used as catalyst.

In hydrogenation reactions Ni is used as catalyst etc.

Magnetic Behavior

Those elements which are attracted towards magnetic are called para magnetic elements and those elements which are not attracted towards magnet are called diamagnetic elements.

Most of the transition elements are paramagnetic in nature due to the presence of unpaired electron. Unpaired electrons give raise to magnetic behavior in an element.

The elements of group II-B do not have unpaired electron, that's why they are diamagnetic.

Alloy Formation

The combination of two or more than two metals is called alloy. Transition elements have the ability to form alloy.

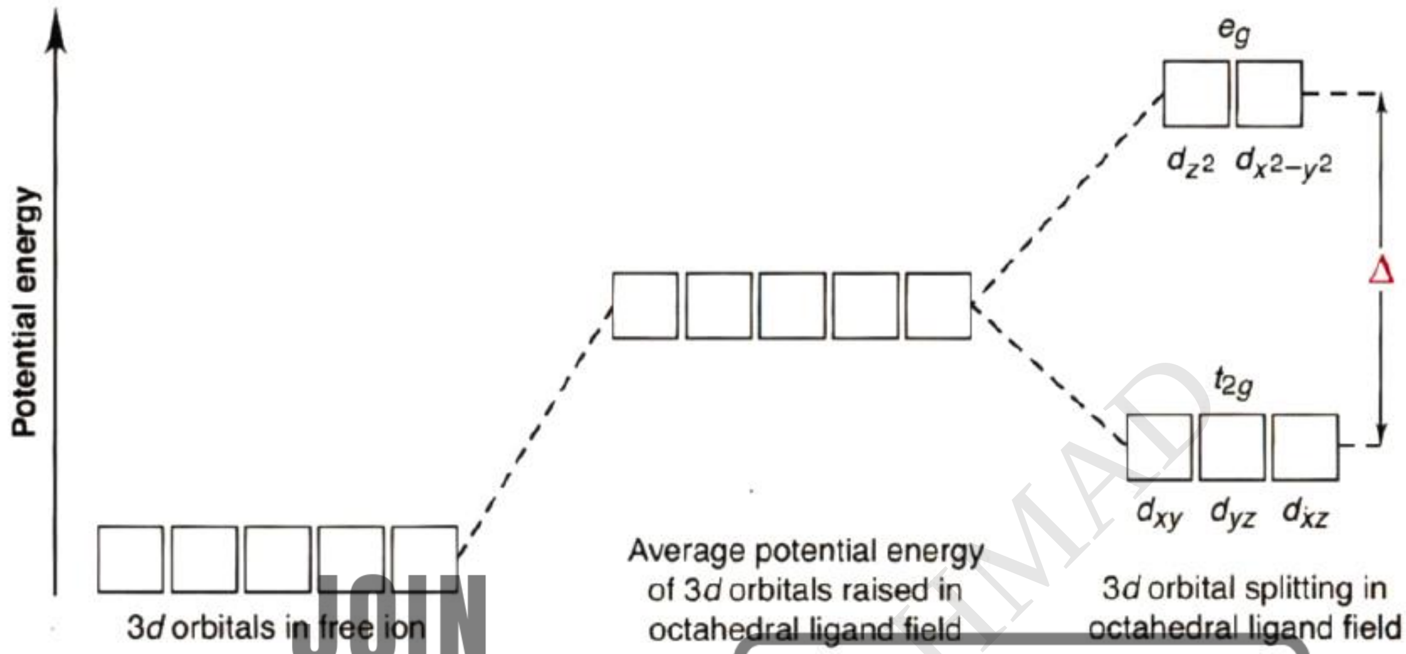
Alloys	Compositions	Important Uses
Stainless steel	Iron, Chromium and Nickel	In making cutlery, and surgical instruments.
Duralumin	Aluminum, Copper Magnesium and Manganese	In making utensils, aeroplane etc.
Brass	Copper and Zinc	In plumbing and automotive parts etc
Bronze	Copper and Aluminum	In making medals, statues, coins etc

Colour of Complexes

Transition elements can form colored compounds which can be explained by Crystal Field Theory (CFT). According to this theory, d-orbitals split into two parts i.e; t_2g and e.g orbitals. t_2g has lower energy than e.g orbitals. The difference in energies between t_2g and e.g orbital is Δ_o. When light rays fall on any transition metal compound then t_2g orbitals absorb light of a specific wavelength and jumps to e.g orbital. When electrons from e.g orbitals return back to t_2g orbital, they emit light rays of reciprocal wavelength.

For example, Copper Sulphate ($CuSO_4$) contains Cu^{+2} ions. Cupric ions absorb red and green light. They radiate blue light afterwards so that copper sulphate appears blue in color.

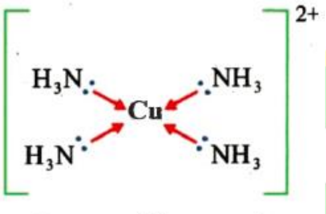
Elements of group II-B have full filled valence orbital so that d-d transition is not possible. Due to this reason, they form white compounds instead of colored compounds. Hence, they are called pseudo transition elements.



COORDINATION COMPOUNDS

Those compounds in which a transition element is bonded to a ligand by means of co-ordinate covalent bond is called co-ordination compound. It's also called complex compound because it contains a complex ion. The complex ion may be cationic or anionic. complex ion is written inside a large bracket which is called co-ordination sphere.

Let's take the following example of a complex ion,



($[Cu(NH_3)_4]^{2+}$ Complex)

Here, Cu is a transition metal which is also called central metal atom. NH_3 is the ligand which is donating lone pair of electrons to central metal atom. Since, there are four molecules of NH_3 which is bonded to copper hence the co-ordination number is 4.

The general formula of a complex ion is given by: **$[M(:L)_n]^{-/+}$**

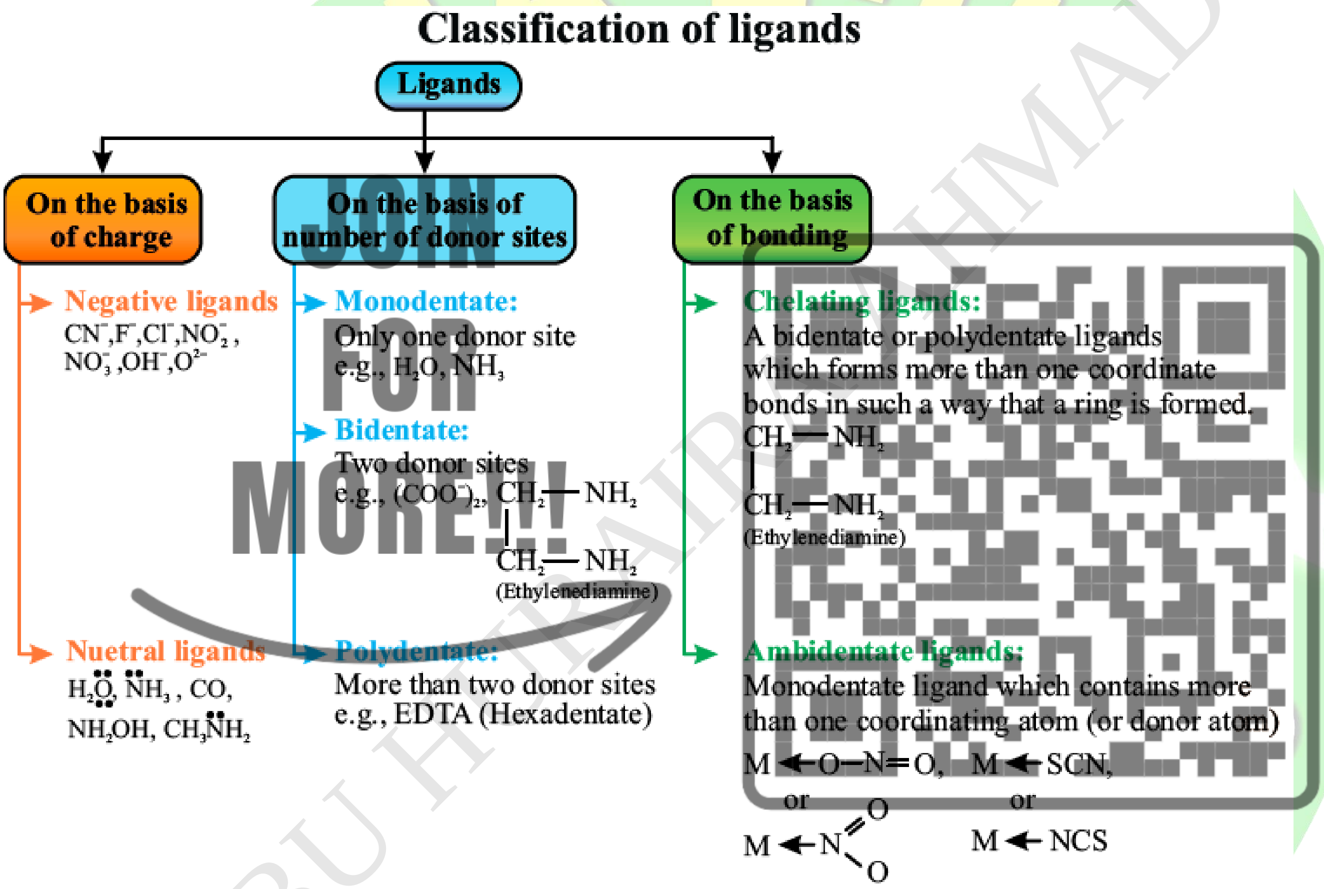
Here, M is the central metal atom.

L is ligand

n is co-ordination number

LIGANDS:

Ligands are the species that can donate lone pair of electrons to central metal atom. They are Lewis bases.



Co-Ordination Number:

The total number of lone pair of electrons donated by ligands is called co-ordination number.

Denticity:

The number of electron pairs donated by a ligand to central metal atom is called denticity.

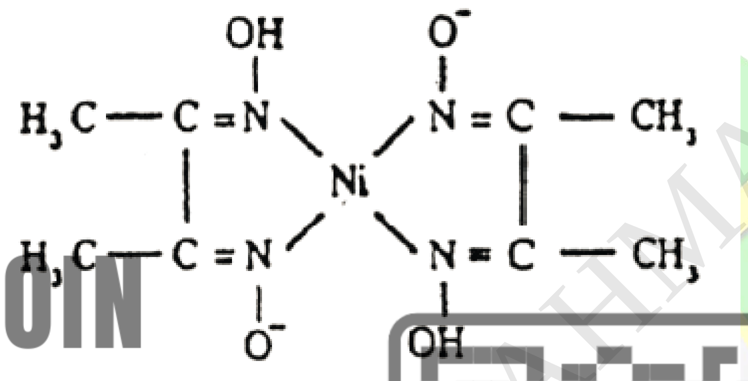
If a ligand donates 1 pair of electrons, then it is called mono-dentate ligand.

If a ligand donates 2 pair of electrons, then it is called bi-dentate ligand.

If a ligand donates 3 pair of electrons, then it is called tri-dentate ligand and so on.

Chelating Ligands:

Polydentate or multidentate ligands are also known as chelating ligands because when they are bonded to a central metal atom, they form a chelate. Chelate is a Greek word which means Crab's claw.



(Nickel dimethyl glyoximate)
(Chelate)

General rules of IUPAC naming of coordination compounds

Co-ordination Compound General Formula: **$C[M(:L)_n]A$**

Naming Pattern: **C + L + M + A**

- Use only small letters
- Don't leave any space between words

1. Write the name of cation first if cation is present in the compound.

2. Write the name of ligand. If more than one type of ligand is present then follow alphabetical order. For inorganic ligands write **di/tri/tetra/penta** etc. for multiple ligand of same type and for inorganic ligands write **bis/tris/tetrakis/pentakis** etc. for multiple ligand of same type.

3. Write the name of metal. If complex contains a +ve charge then write the english name of metal. If complex contains a -ve charge then write the Latin name of metal. While writing Latin names replace -um with -ate.

Symbol	English Name	Latin Name	Um → ate
Fe	Iron	Ferrum	Ferrate
W	Tungsten	Wolfram	Wolfrate
Pb	Lead	Plumbum	Plumbate
Sn	Tin	Stannum	Stannate

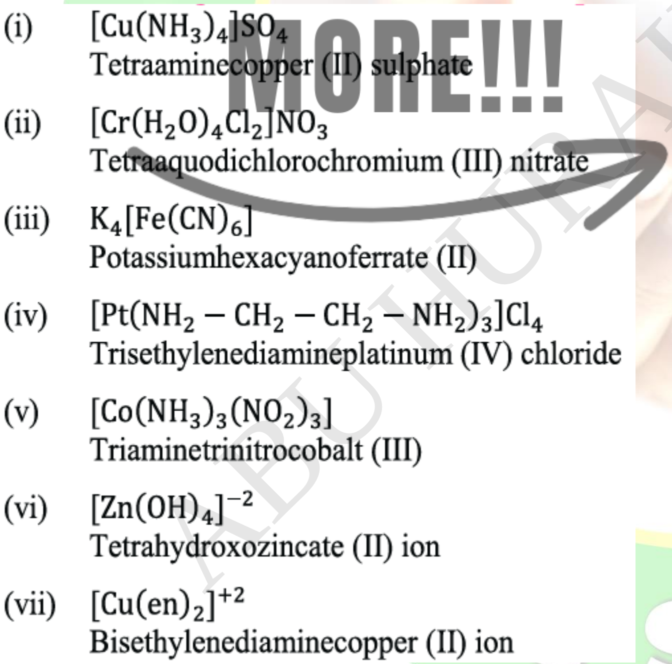
Ag	Silver	Argentum	Argentate
Au	Gold	Aurum	Aurate
Hg	Mercury	Hydrargyrum	Hydragyrate
Cu	Copper	Cuprum	Cuprate
Al	Aluminum	-	Aluminate
Ni	Nickel	-	Nickelate
Co	Cobalt	-	Cobaltate
Cr	Chromium	-	Chromate
Mn	Manganese	-	Manganate
Pt	Platinum	-	Platinate
Zn	Zinc	-	Zincate

4. Write the oxidation number of metal is parenthesis in roman numerals. Remember that 0 oxidation state is also possible.

5. Name the anion, if anion is present in the compound.

6. Write ‘ion’ at the end if the compound contains a positive or negative charge.

Look at the following examples:



(i) $[Cu(NH_3)_4]SO_4$
Tetraaminecopper (II) sulphate

(ii) $[Cr(H_2O)_4Cl_2]NO_3$
Tetraaquodichlorochromium (III) nitrate

(iii) $K_4[Fe(CN)_6]$
Potassiumhexacyanoferrate (II)

(iv) $[Pt(NH_2-CH_2-CH_2-NH_2)_3]Cl_4$
Trisethylenediamineplatinum (IV) chloride

(v) $[Co(NH_3)_3(NO_2)_3]$
Triaminetrinitrocobalt (III)

(vi) $[Zn(OH)_4]^{-2}$
Tetrahydroxozincate (II) ion

(vii) $[Cu(en)_2]^{+2}$
Bisethylenediaminecopper (II) ion

Self Assessment

Write the IUPAC names of the following complexes.

- $[Pt(H_2O)_5Cl](NO_3)_3$
- $[Cr(NH_3)_4]^{+3}$
- $K_2[Cu(CN)_4]$
- $[AlF_6]^{-3}$

1. pentaaquachloroplatinum(IV)nitrate
2. tetraamminechormium(III)ion
3. potassiumtetracyanocuprate(II)
4. hexafluoroalumiate(III)ion

1. Write the IUPAC names of the following:

(i) $Na_2[Pt(OH)_4]$

(ii) $K_2[Fe(CN)_5NO]$

(iii) $[Zn(NH_3)_4]^{+2}$

(iv) $[Ni(SCN)_4]^{-2}$

Answers:

(i) sodiumtetrahydroxoplatinate(II)

(ii) potassiumpentacyanonitrosylferrate(III)

(iii) tetraamminezinc(II)ion

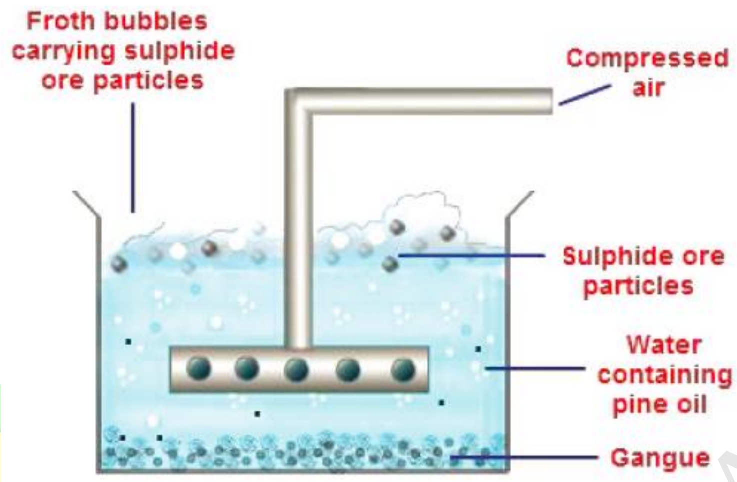
(iv) tetrathiocyanonickelate(II)ion

Metallurgy of Copper

The chief ore of copper metal is copper pyrite or chalcopyrite having chemical formula $CuFeS_2$. This ore contains 6% $CuFeS_2$ and 94% gangue particles or impurities. There are five steps for the extraction of 100% pure copper metal from its chalcopyrite ore.

STEP#1 (CONCENTRATION OF THE ORE)

First of all, the gangue particles from copper pyrite ore are removed. It's done by means of froth floatation process. The crushed copper pyrite ore is mixed with a mixture of water and pine oil. Air is introduced into the mixture so that the gangue particles settle down while copper pyrite ore is deposited at the top.



STEP#2 (ROASTIN OF CONCENTRATED ORE)

In this step the concentrated copper pyrite ore is heated at high temperature in a kiln or reverberatory furnace. Copper pyrite ore is thermally decomposed into cuprous sulphide (Cu_2S), ferrous oxide (FeO) and Sulphur dioxide gas (SO_2).

$$2CuFeS_2 + 4O_2 \longrightarrow Cu_2S + 2FeO + 3SO_2$$

STEP#3 (SMELTING OF ROASTED PYRITE ORE)

Roasted copper pyrite ore is then introduced into a blast furnace along-with silica (SiO_2) and coal. Hot air is blown inside the furnace by means of tuyeres. The temperature inside furnace reaches to 1200 °C to 1500 °C. At this temperature, ferrous oxide reacts with silica to form ferrous silicate which is also known as slag. The slag remains at the top of molten matte (Cu_2S). Slag is removed from the top and it can be used for making roads.

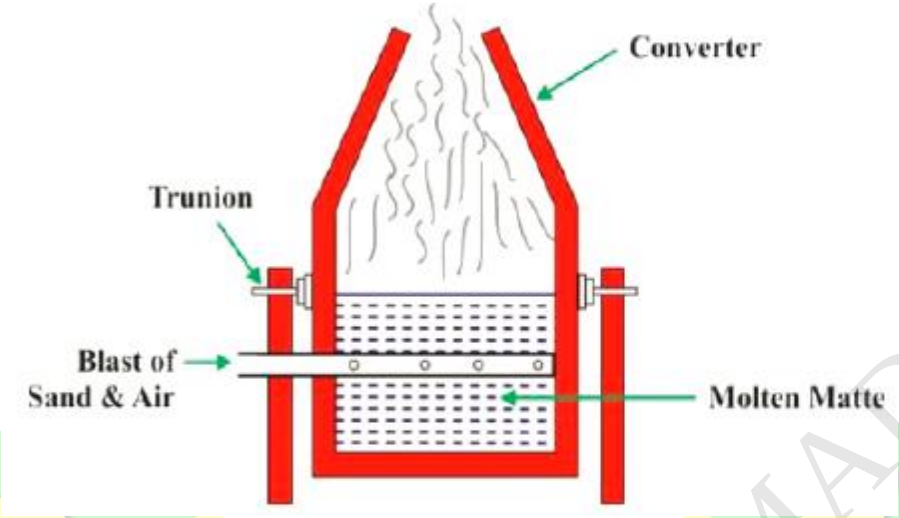
$$\underset{\text{(Iron oxide)}}{FeO} + \underset{\text{(Silica)}}{SiO_2} \xrightarrow{1200°C-1500°C} \underset{\text{(Slag)}}{FeSiO_3}$$

STEP#4 (BESSEMERIZATION OF MATTE)

Matte (Cu_2S) is then transferred into Bessemer converter in which matte reacts with oxygen gas to form a mixture of cuprous oxide (Cu_2O) and Sulfur dioxide gas (SO_2). Cuprous oxide finally reacts with cuprous sulphide to produce blister copper which is 99% pure. Due to the evolution of SO_2 gas from copper, blisters are formed on its surface. Hence, it's known as blister copper. Blister copper contains 1% impurities that's why it is not suitable for making wires as it the impurities produces resistance in the flow of electric current.

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$



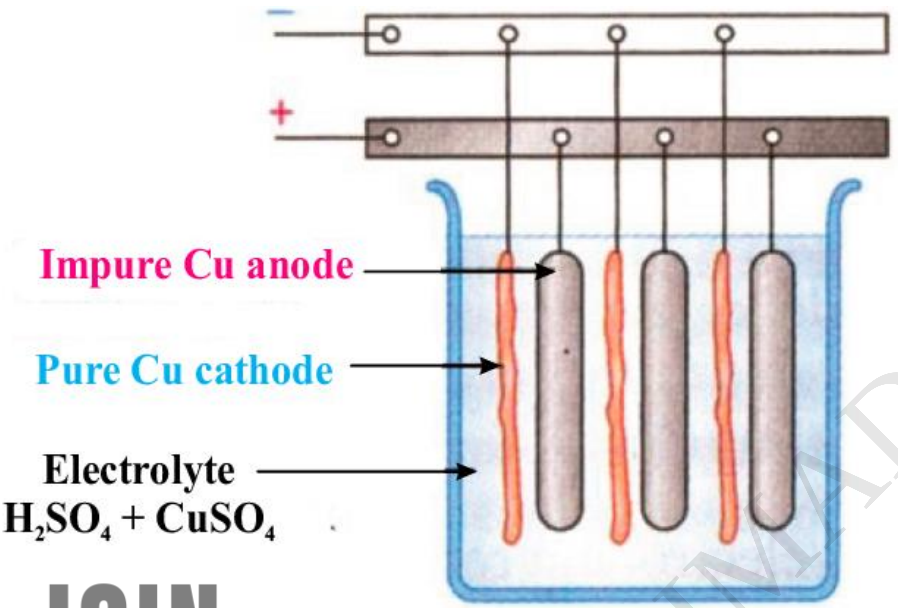
STEP#5 (ELECTROLYTIC REFINING OF BLISTER COPPER)

The impurities of blister copper can be removed by electrolytic method. The electrolytic cell used for this purpose is made up of blister copper anode and pure copper cathode. Copper sulphate solution is used as electrolyte.

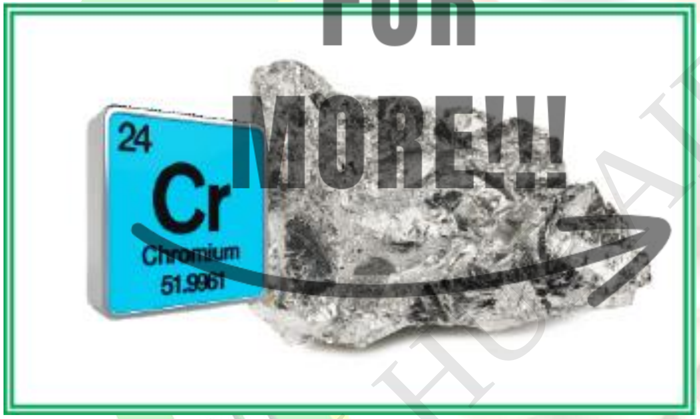
When an electric current of 1.3 volts is passed through the cell, copper metal is oxidized at anode to form Cu^{+2} ions by the loss of two electrons. Cu^{+2} ions are reduced into pure copper metal at cathode by the gain of two electrons. The impurities of blister copper are deposited below anode as anode mud. In this manner, 100% pure copper metal is produced which can be used for making wires.

$$\underset{\text{(Blister copper)}}{Cu} \longrightarrow Cu^{+2} + 2\bar{e} \text{ (oxidation at anode)}$$

$$Cu^{+2} + 2\bar{e} \longrightarrow Cu \text{ (reduction at cathode)}$$



Chromium



Chromium is a transition metal and it belongs to 3d series. It has a silvery grey color and metallic luster.

Chromium reacts with dilute hydrochloric acid to liberate hydrogen gas.

$$2Cr_{(s)} + 6HCl_{(aq)} \longrightarrow 2CrCl_{3(aq)} + 3H_{2(g)}$$

Chromium reacts with oxygen to form chromium oxide.

$$4Cr_{(s)} + 3O_{2(g)} \xrightarrow{\text{Heat}} 2Cr_2O_{3(s)}$$

Chromium reacts with steam at high temperatures to form chromium oxide with the liberation of hydrogen.

$$2Cr_{(s)} + 3H_2O_{(s)} \xrightarrow{\text{Heat}} Cr_2O_{3(s)} + 3H_{2(g)}$$

Chromium is used to make stainless steel, chrome plating and pigments.

Chemistry of Potassium dichromate

Potassium dichromate is a red crystalline solid that is highly soluble in water.

If it dissolves in water a chromate and dichromate equilibrium is formed which shows an orange – red color.

$$\underset{\textbf{(red)}}{Cr_2O_7^{-2}{}_{(aq.)}} + H_2O_{(\ell)} \rightleftharpoons \underset{\textbf{(yellow)}}{2CrO_4^{-2}{}_{(aq.)}} + 2H^+_{(aq.)}$$

This equilibrium between chromate and dichromate ions is pH sensitive. When an acid is added, the equilibrium shifts to the left, resulting in the formation of a red dichromate solution. On the other hand if a base is added, the equilibrium shifts to the right, leading to the formation of a yellow chromate solution.

Potassium dichromate is used as an oxidizing agent in various chemical reactions since it possesses the highest oxidation state of chromium (+6).

$$\underset{\textbf{(orange)}}{Cr_2O_7^{-2}} + 6Fe^{+2} + 14H^+ \longrightarrow \underset{\textbf{(green)}}{2Cr^{+3}} + 6Fe^{+3} + 7H_2O$$

Manganese

Manganese is an outer transition element belonging to 3d series. Its symbol is “Mn”.

Manganese reacts with chlorine to form manganese chloride.

$$Mn_{(s)} + Cl_2 \longrightarrow MnCl_{2(s)}$$

Manganese when dissolves in dilute sulphuric acid, it liberates hydrogen gas.

$$Mn_{(s)} + H_2SO_{4(aq)} \longrightarrow MnSO_{4(aq)} + H_{2(g)}$$

Chemistry of Potassium Permanganate

The formula of potassium permanganate is $KMnO_4$. It is a deep purple crystalline solid. It is highly soluble in water. Mn has +7 oxidation state in potassium permanganate. Due to the highest oxidation state of manganese, $KMnO_4$ is an oxidizing agent in acidic, basic and neutral medium.

The reaction of potassium permanganate with ferrous sulphate and Mohr’s salt is given as;

$$MnO_4^- + 5Fe^{+2} + 8H^+ \longrightarrow Mn^{+2} + 5Fe^{+3} + 4H_2O$$

Iron

Iron is an outer transition metal belonging to 3d series. Its symbol is Fe because it is called Ferrum in Latin language. It’s the fourth most abundant element in Earth crust. Red color of blood is due to Hemoglobin and it contains iron as well.

When iron is exposed to air, it oxidizes and forms an oxide film on its surface which is rusting of iron.

$$4Fe_{(s)} + 3O_{2(g)} \longrightarrow 2Fe_2O_{3(s)}$$

When it reacts with excess of chlorine, it forms ferric chloride.

$$2Fe_{(s)} + 3Cl_{2(g)} \longrightarrow 2FeCl_{3(s)}$$

Steel

Steel is a widely used alloy comprised primarily of iron combined with some other elements. By the inclusion of carbon and other alloying elements in steel enhances its mechanical, thermal and chemical properties compared with simple iron.

There are several types of steel each characterized by unique compositions and properties suited for specific applications.

Type of Steel	Applications
Carbon Steel	Construction tools, machinery, pipes, tubes, automotive etc.
Stainless Steel	Kitchen appliances, Cutlery and Medical equipment
Tool Steel	Cutting and drilling equipment
Alloy Steel	Fry pan, Toaster etc

Table 2.4 Commercial applications of some common transition elements

Transition Elements	Commercial Applications
Titanium	In making artificial joints, bone plates, screws and dental implants.
Vanadium	Use in batteries, as a catalyst and as a pigment in glass making
Iron	Building and bridge construction and tool making.
Copper	In making copper wires, alloys and sanitary works.
Zinc	Galvanizing, alloying and also use in batteries
Platinum	In making jewellery and also serves as a catalyst.
Mercury	Use in thermometers, B.P. apparatus, and amalgam formation

Multiple Choice Questions

(i) Zn^{+2} ion is colourless because:
(a) Its undergoes d-d transition of electron
(b) Its 3d orbitals have all unpaired electrons
[✓ (c) Its 3d orbitals have all paired electrons]
(d) Its d orbitals split up into t_2g and eg

(ii) The coordination number of cobalt in $Na_4[Co(C_2O_4)_3]$ is:
(a) 3　　(b) 4
[✓ (c) 6]　　(d) 7

(iii) An example of a bidentate ligand among the following is:
(a) $O\bar{H}$　　[✓ (b) $C_2O_4^{-2}$]
(c) Cl^-　　(d) $C\bar{N}$

(iv) A highly paramagnetic ion among the following is:
(a) Fe^{+2}　　[✓ (b) Fe^{+3}]
(c) Co^{+2}　　(d) Cr^{+3}

(v) The highest oxidation state of chromium is:
(a) +4 (b) +5
[✓ (c) +6] (d) +7

(vi) The element is not used for electroplating:
(a) Zinc (b) Tin
(c) Chromium [✓ (d) Manganese]

(vii) The steel is typically used in making Fry pans:
(a) Carbon steel (b) Stainless steel
(c) Tool Steel [✓ (d) Alloy Steel]

(viii) The step which involved in the extraction of copper from chalcopyrite ore in the elimination of gangue impurities is:
[✓ (a) Concentration] (b) Roasting
(c) Smelting (d) Bessemerization

(ix) 5d series of outer transition elements is:
(a) Sc to Zn (b) Y to Cd
[✓ (c) La to Hg] (d) Ac to Cn

(x) Oxidation of manganese in air gives the following oxide:
(a) MnO (b) MnO_3
(c) Mn_2O_3 [✓ (d) Mn_3O_4]

Short Questions

2. Give reasons for the following:

(i) Why do transition elements show variable oxidation states?
(ii) Why transition elements have ability to form alloys?
(iii) Why Cu^{+2} ion is blue but Zn^{+2} is colourless?
(iv) Why chromium exists in $4s^1\ 3d^5$ configuration but not in $4s^2\ 3d^4$?
(v) Why binding energy of zinc is least in 3d series?

Answers:

(i) Transition elements show variable oxidation states because they can make bond with ns orbital and (n-1)d orbital as well due to very less energy difference between them.

(ii) Transition elements can form alloys because they have ability to form non-stoichiometric compounds. They have interstitial spaces on their surfaces in which the atoms of other elements adsorb to form alloy,

(iii) d-d transition is possible in Cu^{+2} ions so they absorb light of specific wavelength of red and green color, they release light energy in the form of light having wavelength of blue color. d-d transition is not possible in Zn^{+2} ions because of fully filled d-orbital. That's why they reflect all the light falling on it, hence the compounds of Zinc are white.

(iv) $4s^2$, $3d^4$ is unstable electronic configuration of chromium and $4s^1$, $3d^5$ stable electronic configuration of chromium.

(v) Binding energy of Zn is least because of its fully filled d sub shell.

3. Write down the balanced chemical equations for the following reactions.
   - (i) Reaction of conc. nitric acid with copper
   - (ii) Reaction of conc. sulphuric acid with copper
   - (iii) Reaction of permanganate with oxalic acid
   - (iv) Reaction of dichromate with ferrous sulphate
   - (v) Reaction of manganese with dilute sulphuric acid
   - (vi) Reaction of iron with chlorine

Answers:

(i)

$$Cu + 4HNO_{3(conc.)} \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

(ii)

$$Cu + 2H_2SO_{4(conc.)} \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

(iii)

$$2MnO_4^- + 5C_2O_4^{-2} + 16H^+ \longrightarrow 2Mn^{+2} + 10CO_2 + 8H_2O$$

(iv)

$$\underset{\textbf{(orange)}}{Cr_2O_7^{-2}} + 6Fe^{+2} + 14H^+ \longrightarrow \underset{\textbf{(green)}}{2Cr^{+3}} + 6Fe^{+3} + 7H_2O$$

(v)

$$Mn_{(s)} + H_2SO_{4(aq)} \longrightarrow MnSO_{4(aq)} + H_{2(g)}$$

(vi)

$$2Fe_{(s)} + 3Cl_{2(g)} \longrightarrow 2FeCl_{3(s)}$$

4. Why d-block elements are called outer transition elements?

Ans. d-block elements are also called outer transition elements because they are present outside in the periodic table in contrast to inner transition elements which are present inside lanthanum and actinium.

5. Write down the effect of pH changes on dichromate equilibrium in water.

Ans. In acidic medium, dichromate ion is prominent and in basic medium chromate ion is prominent.

6. Melting point of d-block elements increase up to middle of the series and then decrease why?

Ans. d-block elements usually have high melting points due to the covalent bonding formed by the empty or partially filled d-orbitals and unpaired electrons.

Since electrons get paired in the d-orbital after d^5 configuration, the melting point of elements in the d-block increases from d^1 configuration to d^5 configuration and then starts to decrease.

7. Give the composition and applications of stainless steel, brass and bronze.

Ans. Stainless steel is made up of iron, chromium and nickel. It is used to make kitchen utensils, surgical instruments etc.

Brass is an alloy of copper and zinc. It is used to make taps, moving parts of clock, musical instruments, coins etc.

Bronze is an alloy of copper and tin. It is used to make coins, statues, medals etc.

Descriptive Questions

1. Explain the trend of following properties of 3d-series of transition elements.
   (a) Paramagnetic behavior
   (b) Variable oxidation state
   (c) Colour formation.

See the topic of general properties of transition metals

2. How can you define a coordination complex and a chelating ligand? Explain various types of ligands with examples.

See the topic of Co-ordination compounds

3. Describe how 99.99% pure copper is obtained from its chalcopyrite ore.

See the topic of Metallurgy of Copper

4. Explain why transition elements and their compounds serve as catalysts in many chemical reactions.

See the topic of Catalytic Property of transition element

5. What is meant by binding energy? Write down the trend of binding energy in 3d series of transition elements.

2.1.2 Binding Energy

"The amount of energy required to separate the constituents of a bound system, such as atoms, nuclei, or particles". It represents the strength of the attractive forces holding the system together.

The d-block elements have partially filled d orbitals, which contribute to their unique properties. Their binding energy is higher than that of other elements due to the strong attraction to their outermost d electrons. The binding energy increases across a period from left to right in the d-block elements due to increasing nuclear charge and decreasing atomic radius. The stronger positive charge attracts the d electrons more, requiring more energy to remove them.

Down a group, the binding energy tends to decrease in the d-block elements. This is because the increasing atomic size and shielding effect reduce the effective nuclear charge felt by the outermost d electrons, making them easier to remove.

CHAPTER 3

ORGANIC COMPOUNDS

ORGANIC CHEMISTRY:

It is the branch of chemistry that deals with the study of those compounds which we get from living organisms such as plants and animals.

OR

It is the branch of chemistry that deals with the study of carbon compounds with the exception of carbon monoxide (CO), Carbon dioxide (CO_2), Carbonates (CO_3^{-2}), bicarbonates (HCO_3^{-1}) and carbides.

OR

It is the branch of chemistry that deals with the study of hydrocarbons. Hydrocarbons are the compounds which contain carbon and hydrogen such as methane gas (CH_4)

VITAL FORCE THEORY:

Vital Force Theory (VFT) was given by J. Berzelius. According to this theory, only living things have the ability to make organic compounds and we cannot make it in laboratory.

WOHLER'S EXPERIMENT:

In 1828, a German chemistry, Fredrich Wohler rejected vital force theory and prepared the first organic compound in laboratory. That's why he is known as the father of organic chemistry.

Wohler boiled ammonium cyanate (NH_4CNO), an inorganic compound, in water. He observed that urea is obtained which is an organic compound.

$$\underset{\text{(ammonium cyanate)}}{NH_4CNO} \xrightarrow{\text{Heat}} \underset{\text{(urea)}}{CO(NH_2)_2}$$

SOURCES OF ORGANIC COMPOUNDS

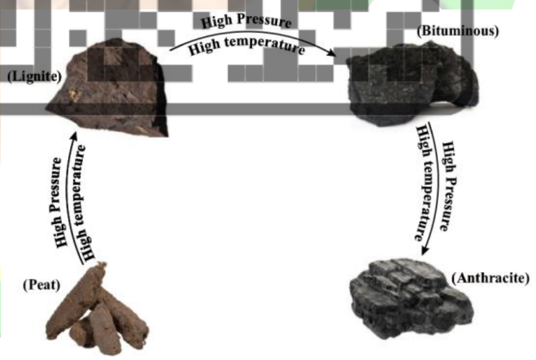
1. Fossil Fuel (Coal, Petroleum, Natural Gas)

Fossils are formed when an organism dies and its remains are quickly buried by sediment without decomposition. The buried remains become compressed and the organic material in the remains is slowly transformed into fossil fuel leaving behind the minerals of the rock. Fossil fuels are nonrenewable energy source. The three main types of fossil fuels are coal, petroleum and natural gas.

Coal

Coal is a plant-derived black mineral found beneath the earth's crust and is a solid fossil fuel that has significance all over the world. Plants that were buried underneath the earth crust millennia ago were slowly turned to coal under high temperature and pressure owing to bacterial and chemical processes

Coal type	% age of carbon contents	Properties and uses
Peat	45 – 60%	It is the earliest stage of coal formation resulting from the decomposition of fossilized remains. It has very low heat contents and use for domestic heating as an alternate of fire wood.
Lignite	60 – 70%	It is a brownish black coloured soft coal. It is typically used to generate electricity in power plants.
Bituminous	70 – 85%	It is a black coloured soft coal. It has a higher carbon content than lignite. It is often used for electric generation and steel production.
Anthracite	90 – 95%	It is a dark black coloured hard coal. It is the highest ranking coal with the highest carbon content. It is used in furnaces, power stations and as a domestic fuel.



Destructive Distillation of Coal:

The process in which coal is heated in the absence of air to produce a range of useful products is known as destructive distillation. The process required an elevated temperature typically 400°C to 900°C in a closed container. The principal products of destructive distillation of coal are coke, coal tar, coal gases and ammonia liquor.

Coke: It is a black hard solid contains 98 – 99% carbon. It is used as fuel and reducing agent.

Coaltar: It is a thick black liquid. Its fractional distillation gives many useful organic compounds such as benzene, toluene, xylene, naphthalene, phenol etc.

Coal Gases: It is a mixture of methane and water gas. It is highly flammable.

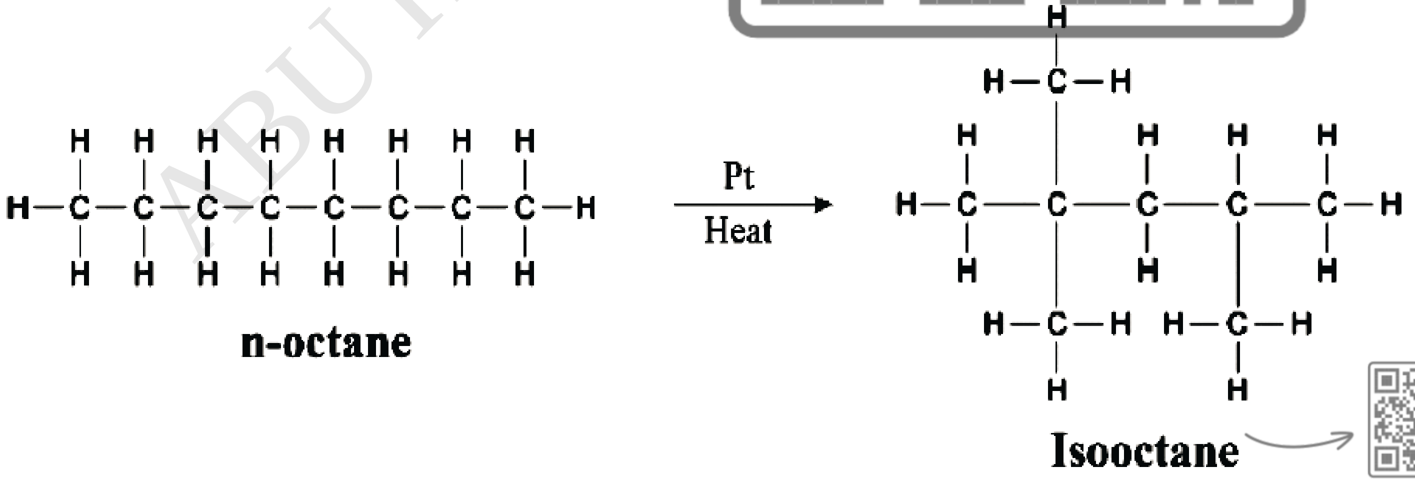
Petroleum

The term petroleum refers to rock oil or crude oil since it is a thick black liquid that oozes out of the earth (Latin words: 'petra' which means rock and 'oleum' means oil). It is a complex combination of alkanes, cycloalkanes and aromatic hydrocarbons etc.

Petroleum is formed from the ancient marine animals that were buried millions of years ago in the earth's crust. It is used for transportation, power generation and many other purposes. Some important products that are extracted from petroleum include gasoline, kerosene, diesel, naphtha, paraffin wax etc.

Reforming of Gasoline:

"The process of conversion of hydrocarbons (gasoline) with low octane rating into those with higher octane rating that can be utilized as a fuel in internal combustion engine is known as reforming". The process of reforming is carried out under high pressure and temperature using platinum catalyst.



Low quality gasoline can cause knocking when ignited in an internal combustion engine. Knocking produces a sharp sound. High quality gasoline tends to product less knocking. To measure a fuel's resistance to knocking, chemists use octane number or octane rating.

The octane number of iso-octane is 100.

The octane number of n-heptane is 0.

Previously, Tetra Ethyl Lead $(C_2H_5)_4Pb$ was used to prevent knocking. This method was banned due to toxic nature of lead.

Natural Gas

Natural gas produced by the decomposition of marine microorganisms over the millions of years.

Natural gas is a mixture of methane, ethane, propane and butane. The highest composition in natural gas is methane (85 - 90% approximately). Natural gas is a more beneficial source of energy than coal and petroleum because its combustion causes less pollution.

2. Plants and Animals

Many organic compounds are isolated from plants, animals and microbes. These are referred to as natural products. Some examples of natural products are glucose, cellulose, insulin, cholesterol, caffeine, nicotine, menthol etc.

3. Partial and Total Synthesis

Partial synthesis involves starting with a simpler molecule and modifying it through a series of chemical reactions to create a more complex target molecule.

One example of partial synthesis is the production of the anti-inflammatory drug ibuprofen from a compound called cumene. Cumene undergoes several chemical transformations, including oxidation and rearrangement to yield ibuprofen.

Total synthesis involves building a complex target molecule entirely from simple starting materials.

For example, the total synthesis of the anti-cancer drug "Taxol" involves numerous steps to construct the molecule from simple building blocks.

4. Products of Biotechnology

Biotechnology is the field of biological sciences that deals with the involvement of living organisms in preparation of valuable products.

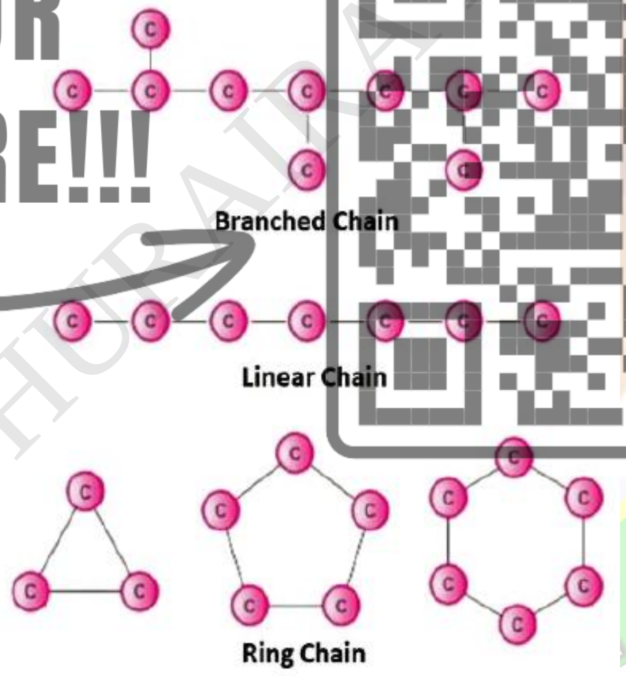
For example, ethyl alcohol is commercially manufactured by fermentation process in which certain enzymes secreted by microorganism.

CHARACTERISTICS OF ORGANIC COMPOUNDS

Catenation

The ability of carbon to form long chain and rings is called catenation.

It is due to the tetravalency and small size of carbon atom. A large number of organic compounds are there due to catenation.



Non Ionic Nature

Organic compounds are made up of carbons and a carbon atom contains four valence electrons. It does not have the ability to lose or gain four electrons since it requires very high energy. Therefore, in contrast with inorganic compounds, it forms covalent bonds by the sharing of electrons.

Solubility

The solubility of organic compounds can vary widely depending on their chemical structure and the solvent in which they are dissolved. For examples:

Water-soluble organic compounds: Organic compounds that contain polar functional groups, such as hydroxyl (-OH) or carboxyl (-COOH) groups, tend to be soluble in water due to the ability to form hydrogen bonds with water molecules. For example, ethanol (C_2H_5OH) and acetic acid (CH_3COOH) are both water-soluble organic compounds.

Nonpolar organic compounds: Nonpolar organic compounds, such as hydrocarbons, generally have low solubility in water but are soluble in nonpolar solvents like hexane or diethyl ether. For instance, hexane (C_6H_{14}) and toluene ($C_6H_5CH_3$) are nonpolar organic compounds that exhibit poor solubility in water but dissolve readily in nonpolar solvents.

Low Melting and Boiling Point

Organic compounds in comparison to inorganic compounds have lower melting and boiling points. This is due to the comparatively weak intermolecular forces found in these molecules. They exist as gases, liquids and soft solids.

Flammability

The majority of organic compounds are combustible and readily react with oxygen to form carbon dioxide and water, thereby releasing heat. As a result, most fuels are organic, such as wood, coal, oil, gasoline, and natural gas.

Reactivity

Organic compounds react at a substantially slower rate than the ionic reactions that are often found in inorganic compounds. To accelerate the reaction, they generally require heating, mixing, and a catalyst.

Isomerism

The organic compounds having same molecular formula but different molecular structures are called isomers and this phenomena is called isomerism.

For example: there are two isomers of butane: n-butane and isobutane.

n-Butane: $CH_3-CH_2-CH_2-CH_3$
Isobutane: $CH_3-CH(CH_3)-CH_3$

Polymerization

Many small organic molecules (monomers) can unite through addition or condensation process to form a single large molecule. This process is known as polymerization and the macromolecule thus formed is called as a polymer.

For example, the polymerization of terephthalic acid (A dicarboxylic acid) with ethylene glycol forms polyethylene terephthalate (PET) which is used for making plastic bottles.

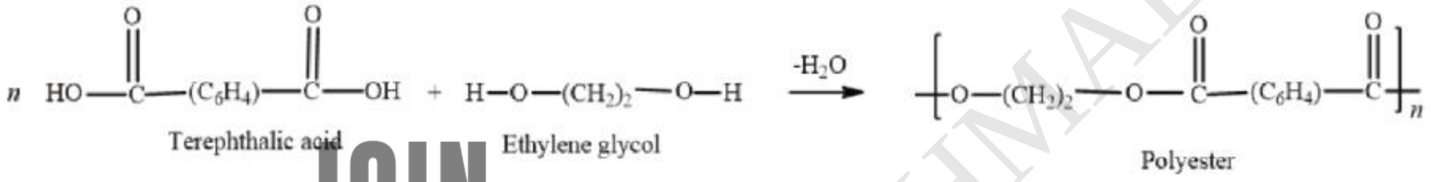
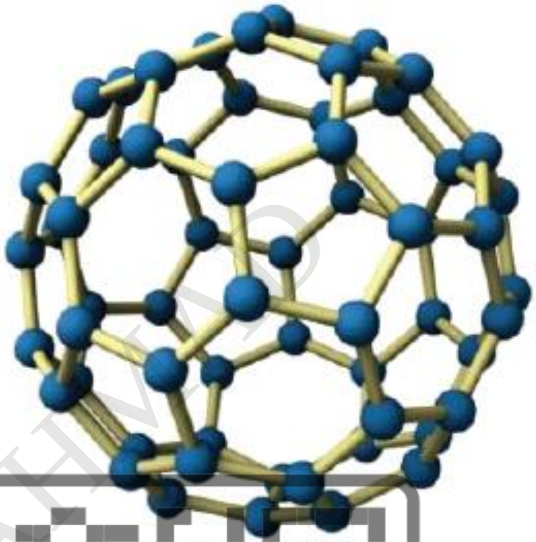


Table 3.2 **Use of common organic compounds**

Organic Compounds	Common Use
Gasoline	Fuel for automobiles
Natural gas	Domestic fuel
Ethene	Ripening of fruits
Ethyne	Gas Welding
Formalin	Preservative of biological specimen
Ethylene glycol	Antifreeze and coolant in automobiles
Phenol	Antiseptics and ink preservatives
Diethyl ether	Anaesthesia
Acetic acid	Vinegar
Ethyl acetate	Artificial flavors and essences
Acetone	Nail polish remover
Nylon	Ropes and fish nets
Poly ester	Fabrics
Carbohydrate, protein, fats, vitamins	Food components

NEW ALLOTROPIC FORM OF CARBON (BUCKY BALLS)



In **1985**, **Richard Smalley** and **Harry Kroto** introduced a new allotropic form of carbons that consist of 60 carbon atoms.

The shape of this newly discovered form of carbon was similar to the dome developed by American architect **'Richard Buckminster Fuller'**. The name of this new form of $\mathbf{C_{60}}$ was suggested as **Buckminster Fullerene** or **Bucky Ball.**

It consists of 12 fiver membered ring and 20 six membered ring.

Bucky balls are good conductors of electricity and they are used in nanotechnology.

Functional Group

Atoms or group of atoms which are responsible for all the physical and chemical properties of organic compounds is called functional group.

Class of Compound	Structure of Functional Group	Class of Compound	Structure of Functional Group
Alkane	$>C-C<$	Carboxylic acid	$-\overset{O}{\overset{\Vert}{C}}-OH$
Alkene	$>C=C<$	Ester	$-\overset{O}{\overset{\Vert}{C}}-O-$
Alkyne	$-C\equiv C-$	Nitrile	$-C\equiv N$
Alcohol	$-OH$	Thiol	$-SH$
Ether	$-O-$	Alkyl Halide	$-X$
Amine	$-NH_2$		
Aldehyde	$-\overset{O}{\overset{\Vert}{C}}-H$	Acyl halide	$-\overset{O}{\overset{\Vert}{C}}-X$
Ketone	$-\overset{O}{\overset{\Vert}{C}}-$	Amide	$-\overset{O}{\overset{\Vert}{C}}-NH_2$

Homologous Series

The consecutive members of organic compounds differ with a fix ratio of CH_2 forming a series of compound which is called homologous series.

The general characteristics of homologous series are given below:

(i) The composition of all the members of a homologous series can be expressed by a general formula.

Alkane	C_nH_{2n+2}	Alcohol	$C_nH_{2n+1}OH$
Alkene	C_nH_{2n}	Alkyl halide	$C_nH_{2n+1}X$
Alkynes	C_nH_{2n-2}	Amine	$C_nH_{2n+1}NH_2$

(ii) The molecular mass of each member of homologous series differs from the next higher or lower member by **14 a.m.u.**

(iii) All the members of homologous series show similar chemical properties due to the presence of similar functional group.

(iv) There is a gradual variation in the physical properties such as physical state, solubility, melting and boiling points etc as the number of carbon atoms per molecule increases.

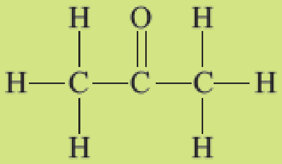
Self Assessment

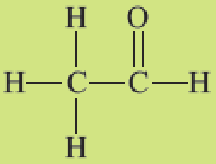
➤ Write the names of ten organic compounds used in daily life.

1) Sugar	6) Diesel
2) Glucose	7) Paraffin Wax
3) Vinegar	8) Polyethene
4) Methane gas	9) Paracetamol
5) Gasoline	10) Aspirin

Self Assessment

Predict the functional group present in the structures given below:


(a)


(b)

a) Ketone functional group is present   b) Aldehyde functional group is present

Self Assessment

Write down the general molecular formula of the homologous series of ethers and alcohols.

General formula of ethers is **$C_nH_{2n+2}O$**

General formula of alcohols is **$C_nH_{2n+2}O$**

Multiple Choice Questions

(i) The functional group that contains a nitrogen atom is:

(a) Alcohol (b) Ketone

(c) Ester [✓ (d) Amide]

(ii) The compound belongs to the alkene family is:

(a) CH_4 (b) C_2H_6

(c) C_3H_8 [✓ (d) C_2H_4]

(iii) Destructive distillation of coal gives coke, coaltar, coal gas and:

(a) Natural gas (b) Petroleum

(c) Naphtha [✓ (d) Ammonia liquor]

(iv) The knocking of internal combustion engine can be reduced by the following petroleum process:

[✓ (a) Reforming] (b) Refining

(c) Distillation (d) Condensation

(v) The general formula of the homologous series of alcohol is:
(a) C_nH_{2n}
(b) C_nH_{2n+2}
[✓ (c) $C_nH_{2n+1}OH$]
(d) $C_nH_{2n-1}OH$

(vi) The number of five membered and six membered rings in C_{60} Bucky ball are respectively:
(a) 12 and 12
(b) 5 and 15
[✓ (c) 12 and 20]
(d) 40 and 20

(vii) The pair of compounds that exhibit isomerism is:
(a) C_2H_5-OH and C_3H_7-OH
[✓ (b) CH_3-CH_2-CH_2-CH_3 and CH_3-CH(CH_3)-CH_3]
(c) C_2H_5-CH_2-Cl and C_3H_7-CH_2-Cl
(d) CH_3-NH_2 and CH_3-CH_2-NH_2

(viii) The type of coal that is hard and high ranked is:
(a) Peat
(b) Lignite
(c) Bituminous
[✓ (d) Anthracite]

(ix) Which of the following hydrocarbon is the chief constituent of natural gas?
[✓ (a) CH_4]
(b) C_2H_6
(c) C_3H_8
(d) C_4H_{10}

(x) Urea was first synthesized by Wohler from an inorganic material named as:
(a) Ammonium nitrate
(b) Ammonium chloride
[✓ (c) Ammonium cyanate]
(d) Ammonium bicarbonate

CHAPTER
4

NOMENCLATURE OF ORGANIC COMPOUNDS

Usefulness of IUPAC System

The IUPAC system continues to hold great significance in modern science society and technology for several key reasons.

(i) It plays a crucial role by offering a uniform language to chemists globally.

(ii) The established rules and guidelines for organic compounds enable advancement in research and sharing of scientific knowledge among scientists.

HYDROCARBONS

Number of carbon atoms in chain	Prefixes	Alkane	Alkene	Alkyne
1	Meth-	Methane		
2	Eth-	Ethane	Ethene	Ethyne
3	Prop-	Propane	Propene	Propyne
4	But-	Butane	Butene	Butyne
5	Pent-	Pentane	Pentene	Pentyne
6	Hex-	Hexane	Hexene	Hexyne
7	Hept-	Heptane	Heptene	Heptyne
8	Oct-	Octane	Octene	Octyne
9	Non-	Nonane	Nonene	Nonyne
10	Dec-	Decane	Decene	Decyne
11	Undec-	Undecane	Undecene	Undecyne
12	Dodec-	Dodecane	Dodecene	Dodecyne

NOMENCLATURE OF ALKANES

Common System

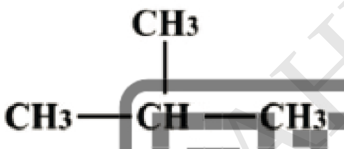
(i) The prefix n- is utilized for alkanes where all the carbon atoms are arranged in a single uninterrupted straight chain.

(ii) The prefix Iso- is utilized if in the structure of alkane molecule one branch (e.g. $-CH_3$) is attached to the second last carbon atom of the chain.

(iii) The prefix Neo- is utilized if two branches are attached on the second last carbon of alkanes.

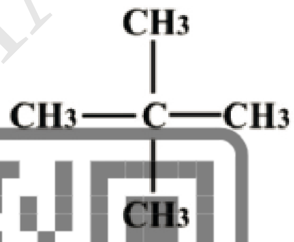
$CH_3-CH_2-CH_2-CH_3$

(n-Butane)



$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_3$

(Isobutane)



$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

(Neopentane)

IUPAC System

(i) Select the longest continuous carbon chain in the molecule and number the carbon chain from one of its terminal. The name of the chain is retained as propane, butane, pentane, hexane etc.

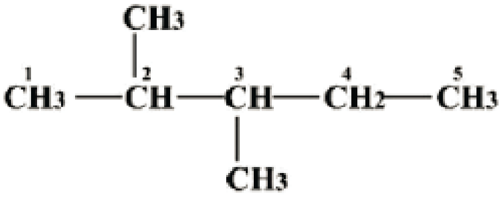
(ii) The numbering of carbon chain should be assigned, starting from the terminal where functional group or an alkyl group (substituent) is nearest.

(iii) If the identical substituents are attached at the same position from both ends of main carbon chain, numbering can be done from either terminal. However, if the identical substituents are attached at different positions, the numbering should be done from the side where the substituent is nearer.

(iv) When two different substituents are attached at the same position from either side of the carbon chain, the numbering of chain is determined from the terminal where the substituent with the lower alphabetical order is nearer.

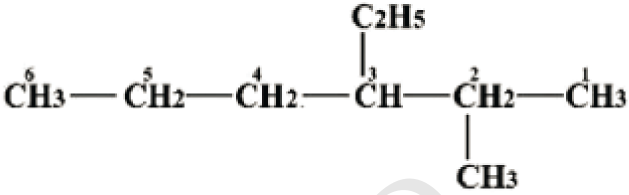
(v) When two or more same substituents are attached to the carbon chain, indicate the quantity of each substituent by using di, tri and so forth.

(vi) Prefix cyclo is used to name cycloalkanes.



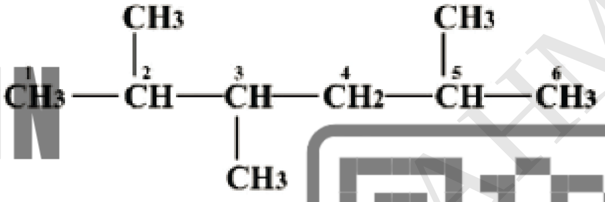
$$\overset{1}{C}H_3-\overset{2}{C}H(CH_3)-\overset{3}{C}H(CH_3)-\overset{4}{C}H_2-\overset{5}{C}H_3$$

(2, 3-Dimethylpentane)



$$\overset{6}{C}H_3-\overset{5}{C}H_2-\overset{4}{C}H_2-\overset{3}{C}H(C_2H_5)-\overset{2}{C}H(CH_3)-\overset{1}{C}H_3$$

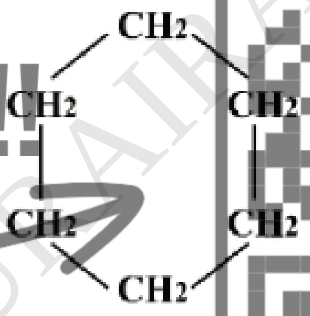
(3-Ethyl-2-methylhexane)



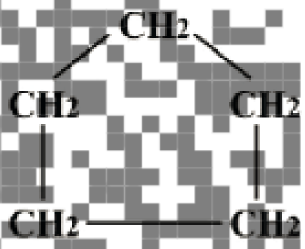
$$\overset{1}{C}H_3-\overset{2}{C}H(CH_3)-\overset{3}{C}H(CH_3)-\overset{4}{C}H_2-\overset{5}{C}H(CH_3)-\overset{6}{C}H_3$$

(2, 3, 5-Trimethylhexane)

(Cyclobutane)



(Cyclohexane)



(Cyclopentane)

NOMENCLATURE OF ALKENES

Common system

In common system, alkenes are named by replacing the suffix "ane" with "ylene" for example ethylene, propylene, butylene.

$CH_2 = CH_2$
(Ethylene)

$CH_3 - CH = CH_2$
(Propylene)

An alternative way of naming alkenes is by considering them as derivatives of ethylene.

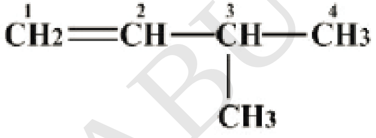
For example

$C_2H_5 - CH = CH - C_2H_5$
(Diethylethylene)

$CH_3 - CH = CH_2$
(Methylethylene)

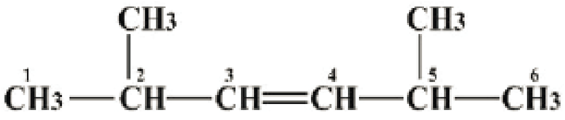
IUPAC System

(i) Select the longest carbon chain which must contain double bonded carbon atoms.
(ii) The numbering of the longest chain starts from that end nearest to the carbon-carbon double bond irrespective of the location of alkyl radicals.
(iii) Indicate the position of double bond by specifying the location of carbon atoms involved in the double bond.
(iv) If there are more than one double bonds present within the carbon chain they are indicated by adding the prefixes di, tri etc. before the suffix "ene".



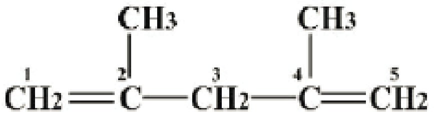
$\overset{1}{C}H_2=\overset{2}{C}H-\underset{\displaystyle CH_3}{\overset{3}{C}H}-\overset{4}{C}H_3$

(3-Methyl-1-butene)



$\overset{1}{C}H_3-\overset{\displaystyle CH_3}{\overset{2}{C}H}-\overset{3}{C}H=\overset{4}{C}H-\overset{\displaystyle CH_3}{\overset{5}{C}H}-\overset{6}{C}H_3$

(2, 5-Dimethyl-3-hexene)



$\overset{1}{C}H_2=\overset{\displaystyle CH_3}{\overset{2}{C}}-\overset{3}{C}H_2-\overset{\displaystyle CH_3}{\overset{4}{C}}=\overset{5}{C}H_2$

(2, 4-Dimethyl-1, 4-pentadiene)

NOMENCLATURE OF ALKYNES

Common System

$HC \equiv CH$
(Acetylene)

$H_3C - C \equiv CH$
(Methylacetylene)

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

$C_2H_5 - C \equiv C - CH_3$
(Ethylmethylacetylene)

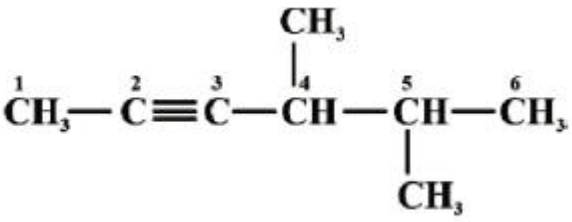
$CH_2 = CH - C \equiv C - CH = CH_2$
(Divinylacetylene)

IUPAC System

(i) Select the longest continuous carbon chain which must include both the carbon atoms containing triple bond.
(ii) The numbering of carbon chain starts from the terminal which is nearest to the carbon-carbon triple bond.
(iii) Write the name of parent alkanes for the same number of carbon atoms, replacing suffix “ane” with “yne” to indicate the presence of triple bond.
(iv) Indicate the position of triple bond by specifying the location of the carbon atom involved in the bond.
(v) If two or more triple bond are present in the chain then they are indicated by adding the prefix di, tri etc. before the suffix -yne.
(vi) When both double and triple bonds are present in the molecule at different positions then the numbering starts from the end where the bond (double or triple) is nearest.
(vii) When double and triple bonds are present in the molecule at equal positions from the end, then the preference of numbering is given to double bond.

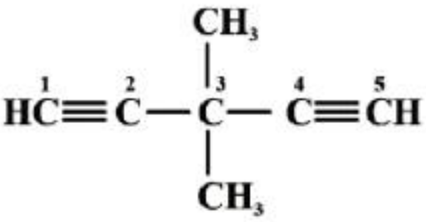
$\overset{1}{C}H_3-\overset{2}{C}\equiv\overset{3}{C}-\overset{4}{C}H_3$

(2-Butyne)



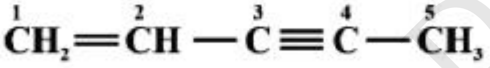
$\overset{1}{C}H_3-\overset{2}{C}\equiv\overset{3}{C}-\overset{CH_3}{\overset{|}{\overset{4}{C}H}}-\underset{\underset{CH_3}{|}}{\overset{5}{C}H}-\overset{6}{C}H_3$

(4,5-Dimethyl-2-hexyne)



$H\overset{1}{C}\equiv\overset{2}{C}-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{\overset{3}{C}}}}-\overset{4}{C}\equiv\overset{5}{C}H$

(3,3-Dimethyl-1, 4-pentadiyne)



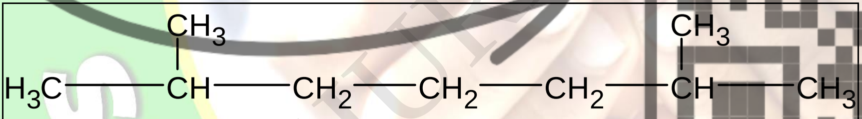
$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}\equiv\overset{4}{C}-\overset{5}{C}H_3$

(1- Pentene-3-yne)

Self Assessment

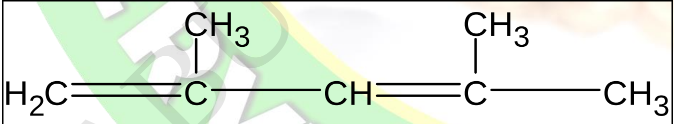
Name the following compounds by IUPAC method.

- $(CH_3)_2\,CH-(CH_2)_3-CH(CH_3)_2$
- $CH_2=C(CH_3)-CH=C(CH_3)-CH_3$
- $CH\equiv C-CH_2-C\equiv C-CH_3$
- $CH_2=C(CH_3)-CH_2-C\equiv CH$



$H_3C-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_3$

2,6-dimethylheptane

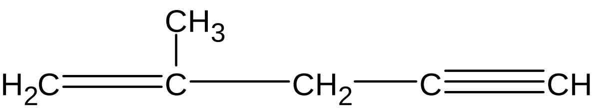


$H_2C=\overset{CH_3}{\overset{|}{C}}-CH=\overset{CH_3}{\overset{|}{C}}-CH_3$

2,4-dimethylpenta-1,3-diene

$HC\equiv C-CH_2-C\equiv C-CH_3$

hexa-1,4-diyne



$H_2C=\overset{CH_3}{\overset{|}{C}}-CH_2-C\equiv CH$

2-methylpent-1-en-4-yne

NOMENCLATURE OF ALKYL HALIDES

Alkyl halides are the derivatives of alkanes in which one or more hydrogen of alkanes are replaced by halogen atom.

Common System

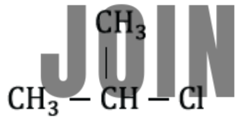
The common name of an alkyl halide is formed by naming the alkyl group first, followed by the term "halide".

CH_3-Cl **(Methyl chloride)**

CH_3-CH_2-Br **(Ethyl bromide)**

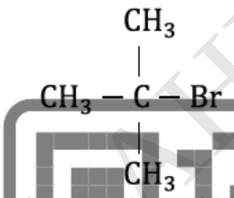
$CH_3-CH_2-CH_2-I$ **(Propyl iodide)**

The term secondary (sec.) and tertiary (tert.) are used as prefix if the carbon atom bonded to halogen is further attached to two and three other carbon atoms respectively.



$$CH_3-\overset{\displaystyle CH_3 \atop |}{CH}-Cl$$

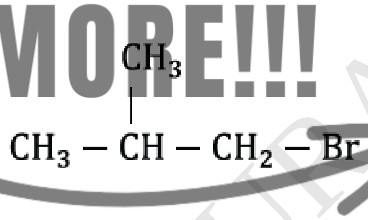
(sec-Propyl chloride)



$$CH_3-\overset{\displaystyle CH_3 \atop |}{\underset{| \atop \displaystyle CH_3}{C}}-Br$$

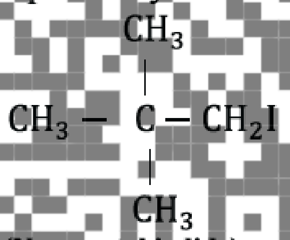
(tert-Butyl bromide)

The term iso and neo are also used as prefix when penultimate carbon is further attached to two or three other carbon atoms respectively.



$$CH_3-\overset{\displaystyle CH_3 \atop |}{CH}-CH_2-Br$$

(Isobutyl bromide)



$$CH_3-\overset{\displaystyle CH_3 \atop |}{\underset{| \atop \displaystyle CH_3}{C}}-CH_2I$$

(Neo pentyl iodide)

IUPAC System

(i) Determine the longest carbon chain that contains the carbon atom directly bonded to halogen.

(ii) Number the carbon atoms in the chain from the end closest to the halogen atom.

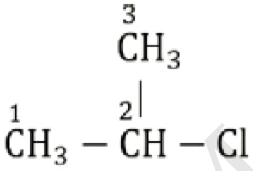
(iii) When a double or triple bond is present in the halogenated carbon chain it is recommended to number the chain from the end nearest to the double or triple bond.

(iv) Prefix di, tri, tetra etc are used to indicate the number of halogens attached to the main carbon chain.

(v) When two different halogens are attached to the carbon chain at the same position from opposite ends, the halogen name will be written by its alphabetical order.

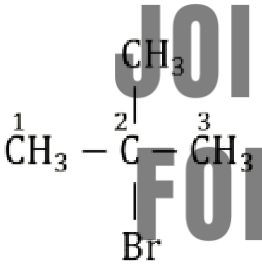
$CH_3 - CH_2 - Br$

(Bromoethane)



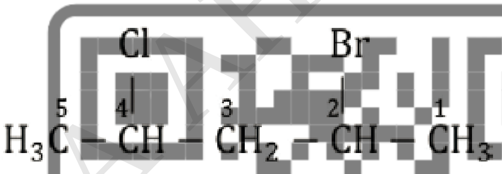
$\overset{1}{CH_3} - \overset{\overset{3}{CH_3}}{\overset{|}{\overset{2}{CH}}} - Cl$

(2-Chloropropane)



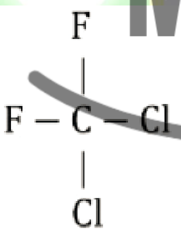
$\overset{1}{CH_3} - \underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{\overset{2}{C}}} - \overset{3}{CH_3}$

(2-Bromo-2-methylpropane)



$H_3\overset{5}{C} - \overset{\overset{Cl}{|}}{\overset{4}{CH}} - \overset{3}{CH_2} - \overset{\overset{Br}{|}}{\overset{2}{CH}} - \overset{1}{CH_3}$

(2-Bromo-4-chloropentane)



$F - \underset{\underset{Cl}{|}}{\overset{\overset{F}{|}}{C}} - Cl$

(Dichlorodifluromethane)

NOMENCLATURE OF AMINES

Amines are organic compounds that contain a nitrogen atom bonded to one or more alkyl or aryl groups. Primary amines contains one alkyl group bonded to the nitrogen atom while secondary and tertiary amine are identified by the direct attachment of two and three alkyl groups with the nitrogen atom respectively.

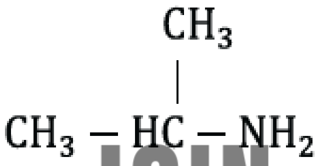
Common System

The common name of a primary amine is formed by combining the name of alkyl group with the suffix “amine”.

$CH_3 - NH_2$
(Methyl amine)

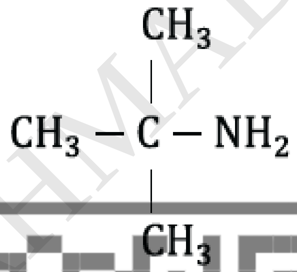
$CH_3 - CH_2 - NH_2$
(Ethyl amine)

The prefix sec. and tert. are used if the carbon atom bonded to nitrogen is further attached with two or three alkyl radicals.



$$CH_3 - \overset{\overset{CH_3}{|}}{HC} - NH_2$$

(sec-Propyl amine)



$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - NH_2$$

(tert-Butyl amine)

IPUAC System

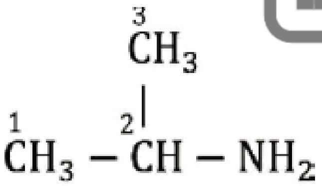
In IUPAC system, primary amines are named as alkanamine

(i) Select the longest carbon chain that contain the carbon atom directly bonded to $-NH_2$ group.

(ii) Write the name of compound by replacing the ending “e” of alkane chain by adding the suffix “amine”.

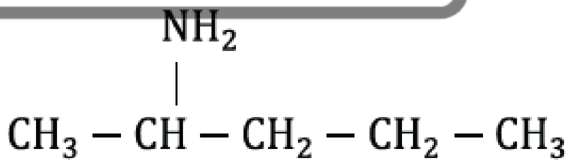
$CH_3 - CH_2 - NH_2$

(Ethanamine)



$$\overset{1}{CH_3} - \overset{\overset{\overset{3}{CH_3}}{|}}{\overset{2}{CH}} - NH_2$$

(2-Propanamine)



$$CH_3 - \overset{\overset{NH_2}{|}}{CH} - CH_2 - CH_2 - CH_3$$

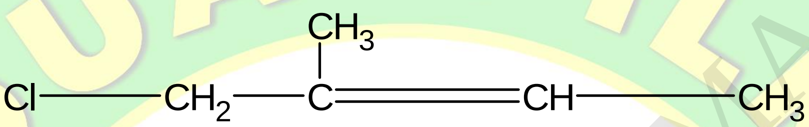
(2-Pentanamine)

Self Assessment

Write the structure of the following organic compounds.

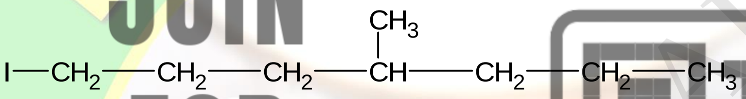
- 1-chloro-2-methyl-2-butene
- Neobutyl iodide
- 1-iodo-4-methylheptane
- 3-methyl-2-butanamine

- 1-chloro-2-methyl-2-butene



$$Cl-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_3$$

- 1-iodo-4-methylheptane

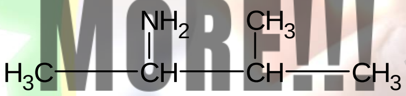


$$I-CH_2-CH_2-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2-CH_3$$

- Neobutyl iodide

This structure is not possible.

- 3-methyl-2-butanamine



$$H_3C-\overset{NH_2}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH_3$$

NOMENCLATURE OF ALCOHOLS

Organic compounds that contain one or more hydroxyl (-OH) functional group attached to the carbon chain are called alcohols.

Common System

Since alcohols are hydroxyl derivatives of hydrocarbons, their common names are formed by combining the name of alkyl group with the suffix "alcohol".

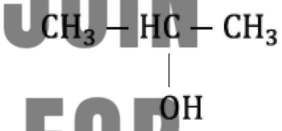
$CH_3 - OH$

(Methyl alcohol)

$CH_3 - CH_2 - CH_2 - OH$

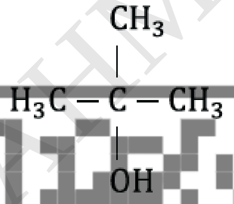
(Propyl alcohol)

If the carbon atom bearing the hydroxyl group is directly connected to two or three other carbon atoms, the term secondary and tertiary is used as a prefix.



$$CH_3 - \underset{\displaystyle OH}{\underset{|}{HC}} - CH_3$$

(sec-Propyl alcohol)



$$H_3C - \underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}} - CH_3$$

(tert-Butyl alcohol)

IUPAC System

The set of rules established by IUPAC system for the naming of alcohol is given as follow:

(i) Identify the longest continuous carbon chain that include the carbon atom bearing the hydroxyl group (-OH).

(ii) Number the carbon atoms in the chain starting from the end nearest to the hydroxyl group.

(iii) The end "e" of the parent alkane is replaced by "ol".

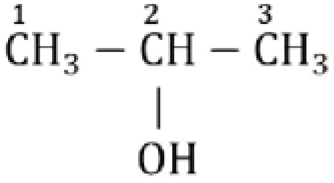
(iv) If the molecule of alcohol has substituents (CH_3, C_2H_5, Br, Cl, I etc), name them as prefixes.

(v) If two or more hydroxyl groups are present in the carbon chain, use di, tri etc. before the suffix "-ol".

(vi) The positions of substituents should be written in alphabetical order.

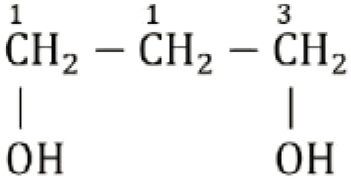
$CH_3 - CH_2 - OH$

(Ethanol)



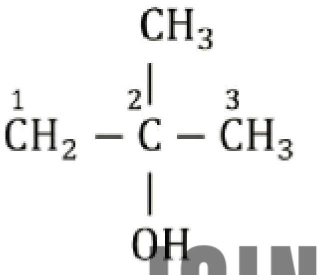
$$\overset{1}{C}H_3 - \underset{\displaystyle OH}{\overset{2}{C}H} - \overset{3}{C}H_3$$

(2-Propanol)



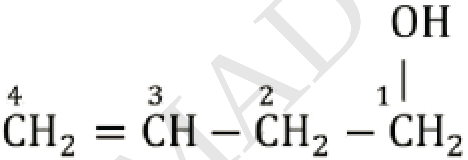
$$\underset{\displaystyle OH}{\overset{1}{C}H_2} - \overset{1}{C}H_2 - \underset{\displaystyle OH}{\overset{3}{C}H_2}$$

(1, 3-Propandiol)



$$\overset{1}{C}H_2 - \underset{\displaystyle OH}{\overset{\displaystyle CH_3}{\overset{2}{C}}} - \overset{3}{C}H_3$$

(2-Methyl-2-propanol)

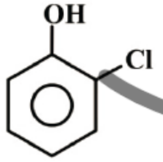


$$\overset{4}{C}H_2 = \overset{3}{C}H - \overset{2}{C}H_2 - \overset{\displaystyle OH}{\overset{1}{C}H_2}$$

(3-Buten-1-ol)

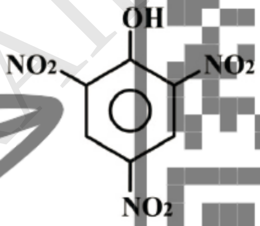
NOMENCLATURE OF PHENOLS

The class of organic compounds in which one or more hydroxyl group are lirectly attached with the benzene ring are called as phenols.

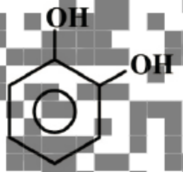


(2-Chlorophenol)
(o-Chlorophenol)

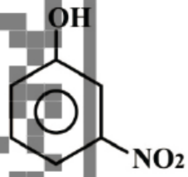
(4-Methylphenol)
(p-Cresol)



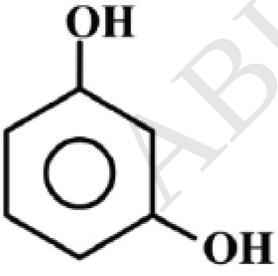
(2, 4, 6-Trinitrophenol)
(Picric acid)



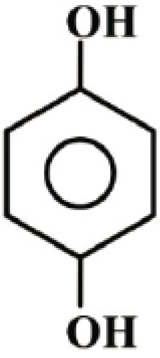
(1, 2-Benzenediol)
(Catechol)



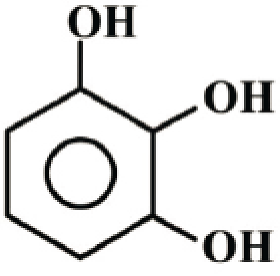
(3-Nitrophenol)
(m-Nitrophenol)



(1, 3-Benzenediol)
(Resorcinol)



(1, 4-Benzenediol)
(Hydroquinone)



(1, 2, 3-Benzenetriol)
(Pyrogallol)

NOMENCLATURE OF ETHERS

Ether is a family of organic compounds in which two alkyl or aryl radicals are attached to an oxygen atom. These compounds are represented by R–O–R'.

Common System

In the common system of naming of ethers, the two alkyl groups are written in alphabetical order and the term ether is added at the end of the name.

$CH_3 - O - C_2H_5$ **(Ethyl methyl ether)**

$C_2H_5 - O - C_2H_5$ **(Diethyl ether)**

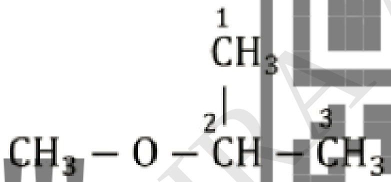
$C_6H_5 - O - CH_3$ **(Methyl phenyl ether)**

IUPAC System

In IUPAC system of nomenclature, ethers are referred to as alkoxy derivatives of alkanes. The alkyl group of larger number of carbon atoms is considered as the main carbon chain whereas the smaller alkyl group, along with its oxygen is named as alkoxy group. The alkoxy group is taken as prefix.

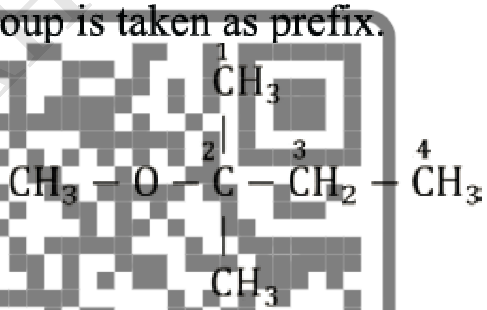
$CH_3 - O - CH_2 - CH_3$

(Methoxyethane)



$$CH_3 - O - \overset{\overset{1}{CH_3}\,|}{\overset{2}{CH}} - \overset{3}{CH_3}$$

(2-Methoxypropane)



$$CH_3 - O - \underset{|\,CH_3}{\overset{\overset{1}{CH_3}\,|}{\overset{2}{C}}} - \overset{3}{CH_2} - \overset{4}{CH_3}$$

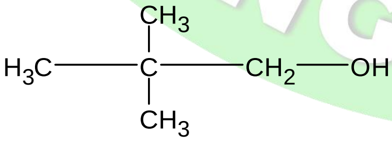
(2-Methoxy-2-methylbutane)

Self Assessment

Write the structure of the following organic compounds.

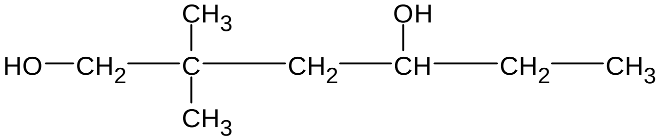
- Neopentyl alcohol
- Ethyl, tert-butyl ether
- 2,2-Dimethyl-1,4 hexandiol
- 2,4,6-Tribromophenol

- Neopentyl alcohol



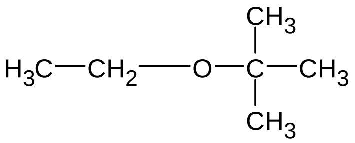
$$H_3C - \underset{|\,CH_3}{\overset{CH_3\,|}{C}} - CH_2 - OH$$

- 2,2-dimethyl-1,4-hexandiol

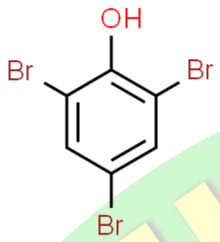


$$HO - CH_2 - \underset{|\,CH_3}{\overset{CH_3\,|}{C}} - CH_2 - \overset{OH\,|}{CH} - CH_2 - CH_3$$

- Ethyl tert-butyl ether



- 2,4,6-tribromophenol



NOMENCLATURE OF ALDEHYDES AND KETONES

Aldehydes and ketones are characterized by the presence of a carbonyl group. ($>$C=O). Aldehydes have carbonyl group at the end of carbon chain whereas ketones have the carbonyl group within the carbon chain.

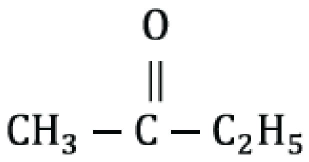
Common System

Latin Number + Aldehyde

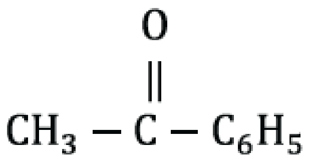
Latin Numbers (1=form, 2=acet, 3=propion, 4=butyr, 5=valer, 6=capro)

Aldehyde
$H-\overset{\overset{O}{\|}}{C}-H$ **(Formaldehyde)**
$CH_3-\overset{\overset{O}{\|}}{C}-H$ **(Acetaldehyde)**

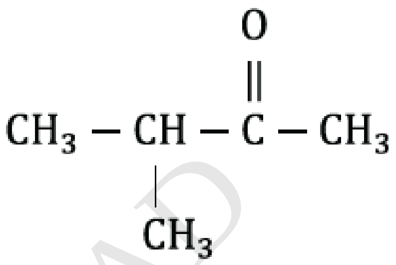
The common naming system of ketones is quite similar to that of ether. The two alkyl groups attached to the carbonyl carbon are named in alphabetical order and the term ketone is added at the end of the name.


$CH_3-\overset{\overset{O}{\|}}{C}-C_2H_5$

(Ethyl methyl ketone)


$CH_3-\overset{\overset{O}{\|}}{C}-C_6H_5$

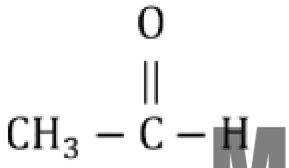
(Methyl phenyl ketone)


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

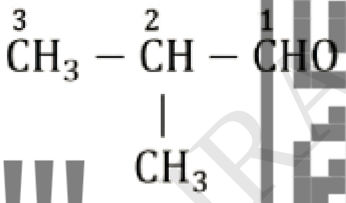
(Methyl isopropyl ketone)

IUPAC System

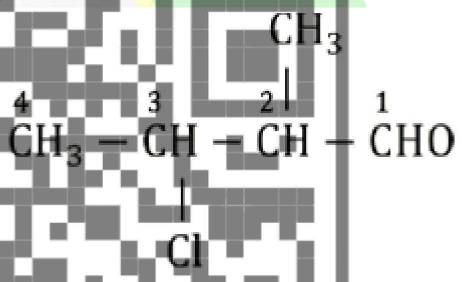
General IUPAC name of aldehydes is Alkanal in which we count all the carbon atoms.


$CH_3-\overset{\overset{O}{\|}}{C}-H$

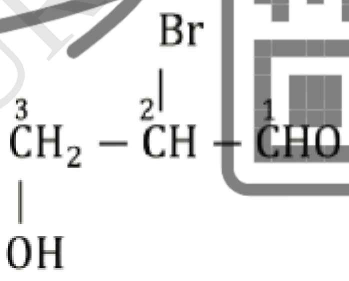
(Ethanal)


$\overset{3}{C}H_3-\underset{\underset{CH_3}{|}}{\overset{2}{C}H}-\overset{1}{C}HO$

(2-Methylpropanal)

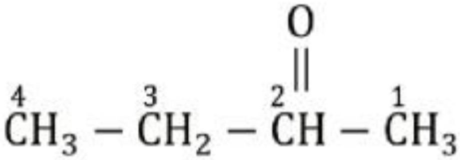

$\overset{4}{C}H_3-\underset{\underset{Cl}{|}}{\overset{3}{C}H}-\overset{\overset{CH_3}{|}}{\overset{2}{C}H}-\overset{1}{C}HO$

(3-Chloro-2-methylbutanal)


$\underset{\underset{OH}{|}}{\overset{3}{C}H_2}-\overset{\overset{Br}{|}}{\overset{2}{C}H}-\overset{1}{C}HO$

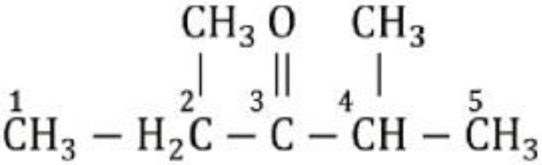
(2-Bromo-3-hydroxypropanal)

General IUPAC name of ketones is **propanone** in which we count all the carbon atoms.



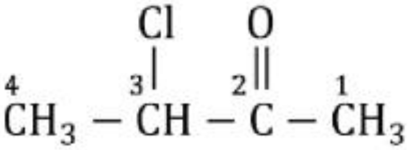
$$\overset{4}{C}H_3 - \overset{3}{C}H_2 - \overset{\overset{\displaystyle O}{\|}}{\overset{2}{C}H} - \overset{1}{C}H_3$$

(2-Butanone)



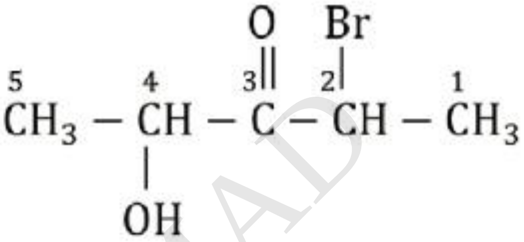
$$\overset{1}{C}H_3 - \overset{\overset{\displaystyle CH_3}{|}}{H_2\overset{2}{C}} - \overset{\overset{\displaystyle O}{\|}}{\overset{3}{C}} - \overset{\overset{\displaystyle CH_3}{|}}{\overset{4}{C}H} - \overset{5}{C}H_3$$

(2, 4-Dimethyl-3-pentanone)



$$\overset{4}{C}H_3 - \overset{\overset{\displaystyle Cl}{|}}{\overset{3}{C}H} - \overset{\overset{\displaystyle O}{\|}}{\overset{2}{C}} - \overset{1}{C}H_3$$

(3-Chloro-2-butanone)



$$\overset{5}{C}H_3 - \underset{\underset{\displaystyle OH}{|}}{\overset{4}{C}H} - \overset{\overset{\displaystyle O}{\|}}{\overset{3}{C}} - \overset{\overset{\displaystyle Br}{|}}{\overset{2}{C}H} - \overset{1}{C}H_3$$

(2-Bromo-4-hydroxy-3-pentanone)

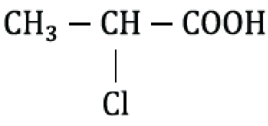
NOMENCLATURE OF CARBOXYLIC ACIDS

Organic compounds which contain carboxyl group (-COOH) are known as carboxylic acids.

Common System

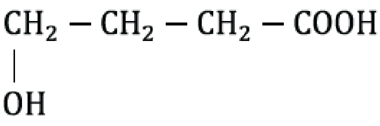
Structure	Common name
$HCOOH$	Formic acid
CH_3COOH	Acetic acid
CH_3CH_2COOH	Propionic acid
$CH_3(CH_2)_2COOH$	Butyric acid
$CH_3(CH_2)_3COOH$	Valeric acid
$CH_3(CH_2)_4COOH$	Caproic acid

Common names of carboxylic acid are given as



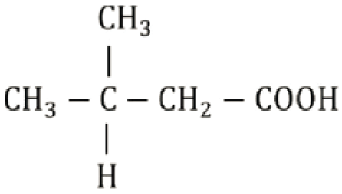
$$CH_3 - \underset{\underset{\displaystyle Cl}{|}}{CH} - COOH$$

(∝-Chloro propionic acid)



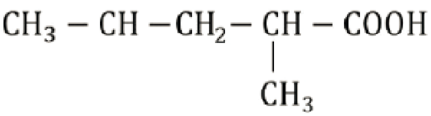
$$\underset{\underset{\displaystyle OH}{|}}{CH_2} - CH_2 - CH_2 - COOH$$

(γ-Hydroxy butyric acid)



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

(β-Methyl butyric acid)

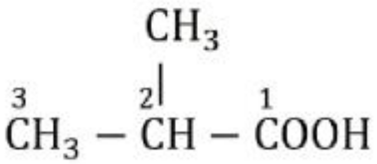


$$CH_3 - CH - CH_2 - \underset{\underset{\displaystyle CH_3}{|}}{CH} - COOH$$

(∝, β-Dimethyl valeric acid)

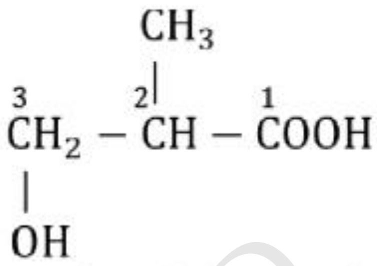
IUPAC System

The name of carboxylic acid in IUPAC system is referred as alkanoic acid.



$\overset{3}{C}H_3 - \overset{\overset{CH_3}{|}}{\overset{2}{C}H} - \overset{1}{C}OOH$

(2-Methyl propanoic acid)

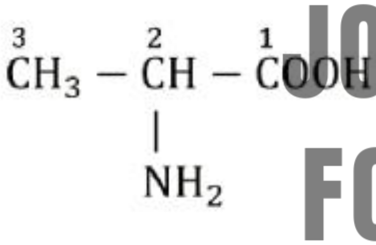


$\underset{\underset{OH}{|}}{\overset{3}{C}H_2} - \overset{\overset{CH_3}{|}}{\overset{2}{C}H} - \overset{1}{C}OOH$

(3-Hydroxy-2-methyl propanoic acid)

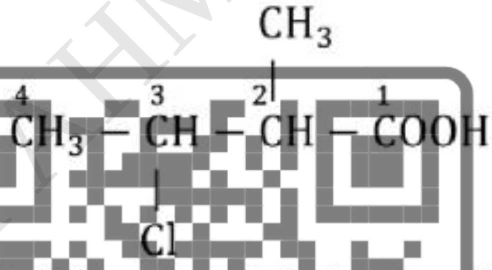
$HOO\overset{4}{C} - \overset{3}{C}H = \overset{2}{C}H - \overset{1}{C}OOH$

(2-Buten-1,4dioic acid)



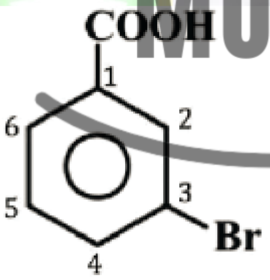
$\overset{3}{C}H_3 - \underset{\underset{NH_2}{|}}{\overset{2}{C}H} - \overset{1}{C}OOH$

(2-Aminopropanoic acid)

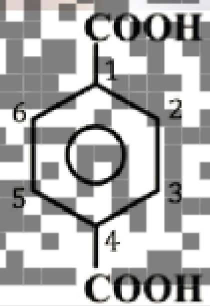


$\overset{4}{C}H_3 - \underset{\underset{Cl}{|}}{\overset{3}{C}H} - \overset{\overset{CH_3}{|}}{\overset{2}{C}H} - \overset{1}{C}OOH$

(3-Chloro-2-methylbutanoic acid)



(3-Bromobenzoic acid)

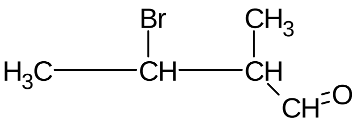


(Benzen-1, 4-dioic acid)

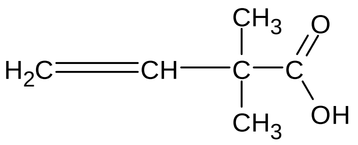
Self Assessment

Write the IUPAC name of the following molecules.

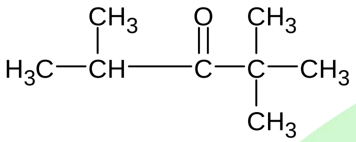
- $CH_3 - CH(Br) - CH(CH_3) - CHO$
- $CH_2 = CH - C(CH_3)_2 - COOH$
- $(CH_3)_2\,CH - CO - C(CH_3)_3$
- $HOOC - CH_2 - HC = CHCOOH$



3-bromo-2-methylbutanal

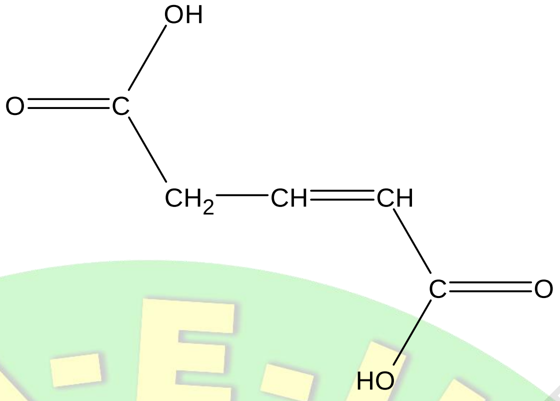


2,2-dimethylbut-3-enoic acid



$H_3C-CH(CH_3)-C(=O)-C(CH_3)_2-CH_3$

2,2,4-trimethylpentan-3-one



pent-2-enedioic acid

NOMENCLATURE OF ESTERS

Structure of Ester	Common Name	IUPAC Name
$HCOOC_2H_5$	Ethyl formate	Ethyl methanoate
$CH_3-CH_2-COO-CH_3$	Methyl propionate	Methyl propanoate
$CH_3(CH_2)_2COOC_2H_5$	Ethyl butyrate	Ethyl butanoate
$CH_3COOCH(CH_3)_2$	Isopropyl acetate	Isopropyl ethanoate

NOMENCLATURE OF AMIDE

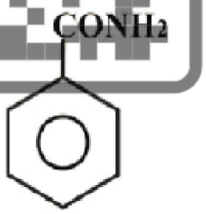
Amides are the derivate of carboxylic acids formed by replacing –OH group of carboxylic acid by –NH_2 group. The nomenclature of amide is based on replacing the suffix -oic acid with amide. For example

$CH_3-CH_2-CONH_2$

(Propanamide)

$CH_3-(CH_2)_2-CONH_2$

(Butanamide)



(Benzamide)

NOMENCLATURE OF ACYL HALIDES

Acyl halides or acid halides are derived from carboxylic acids.

$CH_3-CH_2-CO-Br$

Propanoyl bromide (IUPAC)

Propionyl bromide (common)

CH_3-COCl

Ethanoyl chloride (IUPAC)

Acetyl chloride (common)

Multiple Choice Questions

(i) Which of the following molecule possess acyl functional group:

[✓ (a) R-CO-X]
(b) $R\text{-}CONH_2$
(c) $R\text{-}COO\text{-}CH_3$
(d) R-CO-R

(ii) A hydrocarbon with the molecular formula C_7H_{12} is possibly:

(a) Heptane
(b) Heptene
[✓ (c) Heptyne]
(d) Hepta diene

(iii) An organic compound possesses the structural formula $CH_3CH = CH - C \equiv CH$, its correct IUPAC name is:

(a) 1-pentyne-3-ene
(b) 3-pentene-1-pentyne
[✓ (c) 3-penten-1-yne]
(d) 2-pentene-3-yne

(iv) IUPAC name of isopropyl alcohol is:

(a) 1-propanol
[✓ (b) 2-propanol]
(c) 1-butanol
(d) 2-butanol

(v) Resorcinol is a phenol, it contains two –OH groups at:

(a) Position 1 and 2
[✓ (b) Position 1 and 3]
(c) Position 1 and 4
(d) Position 2 and 4

(vi) Formula of a saturated hydrocarbon is C_4H_8, it should be:
(a) Butane
(b) Butene
(c) Butyne
[✓ (d) Cyclobutane]

(vii) In the IUPAC naming of ketones the ending –e of main carbon chain is replaced by:
(a) yl
(b) ol
(c) al
[✓ (d) one]

(viii) In the common system, carboxylic acid with six carbon atoms in straight chain is named as:
(a) propionic acid
(b) valeric acid
[✓ (c) caproic acid]
(d) steric acid

(ix) The correct structure of 1, 3-penta diene is:
(a) $H_3C-CH=CH-HC=CH_2-CH_3$
(b) $CH_2=CH-CH_2-CH=CH_2$
[✓ (c) $CH_2=CH-HC=CH-CH_3$]
(d) $CH_3-CH=C=CH-CH_3$

(x) The IUPAC name of $CH_3COOCH(CH_3)_2$ is:
(a) propyl ethanoate
(b) ethyl propanoate
(c) isopropyl acetate
[✓ (d) isopropyl ethanoate]

Short Questions

1. Why IUPAC system of nomenclature is preferred on common system of naming of organic compounds?

Ans.

- The IUPAC system of naming has provided unique names for more than fifteen millions organic compounds and offer the name of millions of compounds that are yet to be discovered.
- The disadvantage of common or trivial name of organic compound in that they do not describe the structure and functional group of the compounds.
- The IUPAC naming has established some general rules for naming organic compounds. These rules were revised in 2013.

2. Write the name of five organic families and mention the functional group present in them.

Answer.

1. Alcohol Family (R-OH) contains hydroxy (-OH) functional group.
2. Ether Family (R-O-R) contains alkoxy (-OR) functional group.
3. Alkyl Halide Family (R-X) contains halide (-X) functional group.
4. Aldehyde Family (R-CHO) contains aldehydic (-CHO) functional group.
5. Ketone Family (R-COR) contains ketonic (-COR) functional group.

3. Write down basic rules for IUPAC naming of organic compound.

Answer.

The general rules set for IUPAC method of naming organic compounds are as follow:

(i) Identify the longest unbroken carbon chain within the molecule which will act as parent chain.

(ii) Allocate numerical designations to the carbon atoms within the parent chain to the terminal side, to which functional group is nearer.

(iii) Identify substituents and name them using prefix such as methyl, ethyl, methoxy, chloro, bromo etc. and mention their position in the longest carbon chain.

(iv) If any functional group is present in the molecule, name it by using appropriate suffix such as "one" for ketone, "-al" for aldehyde and "–ol" for alcohol etc.

(v) If there are more than one functional group present in the molecule, write their name on priority basis set by priority rules i.e. (-COOH) > (-CHO) > (C = O) > (-OH) > ($-NH_2$) > (-O-) > (=) > (≡).

4. We often use the term Iso and Neo in the common system of naming of alkanes. Explain with example

Ans.

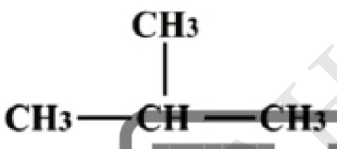
(i) The prefix n- is utilized for alkanes where all the carbon atoms are arranged in a single uninterrupted straight chain.

(ii) The prefix Iso- is utilized if in the structure of alkane molecule one branch (e.g. $-CH_3$) is attached to the second last carbon atom of the chain.

(iii) The prefix Neo- is utilized if two branches are attached on the second last carbon of alkanes.

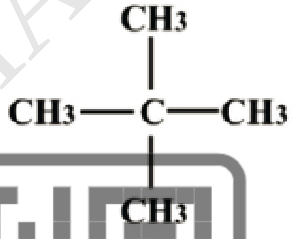
$CH_3-CH_2-CH_2-CH_3$

(n-Butane)



$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_3$

(Isobutane)



$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

(Neopentane)

5. Write the common names of first five members of carboxylic acid.

Common name
Formic acid
Acetic acid
Propionic acid
Butyric acid
Valeric acid

6. If an organic compound contains both double and triple bond, in the main carbon chain, what rules you follow to write its IUPAC name. Explain by giving an example.

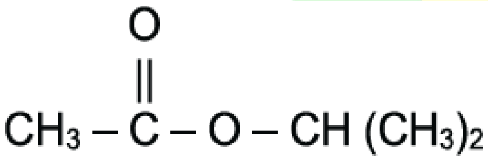
Ans.

- First of all, we have to draw a chain which contains all the double and triple bonds.

- We have to number the chain from where the double or triple bond is nearby.
- If both double and triple bond are near then do numbering from double bond.
- First of all, write the name of double bond along-with its position.
- Finally mention the positions of triple bond and write ‘yne.’

Descriptive Questions

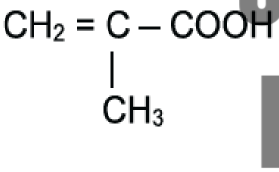
1. Give the IUPAC names of the following organic molecules.

(a)

$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH(CH_3)_2$

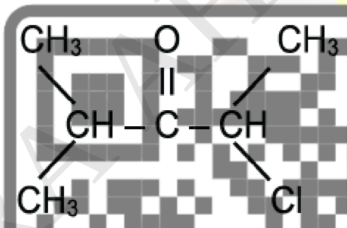
isopropylethanoate

(b) $HC\equiv C-CH(CH_3)-CH=CH_2$

3-methyl-1-pentene-4-yne

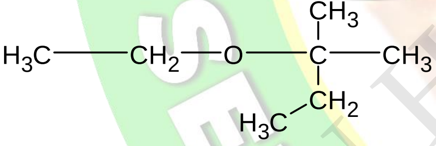
(c)

$CH_2=\underset{\underset{\displaystyle CH_3}{|}}{C}-COOH$

2-methylpent-2-en-1-oic acid

(d)


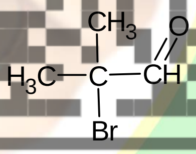
2-chloro-4-methylpentan-3-one

(e) $CH_3-CH_2-OC(CH_3)_2C_2H_5$

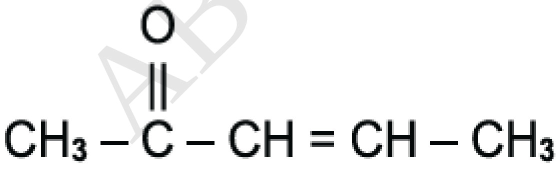


2-ethoxy-2-methylbutane

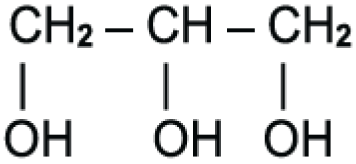
(f) $(CH_3)_2CBrCHO$



2-bromo-2-methylpropanal

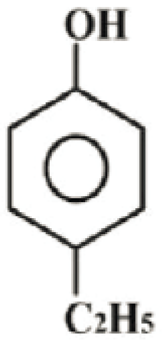
(g)

$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH=CH-CH_3$

pent-3-en-2-one

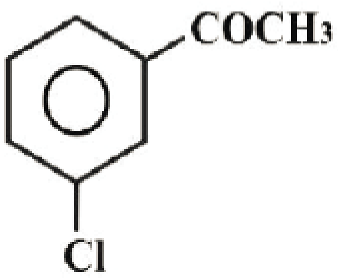
(h)

$\underset{\underset{\displaystyle OH}{|}}{CH_2}-\underset{\underset{\displaystyle OH}{|}}{CH}-\underset{\underset{\displaystyle OH}{|}}{CH_2}$

1,2,3-propantriol

(i)



(j)

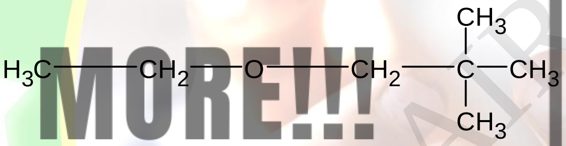


4-ethylphenol

3-chloroacetophenone

2. Outline the structure of each of the following molecules.

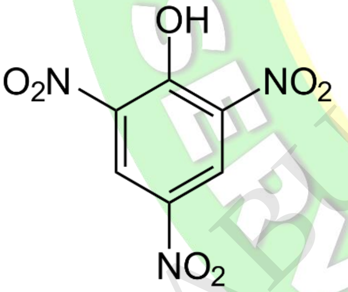
(a) Ethyl neo-pentyl ether



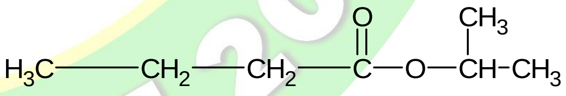
$H_3C-CH_2-O-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

(b) Resorcinol

(c) Picric acid

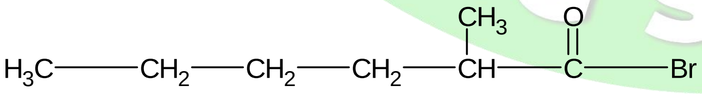


(d) Isopropylbutanoate



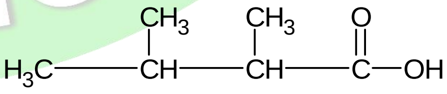
$H_3C-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-\overset{CH_3}{CH}-CH_3$

(e) 1-Bromo-3-methyl hexane-2-one



$H_3C-CH_2-CH_2-CH_2-\overset{CH_3}{CH}-\overset{O}{\overset{\|}{C}}-Br$

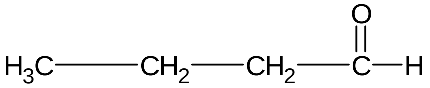
(f) α, β-dimethyl butyric acid



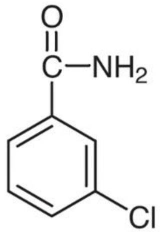
$H_3C-\overset{CH_3}{CH}-\overset{CH_3}{CH}-\overset{O}{\overset{\|}{C}}-OH$

(g) Butyraldehyde

(h) 3-Chlorobenzamide

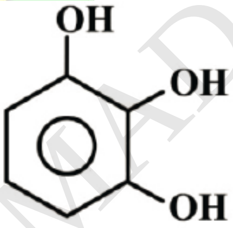


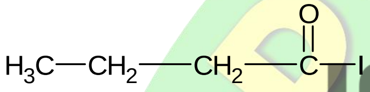
$H_3C-CH_2-CH_2-\overset{\overset{\displaystyle O}{\parallel}}{C}-H$



(i) Butanoyl iodide

(j) 1, 2, 3-benzentriol

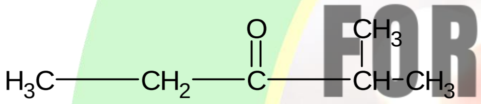




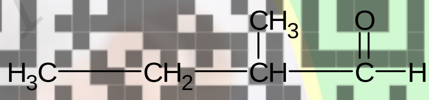
$H_3C-CH_2-CH_2-\overset{\overset{\displaystyle O}{\parallel}}{C}-I$

(k) Ethyl isopropyl ketone

(l) ∝-Methyl butyraldehyde

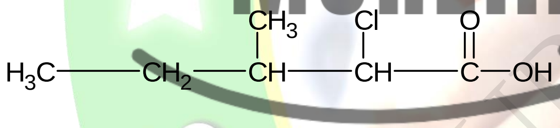


$H_3C-CH_2-\overset{\overset{\displaystyle O}{\parallel}}{C}-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_3$



$H_3C-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-\overset{\overset{\displaystyle O}{\parallel}}{C}-H$

(m) ∝-Chloro-β-methyl valeric acid



$H_3C-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-\overset{\overset{\displaystyle Cl}{|}}{CH}-\overset{\overset{\displaystyle O}{\parallel}}{C}-OH$

CHAPTER 5

INTRODUCTION TO HYDROCARBONS

Organic compounds which are made up of hydrogen and carbon atoms are known as hydrocarbons.

TYPES OF HYDROCARBONS

Aliphatic Hydrocarbons

Those hydrocarbons which contain a straight or branched chain are called aliphatic hydrocarbons. Carbon atoms maybe bonded through single, double or triple covalent bond. They are also called open chain hydrocarbons. The word 'Aliphatic' comes from 'fat' because these hydrocarbons were first extracted from fats and oils.

Aliphatic hydrocarbons can be further classified into saturated and unsaturated hydrocarbons.

Saturated Hydrocarbons:

In these hydrocarbons, all carbon atoms are attached to each other by a **single bond** only.

They are further classified into alkanes and cyclo alkanes.

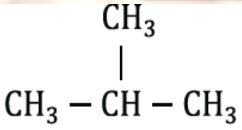
The general formula of alkanes is C_nH_{2n+2}

The general formula of cyclo alkanes is C_nH_{2n}

For example:

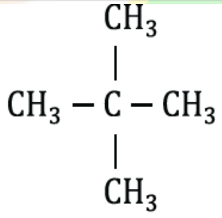
$H_3C-CH_2-CH_2-CH_3$

(n – butane)



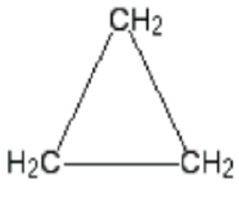
$CH_3-CH(CH_3)-CH_3$

(iso butane)

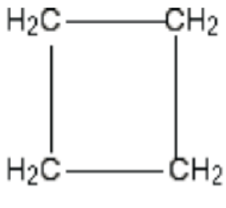


$CH_3-C(CH_3)_2-CH_3$

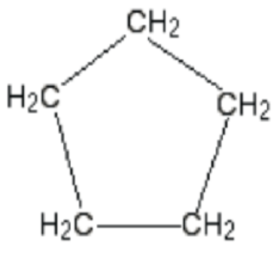
(neo pentane)



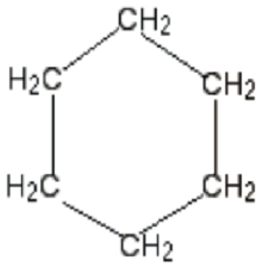
(cyclopropane)



(cyclobutane)



(cyclopentane)



(cyclohexane)

Saturated Hydrocarbons:

“These hydrocarbons contain one or more double or triple bonds between the two adjacent carbon atoms in their structure.”

Unsaturated hydrocarbons are generally referred as alkanes and alkynes. The general formula for their homologous series is **C_nH_{2n}** and **C_nH_{2n-2}** respectively.

For example:

$$CH_2 = CH - CH_3$$

(1-propene)

$$CH_3 - C \equiv C - CH_3$$

(2-butyne)

$$CH_2 = CH - CH = CH_2$$

(1, 3-buta diene)

Self Assessment

Identify the following hydrocarbons as saturated and unsaturated.

C_3H_6, C_7H_{12}, C_8H_{18}, C_5H_{10}, C_5H_8

C_3H_6 → Unsaturated Hydrocarbon

C_7H_{12} → Unsaturated Hydrocarbon

C_8H_{18} → Saturated Hydrocarbon

C_5H_{10} → Unsaturated Hydrocarbon

C_5H_8 → Unsaturated Hydrocarbon

Aromatic Hydrocarbons

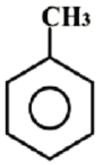
The term aromatic originates from Greek word “aroma” which means fragrance, as these compounds were initially isolated from pleasant smelling plants. The parent member of this class is benzene which is why aromatic compounds are often referred as benzene and its derivatives.

“Aromatic hydrocarbons are those which are characterized by a cyclic arrangement of atoms that are connected by alternating double bonds, they generally follow the Huckle’s rule (4n+2 π electrons.)”

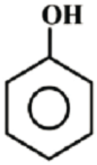
Huckle's Rule: It states that aromaticity is exhibited by planar cyclic compounds with 4n+2 π electrons. where 'n' is a non-negative integer. These compounds possess enhanced stability due to the delocalization of π electrons.

Few examples of aromatic compounds are as follows:

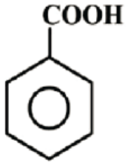
(Benzene)



(Toluene)



(Phenol)



(Benzoic acid)

Physical properties of alkanes

(i) Alkanes are nonpolar organic compounds that are insoluble in water but soluble in organic solvents.

(ii) Boiling point of alkanes is very low, it increases with the length of the carbon chain.

(iii) The boiling point of straight chain alkanes is more than branched chain alkanes.

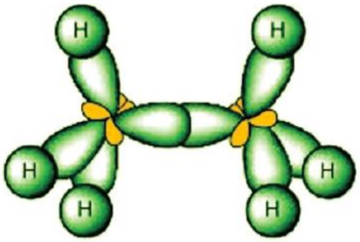
(iv) Alkanes which consist of C_1 to C_4 are gases C_5 to C_{17} are liquids and above C_{17} are waxy solids.

Structure of Alkanes

STRUCTURE OF ETHANE (C_2H_4)

To illustrate the structure of alkanes, the molecule of ethane is taken as a representative example.

Ethane is composed of two carbon atoms and six hydrogen atoms (C_2H_6). Each carbon atom in ethane is sp^3 hybridized containing four sp^3 hybrid orbitals. These four sp^3 hybrid orbitals are arranged in a tetrahedral fashion. Out of four sp^3 hybrid orbitals of each carbon atom, three sp^3 hybrid orbitals are utilized in the formation of sigma bonds with three hydrogen atoms whereas the remaining sp^3 hybrid orbital of one carbon atom overlaps with the sp^3 hybrid orbital of another carbon atom. The bond length between the carbon and carbon atoms is approximately 1.54 Å, and the bond angle between carbon, carbon and hydrogen atoms is approximately 109.5°.



Reactivity of Alkanes

Alkanes are less reactive under normal conditions. This is because they are non polar in nature and hence a polar reagent finds no reaction site. Further, the stronger carbon-carbon bond requires high bond energy for its breaking. They are often called as paraffin. The term paraffin is said to have originated from the Latin word "parum" meaning "little" and "affin" meaning affinity. However under certain conditions, they undergo halogenations, combustion and cracking which can be used in industrial processes to produce a variety of useful products.

SUBSTITUTION REACTIONS:

Saturated hydrocarbons always undergo substitution reactions. Sigma bond breaks down in free radical reactions. In this reaction, a hydrogen is substituted by any other atom or group of atoms which is called substituent. Substituents may be a free radical, electrophile or nucleophile.

TYPES OF SUBSTITUTION REACTIONS:

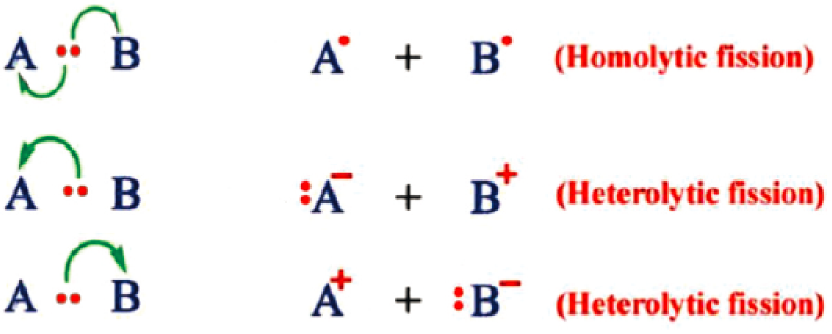
There are three types of substitution reactions.

(i) Free Radical substitution reactions → Characteristic reactions of alkanes

(ii) Electrophilic substitution reactions → Characteristic reactions of Benzene

(iii) Nucleophilic substitution reactions → Characteristic reactions of Alkyl halides

"The cleavage of chemical bond takes place in the organic molecule either by homolytic fission or heterolytic fission". In homolytic fission the bond cleavage takes place evenly, with each atom receiving one of the electron from the bond. In heterolytic fission, the cleavage is uneven with one atom receiving both electrons from the bond and the other atom receiving none.



FREE RADICAL SUBSTITUTION REACTIONS:

Free radical substitution reactions are typically carried out by homolytic fission. The reaction between methane and chlorine in UV light takes place through free radical reaction.

The mechanism of free radical consists of three steps.

Step-1: Chain Initiation

The reaction begins with the breaking of the chlorine-chlorine bond in the presence of UV light producing two chlorine free radicals.

$$Cl:Cl \xrightarrow{\text{U.V. light}} Cl\cdot + Cl\cdot$$

Step-2: Chain Propagation

The chlorine radical is produced during chain initiation by attacking the methane molecule and abstracting a hydrogen atom. This process results in the formation of a molecule of hydrogen chloride and a methyl free radical.

$$Cl\cdot + H:CH_3 \longrightarrow H:Cl + \cdot CH_3$$

The methyl free radical then attacks another chlorine molecule, removing a chlorine atom to produce methyl chloride.

$$Cl:Cl + \cdot CH_3 \longrightarrow CH_3:Cl + \cdot Cl$$

Step-3: Chain Termination

This step leads to the completion of reaction when all free radicals combine to form three possible stable molecules.

$$Cl\cdot + \cdot Cl \longrightarrow Cl:Cl$$

$$CH_3\cdot + \cdot Cl \longrightarrow CH_3:Cl$$

$$CH_3\cdot + \cdot CH_3 \longrightarrow CH_3:CH_3$$

Overall Reaction:

$$\underset{\text{(Methane)}}{CH_4 + Cl_2} \xrightarrow{\text{Sunlight}} \underset{\text{(Methyl chloride)}}{CH_3Cl} + HCl$$

$$CH_3-Cl + Cl_2 \xrightarrow{\text{Sunlight}} \underset{\text{(Methylene dichloride)}}{CH_2Cl_2} + HCl$$

$$\underset{\text{(Methylene dichloride)}}{CH_2Cl_2} + Cl_2 \xrightarrow{\text{Sunlight}} \underset{\text{(Chloroform)}}{CHCl_3} + HCl$$

$$\underset{\text{(Chloroform)}}{CHCl_3} + Cl_2 \xrightarrow{\text{Sunlight}} \underset{\text{(Carbon tetrachloride)}}{CCl_4} + HCl$$

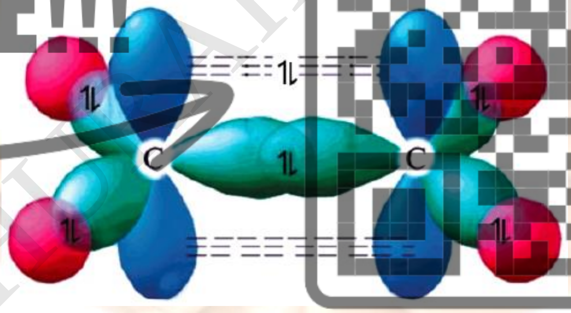
ALKENES

Alkenes are a class of unsaturated hydrocarbons, they contain one or more carbon-carbon double bonds in the chain. Olefins is another term used to refer alkenes. The term olefin derives from Latin oleum meaning oil. This is because some of early discovered alkenes were oil like.

Structure of Ethene

To describe the structure of alkene, ethene can be taken as a representative example.

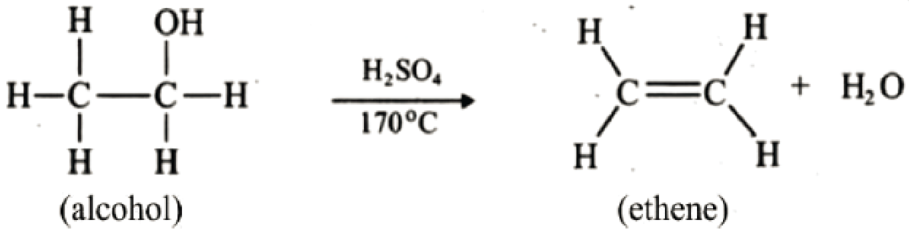
The structure of ethene is characterized by two sp^2 hybrid carbon atoms that are arranged in a trigonal planar geometry. The double bond between the carbon atoms is composed of a sigma bond, which arises from the overlap of two sp^2 hybrid orbitals from each carbon atom and a pi bond which forms due to lateral overlapping of two unhybrid p orbitals, one from each carbon atom. Each carbon in ethene is also bonded with two hydrogen atoms through sp^2-s sigma bonding. The bond length for the C-C single sigma bond is approximately 1.34 Å and bond angle between the two carbon-hydrogen (C-H) bonds is approximately 120 degrees.



Preparation of Alkenes

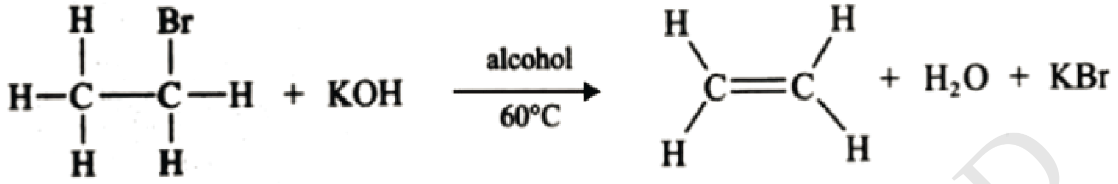
1. Dehydration of Alcohol:

When an alcohol is heated in the presence of a dehydrating agent such as concentrated sulphuric acid, it undergoes elimination of water molecule and gives an alkene.



2. Dehydrohalogenation of Alkyl Halide:

When ethyl halide is treated with an alcoholic solution of potassium hydroxide (KOH), the elimination of a hydrogen and a halogen atom takes place from two adjacent carbon atoms of alkyl halide, giving an alkene.



(ethyl bromide) (ethene)

Reactivity of Alkenes

Alkenes are more reactive than alkanes due to the presence of π bond. π bonds are weaker than σ bonds that's why they can easily be broken by providing a very little amount of energy. Alkenes undergo addition reactions due to the cleavage of pi bonds. They follow electrophilic addition reaction mechanism.

Reactions of Alkenes

1. Hydrogenation:

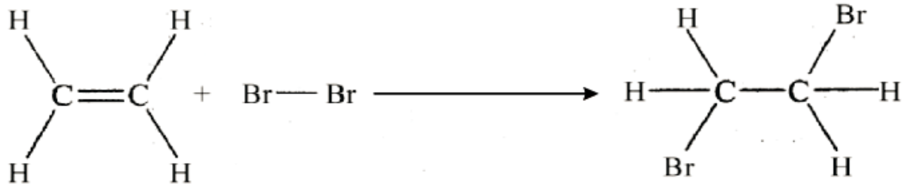
In this reaction, hydrogen gas (H_2) is added across a carbon-carbon double bond of alkene. The reaction is carried out in the presence of metal catalyst such as platinum (Pt), palladium (Pd) or nickel (Ni) at a temperature of 250 to 300°C.

$$H_2C = CH_2 + H_2 \xrightarrow[\text{Ni, Pt or Pd}]{250\text{-}300°C} CH_3 - CH_3$$

(ethene) (ethane)

2. Halogenation:

In this reaction, a halogen (X_2) such as Cl_2 or Br_2 is added to produce 1,2-dihaloalkane or vicinal dihalide.



(ethene) (1,2-dibromo ethene)

3. Hydrohalogenation:

The addition of a halogen acid (HX) on an alkene to give an alkyl halide is known as hydrohalogenation of alkene.

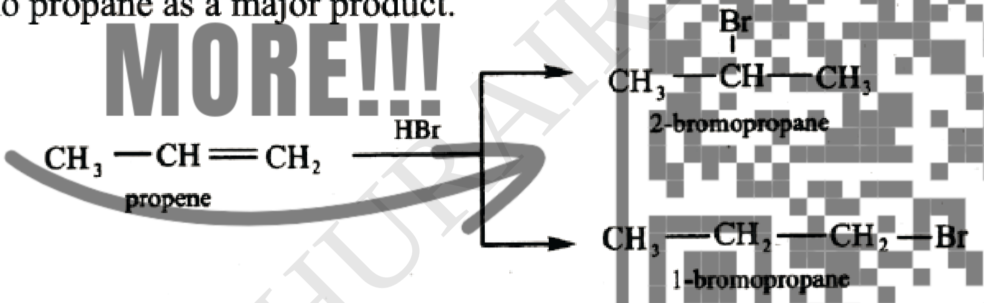
$$\underset{\text{(ethene)}}{CH_2=CH_2} + H-Br \longrightarrow \underset{\text{(ethyl bromide)}}{CH_3-CH_2-Br}$$

The order of reactivity of halogen acid (HX) is HI > HBr > HCl.

Markovnikov's Rule:

The addition of halogen acid on an unsymmetrical alkene is governed by Markovnikov's rule which states that **"when an unsymmetrical alkene undergoes addition reactions, the negative part of attacking reagent is added to that double bonded carbon atom which holds lesser number of hydrogen atoms while the hydrogen atom is attached to the carbon atom with the highest number of hydrogen substituents"**.

For example the reaction of propene with hydrogen bromide (HBr) gives 2-bromo propane as a major product.



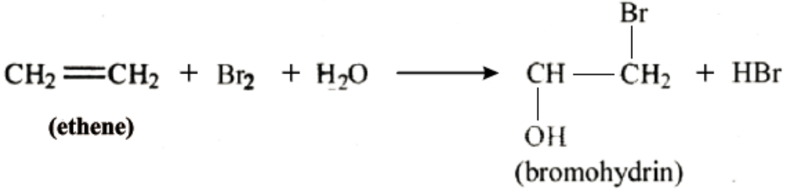
4. Hydration:

The addition of water on an alkene to give alcohol is known as hydration of alkene. This reaction is carried out by acid catalysis at 80-100°C.

$$\underset{\text{(ethene)}}{H_2C=CH_2} + H_2O \xrightarrow[100^\circ C]{H_2SO_4} \underset{\text{(ethyl alcohol)}}{CH_3-CH_2-OH}$$

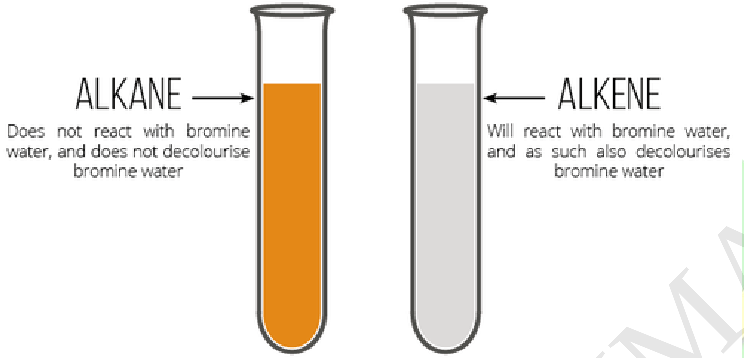
5. Halohydration: (Confirmatory Test for Alkene or Unsaturation Test)

Halohydration is a reaction in which a halogen reacts with alkene in presence of water and forms halohydrin.



$$\underset{\text{(ethene)}}{CH_2=CH_2} + Br_2 + H_2O \longrightarrow \underset{\text{(bromohydrin)}}{\underset{\underset{OH}{|}}{CH}-\overset{\overset{Br}{|}}{CH_2}} + HBr$$

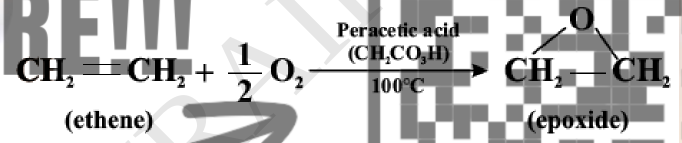
Brown color of bromine water decolorizes in this reaction. When alkane in treated with bromine water then brown color of bromine water does not discharge which confirms the absence of π bond in it.



ADDITION OF BROMINE WATER TO ALKANES & ALKENES

6. Epoxidation:

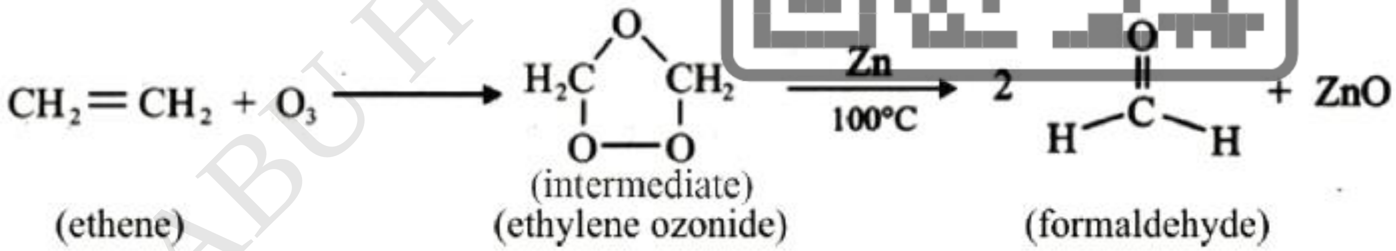
The addition of oxygen to the double bond of an alkene is known as epoxidation. The product of this reaction is an epoxide which is a three membered cyclic ether.



$$CH_2{=}CH_2 + \frac{1}{2}O_2 \xrightarrow[100^\circ C]{\text{Peracetic acid } (CH_3CO_3H)} \overset{O}{CH_2-CH_2}$$

(ethene) (epoxide)

7. Ozonolysis:



8. Polymerization:

Polymerization of alkene involves the linking of many alkene monomers together to produce a polymer chain.

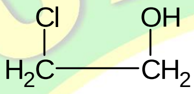
$$nH_2C{=}CH_2 \xrightarrow[2000\ atm]{200^\circ C} \left[CH_2-CH_2 \right]_n$$

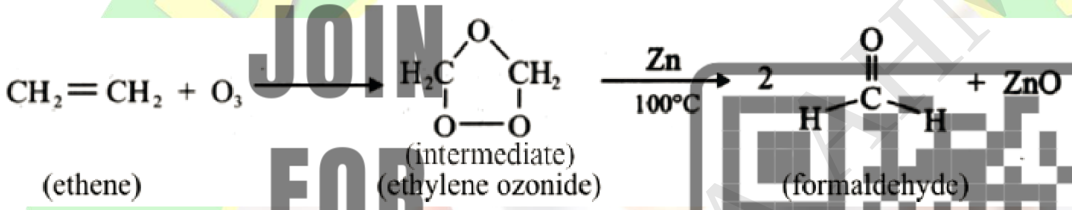
(ethene) (polyethene)

Self Assessment

What major product obtained when
(i) Propene reacts with hydrogen iodide
(ii) Ethene reacts with chlorine water
(iii) Ethylene reacts with ozone

i) $C_3H_6 + HI \rightarrow C_3H_7I$ (Propyl iodide / iodo propane)

ii) $C_2H_4 + Cl_2 + H_2O \rightarrow$ 
$H_2\overset{Cl}{C}-\overset{OH}{C}H_2$ (Chloro Hydrin)

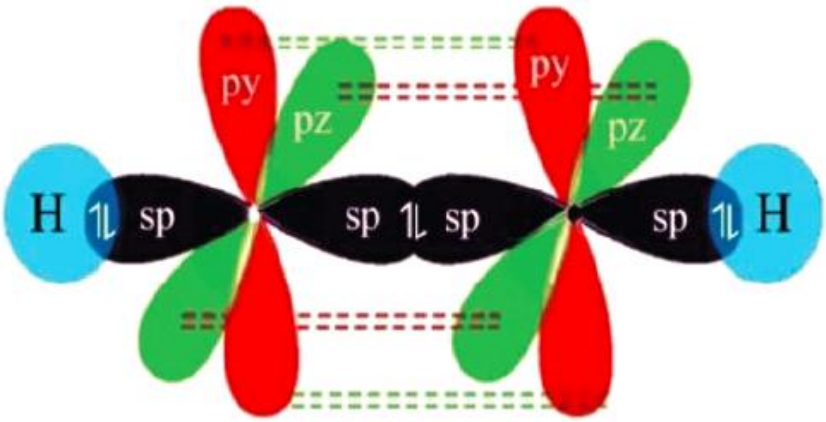
iii) 

ALKYNES

Alkynes are hydrocarbons that contain a triple bond between the two carbon atoms.

Structure of Ethyne

Ethyne is the first member of alkynes family in which both carbon atoms are sp hybridized. Each carbon has two sp hybrid orbitals and two unhybrid 'p' orbitals (Py and Pz). Two hybrid orbitals form two sigma bonds, one with carbon and other with hydrogen, whereas two unhybrid orbitals form two pi bonds by parallel overlapping. Hence the shape is linear with an angle of 180°.

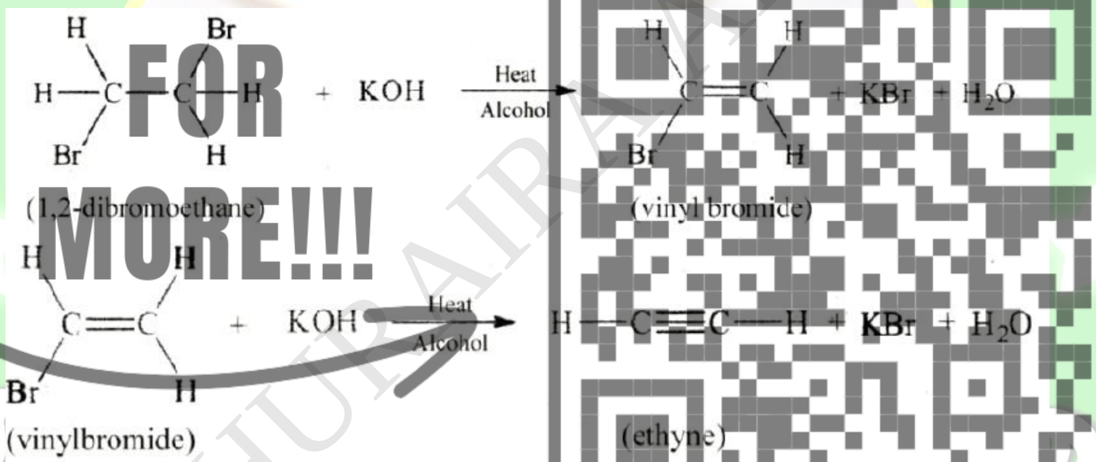


PHYSICAL PROPERTIES OF ALKYNE:

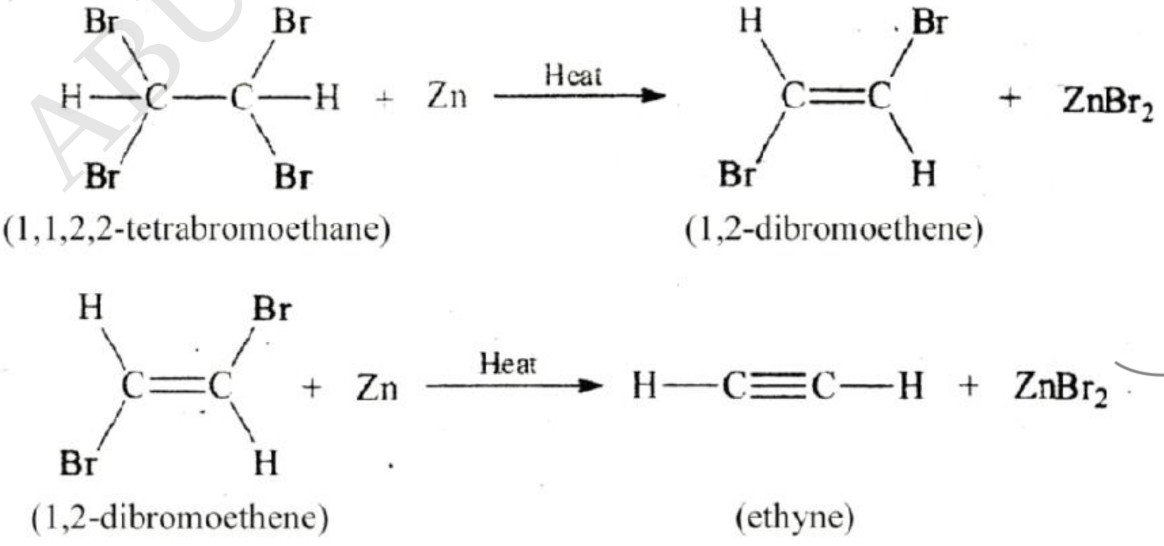
- Alkynes are colourless and odourless except for acetylene gas which has garlic like odour.
- Alkynes are insoluble in water but soluble in the organic solvents like acetone, ether, Ethyl acetate etc.
- Melting and boiling points increase with increasing molecular mass of alkynes.
- First three members are gases and next members up to 12 carbons are liquids.

PREPARATION OF ALKYNE:

1. Dehydrohalogenation of Vicinal dihalides:



2. Dehalogenation of tetrahalides:



CHEMICAL PROPERTIES OF ALKYNE:

Acidity of Terminal Alkynes

Hydrocarbons containing a triple bond on the terminal carbon, (ethyne, 1-propyne, 1-butyne etc) are characterized as weak acids.

In terminal alkynes, the hydrogen is bonded to sp hybridized carbon atom which is more strongly bonded to other carbon atom with a sigma and 2 pi bonds. Due to this the sigma bond between terminal hydrogen and carbon becomes weaker and it is easily lost.

$$HC \equiv CH + 2AgNO_3 \xrightarrow{NH_3} AgC \equiv CAg + 2H_2O$$

(silver acetylide)
(white ppt)

$$HC \equiv CH + Cu_2Cl_2 \xrightarrow{NH_3} CuC \equiv CCu + 2H_2O$$

(copper acetylide)
(red ppt)

Since silver acetylide and copper acetylide appear in the form of precipitates, these reactions are often used to identify terminal alkynes in the laboratory. It is also used to distinguish ethyne from ethene.

Self Assessment

How can you distinguish between an ethene and an ethyne by simple chemical test?

Ethene and ethyne can be distinguished by acidic character test. Ethyne is acidic nature so it will form precipitates which ethene is not acidic so it cannot form precipitates.

$$HC \equiv CH + 2AgNO_3 \xrightarrow{NH_3} AgC \equiv CAg + 2H_2O$$

(silver acetylide)
(white ppt)

C_2H_4 + $AgNO_3$ → No white precipitates

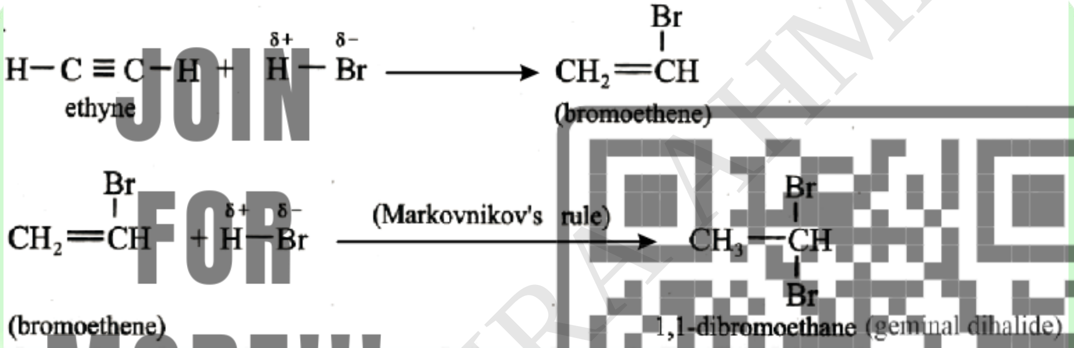
Addition reaction of alkynes

1. Hydrogenation:

$$\underset{\text{(ethyne)}}{HC\equiv CH} + H_2 \xrightarrow[\text{Ni, Pt or Pd}]{250\text{-}300^\circ C} \underset{\text{(ethene)}}{H_2C=CH_2}$$

$$\underset{\text{(ethene)}}{H_2C=CH_2} + H_2 \xrightarrow[\text{Ni, Pt or Pd}]{250\text{-}300^\circ C} \underset{\text{(ethane)}}{CH_3-CH_3}$$

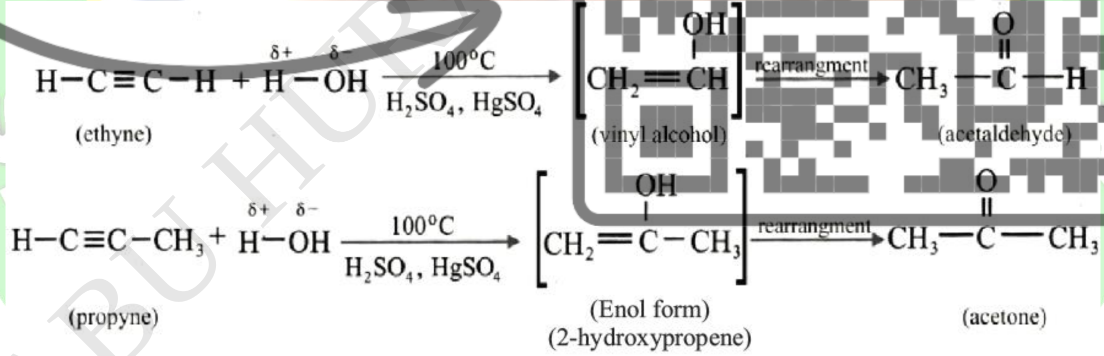
2. Halogenation:



$$\underset{\text{ethyne}}{H-C\equiv C-H} + \overset{\delta+}{H}-\overset{\delta-}{Br} \longrightarrow \underset{\text{(bromoethene)}}{CH_2=\overset{Br}{CH}}$$

$$\underset{\text{(bromoethene)}}{CH_2=\overset{Br}{CH}} + \overset{\delta+}{H}-\overset{\delta-}{Br} \xrightarrow{\text{(Markovnikov's rule)}} \underset{\text{1,1-dibromoethane (geminal dihalide)}}{CH_3-\underset{Br}{\overset{Br}{CH}}}$$

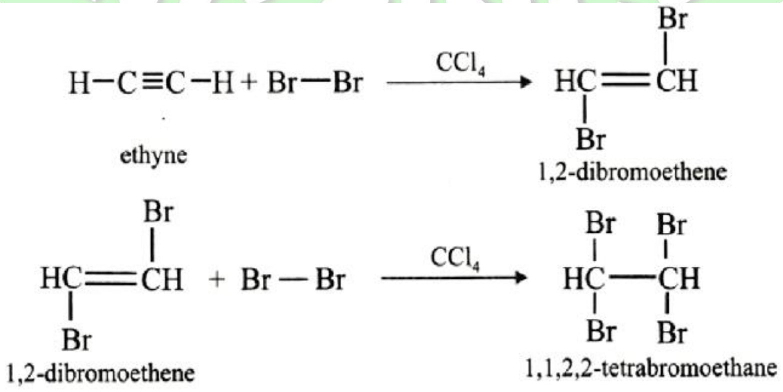
3. Hydration:



$$\underset{\text{(ethyne)}}{H-C\equiv C-H} + \overset{\delta+}{H}-\overset{\delta-}{OH} \xrightarrow[H_2SO_4,\ HgSO_4]{100^\circ C} \underset{\text{(vinyl alcohol)}}{\left[CH_2=\overset{OH}{CH}\right]} \xrightarrow{\text{rearrangment}} \underset{\text{(acetaldehyde)}}{CH_3-\overset{O}{\overset{\|}{C}}-H}$$

$$\underset{\text{(propyne)}}{H-C\equiv C-CH_3} + \overset{\delta+}{H}-\overset{\delta-}{OH} \xrightarrow[H_2SO_4,\ HgSO_4]{100^\circ C} \underset{\substack{\text{(Enol form)}\\ \text{(2-hydroxypropene)}}}{\left[CH_2=\overset{OH}{C}-CH_3\right]} \xrightarrow{\text{rearrangment}} \underset{\text{(acetone)}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3}$$

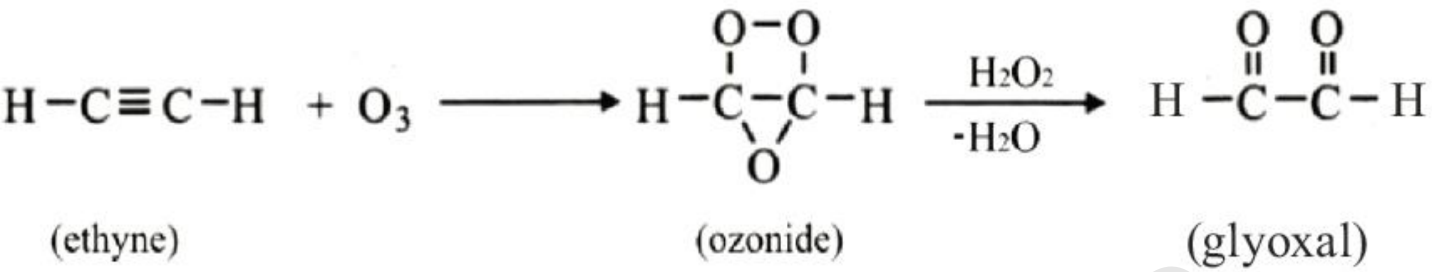
4. Halogenation:



$$\underset{\text{ethyne}}{H-C\equiv C-H} + Br-Br \xrightarrow{CCl_4} \underset{\text{1,2-dibromoethene}}{\underset{Br}{HC}=\overset{Br}{CH}}$$

$$\underset{\text{1,2-dibromoethene}}{\underset{Br}{HC}=\overset{Br}{CH}} + Br-Br \xrightarrow{CCl_4} \underset{\text{1,1,2,2-tetrabromoethane}}{\underset{Br}{\overset{Br}{HC}}-\underset{Br}{\overset{Br}{CH}}}$$

5. Ozonolysis:



Alkanes	Alkenes	Alkynes
Alkanes are chemically less reactive since the sigma bond between carbon-carbon requires high energy to break.	Alkenes are more reactive because the electron density of pi electrons spreads above and below the axis which offers an electrophile to attack on the substrate molecule.	Alkynes display higher reactivity than alkanes but lower reactivity than alkenes because pi electrons are not entirely exposed owing to the short length of triple bond.
They do not oxidized by $KMnO_4$.	They oxidize by $KMnO_4$.	They oxidize by $KMnO_4$.

ISOMERISM

"A wide range of organic compounds studied in organic chemistry exhibit the same molecular formula, yet differ in their structure or sterio chemistry. These compounds are known as isomers and the phenomenon is referred as isomerism".

Isomers are initially classified into following two categories.

(i) Structural isomers (ii) Stereo isomers

Structural Isomerism

Organic molecules having the same molecular formula but differing in the way their atoms are connected to each other are called as structural isomers. These are further classified into the following types.

1. Chain Isomerism

2. Position Isomerism

3. Functional Group Isomerism

4. Metamerism

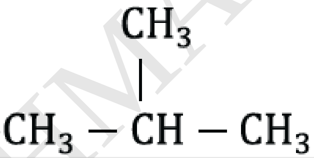
1. Chain Isomerism:

"It is a type of structural isomer in which the molecules differ from each other with respect to carbon skeleton".

For example C_4H_{10} exists in the following two chain isomers.

$H_3C - CH_2 - CH_2 - CH_5$

(n – butane)



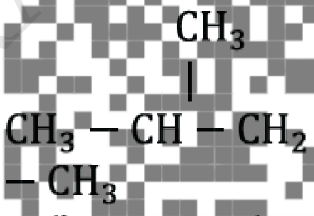
$$\begin{array}{c} CH_3 \\ | \\ CH_3 - CH - CH_3 \end{array}$$

(isobutene)

Similarly C_5H_{12} has the following three possible chain isomers.

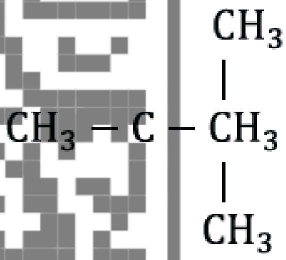
$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$

(n - pentane)



$$\begin{array}{l} \quad\quad\;\; CH_3 \\ \quad\quad\;\;\; | \\ CH_3 - CH - CH_2 \\ - CH_3 \end{array}$$

(isopentane)



$$\begin{array}{c} CH_3 \\ | \\ CH_3 - C - CH_3 \\ | \\ CH_3 \end{array}$$

(neopentane)

2. Position Isomerism:

"In this type of isomerism, the structural difference is based on the change in the position of functional group".

For example C_4H_8 has two position isomers.

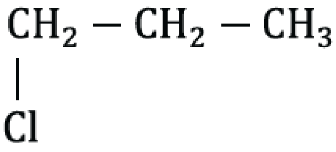
$CH_3 - CH = CH - CH_3$

(2 – butene)

$CH_3 - CH_2 - CH = CH_2$

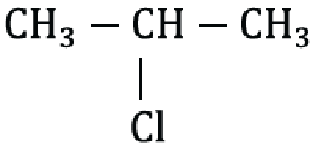
(1 – butane)

Similarly the two possible position isomers of C_3H_7Cl are given as.



$$\begin{array}{l} CH_2 - CH_2 - CH_3 \\ | \\ Cl \end{array}$$

(1 – chloropropane)



$$\begin{array}{c} CH_3 - CH - CH_3 \\ | \\ Cl \end{array}$$

(2 – chloropropane)

3. Functional Group Isomerism:

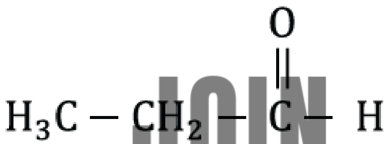
"Two molecules having the same molecular formula but differing from each other by the change of functional groups are called functional group isomers".

For example the two possible functional group isomers of C_2H_6O are given as.

$CH_3 - CH_2 - OH$
(ethyl alcohol)

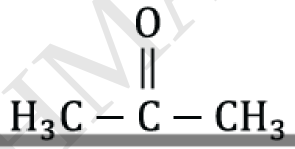
$CH_3 - O - CH_3$
(Diethyl ether)

Another example of molecule exhibiting functional group isomerism is C_3H_6O.



$$H_3C - CH_2 - \overset{\overset{O}{||}}{C} - H$$

(propanal)



$$H_3C - \overset{\overset{O}{||}}{C} - CH_3$$

(2 – propanone)

4. Metamerism:

"Organic molecule which exhibits unequal distribution of alkyl group on either side of functional group is known as metamerism".

For example two possible metamers of the formula $C_4H_{10}O$ are.

$CH_3 - O - C_3H_7$
(methyl propyl ether)

$C_2H_5 - O - C_2H_5$
(Diethyl ether)

Self Assessment

- Draw the possible position isomers of C_4H_{10}, C_5H_{12}, C_4H_8, C_5H_{10}, C_4H_6, C_5H_8 with their IUPAC names.
- Draw the possible functional group isomers of C_2H_6O, C_3H_6O, $C_2H_4O_2$ with their IUPAC names.

Position isomers of C_4H_{10} and C_5H_{12} is not possible as they don't contain any functional group.

Position isomers of C_4H_8 are:

$CH_3 - CH = CH - CH_3$
(2 – butene)

$CH_3 - CH_2 - CH = CH_2$
(1 – butane)

Position isomers of C_5H_{10} are:

$H_2C{=}CH{-}CH_2{-}CH_2{-}CH_3$

pent-1-ene

$H_3C{-}CH{=}CH{-}CH_2{-}CH_3$

pent-2-ene

Position isomers of C_4H_6 are:

$HC{\equiv}C{-}CH_2{-}CH_3$

but-1-yne

$H_3C{-}C{\equiv}C{-}CH_3$

but-2-yne

Position isomers of C_5H_8 are:

$HC{\equiv}C{-}CH_2{-}CH_2{-}CH_3$

pent-1-yne

$H_3C{-}C{\equiv}C{-}CH_2{-}CH_3$

pent-2-yne

Functional group isomers of C_2H_6O

CH_3-CH_2-OH

(ethyl alcohol)

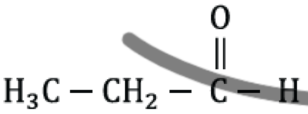
(ethanol)

CH_3-O-CH_3

(Diethyl ether)

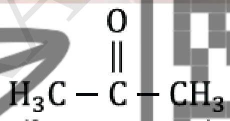
(methoxy methane)

Functional group isomers of C_3H_6O



$$H_3C-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

(propanal)



$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

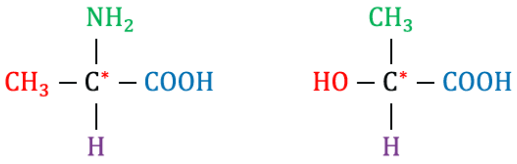
(2 – propanone)

Functional group isomers of $C_2H_4O_2$

CH_3COOH (Ethanoic Acid) and $HCOOCH_3$ (methyl methanoate)

Chiral Centre

“A chiral centre is formed in a molecule when a carbon atom is bonded to four different atoms or groups”. The carbon atom on which these different groups are attached is called chiral carbon and the phenomenon is referred as chirality.



$$CH_3-\overset{\overset{\displaystyle NH_2}{|}}{\underset{\underset{\displaystyle H}{|}}{C^*}}-COOH \qquad HO-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C^*}}-COOH$$

Fig 5.4: Structure of (a) amino acid and (b) lactic acid showing chiral carbon

Optical Activity

When plane polarized light is passed through a solution containing chiral carbon then the plane polarized light is rotated either in clockwise or in anticlockwise direction. This rotation of plane polarized light is called optical activity. The device which is used to measure optical activity is called **polarimeter.**

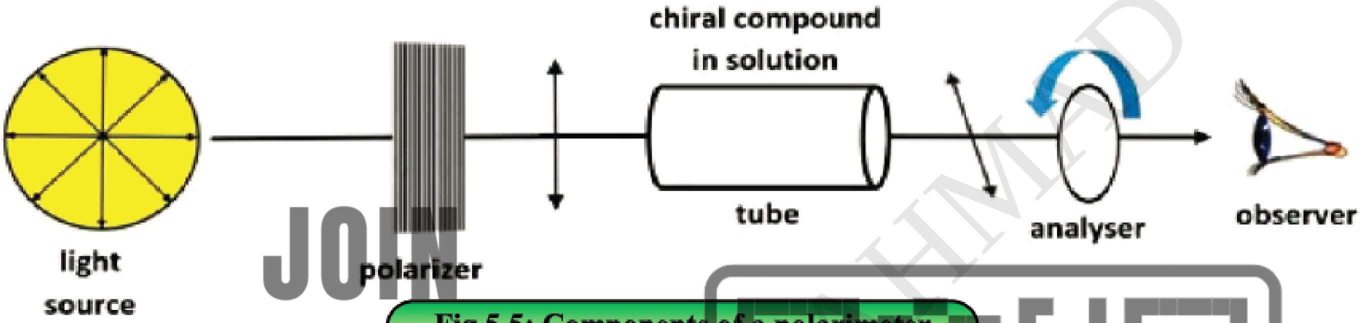


Fig 5.5: Components of a polarimeter

Optical Isomers

"Two compounds having the same molecular formula and same molecular structure but different from each other by the optical rotation of plane polarized light are called <u>optical isomers</u> or <u>enantiomers</u>."

The compounds that rotate the plane of polarized light in a clockwise direction is known as dextrorotatory or D-isomer while the compound that rotates the plane of polarized light in anticlockwise direction is called levorotatory or L-isomer. These two optical isomers are mirror images to each other.

A **<u>racemic mixture</u>** is formed if both D and L isomers of a compound are present in equal amounts within a solution. The solution exhibits no rotation of polarized light.

Stereoisomerism (Geometrical isomers)

Stereoisomers are a type of isomers that have the same molecular formula and connectivity of atoms but differ in the spatial arrangement of atoms in three-dimensional space, resulting in distinct physical and chemical properties.

Geometrical isomers are a type of stereo isomers and are found in the compounds having two different groups on double bonded carbon atoms. Both compounds have restricted movement of atoms of groups around double bond.

"Geometrical isomers are of two types, one is called cis and other is called trans". If the same groups lie on the same side of molecule, this is called cis isomer where as if the same groups lie on opposite direction in the molecule, this is referred as trans-isomer (Fig:5.7).

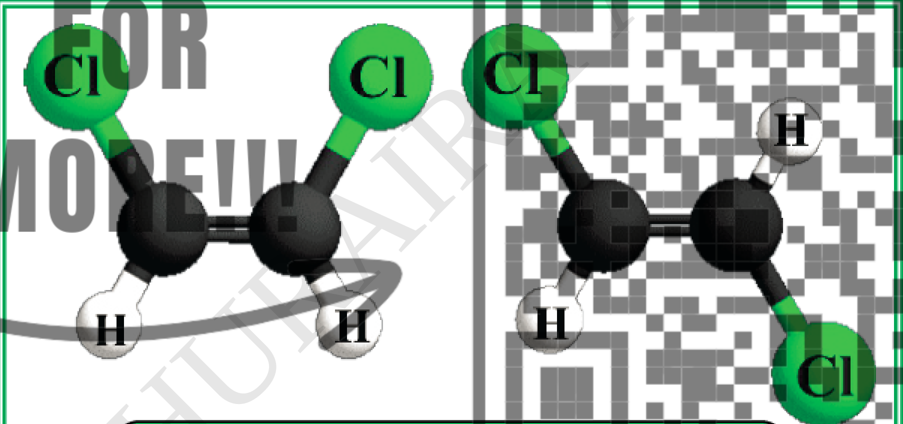


Fig 5.7: Cis and trans isomers of 1,2-dichloro ethene

BENZENE AND ITS DERIVATIVES

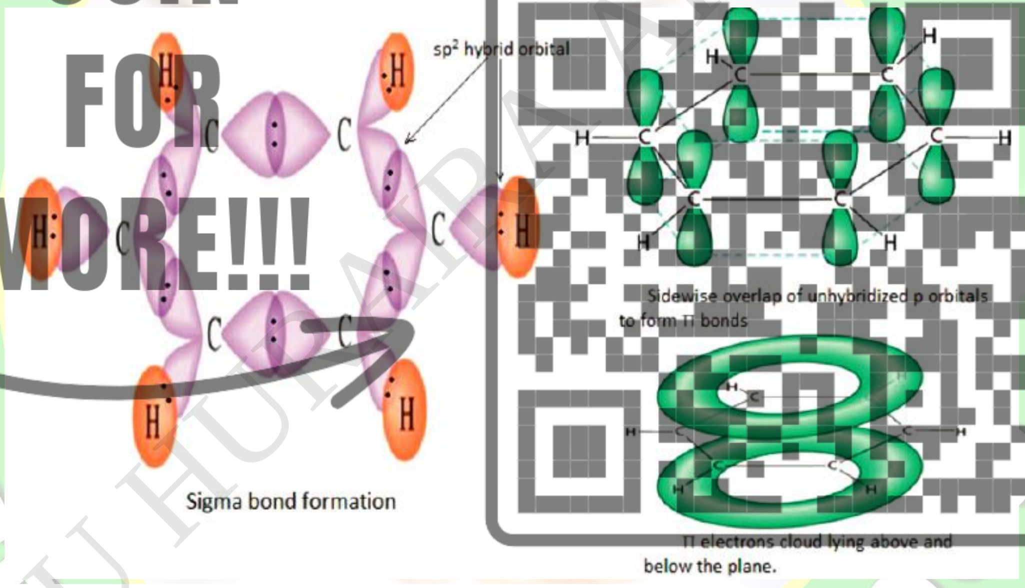
- Benzene is the simplest aromatic compound
- It's a colorless, carcinogenic and highly inflammable liquid.
- It burns with black soot due to high percentage of carbon.
- Its molecular formula is C_6H_6
- It was first isolated by Michael Faraday in 1825.
- It is insoluble in water but soluble in organic solvents.

Molecular orbital structure of benzene

Benzene consists of six carbon atoms in ring, each carbon is sp^2 hybridized and has three sp^2 hybrid orbitals.

Two hybrid orbitals of each carbon atoms are used to make sigma bond with the adjacent carbon atom through $sp^2 - sp^2$ overlapping. The third sp^2 hybrid orbital is involved in sigma bonding with hydrogen atoms through $sp^2 - s$ overlapping. Carbon atoms have a trigonal planar shape with 120° bond angle. In benzene, the C – C bond length and C = C bond length is approximately 1.39 Å.

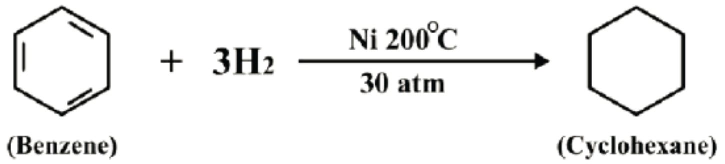
The six carbon atoms in benzene possess six unhybridized p-orbitals that are oriented perpendicular to the sigma bonds. The side wise overlapping of p orbitals gives six delocalized pi molecular orbitals where half of them is located above the plane while other half below the plane of sigma bonds. The six electrons present in pi molecular orbitals are delocalized over all six carbon atoms in molecule.



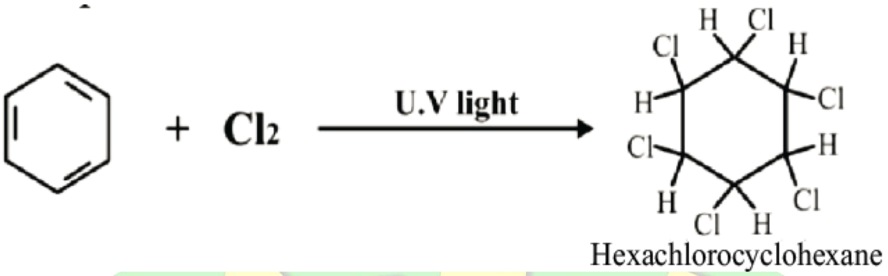
Addition reactions of benzene

Benzene, being an aromatic compound, is highly resistant to addition reactions due to its stability. However, under specific conditions, it can undergo addition reactions. So far only the addition of hydrogen and chlorine to benzene has been observed.

1. Addition of Hydrogen:



2. Addition of Halogen:



Electrophilic substitution reactions of benzene

Electrophilic substitution reactions are a type of organic reaction in which an electrophile reacts with benzene and replace its hydrogen. The general mechanism of electrophilic substitution reaction of benzene consists of following steps:

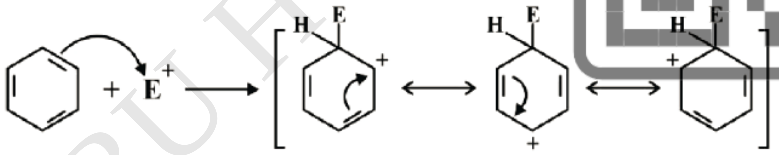
Step-1: Generation of an electrophile

An electrophile (E^+) is generated by reaction of catalyst with the reagent.

$$E - Z + \text{Catalyst} \longrightarrow E^+ + [Z - \text{catalyst}]$$

Step-2: Formation of Arenium ion

The electrophile attacks on pi system of benzene and forms a carbocation known as arenium ion.

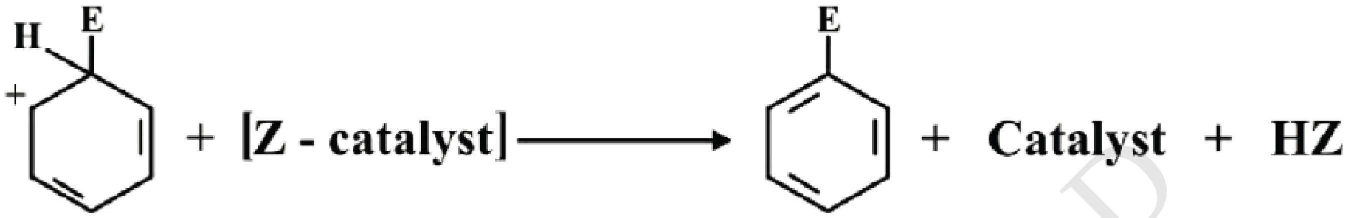


(Sigma complex)

In this attack, one carbon of benzene becomes sp^3 hybridized and hence the aromaticity of benzene has lost.

Step-3: Abstraction of proton

The unstable non aromatic arenium ion then loses a proton and changes into the product.



TYPES OF ELECTROPHILIC SUBSTITUTION REACTIONS:

There are 5 types of electrophilic substitution reactions.

(i) Nitration

(ii) Sulphonation

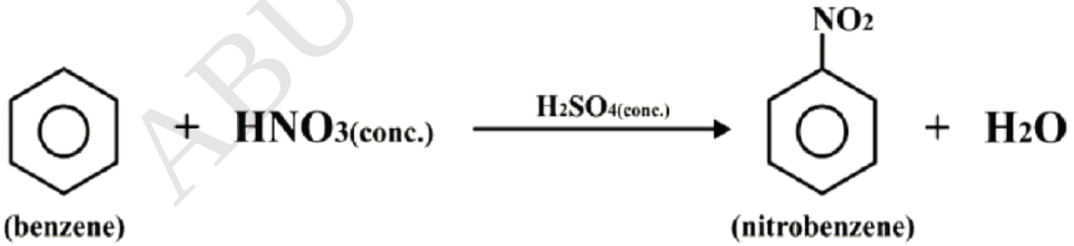
(iii) Halogenation

(iv) Friedel – Craft's Alkylation

(v) Friedel – Craft's Acylation

1. Nitration:

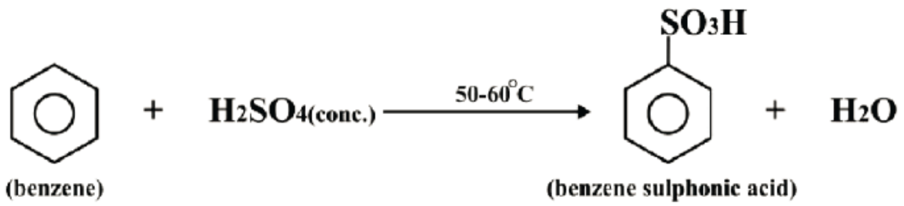
The reaction of benzene with conc. nitric acid to produce nitrobenzene is known as nitration. This reaction is carried out at 50°C in the presence of conc. sulphuric acid.



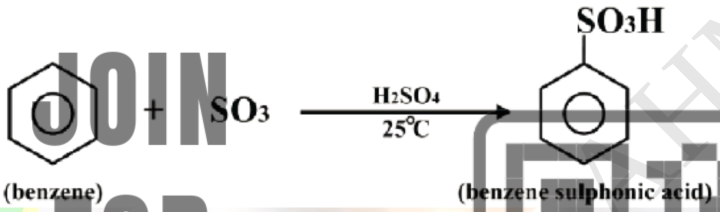
In this reaction, one hydrogen of benzene is replaced by a nitronium ion (NO_2^+).

2. Sulphonation:

Benzene reacts with conc. sulphuric acid at 50 to 60°C to give benzene sulphonic acid.

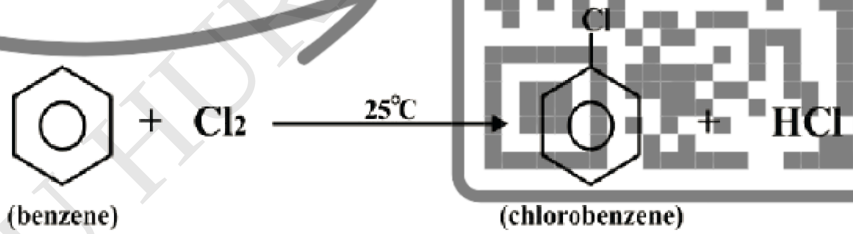


This reaction may also be carried out at room temperature if fuming sulphuric acid is used.



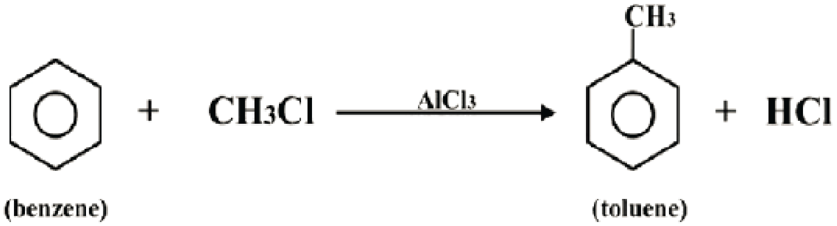
3. Halogenation:

Benzene reacts with halogens (Cl_2, Br_2) at room temperature in the presence of a Lewis acid ($FeCl_3$) to give a halobenzene.



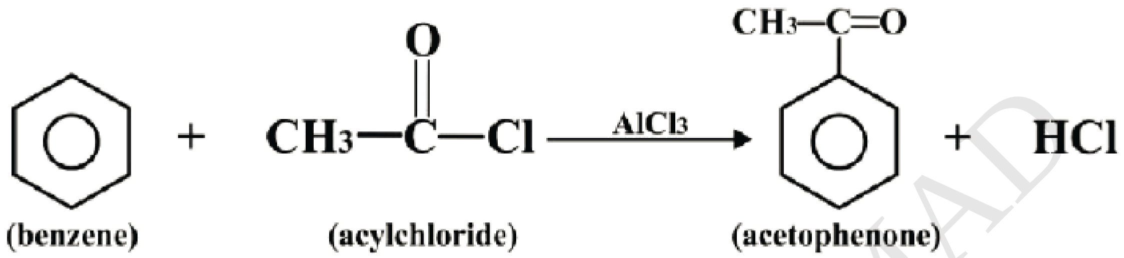
4. Friedel-Craft's Alkylation:

Benzene undergoes reaction with an alkyl halide in the presence of a Lewis acid ($AlCl_3$) to produce an alkyl benzene.



5. Friedel-Craft's Acylation:

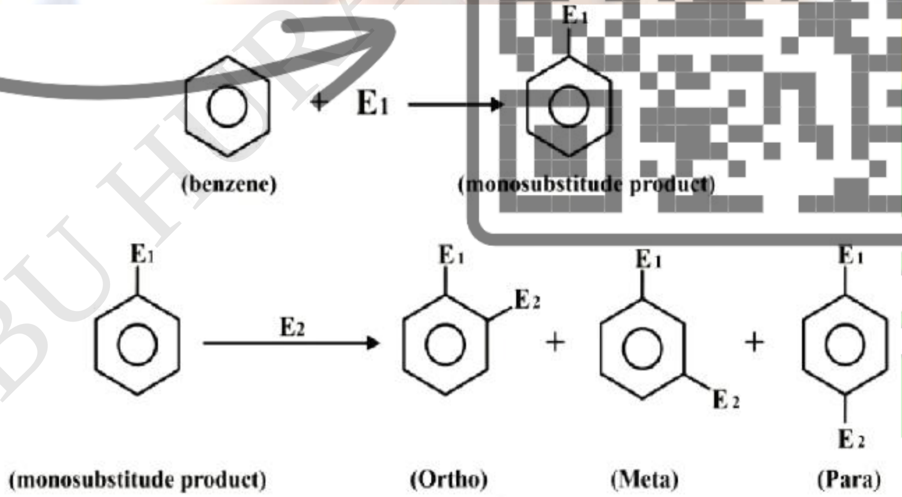
The reaction of benzene with an acylhalide (RCOCl) in the presence of lewis acid ($AlCl_3$) is known as Friedal Craft acylation.



Substituent Effect

When an electrophile reacts with benzene, a monosubstituted product is obtained. The second electrophile is substituted according to the substituent effect of first electrophile,

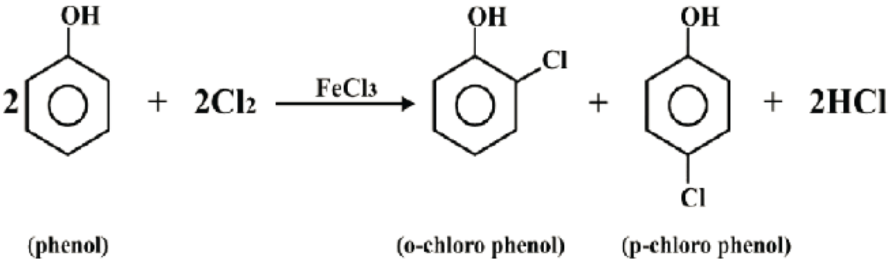
"The effect of first substituent on the incoming electrophilic reagent is known as substituent effect or orientation in benzene"



(i) Ortho, para directing groups

"These substituent groups when attached to benzene ring, direct incoming Electrophilic substituents to the ortho and para positions". They increase the electron density on ortho and para positions through resonance effect. The increased electron density on these positions make more attraction for the incoming electrophile to attack.

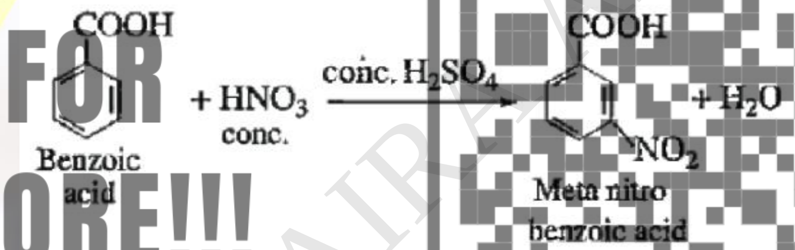
For example the $-OH$ group of phenol is ortho, para director



(ii) Meta direction group

The presence of these groups in benzene ring decreases the electron density at ortho and para positions due to inductive effect and hence the incoming electrophile attacks on meta position.

For example the $-COOH$ part of benzoic acid is meta directing.



DIFFERENCE BETWEEN ORTHO-PARA DIRECTORS AND META DIRECTORS

Ortho para directors	Meta director
They release electron to the aromatic ring and increasing the electron density on ortho para position.	They withdraw electron from benzene ring and decrease the electron density on ortho para position.
When they attached with the benzene rings they allow the incoming electrophilic reagent toward ortho and para positions.	When they attached with the benzene ring, they invite the incoming electrophilic reagent towards meta positions.
Example are –R, –RCO, –OR $-Cl$, $-Br$, $-CH_3$, $-OH$ etc	Examples are –COOR, –CHO $-COOH$, $-NO_2$, $-COCH_3$, $-SO_3H$ etc

EXERCISE

Multiple Choice Questions

(i) The final product obtained when hydrogen bromide (HBr) is added to an ethyne molecule:
(a) Bromo ethene
[✓ (b) 1, 1-dibromo ethane]
(c) 1,2-bromo ethane
(d) 1,1,2,2 tetra bromoethane

(ii) The formula of a saturated hydrocarbon is C_3H_6, it should be:
(a) Propane
(b) Propene
(c) Propyne
[✓ (d) Cyclopropane]

(iii) Ozonide on heating with zinc dust produce:
(a) Alcohol
[✓ (b) Aldehyde]
(c) Alkene
(d) Ether

(iv) Which of the following pairs of compounds represent functional group isomerism?
(a) 1-butene and 2-butene
[✓ (b) Ethanol and dimethyl ether]
(c) n-butane and iso butane
(d) Diethyl ketone and methyl propyl ketone

(v) The substituent that can act as a meta director is:
(a) -Cl
(b) $-CH_3$
(c) -OH
[✓ (d) -COOH]

(vi) Welding gas among the following is:
(a) Ethylene
[✓ (b) Acetylene]
(c) Ethane
(d) Methane

(vii) Benzene burns with smokey flame because of its:
(a) Inflammability
[✓ (b) High carbon % age]
(c) High resonance energy
(d) Aromaticity

(viii) Select the suitable chemical to distinguish between Ethene and Ethyne:
(a) Alkaline $KMnO_4$
(b) Acidified $KMnO_4$
(c) Bromine water
[✓ (d) Ammonical $AgNO_3$]

(ix) Meta directing group among the following is:
(a) – OH (b) – NH_2
(c) – CH_3 (d) – NO_2

(x) Acylation of benzene in the presence of $AlCl_3$ gives:
(a) Toluene (b) Acetophenone
(c) Phenol (d) Xylene

Short Questions

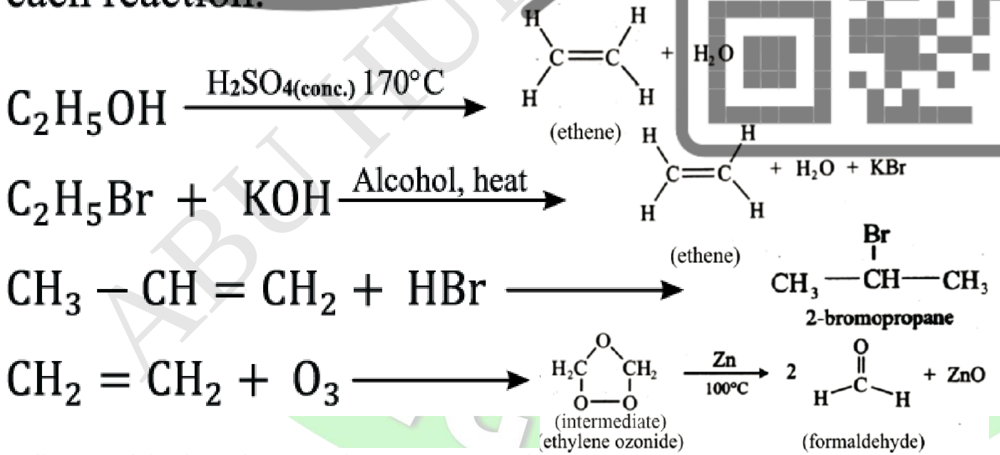
1. Give three differences between aliphatic and aromatic hydrocarbons?

Aliphatic Hydrocarbons	Aromatic Hydrocarbons
1) It has less percentage of carbon.	*1) It has more percentage of carbon.*
2) It doesn't burn with black soot.	*2) It burns with black soot.*
3) It can be cyclic and acyclic.	*3) It is always cyclic.*

2. Give the mechanism of free radical reaction between methane and chlorine in the presence of sunlight.

Already discussed above

3. Complete the following reactions and name the major product formed in each reaction.

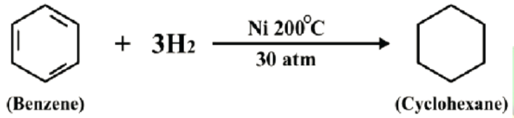


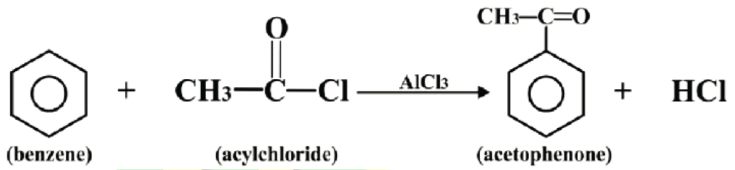
4. Define a chiral carbon? Give an example to justify your answer.

Already discussed above

5. Write the equations with all required conditions for the reaction of benzene with the following:

(i) H_2 (ii) CH_3COCl (iii) $HNO_{3(conc.)}$ (iv) $H_2SO_{4(conc.)}$

(i)


(ii)


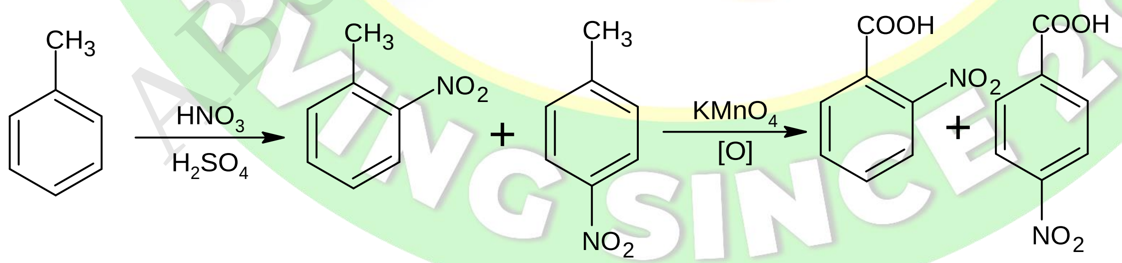
(iii)


(iv)

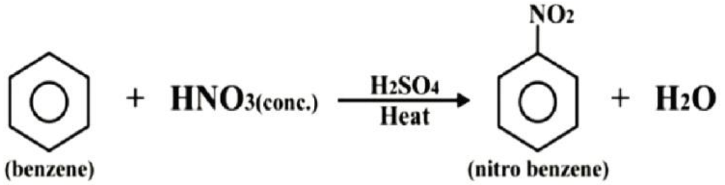

6. Bring about the following conversions.

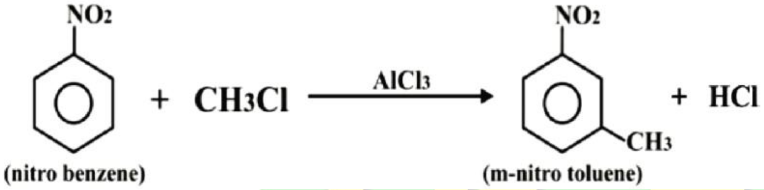
(i) Toluene to ortho-para nitro benzoic acid

(ii) Benzene to m-nitro toluene



(i)





(ii)

7. How can you prepare ethene from dehydration of ethanol and ethyne from dehydro halogenations of ethyl chloride?

Already discussed above

8. Alkanes are generally referred as parafins due to their less reactivity, why are they stable towards chemical reactions?

Ans. A Sigma bond is present between carbon atoms of alkanes. Sigma bond is stronger bond due to head-to-head overlapping. It's more difficult to break sigma bond that's why alkanes are less reactive towards chemical reactions.

Descriptive Questions

1. Draw the orbital structures of the following hydrocarbons.
   (i) Ethane (ii) Ethylene (iii) Acetylene

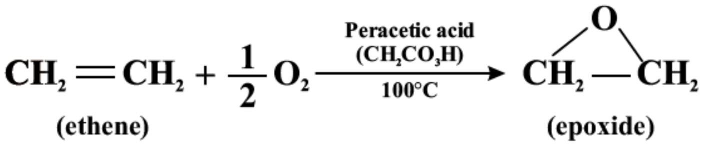
Already discussed above

2. Write the equations of the following chemical processes.
   (i) Ethylene is heated at high temperature and pressure.

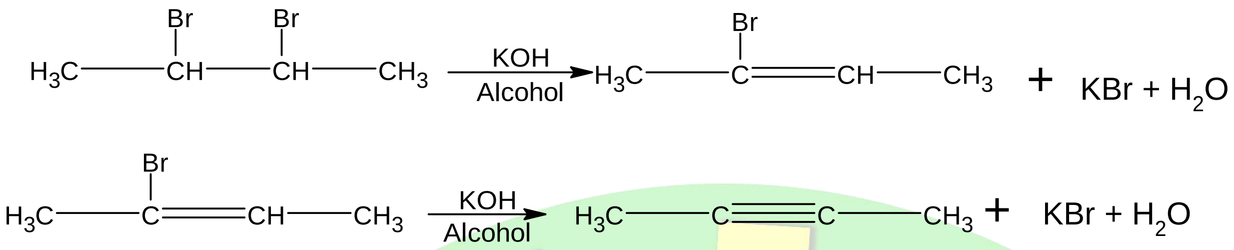
$$nH_2C{=}CH_2 \xrightarrow[2000\text{ atm}]{200^\circ C} \left[CH_2-CH_2 \right]_n$$

(ethene) (polyethene)

(ii) Ethene is burnt in air in the presence of per acetic acid.



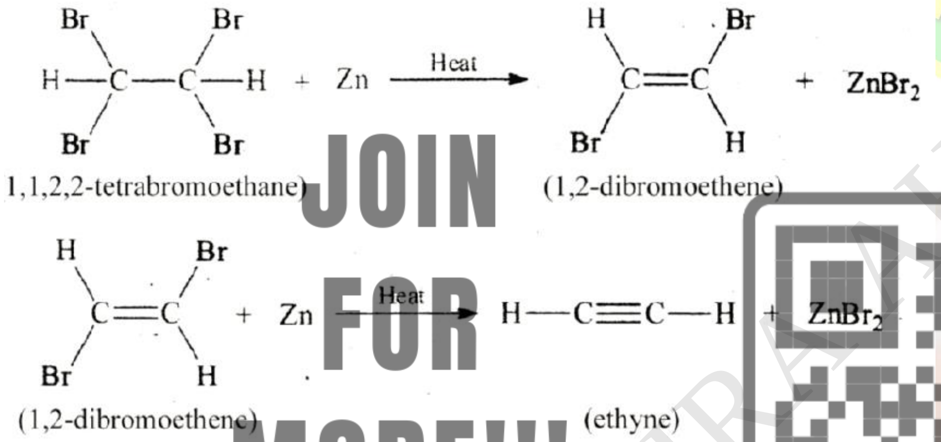
(iii) 1,2-di bromo butane is heated with alcoholic potassium hydroxide.



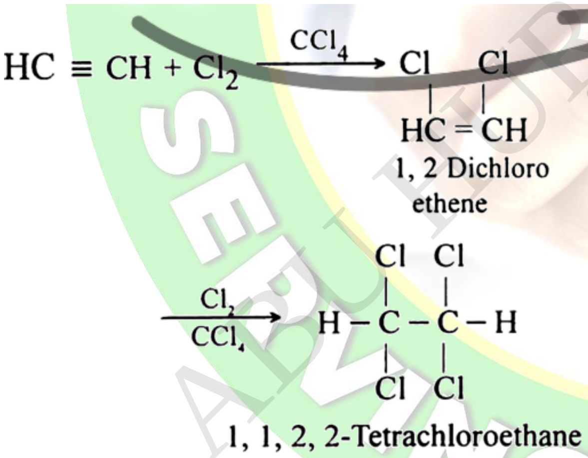
$$H_3C-\overset{Br}{CH}-\overset{Br}{CH}-CH_3 \xrightarrow[\text{Alcohol}]{\text{KOH}} H_3C-\overset{Br}{C}=CH-CH_3 + KBr + H_2O$$

$$H_3C-\overset{Br}{C}=CH-CH_3 \xrightarrow[\text{Alcohol}]{\text{KOH}} H_3C-C\equiv C-CH_3 + KBr + H_2O$$

(iv) 1,1,2,2 tetra bromo ethane is heated with zinc powder.



(v) Reaction of chlorine with acetylene



3. Ethene is more reactive than ethane but less reactive than ethyne, how can you explain this behavior?

Ans. Ethene is more reactive than ethane due to the presence of pi bond which is weaker than sigma bond. Ethene is less reactive than ethyne because ethyne contains two pi bonds.

4. What is meant by isomerism? Explain four different types of structural isomers and give one example of each.

Already discussed above

5. Explain the following with suitable examples.
   (a) Optical isomers (b) Geometrical isomers

Already discussed above

6. Describe the molecular orbital structure of benzene.

Already discussed above

7. Give the mechanism of following Electrophilic substitution reaction of benzene.
   (a) Nitration (b) Acylation (c) Chlorination

Already discussed above

8. What is meant by ortho, para and meta directing groups. Explain the influence of substituent of benzene to the incoming Electrophile.

Already discussed above

9. Why ethyne terminal hydrogen is acidic in nature? Give two reactions of ethyne to show their acidic behavior.

Already discussed above

CHAPTER 6

AKYL HALIDES & AMINES

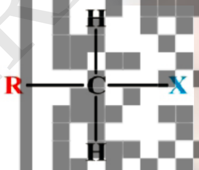
“Organic compounds that contain at least one halogen atom (fluorine, chlorine, bromine or iodine) bonded to an alkyl group are called haloalkanes.”

Types of Haloalkanes:

- **Monohaloalkanes** have only one halogen atom. (They are also called **alkyl halides**)
  The general formula of alkyl halides in R-X, where R is alkyl group and X is halogen atom (functional group).
  Another general formula is $C_nH_{2n+1}X$ where n represents the number of carbon atoms.
- **Dihaloalkanes** have only two halogen atoms.
- **Trihaloalkanes** have only three halogen atoms.

Classification of Alkyl Halides:

- **Primary alkyl halides or 1° alkyl halides:** Only one alkyl radical is bonded to α carbon.

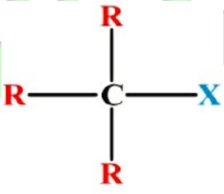


(1°- Alkyl halide)

  For example: 1-bromo propane ($CH_3CH_2CH_2Br$)
- **Secondary alkyl halides or 2° alkyl halides:** Two alkyl radical is bonded to α carbon.

(2°- Alkyl halide)

  For example: 2-bromo propane ($CH_3CHBrCH_3$)
- **Tertiary alkyl halides or 3° alkyl halides:** Three alkyl radical is bonded to α carbon.

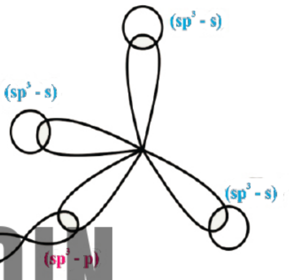


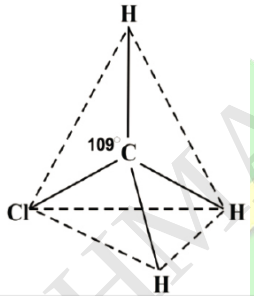
(3°- Alkyl halide)

  For example: 2-bromo-2-methylpropane $CH_3C(CH_3)_2Br$

Structure of Alkyl Halide

Let us consider methyl chloride (CH_3-Cl) as an alkyl halide. The geometry of molecule is explained by hybrid orbital theory. Carbon of methyl halide is bonded with four atoms which means carbon is utilizing its all four valence electrons to produce four sp^3 hybrid orbitals, which are oriented at an angle of 109° to give a tetrahedral geometry. These four sp^3 hybrid orbitals are shared with three s-orbitals of hydrogen atoms and one p-orbital of chlorine by head on overlapping to make four sigma bonds (Fig.6.1).





Physical Properties of Alkyl Halides

- They are mostly gases and liquids.
- Alkyl halides with more than 18 carbons atoms are colorless solids.
- They are soluble in organic solvents.
- They have higher melting and boiling point than alkanes.

Preparation of Alkyl Halides

1. Reaction of Alcohol with Hydrogen Halides:

$$R-OH + HX \longrightarrow R-X + H_2O$$

$$\underset{\text{(Ethyl alcohol)}}{CH_3CH_2OH} + \underset{\text{(Hydrogen chloride)}}{HCl} \xrightarrow{ZnCl_2} \underset{\text{(Ethyl chloride)}}{CH_3CH_2Cl} + H_2O$$

2. Reaction of Alcohol with halogenating agents:

$$3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3$$

$$\underset{\text{(Ethyl alcohol)}}{3CH_3CH_2OH} + \underset{\text{(Phosphorous tri chloride)}}{PCl_3} \longrightarrow \underset{\text{(Ethyl chloride)}}{3CH_3CH_2Cl} + \underset{\text{(Phosphorous acid)}}{H_3PO_3}$$

$$R-OH + SOX_2 \longrightarrow R-X + SO_2 + HX$$

$$\underset{\text{(Ethyl alcohol)}}{CH_3CH_2OH} + \underset{\text{(Thionyl chloride)}}{SOCl_2} \xrightarrow{\text{Pyridine}} \underset{\text{(Ethyl chloride)}}{CH_3CH_2Cl} + SO_2 + HCl$$

3. By the halogenation of alkane:

$$CH_4 + Cl_2 \xrightarrow{UV} CH_3Cl + HCl$$

(Methane) (Chlorine) (Methyl chloride)

Nucleophilic Substitution Reactions

"A type of chemical reactions in which a strong nucleophile (electron efficient species) replaces the weak nucleophile of the substrate is termed as nucleophilic substitution reactions."

$$R-X + Nu \longrightarrow R-Nu + X^-$$

(Alkyl halide Substrate) (Attacking Nucleophile) (Product) (Leaving Nucleophile)

Different strong nucleophilic can produce a variety of organic compounds when treated with an alkyl halide.

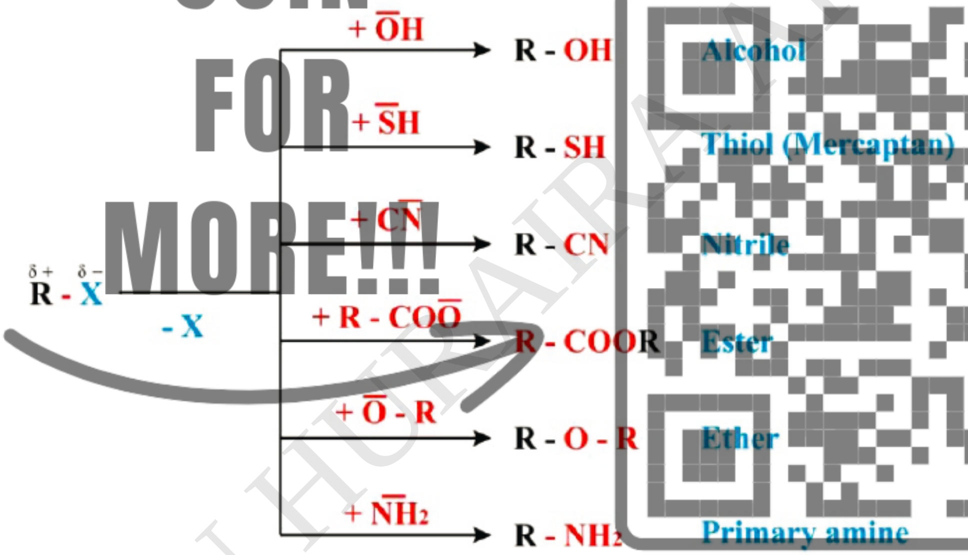


Table 6.1 Some common strong Nucleophiles along with their typical reagents.

Nucleophiles	Typical Reagent
^-OH	NaOH, KOH
^-SH	KSH
CN^-	NaCN
$CH_3\text{-}COO^-$	$CH_3\text{-}COONa$
$CH_3\text{-}CH_2\text{-}O^-$	$CH_3\text{-}CH_2\text{-}ONa$
NH_2^-	$NaNH_2$

Self Assessment

Why alkyl halide undergoes nucleophilic substitution reaction? Which reagent is required to convert a methyliodide into:
(i) Methanol (ii) Methyl cyanide (iii) Dimethyl ether (iv) Thiol

Ans. Alkyl halide undergoes nucleophilic substitution reaction because of the presence of polar covalent bond between carbon atom and halogen atom. Due to the high electronegativity of halogens, it carries a partial negative charge and carbon carries a partial positive charge. Carbon with a positive charge is called carbonium ion or carbocation. Carbonium ion is a good place for the attack of nucleophile. Nucleophile makes bond with carbon and the halogen is removed.

(i) H_2O

(ii) KCN

(iii) CH_3Ona

(iv) KSH

Mechanism of nucleophilic substitution reactions

The mechanism of nucleophilic substitution reaction is divided into:

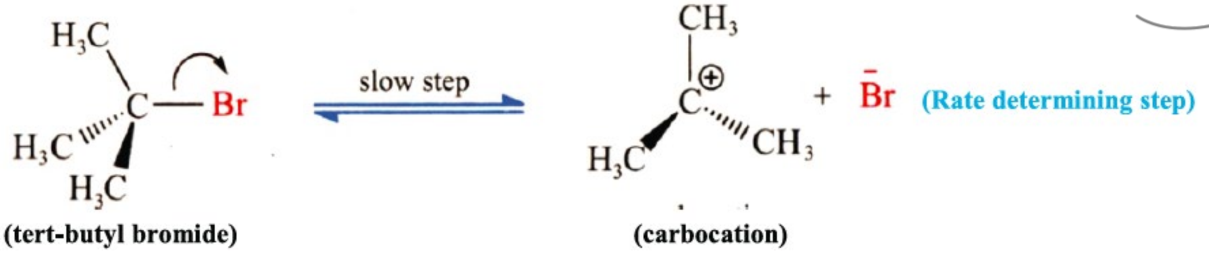
(i) $S_N{}^1$ Reactions

(ii) $S_N{}^2$ Reactions

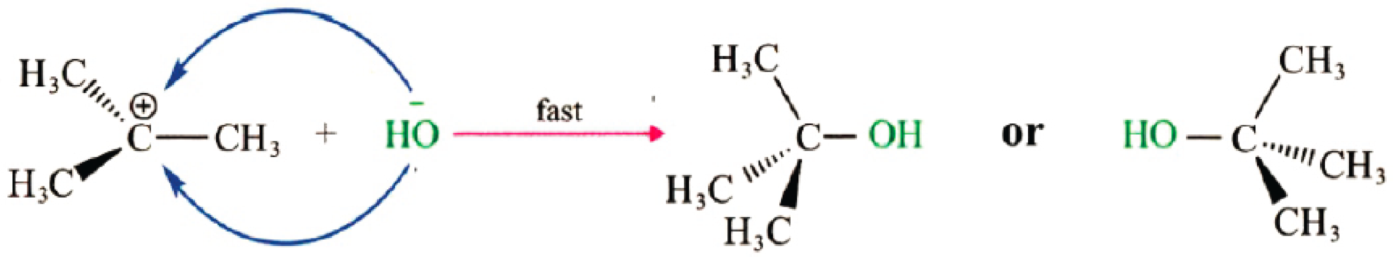
SN^1 mechanism

It is unimolecular bi-step SN reaction. **"The SN1 reaction mechanism proceeds in two distinct steps, with the first step involving the departure of the leaving group (the halogen atom) from the substrate molecule, leading to the formation of a carbocation intermediate, followed by nucleophilic attack in the second step".**

Step-1: Departure of halogen from substrate to form carbocation



Step-2: Attack of strong nucleophile on carbocation to form product



(carbocation) **(nucelophile)** **(product)**

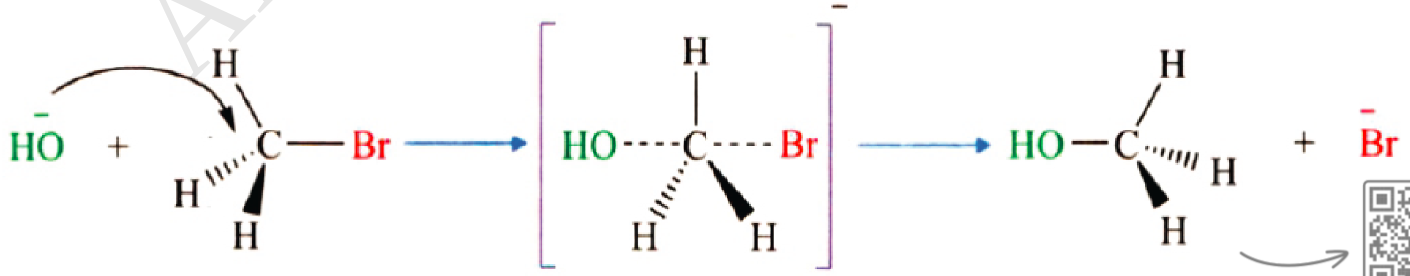
Tertiary alkyl halides undergo SN^1 reactions more readily than primary or secondary alkyl halides due to the stabilizing effect of electron-donating alkyl groups, and favoring the formation of the carbocation intermediate, thus facilitating the SN^1 reaction.

Chemical reactions that processed via the SN^1 mechanism exhibit first-order Kinetics, and the rate of the reaction is dependent on the concentration of the substrate, not on the nucleophile involved in the reaction.

$$R = K\,[\text{Substrate}]$$

SN^2 mechanism

It is bimolecular single step SN reaction **"In the SN2 mechanism, bond formation and bond breaking occur simultaneously in a single step process".** The nucleophile directly attacks the electrophilic carbon atom of the substrate, leading to the departure of the halogen atom attached to the electrophilic carbon. The nucleophile attacks from the back side because the front side is sterically hindered by the nucleophile of the substrate.



(Attacking Nucleophile) **(Substrate)** **(Transition state)** **(Product)**

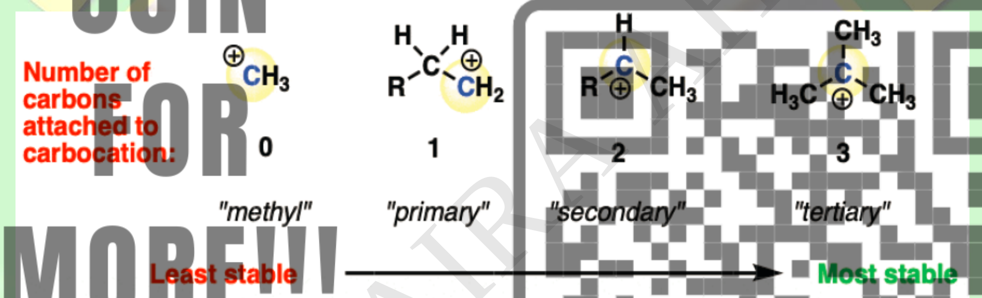
The SN^2 mechanism is typically observed in primary alkyl halides and methyl haldies because primary carbocation and methyl carbocation are highly unstable due to the lack of electron donating alkyl groups.

The SN^2 mechanism is followed by second order kinetics which means that the reaction rate is dependent upon the concentration of both substrate and attacking nucleophile.

$$\mathbf{R = K\,[Substrate]\,[N\bar{u}]}$$

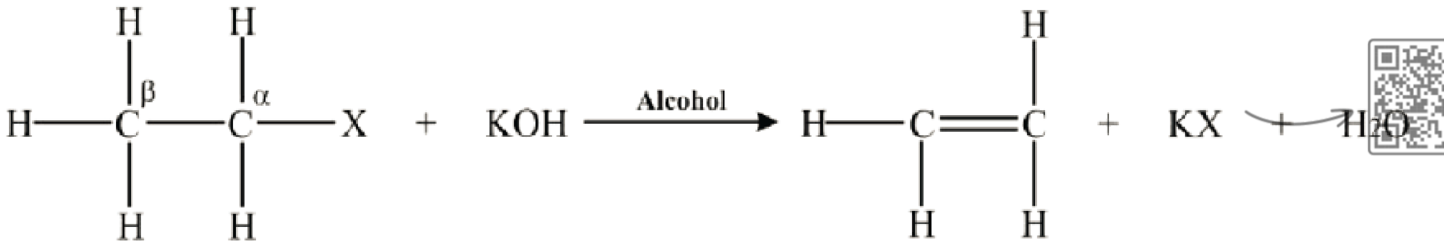
Carbocations and their stability

"Carbocations are organic ions that have a positively charged carbon atom. They are formed when a carbon atom loses a pair of electrons."



Elimination Reactions

An elimination reaction refers to a type of organic reaction where the substituents are removed from the adjacent carbon atoms of substrate molecule. **"When an alkyl halide reacts with alcoholic potassium hydroxide, the removal of hydrogen and halogen atoms from two adjacent carbon atoms of substrate takes place, giving a multiple bond product"**. It is referred as 1, 2-elimination or β–elimination reaction.



$$H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}_{\beta}-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}_{\alpha}-X + KOH \xrightarrow{\text{Alcohol}} H-\underset{H}{\underset{|}{C}}=\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}} + KX + H_2O$$

(Alkyl halide) **(Base)** **(Alkene)**

There are two common types of β–elimination reactions named as E_1 and E_2.

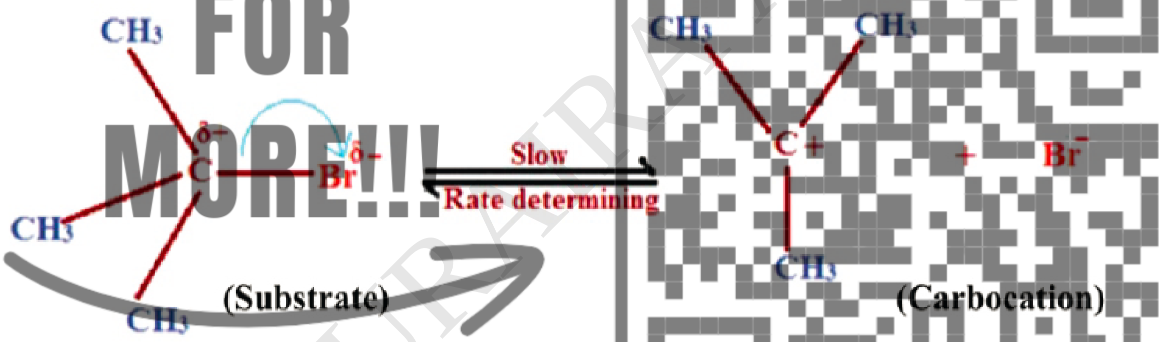
(i) E_1 (Uni molecular elimination reactions)

(ii) E_2 (Bi molecular elimination reactions)

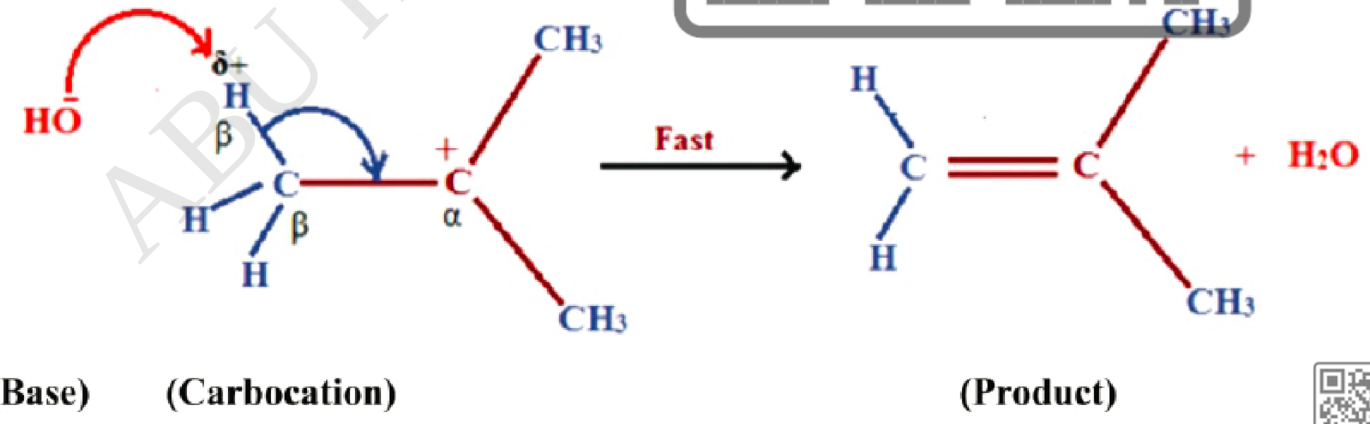
Mechanism of E_1 Reaction

E1 reactions, known as unimolecular elimination reactions, occur in two steps. In the first step, the halogen atom departs from the substrate, forming a carbocation intermediate, which is the slow and rate-determining step. In the second step, a base abstracts a proton from the carbon next to the halogenated carbon, leading to the formation of a double bond between the two adjacent carbon atoms.

Step-1: Formation of carbocation



Step-2: Attack of Base on β-H & formation of multiple bond

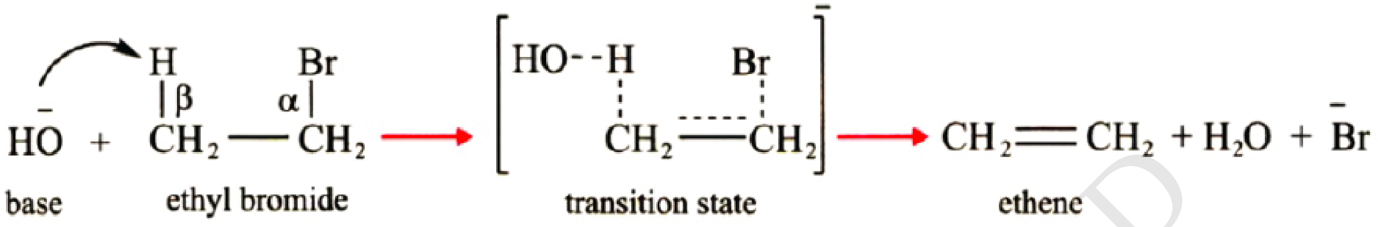


The rate determining step in E^1 mechanism involves the unimolecular ionization of the substrate molecule. Therefore, the rate of the reaction depends only on the concentration of reactant, and not on the concentration of base.

$$R = K[\text{Substrate}]$$

Mechanism of E_2 – reaction

E_2-reaction is referred as bimolecular elimination reaction. The mechanism completes in single step in which both substrate and attacking base are involved.



$$\overset{-}{HO} + \overset{H}{\underset{\beta}{CH_2}} - \overset{Br}{\underset{\alpha}{CH_2}} \longrightarrow \left[\overset{HO--H}{CH_2} \text{-----} \overset{Br}{CH_2} \right]^{-} \longrightarrow CH_2{=}CH_2 + H_2O + \overset{-}{Br}$$

Mechanism of E_2 reaction is feasible in primary alkyl halides for example when ethyl bromide is allowed to react with hot alcoholic potassium hydroxide, it gives ethene followed by E_2-mechanism. Base first attacks on ethyl bromide and abstracts a proton from β-carbon. Simultaneous halide ion eliminates from ∝-carbon and the lone pair of electrons is shifted between ∝ and β carbon to give an ethene.

Therefore, as far as kinetics of E_2 reaction is concerned, the rate of this reaction depends upon the concentration of both substrate and attacking base, the rate law may be written as

$$R = K\,[Sub]\,[base]$$

Self Assessment

Explain the following:

- ➢ Why β-elimination reactions are not possible in methyl halides?
- ➢ Why SN^2 reaction is not favourable in tertiary alkyl halides?
- ➢ Why tertiary carbocation is more stable than secondary and primary carbocations?

(i) β-elimination reactions lead to the formation of alkene via elimination of β hydrogen. Since, methyl halides don't contain β hydrogen. That's why β-elimination reactions is not possible.

(ii) SN^2 reaction is not favorable in tertiary alkyl halides because of high steric hindrance of alkyl radicals. It is also the reason for high stability of tertiary alkyl halides.

(iii) tertiary carbocation is more stable than secondary and primary carbocations because of high steric hindrance.

(ORGANOMETALLIC COMPOUNDS)

"Organic compounds that possess at least one bond between a carbon atom and a metal atom are called organometallic compounds."

Some common examples of organometallic compounds are as follows:

(i) Grignard's Reagent (R-Mg-X)

(ii) Tetraethyl lead $(C_2H_5)_4Pb$ → It is used as knock inhibitor in petroleum industry

GRIGNARD'S REAGENT:

"Grignard's reagent is an organometallic compound that contains a carbon-magnesium (C-Mg) bond."

The name Grignard is derived from a French chemist Victor Grignard, who first synthesized this compound and was subsequently awarded the Nobel Prize in Chemistry in 1912.

Preparation of Grignard Reagent

Grignard reagents are prepared in the laboratory by the reaction of an alkyl halide with magnesium metal in the presence of anhydrous ether.

$$R-X + Mg \xrightarrow{\text{anhydrous ether}} R-MgX$$

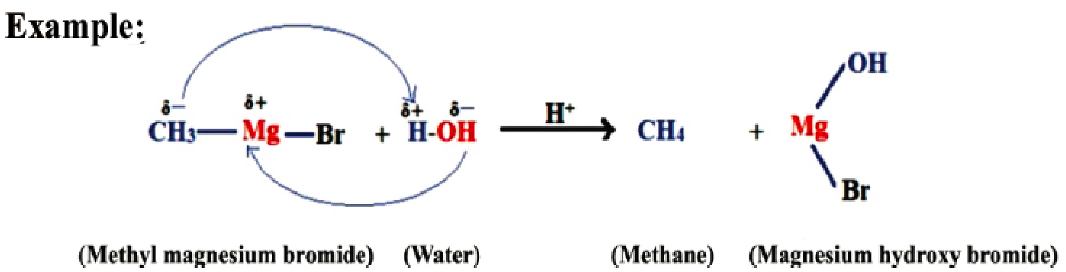
Where R = alkyl group, for example $-CH_3$, $-C_2H_5$ etc

X = halogen, for example $-Cl$, $-Br$, $-I$

$$\underset{\text{Ethyl halide}}{CH_3CH_2X} + \underset{\text{Magnesium}}{Mg} \xrightarrow{\text{Ether}} \underset{\substack{\text{Grignard Reagent} \\ \text{(Ethyl magnesiumhalide)}}}{CH_3CH_2MgX}$$

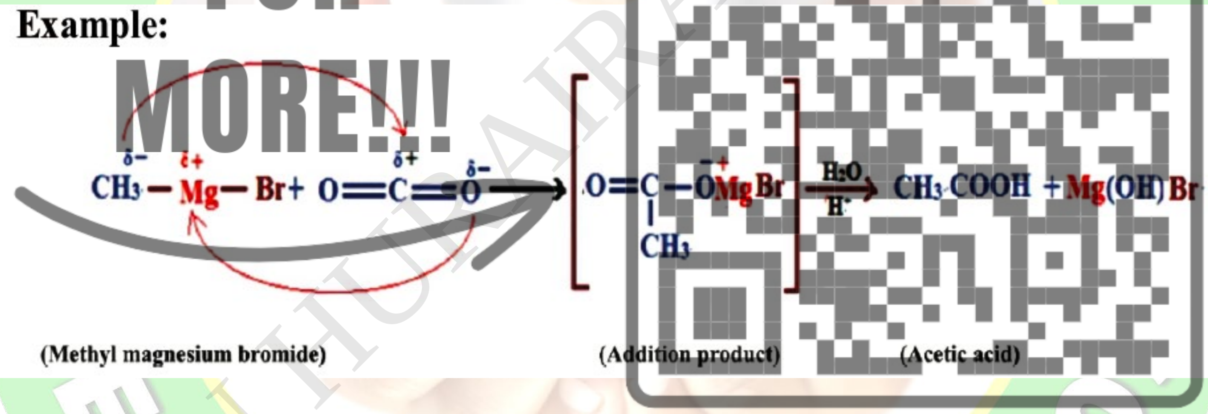
Reactions of Grignard Reagent

(i) Reaction with water:

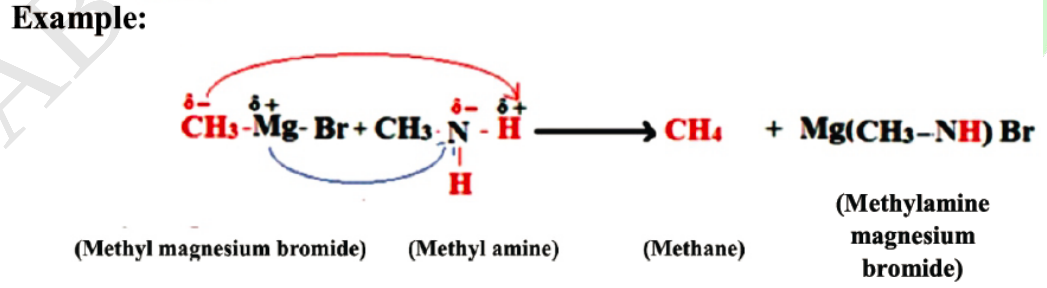


(ii) Reaction with Ester:

(iii) Reaction with CO_2:



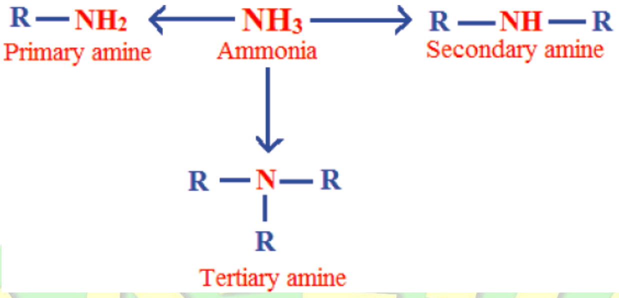
(iv) Reaction with Primary Amine:



AMINES

"Organic compounds that contain a nitrogen atom bonded to one or more alkyl or aryl group are known as amines."

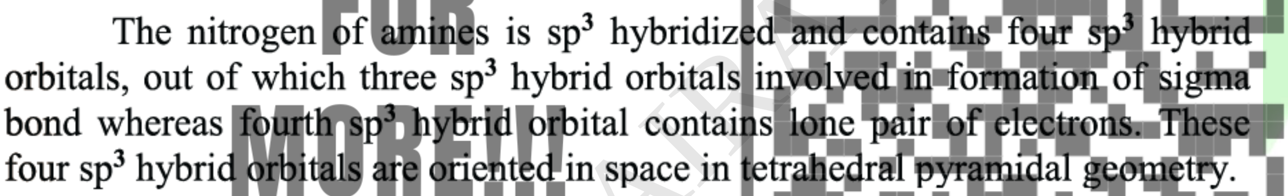
Amines are derivate of ammonia where one or more hydrogen atoms of ammonia are replaced by an alkyl or aryl group.



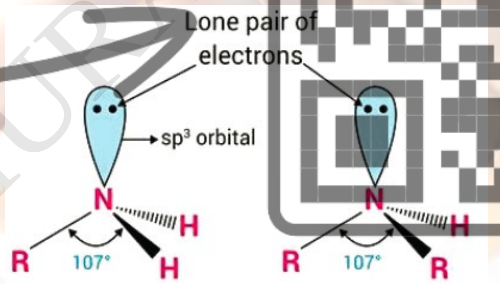
PHYSICAL PROPERTIES OF AMINE:

- Methyl amine (CH_3NH_2) is a gas and higher members are liquids.
- They have an unpleasant smell. For example: trimethylamine **$N(CH_3)_3$** has a strong fishy odor and is found in decaying fish and other organic matter.

STRUCTURE OF AMINE:



The nitrogen of amines is sp^3 hybridized and contains four sp^3 hybrid orbitals, out of which three sp^3 hybrid orbitals involved in formation of sigma bond whereas fourth sp^3 hybrid orbital contains lone pair of electrons. These four sp^3 hybrid orbitals are oriented in space in tetrahedral pyramidal geometry.



BASICITY OF AMINES:

Amines are basic in nature. The basicity of amines is explained by the presence of lone pair of electrons on nitrogen atom.

$$R - NH_2 + HCl \longrightarrow [R - NH_3]^+ Cl^-$$

(Primary amine) **(Alkylammonium chloride salt)**

Preparation of Amines

(i) Alkylation of Ammonia by Alkyl Halides

$$CH_3-I + NH_3 \longrightarrow CH_3-NH_2 + HI$$

(Primary amine)

$$CH_3-NH_2 + CH_3-I \longrightarrow CH_3-NH-CH_3 + HI$$

(Secondary amine)

$$CH_3-NH-CH_3 + CH_3-I \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{N}-CH_3 + HI$$

(Tertiary amine)

(ii) Reduction of Nitriles

$$CH_3-C\equiv N + 4[H] \xrightarrow{LiAlH_4} CH_3-CH_2-NH_2$$

(methyl cyanide) (Ethyl amine)

(iii) Reduction of Amides

$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2 + 4[H] \xrightarrow{LiAlH_4} CH_3\text{-}CH_2\text{-}NH_2 + H_2O$$

(Amide) (Ethyl amine)

Reactions of Amines

(i) Alkylation of Amines by Alkyl Amines

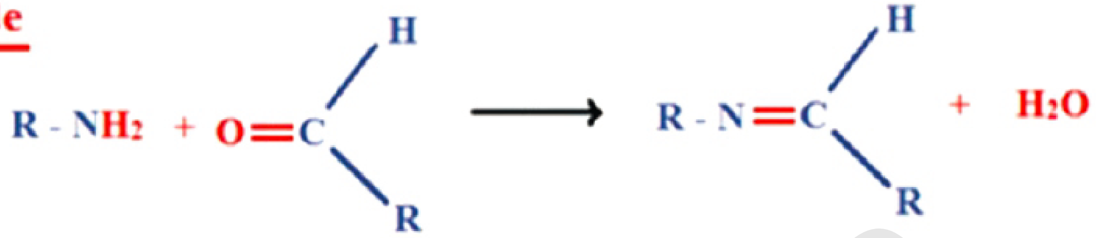
$$CH_3-NH_2 \xrightarrow[-HI]{CH_3I} (CH_3)_2NH \xrightarrow[-HI]{CH_3I} (CH_3)_3N$$

(Methylamine) (Dimethylamine) (Trimethylamine)

(ii) Reaction of Amine with aldehyde and ketone

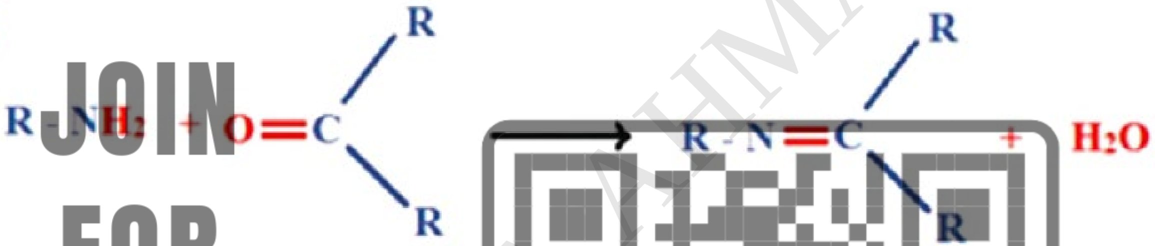
Primary amines can react with aldehydes and ketones to produce "imines" which also referred as Schiff bases.

with Aldehyde



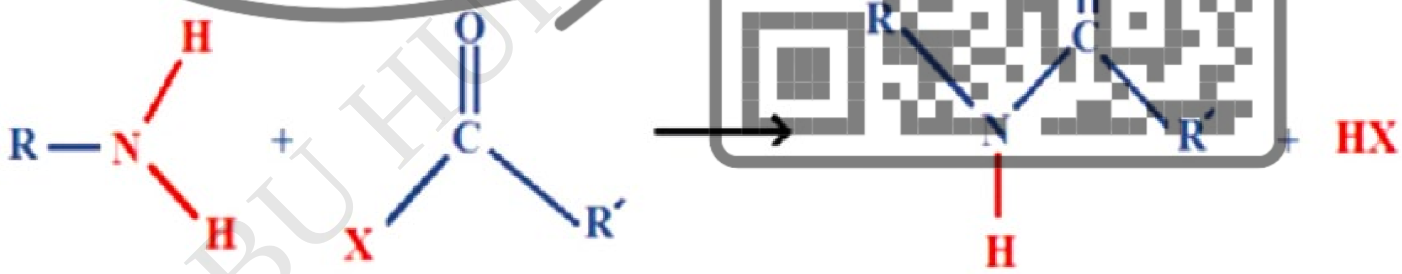
(Primary amine) (Aldehdye) (imine)

with ketone



(Primary amine) (Ketone) (imine)

(iii) Preparation of Amides



(Primary amine) (acyl halide) (Sec: amide)

(iv) Preparation of Diazonium salts

$$\underset{\text{(Amine)}}{R-NH_2} + \underset{\text{(Nitrous acid)}}{HNO_2} + HCl \xrightarrow{\text{Below } 10^\circ C} \underset{\text{(Diazonium chloride)}}{R-N^+ \equiv NCl^-} + 2H_2O$$

Multiple Choice Questions

(i) Which of the following composition justifies the secondary alkyl halide?

(a) R_3CX [✓ (b) R_2CHX]
(c) RCH_2X (d) CH_3X

(ii) Which of the following alkyl halide cannot produce an alkene while treated with alcoholic potassium hydroxide:

[✓ (a) Methyl bromide] (b) Ethyl bromide
(c) Propyl bromide (d) Butyl bromide

(iii) Ethyl magnesium bromide with carbon dioxide yields.

(a) Methanoic acid (b) Ethanoic acid
[✓ (c) Propanoic acid] (d) Butanoic acid

(iv) Grignard reagent with ester produces:

(a) Aldehyde (b) Carboxylic acid
[✓ (c) Ketone] (d) Ether

(v) Amines act as bases because:

(a) They accept OH^- [✓ (b) They accept H^+]
(c) They donate H^+ (d) They donate the OH^-

(vi) The structure of Primary amine is:

(a) Planar trigonal (b) Linear
[✓ (c) Tetrahedral pyramidal] (d) Regular tetrahedral

(vii) Alkyl amine when reacts with nitrous acid in the presence of hydrochloric acid, yields:
[✓ (a) Diazonium salt]
(b) Aldehyde
(c) Ketone
(d) Alcohol

(viii) SN^2 reaction occurs most easily if the substrate molecule is:
[✓ (a) A methyl iodide]
(b) An ethyl iodide
(c) 2-iodo propane
(d) 2-iodo butane

(ix) Suitable reagent required for the synthesis of propane from methyl magnesium iodide is:
[✓ (a) H_2O]
(b) NH_3
(c) CH_3OH
(d) CH_3NH_2

(x) The rate of SN^1 mechanism depends upon:
[✓ (a) Conc. of substrate only]
(b) Conc. of attacking nucleophile only
(c) Conc. of both substrate and attacking nucleophile
(d) Polar solvent

Short Questions

1. How are alkyl halides prepared by the reaction of alcohol with (i) HX (ii) PX_3 (iii) $SOCl_2$. Give the equations.

ALREADY DISCUSSED ABOVE

2. How are amines prepared from nitriles, give the equations.

ALREADY DISCUSSED ABOVE

3. Why are secondary and tertiary amines more alkaline than primary amines?

WRONG QUESTION

The correct order of basicity is **Primary > Secondary > Tertiary**

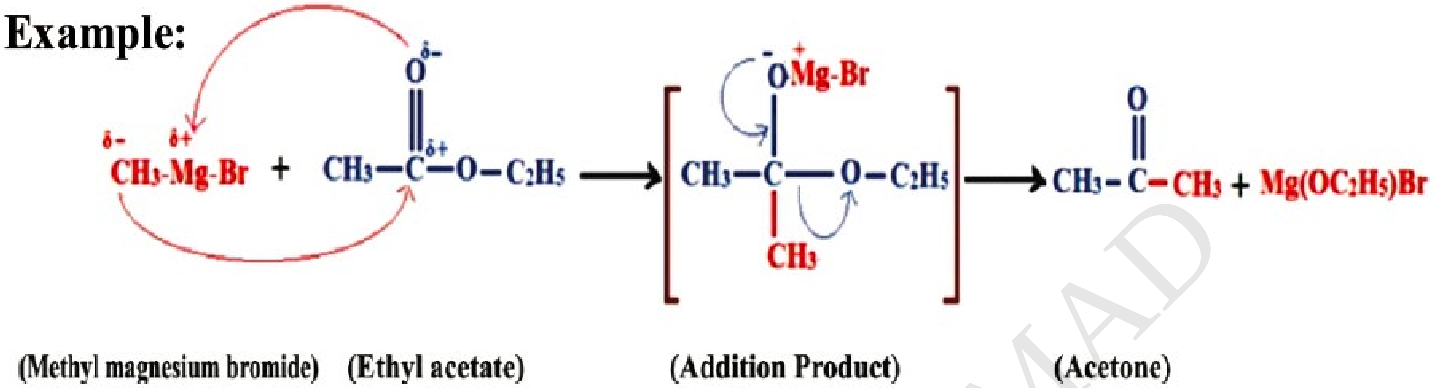
4. Why the alkyl part of Grignard reagent is nucleophilic in nature?

Ans. Alkyl part of Grignard's reagent is nucleophilic in nature due to high electro positivity of magnesium. Magnesium metal has the tendency to loss electron which creates a partial negative charge on alkyl radical. Hence, it behaves as a nucleophile.

5. Convert the followings:

(a) Methyl magnesium bromide into acetone

Example:



(b) Ethyl chloride into ethyl amine

$$C_2H_5Cl + NH_3 \rightarrow C_2H_5NH_2 + HCl$$

(c) Ethyl chloride into ethyl alcohol

$$H_3C\ CH_2\ Cl + KOH \xrightarrow{H_2O} H_3C\ CH_2\ OH + KCl$$

(d) Ethyl amine into imine

$$H_3C\ CH_2\ NH_2 + O\ \overset{H}{\underset{H}{C}} \longrightarrow H_3C\ CH_2\ N\ \overset{H}{\underset{H}{C}} + H_2O$$

6. How is primary amine converted into secondary and tertiary amines, give the equations.

ALREADY DISCUSSED ABOVE

7. Give an account on the basicity of amines.

ALREADY DISCUSSED ABOVE

8. How can you justify the fact that alkyl halides are water insoluble?

Alkyl halides are soluble in organic solvents but are slightly soluble in water, this is due to the inability of alkyl halides to form hydrogen bonds with water.

9. How can you define a nucleophile? Write the names of four nucleophiles along with their typical reagents.

Ans. Nucleophile is a chemical species within a molecule that can donate a pair of electrons to form a covalent bond with another atom or molecule.

Nucleophile	Reagent
OH^-	KOH
CN^-	KCN
SH^-	KSH
OR^-	RONa

10. Why the mechanism of SN^2 reaction completes in one step?

Ans. Because of less steric hindrance the removal of halogen and formation of C-Nu bond takes place in the same time in primary alkyl halides. That's why SN^2 reaction completes in one step.

Descriptive Questions

1. How can you define nucleophilic substitution reactions? Describe the mechanisms of SN^1 and SN^2 reactions.

ALREADY DISCUSSED ABOVE

2. What is β-elimination? Discuss the mechanisms of E_1 and E_2 reactions.

ALREADY DISCUSSED ABOVE

3. What are organometallic compounds? How is Grignard reagent prepared? Write down the reactions of Grignard reagent with water, carbon dioxide, ester and amines.

ALREADY DISCUSSED ABOVE

4. What are alkyl halides? Define primary, secondary and tertiary alkyl halides.

ALREADY DISCUSSED ABOVE

5. Draw the orbital structure of methyl iodide and explain the type of hybridization in it.

The structure of methyl chloride has been discussed above. Just change chloride with iodide and the whole answer will remain same.

6. Give a comparative study between nucleophilic substitution reactions and elimination reactions of alkyl halides.

Nucleophilic Substitution Reaction	Elimination Reaction
It follows SN^1 and SN^2 mechanism	It follows E^1 and E^2 mechanism
It occurs in aqueous medium.	It occurs in alcoholic medium
No pi bond is formed in this reaction.	Pi bond is formed in this reaction.
It is favored by polar medium	It is favored by non-polar medium

CHAPTER 7

Alcohols, Phenols and Ethers

ALCOHOL

Alcohol is a class of organic compounds in which hydroxyl group (-OH) is attached to an aliphatic carbon atom.

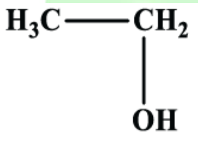
CLASSIFICATION OF ALCOHOL:

Alcohols are classified into three types on the basis of number of hydroxyl group attached to carbon.

(i) Monohydric Alcohol – It contains 1 OH group

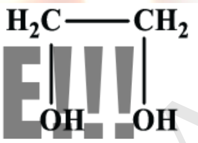
(ii) Dihydric Alcohol – It contains 2 OH groups

(iii) Trihydric Alcohol – It contains 3 OH groups



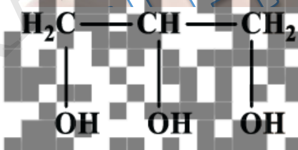
$H_3C-\underset{\displaystyle OH}{\underset{|}{CH_2}}$

Ethanol
(monohydric alcohol)



$\underset{\displaystyle OH}{\underset{|}{H_2C}}-\underset{\displaystyle OH}{\underset{|}{CH_2}}$

Ethylene glycol
(Dihydric alcohol)



$\underset{\displaystyle OH}{\underset{|}{H_2C}}-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH_2}}$

Glycerol
(Trihydric alcohol)

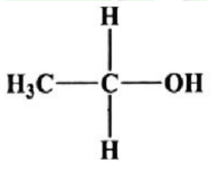
CLASSIFICATION OF MONO HYDRIC ALCOHOLS:

Monohydric alcohols can be further classified into three types.

(a) **Primary or 1° Alcohols** – 1 Alkyl radical is attached to α carbon

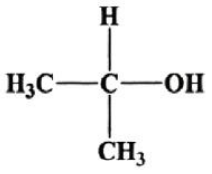
(b) **Secondary or 2° Alcohols** – 2 Alkyl radicals is attached to α carbon

(c) **Tertiary or 3° Alcohols** - 3 Alkyl radicals is attached to α carbon



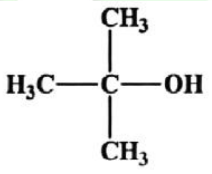
$H_3C-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C}}}}-OH$

(1° - alcohol)
(ethyl alcohol)



$H_3C-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH$

(2° - alcohol)
(isopropyl alcohol)

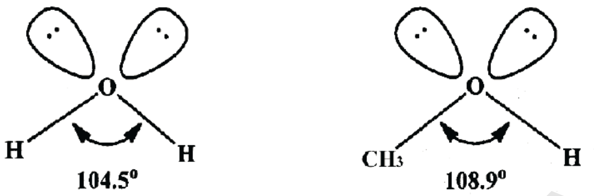


$H_3C-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH$

(3° - alcohol)
(t-butyl alcohol)

Structure of Alcohol

The structure of an alcohol molecule is similar to that of water molecule. The carbon which is boned to hydroxyl group is sp^3 hybridized. The oxygen atom of -OH group is also sp^3 hybridized. Oxygen atom utilizes its two sp^3 hybrid orbitals in the formation of sigma bond with carbon and hydrogen atom while the remaining two sp^3 hybrid orbitals of oxygen contain lone pairs of electrons.



PHYSICAL PROPERTIES OF ALCOHOL:

- Alcohols from methanol to butanol are colorless liquids. Higher members are waxy solids.
- BP of alcohol is more than alkanes due to the presence of hydrogen bond. The greater the number of carbons in the molecule, the higher the boiling point of alcohol. Further, the boiling point of straight chain alcohol is higher than branched chain alcohol.
- Alcohols are soluble in water due to hydrogen bond. Solubility decreases with increasing the number of alkyl groups because it will increase the non-polar nature.

Self Assessment

Arrange the following alcohol molecules in increasing order of their boiling point.

C_2H_5OH, $CH_3(CH_2)_3OH$, $CH_3CH(OH)CH_3$, $CH_3C(CH_3)_2OH$

$$C_2H_5OH < CH_3CH(OH)CH_3 < CH_3C(CH_3)_2OH < CH_3(CH_2)_3OH$$

Acidity of Alcohol

Alcohols are generally classified as weak acids due to their ability to donate a proton to a strong base. The order of acidity is as follows:

Primary Alcohols > Secondary Alcohols > Tertiary Alcohols

$$\underset{\text{(Ethyl alcohol)}}{2\,C_2H_5OH} + 2Na \longrightarrow \underset{\text{(Sodium ethoxide)}}{2\,C_2H_5ONa} + H_2\uparrow$$

Preparations of Alcohols

1. Hydration of Alkenes:

$$\underset{\text{(Ethene)}}{H_2C{=}CH_2} + H_2O \xrightarrow[100^\circ C]{H_2SO_4\,(\text{conc.})} \underset{\text{(Ethyl alcohol)}}{H_3C{-}CH_2{-}OH}$$

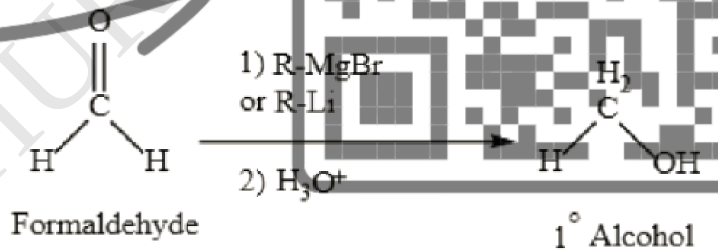
2. Hydrolysis of an Alkyl Halide:

$$\underset{\text{(Ethyl Chloride)}}{C_2H_5Cl} + NaOH \xrightarrow[\text{Heat}]{H_2O} \underset{\text{(Ethyl alcohol)}}{C_2H_5OH} + NaCl$$

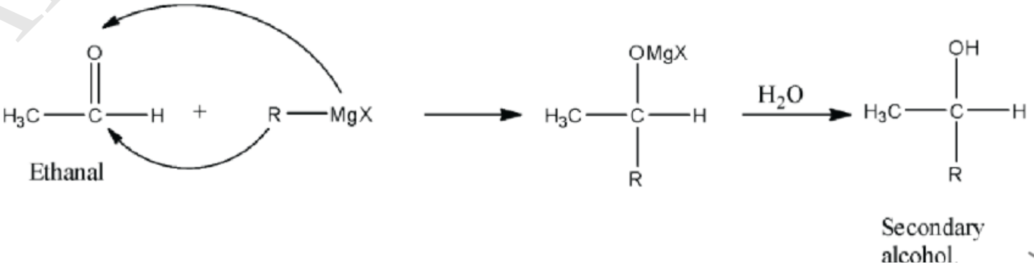
3. Reaction of Grignard's Reagent with Aldehyde & Ketone:

Grignard reagent when reacts with a formaldehyde, acetaldehyde and acetone molecule, it gives primary, secondary and tertiary alcohols respectively.

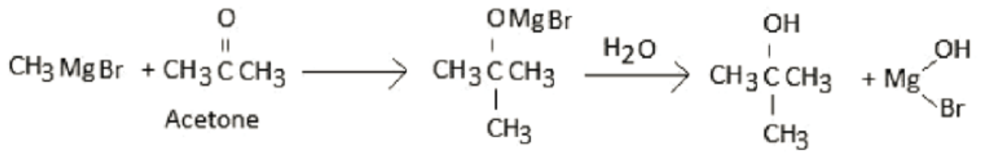
(i) Reaction with formaldehyde



(ii) Reaction with acetaldehyde (ethanal)



(iii) Reaction with acetone

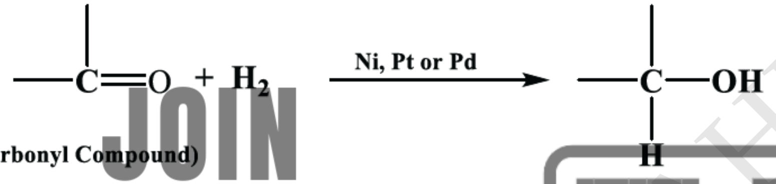


$$CH_3MgBr + CH_3\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow CH_3\overset{OMgBr}{\underset{CH_3}{C}}CH_3 \xrightarrow{H_2O} CH_3\overset{OH}{\underset{CH_3}{C}}CH_3 + Mg\begin{smallmatrix}OH\\Br\end{smallmatrix}$$

2-methyl-2-propanol

4. Reduction of Aldehyde and Ketone:

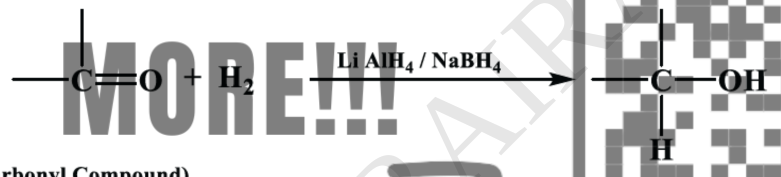
(a) Hydrogenation of aldehyde and ketone at high temperature and pressure in the presence of catalyst like nickel (Ni), platinum (Pt) or palladium (Pd).



$$-\overset{|}{C}=O + H_2 \xrightarrow{\text{Ni, Pt or Pd}} -\overset{|}{\underset{H}{C}}-OH$$

(Carbonyl Compound) (Alcohol)

(b) Reaction of aldehyde and ketone with a reducing agent like lithium aluminum hydride (Li AlH₄) or sodium borohydride (NaBH₄).

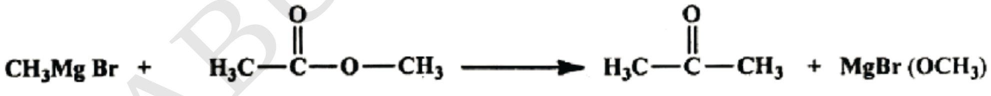


$$-\overset{|}{C}=O + H_2 \xrightarrow{\text{Li AlH}_4\text{ / NaBH}_4} -\overset{|}{\underset{H}{C}}-OH$$

(Carbonyl Compound) (Alcohol)

It is important to note that aldehydes on reduction give primary alcohols, and ketones on reduction give secondary alcohols.

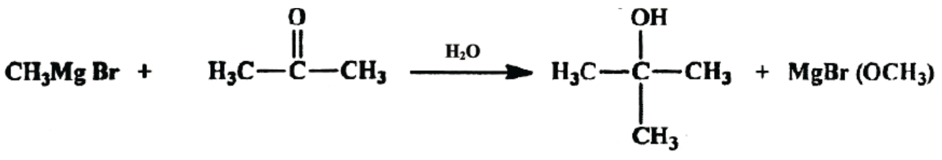
5. Reaction of Grignard's reagent with esters:



$$CH_3MgBr + H_3C-\overset{O}{\overset{\|}{C}}-O-CH_3 \longrightarrow H_3C-\overset{O}{\overset{\|}{C}}-CH_3 + MgBr(OCH_3)$$

(Grignard reagent) (Methyl acetate) (Acetone)

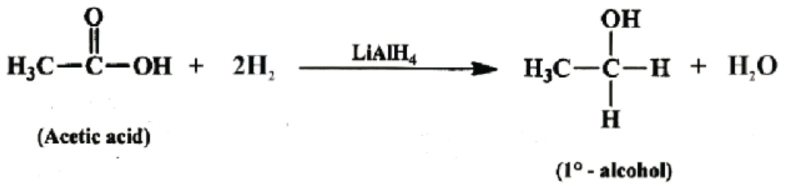
The carbonyl compound this formed then reacts with another molecule of Grignard's reagent and finally gives an alcohol.



$$CH_3MgBr + H_3C-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{H_2O} H_3C-\overset{OH}{\underset{CH_3}{C}}-CH_3 + MgBr(OCH_3)$$

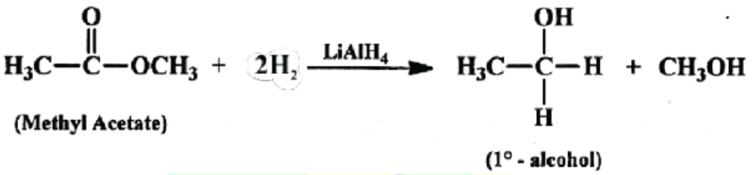
(Grignard reagent) (Acetone) (3° - alcohol)

6. Reduction of Carboxylic Acid & Esters



$$H_3C-\overset{\overset{O}{\|}}{C}-OH + 2H_2 \xrightarrow{LiAlH_4} H_3C-\underset{H}{\overset{OH}{C}}-H + H_2O$$

(Acetic acid) (1° - alcohol)



$$H_3C-\overset{\overset{O}{\|}}{C}-OCH_3 + 2H_2 \xrightarrow{LiAlH_4} H_3C-\underset{H}{\overset{OH}{C}}-H + CH_3OH$$

(Methyl Acetate) (1° - alcohol)

Reactions of Alcohols

(i) The C-O bond in an alcohol molecule breaks when it is attacked by a nucleophile.
(ii) The H-O bond in an alcohol molecule breaks when it is attacked by an electrophile.

Type of Bond Breaking	Type of Attacking Reagent	Order of reactivity of alcohols
O – H	Electrophile	1° > 2° > 3°
C – O	Nucleophile	3° > 2° > 1°

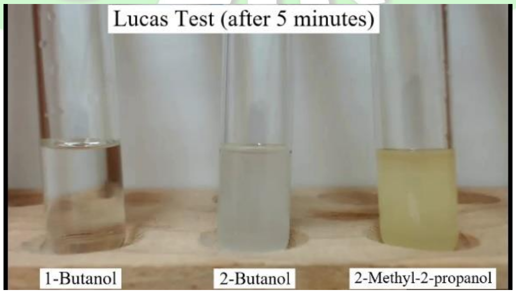
1. Reaction with Halogen Acids (HX)

$$C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O$$

(Ethyl alcohol) (Ethyl chloride)

The mixture of concentrated HCl and $ZnCl_2$ is called "Lucas Reagent and it is used to distinguish between primary, secondary and tertiary alcohol.

In the Lucas test, primary alcohols show no immediate reaction, secondary alcohols form turbidity within few minutes, and tertiary alcohols produce an immediate and vigorous formation of cloudy precipitate.



Lucas Test (after 5 minutes)

2. Reaction with $SOCl_2$ and PX_3

$$3\,C_2H_5OH + PCl_3 \longrightarrow 3\,C_2H_5Cl + H_3PO_3$$

(Ethyl alcohol) (Ethyl chloride)

$$C_2H_5OH + SOCl_2 \xrightarrow{\text{Pyridine}} C_2H_5Cl + SO_2 + HCl$$

(Ethyl alcohol) (Ethyl chloride)

3. Dehydration of Alcohol

$$C_2H_5OH \xrightarrow[170°C]{\text{Conc. } H_2SO_4} H_2C{=}CH_2 + H_2O$$

(Ethyl alcohol) (Ethene)

The ease of acid catalyzed dehydration of alcohol is given as

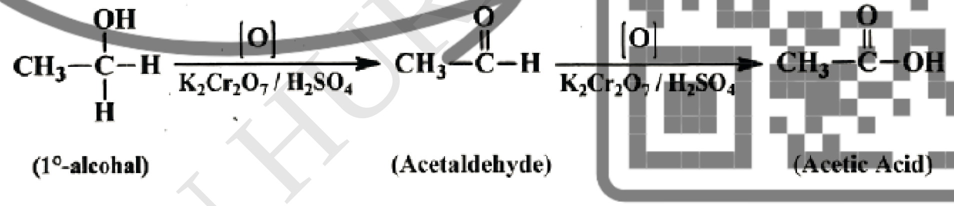
3°-alcohol > 2°-alcohol > 1°-alcohol

4. Oxidation of Alcohol

Primary alcohols yield aldehyde on oxidation.

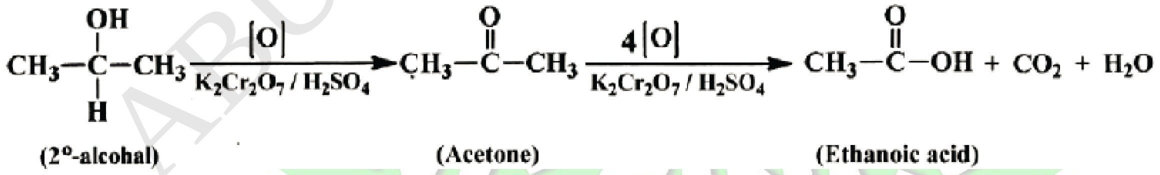
Secondary alcohols yield ketone on oxidation.

Tertiary alcohols cannot be oxidized.



$$CH_3-CH_2-OH \xrightarrow[K_2Cr_2O_7 / H_2SO_4]{[O]} CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[K_2Cr_2O_7 / H_2SO_4]{[O]} CH_3-\overset{O}{\overset{\|}{C}}-OH$$

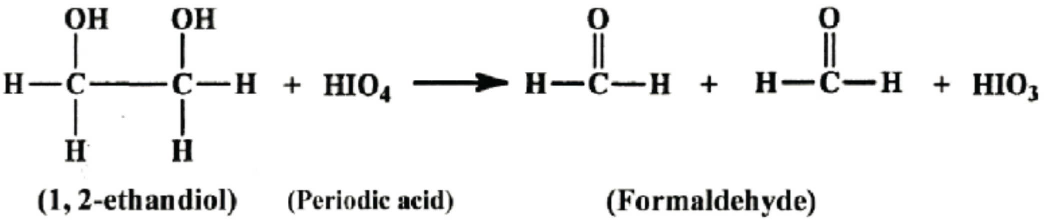
(1°-alcohal) (Acetaldehyde) (Acetic Acid)



$$CH_3-\underset{H}{\overset{OH}{C}}-CH_3 \xrightarrow[K_2Cr_2O_7 / H_2SO_4]{[O]} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[K_2Cr_2O_7 / H_2SO_4]{4[O]} CH_3-\overset{O}{\overset{\|}{C}}-OH + CO_2 + H_2O$$

(2°-alcohal) (Acetone) (Ethanoic acid)

5. Cleavage of 1,2-diols



$$H-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-H + HIO_4 \longrightarrow H-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-H + HIO_3$$

(1, 2-ethandiol) (Periodic acid) (Formaldehyde)

Self Assessment

Mention the reagents required for the following conversions.

(i)	Ethanol to Ethene	(ii)	Acetic acid to Ethanol
(iii)	Ethanol to Acetic acid	(iv)	Ethylene glycol to formaldehyde

(i) Concentrated H_2SO_4 (ii) $LiAlH_4$ (iii) $K_2Cr_2O_7/H_2SO_4$ (iv) HIO_4

Uses of Alcohol

(i) Methanol is used as antifreeze solution and also in the preparation of perfumes, dyes, drugs etc.

(ii) Ethanol is used as a raw material in the synthesis of a variety of organic compounds such as gums, resins, tinctures, chloroform, esters, acetone and acetic acid.

(iii) The mixture of isopropyl alcohol in water is used as rubbing alcohol (antiseptic).

PHENOLS

Organic compounds in which hydroxy group (-OH) is directly attached to benzene ring are called phenols. The parent compound of this family is hydroxy benzene which is also known as carbolic acid or benzenol.

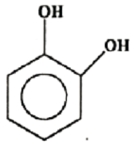
CLASSIFICATION OF PHENOLS

Phenols can be classified into three types:

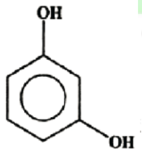
(a) Monohydroxy phenol – It contains 1 OH group

(Benzenol)

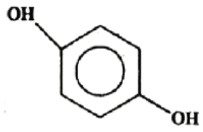
(b) Dihydroxy phenol – It contains 2 OH groups



(Catechol)

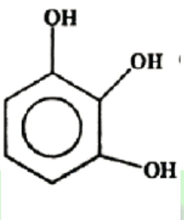


(Resorcinol)



(Hydroquinone)

(c) Trihydroxy phenol – It contains 3 OH groups

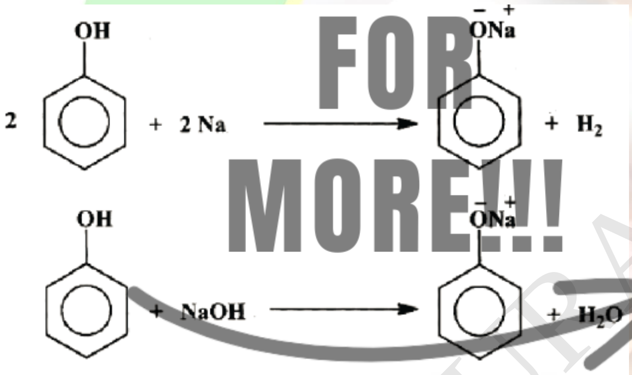


(Pyrogallol)

PHYSICAL PROPERTIES OF PHENOLS

- It is a white crystalline solid at room temperature.
- Phenol is toxic in nature.
- It is soluble in water due to the presence of hydrogen bond.

Acidity of Phenol



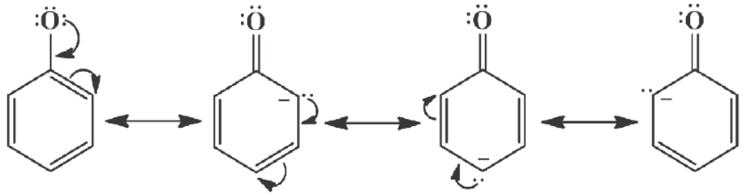
(Phenol) (Sodium phenoxide)

Phenol is a stronger acid than alcohol but weaker than carboxylic acids.

Comparing phenoxide ion with ethoxide ion, it is noted that the negative charge on oxygen atom of phenoxide is delocalized over the entire ring through a process called as resonance and make the phenoxide ion stable.

$$C_6H_5OH + H_2O \rightleftharpoons C_6H_5\bar{O} + H_3O^+$$

(Phenol) (Phenoxide ion)



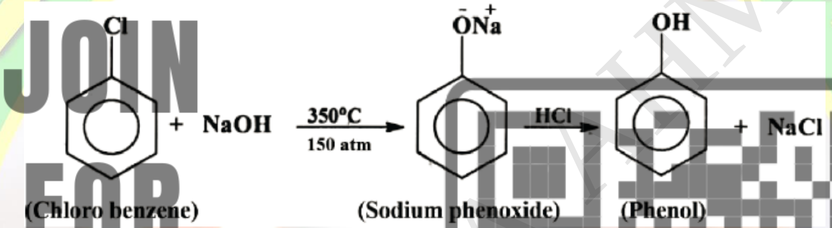
On the other hand, in ethoxide ion the negative charge is localized on the oxygen atom due to the absence of aromatic ring result in a less stable structure compared to phenoxide ion.

$$C_2H_5OH + H_2O \rightleftharpoons C_2H_5\bar{O} + H_3O^+$$

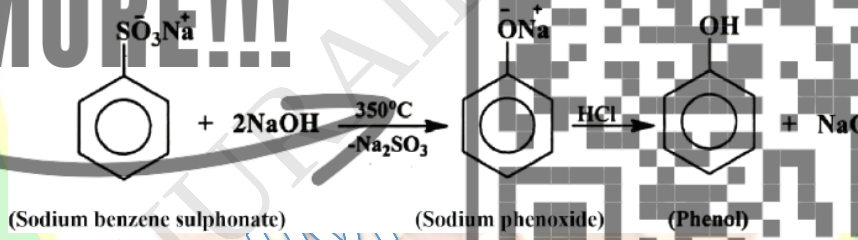
(Ethanol) (Ethoxide ion)

Preparation of Phenol

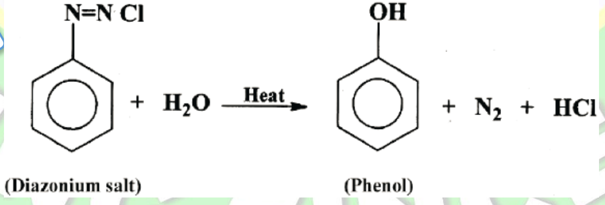
1. From Chlorobenzene (Dow's Process)



2. From Sodium Benzene Sulphonate



3. Hydrolysis of Diazonium Salt



Reactions of Phenol

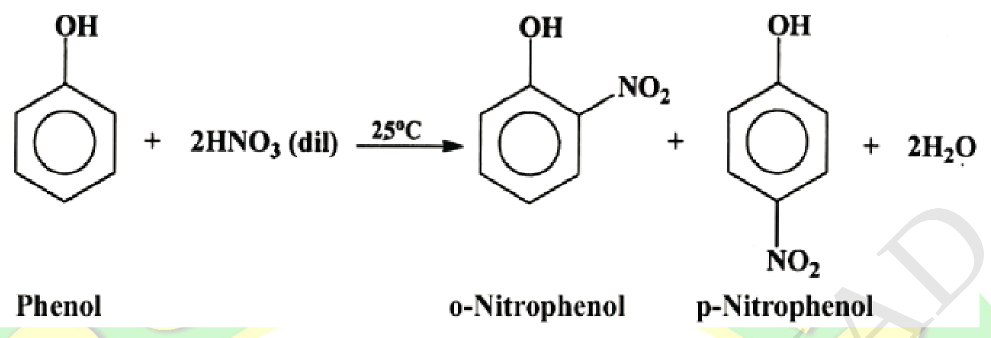
Phenol typically undergoes two types of reactions:

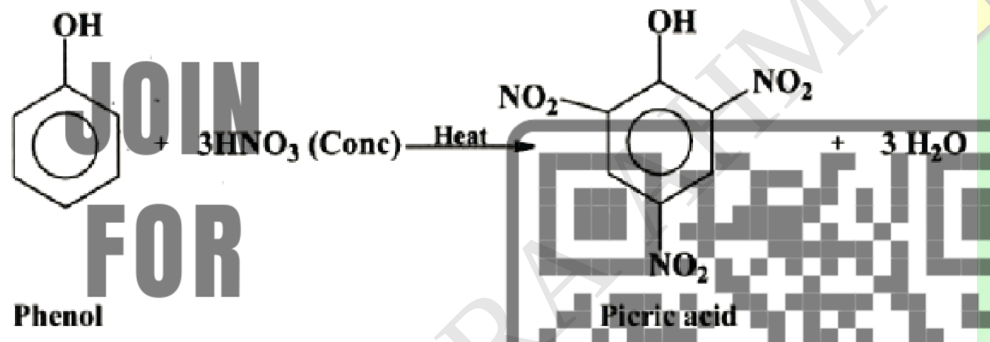
a) Those reactions in which hydroxyl group is involved

b) Those reactions in which aromatic ring is involved

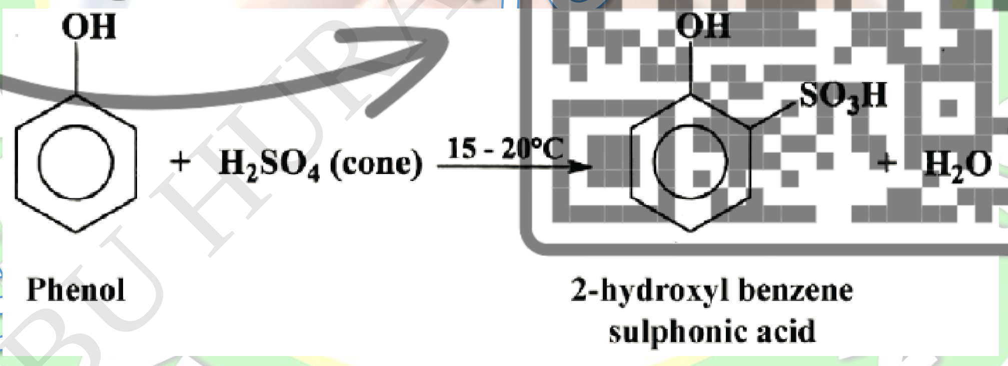
Electrophilic Aromatic Substitutions

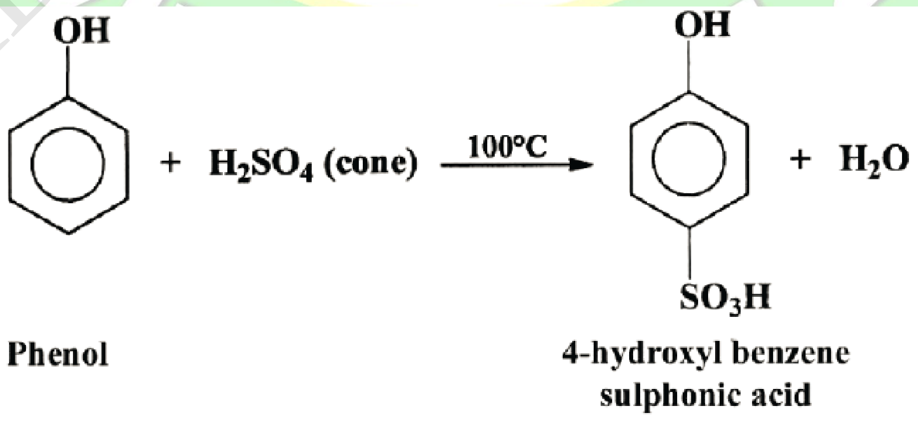
1. Nitration of Phenol



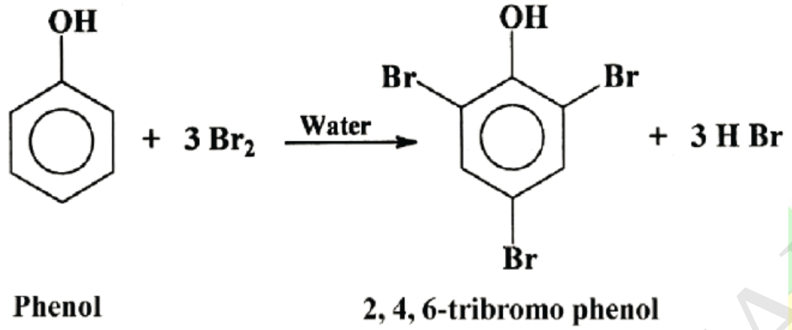


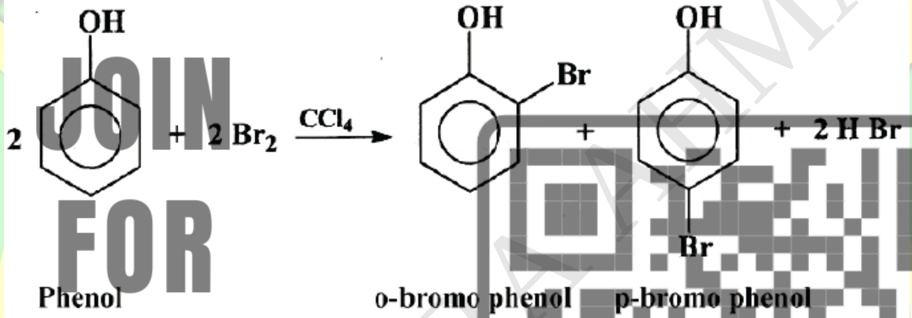
2. Sulphonation of Phenol



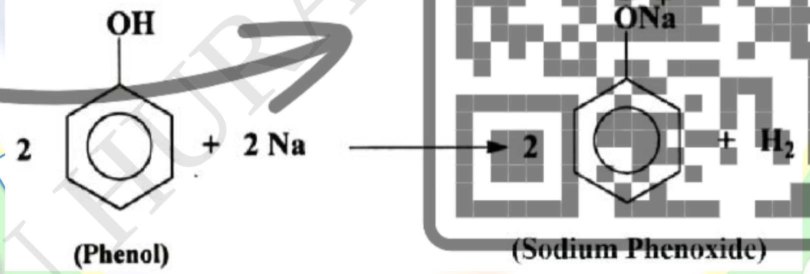


3. Halogenation of Phenol

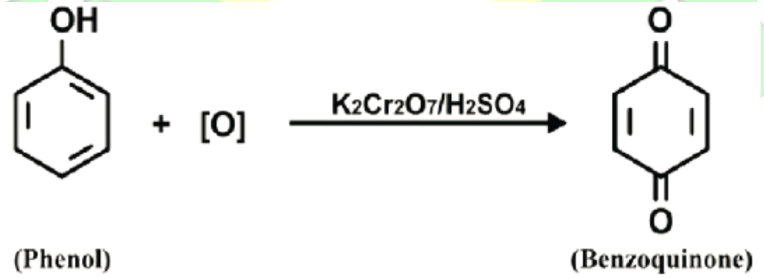




Reaction with Sodium Metal



Oxidation of Phenol



Difference between Alcohol and Phenol

Property	Alcohol	Phenol
Functional Group	-OH attached to alkyl carbon (R-OH)	-OH attached to aryl carbon (Ar-OH)
Hydrogen Bonding	Can form intermolecular hydrogen bonding	Can form stronger hydrogen bonding
Boiling Point	Generally lower than phenol	Generally higher than alcohols
Acidity	Weaker acids (higher pKa values)	Stronger acids (lower pKa values)
Solubility in Water	Readily soluble in water	Lower solubility in water
Aromatic Properties	Lacks aromatic properties	Contains an aromatic ring

Uses of Phenol

(i) It is used as an antiseptic and disinfectant

(ii) It is used in the manufacturing of soap, Plastics, ointments and lozenges etc.

(iii) It is used in the preparation of picric acid and, phenolphthalein.

(iv) It is used as ink preservative.

ETHERS

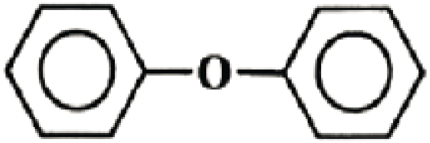
Ethers are organic compounds having a general formula R-O-R’, characterized by an oxygen atom bonded to two alkyl or aryl groups. It has low reactivity and it is commonly used as solvent in various chemical reactions.

Ethers can be classified into two types:

(i) Symmetrical ethers or Simple Ethers (Both the alkyl radicals are same.)

$H_3C-O-CH_3$

Dimethyl ether

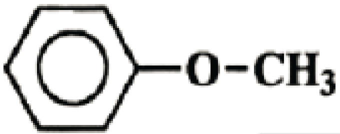


Diphenyl ether

(ii) Asymmetrical ethers or Mixed ethers (Both the alkyl radicals are different)

$C_2H_5-O-CH_3$

Ethyl methyl ether



Phenyl methyl ether

Preparation of Ether

(i) Dehydration of alcohol

$$C_2H_5OH + HOC_2H_5 \xrightarrow[140°C]{H_2SO_4} C_2H_5-O-C_2H_5 + H_2O$$

(Ethyl alcohol) (Ethyl alcohol) (Diethyl ether)

(ii) Williamson synthesis

$$C_2H_5\overset{-}{O}\overset{+}{Na} + C_2H_5Cl \longrightarrow C_2H_5-O-C_2H_5 + NaCl$$

(Sodium ethoxide) (Ethyl chloride) (Diethyl ether)

Physical Properties of Ether

1. Dimethyl ether (CH_3-O-CH_3) and Ethyl Methyl Ether (CH_3-O-C_2H_5) are gases. Other higher members of ether family are volatile liquids.

2. The boiling point of ether is less than alcohol due to the absence of hydrogen bond.

3. Ethers are moderately soluble in water due to its polar nature because of the presence of oxygen atom. Solubility decreases with increase in number of alkyl group as it increases the non-polar nature of molecules.

Chemical Reactivity of Ether

Ether are less reactive organic compounds due to the presence of alkyl radicals on both side of oxygen atom which produces a steric hindrance and makes the molecule stable.

Self Assessment

- Provide an example of a symmetrical ether.
- Can ethers form hydrogen bonds with water? Why or why not?

- An example of symmetrical ether is dimethyl ether (CH_3-O-CH_3)
- Ethers can form hydrogen bonds with water due to presence of oxygen atom in its molecule.

Uses of Ethers

(i) Ether is used as solvent in the manufacturing of waxes, gums, resins, oils etc.

(ii) Diethyl ether is used as solvent in Wurtz reaction and in the preparation of Grignard reagent.

Multiple Choice Questions

(i) In the molecule of phenol, the carbon atom which is attached to hydroxyl group is.
(a) sp-hybridized [✓ (b) sp^2-hybridized]
(c) sp^3-hybridized (d) Unhybridized

(ii) Which of the following is a trihydric phenol?
(a) Resorcinol (b) Cresol
[✓ (c) Pyrogallol] (d) Catechol

(iii) Ethanol reacts with PCl_3 to form.

(a) Diethyl ether
(b) Ethene
[✓ (c) Ethyl chloride]
(d) Ethanoic acid

(iv) Which of the following alcohols has highest boiling Point

(a) Ethyl alcohol
[✓ (b) n-pentyl alcohol]
(c) iso-pentyl alcohol
(d) neo-pentyl alcohol

(v) Which of the following Products is mainly formed if ethanol is dehydrated with concentrated sulphuric acid at 170°C?

[✓ (a) Ethene]
(b) Ethyne
(c) Ethanol
(d) Diethyl ether

(vi) Lucas reagent is a mixture of

(a) Zn and Hg
(b) Zn and HCl
[✓ (c) $ZnCl_2$ and HCl]
(d) NaOH and CaO

(vii) Oxidative cleavage of 1, 2 – diol occur in the presence of

(a) $K_2Cr_2O_7$
(b) $KMnO_4$
(c) HNO_3
[✓ (d) HIO_4]

(viii) Which of the following molecule cannot form hydrogen bonding with water molecule?

(a) Phenol
(b) Resorcinol
[✓ (c) Ethyl chloride]
(d) Ethyl alcohol

(ix) Secondary alcohols, undergo oxidation with potassium dichromate to produce carboxylic acid through an intermediate product known as:

(a) Aldehyde
[✓ (b) Ketone]
(c) Ether
(d) Alkyl halide

(x) Which of the following is an anaesthetic agent

(a) Phenol
(b) Ethyl alcohol
[✓ (c) Diethyl ether]
(d) Acetone

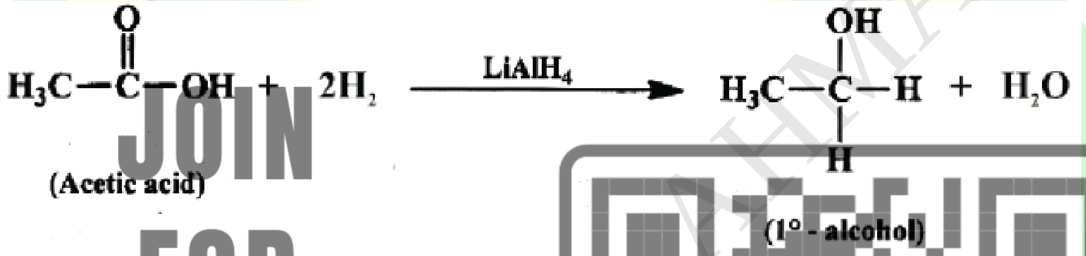
Short Questions

1. Define Phenol? Write the equations for the preparation of Phenol from.
   - (i) Chlorobenzene
   - (ii) Sodium benzene sulphonate

ALREADY DISCUSSED ABOVE

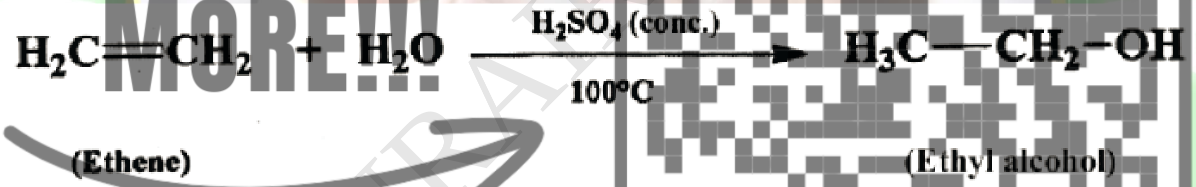
2. Write the equations for the following chemical Process

(i) Reduction of acetic acid with $LiAlH_4$.



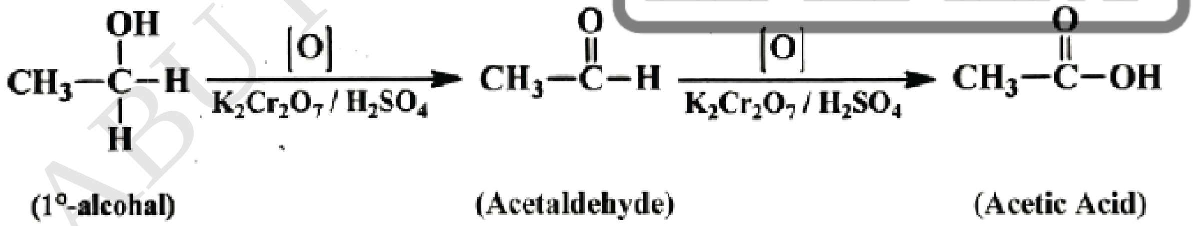
$$CH_3COOH + 2H_2 \xrightarrow{LiAlH_4} CH_3CH_2OH + H_2O$$

(ii) Hydration of ethene with hot concentrated H_2SO_4



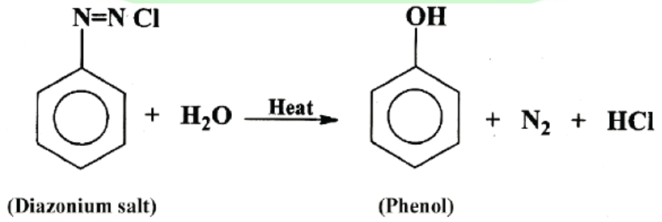
$$H_2C{=}CH_2 + H_2O \xrightarrow[100°C]{H_2SO_4\,(conc.)} H_3C{-}CH_2{-}OH$$

(iii) Oxidation of ethanol with acidified dichromate.



$$CH_3CH_2OH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} CH_3CHO \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} CH_3COOH$$

(iv) Hydrolysis of diazonium salt



3. Explain the following with scientific reason

(i) Boiling point of ether is less than alcohol?

Ans. Boiling point of ether is less than alcohol because ether do not contain hydrogen bonding. Hence, they have low boiling point due to the presence of weaker intermolecular forces.

(ii) Alcohols are soluble in water?

Ans. Alcohols are soluble in water due to the presence of hydrogen bonding.

(iii) Ethanol is liquid but ethyl chloride is gas at room temperature?

Ans. Ethanol contains hydrogen bonding that's why it is a liquid but ethyl chloride does not contain hydrogen bonding that's why it is a gas at room temperature.

4. Identify each of following with two laboratory tests.

(i) Phenol

(ii) Alcohol

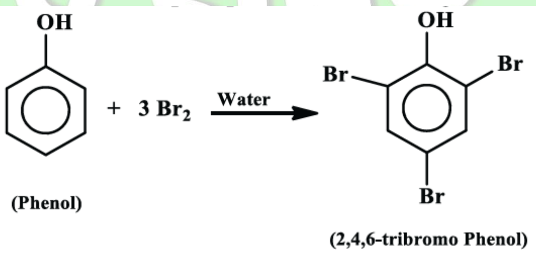
Tests for identification of Phenol

(i) Ferric chloride test

$$\underset{\text{(Phenol)}}{6\,C_6H_5OH} + FeCl_3 \longrightarrow \underset{\text{(Voilet or Purple Ferric Phenoxide Complex)}}{H_3[Fe(C_6H_5O)_6]} + 3HCl$$

Appearance of violet, blue or purple coloration indicates the formation of complex and identifies the presence of phenol.

(ii) Bromine water test



Disappearance of brown color of bromine and appearance of white precipitates of 2,4,6-tribromophenol identifies the presence of phenols

Tests of identification of Alcohol

(i) Sodium metal test

$$C_2H_5OH + Na \rightarrow C_2H_5ONa + \frac{1}{2} H_2$$

Brisk effervescence in the solution indicates the presence of alcoholic group in the given organic molecule.

(ii) Ester test

$$\underset{\text{(Ethyl alcohol)}}{C_2H_5OH} + \underset{\text{(Acetic acid)}}{CH_3COOH} \underset{\text{Heat}}{\overset{H_2SO_4\ \text{Conc.}}{\rightleftharpoons}} \underset{\text{(Ethyl acetate)}}{CH_3COOC_2H_5} + H_2O$$

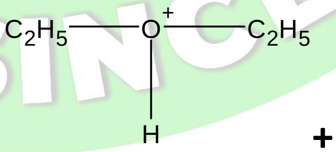
Fruity smell of ester indicates the presence of alcoholic group in the given organic compound.

5. What is Lucas reagent? Describe its use to distinguish between primary, secondary and tertiary alcohol.

ALREADY DISCUSSED ABOVE

6. What is oxonium ion? How can ether form oxonium ion?

Ans. If oxygen contains a positive charge, then it is called an oxonium ion. It is denoted by O^+. Ether can form oxonium ions by reaction with hydrogen iodide (HI)



$$C_2H_5\text{-}O\text{-}C_2H_5 + HI \rightarrow C_2H_5-\underset{\underset{H}{|}}{\overset{+}{O}}-C_2H_5 + I^-$$

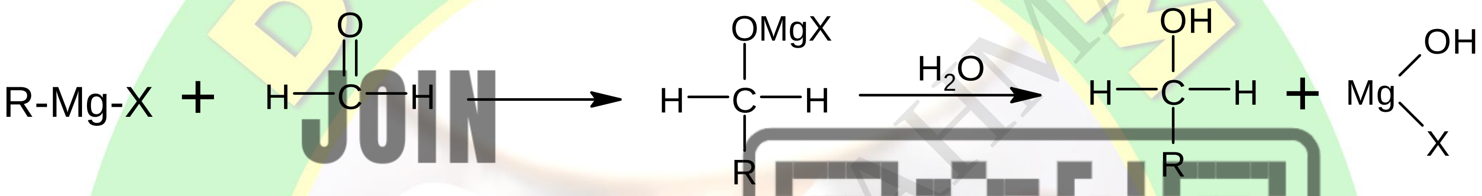
Descriptive Questions

1. (a) What are alcohols? How alcohols are they classified?

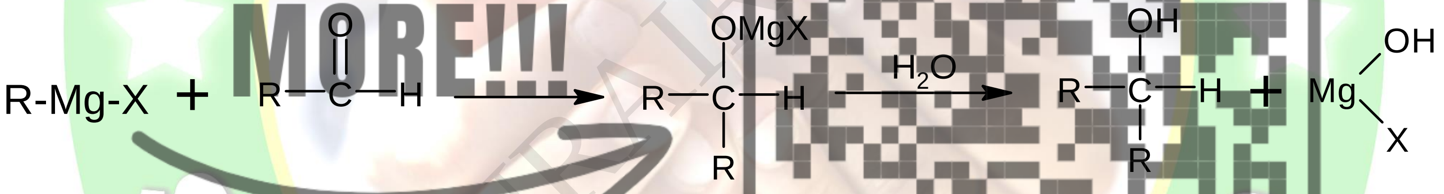
ALREADY DISCUSSED ABOVE

(b) Starting from Grignard reagent how is primary, secondary and tertiary alcohol prepared?

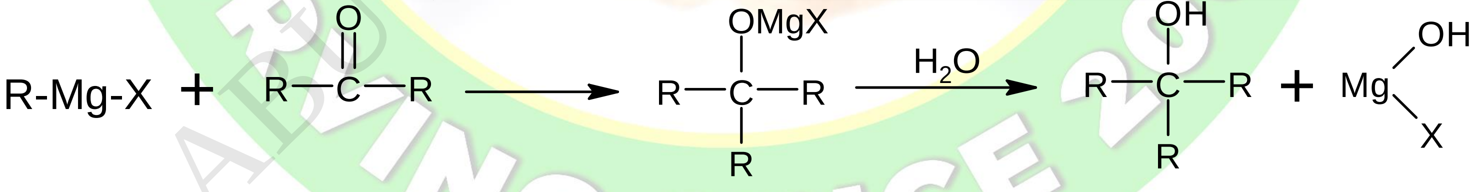
Ans. Primary alcohols can be prepared by the reaction of Grignard's reagent with form aldehyde.



Secondary alcohols can be prepared by the reaction of Grignard's reagent with aldehyde other than form aldehyde.



Tertiary alcohols can be prepared by the reaction of Grignard's reagent with ketones.

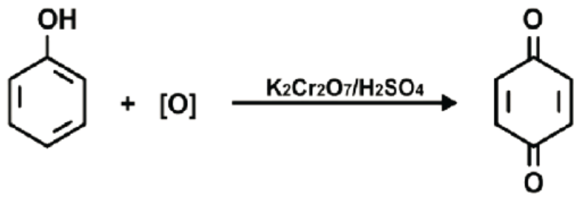


2. Write the equations for the following possible conversions.

(i) Ethyl alcohol to diethyl ether

$$\underset{\text{(Ethyl alcohol)}}{C_2H_5OH} + \underset{\text{(Ethyl alcohol)}}{HOC_2H_5} \xrightarrow[140°C]{H_2SO_4} \underset{\text{(Diethyl ether)}}{C_2H_5-O-C_2H_5} + H_2O$$

(ii) Phenol to benzoquinone

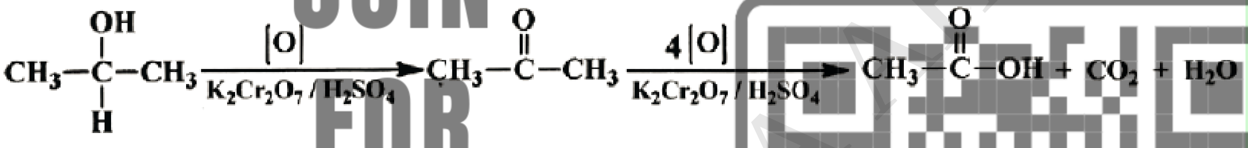


(Phenol) (Benzoquinone)

(iii) Ethyl bromide to ethanol

$$H_3C-CH_2-Br + KOH \xrightarrow{H_2O} H_3C-CH_2-OH + KBr$$

(iv) 2°- alcohol to carboxylic acid



$$CH_3-\overset{OH}{\underset{H}{C}}-CH_3 \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[K_2Cr_2O_7/H_2SO_4]{4[O]} CH_3-\overset{O}{\overset{\|}{C}}-OH + CO_2 + H_2O$$

(2°-alcohal) (Acetone) (Ethanoic acid)

3 Differentiate between alcohol and phenol on the basis of
- (i) Solubility in water
- (ii) Boiling Point
- (iii) Acidic character

ALREADY DISCUSSED ABOVE

4. Write the equation and name the final product when phenol reacts with the following
- (i) Hot and concentrated nitric acid.
- (ii) Concentrated sulphuric acid at 100°C
- (iii) Bromine water
- (iv) Sodium metal

ALREADY DISCUSSED ABOVE

5. Enlist the commercial applications of alcohol, phenol and ether.

Ans. Commercial Applications of Alcohol:

(i) Alcohols are used as beverage for drinking purpose.

(ii) Wood spirit is used as a fuel.

(iii) Isopropyl alcohol is used as rubbing alcohol.

(iv) Ethyl alcohol is used to make perfume.

(v) Ethanol is used as petrol substitute.

(vi) Ethanol is used for making thermometers.

(vii) Ethanol is used to make tincture.

Commercial Applications of Phenol:

(i) Phenol is used as antiseptic.

(ii) Phenol is used to make ointments and lozenges.

(iii) Phenol is used to make picric acid which is an explosive.

(iv) Phenol is used to make plastics such as Bakelite.

Commercial Applications of Ether:

(i) Diethyl ether is used as anesthesia.

(ii) Diethyl ether is mixed with ethanol to form Bloor's reagent which can dissolve lipids.

(iii) Ethers are used as solvent in many chemical reactions such as Wurtz Reactions, preparation of Grignard's Reagent etc.

CHAPTER 8

CARBOYNL COMPOUNDS 1: ALDEHYDES AND KETONES

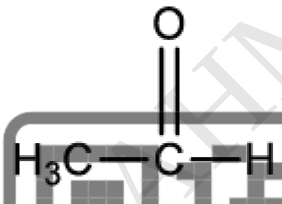
Carbonyl Compounds:

Those compounds which contain carbonyl group (-CO-) are called carbonyl compounds.

Aldehydes and ketones are included in carbonyl compounds.

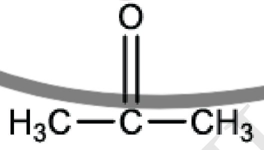
Aldehydes contains (-COH) Functional group and their general formula is R-COH.

(Formoldehyde)

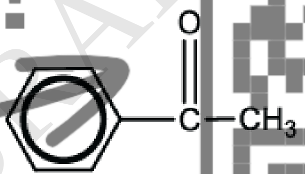


(Acetaldehyde)

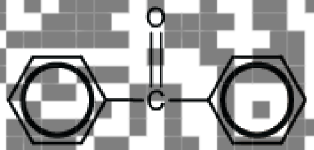
Ketones contains (-COR) functional group and their general formula is R-COR.



(Acetone)



(Acetophenone)



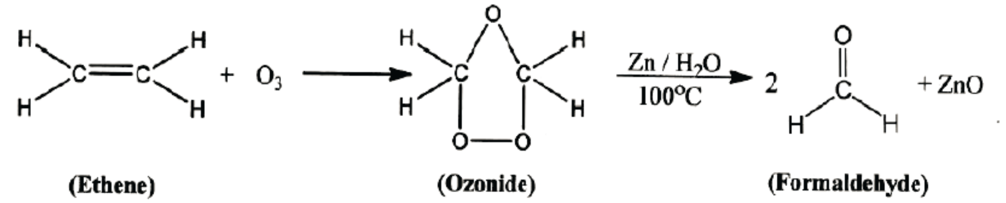
(Benzophenone)

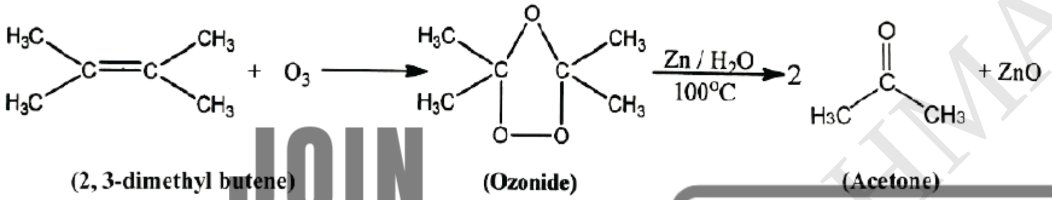
Physical Properties of Aldehyde:

- Methanal and ethanal are gases, other aldehydes are colorless liquids and aldehydes with more than 20 carbon atoms are solids at room temperature.
- Most of the ketones are liquids and ketones with more than 20 carbon atoms are solids.
- Lower aldehydes have a pungent smell whereas ketones and higher aldehydes have a pleasant smell.
- Carbonyl compounds have higher boiling point than alkanes due to polarity but they have lesser boiling points than alcohols or carboxylic acids due to the absence of hydrogen bond.
- Carbonyl compounds are soluble in water due to their polar nature. Solubility decreases with increase in carbon atoms.

PREPARATION OF ALDEHYDE AND KETONE

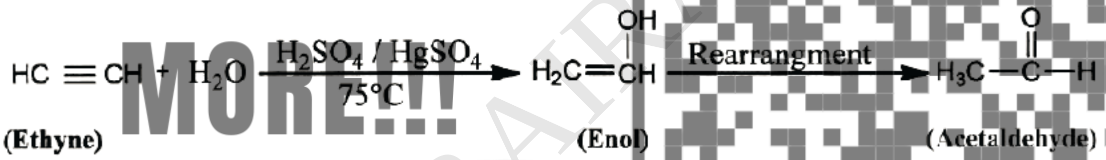
1. OZONOLYSIS OF ALKENES



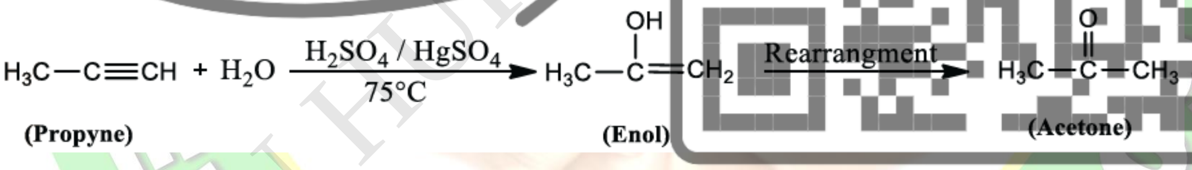


2. HYDRATION OF ALKYNE

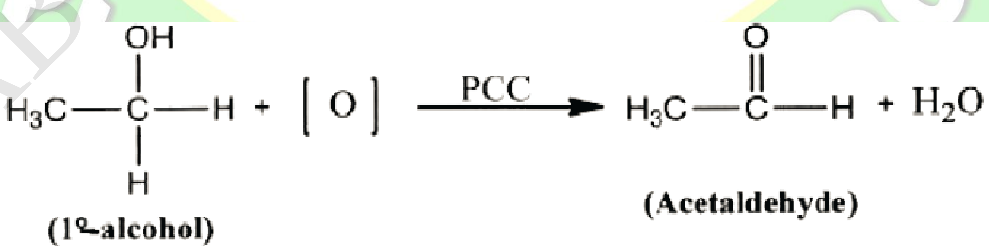
(i) The hydration of ethyne gives acetaldehyde

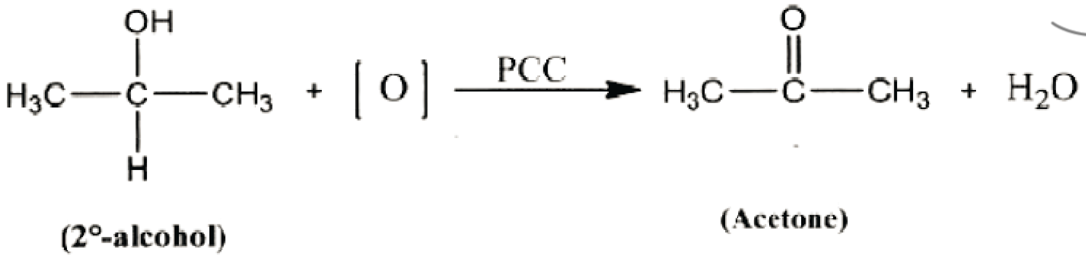


(ii) The hydration of propyne gives propanone

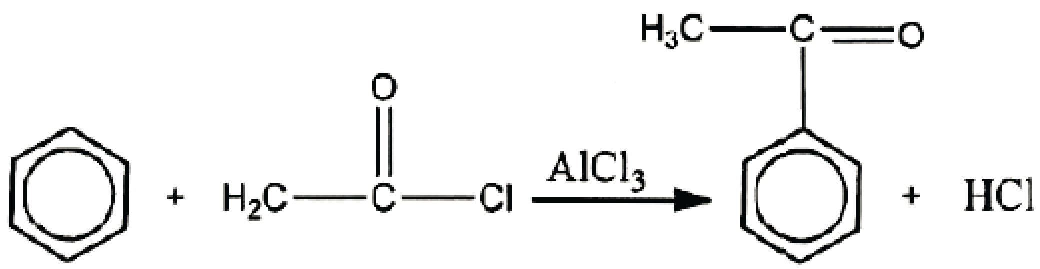


3. OXIDATION OF ALCOHOL





4. FRIEDEL-CRAFT'S ACYLATION OF AROMATIC COMPOUNDS



(Benzene) **(Acylchloride)** **(Acetophenone)**

REACTIONS OF ALDEHYDE AND KETONES

Aldehyde and ketone undergo following types of reactions.

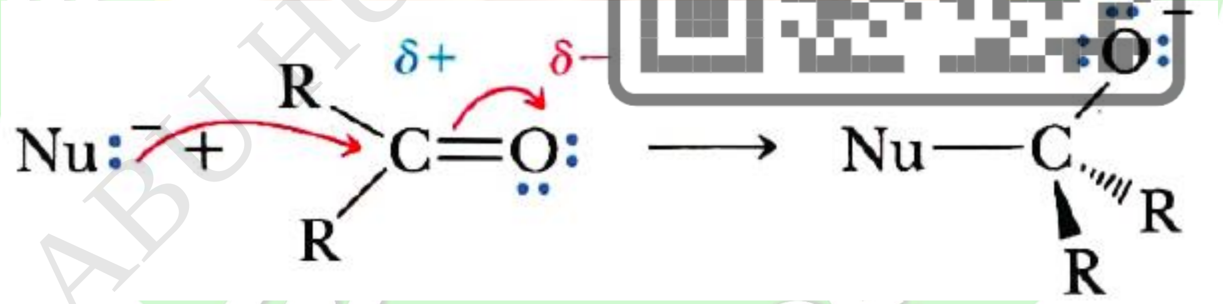
(i) Nucleophilic addition reactions

(ii) Reduction reaction

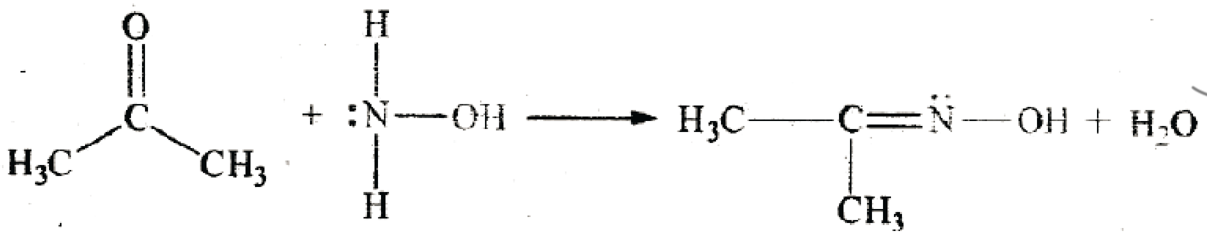
(iii) Oxidation reaction

1 Nucleophilic addition reaction

In this reaction a nucleophile attacks the carbonium ion by the cleavage of pi bond. The hybridization of carbon atom changes from sp^2 to sp^3.

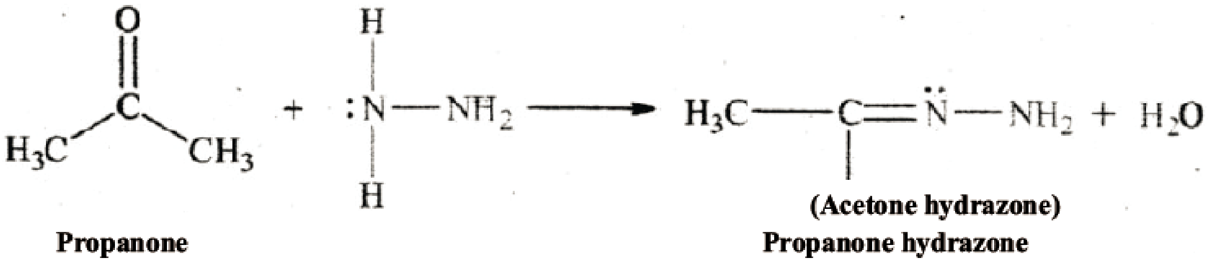


a) Reaction with hydroxyl amine (NH_2-OH)

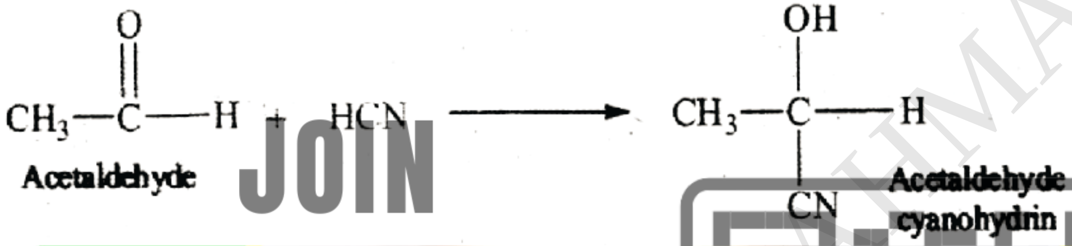


Propanone **Hydroxyl amine** **Propanone oxime**

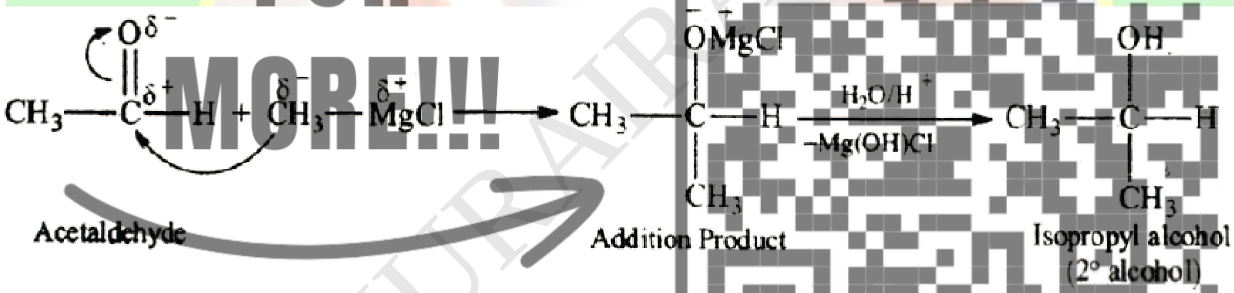
b) Reaction with hydrazine (NH_2-NH_2)



c) Reaction with HCN



d) Reaction with Grignard's Reagent

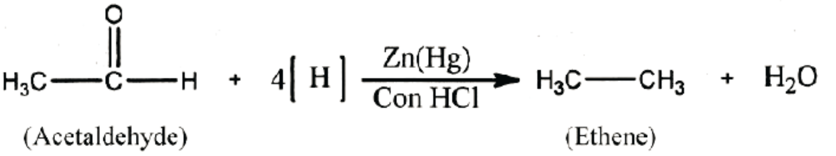


2 Reduction of Aldehyde and Ketone

1. Reduction to Hydrocarbon

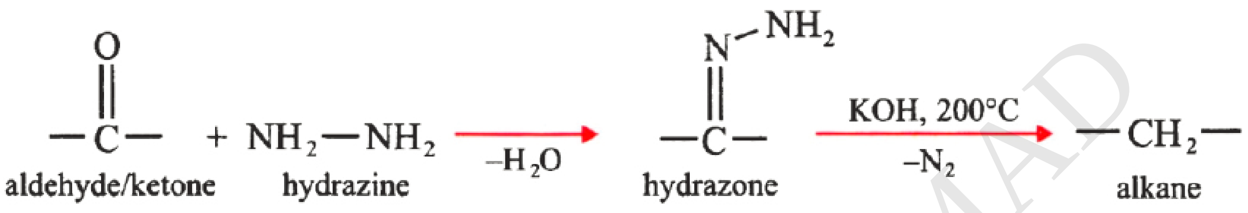
(a) Clemmensen Reduction

The reduction of aldehyde and ketone into saturated hydrocarbons is carried out if a mixture of zinc amalgam and concentrated HCl is used. This is known as Clemmensen reduction.



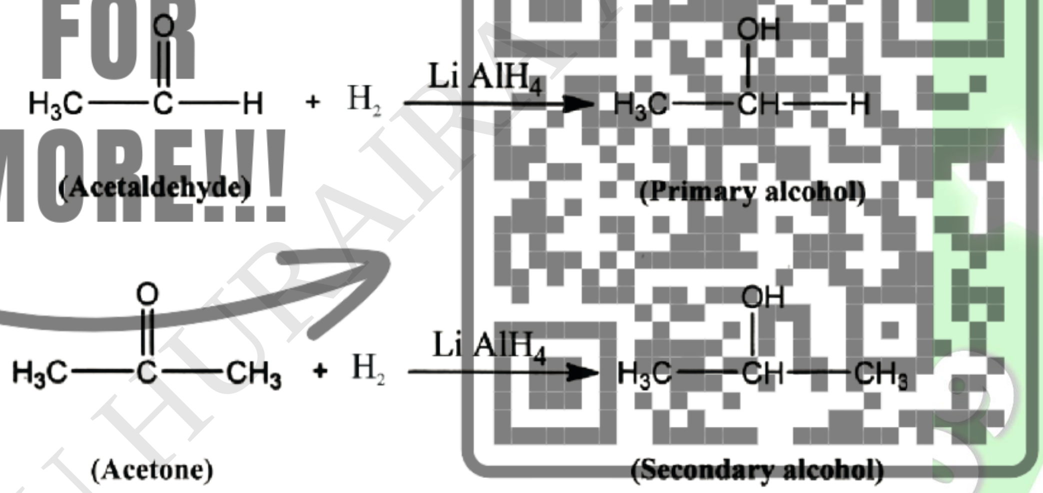
(b) Wolf Kishner Reduction

Aldehyde and ketone can also be converted into alkane by using hydrazine (NH2-NH2) and postassium hydroxide. This is known as Wolf Kishner reaction.

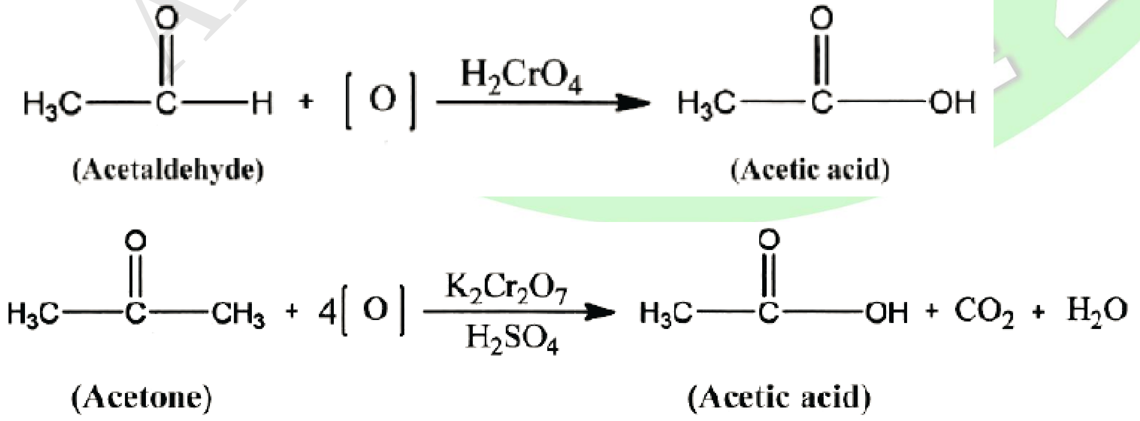


2. Reduction to Alcohol

In this reaction, a reducing agent is used such as $NaBH_4$ or $LiAlH_4$.



3 Oxidation Reaction



Laboratory test to distinguish between aldehydes and ketones

(i) Silver mirror test

The reagent used for this test is ammoniacal silver nitrate (Tollen’s reagent). Since this reagent has short shelf life, it should be freshly prepared in laboratory by mixing silver nitrate and ammonium hydroxide.

$$RCHO + 2[Ag(NH_3)_2]OH \xrightarrow{\text{Heat}} RCOO^-NH_4^+ + 3NH_3 + H_2O + 2Ag\downarrow$$

While performing the test tollen’s reagent is mixed with the given carbonyl compound and heated to boiling. If aldehyde is present, a silver mirror will form on the inside of the test tube.

(ii) Fehling test

There are two Fehling solutions available in laboratory. Fehling A is an aqueous copper (II) sulphate solution while Fehling B is an aqueous solution of sodium hydroxide (NaOH).

To carry out the Fehling’s test, mix equal volumes of Fehling A and B in a test tube, heat the mixture to boiling and then add a small amount of given carbonyl compound into the test tube. If aldehyde is present, the blue color of Fehling solution (Cu^{+2}) changes to red precipitates (ppt) of copper (I) oxide.

$$\underset{\text{(Aldehyde)}}{RCHO} + \underset{\text{(Fehling Solution)}}{2Cu^{+2}} + 5\bar{O}H \longrightarrow RCOO^- + \underset{\text{(Red-brown ppt.)}}{Cu_2O} + 3H_2O$$

Multiple Choice Questions

(i) Ketones when treated with $LiAlH_4$, they reduce to:
(a) Primary alcohol [✓ (b) Secondary alcohol]
(c) Tertiary alcohol (d) Dihyderic alcohol

(ii) The reagent used to oxidizes ketones into carboxylic acids is:
(a) Ammoniacal silver nitrate [✓ (b) Potassium dichromatic]
(c) Fehling solution (d) Benedict solution

(iii) The carbonyl carbon of aldehydes and ketones is:
(a) Sp hyrbidized [✓ (b) Sp^2 hyrbidized]
(c) Sp^3 hyrbidized (d) dsp^3 hyrbidized

(iv) Acetophenone is the member of ketone family, it contains:
(a) Two alkyl groups (b) Two aryl group
[✓ (c) One alkyl and one aryl group] (d) One aryl and one hydrogen atom

(v) The most reactive molecule towards nucleophilic addition in the following is:
[✓ (a) Formaldehyde] (b) Acetaldehyde
(c) Diethyl ketone (d) Acetophenone

(vi) Clemmensen reduction is the conversion of aldehydes and ketones into:
[✓ (a) Alkanes] (b) Alkenes
(c) Alkyl halides (d) Alcohols

(vii) Hydration of propyne in the presence of H_2SO_4 and $HgSO_4$ gives:
(a) Formaldehyde (b) Methyl ethyl ketone
[✓ (c) Acetone] (d) Acetaldehyde

(viii) Which of the following carbonyl compound is most soluble in water?
[✓ (a) Formaldehyde] (b) Acetaldehyde
(c) Benzaldehyde (d) Acetophenone

(ix) Which of the following gives silver test with Tollen's reagent?
[✓ (a) HCHO] (b) $CH_3\text{-}O\text{-}CH_3$
(c) C_2H_5OH (d) CH_3COOH

(x) On reduction of a carbonyl compound by Zn-Hg and Conc. HCl, it is converted to an alkane. This reaction is known as;
(a) Dow reduction (b) Cope reduction
[✓ (c) Clemmensen reduction] (d) Wolf-Kishner reduction

Short Questions

1. Give reasons for the following:
   i. The boiling point of aldehydes and ketones is lower than alcohol.

Ans. Aldehydes and ketones do not have hydrogen bond that's why they have lower boiling point than alcohol.

ii. Formaldehyde is highly soluble in water as compared to other aldehydes.

Ans. Form aldehyde is highly soluble in water because of the presence of only one carbon atom. The greater number of carbon atoms increases non-polar nature and hinders solubility in water.

iii. Oxidation of aldehydes is faster than ketones.

Ans. Oxidation of aldehyde is faster than ketones due to less steric hindrance. Ketones have more steric hindrance due to the presence of alkyl radicals on both sides of carbonyl group.

2. Write the equation for the reaction of acetaldehyde with the following:
   i. Chromic acid (H_2CrO_4)
   ii. Lithium Aluminum hydride ($LiAlH_4$)
   iii. Zinc mercury amalgam

ALREADY DISCUSSED ABOVE

3. How is formaldehyde prepared by ozonolysis?

ALREADY DISCUSSED ABOVE

4. Why is formaldehyde more reactive towards Nucleophilic addition reactions compared with ketones.

Ans. Formaldehyde is more reactive towards nucleophilic addition reactions due to less steric hindrance. Ketones have more steric hindrance due to the presence of alkyl radicals on both sides of carbonyl group that's why they have less reactivity towards nucleophilic addition reactions.

5. How does the oxidation of ketones differ from the oxidation of aldehydes?

Oxidation into Carboxylic acid: Ketones oxidizes to carboxylic acid with strong oxidizing agent such as potassium dichromate ($K_2Cr_2O_7$) and potassium permanganate ($KMnO_4$) while aldehydes can easily be oxidized to carboxylic acid with mild oxidizing agent such as chromic acid (H_2CrO_4), Tollen's reagent and Fehling solution and Benedict solution.

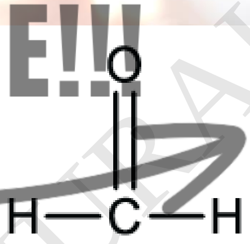
6. Why are ethers considered as good solvents in organic reactions?

Ans. Ethers are considered as good solvents in organic reactions because of their inert nature.

Descriptive Questions

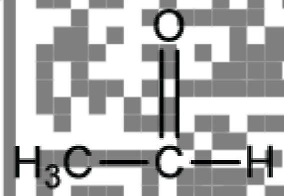
1. What are aldehydes and ketones? Describe the structure and type of hybridization in them.

Ans. Aldehydes contains (-COH) Functional group and their general formula is R-COH.



$H-\overset{\overset{\displaystyle O}{\|}}{C}-H$

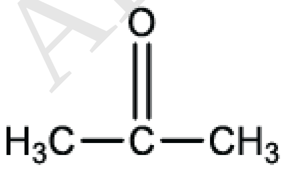
(Formoldehyde)



$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-H$

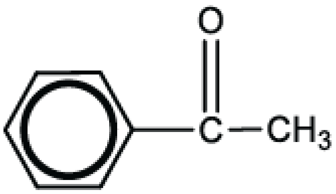
(Acetaldehyde)

Ketones contains (-COR) functional group and their general formula is R-COR.

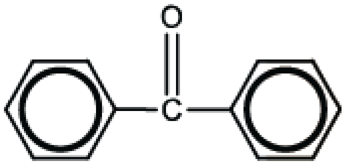


$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

(Acetone)



(Acetophenone)



(Benzophenone)

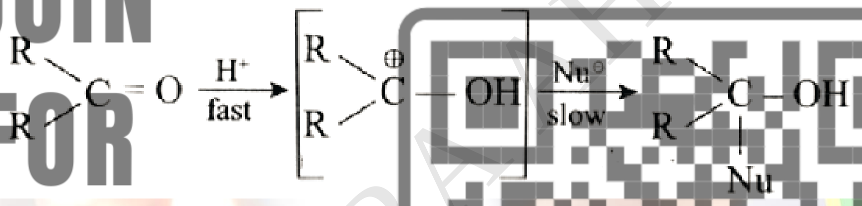
In aldehydes and ketones, the carbon atom of carbonyl group is sp^2 hybridized with a trigonal planar structure and 120° bond angle.

2. Explain the acid-catalyzed and base-catalyzed nucleophilic addition reactions in aldehydes and ketones.

Ans.

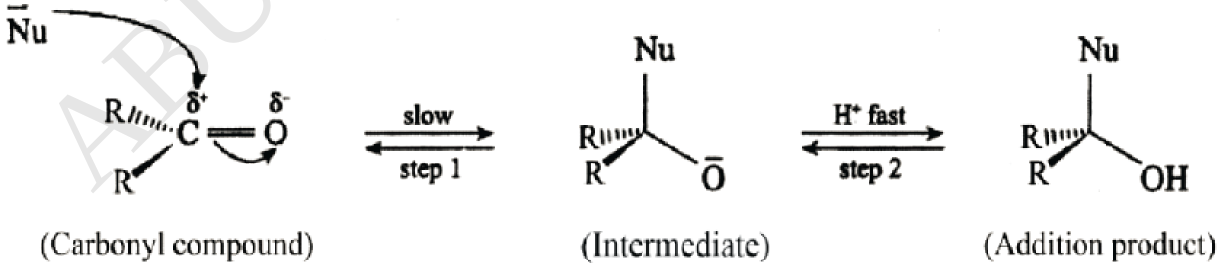
(i) Acid catalysed Nucleophilic addition reactions

An acid catalyst is employed in a case where a carbonyl compound reacts with weak nucleophile for addition. The acidic proton, attacks the carbonyl atom, resulting in the formation of a protonated carbonyl group. This protonation enhances the electrophilic behavior of the carbonyl carbon making it more responsive to a necleophile. Thus, a weak nucleophile can easily attack on carbonyl carbon and give the addition product. The general mechanism of acid catalysed nucleophilic addition on aldehyde and ketone is written as.



(ii) Base catalysed Nucleophilic addition reaction

Addition of strong nucleophilic reagents on aldehyde and ketone is catalysed by base. The base first reacts with the reagent to generate a nucleophile. The nucleophile then attacks on carbonyl carbon. The pi electron of C=O is then shifted towards oxygen atom to form tetrahedral alkoxide ion as intermediate. This intermediate captures a proton or the electrophile to give the product. General mechanism of base catalysed Nucleophilic addition reaction is given as.



3. Describe how aldehydes are distinguished from ketones by the following laboratory test.

(i) Tollen's reagents (ii) Fehling solution

ALREADY DISCUSSED ABOVE

4. Write the equation and give the name of major product in the following chemical process.
   i. Oxidation of acetone with acidified $K_2Cr_2O_7$.
   ii. Reduction of acetaldehyde with $NaBH_4$.
   iii. Hydration of ethyne in the presence of $H_2SO_4/HgSO_4$
   iv. Acylation of benzene in the presence of $AlCl_3$.

ALREADY DISCUSSED ABOVE

5. Give four differences between aldehydes and ketones.

Ans.

(1) The general formula of aldehyde is RCOH and general formula of aldehyde is RCOR.

(2) Aldehydes are more reactive than ketones.

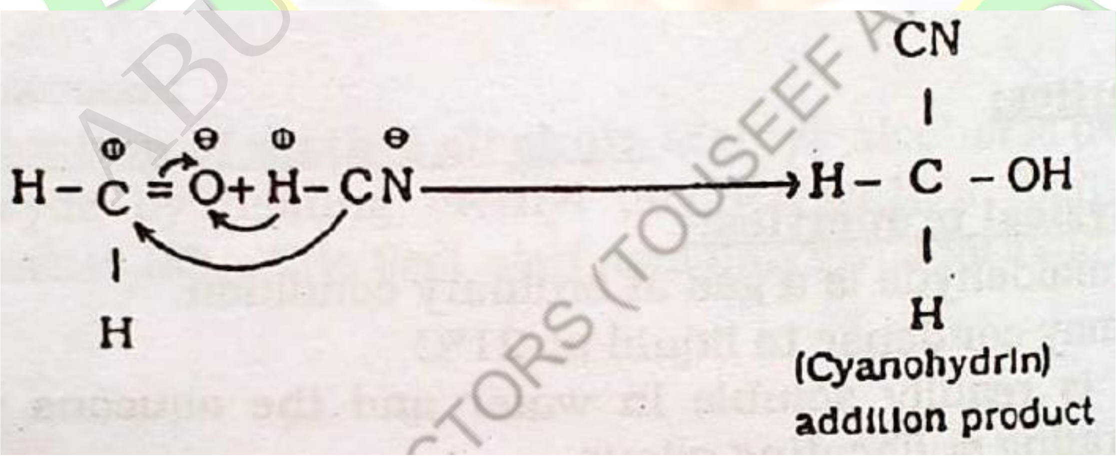
(3) Boiling point of aldehyde is higher than aldehyde.

(4) Aldehydes are reduced to form primary alcohol and ketones are reduced to form secondary alcohols.

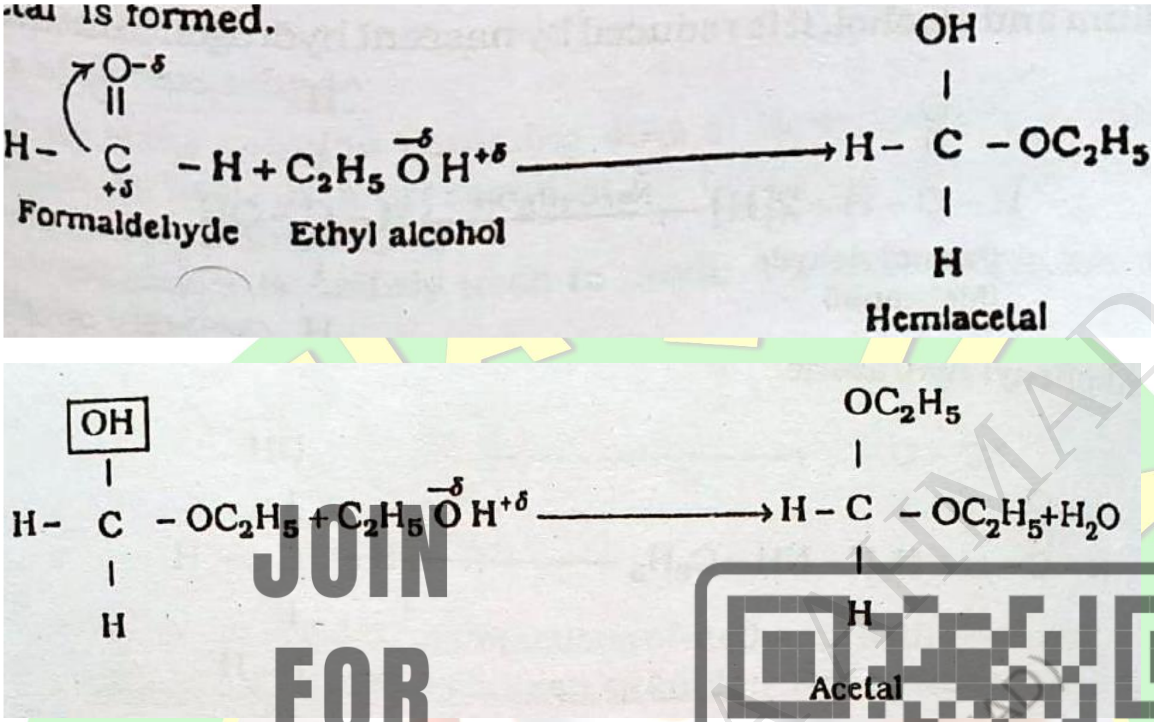
6. Write the equation for the nucleophilic addition reaction if formaldehyde treated with

i.	Hydrogen cyanide	ii.	Primary alcohol
iii.	Methyl magnesium bromide	iv.	Ammonia

(i)



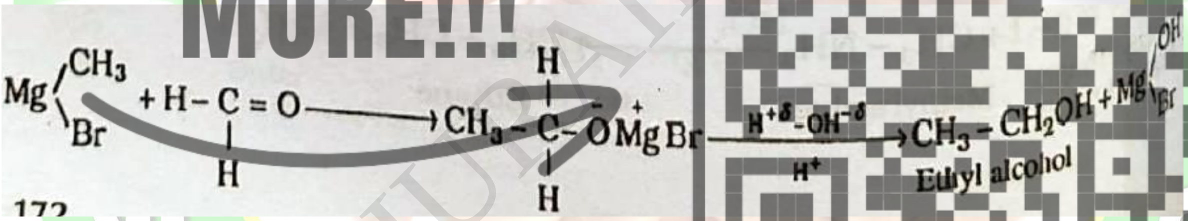
(ii)



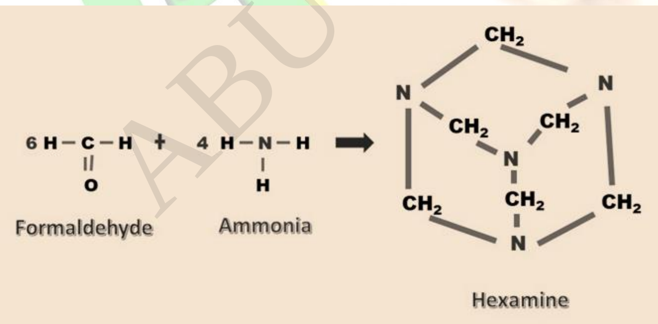
$H-\overset{O^{-\delta}}{\overset{||}{C}}{}^{+\delta}-H + C_2H_5\overset{-\delta}{O}H^{+\delta} \longrightarrow H-\underset{H}{\overset{OH}{C}}-OC_2H_5$

$H-\underset{H}{\overset{\boxed{OH}}{C}}-OC_2H_5 + C_2H_5\overset{-\delta}{O}H^{+\delta} \longrightarrow H-\underset{H}{\overset{OC_2H_5}{C}}-OC_2H_5 + H_2O$

(iii)



(iv)



7. Explain the factors that influence the reactivity of carbonyl compounds towards nucleophilic addition reaction.

ALREADY DISCUSSED ABOVE

CHAPTER 9

CARBONYL COMPOUNDS II: CARBOXYLIC ACID AND FUNCTIONAL DERIVATIVES

“Organic compounds which contain carbonyl group (C=O) attached to hydroxyl group (-OH) are referred as carboxylic acid.”

PHYSICAL PROPERTIES OF CARBOXYLIC ACID:

- They are liquids with a sharp odor.
- They are soluble in polar solvents such as water.
- They have high boiling point as compared to alcohols due to stronger hydrogen bond.

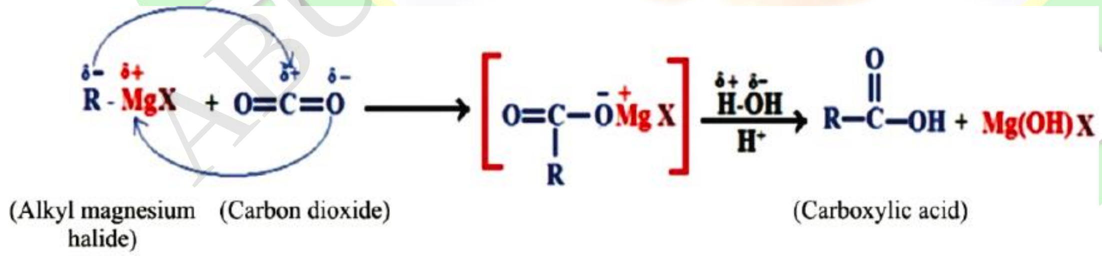
ACIDITY OF CARBOXYLIC ACID:

“Carboxylic acids are stronger acids than alcohols, phenols and water. However, they are weaker acids compared to mineral acids.”

Name of Compound	Molecular Formula	pKa Value
Acetic acid	CH_3COOH	5
Phenol	C_6H_5OH	10
Ethyl alcohol	C_2H_5OH	16
Water	H_2O	15.7

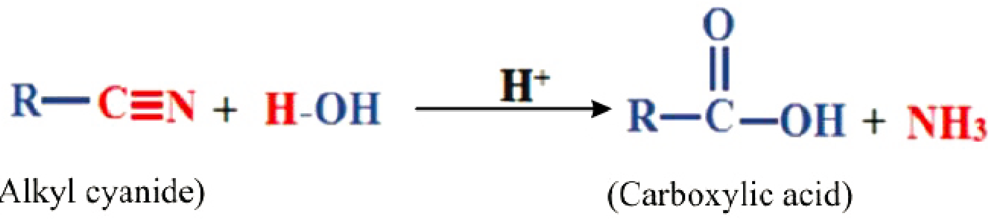
PREPARATION OF CARBOXYLIC ACID:

1 By the Carbonation of Grignard Reagent



$$\overset{\delta-}{R}-\overset{\delta+}{MgX} + O=\overset{\delta+}{C}=\overset{\delta-}{O} \longrightarrow \left[O=\underset{R}{C}-\overset{-}{O}\overset{+}{Mg}X\right] \xrightarrow[H^+]{\overset{\delta+\ \delta-}{H\text{-}OH}} R-\overset{O}{\overset{\|}{C}}-OH + Mg(OH)X$$

2 By the Hydrolysis of Nitriles



$$R-C\equiv N + H\text{-}OH \xrightarrow{H^+} R-\overset{O}{\overset{\|}{C}}-OH + NH_3$$

3 By the Oxidation of Primary Alcohols

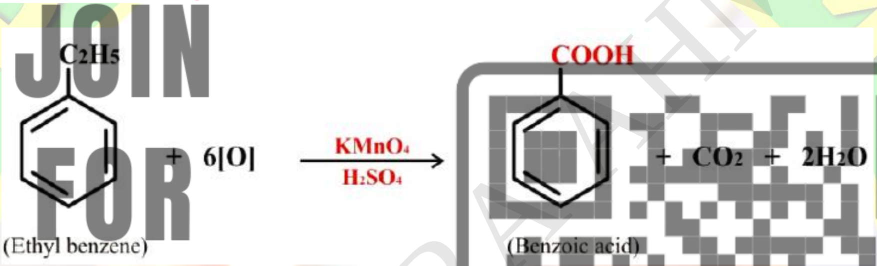
$$\underset{\text{(Primary alcohol)}}{R\text{-}CH_2\text{-}OH} + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\text{(Aldehyde)}}{R\text{-}CHO} + H_2O$$

$$\underset{\text{(Acetaldehyde)}}{CH_3\text{-}CHO} + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\text{(Acetic acid)}}{CH_3\text{-}COOH}$$

4 By the Oxidation of Aldehyde

$$\underset{\text{(Aldehyde)}}{R\text{-}CHO} + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\text{(Carboxylic acid)}}{R\text{-}COOH}$$

5 By the Oxidation of Alkyl Benzene



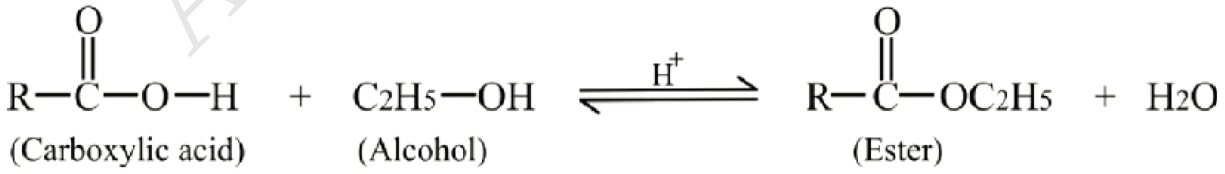
DERIVATIVES OF CARBOXYLIC ACIDS

Certain compounds are structurally derived from carboxylic acids by replacing a part of functional group of the carboxylic acid. Some common derivatives of carboxylic acids are given as:

(i) Esters: They are formed by replacing the hydrogen atom of carboxylic group with an alkyl or aryl group. Their general formula is R-COOR.

Conversion of Carboxylic Acids into Ester

The process in which carboxylic acid reacts with alcohol to form ester is called esterification.



$$\underset{\text{(Carboxylic acid)}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-O-H} + \underset{\text{(Alcohol)}}{C_2H_5-OH} \underset{}{\overset{H^+}{\rightleftharpoons}} \underset{\text{(Ester)}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5} + H_2O$$

e.g: Ethyl acetate ($CH_3COOC_2H_5$), Methyl propionate ($C_2H_5COOCH_3$)

(ii) Acid Halides: They are formed by replacing the hydroxyl group of carboxylic acid with a halogen atom (X). Their general formula is RCOX.

e.g. Acetyl chloride (CH_3COCl), Propionyl chloride (C_2H_5COCl) etc.

Conversion of carboxylic acids into acyl halides

$$\underset{\text{(carboxylic acid)}}{R-COOH} + PCl_5 \longrightarrow \underset{\text{(Acyl halide)}}{R-CO-Cl} + POCl_3 + HCl$$

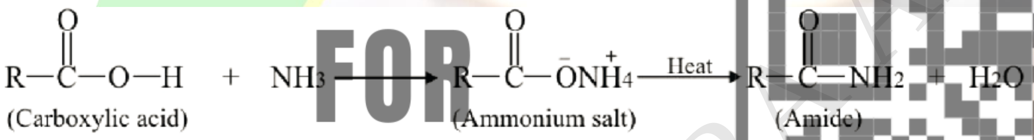
$$\underset{\text{(carboxylic acid)}}{3R-COOH} + PCl_3 \longrightarrow \underset{\text{(Acyl halide)}}{3R-CO-Cl} + H_3PO_3$$

$$\underset{\text{(carboxylic acid)}}{R-COOH} + SOCl_2 \longrightarrow \underset{\text{(Acyl halide)}}{R-CO-Cl} + SO_2 + HCl$$

(iii) Amides: **They are formed by replacing the hydroxyl group of carboxylic acid with an amino group. Their general formula is $RCONH_2$.**

e.g. Acetamide (CH_3CONH_2), Benzamide ($C_6H_5CONH_2$) etc.

Conversion of Carboxylic Acids into Amides

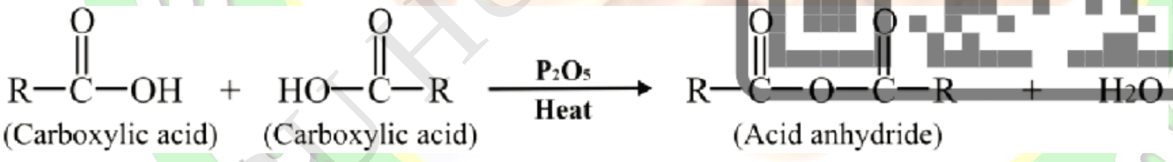


$$\underset{\text{(Carboxylic acid)}}{R-\overset{O}{\overset{\|}{C}}-O-H} + NH_3 \longrightarrow \underset{\text{(Ammonium salt)}}{R-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{N}H_4} \xrightarrow{\text{Heat}} \underset{\text{(Amide)}}{R-\overset{O}{\overset{\|}{C}}-NH_2} + H_2O$$

(iv) Acid Anhydrides: **They are formed by removing a water molecule from two carboxylic molecules. Their general formula is $(RCO)_2O$.**

e.g. Acetic Anhydride $(CH_3CO)_2O$

Conversion of Carboxylic Acids into Acid Anhydirdes



$$\underset{\text{(Carboxylic acid)}}{R-\overset{O}{\overset{\|}{C}}-OH} + \underset{\text{(Carboxylic acid)}}{HO-\overset{O}{\overset{\|}{C}}-R} \xrightarrow[\text{Heat}]{P_2O_5} \underset{\text{(Acid anhydride)}}{R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R} + H_2O$$

Conversion of Carboxylic Acids into Alcohols

$$\underset{\text{(Carboxylic acid)}}{R-COOH} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{(Alcohol)}}{R-CH_2-OH} + H_2O$$

Conversion of Carboxylic Acids into Alkane

Carboxylic acids when reacted with caustic soda (base) they form salt of carboxylic acid which on further heating with soda-lime yield alkanes.

$$\underset{\text{(Acetic acid)}}{CH_3\text{-}COOH} + NaOH \longrightarrow \underset{\text{(Sod. acetate)}}{CH_3\text{-}COONa} + H_2O$$

$$\underset{\text{(Sod. acetate)}}{CH_3\text{-}COONa} + NaOH \xrightarrow{CaO/Heat} \underset{\text{(Methane)}}{CH_4} + Na_2CO_3$$

Self Assessment

Show the following conversions by means of chemical reactions:

- Methyl cyanide into acetic acid
- Acetic acid into an amide
- Ethanoic acid into ethanol

- $CH_3CN + 2H_2O \rightarrow CH_3COOH + NH_3$
- $CH_3COOH + NH_3 \rightarrow CH_3COONH_4$ ------heat------>$CH_3COONH_2 + H_2O$
- $CH_3COOH + 4[H]$ -------$LiAlH_4$-------> $C_2H_5OH + H_2O$

Uses of some common carboxylic acids and their derivatives

- Citric acid is used as flavor enhancer.
- Maleic acid is used as food additive.
- Tartaric Acid is used in food industry.
- Acetic acid is used as vinegar.
- Salicylic acid is used in the production of aspirin.
- Acet amide is used in drug synthesis.
- Acetic anhydride is used in making cellulose acetate.

Common name	Structure	Occurrence and derivation of name	Applications
Formic acid	$HCOOH$	Ants (Latin; Formica)	Preservative and antibacterial agent in livestock feed
Acetic acid	CH_3COOH	Vinegar (Latin; Acetum)	Vinegar production, food preservative and flavoring agent
Propionic acid	CH_3CH_3COOH	Milk, butter and cheese (Greek Protos, First; pion, fat)	Animal feed additive for preventing mold growth
Butyric acid	$CH_3(CH_2)_2COOH$	Butter (Latin; Butyrum)	Flavoring agent in food products
Valeric acid	$CH_3(CH_2)_3COOH$	Valerian root (Latin; Valere, to be strong)	Manufacture of valerate esters used in perfumes
Caproic acid	$CH_3(CH_3)_4COOH$	Goat (Latin; Caper)	Pharmaceuticals and plasticizers

Multiple Choice Questions

(i) The most common compound found in pineapple is:
(a) Acetic acid
(b) Ethanol
(c) Acetone
[✓ (d) Ethyl butanoate]

(ii) Two molecules of acetic acid on condensation gives:
(a) Ethyl acetate
(b) Aceticamide
(c) Acylhalide
[✓ (d) Acetic anhydride]

(iii) Carboxylic acid is stronger acid than:
(a) HCl
(b) HNO_3
[✓ (c) C_2H_5OH]
(d) H_2SO_4

(iv) The reagent that cannot produce an acyl halide in reaction with a carboxylic acid is:
(a) PCl_3
(b) PCl_5
[✓ (c) HCl]
(d) $SOCl_2$

(v) Benzoic acid is the product of oxidation of:
(a) Benzene
[✓ (b) Ethyl Benzene]
(c) Aniline
(d) Phenol

(vi) Formation of acyl halide and amide by carboxylic acid involved
(a) Replacement of hydrogen
(b) Replacement of carbonyl group
[✓ (c) Replacement of hydroxyl group]
(d) Replacement of oxygen

(vii) Formic acid is naturally found in:
[✓ (a) Venom of ants]
(b) Bees string
(c) Vinegar
(d) Butter

(viii) Among the following compounds, the one with the highest boiling point is:
(a) Ethanol
(b) Acetaldehyde
[✓ (c) Acetic acid]
(d) Ethyl chloride

(ix) The formula of caproic acid is:
(a) C_4H_9COOH
[✓ (b) $C_5H_{11}COOH$]
(c) $C_6H_{13}COOH$
(d) $C_7H_{15}COOH$

(x) The reaction of acetic acid with ethanol in the presence of conc. sulphuric acid gives:
[✓ (a) Ethyl acetate]
(b) Acetamide
(c) Ethane
(d) Acetic anhydride

Short Questions

1. Explain why?
   i) The boiling points of carboxylic acids are high than alcohol?

Ans. The hydrogen bonding is stronger in carboxylic acid than alcohol that's why they have higher boiling point.

ii) The structure of carboxylic acid is trigonal planar?

Ans. The carbon atom in carboxylic acid is sp^2 hybridized and sp^2 hybrid orbitals have a trigonal planar shape with 120° bond angle due to maximum repulsion of electron. Due to this fact, carboxylic acids have a trigonal planar structure.

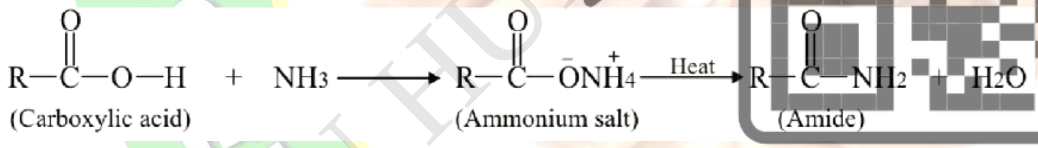
2. What happens when:
   i) Formaldehyde reacts with a mixture of Potassium dichromate & sulphuric acid.

$HCHO + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} HCOOH$ **(Formic Acid)**

ii) Carboxylic acid reacts with thionyl chloride

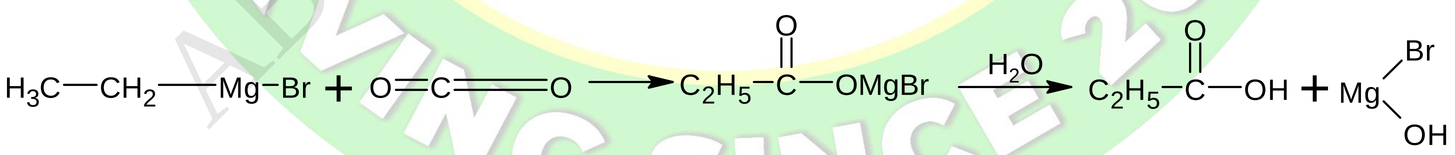
$$\underset{\text{(carboxylic acid)}}{R-COOH} + SOCl_2 \longrightarrow \underset{\text{(Acyl halide)}}{R-CO-Cl} + SO_2 + HCl$$

iii) Carboxylic acid reacts with ammonia



$$\underset{\text{(Carboxylic acid)}}{R-\overset{O}{\overset{\|}{C}}-O-H} + NH_3 \longrightarrow \underset{\text{(Ammonium salt)}}{R-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{N}H_4} \xrightarrow{Heat} \underset{\text{(Amide)}}{R-\overset{O}{\overset{\|}{C}}-NH_2} + H_2O$$

iv) Ethyl magnesium bromide reacts with carbon dioxide



$$H_3C-CH_2-Mg-Br + O=C=O \longrightarrow C_2H_5-\overset{O}{\overset{\|}{C}}-OMgBr \xrightarrow{H_2O} C_2H_5-\overset{O}{\overset{\|}{C}}-OH + Mg\begin{matrix}Br\\OH\end{matrix}$$

3. Write down the commercial applications of carboxylic acids.

Already Discussed Above

4. Write the natural sources of following carboxylic acids.
   (a) Formic acid (b) Acetic acid (c) Valeric acid (d) Caproic acid

Already Discussed Above

Descriptive Questions

1. How is carboxylic acid prepared by:
   - i) Carbonation of Grignard reagent
   - ii) Hydrolysis of alkyl nitriles
   - iii) Oxidation of primary alcohols

Already Discussed Above

2. Explain the structure of carboxylic acid.

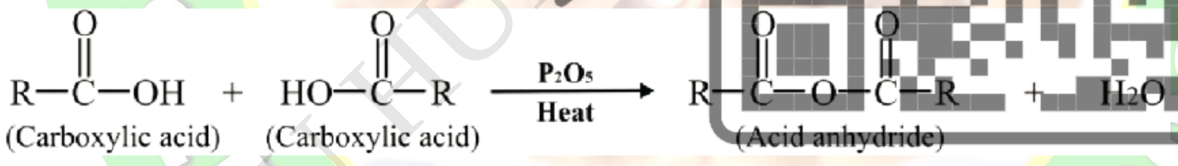
Ans. Structure of carboxylic acid is explained by hybrid orbital theory. The carbonyl carbon is sp^2 hybridized, possessing three sp^2 hybrid orbitals and one p_z unhybridized orbital. These three sp^2 hybrid orbitals are oriented almost at an angle of 120° to give trigonal geometry whereas p_z unhybridized orbital of carbonyl carbon form pi bond with p_z orbital of oxygen atom.

3. Discuss the acidic nature of carboxylic acid. How is it stronger than other organic compounds and weaker than mineral acids?

Already Discussed Above

4. Convert the followings:
   - i) Carboxylic acid into acid anhydride
   - ii) Ester into carboxylic acid
   - iii) Toluene into benzoic acid

i)



$$R-\overset{O}{\overset{\|}{C}}-OH + HO-\overset{O}{\overset{\|}{C}}-R \xrightarrow[Heat]{P_2O_5} R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R + H_2O$$

(Carboxylic acid) (Carboxylic acid) (Acid anhydride)

ii) $RCOOR + H_2O \rightleftharpoons RCOOH + ROH$

iii) $C_6H_5CH_3 + 3[O]$ ----$KMnO_4$----> $C_6H_5COOH + H_2O$

5. Explain the following physical properties of carboxylic acids:
   (a) Solubility (b) Boiling point

Already Discussed Above

6. Write the names of four derivatives of carboxylic acids and give the equation for their preparation from acetic acid.

Already Discussed Above

CHAPTER 10 BIOCHEMISTRY

"Biochemistry is the branch of science that deals with the chemical process taking place in the organisms."

DO YOU KNOW?

- 1 gram of carbohydrate provides approximately 4 calories.
- 1 gram of protein provides approximately 4 calories.
- 1 gram of fat (lipid) provides approximately 9 calories.

CARBOHYDRATES

"Polyhydroxy aldehydes and ketones are called carbohydrates."

Carbohydrate is a nutrient for human beings and animals.

Classification based on structure

On the basis of structures, carbohydrates can be classified into four categories:

1) Monosaccharides
2) Disaccharides
3) Oligosaccharides
4) Polysaccharides

1) Monosaccharides

Monosaccharides contain a single sugar unit.

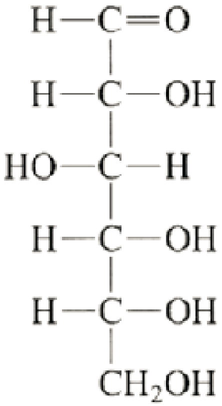
For example: glucose, fructose, galactose etc.

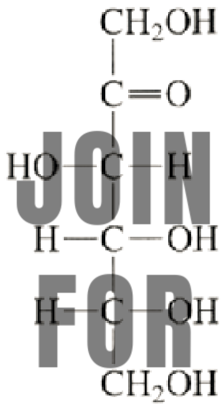
Monosaccharides are further classified on the basis of number of carbon atoms.

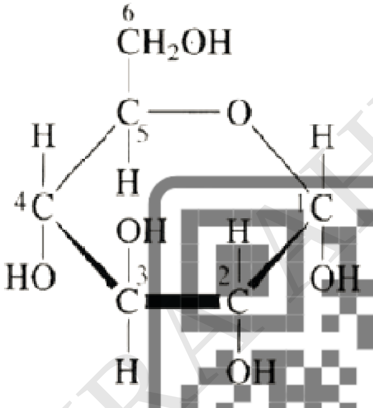
Class of Monosaccharide	Formula	Examples
Triose	$C_3H_6O_3$	Glyceraldehyde
Tetrose	$C_4H_8O_4$	Erythrose
Pentose	$C_5H_{10}O_5$	Ribose
Hexose	$C_6H_{12}O_6$	Glucose

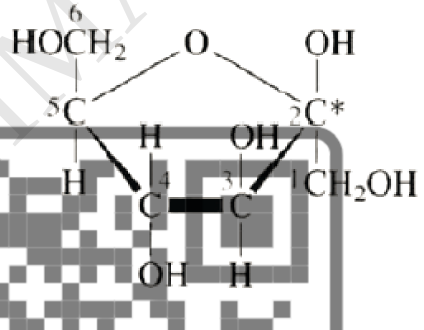
Hexose sugars are classified into **aldohexose** and **ketohexose**. Glucose is an example of aldohexose because it contains aldehyde group while fructose is an example of ketohexose because it contains ketone group.

Glucose and fructose exist in both open chain and closed chain form. However, the open chain form is relatively unstable. The close chain form of glucose is called pyranose (6 membered ring) whereas the close chain form of fructose is called furanose (5 membered ring).


(a) Glucose


(b) Fructose


(c) Glucopyranose


(d) Fructofuranose

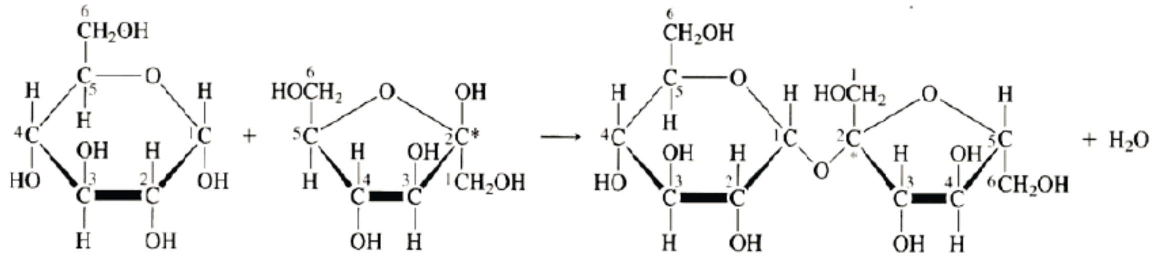
2) Disaccharides:-

Disaccharides contain two sugar units.

For example: sucrose lactose, maltose etc.

Monosaccharides are joined together though ‘glycosidic bond’ to form disaccharide. (O-C-O) bond is called glycosidic bond. It’s formed through a condensation reaction by the elimination of water molecule.

Disaccharides are water soluble crystalline solids and represented by molecular formula $C_{12}H_{22}O_{11}$.


(α-glucopyranose) (β-fructofuranose) (sucrose)

3) Oligosaccharides (Oligo = Few)

Oligosaccharides contain 3 to 10 sugar units.

For example: kestose (glucose+fructose+fructose), melezitose (glucose+fructose+glucose)

4) Polysaccharides

Polysaccharides contain more than 10 sugar units.

For example: cellulose, starch, glycogen etc.

Polysaccharides are macromolecules or polymers of monosaccharides. They are amorphous, water insoluble and made up of more than 10 hexose sugars.

Hexose units are joined together by glycosidic bond.

Polysaccharides are further classified into animal polysaccharides and plant polysaccharides.

An example of animal polysaccharide is glycogen, which is found in the liver of animals. It's a storage of carbohydrate and commonly known as anima starch.

Examples of plant polysaccharide are starch and cellulose. Starch is found in potato, wheat, barley etc. Cellulose is found in the cell wall of plant.

Role of Common Carbohydrates in Health and Disease

Glucose

It's a vital component of our blood. The normal range of glucose in blood ranges between 70 to 110 mg per 100 dl. However, if glucose level exceeds this range, it can lead to Diabetes.

Fructose

It is found in fruits and honey. It's the sweetest sugar.

Lactose

It's a disaccharide. It's found in milk so it's also known as milk sugar. It's broken down into glucose and galactose in the alimentary canal by the enzymic activity.

Sucrose

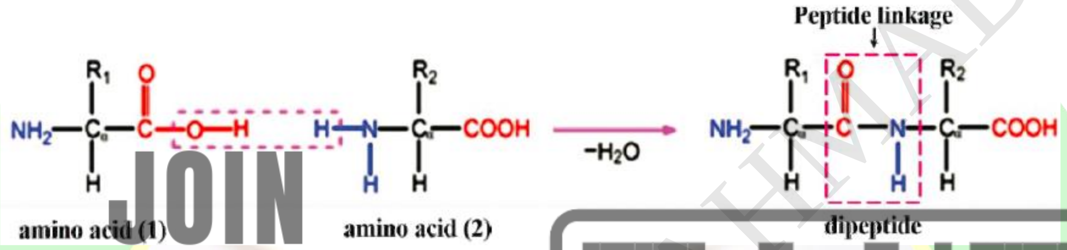
It's also a disaccharide and made up of a glucose and a fructose sugar. It's known as table sugar or cane sugar. An excess amount of sucrose in our diet can cause the development of gum disease such as plaque formation in the teeth and even tooth decay.

PROTEINS

Proteins are naturally occurring macromolecules made up of long chain of amino acids.

$$H_2N-\underset{}{\overset{R}{\overset{|}{C}}}H-COOH$$

There are 22 types of α amino acids that can be used to build proteins. Each amino acid consists of an amino group as well as a carboxyl group. These amino acids are associated with each other through poly peptide linkage (CONH).



Classification of proteins

Proteins may be classified on the basis of their functions and structures.

CLASSIFICATION OF PROTEINS ON THE BASIS OF FUNCTION:

Based on functions, proteins are classified into following types.

(i) Catalytic Proteins (Enzymes)

Enzymes are biological catalysts. They increase the rate of the biological reaction multiple fold as compared to a chemical catalyst. Our bodies contain numerous catalytic proteins which facilitate the chemical reactions inside the body. For example, lipase catalysis the decomposition of lipids into fatty acids in our alimentary canal.

$$\text{Starch} + H_2O \xrightarrow{\text{Amalyase}} \text{Glucose}$$

$$\text{Protein} + H_2O \xrightarrow{\text{Protease}} \text{Amino acid}$$

$$\text{Lipid} + H_2O \xrightarrow{\text{Lipase}} \text{Fatty acid}$$

(ii) Storage Proteins:

These proteins store nutrients or metal ions in a particular part of plants or animals. For example, Albumin, Globulin and Casein etc.

(iii) Transport Proteins:

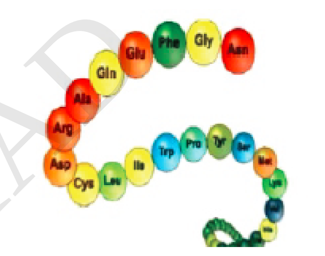
These proteins facilitate the movement of molecules, ions and other substances across cellular membrane and in the blood stream. For example: hemoglobin.

(iv) Hormonal Proteins:

These proteins play a critical role in regulating the function of body by transmitting signals between the cells.

CLASSIFICATION OF PROTEINS ON THE BASIS OF STRUCTURE:

Proteins are classified into four main types based on their structures.

Primary	➢ It is a linear sequence of amino acids in the protein chain. ➢ This sequence plays a crucial role in determining the overall shape and function of the protein.	
Secondary	➢ It refers to the folding patterns in polypeptide chains due to interactions between nearby amino acids. ➢ The two secondary common structures are alpha helix and beta sheets. ➢ The Stabilization of secondary structure is due formation of hydrogen bonds between N-H and C=O groups of amino acids	
Tertiary	➢ It refers to three-dimensional arrangement of a protein molecule having folded and refolded polypeptide chain. ➢ The stability of molecule is due to the presence of following types of forces among polypeptide chain; • Salt bridge (ionic bond) • Disulfide bridge (covalent bond) • Van der Waals forces • Hydrogen bond ➢ Example: Myoglobin exhibits a tertiary structure.	
Quaternary	➢ It is a large complex protein molecule and formed by the interaction of multiple protein subunits. Example: Hemoglobin, which consists of four subunits and illustrates the quaternary structure.	

Properties of proteins

(i) Proteins are water soluble due to the di polar terminal of amino acids in the polypeptide chain.
(ii) Proteins are amphoteric in nature because of the presence of $-COOH$ as well as $-NH_2$ group in their structure of amino acid sequences.
(iii) Proteins exhibit flexibility due to the ability of amino acid chain rotation.
(iv) Certain proteins exist in various colours i.e. haemoglobin.
(v) Proteins are thermally stable, however the structure of proteins are disrupted by heating, at elevated temperature or by a sharp change in the pH.

Importance of proteins

(i) Proteins provide energy for the body and in a rough estimation, 1g of protein provides four calories.
(ii) Haemoglobin is a protein, it transports oxygen from the lungs to every tissue of the body.
(iii) Harmones are proteins which regulate various physiological functions in the body.
(iv) Antibodies are proteins which play a very important role in the immune system of the body.

LIPIDS

“Lipids are naturally occurring heterogenous organic compounds that are insoluble in water but soluble in Bloor’s reagent.”

Bloor’s reagent is a mixture of diethyl ether and ethyl alcohol.

Classification of lipids

Lipids are classified into three main groups.

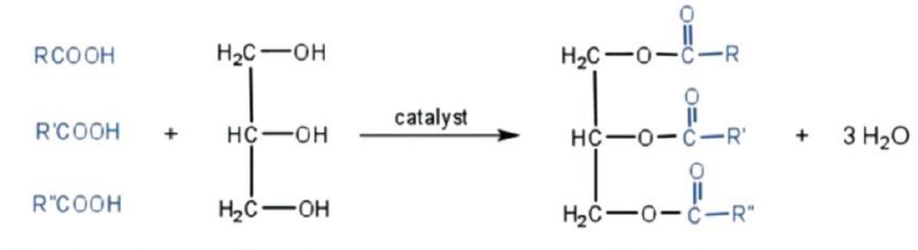
a) Simple lipids b) Compound lipids c) Steroids

a) Simple Lipids

These lipids are chemically esters, made up of fatty acids and alcohols.

Such lipids are further classified into fat, oil and waxes.

Fats and Oils: They are also known as triglycerides or triesters. They are formed by the condensation of three fatty acid and a glycerol molecule.



(Three fatty acids) (Glycerol) (Triglyceride)

Fatty acids are carboxylic acids with contains 12 to 24 carbon atoms which may be saturated or unsaturated. Oils are made up of unsaturated fatty acids and they are liquids at room temperature. Fats are made up of saturated fatty acids.

Type of Fatty Acid	Description	Examples
Saturated Fatty Acid	Contains only single bonds between carbon atoms	Stearic Acid, Palmitic Acid
Unsaturated Fatty Acid	Contains at least one double bond between carbon atoms	Oleic Acid, Linoleic Acid.

Waxes: Waxes are naturally occurring esters of long-chain fatty acids and long chain alcohols.

For example:

$$C_{15}H_{31} - COO - C_{16}H_{33}$$

(Bees wax)

b) Compound Lipids

These are esters of glycerol with two fatty acids and some other compounds sch as carbohydrates, amino acids, phosphoric acid etc.

c) Steroids

Non-saponifiable lipids are called steroids. It contains a polycyclic structure.

Examples of steroids are cholesterol and cholic acid.

Properties of lipids

A. Physical Properties

- Lipids exist in different physical states depending upon their chemical nature and temperature. For example, fat exists in solid state, wax is semisolid state and oil in liquid state at room temperature.
- Lipids are translucent or opaque in nature.
- Lipids are insoluble in water and soluble in the organic solvents; like Bloor's reagent.
- Lipids have low density which enables them to float on water.
- Melting point of saturated lipids is higher than unsaturated lipids.

B. Chemical Properties

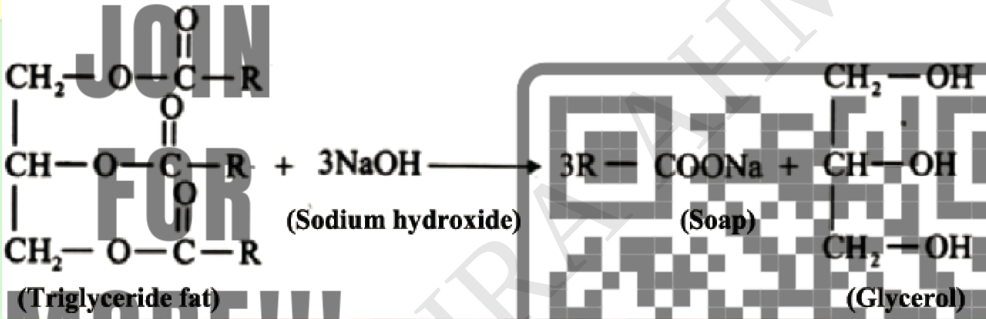
i) Addition Reactions:

Oils undergo addition reactions with hydrogen in the presence of nickel catalyst to produce fats.

$$R\text{-}CH{=}CH\text{-}COOH + H_2 \text{ ----------------- } R\text{-}CH_2\text{-}CH_2\text{-}COOH$$

ii) Saponification

Fats and oils are hydrolyzed when heated with an alkali to produce soap and glycerol, this process is known as saponification.



iii) Rancidity

When animal fats are exposed to moist air, they undergo oxidation and hydrolysis reactions simultaneously leading to the development of an unpleasant taste and odor. This process is called rancidity.

Importance of lipids

(i) They store chemical energy in the form of triglycerides in adipose tissues. They store more than twice energy as compared to carbohydrates and proteins. This stored energy is used during fasting.

(ii) They are fundamental building blocks of cell membranes. Due to their water insolubility, they protect the cell by forming a phospholipid layer which allows the movement of substances in and out of the cell.

(iii) Lipids in adipose tissues help maintaining the body temperature and serve as insulation of the body.

(iv) They help in the absorption and utilization of fat soluble vitamins such as vitamin A, D, E and K.

IMPORTANCE OF MINERALS IN OUR BODY:

1. IRON:

It involves in the oxygen transport, immune function and the production of red blood cells.

2. CALCIUM:

Calcium is used to build strong bones and teeth. It also helps in immune system.

3. PHOSPHORUS:

Being a part of DNA and RNA, it is important for protein synthesis and transferring genetic information.

4. Zinc:

It improves our immune system and enhances insulin activity. It also activates our sense of smell and taste. Deficiency of zinc causes loss of weight, appetite and taste.

Multiple Choice Questions

(i) Starch and Sucrose are examples of:
(a) Monosaccharides and Disaccharides
(b) Disaccharides and Oligosaccharides
[✓ (c) Polysaccharides and Disaccharides]
(d) Monosaccharides and Polysaccharides

(ii) Amino acid units bonded in protein molecule through:
(a) Glycosidic linkage (b) Ether linkage
[✓ (c) Peptide linkage] (d) Hydrogen bridge

(iii) Proteins are composed of:
[✓ (a) Amino acids] (b) Carbohydrates
(c) Lipids (d) Nucleic acids

(iv) A condensation polymer of amino acid is:
[✓ (a) Protein] (b) Lipids
(c) Starch (d) Glycogen

(v) Saponification is the formation of soap by the reaction of fat and oil with:
[✓ (a) An alkali] (b) An acid
(c) Sugar (d) Glycerol

(vi) Which of the following mineral is considered to be essential for immune system:
(a) Iron
[✓ (b) Zinc]
(c) Magnesium
(d) Calcium

(vii) Rancidity is a chemical process involving:
[✓ (a) Oxidation and hydrolysis]
(b) Condensation and reduction
(c) Polymerization
(d) Decarboxylation

(viii) Lipid which is a major component of cell membrane is:
(a) Triglyceride
[✓ (b) Phospholipid]
(c) Glycolipid
(d) Steroid

(ix) Total numbers of alpha amino acids are:
(a) 19
[✓ (b) 22]
(c) 25
(d) 28

(x) Sugar molecules are classified as:
(a) Fats
(b) Proteins
[✓ (c) Carbohydrates]
(d) Lipids

Short Questions

1. Mention the three main functions of lipids.

ALREADY DISCUSSED ABOVE

2. Comparing with other nutrients, why lipids are better source of energy?

Ans. Lipids are better source of energy because they can provide more energy in a little amount.

3. Carbohydrates are necessary component of our diet. Give two dietary importance of carbohydrates.

ALREADY DISCUSSED ABOVE

4. What is meant by saponification? Give the reaction.

ALREADY DISCUSSED ABOVE

5. What is rancidity which chemical reaction involves in this process?

ALREADY DISCUSSED ABOVE

6. Write three essential functions of protein in the body.

ALREADY DISCUSSED ABOVE

7. Write down the sources from which we intake fructose and lactose.

ALREADY DISCUSSED ABOVE

Descriptive Questions

1. What are Carbohydrates? Give their classification on the basis of structure.

ALREADY DISCUSSED ABOVE

2. Explain the role of glucose, fructose, sucrose and lactose in the health of human being.

ALREADY DISCUSSED ABOVE

3. What are Proteins? Classify various types of proteins on the basis of their function.

ALREADY DISCUSSED ABOVE

4. What are Lipids? Give their classification, properties and biological significance.

ALREADY DISCUSSED ABOVE

5. How can you explain primary, secondary and tertiary structure of proteins?

ALREADY DISCUSSED ABOVE

6. Describe physical properties of proteins.

ALREADY DISCUSSED ABOVE

7. Why minerals are essential for our health? Give the biological significance of Calcium, Iron, Zinc, and phosphorus.

ALREADY DISCUSSED ABOVE

CHAPTER 11

INDUSTRIAL CHEMISTRY

Industrial chemistry is the branch of chemistry which deals with the conversion of raw materials into useful product through chemical process.

CHEMICAL INDUSTRIES

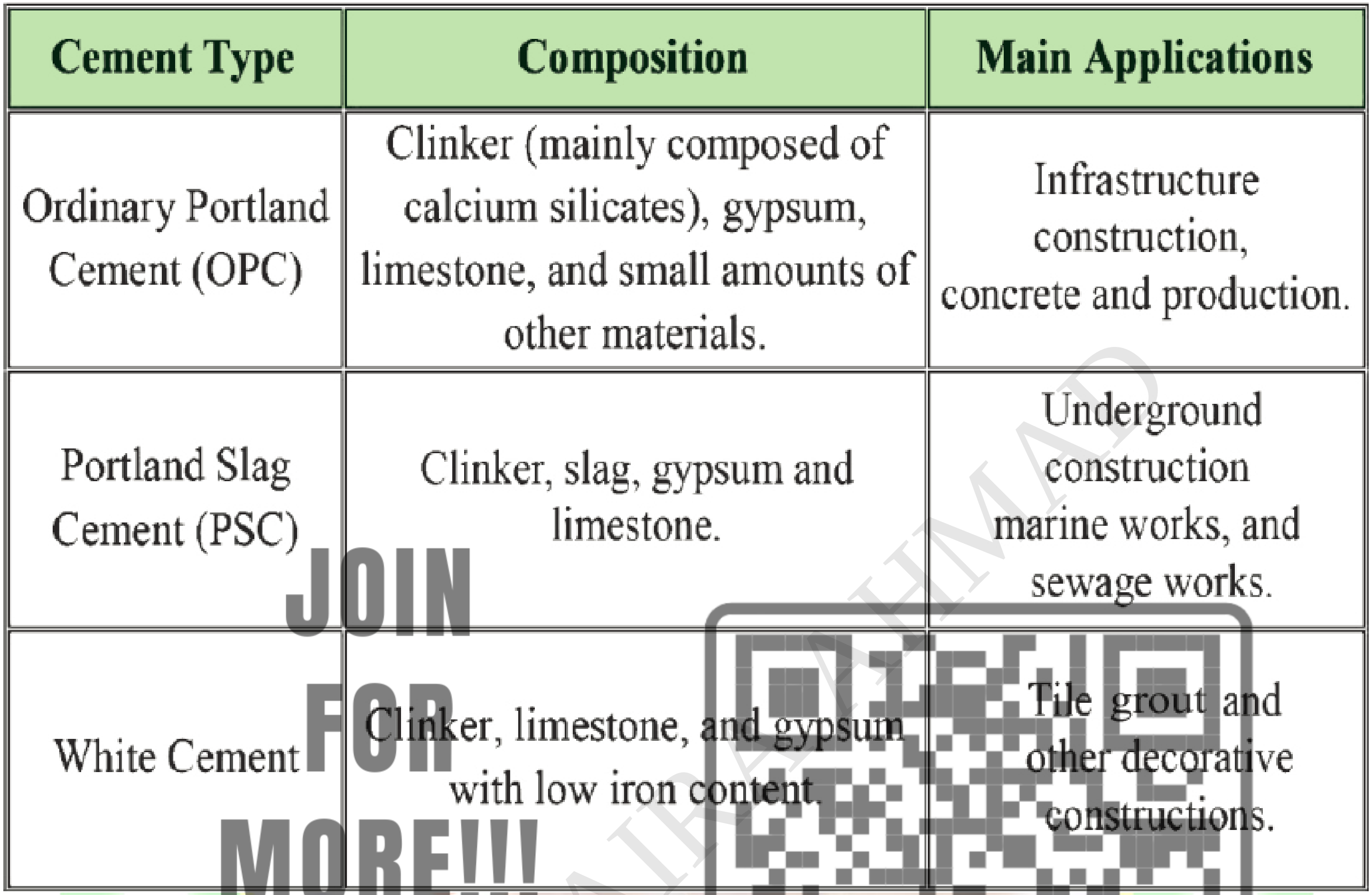
“The term chemical industries refer to all those compounds that manufacture chemicals.”

Synthetic Fertilizer	Chemical Formula	Nutrients Provided	Uses
Ammonium Nitrate	NH_4NO_3	Nitrogen	Development of roots and maintaining pH soil
Urea	$CO(NH_2)_2$	Nitrogen	Development of leaf, steam and fruits
Diammonium Phosphate (DAP)	$(NH_4)_2HPO_4$	Nitrogen, Phosphorus	Development of early stage of plants growth
Potassium Chloride (MOP)	KCl	Potassium	Help enzyme activities and photosynthesis

Synthetic Textile Products	Description	Uses
Polyester	A synthetic fiber made from petrochemicals	Clothing (shirts, pants, dresses, jackets), curtains, bedding etc.
Nylon	A strong and durable synthetic fiber	Stockings, hosiery, swimwears, ropes, parachutes, and various sportswears.
Acrylic	A soft and light weight synthetic fiber.	Sweaters, blankets, faux fur carpets,

Paint Products	Description	Common Uses
Water-Based Paint	It is also known as latex. In this paint water is used as a carrier solvent	Interior and exterior walls, ceilings, and various surfaces.
Oil-Based Paint	It contains organic solvents as a carrier.	Woodwork, metal surfaces and surfaces that require durability.
Enamel Paint	A type of oil-based or water-based paint with a hard, glossy finish.	Metal surfaces, kitchen appliances, and surfaces that need high durability.
Epoxy Paint	A two-part paint that consists of a resin and a hardener, creating a tough and durable coating.	Industrial floors, garage floors, marine applications, and metal surfaces.

Detergent Products	Composition	Main Uses
Laundry Detergent	Surfactants, builders, enzymes, fragrance, water softeners	Cleaning clothes in washing machines
Dishwashing Detergent	Surfactants, enzymes, fragrance, water softeners	Washing dishes by hand or in dishwashers
All-Purpose Cleaner	Surfactants, solvents, fragrance, water	Cleaning various surfaces and floors
Hand Soap	Surfactants, moisturizers, fragrance, antibacterial agents	Hand hygiene and cleansing



Cement Type	Composition	Main Applications
Ordinary Portland Cement (OPC)	Clinker (mainly composed of calcium silicates), gypsum, limestone, and small amounts of other materials.	Infrastructure construction, concrete and production.
Portland Slag Cement (PSC)	Clinker, slag, gypsum and limestone.	Underground construction marine works, and sewage works.
White Cement	Clinker, limestone, and gypsum with low iron content.	Tile grout and other decorative constructions.

PHARMACEUTICAL INDUSTRY

Pharmaceutical industries refers to the companies where drugs are manufactured. Drug is a substance that is used to treat or cure a disease in human or animals. Some common drugs are described below:

1. Analgesics:

A drug that specifically targeted on central nervous system to provide pain relief is known as analgesic drug.

Foe example: Aspirin (chemical name: Acetyl salicyclic acid)

2. Antibiotics:

It suppress the growth or kills micro organisms. “Penicillin” was the first discovered antibiotic.

3. Antipyretic medicines:

A drug which lowers the body temperature to normal is known as antipyretic. The most widely used antipyretic is “Paracetamol”.

4. Anti Fungal medicine:

These drugs are used to kill fungi that cause infections on skin. The most common skin infections are ringworm and dandruff. Example of antifungal drug is “fluconazole”.

5. Anti Inflammatory medicine:

These drugs helps to reduce inflammation, and relieve pain. Ibuprofen (Brufen) is an example of anti inflammatory medicine.

6. Anti Allergic medicine:

These are also called antihistamines. Histamine is a chemical produced in the body due to decarboxylation of an amino acid known as histidine. The adminstration of these drugs reduces the histamine level in the body.

For example: Dephenyl hydramine (Acefyl)

7. Anti Malarial medicine:

Anti protozoal or anti malarial drugs are used to treat mosquito bite infectious disease such as malaria. Most commonly used anti malerial drug is chloroquine.

PESTICIDES

“Chemical which are used to control, repel or kill pets or insects or fungus are known as pesticides”.

Types of Pesticides

Pesticides are classified into three major classes named as insecticides, fungicides and herbicides.

1. Insecticides

“Chemical substances which use to kill insects are called as insecticides”. The best known insecticide is Dichlorodiphenyltrichloroethane (DDT),

2. Herbicides

Herbicides are the chemicals which either destroy or stop growing weeds.

3. Fungicides

Fungicides ae chemcial substances employed to eliminate undesired fungi that develop within crops.

SYNTHETIC POLYMERS

"Polymer is a high molecular mass compound that forms by the combination of a large number of one or more types of molecules of low molecular mass".

Types of Polymers:

There are two types of polymers.

1. Natural Polymers such as rubber, cellulose, starch etc.

2. Synthetic Polymers such as PVC, Polyethene, Bakelite etc.

Types of Synthetic Polymers:

1. **Addition Polymerization:** In this process monomers are added to form polymers by the cleavage of pi bond.

For example: Polythene, PVC, PVA etc.

2. Condensation Polymerization: In this process monomers are added to form polymers by elimination of simple molecules such as H_2O.

For example: Bakelite, Protein etc.

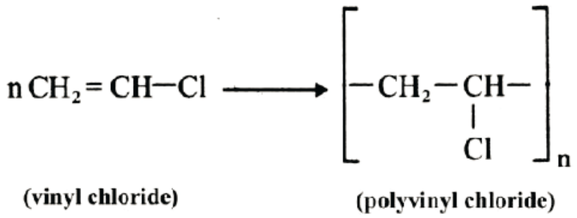
Types of Plastics:

1. Thermoplastics: They softern onn heatin and regain their original properties on cooling. Such as polyethene.

2. Thermosetting Plastics: They undergo irreversible transformation, becoming hard and rigid upon heating. such as Bakelite.

Polyvinyl chloride (PVC)

Polyvinyl chloride (PVC) is a widely used thermoplastic due to its versatility and durability. It is known for its excellent electric insulation, light weight and low cost. PVC is an addition polymer of vinyl chloride it is prepared by heating vinyl chloride at 60-70°C in the presence of Hydrogenperoxide (H_2O_2).



$$n\,CH_2=CH-Cl \longrightarrow \left[-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-\right]_n$$

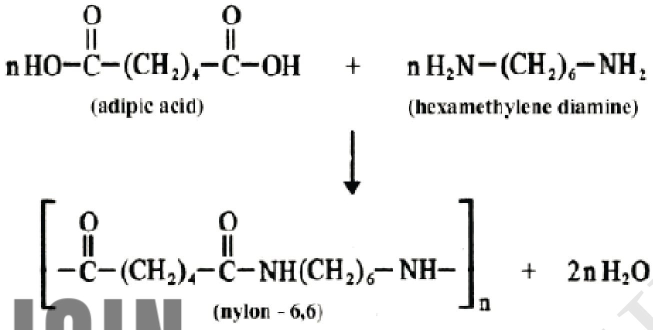
(vinyl chloride) (polyvinyl chloride)

PVC is used in the manufacturing of bottles, pipes, medical tubes, blood bags and insulation material on electric wires.

Nylon 6, 6

Nylon 6, 6 is a type of synthetic polymer. It is known due to its high strength, light weight and excellent mechanical properties.

Nylon 6, 6 is chemically a polyamide and prepared by the process of condensation polymerization between hexamethylenediamine and adipic acid (hexanedioic acid) with the elimination of water molecules.



$$n\,HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH + n\,H_2N-(CH_2)_6-NH_2 \longrightarrow \left[-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH(CH_2)_6-NH-\right]_n + 2n\,H_2O$$

It is used in making tents, parachutes, ropes, fish net, bristles of brushes etc.

COSMETICS

The word cosmetic is derived from the Greek word “kosmetiko” which means butification of skin.

“Cosmetics are the products that are used to enhance or alter the appearance of face, body, nails or hairs.”

(i) **Lipstick:** **“Lipstick is a chemical used to colour, moisturization and protection of the lips”**. It is a type of makeup that usually available in a stick and is applied directly to the lips. Lipstick is typically made from a mixture of oils, waxes, pigments, fragrance and moisturing agent.

(ii) **Nail Polish:** It is a type of lacquer that is used to enhance the appearance of nails in women. It comes in a variety of colours including red, pink, brown and others. The basic components of nail polish include pigments, resin, plasticizers and film former.

(iii) **Nail Polish Remover:** It is an organic solvent such as “acetone”

(iv) **Hair Dyes:** These are chemicals that change the colour of hairs.

Hair dyes can be temporary or permanent. The permanet hair dyes contains Hydrogen Per Oxide (H_2O_2) as an oxidizing agent.

(v) **Perfumes:** These are complex mixtures of aromatic compounds.

ADHESIVES

"Adhesives or glue are chemical substance that use to stick materials together". They are liquids or semi solids. They create a bond between the two surface through either physical or chemical processes. A wide variety of adhesive are available, each possessing unique properties and appropriate applications. Some of frequently used adhesive are described below.

Starch

It is a natural adhesive and prepared by heating starch suspension in water.

It has low adhesive strength but widely used because it is easiy prepared and low cost.

For example: Flour is mixed in water and then it is heated.

Epoxy Resins

These are strong synthetic adhesives and commonly used for bonding metals, plastics, glasses and ceramic items.

For example: Magic Depoxy Steel

Silicon Resins

These are known with their high strength, high thermal stability and water repellent ability. For example: UHU

Super Glue

It is chemically named as cyanoacrylate. It is fast acting adhesive that bond quickly of broken items such as jewellery, toys, automotives etc.

For example: Elfy

Multiple Choice Questions

(i) Super glue is chemically named as:
[✓ (a) Cyano acrylate] (b) Polyvinyl acetate
(c) Epoxy resins (d) Polyurethane

(ii) DDT is a chemical which commercially known as:
[✓ (a) Insecticide] (b) Herbicide
(c) Pesticide (d) Fungicide

(iii) Nail polish remover is mainly consists of:
(a) Pigments [✓ (b) Acetone]
(c) Diethyl ether (d) Ethyl alcohol

(iv) Antimalarial drug among the following is:
(a) Ibuprofin [✓ (b) Chloroquine]
(c) Paracetamol (d) Diphenyl hdramine

(v) Asprin is a pain reliever, its chemical name is:
(a) Ascorbic acid (b) Nicotinic acid
[✓ (c) Acetyl salisylic acid] (d) Benzoic acid

(vi) Nylon 6, 6 is a condensation polymer of hexamethylene diamine and:
(a) Benzoic acid [✓ (b) Adipic acid]
(c) Pthalic acid (d) Valeric acid

(vii) Which of the following is not a synthetic plastic:
(a) Nylon (b) Teflon
[✓ (c) Cellulose] (d) Polyethene

(viii) Drugs that lower the body temperature to normal are known as:
(a) Antibiotics [✓ (b) Antipyretic]
(c) Antiallergic (d) Anti histamins

(ix) Which of the following chemical is used as an oxidizing agent in permanent hair dyes:
(a) Acetone [✓ (b) Hydrogen peroxide]
(c) Polyvinyl acetate (d) Resorcinol

(x) An example of thermosetting plastic is:
(a) Polyethene (b) PVC
(c) Nylon [✓ (d) Bakelite]

Short Questions

1. Give the scope of pharmaceutical industries in Pakistan.

Ans. There are hundreds of pharmaceutical industries operating in Pakistan. Health ministry of Government of Pakistan play important role in the availability and accessibility of drugs in public sector.

2. What is antihistamine drug? Give the symptoms in which it is used.

ALREADY DISCUSSED ABOVE

3. Write the names of two synthetic and two natural polymers.

ALREADY DISCUSSED ABOVE

4. Write the name of four main components of Nail polish?

ALREADY DISCUSSED ABOVE

Descriptive Questions

1. How can you define Cosmetics? Describe four cosmetics which are commonly used.

ALREADY DISCUSSED ABOVE

2. What are pesticides? Explain various types of pesticides along with their specific use.

ALREADY DISCUSSED ABOVE

3. Describe the preparation, properties and uses of Nylon and polyvinyl chloride.

ALREADY DISCUSSED ABOVE

4. What are adhesives? Explain the significance of super glue and silicon resins.

ALREADY DISCUSSED ABOVE

CHAPTER 12

ENVIRONMENTAL CHEMISTRY

ENVIRONMENTAL CHEMISTRY:

"It deals with the study of chemical processes happening in Earth's environment and their direct or indirect impact on organisms that live on Earth."

POLLUTION:

The presence of undesirable substances in the environment that harm the natural balance of eco systems is known as environmental pollution.

PARTS OF ENVIRONMENT:

Earth's atmosphere consists of four interconnected parts that work together to sustain life.

1. Lithosphere: It comprises Earth crust and soil covering with rocks.

2. Hydrosphere: It comprises all surface and underground water.

3. Biosphere: It includes the entire living being on the Earth.

4. Atmosphere: It is extended to 500 KM above Earth's surface and consists of gases.

LAYERS OF ATMOSPHERE:

1. Troposphere: It's the lowest layer of atmosphere extending from Earth's surface to an altitude of 11 km.

2. Stratosphere: It starts from the top of troposphere and extending up to 50 km above the Earth's surface.

3. Mesosphere: It lies above stratosphere stretching from 50 km to 85 km above the Earth's surface.

4. Thermosphere: It is the uppermost layer of the Earth's atmosphere extending from 85 km to 500 km.

AIR POLLUTANTS:

Carbon Oxides (CO_x), Nitrogen oxides (NO_x), Sulphur oxides (SO_x), volatile organic compounds (VOCs) and Ozone (O_3) are air pollutants.

1. CO_x

The oxides of carbon in troposphere are carbon monoxide (CO) and carbon dioxide (CO_2). CO is a very toxic gas. It is released by the partial combustion of fuel in automobile or forest fire. CO in troposphere is broken down by UV rays into free carbon particles which are responsible for the smog formation.

$$CO_{(g)} + h\upsilon \longrightarrow C_{(s)} + \frac{1}{2}O_{2(g)}$$

CO_2 is added to atmosphere due to the combustion of fossil fuels such as coal, petroleum etc. It's also released during the respiration of animals. The increased level of carbon dioxide in atmosphere causes suffocation and respiratory disease.

2. NO_x

There are two main oxides of nitrogen which causes air pollution. These are nitric oxide (NO) and nitrogen dioxide (NO_2). The high concentration of NO and NO_2 gases in air is harmful because they form acid rain.

3. SO_x

There are two oxides of sulfur found in the air named as SO_2 and SO_3. They are produced by volcanic eruption. The presence of these gases in atmosphere causes cardiac and respiratory disease and also affects crops production.

4. Volatile Organic Compounds (VOCs)

All those solvents which evaporate into atmosphere and contribute the atmospheric pollution are known as volatile organic compound. They are responsible for ozone depletion. Examples of VOCs include formaldehyde, benzene, toluene etc.

5. Ozone (O_3)

Ozone is an allotropic form of oxygen. It's present in a very low concentration in troposphere. Its side effects include respiratory issues, cardiac issues and irrigation of plants and crops.

CATALYTIC CONVERTER:

The burning of gasoline in a car engine results in the formation of air pollutants. To solve this issue, modern car engines are equipped with catalytic converters. The purpose of catalytic converter is to transform the harmful chemicals produced during internal combustion engine into less harmful or non-harmful substances such as CO_2, N_2, O_2 and H_2O. Catalytic converter contains a mixture of Pt and Pd which serves as catalyst.

Q. Can a vehicle run without catalytic converter?

Ans. Yes, a vehicle can run without catalytic convertor but it will produce air pollution.

Q. How dies catalytic converter contribute to reducing air pollution?

Ans. Catalytic converter converts harmful air pollutants into harmless substances.

INDUSTRIAL SMOG:

Smog is a type of air pollution. This term is a combination of smoke and fog. Smog is a mixture of SO_2, aerosols and volatile organic compounds ejected through the chimney of industries. It forms a brown-yellow layer usually in the industrial areas. Smog has many harmful side effects on human health, plant growth and overall, a major contributor of environmental pollution.

GLOBAL WARMING / GREEN HOUSE EFFECT:

The temperature of our Earth is regulated by certain gases present in the atmosphere such as CH_4, CO_2, N_2O and H_2O known as green house gases. The change in concertation of these gases can lead to alternation in the Earth's climate.

Global warming refers to the gradual rise in Earth's average surface temperature. The average temperature of earth is approximately 15°C but due to long term climate change resulting from global warming is causing shifts in average temperature.

To prevent global warming, we need to reduce green house gas emissions.

ACID RAIN:

The term caid rain was first introduced by an English chemist Robert Angus in 1872. Acid rain refers to rainfall that has acidic components such as nitric acid, sulfuric acid and carbonic acid.

The pH of normal rainfall generally ranges between 6 to 6.5 but the pH of acid rain is below 5.

Pollutants like oxides of carbon, nitrogen and sulfur are present in the atmosphere. These oxides may undergo chemical reaction with atmospheric water to produced sulfuric acid, nitric acid and carbonic acid. These acidic components mixed with rainwater and fall to the earth as acid rain.

Acid rain has several adverse effects on the environment and human life. For example:

1. Acid rain increases the acidity of rivers, which affect negatively on aquatic animal and plants causing a disturbance of eco system.
2. Acid rain reduces soil fertility due to lowing in soil pH from their normal range and ultimately affects on crops production.
3. Acid rain causes corrosion of building, bridges and other concrete and metal things.
4. Acid rain makes underground water toxic and undrinkable.

OZONE FORMATION & OZONE DEPLETION

Ozone layer is present in stratosphere. This layer plays a vital role in blocking and absorbing maximum portion of Sun's harmful radiations. The life on Earth would not be possible without the protection of this layer.

Ozone is produced in stratosphere due to photochemical reaction of sun rays and oxygen gas. UV radiations of sunlight breaks O_2 into free radicals. The oxygen free radicals are then combined with another oxygen molecule to produce ozone.

$$O_2 \xrightarrow{\text{U.V radiations}} O\bullet + \bullet O$$

$$O\bullet + O_2 \longrightarrow O_3$$

Human activities can contribute to the depletion of ozone layer through the emission of certain chemicals known as Ozone Depletion Substances (ODS). The most considerable human activity that have been responsible for ozone depletion is the release of gases from cooling devices such as refrigerator and air conditioners.

Chlorofluoro Carbons (CFCs) is a highly stable gas used as coolant in refrigeration and also a repellent in aerosol spray. When CFC reaches into stratosphere region, it breaks down into free chlorine and fluorine atoms which then react with ozone in UV light and decompose it into oxygen.

The best alternative is Hydro Fluro Carbons (HFCs) which do not have chlorine and do not contribute to ozone depletion.

WATER POLLUTION

Any undesirable change in the quality of water which affects the life adversely is called water pollution.

WASTE WATER ANALYSIS

Sample of waste water are collected from many different areas and they are analyzed by a series of tests.

1. Physical Test: This includes estimation of odor, color and taste.

2. Chemical test: This involves the checking of pH and presence of toxic chemical.

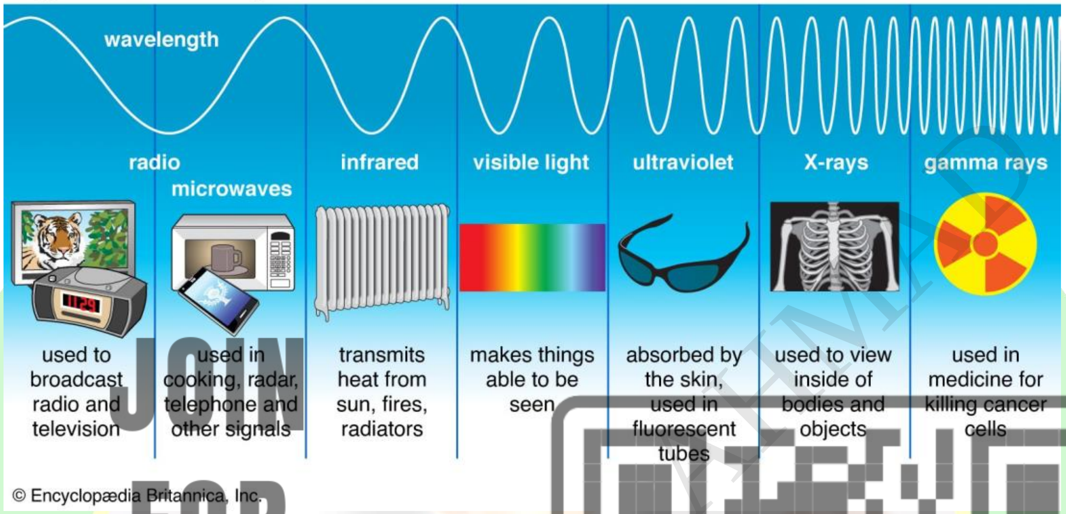
3. Microbiological test: This test involves checking for the presence of pathogens.

4. Organic test: This test is performed to check the presence of pesticides and volatile organic solvents such as petrol, benzene, toluene etc.

CHAPTER 13

SPECTROSCOPY

Types of Electromagnetic Radiation



© Encyclopædia Britannica, Inc.

SPECTROSCOPY:

Spectroscopy is the study of interaction of electromagnetic radiation of light with matter. It's a powerful analytical technique for the determination of structure of molecules.

TYPES OF SPECTROSCOPY:

1. Infrared (IR) Spectroscopy
2. Ultraviolet/Visible (UV-Vis) Spectroscopy
3. Nuclear Magnetic Resonance (NMR) Spectroscopy
4. Atomic Absorption and Emission Spectroscopy
5. Mass Spectrometry

1. Infrared (IR) Spectroscopy

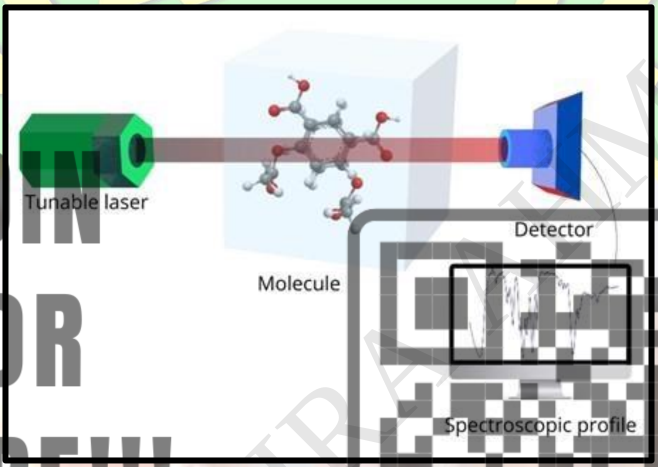
Infrared spectroscopy is used to detect the type of bond and the functional groups present in molecule. The atoms in a molecule already undergo vibration and rotation, in their normal routine, however when the molecules absorb radiations, it leads to increased intensity of vibrations. This vibration can be of two types namely **bond stretching** and **bond bending.** In bond stretching, the bond length increases or decreases while in bond bending the bond angle between the atoms changes.

The bending and stretching of each type of bond present in the molecule occurs at a particular frequency of IR spectrum and show the signals at a particular region.

The applications of IR spectroscopy are as follows:

(i) IR spectroscopy provides information for the presence of different functional groups in the organic molecules.

(ii) IR spectroscopy is also useful for identifying the impurities present in the sample to be analyzed.

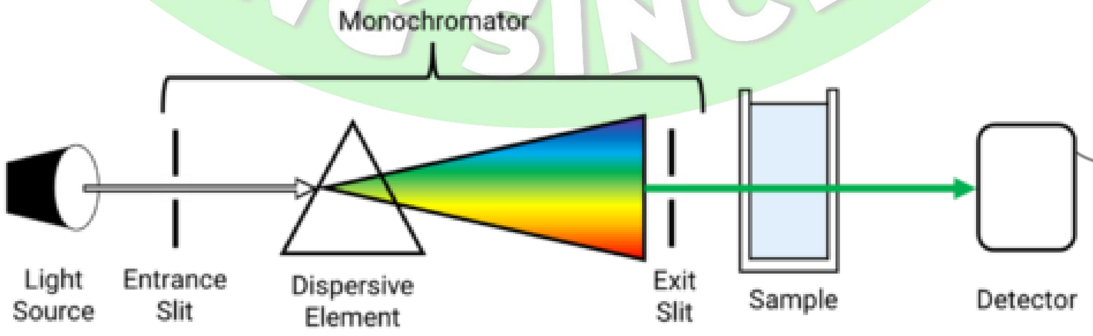


2. Ultraviolet/Visible (UV-Vis) Spectroscopy

It is used to determine the presence of double and triple bonds as well as conjugated system in the molecule. The UV region of electromagnetic spectrum extends from 200 nm to 400 nm and the visible region extends from 400 nm to 800 nm.

When a molecule absorbs electromagnetic radiations of UV – visible range (200 nm – 800 nm) electronic transitions occur. Its electrons are promoted from lower energy level to higher energy level.

UV spectroscopy is extensively used for determining the concentration of unknown compounds in a solution by using Beer-Lambert's law.



3. Nuclear Magnetic Resonance (NMR) Spectroscopy

The nucleus of certain elements exhibits random spin and behave like a tiny magnet due to their charged nature. When an external magnetic field is applied, the spin of nucleus aligned in two ways.

(i) It can align in the same direction of the applied magnetic field and it is said to be low energy spin state.

(ii) It can be opposite direction to the applied magnetic field and said to be high energy spin state.

When a sample of a compound is placed in a strong magnetic field and subjected to radio frequency radiation, the nuclei with specific spin state absorbs energy and flip into a high energy state, this absorption of energy is detected as signals in the NMR spectrum. The solvent used in NMR spectroscopy is usually D_2O or DMSO (Di Methyl SulfOxide)

The graph of NMR consists of the following parameters.

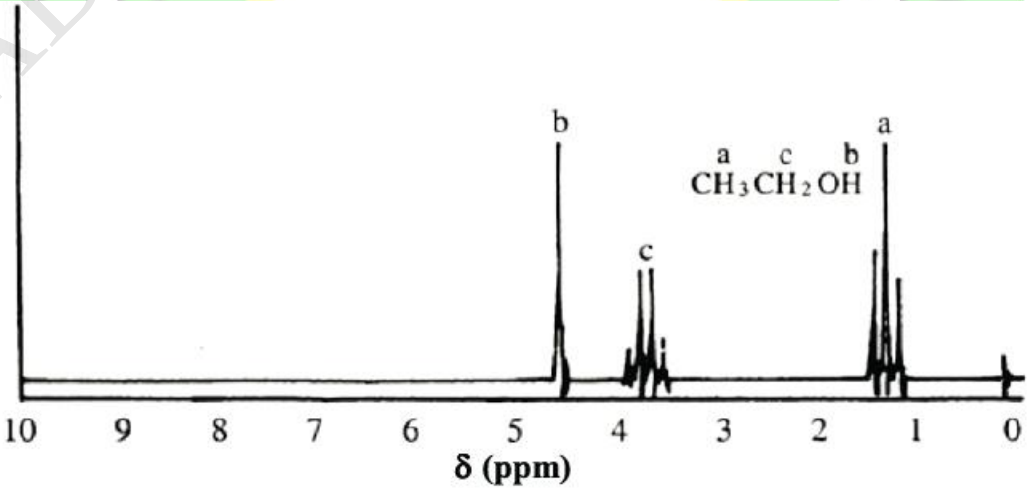
(i) x-axis represents chemical shift which shows position of proton signals relative to TMS (tetramethylsilane). The values are between 0 – 12 ppm relative to TMS.

(ii) y-axis represents absorption which shows the intensity of NMR signals.

(iii) Peak represents splitting pattern (singlet, doublet, triplet, quartet) due to neighboring protons.

Consider the example of ethanol

- Methyl (CH_3) protons appear as triplet around 1.1 to 1.3 ppm
- Methylene (CH_2) protons appear as quartet around 3.5 to 4 ppm
- Hydroxyl (OH) protons appears as a broad singlet around 4 to 5 ppm.



NMR spectroscopy provides valuable information about the chemical structure of organic compounds. Each organic compound exhibits a unique NMR spectrum acting as a ‘fingerprint’ that allows chemists to identify them.

4. Atomic Absorption and Emission Spectroscopy

It is used to identify elements in various samples including metal compounds. Within an atom, electrons are distributed in different energy levels, when atom receive energy from an external source like heat or an electric discharge, electrons can be promoted to higher energy level. These excited electrons then undergo transition involving the absorption or emission of electromagnetic radiations.

a) Atomic absorption spectroscopy

In atomic absorption spectroscopy, the sample is exposed to a wide range of light, the atom selectively absorbs specific wavelength of light that align with the energy needed to elevate electrons to higher energy level. The absorbed wavelength of light appears as dark lines in a unique pattern specific for that element. by examining the absorbed wavelength, a chemist can identify the presence of specific element in the sample.

b) Atomic emission spectroscopy

In atomic emission spectroscopy, the electron in an atom is first excited by providing energy from external source such as heat or electrical energy. When the excited electrons return to their ground state, they emit excess energy in the form of light of specific wavelengths. This emitted light appears as a series of bright lines against a dark background. Since each element has its distinct set of bright lines, chemist can identify the element based on this information.

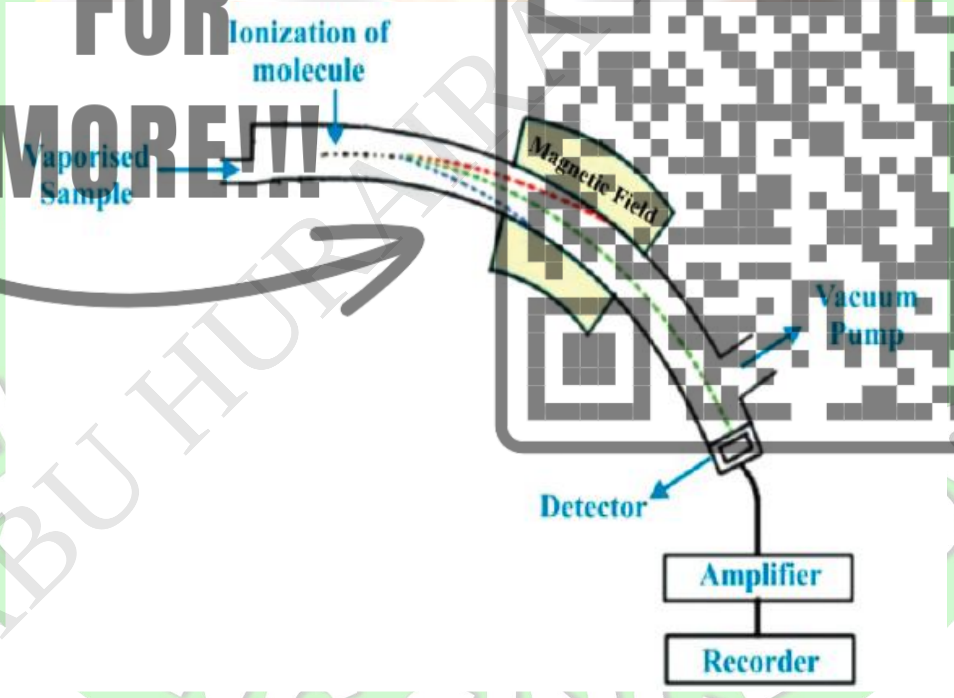
5. Mass Spectrometry

It is a technique used to determine the mass to charge ratio (m/z) of ions in a sample. It provides information about the mass of different fragments of the molecule.

In mass spectrometry, the vapors of compounds are bombarded with beam of high energy electrons from electron gun that makes the neutral molecules loose and electron and change into molecular ion. These molecular ion further break into smaller possible fragments of specific mass to charge ratio (m/z).

$$\underset{\text{(Neutral molecule)}}{Z} \xrightarrow{\text{high energy electron beam}} \underset{\text{(Molecular ion)}}{Z^{+}} + \bar{e}$$

These molecular ions then pass though magnetic field where they follow a curved path. A highly sensitive detector is attached in mass spectrometer which detects the molecular mass of ions and record on paper as specific lines.



It is used to determine the molecular mass of unknown compounds on the basis of mass to charge ratio.

——---- OUR CHANNELS ——----

INTER KARACHI (BIEK)

Channel Link

MDCAT --- Material & Guidance Group

Channel Link

ECAT --- Preparation Group 🛠️🔎

Channel Link

——---- OUR GROUPS ——----

INTER KARACHI

Group Link

- This group provides basic news, information, and study materials. Phone numbers will not be visible to other members.

2nd YEAR

Group Link

- This group serves the same purpose as the previous one. You can vote in this group to express your preferences.

2nd YEAR (2)

Group Link

- This group is identical to the previous one. Please join only one group from this set.

Inter Discussion (Boys)

Group Link

- In this group, you can engage in discussions and share your thoughts and questions. Please note that this group is exclusively for males.

MDCAT --- Material & Guidance Group

Group Link

- Created for MDCAT test preparation and guidance for the 2024 session. Start your preparation from the intermediate level. Group details are available in the description.

ECAT --- Preparation Group 🛠️🔎

Group Link

- Established for ECAT test preparation and guidance for the 2024 session. Begin your preparation from the intermediate level. Further information is provided in the group description.

Admin:

Abu Huraira Ahmad