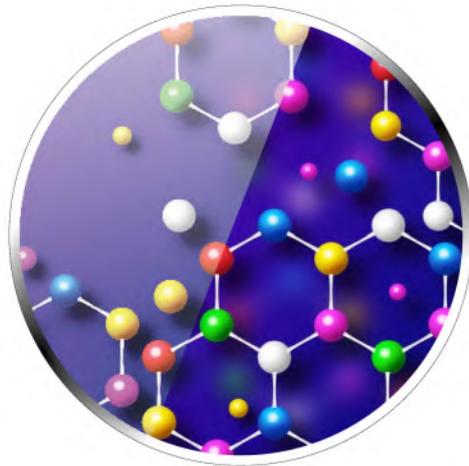


TEST EDITION



THE TEXTBOOK OF
CHEMISTRY

For Class XII



Sindh Textbook Board

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PREFACE

In this age of scientific advancements and technological breakthroughs, the field of chemistry continues to play a vital role in shaping our society and driving technological innovation. As we embark upon the journey of the XII Chemistry Textbook in continuation of XI Chemistry, that was published last year, we recognize the paramount importance of equipping students with the knowledge and skills required to thrive in an ever-evolving scientific landscape and excel in their future endeavors.

This latest edition of the XII Chemistry Textbook aims to provide students with a comprehensive understanding of advanced concepts in chemistry that are not only essential for higher education but also instrumental in unlocking promising career prospects. We have taken great care to ensure that the content presented in this textbook aligns with the national curriculum and offers students a student-friendly language and a well-structured approach to learning.

With each chapter, students will find clear learning objectives that outline the key topics to be covered. To facilitate a deeper understanding, the text is accompanied by a rich collection of illustrations, practical applications, and examples that highlight the relevance of chemistry in our everyday lives. Numerous self-assessment questions are incorporated throughout the book to aid students in their learning journey. Furthermore, at the end of each chapter, students will find a range of multiple-choice questions and reasoning exercises designed to assess their grasp of the concepts learned.

This textbook has been developed in accordance with the revised curriculum prepared by the Ministry of Education, Govt. of Pakistan, Islamabad, and has undergone meticulous review by a team of experts from the Directorate of Curriculum, Assessment and research Sindh Jamshoro.

I extend my sincere and heartfelt gratitude to authors and significantly to the most senior and highly dedicated author Prof. Dr. Moazzam Haider, who contributed to the major portion of this book. I also express my gratitude to the Director (ART) and subject specialist of STBB whose efforts played a significant role in bringing this book to publication.

It is my sincere hope that this XII Chemistry Textbook will serve as a valuable resource for students, empowering them to explore the fascinating world of chemistry, unravel its mysteries, and embrace the limitless possibilities.

Chairman
Sindh Textbook Board

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Periodic Table of Elements showing atomic number, symbol, and atomic weight. The table is color-coded by groups and includes a legend for state and classification.

Legend:

- State:** [S] Solid, [L] Liquid, [G] Gas, [X] Not found in nature
- Classification:** Main Group metals (red), Transition metals (yellow), Lanthanide series (orange), Actinide series (green), Metalloids (purple), Nonmetals (grey), Noble gases (light blue)

1A	2A	3B	4B	5B	6B	7B	8B	9B	10B	11B	12B	13A	14A	15A	16A	17A	18A
1 H Hydrogen 1.0079	2 He Helium 4.0026	3 Li Lithium 6.941	4 Be Beryllium 9.0122	5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.0067	8 O Oxygen 15.9994	9 F Fluorine 18.9984	10 Ne Neon 20.1797	11 Na Sodium 22.9898	12 Mg Magnesium 24.3050	13 Al Aluminum 26.9815	14 Si Silicon 28.0855	15 P Phosphorus 30.9738	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.9559	22 Ti Titanium 47.88	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.9380	26 Fe Iron 55.847	27 Co Cobalt 58.9332	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.9216	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.9059	40 Zr Zirconium 91.224	41 Nb Niobium 92.9064	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 103.9055	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.82	50 Sn Tin 118.710	51 Sb Antimony 121.757	52 Te Tellurium 127.60	53 I Iodine 126.9045	54 Xe Xenon 131.29
55 Cs Cesium 132.9054	56 Ba Barium 137.327	57 La Lanthanum 138.9055	58 Ce Cerium 140.12	59 Pr Praseodymium 140.9076	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.965	64 Gd Gadolinium 157.25	65 Tb Terbium 158.9253	66 Dy Dysprosium 162.50	67 Ho Holmium 164.9303	68 Er Erbium 167.26	69 Tm Thulium 168.9342	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967	
87 Fr Francium (223)	88 Ra Radium 226.0254	89 Ac Actinium 227.0278	90 Th Thorium 232.0381	91 Pa Protactinium 231.0369	92 U Uranium 238.0289	93 Np Neptunium 237.0482	94 Pu Plutonium 244	95 Am Americium 243	96 Cm Curium 247	97 Bk Berkelium 247	98 Cf Californium 251	99 Es Einsteinium 252	100 Fm Fermium 257	101 Md Mendelevium 258	102 No Nobelium 259	103 Lr Lawrencium 260	

* Elements 110-112 have not yet been named.



CHAPTER 1

CHEMISTRY OF REPRESENTATIVE ELEMENTS



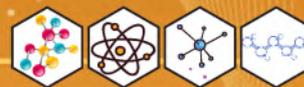
Teaching Periods	22	Assessment	02	Weightage %	18
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1 IA 1A								18 VIIIA 8A
1 H Hydrogen 1.008		13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	2 He Helium 4.003	
3 Li Lithium 6.941	4 Be Beryllium 9.012	5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 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 Aluminium 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		



Students will be able to:

- ✓ Recognize the demarcation of the Periodic Table into s-block, p-block, d-block, and f-block. (Understanding)
- ✓ Describe physical properties like atomic radius, ionization energy, electronegativity, electrical conductivity, oxidation states of elements and melting and boiling points of elements change within groups of representative elements. (Analyzing)
- ✓ Explain reactions of s-Block elements with oxygen, water, Halogens, nitrogen, hydrogen, alcohol and acids. (Understanding)
- ✓ Enlist flame test of s-Block Elements. (Applying)
- ✓ Explain Chemistry of Sodium Hydroxide and bleaching powder. (Understanding)
- ✓ Enlist functions of s-Block Elements and their important compounds in tabular form. (Understanding)
- ✓ Explain reactions of p-Block elements with oxygen, water, Halogens, nitrogen and hydrogen. (Understanding)
- ✓ Differentiate beryllium from other members of its group. (Analyzing)
- ✓ Explain the relative behaviour of halogens as oxidizing agents and reducing agents. (Applying)
- ✓ Compare the acidity of hydrogen halides. (Analyzing)
- ✓ Distinguish between an oxide and a peroxide. (Understanding)
- ✓ Write representative equations for the formation of oxides and sulphides. (Applying)
- ✓ Explain Chemistry of Sulphuric acid (Understanding)
- ✓ Enlist functions of some p-block elements and their important compounds in tabular form (Understanding)



Introduction

Periodic table is a systematic arrangement of elements based on their atomic numbers, electronic configuration and properties.

The long form of periodic table consists of seven horizontal rows known as periods and eighteen vertical columns known as groups. There are two types of groups in the periodic table. Sub group A, referred to as representative elements, and sub group B is known as transition elements. The block in the periodic table refers to specific sections based on the type of orbitals being filled by valence electrons. There are four blocks in the modern periodic table named as s-block, p-block, d-block and f-block. The elements of s-block are located on extreme left in the periodic table. It consists of groups IA and IIA. The valence shell electronic configuration of the elements of this block is ns^1 for alkali metals and ns^2 for alkaline earth metals. The p-block is found on extreme right of the periodic table and includes groups IIIA to VIIIA. Elements belong to this block possess a valence shell electronic configuration of ns^2, np^1 to ns^2, np^6 . The d-block elements are located in the middle of the periodic table and cover up all sub group B. The general valence shell electronic configuration of these elements is $ns^2, (n-1) d^1$ to $ns^2, (n-1) d^{10}$. The f-block elements are located below the main body of periodic table and exist in two horizontal series of fourteen elements each, generally known as lanthanides and actinides. The valence configuration of f-block elements is $ns^{1,2}, (n-2) f^1$ to $ns^{1,2}, (n-2) f^{14}$.

The position of each element in a particular group, period and block can be identified by its electronic configuration. The principal quantum number (n) of the valence electrons represents the period of an element. While the group of an element is predicted from the number of electrons in the valence shell. For example, the atomic number of sulphur is 16 ($1s^2, 2s^2, 2p^6, 3s^2, 3p^4$), therefore it is predicted that sulphur belongs to third period and VIA group. Another feature of the long form of periodic table is the regular changes in the physical properties of elements downward in the group and along with the period except ignoring anomalies in certain places.

1.1 GENERAL GROUP TRENDS OF REPRESENTATIVE ELEMENTS

Elements in the long form of periodic table are arranged according to their increasing atomic number and electronic configuration in such a manner that their general properties are correlated to each other. They exhibit a regular



trend in properties within each group, with some exceptions or anomalies occurring in specific positions.

“The regular variations in the properties of elements in a group of periodic table is called group trend”. In this section we will discuss the group trends of various physical properties of s-block and p-block elements.

Atomic Radii

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

Group Trends

IA and IIA Groups

Elements of group IA are termed as alkali metals. They possess the largest atomic radii in their respective periods. However the atomic radii increase regularly from lithium to francium. It is because the number of energy levels occupied by electrons increases, resulting in an increase in the distance between the nucleus and the outermost electronic shell.

Similarly, the same trend applies to the elements of group IIA (Be to Ra). That means beryllium is the smallest alkaline earth metal (IIA) and barium is the largest, as shown in Table 1.1.

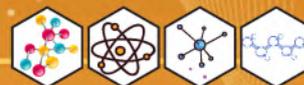
Table 1.1 Atomic radii of group IA and IIA in picometer (pm)

Alkali Metals (Group IA)	Atomic Radii (pm)	Alkaline earth Metals (Group IIA)	Atomic Radii (pm)
Li	152	Be	112
Na	186	Mg	145
K	227	Ca	194
Rb	248	Sr	219
Cs	265	Ba	253
Fr	348	Ra	215

↓ Increase

IIIA Group

Atomic radii of the elements of Boron family (Group IIIA) generally increase down the group (from boron to thallium). However, there is an exception to the trend between aluminum and gallium. Gallium has slightly



smaller atomic radii than aluminum despite being located below it in the group. It is because of poor shielding effect caused by electrons of d-orbitals.

IVA to VIIIA Groups

The atomic radii of elements of Group IVA to Group VIIIA follow the similar group trend, increasing regularly from top to bottom within the group as shown in Table 1.2. The same reason for this trend is discussed as in the group trend of alkali metals.

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)	Ne (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)

Decrease →

↑ Increase

Ionization Energy

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

Group Trends

IA and IIA Groups

The ionization energy of alkali metals (Group IA) and alkaline earth metals (Group IIA) decreases as we move down the group. This is because the outermost electrons of these elements are located farther away from the nucleus as we go from top to bottom, leading to weaker attractive forces between the electrons and the nucleus. As a result, it requires less energy to remove the outer shell electrons from the atom, that is why the ionization energy decreases.



IIIA Group

The ionization energy (IE) trend in group IIIA elements has irregularities as we move down the group. Two exceptions highlight this irregularity. Firstly, gallium (Ga) has a higher ionization energy than aluminum (Al). Secondly, thallium (Tl) exhibits a higher ionization energy than indium (In). These irregularities occur due to insufficient shielding of the nuclear charge in gallium by 3d electrons and in thallium by 4f electrons.

IVA Group

The ionization energy of group IVA elements generally decreases from top to bottom in the group. However, there are irregularities observed between Tin (Sn) and Lead (Pb). This is because both tin and lead have nearly the same atomic radii, which is a result of the lanthanide contraction. Due to this, the attraction between the nucleus and the outer electrons becomes stronger and requires more energy to remove these electrons.

VA, VIA, VIIA and VIIIA Groups

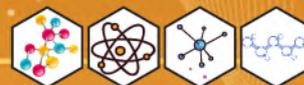
The ionization energy of the remaining groups of representative elements (group VA, VIA, VIIA, VIIIA) follows a regular pattern. It decreases progressively from top to bottom as the atomic radii increase, as shown in Table 1.3.

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



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”.

Group Trends

IA and IIA Groups

The electronegativity (EN) of alkali metals (Group IA) and alkaline earth metals (Group IIA) follows a regular decreasing trend from top to bottom. This trend can be explained by the regular increase in atomic radii as we move down the group. The larger atomic size results in a decreasing tendency for the atom to attract the shared pair of electrons towards itself.

IIIA Group

The electronegativity (EN) of group III elements initially decreases from Boron (B) to Aluminum (Al) and then increases from gallium (Ga) to tellurium (Te). This irregular increase in EN can be attributed to the poor shielding effect of the electrons in the d-orbital and f-orbitals, respectively.

IVA, VA, VIA and VIIA Groups

The electronegativity of groups IVA, VA, VIA, and VIIA decreases regularly from top to bottom. This trend can be explained by the same reason as discussed for alkali metals as shown in Table 1.4.

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)

Decrease

Increase



Electrical Conductivity

“Electrical conductivity is the measurement of a material's capability to conduct electric current”. It is a measure of how easily electric charges, such as electrons, can flow through a substance. Materials with high electrical conductivity allow electric current to pass through them easily, while materials with low electrical conductivity hinder the flow of electric charges.

The electrical conductivity of representative elements can vary widely. Alkali metals and alkaline earth metals generally exhibit high electrical conductivity due to their ability to easily transfer electrons. Group IIIA elements display moderate electrical conductivity, while elements in Group IVA can have variable conductivity ranging from poor (e.g., carbon and lead) to moderate (e.g., silicon and tin). Group VA, VIA, and VIIA elements typically have poor electrical conductivity. Noble gases, on the other hand, have extremely low electrical conductivity as shown in Table 1.5.

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.



The oxidation states of representative elements depend on their position in a particular group of periodic table. Some oxidation states are shown in Table 1.6.

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 melting and boiling points of representative elements can vary widely across the periodic table. Alkali metals have low melting and boiling points due to weak metallic bonding, while alkaline earth metals have higher melting and boiling points due to stronger metallic bonding as shown in Table 1.7. Moving across the p-block elements, the melting and boiling points generally increase gradually.

However, there are exceptions in groups IVA and VA. Carbon has a high melting point due to strong covalent bonds, while nitrogen has low melting and boiling points because it exists as diatomic molecules with weak intermolecular forces. Halogens have low melting and boiling points due to weak intermolecular forces, and noble gases have extremely low melting and boiling points due to weak interatomic forces.

The melting and boiling points of representative elements reflect the different bonding types and intermolecular forces within each group, resulting in a wide range of physical properties.



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)



Self-Assessment

Boiling points of alkali metal decreases regularly and the boiling point of halogens increase regularly in going from top to bottom in their respective groups. How can you explain this behavior?



Unique behavior of Beryllium in group IIA

Beryllium differs markedly from its other members because of its smaller atomic radii and high electronegativity. Some unique characteristics shown by beryllium in comparison to other elements of group IIA are given as:

- Beryllium is harder and more rigid than other members of group IIA.
- Beryllium has relatively low density and high melting point compared with other group members.
- Beryllium exhibits chemical stability due to the formation of protective oxide layer on its surface which prevents further oxidation and corrosion.
- Beryllium has tendency to form covalent bonds with other elements due to its smaller atomic size while other members of the group form ionic bonds.

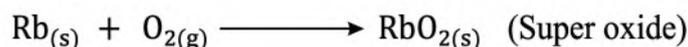
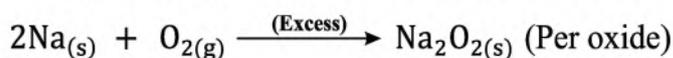
1.2 REACTIONS OF REPRESENTATIVE ELEMENTS

1.2.1 s-block elements

Alkali metals (group IA) and alkaline earth metals (group IIA) are highly reactive because they can easily lose their valence electrons due to low ionization energy (IE). Some common reactions of the elements of group IA and IIA are given as.

1.2.1.1 With oxygen

Alkali metals rapidly react with oxygen to produce oxides. Lithium forms normal oxide (oxidation state of oxygen is -2), sodium forms peroxide (oxidation state of oxygen is -1) in excess of air while the rest of the elements of group IA form superoxides (oxidation state of oxygen is $-\frac{1}{2}$).





The reaction of alkaline earth metals with oxygen takes place at high temperature. However, on oxidation, beryllium, magnesium and calcium form normal oxides while strontium and barium form peroxides.



1.2.1.2 With water

Alkali metals react with water to produce metal hydroxides with the liberation of hydrogen gas. The intensity of reaction increases from lithium to cesium, until a violent reaction is observed often accompanied by an explosion when cesium is put into water.



(Where $M = \text{Li, Na, K, Rb, Cs}$).

Among alkaline earth metals beryllium does not react with either cold or steam, but magnesium reacts with steam. The reason is that these two elements form a stable oxide layer that acts as a barrier preventing direct contact between water and metal. The rest of the members of this group react with water easily and form hydroxides.



DO YOU KNOW?

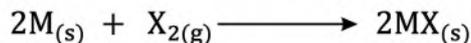
Alkali metals are highly reactive, they react vigorously with water and moist air and can cause fire or explosion that is why they keep in kerosene oil.



(Where $M = \text{Mg, Ca, Sr and Ba}$).

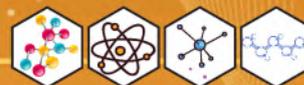
1.2.1.3 With halogens

Alkali metals react vigorously with halogens to form metal halides. The reaction involves the transfer of electron from an alkali metal to a halogen.



(Where $M = \text{Li, Na, K, Rb, Cs}$)

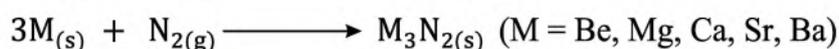
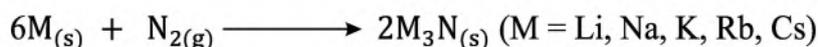
Alkaline earth metals also react with halogens although to a lesser extent when compared with alkali metals.



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

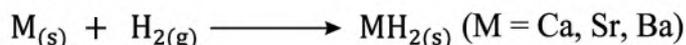
1.2.1.4 With nitrogen

Nitrides are formed when both alkali metals and alkaline earth metals react with nitrogen. The general formula for the nitrides of alkali metals is M_3N and for the nitrides of alkaline earth metals is the formula M_3N_2 .



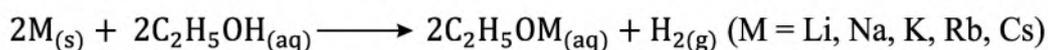
1.2.1.5 With hydrogen

Alkali and alkaline earth metals react with hydrogen at different temperatures to produce ionic hydrides.



1.2.1.6 With alcohols

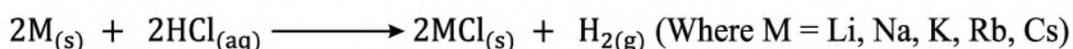
Elements of group IA react vigorously with alcohols to form metal alkoxide with the liberation of hydrogen gas.



Alkaline earth metals have a very limited reactivity with alcohols.

1.2.1.7 With acids

Alkali metals react vigorously with acids to produce salt with the liberation of hydrogen gas. This reaction is highly exothermic and violent.

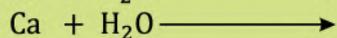
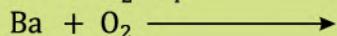
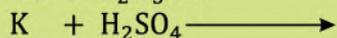
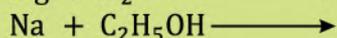


Alkaline earth metals can react with acids but their reactivity is generally lower compared to alkali metals.



Self-Assessment

Complete and balance the following reactions:



1.3 FLAME TEST FOR S-BLOCK ELEMENTS

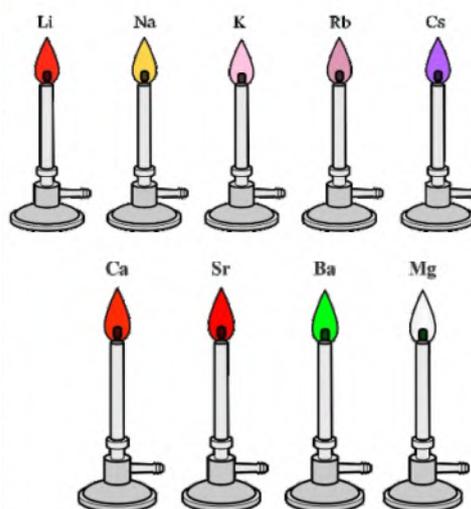
“Flame test is a qualitative method used to identify the presence of alkali metals based on their characteristic flame colours”.

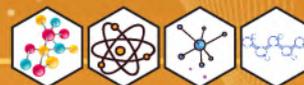
When an alkali metal or its compound burn in flame, the electron in the lower energy orbital jumps to higher energy orbital due to the absorption of energy from the flame. This electron upon returning to lower energy orbital, releases energy in the form of light of a specific colour which can be observed as a colour flame.

Table 1.8

Colour flames of alkali and alkaline earth metals

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





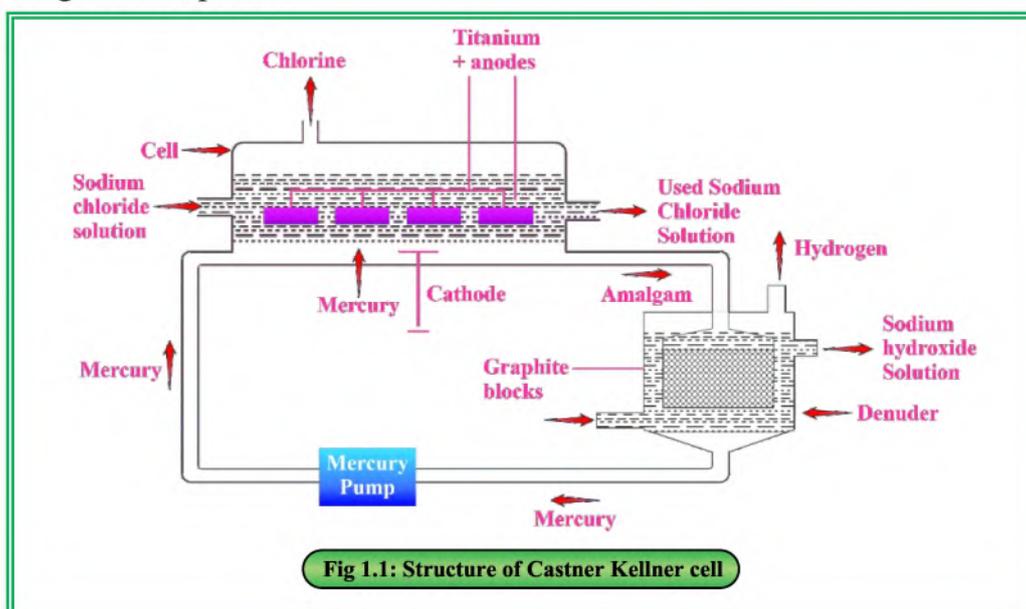
1.4 CHEMISTRY OF IMPORTANT COMPOUNDS OF S-BLOCK ELEMENTS

There are various naturally occurring compounds of alkali and alkaline earth metals found in the earth's crust in the form of minerals and ores. However, many useful compounds of s-block elements are synthesized in industries, such as caustic soda, soda ash, bleaching powder etc.

1.4.1 Sodium Hydroxide (NaOH)

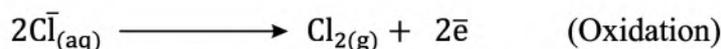
Sodium hydroxide is a highly versatile and widely used chemical compound. It is commonly known as caustic soda due to its ability to cause burns and damage tissues severely.

Caustic soda is manufactured by an electrolytic process in a specially designed cell known as Castner Kellner cell. The cell consists of an upper rectangular vessel and a lower pipe like portion. In the upper part, there are titanium blocks which are submerged in an aqueous solution of sodium chloride acting as an anode as shown in figure 1.1. The lower section is filled with mercury which circulates constantly with the help of a pump and serves as cathode. The upper part of the cell is connected to the lower part by a graphite made chamber known as denuder where the separation of sodium from amalgam takes place.

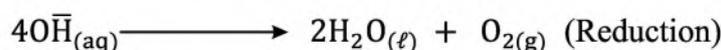




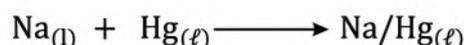
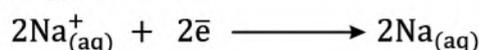
The aqueous solution of sodium chloride in the upper portion consists of mainly sodium ions (Na^+) and chloride ions (Cl^-). On passing electricity through the cell, all Cl^- ions migrate toward titanium anode where they get oxidized. The chlorine gas liberated in this electrolytic process is collected as a by-product.



OH^- ions of water which are in very low quantities, are also oxidized on titanium anode.



Sodium ions on the other hand discharge over mercury surface where an amalgam of Na/Hg (alloy) is formed.



Amalgam is then sent to denuder where sodium reacts with water to form sodium hydroxide.

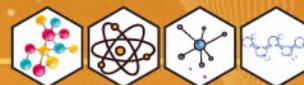


The mercury is recycled to dissolve more sodium and the sodium hydroxide is collected for marketing.

Compared with other processes for the preparation of caustic soda, the Castner Kellner process is more preferable because the two products of the process, sodium hydroxide and chlorine are obtained in separate portions of the cell, which prevents them to react with each other. However, one disadvantage of the process is that, in spite of strict control some mercury vapours escape from the factory. This mercury contaminates seawater. As a result mercury becomes part of tissues of marine animals and plants and thus pollutes the food chain.

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 $318\text{ }^\circ\text{C}$ ($604\text{ }^\circ\text{F}$). At this temperature, it melts and forms a liquid.
- **Solubility:** It is highly soluble in water.



- **Density:** The density of NaOH depends on its concentration and temperature. For a 50% concentration at room temperature, the density is approximately 1.52 g/cm³.
- **Corrosiveness:** It is highly corrosive and can cause burns and irritation to the skin, eyes, and respiratory system.

Chemical Properties

Reaction with acids

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



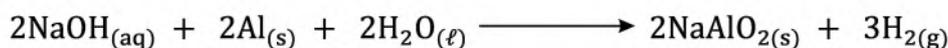
Reaction with Ferric Chloride

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



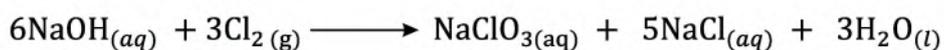
Reaction with Aluminum and Zinc

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



Reaction with Chlorine

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



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.

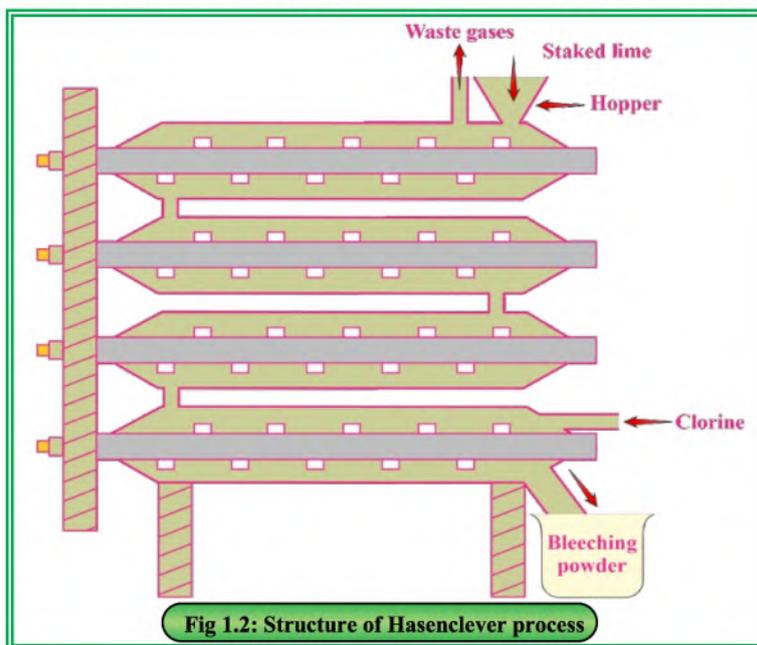


- It is utilized in the canning process to remove the outer skin of fruits and vegetables, ensuring food safety and quality.
- It plays a role in the paper making industry, where it is used for pulping wood fibers and paper recycling processes.

1.4.2 Bleaching Powder(CaOCl_2)

Bleaching powder, also known as calcium hypochloride (CaOCl_2), is a chemical compound widely used as a bleaching agent and disinfectant.

Commercially, it is prepared by Hasenclever Process, as shown in figure 1.2. Dry slaked lime is fed into the Hasenclever plant from the most upper cylinder. The slaked lime is moved forward by revolving blades of rotating shaft. Chlorine gas is passed from the lower cylinder which rises upto upper cylinder and reacts with slaked lime to form bleaching powder.



DO YOU KNOW?

Sometimes accidentally bleach ingestion occurs in children and adults by instead of water due to its clear color, especially when stored in unmarked containers. Common symptoms include sore throat, nausea, vomiting, and difficulty in swallowing. Immediate give them some water to drink and then medical attention is necessary when bleach is ingested.



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

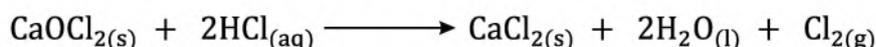
(i) Reaction with Water

Bleaching powder when dissolves in water, it produces calcium hydroxide and hypochlorous acid (HOCl). Hypochlorous acid is a weak acid and commonly used for bleaching and sanitizing.



(ii) Reaction with Acids

The reaction of bleaching powder with hydrochloric acid produces calcium chloride and chlorine gas.



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.

Table 1.9 Functions of some elements and compounds of s-block elements.

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.



Magnesium (Mg)	It helps in muscle contraction and maintain the bones and heart functions.
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 ₂ CO ₃ ·10H ₂ O)	It is used in the manufacturing of glass, soap and borax. It is also used for laundry purpose.
Baking Soda (NaHCO ₃)	It is used in bakeries to prepare various food items.
Potassium Nitrate (KNO ₃)	It is used in fireworks and fertilizer.

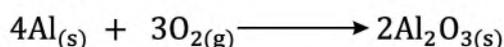
1.5 REACTIONS OF p-BLOCK ELEMENTS

Elements of group IIIA to VIIA in the periodic table exhibit diverse chemical behavior. They can participate in various types of chemical reactions based on their unique properties. Some important chemical reactions involving p-block elements are given below.

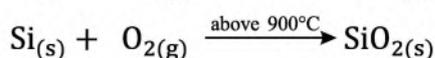
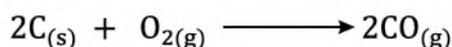
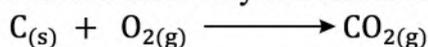
1.5.1 With oxygen

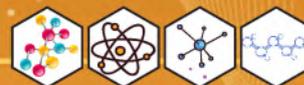
The reactions of p-block elements with oxygen produce either normal oxides or in some cases peroxides.

Elements of group IIIA react with oxygen to produce oxides of the formula M₂O₃.

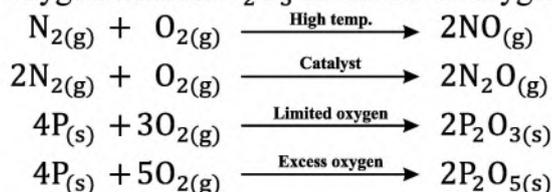


- In group IVA, carbon forms carbon monoxide and carbon dioxide when it reacts with oxygen while silicon form only one stable silicon oxide(SiO₂).





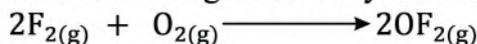
- In group VA, nitrogen forms NO, N₂O and NO₂ when reacts with oxygen depending upon the conditions applied. Phosphorus may form P₂O₃ in limited supply of oxygen whereas P₂O₅ in excess of oxygen.



- In group VIA, sulphur oxidized in air to give sulphur dioxide.



- Halogens can also react with oxygen however their oxides are mostly highly reactive. For example the oxide of fluorine is a highly reactive yellow gas.
- The oxides of halogens are very unstable.



DO YOU KNOW?

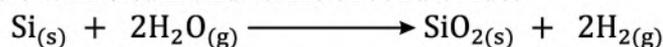
Aluminum is generally considered safe metal for cooking and food storage purposes. It is widely used in kitchen wares due to its light weight. However, it is recommended to avoid cooking or storing highly acidic or alkaline foods in aluminum containers.

1.5.2 With water

- The reaction of p-block elements with water depends on the nature of element and the group to which it belongs.
- Aluminum reacts with water but the reaction is slow due to the presence of a thin oxide film on its surface.



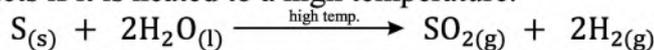
- Silicon reacts with steam and forms silicodioxide.



- Phosphorus reacts vigorously with water to produce phosphoric acid and phosphine.



- Sulphur reacts if it is heated to a high temperature.



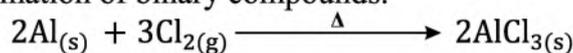
- Halogens such as chlorine and bromine react with water to form a mixture of two acids.





1.5.3 With halogens

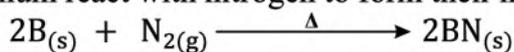
Majority of p-block elements have the capability to react with halogens, resulting in the formation of binary compounds.



1.5.4 With nitrogen

The reaction of p-block elements with nitrogen can vary depending on the specific element and the reaction conditions. For example

- Boron and aluminum react with nitrogen to form their nitrides.



- Carbon and Silicon can form nitrides when heated with nitrogen at high temperatures.



- Phosphorus reacts with nitrogen at high temperatures to form phosphorus nitride (P_3N_5).

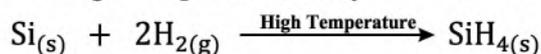


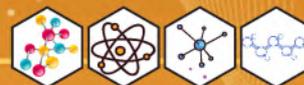
- Halogen (Cl_2 , Br_2) can react with nitrogen to form nitrogen trihalide.



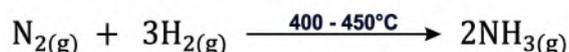
1.5.5 With hydrogen

- Elements of group IIIA and IVA do not directly react with hydrogen, however silicon at high temperatures may form silicon hydrides.

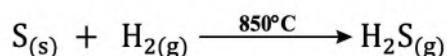




- Nitrogen reacts with hydrogen under high pressure to form ammonia.



- Sulphur reacts with hydrogen at high temperatures to form hydrogen sulphide.



- The reaction of halogen with hydrogen can result in the formation of hydrogen halides.



Self-Assessment

Write the equations for the following chemical processes.

- Silicon is put into steam.
- Phosphorus burns in excess of oxygen.
- Nitrogen gas is passed through hot piece of phosphorus.
- Carbon is heated with nitrogen.
- Aluminum is treated with chlorine gas.

1.6 CHEMICAL BEHAVIOR OF HALOGENS

Halogens include fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At). The reactivity of halogens is determined by their bond enthalpies and their ability to undergo redox reactions.

1.6.1 Bond enthalpies in halogens

The enthalpy is required for the dissociation of halogen-halogen bond in gaseous state and it varies according to size of halogen atom, bond length and the intermolecular attraction.



Table 1.10 Bond enthalpies of halogens

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

It is noted from the Table 1.10 that the bond enthalpies of halogens decrease from chlorine to iodine due to the increase in bond length but fluorine is an exception to this trend. This is due to the large repulsion between the non-bonding electrons of small sized atom in the fluorine molecule.

1.6.2 Acidity of Hydrogen Halides

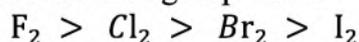
Hydrogen halides (HX) are strong mineral acids and their acidity follows an increasing trend from HF to HI ($\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$). The increasing order of acidity of hydrogen halides can be attributed to their bond energies. Since the bond energy of H-I is the smallest, it can easily donate a proton and serves as the strongest acid compared to other halogen acids.

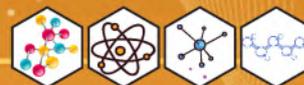
Halogen acids (HX)	H-F	H-Cl	HBr	HI
Bond energies (KJ/mol)	565	432	366	299


 Decrease

1.6.3 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.





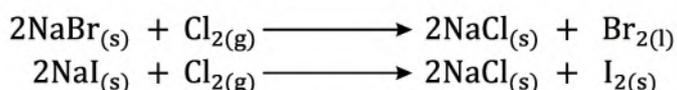
Fluorine is the strongest oxidizing agent due to its highest electronegativity and smallest atomic size allowing it to readily accept electron and attain a negative charge.

1.6.4 Halide ions as a reducing agent

Halide ions (Cl^- , Br^- , I^-) can serve as reducing agents in chemical reactions due to their ability to readily donate electron to an oxidizing species thereby undergoing oxidation.

Among halide ions, there is a trend in relative strength of reducing agents $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$. This means that iodide ion is the strongest reducing agent while fluoride ion is the weakest.

Based on this information, we can infer that chlorine has the ability to displace bromine and iodine from their salts.

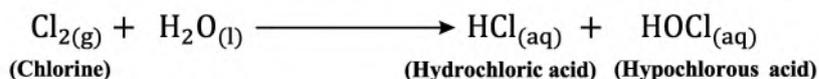


Similarly bromine has the ability to displace iodine from its salt.



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.



DO YOU KNOW?

The deficiency of iodine in the diet can lead to the development of goiter, which is an enlargement of the thyroid gland. To control the deficiency of iodine in the body an efficient way to intake iodide salt and food supplements i.e., Kelp or Seaweed, fish and other sea foods etc.



Self-Assessment

Chlorine can displace bromide and iodide from their salts but fluorine cannot why?

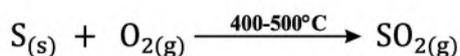


1.7 CHEMISTRY OF SULPHURIC ACID (Contact Process)

Sulphuric acid is a highly corrosive and colourless liquid with a viscous texture. It is one of the most widely used and important industrial chemical compound due to its versatile nature and unique properties. It is often called oil of vitriol because in past it was obtained through the distillation of green vitriol. Sulphuric acid is produced worldwide by Contact process, which involves a series of essential steps.

Step 1: Oxidation of Sulfur to Sulfur Dioxide

Sulfur (S) is burned in the presence of air or oxygen to produce sulfur dioxide (SO₂). The reaction can be represented as follows:



SO₂ gas which is produced in “Sulphur Burner” may contains some impurities of “Arsenic”, “Silica” and “CO₂”. These impurities must be removed from SO₂ gas before entering it into catalytic chamber because catalyst (V₂O₅) get poisoned in the presence of these impurities and hence decreases the rate of formation of SO₃.

Step 2: Conversion of Sulfur Dioxide into Sulfur Trioxide

Sulfur dioxide (SO₂) is then reacted with oxygen (O₂) in the presence of a catalyst (usually vanadium pentoxide, V₂O₅) to form sulfur trioxide (SO₃). This reaction is carried out at high temperatures:



Step 3: Absorption of Sulfur Trioxide to Sulphuric acid

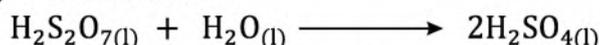
Sulfur trioxide (SO₃) is dissolved in concentrated sulphuric acid (H₂SO₄) to produce oleum, also known as fuming sulphuric acid (H₂S₂O₇). This is an exothermic reaction, and it needs to be carefully controlled to avoid excessive heat release.



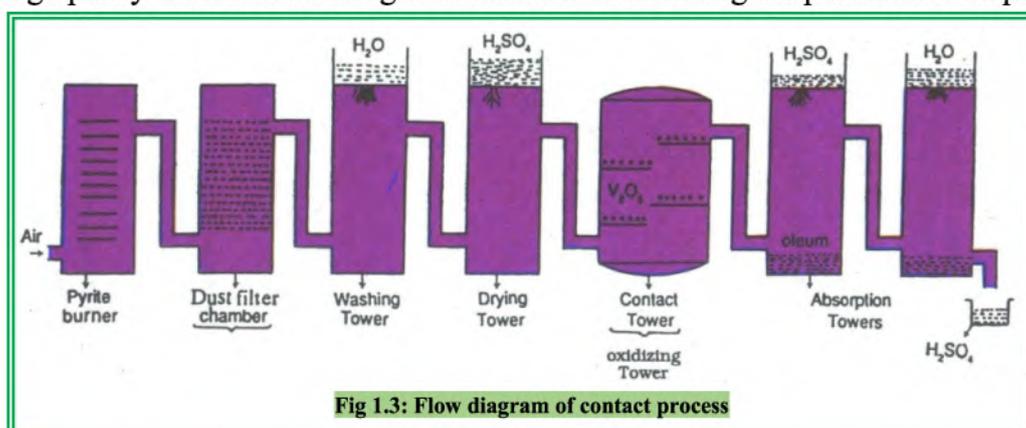


Step 4: Dilution of Oleum to Sulphuric acid

Finally, the oleum ($\text{H}_2\text{S}_2\text{O}_7$) is diluted with water to obtain the desired concentration of sulphuric acid. The reaction is highly exothermic and must be performed slowly and with caution:



Sulphuric acid obtained through the contact process as shown in figure 1.3 is typically of high purity, often reaching a concentration of 98%. The high purity is achieved through careful control including the purification steps.



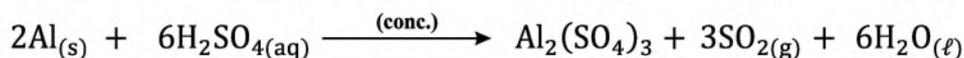
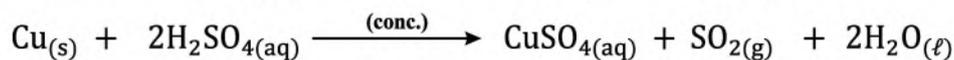
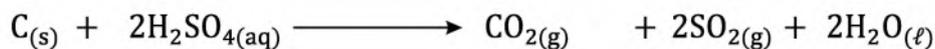
Physical Properties

- **Density:** Sulphuric acid has a high density, typically around 1.84 g/cm^3 .
- **Melting Point:** Sulphuric acid has no distinct melting point since it can supercool below its freezing point. The freezing point of sulphuric acid is approximately 10°C but it can vary depending on the concentration.
- **Boiling Point:** Commercial sulphuric acid has a boiling point of 290°C . 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

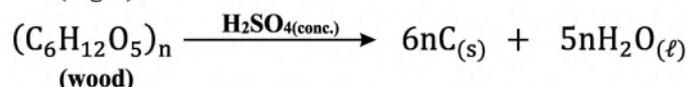
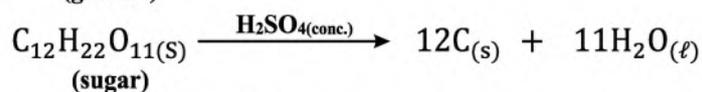
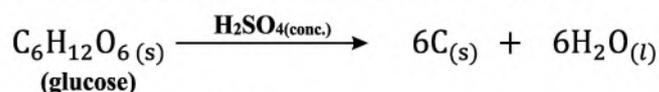
An oxidizing agent

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.



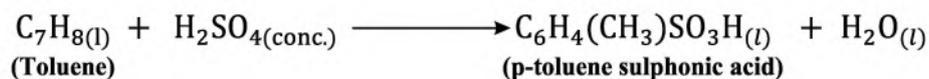
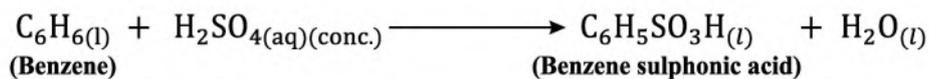
A dehydrating agent

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



A sulphonating agent

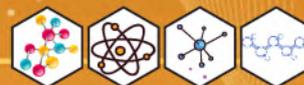
Sulphonation involves the introduction of sulphonic group (SO_3H) into a molecule. Sulphuric acid serves as a source of sulphonic group which can be added to organic compounds to create new molecules.



A dibasic acid

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





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.

1.8 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.

There are three pairs of elements that exhibit the diagonal relationship in the second and third periods of representative elements.

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

1.8.1 Diagonal relationship between lithium and magnesium, Beryllium and Aluminum, Boron and Silicon

➤ Li and Mg

- Both have almost similar atomic radii (Li = 152pm and Mg = 160pm).
- Both have almost similar electronegativities (Li = 1.0 and Mg 1.2)
- Both are lighter in their respective group.
- Oxide of both Li and Mg are very less soluble in water compared to other elements of the respective group.



➤ Be and Al

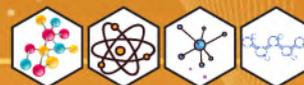
- i. Both Be and Mg have same EN (1.5).
- ii. Both show passivity with conc. Nitric acid.
- iii. BeCl_2 and AlCl_3 both acts as Lewis acid.

➤ B and Si

- i. Both B and Si have closer EN (B = 2.0 and Si 1.8).
- ii. Both B and Si have nearly same density (B = 2.35g/cm^3 , Si = 2.34g/cm^3).
- iii. Both B and Si are metalloids and both of these do not form cation.

Table 1.12 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 ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)	It is used in cleaning, laundry, cosmetics and as flux in welding.
Alum ($\text{K}_2\text{SO}_4 \cdot \text{Al}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$)	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.



SOCIETY, TECHNOLOGY AND SCIENCE

Fluoride Toxicity and Deficiency

Fluoride is an essential mineral. It plays a significant role in maintaining the dental and skeletal health of our bodies. It is obtained from water, tea, fish and certain fruits and vegetables.

The deficiency of fluoride increases the risk of dental cavities, brown colouration of teeth, weakening of teeth and bones etc.

An excessive intake of fluoride over a prolonged period may cause a condition known as fluorosis or fluoride toxicity. It causes white or brown spotting on teeth, pitting of teeth and irregular appearance of teeth etc.



SUMMARY

- Atomic radii of representative elements generally increase downward in the group.
- Melting point and boiling point of alkali metals decrease regularly down the group while the elements of other groups have variations depending upon their position in the periodic table.
- Ionization energy of s-block elements decreases down the group with increasing atomic radii.
- Electronegativities of the elements of group IA and IIA decrease regularly from top to bottom while the EN of the elements of remaining group varies depending upon shielding effect.
- Beryllium differs markedly from other members of group IIA on the basis of its smaller atomic radii, hardness and high melting point.
- Lithium forms normal oxide, sodium forms peroxide while the rest of alkali metals form super oxide when come in contact with air.
- Alkali metals and alkaline earth metals can be identified by flame test. Lithium gives red, sodium yellow and potassium shows violet colour when comes in contact with the flame.



- Castner Kellner process is used for preparation of caustic soda.
- Bleaching powder is prepared by the reaction of lime water with chlorine gas.
- The order of acidic strength of hydrogen halides is $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$.
- Chlorine acts as auto oxidizing and reducing agent in certain chemical reactions.
- Sulphuric acid is a good dehydrating agent.
- Sulphuric acid reacts with metals and non metals, it acts as an oxidizing agent.
- Similarities in the properties exhibited by certain pairs of elements among the groups of representative elements are known as diagonal relationship.

EXERCISE

Multiple Choice Questions

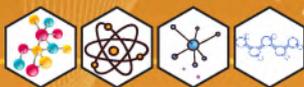
- (i) Melting and boiling points regularly decrease down the group in:
- | | |
|----------------|-----------------|
| (a) Group IA | (b) Group IIIA |
| (c) Group VIIA | (d) Group VIIIA |
- (ii) The s-block element forms super oxide when burned in air is:
- | | |
|--------|--------|
| (a) Li | (b) Na |
| (c) K | (d) Mg |
- (iii) The general formula of nitrides for alkaline earth metal is:
- | | |
|--------------------------|----------------------------|
| (a) MN_3 | (b) M_2N_3 |
| (c) M_3N | (d) M_3N_2 |
- (iv) The alkali metal that gives a yellow color during a flame test is:
- | | |
|--------|--------|
| (a) Na | (b) K |
| (c) Rb | (d) Cs |
- (v) The chemical commonly used in fireworks is:
- | | |
|------------------------|----------------------|
| (a) Sodium bicarbonate | (b) Bleaching powder |
| (c) Potassium nitrate | (d) Potash Alum |
- (vi) Cathode in Castner Kellner cell is:
- | | |
|---------------------|--------------------|
| (a) Titanium blocks | (b) Carbon rods |
| (c) Mercury | (d) Iron container |



- (vii) The diagonal member of beryllium is:
(a) Mg (b) Al
(c) Si (d) C
- (viii) The catalyst commonly used in the conversion of sulfur dioxide to sulfur trioxide during the preparation of sulphuric acid is:
(a) Vanadium pentoxide (V_2O_5) (b) Copper (Cu)
(c) Iron (Fe) (d) Nickel (Ni)
- (ix) Oil of vitriol refers to:
(a) Borax (b) Sulphuric acid
(c) Alum (d) Caustic soda
- (x) The best oxidizing agent among halogens is:
(a) F_2 (b) Cl_2
(c) Br_2 (d) I_2

Short Questions

- Give reasons for the following:
 - Ionization energy decreases from top to bottom in s-block elements?
 - Boiling point of halogens increase down the group in the periodic table?
 - Gallium has smaller atomic radii than aluminum despite being below the aluminum in group IIIA?
 - Electronegativities of alkali metals decrease from Li to Cs?
 - Alkali metals are good conductor of electricity?
 - Acidity of hydrogen halides increase from HF to HI?
 - Fluorine is the strongest oxidizing agent?
- What is flame test? Mention the colour of flame of alkali metals.
- Explain the auto oxidizing and reducing properties of chlorine.
- What is meant by a diagonal relationship? Mention three pairs of representative elements that show diagonal relationship.
- Discuss the group trend of Ionization energy in group IIIA of periodic table.
- Write down three properties of beryllium that show its unique behavior in group IIA.



Descriptive Questions

1. Draw a flow diagram of contact process and describe various steps involved in the manufacturing of sulphuric acid.
2. Explain with the help of a diagram of Castner Kellner cell, how caustic soda is obtained by the electrolysis of aqueous sodium chloride?
3. Write the balance equations for the following chemical process.
 - (i) A piece of aluminum is dipped into concentrated sulphuric acid.
 - (ii) Ferric chloride is mixed with an aqueous solution of caustic soda.
 - (iii) Sodium burns in excess of air.
 - (iv) Magnesium is heated with nitrogen gas.
 - (v) Potassium is put into ethyl alcohol.
 - (vi) Chlorine gas is passed through an aqueous solution of caustic soda.
4. What is bleaching powder? How is it prepared? Give the reaction of bleaching powder with water and hydrochloric acid.
5. Discuss the group trend of atomic radii, ionization energy and electronegativity of alkali metals.



CHAPTER 2 CHEMISTRY OF OUTER TRANSITION ELEMENTS



Teaching Periods	09	Assessment	01	Weightage %	07
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Period	IA	IIA		IIIB	IVB	VB	VIB	VII B	VIII B	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														



Students will be able to:

- ✓ Describe electronic structures of elements and ions of d-block elements. (Applying)
- ✓ Explain why the electronic configuration for chromium and copper differ from those assigned using the Aufbau principle. (Analyzing)
- ✓ Describe general features of transition elements (Understanding)
- ✓ Enlist oxidation states of Cr, Mn, Fe, Co. (Applying)
- ✓ Explain origin of colors and nomenclature of coordination compounds. (Applying)
- ✓ Describe important reactions and uses of Chromium, Manganese, Iron and Copper.
- ✓ Define an alloy and describe some properties of an alloy that are different from the metals that compose it. (Analyzing)
- ✓ Describe the Steel, types and its applications. (Understanding)
- ✓ Enlist alloys of d block elements and their applications in tabular form (Applying).
- ✓ Describe the reactions of potassium dichromate with oxalic acid and Mohr's salt. (Understanding)
- ✓ Describe the reactions of potassium permanganate with ferrous sulphate, oxalic acid and Mohr's salt. (Understanding)
- ✓ Explain clearly the rules of nomenclature of coordination compounds with suitable examples (Applying)
- ✓ Enlist functions of some d-block elements and their important compounds in tabular form.



INTRODUCTION

The elements that possess partially occupied d-orbitals, either in their atomic state or any of their ionic states, are commonly referred as outer transition elements or d-block elements. These elements are positioned in the middle section of the periodic table and are recognized for their intermediate characteristics between s-block and p-block elements. The elements are called d-block elements because they possess partially filled d-electrons in their valence shell. These elements hold considerable significance across numerous domains of chemistry and industries due to their versatile oxidation states, catalytic activity, alloy forming ability, colour, complex forming ability, magnetic behavior and electrical conductivity. The unique electronic structure and broad range of oxidation states exhibited by these elements make significant contributions to the advancement of technology in industry and various scientific fields.

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:

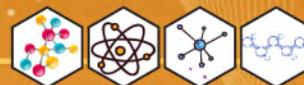
This series is situated in the sixth period and consists of elements from lanthanum (La) to mercury (Hg).

6d – series:

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

2.1 GENERAL FEATURES OF OUTER TRANSITION ELEMENTS

Outer transition elements typically exhibit metallic luster and shiny appearance. They possess hardness, high density and are malleable and ductile. These elements also have elevated melting and boiling points. Being situated in the middle of the periodic table, their atomic radii fall within an intermediate range, neither excessively large nor small.



The general physical properties of the first series of outer transition elements are summarized in Table 2.1.

Table 2.1 Physical properties of 3d series of outer transition elements

Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic No. (z)	21	22	23	24	25	26	27	28	29	30
Atomic size (pm)	144	132	122	117	117	117	116	115	117	125
1 st ionization potential (KJ/mol)	632	661	648	653	716	762	757	736	745	908
Melting Point (°C)	1539	1668	1760	1875	1245	1535	1480	1452	1083	419
Boiling point (°C)	3900	3130	3000	2480	2087	2450	2900	2900	2310	907
Electronegativity	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9	1.6

2.1.1 Electronic Structure

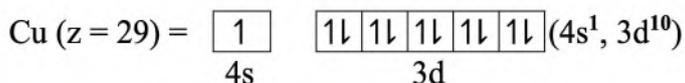
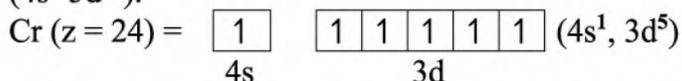
d-block elements have valence electrons both in outer most and second outer most shells (penultimate) therefore the general valence electronic configuration of these elements is represented by $(n-1)d^{1-10}, ns^{1,2}$, where “n” is the outermost shell and n-1 is the penultimate shell.

In the context of the electronic configuration of the 3d series, the filling of electrons occurs in a sequential manner across the row (Sc to Zn). Typically the 4s orbital is filled prior to 3d orbitals. This pattern follows the guidelines set forth by Aufbau principle.

However, there are exceptions observed in chromium and copper where an electron is transferred from 4s orbital to 3d orbital in order to achieve more stable arrangement. Chromium contains four single parallel electrons in its 3d orbitals therefore one electron of 4s orbital jumps into 3d orbital to make it half-filled and reaches the more stable electronic configuration $(4s^1, 3d^5)$.



A similar pattern is observed in the case of copper where a 4s electron is excited and moves into the 3d orbital, resulting in a completely filled 3d sub shell. The electron rearrangement makes a more stable configuration of copper ($4s^1 3d^{10}$).



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.

2.1.3 Variable Oxidation States

The variable oxidation states displayed by transition elements are recognized as one of their distinctive properties. The oxidation states of transition metal ions are in the range of +1 to +7. “This variation is due to very small energy difference between 3d and 4s orbitals”. As a result, electrons of 3d as well as 4s orbitals take part in the bond formation. The oxidation states of 3d series of transition elements increase from scandium to manganese and then decrease up to zinc. The most common oxidation state of transition elements is +2 and the highest oxidation state is +7 for manganese as shown in Table 2.2.



Table 2.2 Oxidation states of the elements of 3d series

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

Argon (Ar) 18 = 1s², 2s², 2p⁶, 3s², 3p⁶



Self-Assessment

Write down the electronic configurations of the following transition metals. Vanadium (V), Manganese (Mn), Nickel (Ni) and Titanium (Ti).

2.1.4 Catalytic Activity

Transition elements are well known for their significant catalytical activity. **“Most of the transition elements and their compounds serve as catalysts in numerous chemical reactions”**. For example nickel (Ni) is used in the addition reaction of alkene, iron is used in the synthesis of ammonia (NH₃) and vanadium pentaoxide (V₂O₅) is used in the manufacturing of sulphuric acid by contact process.

The property of transition metals to serve as catalyst can be explained by the following factors.



DO YOU KNOW?

Ruthenium (Ru) catalysts are being explored for water splitting reactions, which involve the conversion of water into hydrogen and oxygen through electrolysis. These catalysts play a vital role in renewable energy technologies like hydrogen production and fuel cells.



- (i) Transition elements have variable oxidation states. They can easily withdraw or lend electrons from the reagent to form unstable intermediate which then changes into the final product.
- (ii) The surfaces of transition metals offer many active sites where reactant molecules can adsorb.

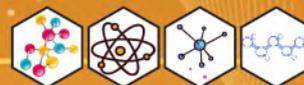
2.1.5 Magnetic Behavior

Atoms, ions or molecules when exposed to a strong external magnetic field, exhibit two distinct behaviors, either they are weakly attracted or repelled by the magnetic field. **“The substances that are attracted by the magnetic field are called paramagnetic substances and those which are repelled by magnetic field are known as diamagnetic substances”.**

Most of the transition elements and their ions show paramagnetic behaviour. This is due to the fact that d-orbitals of these elements possess one or more unpaired electrons and the spinning of unpaired electrons generates a magnetic moment. This magnetic moment causes the ion to interact with the external magnetic field.

Sc (21)	$1\downarrow$	1					 (Paramagnetism)
Ti (22)	$1\downarrow$	1	1				
V (23)	$1\downarrow$	1	1	1			
Cr (24)	1	1	1	1	1	1	
Mn (25)	$1\downarrow$	1	1	1	1	1	
Fe (26)	$1\downarrow$	$1\downarrow$	1	1	1	1	
Co (27)	$1\downarrow$	$1\downarrow$	$1\downarrow$	1	1	1	
Ni (28)	$1\downarrow$	$1\downarrow$	$1\downarrow$	$1\downarrow$	1	1	
Cu (29)	1	$1\downarrow$	$1\downarrow$	$1\downarrow$	$1\downarrow$	$1\downarrow$	
Zn (30)	$1\downarrow$	$1\downarrow$	$1\downarrow$	$1\downarrow$	$1\downarrow$	$1\downarrow$	

The paramagnetic behaviour is more pronounced in the middle of 3d series due to the maximum spin of electrons. However, zinc is diamagnetic since it lacks unpaired electrons in its d-orbitals.



Self-Assessment

Write down the valence electronic configurations of the following transition metal ions.

Cu^{+2} , Cu^{+1} , Fe^{+3} , Cr^{+3} , Fe^{+2} , Mn^{+2} , Co^{+2}

2.1.6 Alloy Formation

“Alloy is a homogenous mixture of two or more elements with at least one of them being a metal”.

Transition elements have the tendency to form alloys because of their similarities in atomic size which enable them to mix easily with one another.

Alloys of transition metals exhibit greater rigidity, strength, light weight and shine compared to pure metals. Moreover, they possess enhanced resistance against corrosion. The composition and uses of some alloys are given in Table 2.3.



DO YOU KNOW?

Brass and Bronze both are copper-based alloys but they have different compositions and properties. Brass is yellowish coloured while bronze is reddish brown coloured. Brass is more resistant to corrosion than bronze.

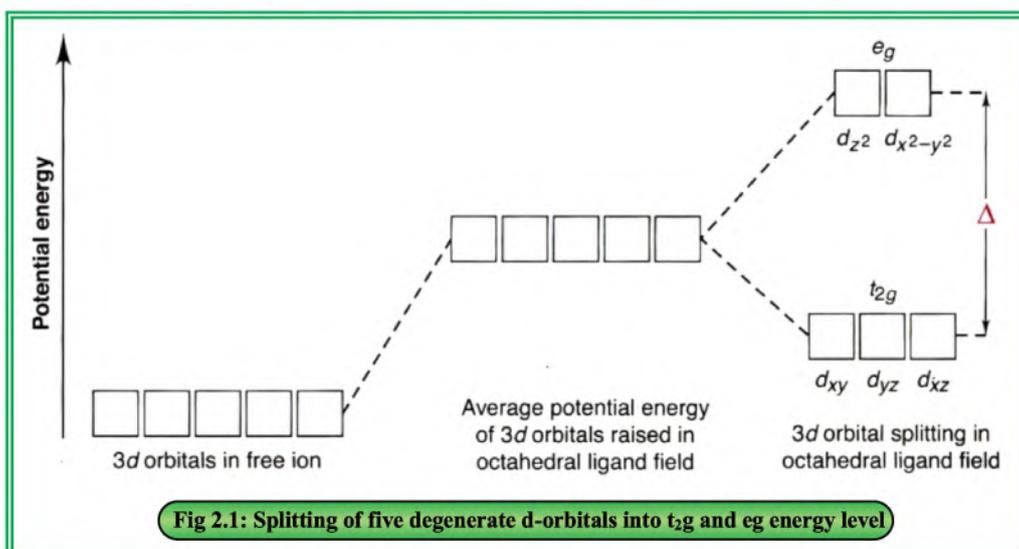
Table 2.3 Compositions and important uses of some alloys of transition-elements

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



2.1.7 Colour of Complexes

Transition elements possess partially filled d-orbitals. **“When a transition metal cation interacts with ligand, its five degenerate d-orbitals split into two sets of energy levels known as t_{2g} (lower energy level) and e_g (higher energy level)”** as shown in figure 2.1.



The energy difference between t_{2g} and e_g orbitals is commonly known as crystal field splitting and is denoted by Δ_o (Δ_o = energy difference for octahedral splitting).

When visible light falls on a sample of a transition metal complex, electrons from the lower energy level (t_{2g}) are promoted to the higher energy level (e_g) by absorbing light of specific wave length. The absorbed light corresponds to the energy difference between the two energy levels (d-d transition). The remaining wavelengths of light are transmitted, which gives characteristic colour.

Different complex ions of transition metals show different colours depending on the

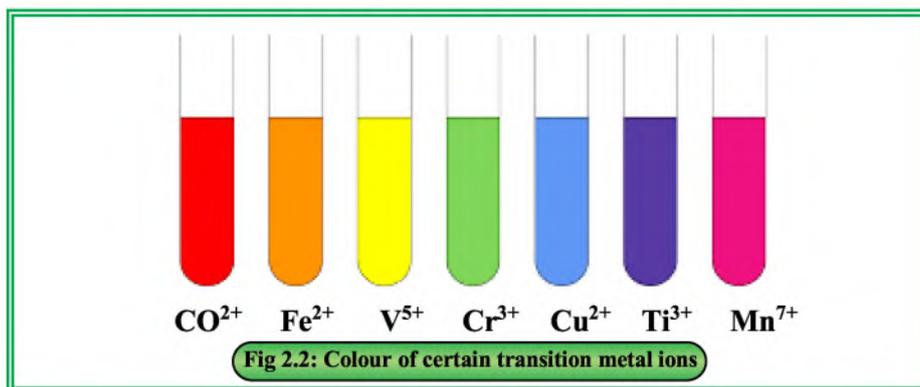


DO YOU KNOW?

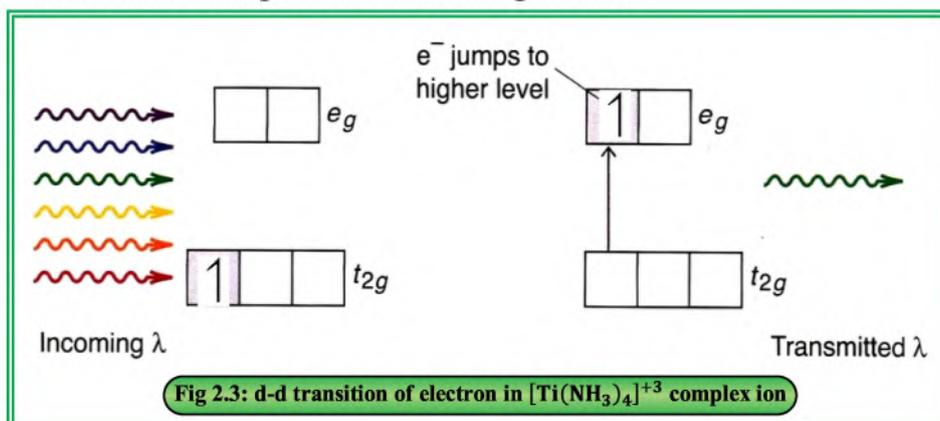
Visible light is composed of seven distinct colours when it interacts with transition metal ion, certain colours are selectively absorbed through d-d transitions while the rest pass through. For example Ti^{+3} complex absorbs yellow and green light while transmitting blue and red light, thereby giving rise to the perception of a violet colour.



oxidation state of the metal ion and the nature of ligands. Zinc complex ions are generally colourless since, there is no unpaired electron available in d-orbitals and hence d-d transition of the electron is not possible in zinc complexes. The Colours of certain transition metal ions are shown in figure 2.2.



For example when visible light fall on a tetraaminetitanium(III) $[\text{Ti}(\text{NH}_3)_4]^{+3}$ Complex ion, most of the component of light absorb in d-d transition while the waves of green colour are transmitted. This give rise to the green colour to the complex as shown in figure 2.3.



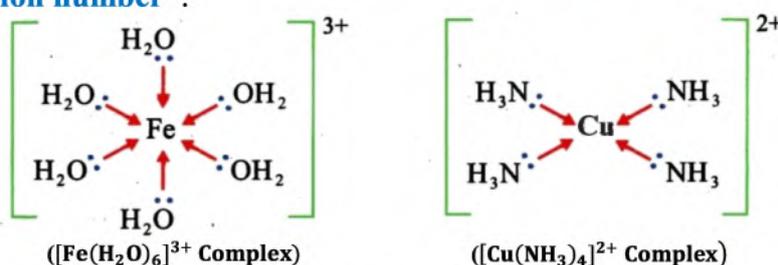
Self-Assessment

Explain why Tetraamminecopper(II) $[\text{Cu}(\text{NH}_3)_4]^{+2}$ complex ion is blue but Tetrahydroxozincate(II) $[\text{Zn}(\text{OH})_4]^{-2}$ is colourless?



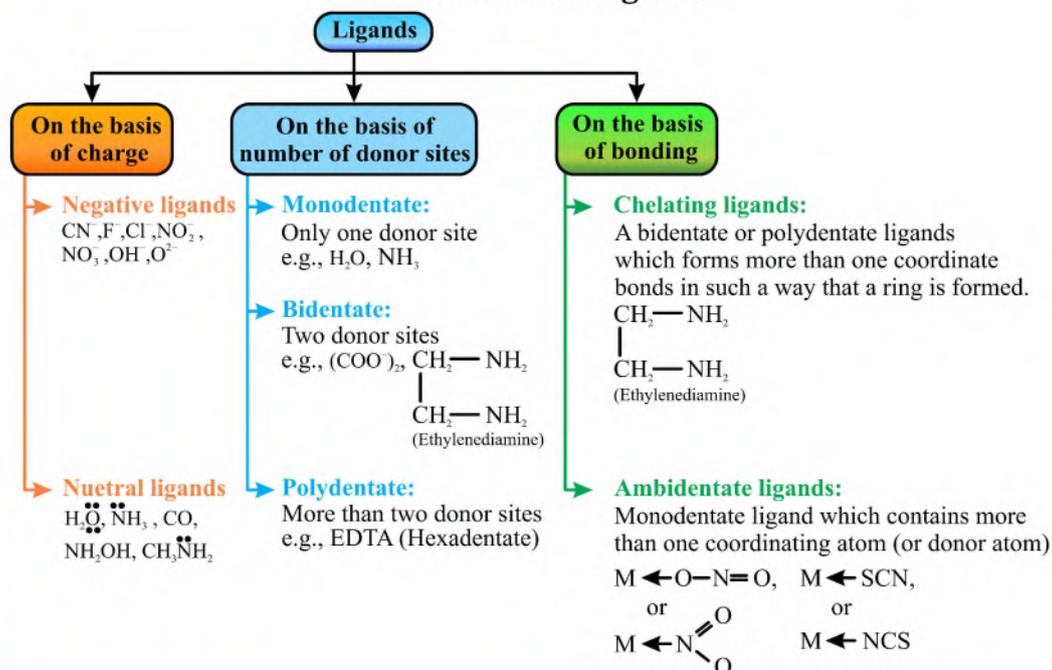
2.2 NOMENCLATURE OF COORDINATION COMPOUNDS

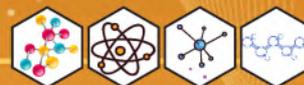
Coordination compounds or coordination complexes are substances in which a central transition metal is surrounded by certain negative ions or neutral molecules known as ligands. These ligands possess one or more lone pairs of electrons that can be donated to the metal ion forming coordinate bond and the coordination number ranges 1-16. **“The number of coordinate bond exist between the metal ion and the surrounding ligands is known as coordination number”.**



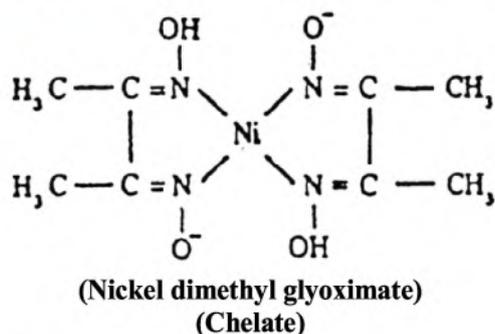
Ligands are the species that directly attached to the central atom or ion in the coordination complex and serve as coordinating group or Lewis base.

Classification of ligands





Bidentate and Multidentate ligands are known as chelating agents because their multipoint attachment to metal ion form a ring structure that resembles the claws of a crab (chelate meaning claw) **“A chelate is a complex of multidentate ligand”**. An example of chelate is nickel dimethyl glyoximate.



General rules of IUPAC naming of coordination compounds

International Union of Pure and Applied Chemistry (IUPAC) recommended following rules for the naming of coordination complexes.

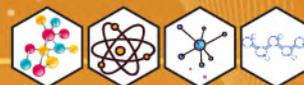
- (i) Cation is always named before anion and there should be a space between the names of cation and anion.
For example, in the complex $\text{Na}_3[\text{Co}(\text{CN})_6]$, sodium (Na) is a simple cation and $[\text{Co}(\text{CN})_6]$ is a complex anion, therefore according to the rule, the name of sodium is written first. Similarly, in the complex $[\text{Cr}(\text{NH}_3)_4]\text{SO}_4$, the $[\text{Cr}(\text{NH}_3)_4]^{+2}$ is a complex cation and SO_4^{-2} is a simple anion therefore the name of $[\text{Cr}(\text{NH}_3)_4]^{+2}$ is written first before SO_4^{-2} ion.
- (ii) The names of ligands are written in alphabetical order before the names of central metal atoms without any space between metal and ligand names.
- (iii) While naming coordination sphere, the name of ligand is written prior to the name of metal.
- (iv) Use Greek prefixes to indicate the number of each type of ligand, for example if there are four water molecules serving as ligand in the complex, use the term tetra. Similarly for six water molecules, it is written as hexa.
- (v) Determine the oxidation state of metal and indicate it in parentheses () by Roman numbers followed by the name of the metal.



- (vi) The number of inorganic ligands are indicated by prefix such as di-, tri-, tetra-, penta and hexa etc, while for organic ligands the prefix bis-, tris-, tetrakis-, etc are used to indicate the number of those ligands.
- (vii) The names of negative ligands are modified to end in “O” for example fluoro (F), chloro (Cl^-), bromo (Br^-) thiocyanato (SCN^-), amido (NH_2^-), oxalato ($\text{C}_2\text{O}_4^{2-}$), carbonato (CO_3^{2-}), hydroxo (OH^-), thiosulphato ($\text{S}_2\text{O}_3^{2-}$) etc.
- (viii) The name of neutral ligand usually remains unchanged for example amine (NH_3), carbonyl (CO), nitrosyl (NO). However, for water its name should be taken as “aquo”.
- (ix) In the case of anionic complex, the metal name will be written suffix “-ate” is added to the metal name after removing “-ium” or “-um” if present in Latin names.
- (x) In case of cationic and neutral complexes, the metal name will be written as English name.

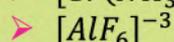
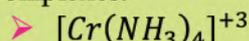
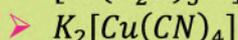
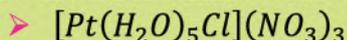
IUPAC naming of so--me coordination complexes

- (i) $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
Tetraamminecopper (II) sulphate
- (ii) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{NO}_3$
Tetraaquadichlorochromium (III) nitrate
- (iii) $\text{K}_4[\text{Fe}(\text{CN})_6]$
Potassiumhexacyanoferrate (II)
- (iv) $[\text{Pt}(\text{NH}_2 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2)_3]\text{Cl}_4$
Trisethylenediamineplatinum (IV) chloride
- (v) $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$
Triaminetrinitrocobalt (III)
- (vi) $[\text{Zn}(\text{OH})_4]^{-2}$
Tetrahydroxozincate (II) ion
- (vii) $[\text{Cu}(\text{en})_2]^{+2}$
Bisethylenediaminecopper (II) ion



Self-Assessment

Write the IUPAC names of the following complexes.



2.3 CHEMISTRY OF SOME IMPORTANT TRANSITION ELEMENTS

2.3.1 Chromium

Chromium is the fourth member of 3d series of transition elements. It is characterized by its silvery grey colour and metallic luster. It is widely used as protective coating on metal surfaces to prevent them from corrosion.

Chromium exhibits various oxidation states (+2, +3, +4, +5, +6) due to the electronic configuration of its atom ($3d^5, 4s^1$). The multiple oxidation states of chromium allow it to play a versatile role in redox reactions. In lower oxidation states, it serves as a reducing agent while in higher oxidation state it works as an oxidizing agent.

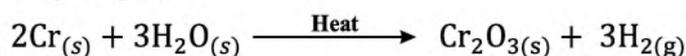
Chromium reacts with dilute hydrochloric acid to liberate hydrogen gas



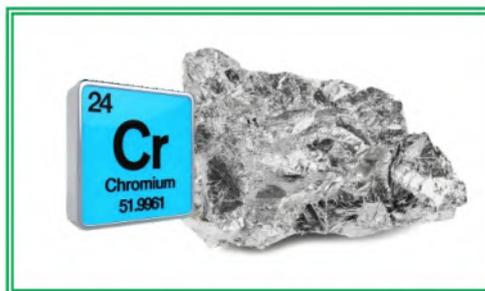
Chromium reacts with oxygen to form chromium oxide



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



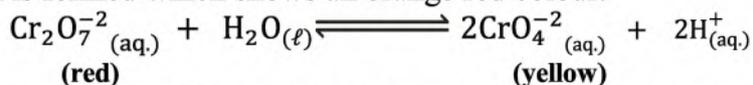
Chromium is used in the production of stainless steel, chrome plating, pigments and as a catalyst in certain chemical reactions.





2.3.1.1 Chemistry of Potassium dichromate

Potassium dichromate is a red crystalline solid that is highly soluble in water. If it dissolves in water at neutral pH, a chromate and dichromate equilibrium is formed which shows an orange red colour.



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.

The preparation of Potassium dichromate is commonly done by using chromates and these chromates are formed by the reaction of chromite ore with sodium or potassium carbonate.

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

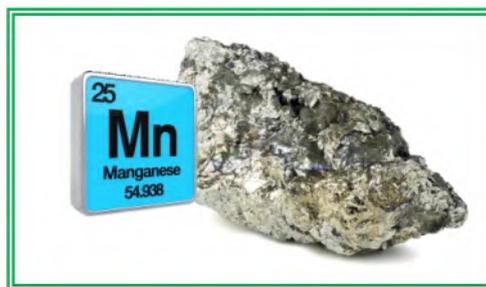
The redox titration of potassium dichromate with oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) and Mohr's salt ($\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$) is commonly carried out in the laboratories for determining the concentration of analyte. The end point of this titration is indicated by the colour change from orange (Cr^{+6}) to green (Cr^{+3}).

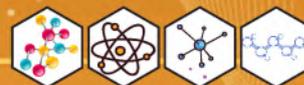


2.3.2 Manganese

Manganese is a greyish white, hard and brittle metal. It ranks as the twelfth most prevalent element within the Earth crust.

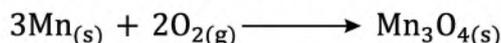
It exists in various oxidation states. For example the oxidation state of manganese in potassium permanganate





(KMnO_4) is +7 and in manganese dioxide (MnO_2) it is +4, where as in manganese chloride (MnCl_2) it is +2.

Manganese reacts with air to form manganese oxide Mn_3O_4 .



Manganese reacts with chlorine to form manganese chloride.



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



Manganese is used in the production of steel, alloys, batteries, ceramics and glasses etc. It is an essential nutrient and play vital role in metabolism, bone development and enzyme function.

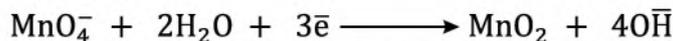
2.3.2.1 Chemistry of Potassium Permanganate

Potassium permanganate is a deep purple crystalline solid. Commercially, potassium permanganate (KMnO_4) is prepared by mixing a solution of potassium hydroxide (KOH) with powdered manganese dioxide (MnO_2) along with an oxidizing agent such as potassium chlorate (KClO_3). It is highly soluble in water, forming a pink solution, potassium permanganate is a powerful oxidizing agent. It works either in acidic, alkaline or neutral medium.

In acidic solutions permanganate ion accept five electrons and change from MnO_4^- to Mn^{+2} .



In basic or neutral medium it accepts three electrons and changes from MnO_4^- to MnO_2 .



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



The reaction of potassium permanganate with oxalic acid is given as



Potassium permanganate is used as a powerful oxidizing agent in various applications, including water treatment for purification and disinfection, and as a chemical reagent in organic synthesis and laboratory experiments.

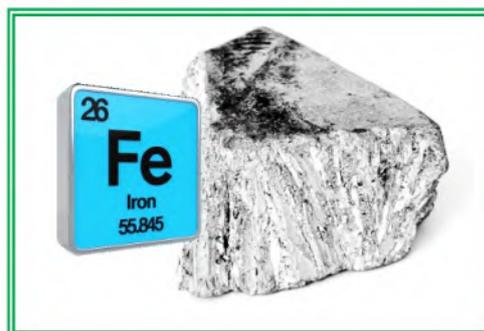


Self-Assessment

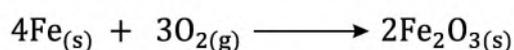
Explain why potassium dichromate and potassium permanganate are generally used in redox titration.

2.3.3 Iron

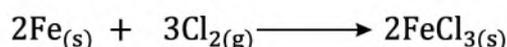
Iron is the fourth most abundant element in the Earth crust. Its strength and magnetic properties make it valuable in industries such as construction and manufacturing. Furthermore, iron is an indispensable component of haemoglobin, emphasizing its critical role in the biological system.



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



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



Iron is mainly used in the construction of buildings and flyovers. It is used in industries for making tools, weapons, appliances, rail tracks, trains, automobiles etc.

2.3.3.1 Steel Types and Applications

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.

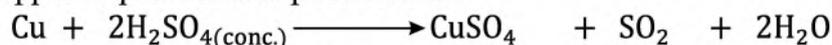
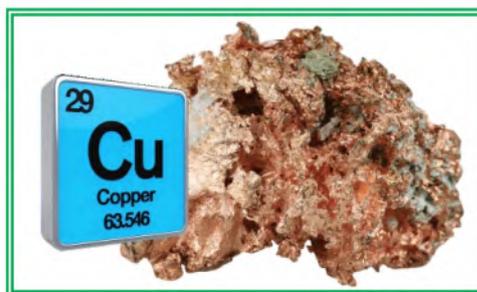
There are several types of steel each characterized by unique compositions and properties suited for specific applications.



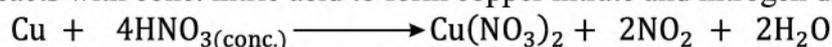
Type of Steel	Applications
Carbon Steel	Construction tools, machinery, pipes, tubes, automotive etc.
Stainless Steel	Kitchen appliances, Cutlery and Medical equipment
Tool Steel	Cutting and drilling equipment
Alloy Steel	Fry pan, Toaster etc

2.3.4 Copper

Copper is a dense metal with a reddish brown colour. It is malleable and ductile, allowing it to be easily shaped and wired. Copper is known for its excellent electrical conductivity and it ranks as second highest (after silver) electrical conductor among pure metals. Copper reacts with conc. sulphuric acid to form copper sulphate and sulphur dioxide.



Copper reacts with conc. nitric acid to form copper nitrate and nitrogen dioxide.



Copper is primarily used in making electric wires, cables, motors and other electrical equipments. It is also used in plumbing, piping, telecommunication, coinage and alloy formation.

2.3.4.1 Metallurgy of Copper

Copper is present in Earth's crust in the combined form referred to as ore. The most abundant ore of copper is chalcopyrite (CuFeS_2). The process of extracting metal like copper from its ore is called metallurgy. The metallurgical



DO YOU KNOW?

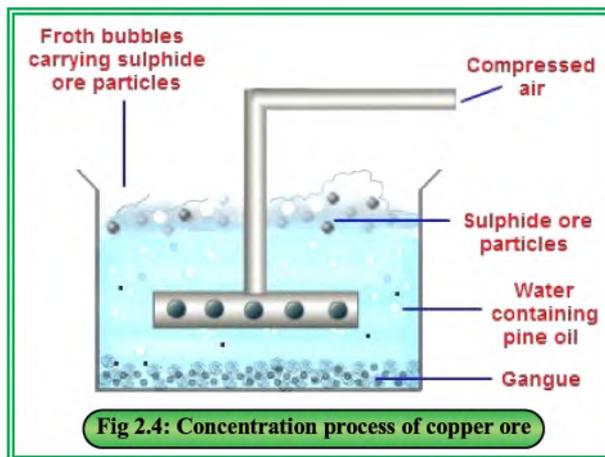
Copper deposits of considerable significance are present in Pakistan, notably in the province of Balochistan. Two prominent copper mining projects in the country are the Saindak copper-gold mine and the Reko-diq copper-gold mine.



operations associated with chalcopyrite ore include series of steps: such as crushing, grinding, Concentration, roasting, smelting and refining.

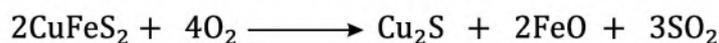
Concentration

In this stage, the objective is to eliminate gangue impurities from the powdered chalcopyrite ore. This is accomplished through a froth floating process, where the ore is blended with water that has pine oil added to it. Subsequently, air is introduced into the water, causing the ore particles to become coated with froth, while the gangue particles settle to the bottom as shown in figure 2.4.



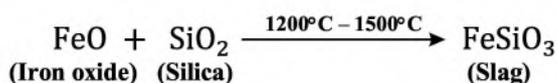
Roasting

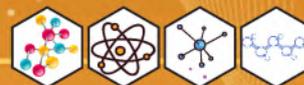
This process involves the heating of ore in the presence of excess air at an elevated temperature in a roasted kiln. As a result, the impurities oxidizes and the ore undergoes decomposition, leading to the formation of cupreous sulphide and ferrous oxide while sulphur dioxide is simultaneously eliminated.



Smelting

Roasted ore along with silica and coal is charged into a blast furnace. The combustion of coal elevates the furnace temperature to approximately 1200°C to 1500°C. Within this environment, ferrous oxide (FeO) present in the ore reacts with silica, resulting in the formation of iron silicate (FeSiO₃) commonly referred to as slag. The slag floats on the surface of the molten matte while the matte (consisting of Cu₂S and some impurities) is separately collected from the slag.



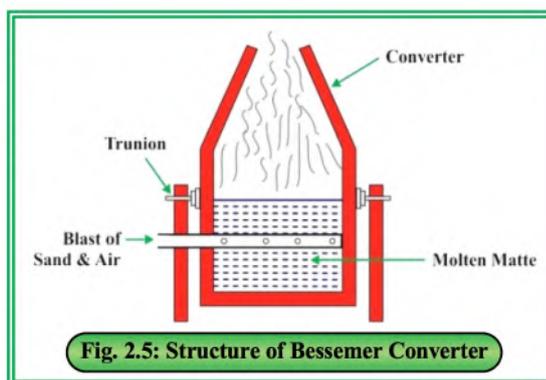


Bessemerization

The matte is subsequently fed into a pear shaped Bessemer converter, where hot gases are introduced from the mid lower portion. Within this converter, cuprous sulphide (Cu_2S) is partly converted into cuprous oxide (Cu_2O), which then reacts with the remaining cuprous sulphide, resulting in the production of molten metallic copper.

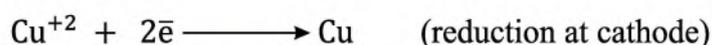
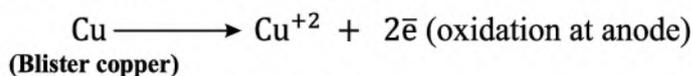


The copper thus produced is called blister copper because as it solidifies hidden sulphur dioxide gas escapes producing blisters on its surface. It is about 99% pure. The blister copper contains impurities mainly iron but small amount of arsenic, zinc, lead, silver and gold. Blister copper is not suitable especially for electrical purposes; therefore, it undergoes a refining process to remove all remaining impurities as shown in figure 2.5.



Refining of Copper

Copper is refined by electrolysis in an electrolytic tank. The blocks of blister copper are used as anodes and thin sheets of pure copper act as cathodes as shown in figure 2.6. The electrolyte is copper sulphate which is acidified with sulphuric acid. By passing electricity through the electrolytic solution, the blister copper undergoes oxidation and the Cu^{+2} ions produced in this oxidation process are then deposited onto cathode. The impurities are left behind which fall to the bottom of the cell as anode mud.





Copper obtained after electrolytic refining is 99.99% pure.

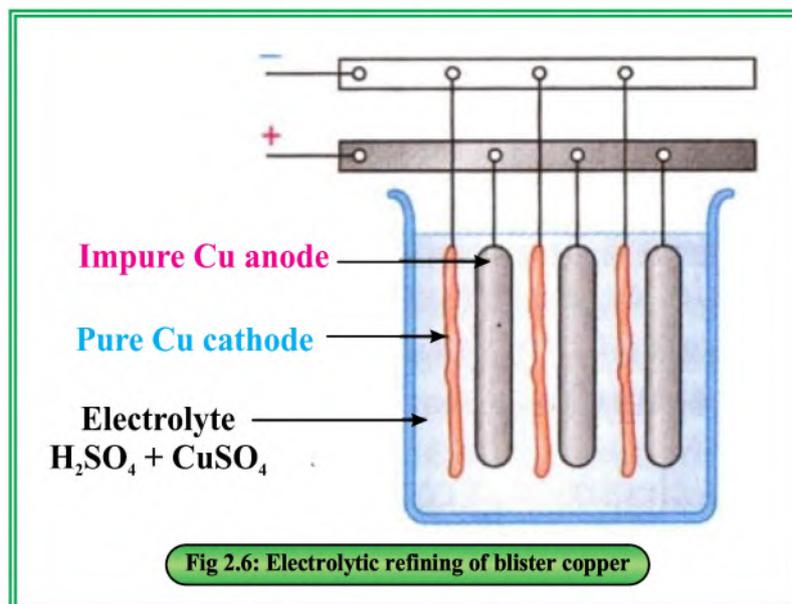
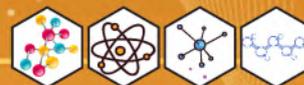


Table 2.4 Commercial applications of some common transition elements

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



SOCIETY, TECHNOLOGY AND SCIENCE

Use of transition metals in paints

Transition elements are widely used in the formulation of paints. They are often employed as pigments. For example, titanium dioxide is used as a white pigment, while iron oxide is used as a brown pigment. Certain transition metals such as zinc and chromium are added to paint formulations for corrosion inhibition. Additionally, certain transition metals, including various forms of zinc and titanium, are used to protect paint surfaces from the damaging effects of ultra violet light.



SUMMARY

- The elements that possess partially filled d-orbitals in their atomic or any of their ionic states are called outer transition elements.
- Transition elements are located in the mid portion of periodic table and cover up 4th, 5th, 6th and 7th periods.
- The general valence electronic configuration of transition elements is $(n - 1) d^{1-10}, ns^{1,2}$.
- Chromium and copper deviate from the general trend of electronic configuration in 3d series of transition elements because of achieving extra stability.
- Binding energy of Mn^{+2} and Fe^{+3} are highest because they possess maximum unpaired electrons in their 3d orbitals.
- The most common oxidation number of transition metal cations is +2.
- Paramagnetic behavior of transition elements is due to the availability of unpaired electrons in their 3d orbitals.
- The colour phenomena of transition elements is due to the excitation of electron from t_{2g} to e_g energy levels by the absorption of light of specific wavelengths.

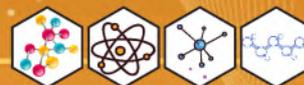


- Coordination number is the number of coordinate bonds formed between ligands and the transition metal in a complex molecule or ion.
- The complexes of multidentate ligands are known as chelates.
- Potassium dichromate and potassium permagnate are powerful oxidizing agents.
- Transition elements have ability to form alloys with each other due to the similarities in their atomic sizes.
- Stainless steel is the most common alloy of iron. It is made up of iron, chromium and nickel.
- The most common ore of copper is chalcopyrite (CuFeS_2).
- Refining of copper is carried out in an electrolytic tank where thick plates of blister copper serve as anode and thin sheets of pure copper act as cathode.

EXERCISE

Multiple Choice Questions

- (i) Zn^{+2} ion is colourless because:
- Its undergoes d-d transition of electron
 - Its 3d orbitals have all unpaired electrons
 - Its 3d orbitals have all paired electrons
 - Its d orbitals split up into t_{2g} and eg
- (ii) The coordination number of cobalt in $\text{Na}_4[\text{Co}(\text{C}_2\text{O}_4)_3]$ is:
- | | |
|-------|-------|
| (a) 3 | (b) 4 |
| (c) 6 | (d) 7 |
- (iii) An example of a bidentate ligand among the following is:
- | | |
|-------------------|---------------------------------|
| (a) OH^- | (b) $\text{C}_2\text{O}_4^{2-}$ |
| (c) Cl^- | (d) CN^- |
- (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) MnO₃
(c) Mn₂O₃ (d) Mn₃O₄

Short Questions

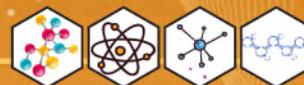
- Write the IUPAC names of the following:
 - $\text{Na}_2[\text{Pt}(\text{OH})_4]$
 - $\text{K}_2[\text{Fe}(\text{CN})_5\text{NO}]$
 - $[\text{Zn}(\text{NH}_3)_4]^{+2}$
 - $[\text{Ni}(\text{SCN})_4]^{-2}$
- Give reasons for the following:
 - Why do transition elements show variable oxidation states?
 - Why transition elements have ability to form alloys?
 - 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?
3. Write down the balanced chemical equations for the following reactions.
- Reaction of conc. nitric acid with copper
 - Reaction of conc. sulphuric acid with copper
 - Reaction of permanganate with oxalic acid
 - Reaction of dichromate with ferrous sulphate
 - Reaction of manganese with dilute sulphuric acid
 - Reaction of iron with chlorine
4. Why d-block elements are called outer transition elements?
5. Write down the effect of pH changes on dichromate equilibrium in water.
6. Melting point of d-block elements increase up to middle of the series and then decrease why?
7. Give the composition and applications of stainless steel, brass and bronze.

Descriptive Questions

- Explain the trend of following properties of 3d-series of transition elements.
 - Paramagnetic behavior
 - Variable oxidation state
 - Colour formation.
- How can you define a coordination complex and a chelating ligand? Explain various types of ligands with examples.
- Describe how 99.99% pure copper is obtained from its chalcopyrite ore.
- Explain why transition elements and their compounds serve as catalysts in many chemical reactions.
- What is meant by binding energy? Write down the trend of binding energy in 3d series of transition elements.

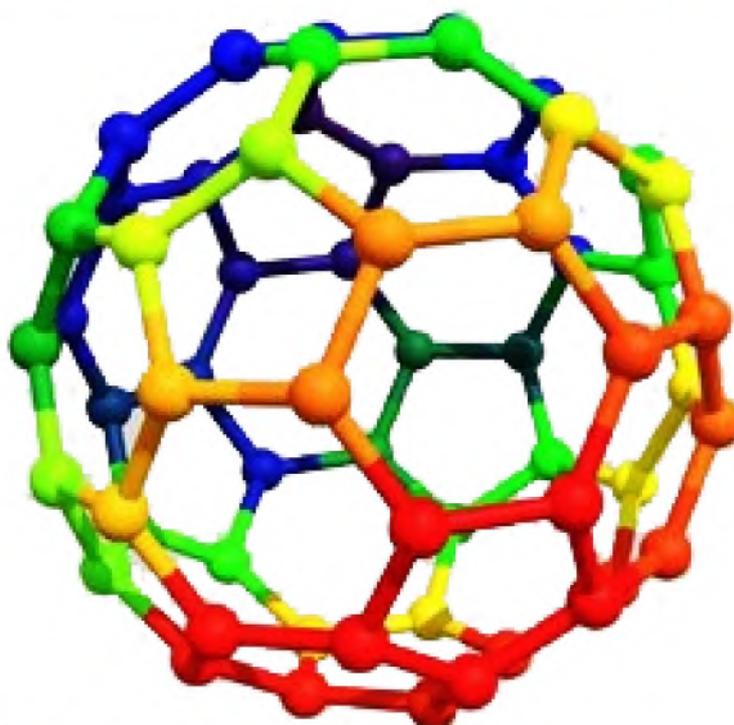


CHAPTER 3

ORGANIC COMPOUNDS



Teaching Periods	04	Assessment	01	Weightage %	03
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Students will be able to:

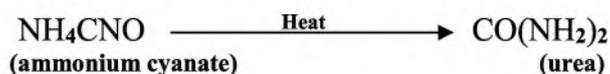
- ✓ Define organic chemistry and organic compounds. (Remembering)
- ✓ Explain why there is such a diversity and magnitude of organic compounds. (Analyzing)
- ✓ Explain the use of coal as a source of both aliphatic and aromatic hydrocarbons. (Understanding)
- ✓ Explain the use of plants as a source of organic compounds. (Understanding)
- ✓ Explain that organic compounds are also synthesized in the lab. (Understanding)
- ✓ Define functional groups and homologous series. (Remembering)
- ✓ Explain reforming of petroleum. (Understanding)
- ✓ Explain different uses of organic compounds in our daily life. (Understanding)
- ✓ Explain Bucky ball. (Understanding)



INTRODUCTION

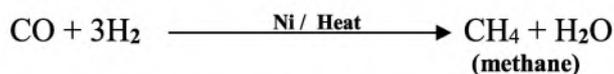
Organic chemistry is the study of properties and structure of carbon containing compounds. Thus “organic chemistry deals with hydrocarbons and their derivatives”. However, a few numbers of carbon containing compounds are excluded from organic chemistry either by their properties or nature of bonding. These are carbonates, bicarbonates, cyanides, carbides, carbon dioxide, carbon monoxide and carbon disulphide etc.

Before the 18th century, the term organic chemistry was used only for those substances that were obtained from animals and plants and could not be prepared in laboratory. It was extensively believed by chemists that there existed a vital force in all living things that was required for the production of organic compounds. In 1828, a German chemist Friedrich Wohler prepared urea in the laboratory by boiling ammonium cyanate with water.



Urea is a typical organic compound that is excreted from urine. Laboratory synthesis of urea by Wohler disapproved the vital force theory and turned the minds of chemists towards synthetic organic chemistry and since then millions of organic compounds have been synthesized.

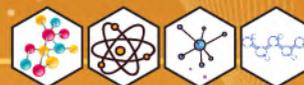
The methane (CH₄) can also be synthesized in the laboratory from hydrogen (H₂) and carbon monoxide (CO) in presence of catalyst at high temperature and moderate pressure.



Organic chemistry is probably the biggest sub-field in chemical sciences and is recognized as the fundamental field for all chemists to study. It serves as a bridge between chemistry and biology.

3.1 SOURCES

Organic compounds are abundant in nature and can be found in various natural sources such as fossil fuels, plants, animals and microorganisms. They play an important role in our society in various aspects.



3.1.1 Fossil Remains (Coal, Petroleum, Natural Gas)

Fossil remains refer to the remnants of ancient animals and plants that have been preserved in rocks and sediments. These remains can include bones, teeth, shells imprints of leaves or other plant parts and provide important clues about the history of life on earth.

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.

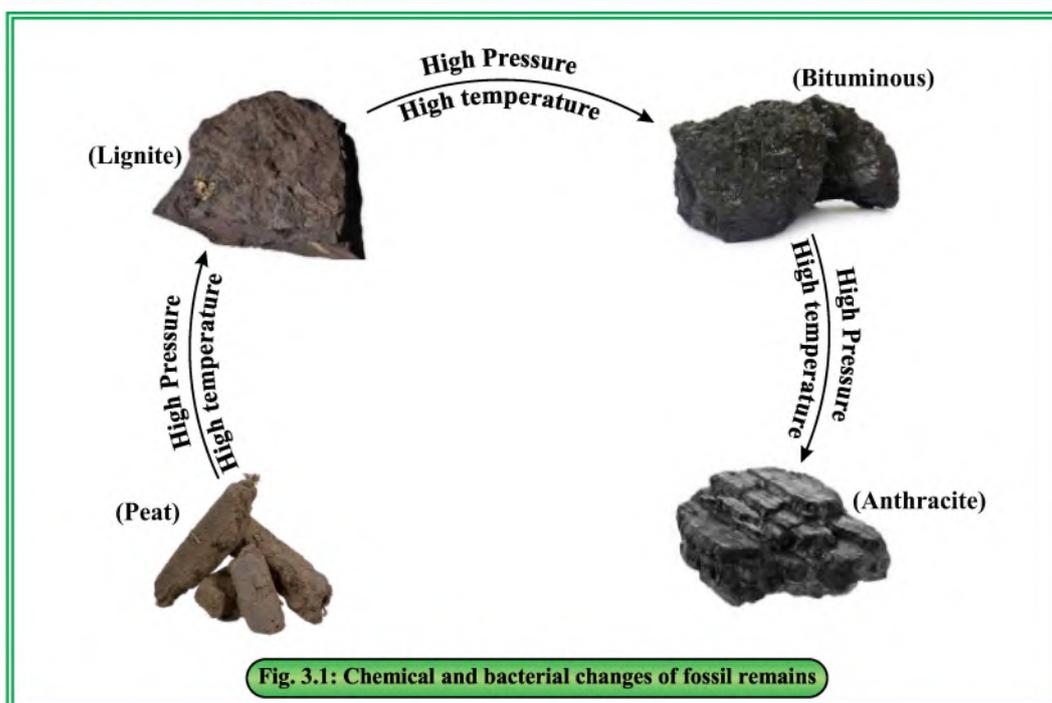


Fig. 3.1: Chemical and bacterial changes of fossil remains

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 (Fig.3.1). The coal types and their some uses are given in Table 3.1.



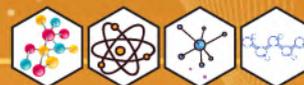
Table 3.1 Coal types and uses

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.

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.



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.

The initial discovery of natural gas in Pakistan dates back to 1952 when it was found in the Sui area of Baluchistan. Subsequently, natural gas deposits were also identified in Khairpur and Ghotki districts in the province of Sindh.



Self-Assessment

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

3.1.2 Natural Products (Plants and Animals)

Many organic compounds are isolated from plants, animals and microbes. These are referred to as natural products. These products are typically produced by living organisms through natural metabolic processes and extracted out through various methods such as distillation, fermentation, purification etc. Natural products have been utilized for millennia for medicinal, cosmetic, and nutritional reasons. Some examples of natural products are glucose, cellulose, insulin, cholesterol, caffeine, nicotine, menthol and peppermint oil etc.

3.1.3 Partial and Total Synthesis

Partial synthesis and total synthesis are two approaches used in organic chemistry to create complex molecules.

Partial 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. This method is particularly useful when the target molecule is challenging to synthesize directly or requires multiple steps.



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:

Total synthesis involves building a complex target molecule entirely from simple starting materials. It requires designing a route that carefully selects and assembles the necessary building blocks through a series of chemical reactions. Total synthesis is often used to produce natural products or pharmaceutical compounds that are not readily available from natural sources.

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

These examples illustrate how partial synthesis modifies an existing compound to create a target molecule, while total synthesis involves constructing the target molecule from scratch using simpler starting materials.

3.1.4 Products of Biotechnology

Biotechnology is the field of biological sciences that deals with the involvement of living organisms or their ingredients in preparation or development of valuable products. **“Products that are made by using living organisms or their constituents such as cells enzymes, DNA, etc are called as products of biotechnology.”**

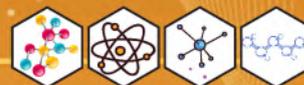
These products have been used across various industries including food production, healthcare, agriculture genetic engineering etc.

These products have been used across various industries including food production, healthcare, agriculture genetic engineering etc. For example, ethyl alcohol is commercially manufactured by fermentation process in which certain enzymes secreted by microorganisms (yeast) are involved.



DO YOU KNOW?

Biotechnology has enabled the development of vaccines for a variety of fatal diseases such as COVID-19. Vaccines consist of inactive pathogens which produce proteins that act as stimulants for our immune system to develop antibodies so that if the virus enters our body, our immune system can easily fight it.



3.2 COAL AS A SOURCE OF ORGANIC COMPOUNDS

Coal mines can be considered a valuable asset for countries. In addition to its widespread use in power generation, coal is also a source of many important organic compounds. These organic compounds can be extracted from coal or obtained as a by product of coal processing. Further, coal can be gasified or liquefied to produce a range of organic compounds such as methane, ethene, ethyne, hexane etc. These compounds can be used as raw materials for the production of many useful chemicals.



DO YOU KNOW?

The largest coal reserves in Pakistan are found in the Thar Desert, Tharparkar district of Sindh province. Tharcoal reserves are considered to be the sixteenth largest in the world containing approximately 175 billion tons of lignite coal.

3.2.1 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 requires an elevated temperature typically 400°C to 900°C in a closed container. The four principal products of destructive distillation of coal are coke, coal tar, coal gases and ammonia liquor.

Coke

It is a greyish black hard solid contain 98 – 99% carbon. It is used as fuel and reducing agent.

Coaltar

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

Coal Gases

It is a mixture of methane and water gas. It is highly flammable and is employed for heating and municipal lighting.

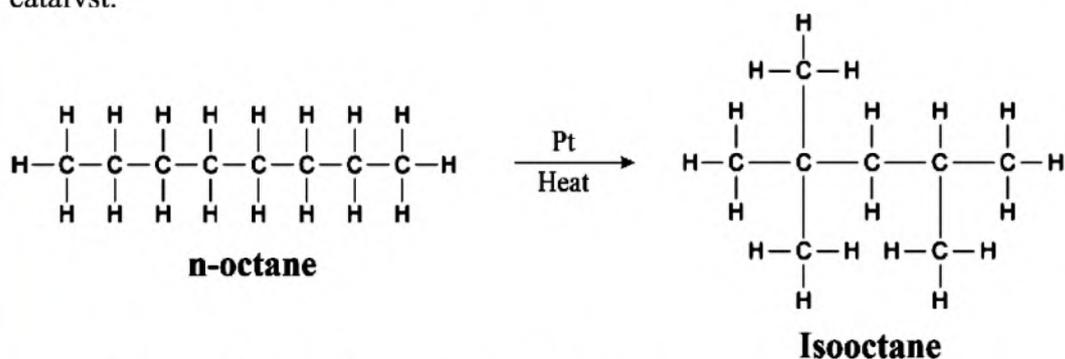
Ammonia Liquor

It is a mixture of ammonium compounds and liquid ammonia and is usually obtained from bituminous coal.



3.2.2 Reforming of Petroleum

“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 due to improper combustion. Knocking produces a sharp sound. Higher-quality gasoline tends to produce less knocking. To measure a fuel's resistance to knocking, chemists use the octane number or octane rating. This standard measure assesses the fuel's ability to resist knocking and helps determine its quality. **“The octane number quantifies a fuel's ability to resist knocking during combustion.”**

Previously, Tetra Ethyl Lead (C_2H_5)₄Pb (TEL) was used as an additive in gasoline to prevent knocking. However, the production of harmful pollutants led to the search for alternatives to reduce atmospheric pollution. Chemists developed a process called reforming as an alternative to TEL. Reforming converts low-octane gasoline into a higher-octane fuel, effectively reducing knocking without the need for TEL. This advancement in the production of higher-octane gasoline helped replace the use of TEL and mitigate its negative environmental impact.



DO YOU KNOW?

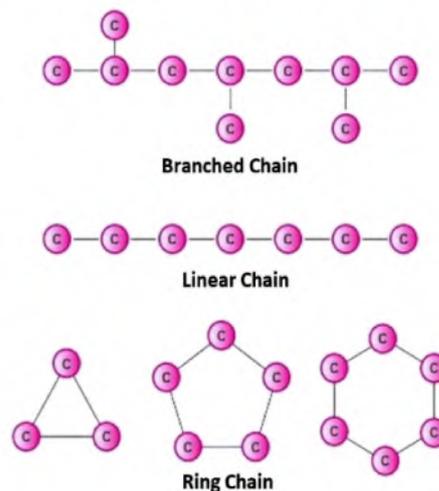
The octane number is measured using the Research Octane Number (RON) scale. RON compares a fuel's performance against a mixture of iso-octane (rated 100) and n-heptane (rated 0) in a standardized engine test. The higher the percentage of iso-octane needed to match the fuel's performance, the higher its octane number.



3.3 CHARACTERISTICS OF ORGANIC COMPOUNDS

Catenation

Organic compounds are made up of carbon atoms. Carbon is distinctive in its ability to bond covalently with other carbon atoms in many different ways to form long chain, branch chain and cyclic compounds. This unique property of organic compounds is known as 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. Burning of organic compounds provide heat energy. The combustion reaction for methane (CH₄) is as follows:



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

Isomerism is a characteristic of organic compounds where compounds with the same number of atoms of each element can arrange those atoms in different ways, resulting in distinct structures and properties. These compounds with different structures but the same molecular formula are called isomers.

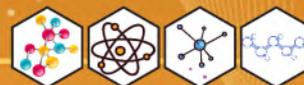
For example: there are two isomers of butane: n-butane and isobutane. In n-butane, the carbon atoms form a straight chain, while in isobutane, the carbon atoms form a branched structure.

n-Butane: CH₃-CH₂-CH₂-CH₃

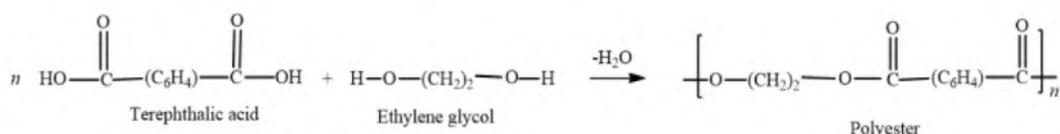
Isobutane: CH₃-CH(CH₃)-CH₃

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 (a diol) forms polyethylene terephthalate (PET), which is a common type of polyester used in various applications, including textiles, packaging, and beverage containers.



3.4 USES OF ORGANIC COMPOUNDS

Organic compounds are widely used in various applications, including pharmaceuticals, agriculture, plastics, fuel, material production, and energy generation.

Table 3.2 displays several organic compounds and their applications that are relevant to our everyday existence.

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



3.5 NEW ALLOTROPIC FORM OF CARBON (BUCKY BALLS)

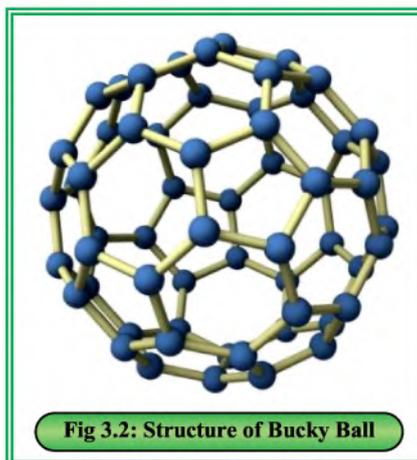
It has been known for centuries that pure carbon exists in two allotropic forms with diamond and graphite. In 1985, Richard Smalley and Harry Kroto introduced a new allotropic form of carbon that consists of 60 carbons.

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

It consists of twelve (12) five membered ring and twenty (20) six membered ring. Structurally each pentagon is surrounded by hexagon. Forming a hollow cage-like structure.

Bucky balls are hollow spheres made up of carbon atoms that have a diameter of approximately one nanometer (Fig.3.1). They have high tensile strength and exhibit high degree of stability with a melting point of 2800°C . They are light weight with a high surface area and are good conductors of electricity and heat.

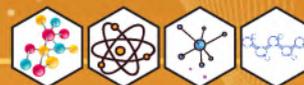
Bucky balls are used in nanotechnology such as nanoscale sensors, drug delivery system and high storage batteries and electronic devices.



3.6 FUNCTIONAL GROUPS AND HOMOLOGOUS SERIES

Functional Group

A large number of organic compounds are considered to be derivatives of hydrocarbons in which one or more hydrogen atoms are replaced by another atom or group of atoms known as a functional group. **“A functional group is a specific group of atoms within the molecule that is responsible for unique chemical properties and determines its characteristic reactions”**. Each functional group has its own chemical characteristic; therefore, all the



compounds having the same functional group behave alike and belong to the same family. For example, alcohol is a class of organic compounds and all the members of this class possess hydroxyl (–OH) functional group.

Some common functional groups and their corresponding classes of organic compounds are listed below Table 3.3.

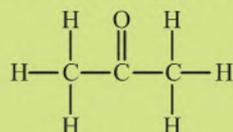
Table 3.3 Name and structure of some common functional groups

Class of Compound	Structure of Functional Group	Class of Compound	Structure of Functional Group
Alkane	$\diagdown \text{C} - \text{C} \diagup$	Carboxylic acid	$\begin{array}{c} \text{O} \\ \\ -\text{C} - \text{OH} \end{array}$
Alkene	$\diagdown \text{C} = \text{C} \diagup$	Ester	$\begin{array}{c} \text{O} \\ \\ -\text{C} - \text{O} - \end{array}$
Alkyne	$-\text{C} \equiv \text{C}-$	Nitrile	$-\text{C} \equiv \text{N}$
Alcohol	$-\text{OH}$	Thiol	$-\text{SH}$
Ether	$-\text{O}-$	Alkyl Halide	$-\text{X}$
Amine	$-\text{NH}_2$		
Aldehyde	$\begin{array}{c} \text{O} \\ \\ -\text{C} - \text{H} \end{array}$	Acyl halide	$\begin{array}{c} \text{O} \\ \\ -\text{C} - \text{X} \end{array}$
Ketone	$\begin{array}{c} \text{O} \\ \\ -\text{C}- \end{array}$	Amide	$\begin{array}{c} \text{O} \\ \\ -\text{C} - \text{NH}_2 \end{array}$

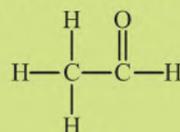


Self-Assessment

Predict the functional group present in the structures given below:



(a)



(b)



Homologous Series

The chemical and physical properties of organic compounds depend to a great extent on their functional group. The physical properties of all the compounds of the same functional group are not precisely same but change with the length of hydrocarbon chain thus “A series refers to a group of organic compounds with similar structural characteristics but differing from each other by the addition of a methylene group ($-\text{CH}_2-$) in their structure 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.

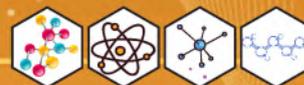
Alkane	$\text{C}_n\text{H}_{2n+2}$	Alcohol	$\text{C}_n\text{H}_{2n+1}\text{OH}$
Alkene	C_nH_{2n}	Alkyl halide	$\text{C}_n\text{H}_{2n+1}\text{X}$
Alkynes	$\text{C}_n\text{H}_{2n-2}$	Amine	$\text{C}_n\text{H}_{2n+1}\text{NH}_2$

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



SOCIETY, TECHNOLOGY AND SCIENCE

Isolation of organic compounds from plants and animals

There are many organic compounds that are obtained from plants and animals. For example, animal **manure** and **seaweed** are gathered from animals and plants respectively which are used as fertilizers in the farms and agricultural lands.

Moreover, countless medicines are directly extracted from plants. For instance, **Caffeine** is obtained from tea, cocoa and coffee beans. It is used as Central Nervous System Stimulant. **Bromelain** is obtained from lemon, orange, grapefruit, etc. and it aids in the treatment of fragility.



SUMMARY

- Urea is a typical organic compound prepared by Friedrich Wohler by boiling ammonium cyanate with water.
- Fossil fuels are nonrenewable energy sources. They include coal, petroleum and natural gases.
- There are four types of coal named as peat, lignite, bituminous and anthracite.
- Petroleum is formed from the ancient marine animals by the chemical and bacterial degradation.
- Organic compounds that are isolated from plants, animals and microbes are known as natural products.
- The process of synthesizing a target molecule directly from an intermediate compound, rather than through stepwise reaction from starting material is called as partial synthesis.
- The process of synthesizing a target molecule from simple starting material using stepwise series of reaction is known as total synthesis.

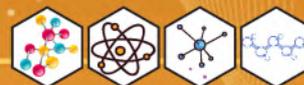


- Products that are made by using living organisms or their constituents such as enzymes, DNA etc are called products of biotechnology.
- The process in which coal is heated in the absence of air to produce coke, coltar, coal gases and ammonia liquor is known as destructive distillation of coal.
- Octane number measures the quality of fuel in terms of its capacity to withstand knocking during combustion.
- The C_{60} molecule of Bucky ball consists of twelve (12) five membered rings and twenty (20) six membered rings.
- Functional group is a specific group of atoms within the molecule which is responsible for unique chemical properties.
- A series of organic compounds in which the various members have similar structural features but differ from each other by methylene group ($-CH_2-$) is called homologous series.

EXERCISE

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

Short Questions

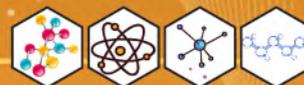
1. Define organic chemistry and give the significance of some organic compounds in everyday life
2. What is Vital force theory? Why was it disapproved?
3. Define functional group and write the structure of three oxygen containing functional group.



4. Define the following terms:
(a) Catenation (b) Isomerism
5. How can you differentiate between total and partial synthesis of organic compounds?
6. What is meant by Reforming? Why is it considered a useful technique?
7. Write down some examples of products that can be produced using biotechnology?
8. Write down some common uses of organic compounds?

Descriptive Questions

1. Describe the natural sources of organic compounds.
2. Define Bucky Ball? Explain its structure and mention its some properties.
3. Explain destructive distillation of coal? What are the various products obtained from it?
4. Describe homologous series of organic compounds? Write three main properties of homologous series.
5. Explain various unique characteristics associated with organic compounds.
6. Describe natural product chemistry and explain the use of plants and animals as sources of organic compounds.
7. Write down the different types of coal and how do they differ from each other?

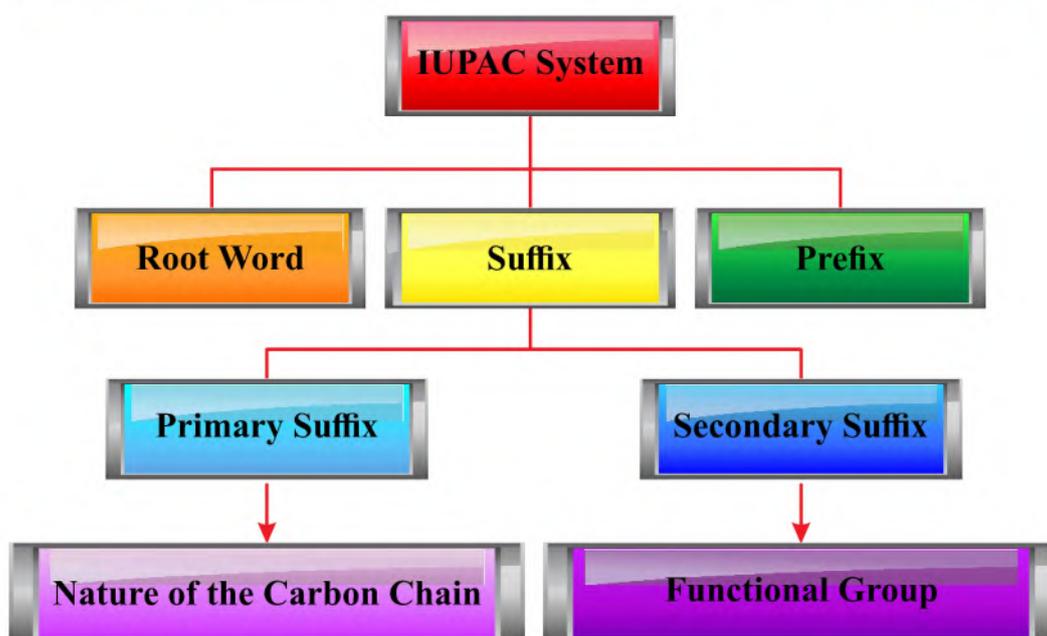


**CHAPTER
4**

**NOMENCLATURE OF
ORGANIC COMPOUNDS**



Teaching Periods	10	Assessment	02	Weightage %	08
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Students will be able to:

- ✓ Enlist the families of organic compound with functional groups. (Remembering)
- ✓ Describe nomenclature rules of each family by applying common name system and IUPAC system. (Understanding)
- ✓ Write nomenclature of alkane, alkene, alkyne cyclo alkanes with five examples of each family. (Applying)
- ✓ Write nomenclature of Alkyl Halide, Amine, Ether, alcohol, Phenol, Aldehyde, Ketone, Carboxylic acid, Ester, Amide and Acyl Halide with at least five examples of each family. (Applying)
- ✓ Explain the outlines to draw structures for IUPAC of organic compounds of each family. (Applying)
- ✓ Explain outlines to draw structures of common names of organic compounds of each family. (Applying)



INTRODUCTION

Organic compounds exhibit a great diversity with millions of known compounds and an infinite numbers of possible isomers. These compounds can possess distinct functional groups, different type of substituents, and variable lengths, branches and cyclic structure of carbon chains leading to a wide range of structural possibilities. It was a big challenge for organic chemists to establish a systematic and simplified method for naming the vast number of organic compounds in a consistent and uniform manner. However this challenge was successfully addressed with the introduction of IUPAC (international union of pure and applied chemistry) naming system which provides comprehensive solution for the nomenclature of organic compounds and allows chemists to identify and understand the vast array of organic compounds that exists in nature or are synthesized in the laboratory.

4.1 HYDROCARBONS AND THEIR DERIVATIVES

Organic compounds are mainly made up of carbon and hydrogen, however certain other elements such as oxygen, nitrogen, sulphur and halogen may also be present in their structures.

A wide range of organic compounds are derivatives of hydrocarbons, formed by substituting one or more hydrogen atoms with a hetero atom or group of atom. These derivatives are distinguished by their unique structures and properties and are categorized into families or groups of organic compounds. Each family is characterized by a specific functional group, which impact distinct chemical and physical properties to the compound within that family.



DO YOU KNOW?

Functional groups are specific group of atoms that are responsible for the characteristic chemical reactions and properties of organic compounds. Organic compounds are categorized into various groups based on the presence and nature of functional group.

A list of certain hydrocarbon families are given in Table 4.1.

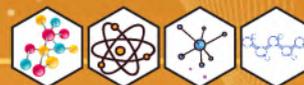


Table 4.1 Names of alkanes , alkenes and alkynes

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

4.2 HISTORY OF NOMENCLATURE

Every organic compound found on Earth possesses a distinct structural feature. Initially the names of organic compounds were assigned on the basis of origin or the person who discovered. These specific designations are referred to as common names or trivial names. With the rapid growth of organic chemistry, the number of compounds increased tremendously, where it became impossible to assign a common name to such an extensive range of compounds and scientists felt the need for a structural or systematic name, that one would accurately reflect the molecular structure of organic compound.

An attempt was made at Geneva conference (1892) to create a unique nomenclature wherein only one official name would be assigned to each compound. In 1958, a



DO YOU KNOW?

The latest updates to the rules of IUPAC system of nomenclature of organic compound were recommended in 2013.



A new commission on nomenclature was appointed by the international union of pure and applied chemistry (IUPAC) for further work on the nomenclature. This new system of nomenclature has set rules for naming organic molecules on the basis of their structures.

4.3 IUPAC SYSTEM

The systematic or scientific system for the naming of organic compound is referred as IUPAC method. This system provides distinct names for over fifteen millions reported organic compounds and can be devised for the millions of organic compounds yet to be synthesized.

IUPAC method considers the arrangement of carbon atoms, types and positions of functional groups and other distinctive features of the compound to generate a standard name.

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. $(-\text{COOH}) > (-\text{CHO}) > (\text{C} = \text{O}) > (-\text{OH}) > (-\text{NH}_2) > (-\text{O}-) > (=) > (\equiv)$.

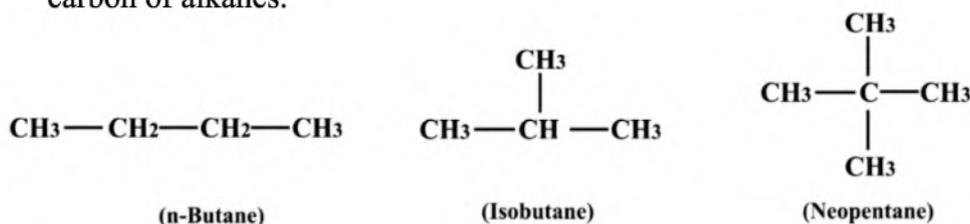
4.4 NOMENCLATURE OF ALKANES

Common System

In this system, all the carbon atoms present in the structure are included in the name, regardless of whether these carbon atoms are attached to each other in straight chain or in a branch form.



- (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. $-\text{CH}_3$) 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.



IUPAC System

The IUPAC names of alkane family is ended with the suffix “ane”. The first four members of this group of organic compounds are written by their trivial names (methane ethane, propane and butane). From the fifth onwards alkanes are named by prefixing the Greek numerals pent (five), hex (six), hept (seven), oct (eight) etc. indicating the number of carbons presents in the molecule to the suffix “ane”.

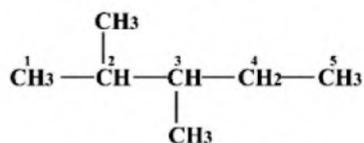
When naming a specific alkane, by IUPAC system it is important to consider the following fundamental rules.

- (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.

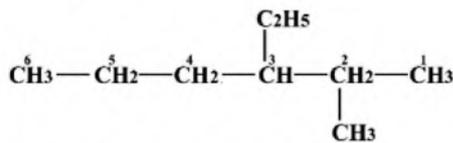


(v) When two or more same substituents are attached to the carbon chain, indicate the quantity of each substituent by using di, tri and so forth.

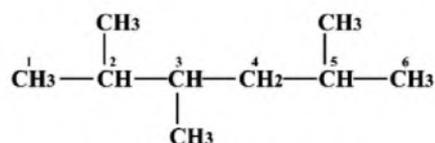
(vi) Prefix cyclo is used to name cycloalkanes.



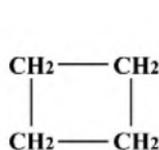
(2, 3-Dimethylpentane)



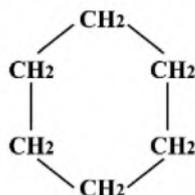
(3-Ethyl-2-methylhexane)



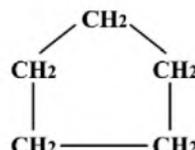
(2, 3, 5-Trimethylhexane)



(Cyclobutane)



(Cyclohexane)

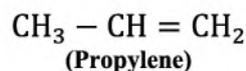
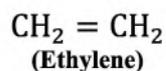


(Cyclopentane)

4.5 NOMENCLATURE OF ALKENES

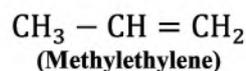
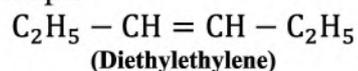
Common system

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



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

For example



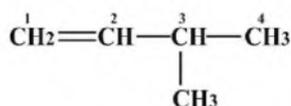


IUPAC System

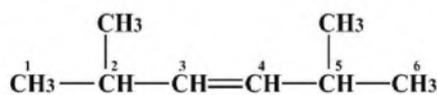
In the IUPAC naming of alkene the suffix “ene” is used to indicate the presence of double bond.

Consider the following general rules as a guidelines for naming alkene molecule according to IUPAC system.

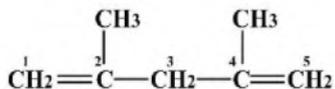
- (i) Select the longest carbon chain which must contain double bonded carbon atoms.
- (ii) The numbering of the longest chain starts from that end nearest to the carbon-carbon double bond irrespective of the location of alkyl radicals.
- (iii) Indicate the position of double bond by specifying the location 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”.



(3-Methyl-1-butene)



(2, 5-Dimethyl-3-hexene)



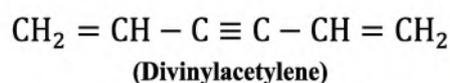
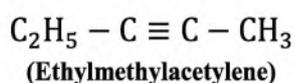
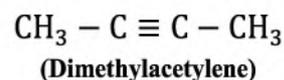
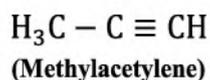
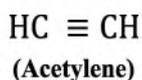
(2, 4-Dimethyl-1, 4-pentadiene)

4.6 NOMENCLATURE OF ALKYNES

Common System

In common system, the first member of alkyne family is named as acetylene (C_2H_2). The name of higher alkynes are derived from acetylene by considering the branched carbon atoms as alkyl radicals.

For example

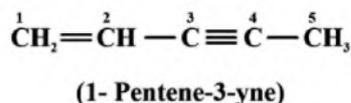
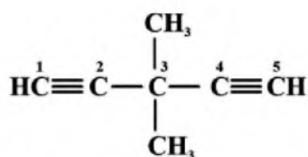
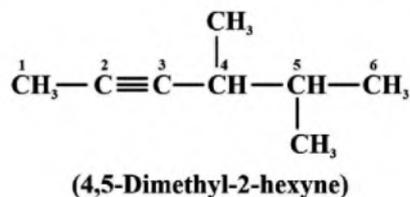
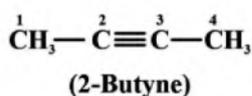




IUPAC System

To write IUPAC names of alkynes, it is necessary to consider the following essential rules.

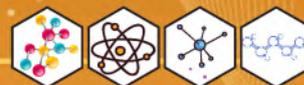
- (i) Select the longest continuous carbon chain which must include both the carbon atoms containing triple bond.
- (ii) The numbering of carbon chain starts from the terminal which is nearest to the carbon-carbon triple bond.
- (iii) Write the name of parent alkanes for the same number of carbon atoms, 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.



Self-Assessment

Name the following compounds by IUPAC method.

- > $(\text{CH}_3)_2\text{CH}-(\text{CH}_2)_3-\text{CH}(\text{CH}_3)_2$
- > $\text{CH}_2 = \text{C}(\text{CH}_3) - \text{CH} = \text{C}(\text{CH}_3) - \text{CH}_3$
- > $\text{CH} \equiv \text{C} - \text{CH}_2 - \text{C} \equiv \text{C} - \text{CH}_3$
- > $\text{CH}_2 = \text{C}(\text{CH}_3) - \text{CH}_2 - \text{C} \equiv \text{CH}$

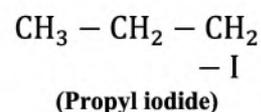
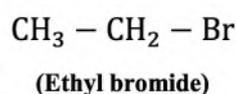
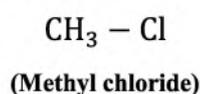


4.7 NOMENCLATURE OF ALKYL HALIDES

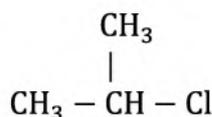
Alkyl halides are the derivatives of alkanes in which one or more hydrogen of alkanes are replaced by halogen atom.

Common System

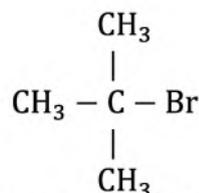
The common name of an alkyl halide is formed by naming the alkyl group first, followed by the term “halide”.



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.

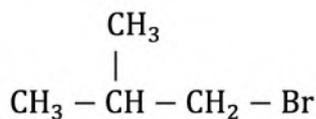


(sec-Propyl chloride)

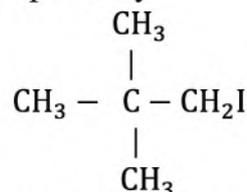


(tert-Butyl bromide)

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



(Isobutyl bromide)



(Neo pentyl iodide)

IUPAC System

In IUPAC system alkyl halides are named as haloalkanes, where halo is chloro, bromo, iodo etc. When naming alkyl halides according to IUPAC system, it is important to adhere to the following rules.

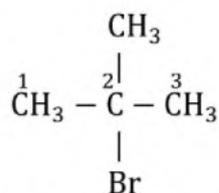
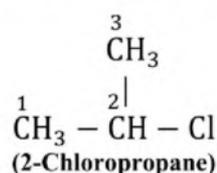
- (i) Determine the longest carbon chain that contains the carbon atom directly bonded to halogen.
- (ii) Number the carbon atoms in the chain from the end closest to the halogen atom.



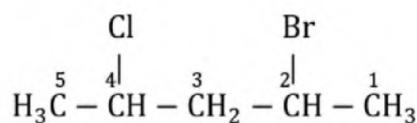
- (iii) When a double or triple bond is present in the halogenated carbon chain it is recommended to number the chain from the end nearest to the double or triple bond.
- (iv) Prefix di, tri, tetra etc are used to indicate the number of halogens attached to the main carbon chain.
- (v) When two different halogens are attached to the carbon chain at the same position from opposite ends, the halogen name will be written by its alphabetical order.



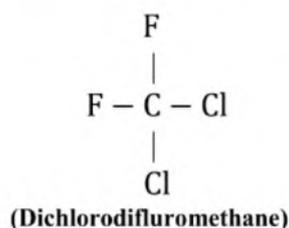
(Bromoethane)



(2-Bromo-2-methylpropane)



(2-Bromo-4-chloropentane)



DO YOU KNOW?

Dichlorodifluoromethane (CCl_2F_2) has been used as a refrigerant gas. It is now replaced by some other environmental friendly alternatives.

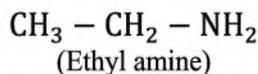
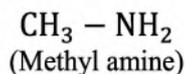
4.8 NOMENCLATURE OF AMINES

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

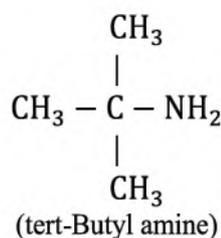
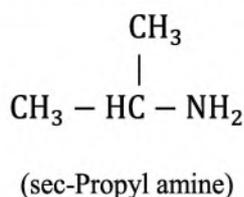


Common System

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



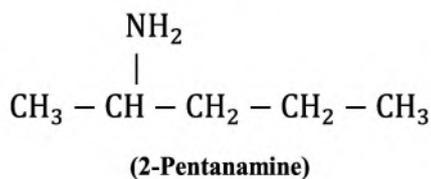
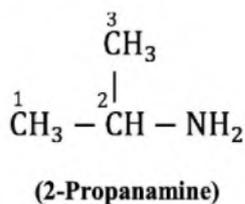
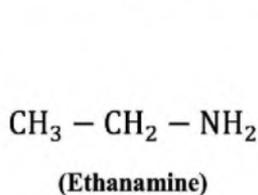
The prefix sec. and tert. are used if the carbon atom bonded to nitrogen is further attached with two or three alkyl radicals.



IPUAC System

In IUPAC system, primary amines are named as alkanamine and based on the following rules.

- (i) Select the longest carbon chain that contain the carbon atom directly bonded to $-\text{NH}_2$ group.
- (ii) Write the name of compound by replacing the ending "e" of alkane chain by adding the suffix "amine".



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

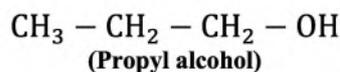
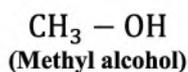


4.9 NOMENCLATURE OF ALCOHOLS

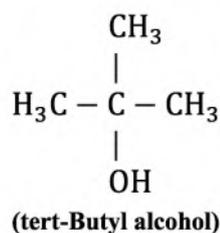
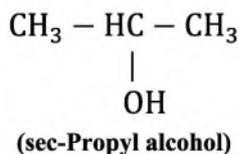
Organic compounds that contain one or more hydroxyl (-OH) functional group attached to the carbon chain are called alcohols.

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".



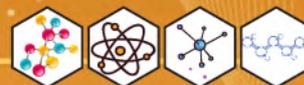
If the carbon atom bearing the hydroxyl group is directly connected to two or three other carbon atoms, the term secondary and tertiary is used as a prefix.



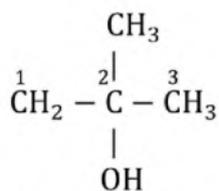
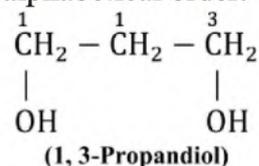
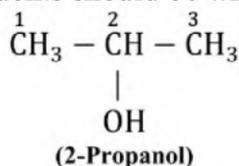
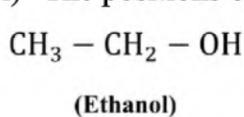
IUPAC System

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

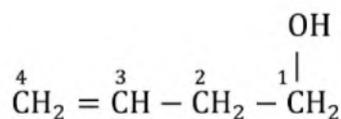
- (i) Identify the longest continuous carbon chain that include the carbon atom bearing the hydroxyl group (-OH).
- (ii) Number the carbon atoms in the chain starting from the end nearest to the hydroxyl group.
- (iii) The end "e" of the parent alkane is replaced by "ol".
- (iv) If the molecule of alcohol 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.



(2-Methyl-2-propanol)

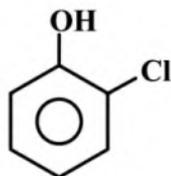


(3-Buten-1-ol)

4.10 NOMENCLATURE OF PHENOLS

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

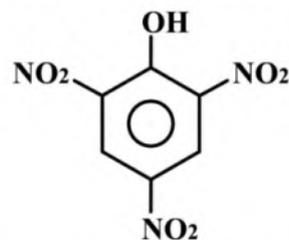
In the IUPAC nomenclature system, the parent molecule is referred phenol while numbering the substituents, the hydroxyl group (OH) is assigned the default first position. The term ortho, (-o), meta (-m) and para (-p) may be used for mentioning the position of substituents. It is important to note that certain phenols are still used by their trivial names in IUPAC system of nomenclature.



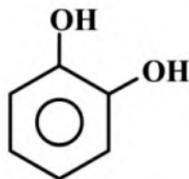
(2-Chlorophenol)
(o-Chlorophenol)



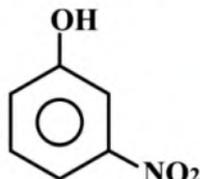
(4-Methylphenol)
(p-Cresol)



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



(1, 2-Benzenediol)
(Catechol)

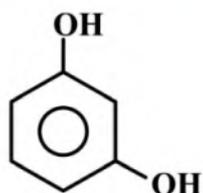


(3-Nitrophenol)
(m-Nitrophenol)



DO YOU KNOW?

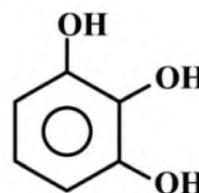
Resorcinol is an important component of hair dyes. It helps in the development of colour by reacting with hydrogen peroxide.



(1, 3-Benzenediol)
(Resorcinol)



(1, 4-Benzenediol)
(Hydroquinone)



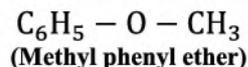
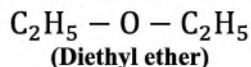
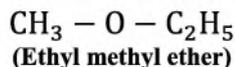
(1, 2, 3-Benzenetriol)
(Pyrogallol)

4.11 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'.

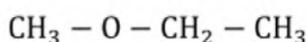
Common System

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.

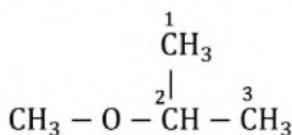


IUPAC System

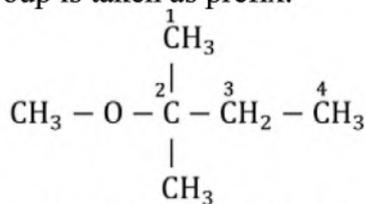
In IUPAC system of nomenclature, ethers are referred to as alkoxy derivatives of alkanes. The alkyl group of larger number of carbon atoms is considered as the main carbon chain whereas the smaller alkyl group, along with its oxygen is named as alkoxy group. The alkoxy group is taken as prefix.



(Methoxyethane)



(2-Methoxypropane)



(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



4.12 NOMENCLATURE OF ALDEHYDES AND KETONES

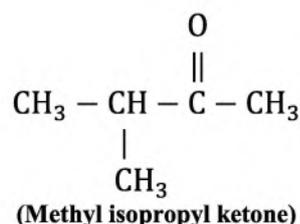
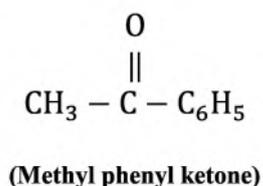
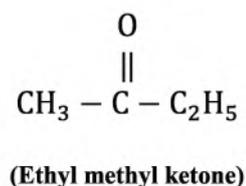
Aldehydes and ketones are characterized by the presence of a carbonyl group. (>C=O). Aldehydes have carbonyl group at the end of carbon chain whereas ketones have the carbonyl group within the carbon chain.

Common System

The common name of aldehyde is derived from the corresponding parent carboxylic acid by replacing -ic acid with the aldehyde. For example

Parent Carboxylic Acid	Aldehyde
$\begin{array}{c} \text{O} \\ \\ \text{H} - \text{C} - \text{OH} \\ \text{(Formic acid)} \end{array}$	$\begin{array}{c} \text{O} \\ \\ \text{H} - \text{C} - \text{H} \\ \text{(Formaldehyde)} \end{array}$
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3 - \text{C} - \text{OH} \\ \text{(Acetic acid)} \end{array}$	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3 - \text{C} - \text{H} \\ \text{(Acetaldehyde)} \end{array}$

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.

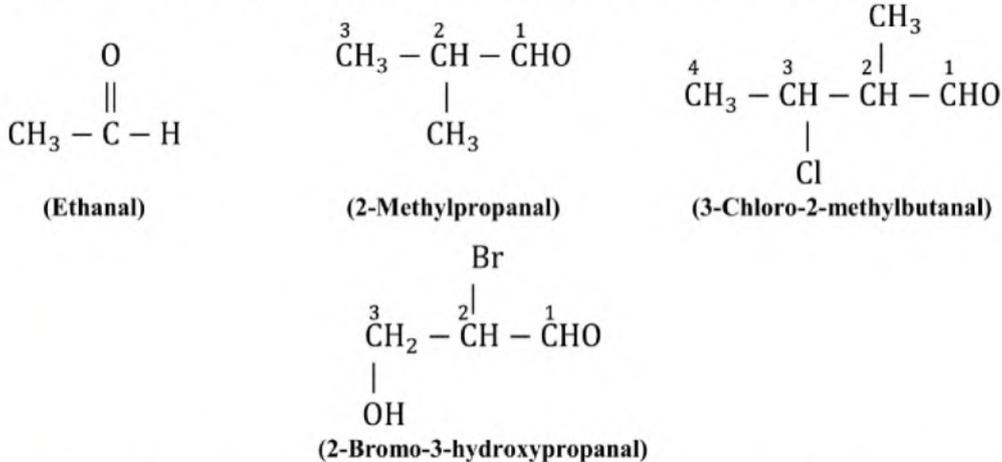


IUPAC System

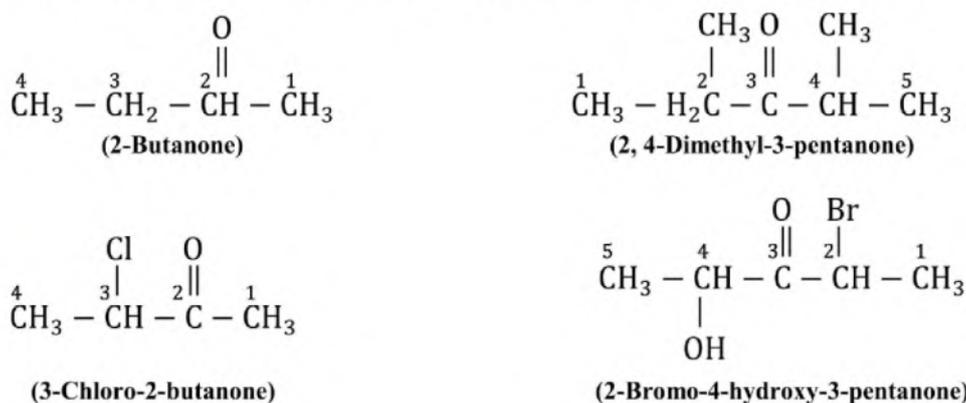
In this system aldehydes are named after the name of corresponding alkanes. The ending "e" of alkane being replaced by suffix -al. The longest carbon chain containing the -CHO group is chosen as the parent chain. The position of substituents are indicated by the numbers of carbon atoms to which they are attached and the carbon atom of the -CHO group is given number one.



The hydroxyl group take preference over double bond and double bond take preference over halogens and alkyl groups if present in the molecule.

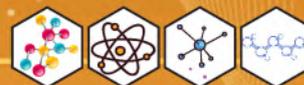


In the IUPAC naming of ketones, the longest carbon chain having the ketonic functional group is chosen as the parent chain and the ketone is named by replacing “-e” of the parent alkane with the suffix “one”. The position of substituents are indicated by numbers of the carbon atoms to which they are attached and the carbon of carbonyl group is given the lowest possible number.



4.13 NOMENCLATURE OF CARBOXYLIC ACIDS

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



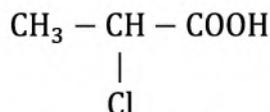
Common System

The common names of mono carboxylic acids refers to their sources rather than their chemical structures. Positions of substituents is designated by α , β and γ etc.

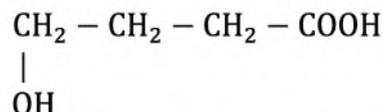
Common names of some carboxylic acids are given below.

Structure	Common name
HCOOH	Formic acid
CH ₃ COOH	Acetic acid
CH ₃ CH ₂ COOH	Propionic acid
CH ₃ (CH ₂) ₂ COOH	Butyric acid
CH ₃ (CH ₂) ₃ COOH	Valeric acid
CH ₃ (CH ₂) ₄ COOH	Caproic acid

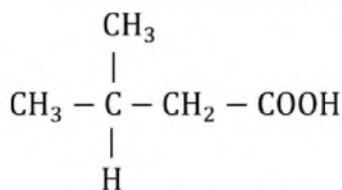
Common names of carboxylic acid are given as



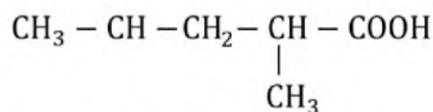
(α -Chloro propionic acid)



(γ -Hydroxy butyric acid)



(β -Methyl butyric acid)



(α , β -Dimethyl valeric acid)

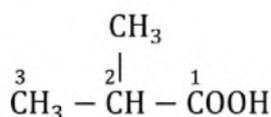
IUPAC System

The name of carboxylic acid in IUPAC system is referred as alcanoic acid. The longest continuous carbon chain containing the $-\text{COOH}$ group is considered the parent chain and the acid is named by replacing $-e$ of the corresponding alkane with "oic acid".

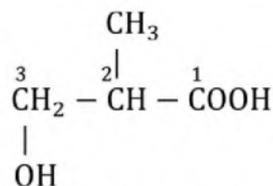
Double bond in the main chain are written by the ending $-\text{enoic acid}$ and its position is designated by numerical prefix. When two $-\text{COOH}$ groups are present in the main chain, use the prefix 'di' before the suffix oic acid. When a



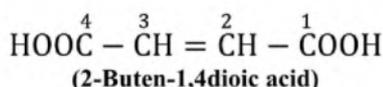
carboxylic acid is attached to benzene ring the parent ring, is named as benzoic acid.



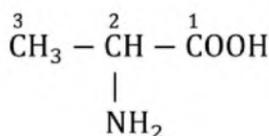
(2-Methyl propanoic acid)



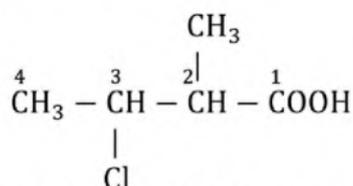
(3-Hydroxy-2-methyl propanoic acid)



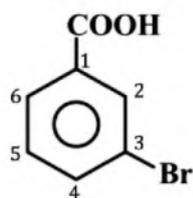
(2-Buten-1,4dioic acid)



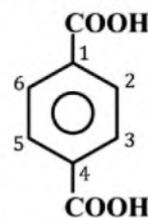
(2-Aminopropanoic acid)



(3-Chloro-2-methylbutanoic acid)



(3-Bromobenzoic acid)



(Benzen-1, 4-dioic acid)



Self-Assessment

Write the IUPAC name of the following molecules.

- $\text{CH}_3 - \text{CH}(\text{Br}) - \text{CH}(\text{CH}_3) - \text{CHO}$
- $\text{CH}_2 = \text{CH} - \text{C}(\text{CH}_3)_2 - \text{COOH}$
- $(\text{CH}_3)_2\text{CH} - \text{CO} - \text{C}(\text{CH}_3)_3$
- $\text{HOOC} - \text{CH}_2 - \text{HC} = \text{CHCOOH}$

4.14 NOMENCLATURE OF ESTERS

Esters are named as alkyl derivatives of carboxylic acids. Following steps should be noted for the naming of ester molecules.

- (i) Find the longest carbon chain which contains -COO- group.



DO YOU KNOW?

Ethyl acetate is naturally present in various fruits such as apples, pine apples and grapes etc.



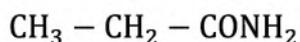
- (ii) Write the name of alkyl group which is attached to R-COO- chain.
 (iii) Name the carbon chain that contain ester functional group using “oate” as a suffix.

Common system of nomenclature of ester is quite similar with IUPAC method. Here “ate” is used as suffix with the main carbon chain.

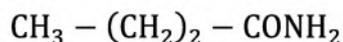
Structure of Ester	Common Name	IUPAC Name
HCOOC_2H_5	Ethyl formate	Ethyl methanoate
$\text{CH}_3 - \text{CH}_2 - \text{COO} - \text{CH}_3$	Methyl propionate	Methyl propanoate
$\text{CH}_3(\text{CH}_2)_2\text{COOC}_2\text{H}_5$	Ethyl butyrate	Ethyl butanoate
$\text{CH}_3\text{COOCH}(\text{CH}_3)_2$	Isopropyl acetate	Isopropyl ethanoate

4.15 NOMENCLATURE OF AMIDE

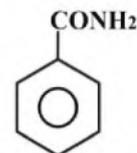
Amides are the derivate of carboxylic acids formed by replacing –OH group of carboxylic acid by –NH₂ group. The nomenclature of amide is based on replacing the suffix -oic acid with amide. For example



(Propanamide)



(Butanamide)

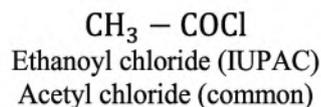
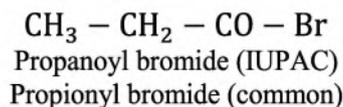


(Benzamide)

4.16 NOMENCLATURE OF ACYL HALIDES

Acyl halides or acid halides are derived from carboxylic acids. They are characterized by the presence of a halogen atom attached to acyl group(R-CO-).

When naming an acyl halide, the work begins with the name of the corresponding carboxylic acid. In both common and IUPAC method the ic acid ending the carboxylic acid is replaced by –yl, and then name the specific halide group. For example





SOCIETY, TECHNOLOGY AND SCIENCE

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.



SUMMARY

- A wide range of organic compounds are derivatives of hydrocarbons and formed by substituting one or more hydrogen atom with hetero atom or group of atoms.
- The presence of distinct functional groups, variable chain lengths, branching, cyclic structures and numerous isomerism has led to synthesis of millions of organic compounds.
- IUPAC naming of organic compounds was first introduced at the Geneva conference in 1892.
- 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.



- The prefix n, Iso and Neo are utilized for the common naming of alkanes where required.
- In IUPAC system the priority for the numbering of carbon chain on the basis of functional group and other substituents is given as.
 $(-\text{COOH}) > (-\text{CHO}) > (\text{C} = \text{O}) > (-\text{OH}) > (-\text{NH}_2) > (-\text{O}-) > (=) > (\equiv)$
- When writing the IUPAC name of organic compounds, first write the name of all prefixes, then name of the carbon chain and finally write the name of suffix.
- In IUPAC system, the suffix of alcohol is $-\text{ol}$, aldehyde is $-\text{al}$, ketone is $-\text{one}$, carboxylic acid is $-\text{oic acid}$ and ester is $-\text{oate}$.

EXERCISE

Multiple Choice Questions

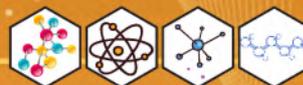
- Which of the following molecule possess acyl functional group:
(a) $\text{R}-\text{CO}-\text{X}$ (b) $\text{R}-\text{CONH}_2$
(c) $\text{R}-\text{COO}-\text{CH}_3$ (d) $\text{R}-\text{CO}-\text{R}$
- A hydrocarbon with the molecular formula C_7H_{12} is possibly:
(a) Heptane (b) Heptene
(c) Heptyne (d) Hepta diene
- An organic compound possesses the structural formula $\text{CH}_3\text{CH}=\text{CH}-\text{C}\equiv\text{CH}$, 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
- IUPAC name of isopropyl alcohol is:
(a) 1-propanol (b) 2-propanol
(c) 1-butanol (d) 2-butanol
- Resorcinol is a phenol, it contains two $-\text{OH}$ 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

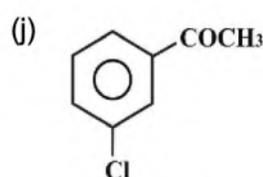
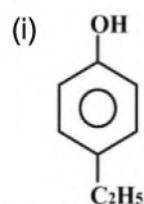
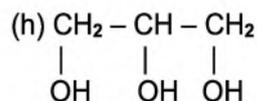
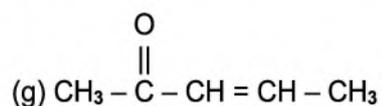
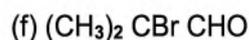
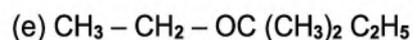
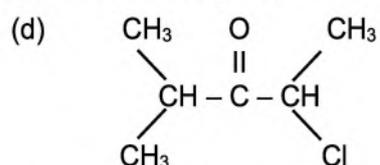
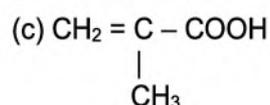
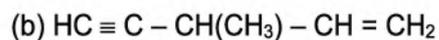
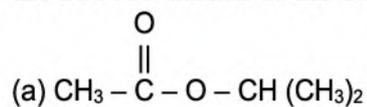
Short Questions

1. Why IUPAC system of nomenclature is preferred on common system of naming of organic compounds?
2. Write the name of five organic families and mention the functional group present in them.
3. Write down basic rules for IUPAC naming of organic compound.
4. We often use the term Iso and Neo in the common system of naming of alkanes. Explain with example
5. Write the common names of first five members of carboxylic 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.



Descriptive Questions

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



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

(a) Ethyl neo-pentyl ether

(b) Resorcinol

(c) Picric acid

(d) Isopropylbutanoate

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

(f) α, β -dimethyl butyric acid

(g) Butyraldehyde

(h) 3-Chlorobenzamide

(i) Butanoyl iodide

(j) 1, 2, 3-benzentriol

(k) Ethyl isopropyl ketone

(l) α -Methyl butyraldehyde

(m) α -Chloro- β -methyl valeric acid

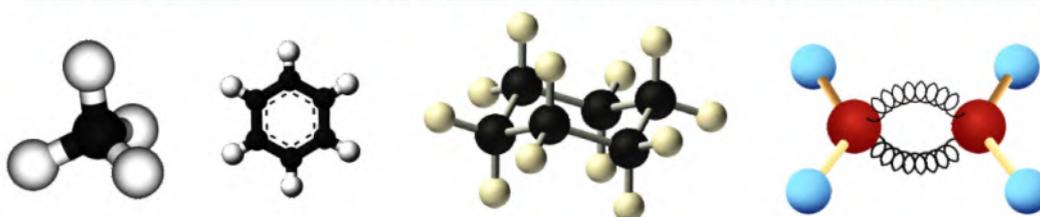


CHAPTER 5

INTRODUCTION TO HYDROCARBONS



Teaching Periods	22	Assessment	02	Weightage %	18
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Students will be able to:

- ✓ Classify hydrocarbons as aliphatic and aromatic. (Understanding)
- ✓ Explain the shapes of alkanes and cycloalkanes exemplified by ethane and cyclopropane. (Applying)
- ✓ Explain unreactive nature of alkanes towards polar reagents. (Applying)
- ✓ Define homolytic and heterolytic fission, free radical initiation, propagation and termination. (Remembering)
- ✓ Describe the mechanism of free radical substitution in alkanes exemplified by methane and ethane. (Understanding)
- ✓ Explain what is meant by a chiral centre and show that such a centre gives rise to optical isomerism. (Understanding)
- ✓ Identify chiral centers in given structural formula of a molecule. (Analyzing)
- ✓ Analyze glucose molecules by optical activity. (Applying)
- ✓ Explain the terms isomerism and structural isomerism with suitable examples. (Remembering)
- ✓ Define stereoisomerism (cis and trans) with example of alkene. (Remembering)
- ✓ Explain shape of ethene molecule in terms of sigma and pi C-C bonds. (Understanding)
- ✓ Describe the structure and reactivity of alkenes as exemplified by ethene. (Applying)
- ✓ Draw all possible isomers of molecular formula C_4H_{10} , C_5H_{12} , C_4H_8 , C_5H_{10} , C_4H_6 , C_5H_8 with their IUPAC names. (Applying)
- ✓ Draw all possible isomers of molecular formula C_3H_7OH , C_3H_7Cl , $C_4H_9NH_2$ with their IUPAC names. (Applying)
- ✓ Draw all possible isomers of molecular formula C_2H_6O , C_3H_8O , $C_2H_4O_2$ with their IUPAC names. (Applying)
- ✓ Explain dehydration of alcohols and dehydrohalogenation of RX for the preparation of ethene. (Understanding)
- ✓ Describe the chemistry of alkenes by the following reactions of ethene: Hydrogenation, hydrohalogenation, hydration, halogenation, halohydrin formation, epoxidation, ozonolysis, polymerization. (Understanding)
- ✓ Explain the shape of benzene molecule (molecular orbital aspect). (Understanding)
- ✓ Describe what is meant by the term delocalized electrons in the context of the benzene ring. (Understanding)
- ✓ Describe addition reactions of Benzene (with hydrogen and halogen). (Understanding)
- ✓ Describe the general mechanism of electrophilic substitution in benzene. (Understanding)
- ✓ Discuss the electrophilic reactions of benzene and toluene (nitration, sulphonation, halogenation, Friedel Craft's alkylation and acylation). (Applying)
- ✓ Apply the knowledge of positions of substituents in the electrophilic substitution of benzene. (Applying)
- ✓ Compare the reactivity of alkanes, alkenes and alkynes. (Analyzing)
- ✓ Discuss the shape of acetylene in terms of sigma and pi bonds. (Applying)
- ✓ Describe the preparation of alkynes using elimination reactions. (Applying)
- ✓ Describe acidity of acetylene. (Understanding)
- ✓ Discuss reaction of alkynes by hydrogenation, hydrohalogenation, hydration, bromination, ozonolysis, and reaction with metals. (Understanding)



INTRODUCTION

Organic compounds made up of hydrogen and carbon atoms are known as hydrocarbons. Hydrocarbons are obtained from fossil fuels like coal, petroleum and natural gases which serve as the primary source of energy for generating heat, electricity and fuel for transportation.

Hydrocarbons are considered as the mother of thousands of organic compounds since the introduction of functional groups to the basic hydrocarbon chain creates new molecules with different properties and structures.

The refining of crude oil yields hundreds of hydrocarbons. Methane is the most basic hydrocarbon. It is the main constituent of natural gas and is commonly found in marshy areas. Hexane, heptanes and octane are derived from petroleum and employed as automotive fuel. Paraffin wax obtained from petroleum has various uses, including as a component in candles, polishes, lubricants and cosmetics. Ethyne is used for welding purposes, ethene is used for ripening fruits. Cycloalkanes have versatile uses, serving as solvents, lubricants and even fuel sources.

5.1 TYPES OF HYDROCARBONS

Hydrocarbons are classified based on their molecular structure and the types of bonds present between carbon atoms. They can be categorized into two main groups; aliphatic hydrocarbons and aromatic hydrocarbons.

Aliphatic Hydrocarbons

It is a class of hydrocarbon in which carbon atoms are arranged in straight or branched chain through single, double or triple bonds. These are often called as open chain hydrocarbons. The name aliphatic was given to those compounds that were initially extracted from fat and oil.

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



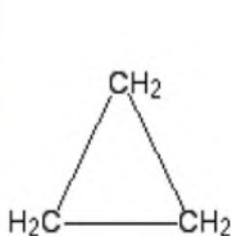
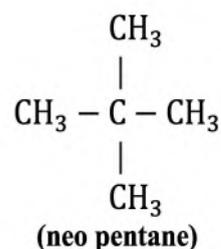
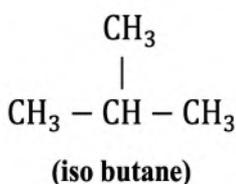
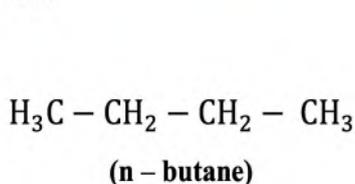
DO YOU KNOW?

Gasoline is a fuel used in automobiles. It chemically consists of C_5 to C_8 carbon atoms. The grading of gasoline is a measure of its resistance to knocking in an internal combustion engine and is referred as the octane number.

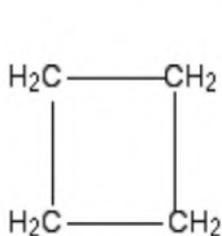


Saturated Hydrocarbons

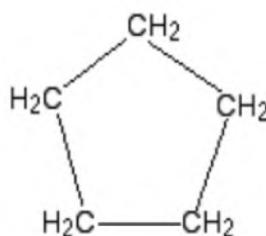
“In these hydrocarbons, all carbon atoms are attached to each other by a single bond only”. These are further classified into alkanes and cycloalkanes.



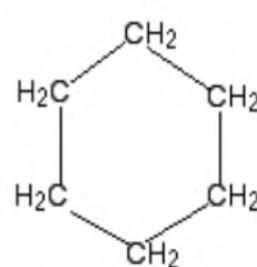
(cyclopropane)



(cyclobutane)



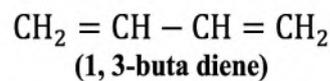
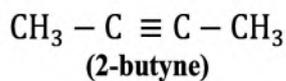
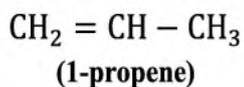
(cyclopentane)



(cyclohexane)

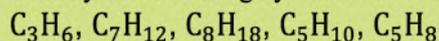
Unsaturated Hydrocarbons

“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 alkenes and alkynes. The general formulas for their homologous series is C_nH_{2n} and $\text{C}_n\text{H}_{2n-2}$ respectively.



Self-Assessment

Identify the following hydrocarbons as saturated and unsaturated.





Aromatic Hydrocarbons

“Aromatic compounds are those which characterized by a cyclic arrangement of atoms that are connected by alternating double bonds they generally follow the Huckle rule ($4n+2\pi$ electrons)”. The term aromatic originates from Greek word “aroma” means fragrant, 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.



DO YOU KNOW?

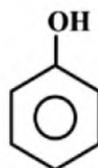
Huckel's Rule states that aromaticity is exhibited by planar cyclic compounds with $4n+2$ π electrons, where "n" is a non-negative integer. These compounds possess enhanced stability due to the delocalization of π electrons, making them highly aromatic.



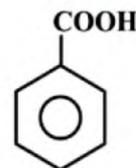
(Benzene)



(Toluene)



(Phenol)



(Benzoic acid)

5.2 ALKANES AND CYCLO ALKANES

Saturated hydrocarbons are represented by both alkanes and cycloalkanes. The fundamental difference between these two lies in the way their carbon atoms are arranged. Alkanes have open-chain or straight chain structures. Cycloalkanes on the other hand, have a close-ring or cyclic structure.

Cycloalkanes are typically nonpolar similar to alkanes. Despite both being saturated hydrocarbons, cyclopropane exhibits distinct properties compared to alkanes. Cycloalkanes are named as cyclopropane, cyclobutane, cyclopentane and cyclohexane etc.

5.2.1 Physical Properties

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 higher than that of branched chain alkanes because straight chain alkanes are more extended, which allows the greater surface area.
- (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.

Physical properties of cycloalkanes

- (i) Cycloalkanes of C_3 and C_4 carbons are gases, while cycloalkanes of C_5 or more carbon atoms are liquids.
- (ii) The boiling point of cycloalkanes is lower than that of straight chain alkanes of comparable molar mass due to the ring strain.

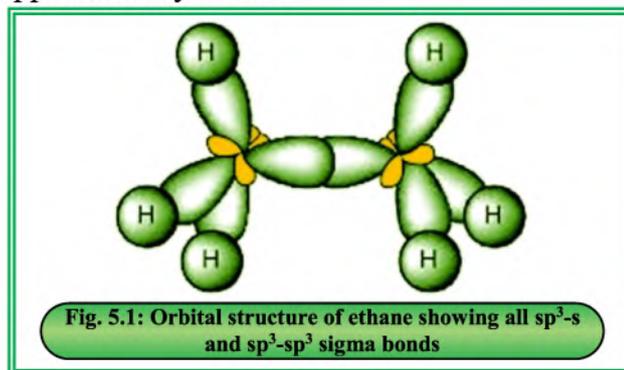
5.2.2 Structure

Structure of Alkanes

Alkanes are open chain saturated hydrocarbons. Each carbon atom in alkanes is tetrahedrally bonded with hydrogen atoms and other carbon atoms.

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

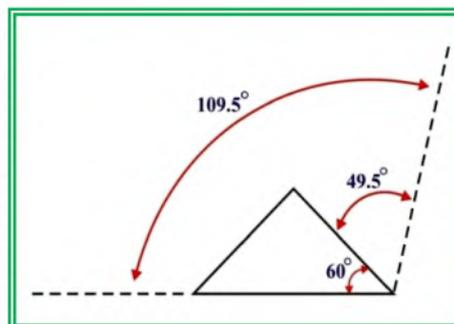
Ethane is composed of two carbon atoms and six hydrogen atoms (C_2H_6). Each carbon atom in ethane is sp^3 hybridized containing four sp^3 hybrid orbitals. These four sp^3 hybrid orbitals are arranged in a tetrahedral fashion. Out of four sp^3 hybrid orbitals of each carbon atom, three sp^3 hybrid orbitals 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 \AA , and the bond angle between carbon, carbon and hydrogen atoms is approximately 109.5° .





Structure of Cycloalkanes

Cyclopropane is the smallest and simplest cycloalkanes with a ring composed of three carbon atoms and six hydrogen atoms. The carbon atoms in cyclopropane are arranged in a trigonal geometry with an internal angle of 60° , which is quite smaller than the bond angle (109.5°) exist in alkanes.



5.2.3 Reactivity

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.

Reactivity of Cycloalkanes

Cycloalkanes are very similar to the alkanes in reactivity, except for the very small ones - especially cyclopropane. Cyclopropane is much more reactive due bond angle strain in ring structure.



Self Assessment

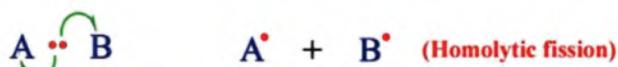
- (i) Draw the structure of cyclopropane and explain the angle strain in it.
- (ii) Boiling point of cyclopropane is less than n-propane explain why?



5.3 RADICAL SUBSTITUTION REACTIONS

Before explaining free radical reaction, we need to understand the concepts of homolytic and heterolytic fission.

“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.



5.3.1 Reaction Mechanism

Free radical substitution reactions are typically carried out by homolytic fission. The reaction between methane and chlorine in U.V light or at high temperature takes place through free radical reaction. The mechanism of free radical reaction consists of following three steps.

Step-1: Chain Initiation

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



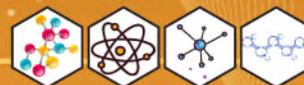
Step-2: Chain Propagation

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.



DO YOU KNOW?

The halogenation of ethane is more difficult than that of methane because of more product formation, firstly due to the presence of six hydrogen atoms in ethane instead of four in methane and secondly because isomerism is possible at the dichlorination step.



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

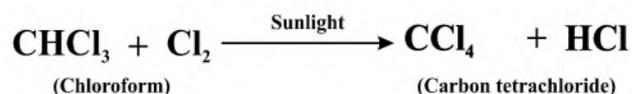
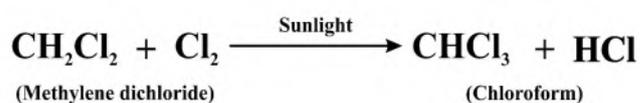
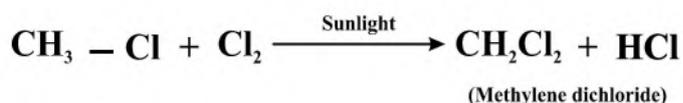
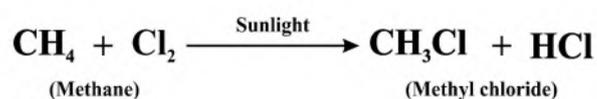


Step-3: Chain Termination

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



In reality, the reaction does not halt after the production of methyl chloride; rather, the remaining three hydrogen atoms in the methyl chloride molecule are substituted by chlorine atoms before the reaction stops.





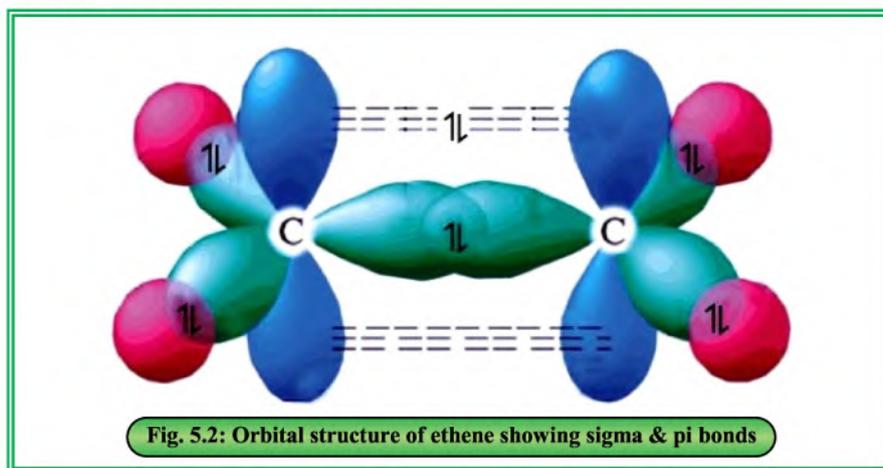
5.4 ALKENES

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.

5.4.1 Structure of Ethene

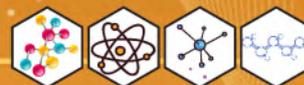
To describe the structure of alkene, ethene can be taken as a representative example.

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.



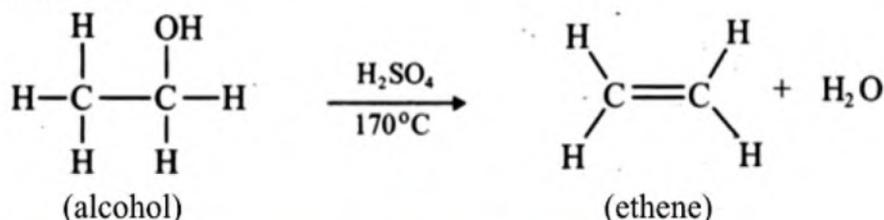
5.4.2 Preparation of Alkenes

Alkenes can be prepared by dehydration of alcohol and dehydrohalogenation of alkyl halides.



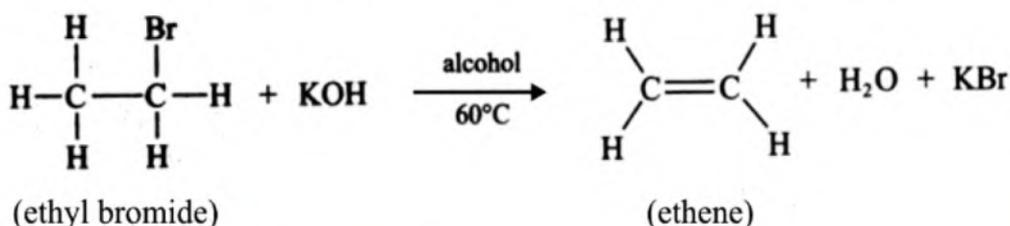
5.4.2.1 Dehydration of Alcohol

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.



5.4.2.2 Dehydrohalogenation of an 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.



5.4.3 Reactivity of Alkenes

“The higher reactivity of alkene as compared to alkane is attributed to the presence of a pi bond between the carbon atoms”. The pi bond is relatively weaker and requires less energy to break. Additionally the electron density associated with the pi bond is distributed above and below the carbon-carbon axis, making the pi electrons more exposed to an Electrophilic species. Consequently, alkenes readily react with electrophile making them more reactive than alkanes.

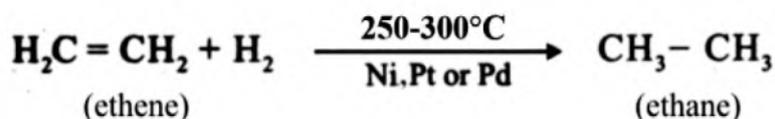
5.4.4 Reactions of Alkenes

Even though alkenes can undergo oxidation and polymerization reactions, the most frequently observed reactions for alkenes are those involving addition reactions.



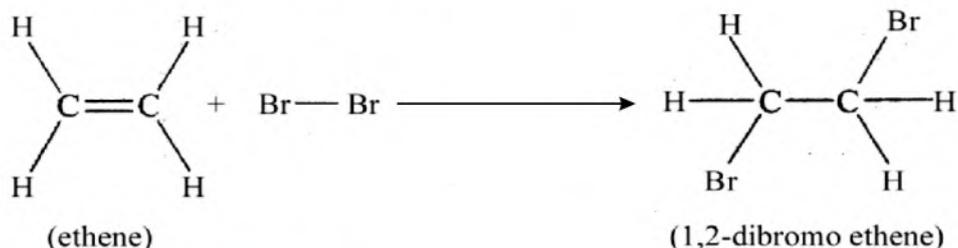
5.4.4.1 Hydrogenation

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.



5.4.4.2 Halogenation

The reaction of ethene with halogen is an addition reaction which gives a dihaloalkane. This reaction takes place in the presence of an inert solvent such as carbon tetrachloride or chloroform.

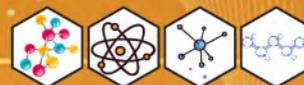


5.4.4.3 Hydrohalogenation

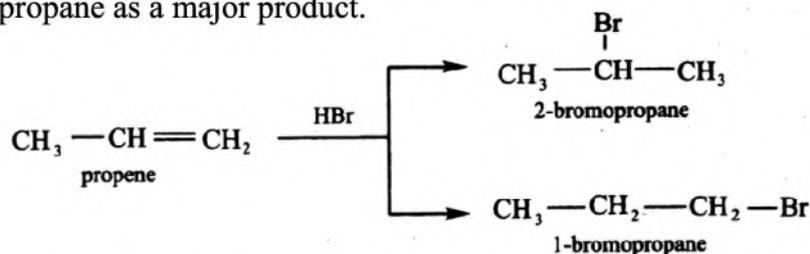
The addition of a halogen acid (HX) on an alkene to give an alkyl halide is known as hydrohalogenation of alkene.



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”**.



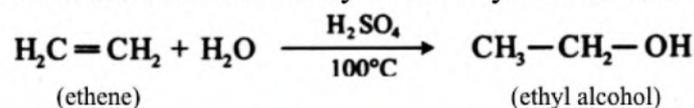
For example the reaction of propene with hydrogen bromide (HBr) gives 2-bromo propane as a major product.



The order of reactivity of halogen acid (HX) is $\text{HI} > \text{HBr} > \text{HCl}$.

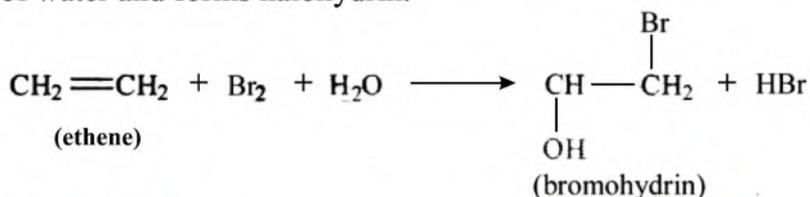
5.4.4.4 Hydration

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 $80\text{--}100^\circ\text{C}$.



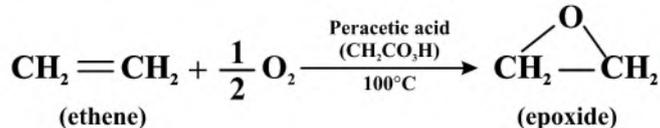
5.4.4.5 Halohydration (confirmatory test for alkene)

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



5.4.4.6 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.



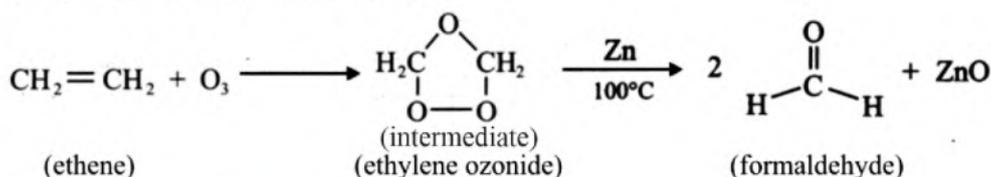
DO YOU KNOW?

Epoxides are used as versatile building blocks in the synthesis of pharmaceuticals, agrochemicals, and various fine chemicals, and they also serve as important intermediates in the production of polymers and surfactants.



5.4.4.7 Ozonolysis

Ozonolysis is a chemical reaction that involves the cleavage of an alkene or alkyne by ozone in the presence of reducing agent such as zinc. The reaction results in the formation of ozonide intermediates which are unstable and quickly decompose to form an aldehyde.



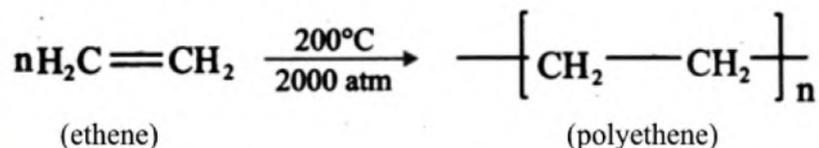
Self-Assessment

What major product obtained when

- (i) Propene reacts with hydrogen iodide
- (ii) Ethene reacts with chlorine water
- (iii) Ethylene reacts with ozone

5.4.4.8 Polymerization

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



5.5 ALKYNES

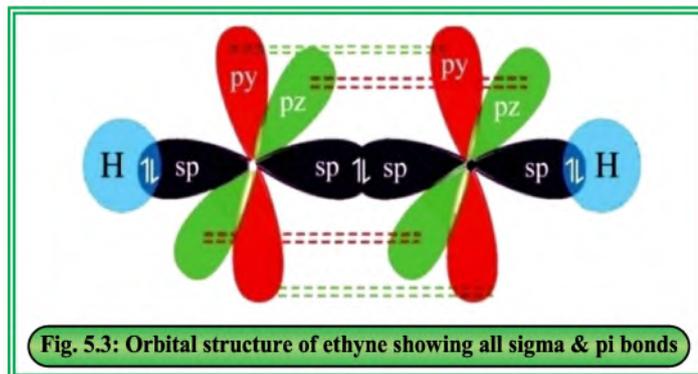
Alkynes are hydrocarbons that contain a triple bond between the two carbon atoms.

5.5.1 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 (P_y and P_z). 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° .



The bond length of the carbon-carbon triple bond ($\text{C}\equiv\text{C}$) in ethyne is approximately 1.20 \AA



5.5.2 Physical Properties

- 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.

5.5.3 Preparation of Alkynes by elimination reaction

Alkynes are generally synthesized through elimination reactions, which involve the removal of atoms or groups from two adjacent carbon atoms.

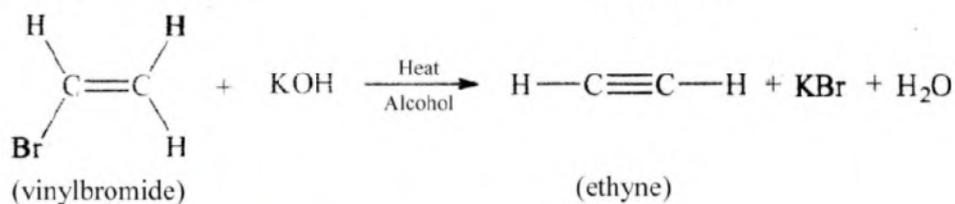
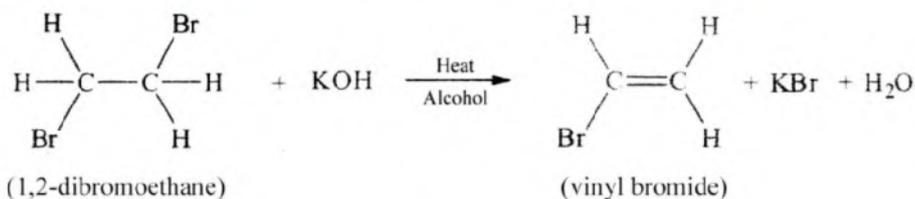
Dehydrohalogenation of Vicinal dihalide

When vicinal dihalide is heated with an alcohol solution of potassium hydroxide (KOH) to give an ethyne. This reaction involves the removal of two halogens and two hydrogens from adjacent carbon atoms.



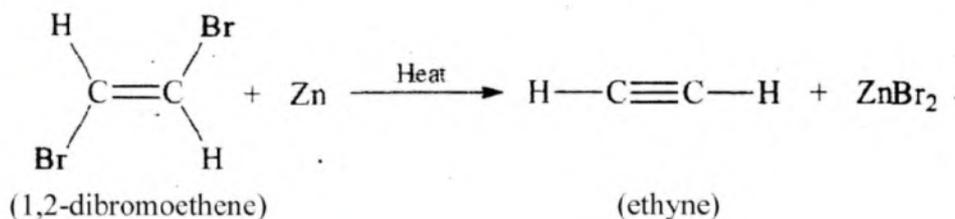
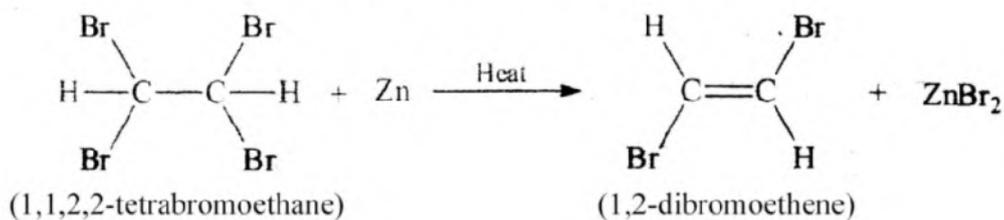
DO YOU KNOW?

When two halogen atoms are attached to two adjacent carbon atoms, it is called vicinal dihalide but if two halogen atoms are attached on the same carbon atom the molecule is said to be geminal dihalide.



Dehalogenation of Tetrahalides

A tetrahalide on heating with zinc dust forms ethyne.



5.5.4 Acidity of Terminal Alkynes

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

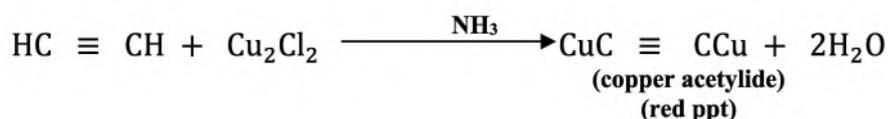
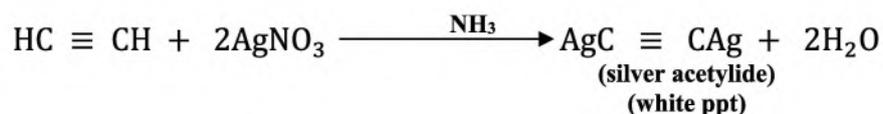
The sp hybridization of carbon in terminal alkyne, such as ethyne, results in their slight acidity. The 50% s character of sp hybrid orbital of carbon makes it slightly electronegative. It cause the hydrogen atom attached to it to be slightly electro positive. This polarity weakens the C-H bond making it easier for a base to abstract the hydrogen atom from terminal carbon.



Table 5.1 s-character and pka values of ethane, ethene and ethyne

Hydrocarbon	Type of Hybridization	% s-character	pka value
Ethane	sp ³	25	-
Ethene	sp ²	33	44
Ethyne	sp	50	25

The acidic nature of terminal alkynes leads to their reaction with metal containing compounds including ammonical silver nitrate and ammonical cuprous chloride.



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?

5.5.5 Addition reaction of alkynes

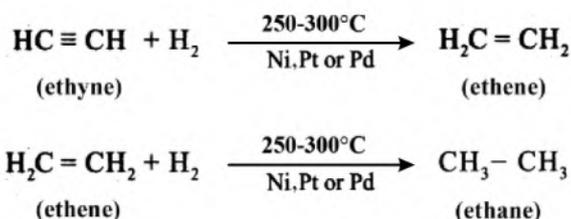
Alkynes undergo addition reactions similar to alkenes however, the reactivity of alkynes towards electrophilic reagents is relatively less than that of alkenes.



The carbon-carbon triple bond in alkyne comprises of one sigma and two pi bonds, with the electron density between the carbon atoms being exceptionally high causing the atoms to be drawn closer together. As a result the electrons in the pi bonds are less exposed compared with the alkene. Consequently, alkynes exhibit lower reactivity than alkenes.

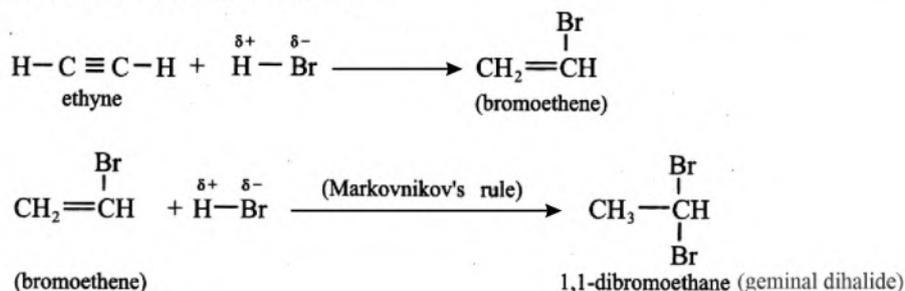
5.5.5.1 Hydrogenation

Alkyne reacts with hydrogen in the presence of metal catalysts such as nickel (Ni), platinum (Pt) and palladium (Pd) to give an alkene which then further reacts with another molecule of hydrogen to produce an alkane.



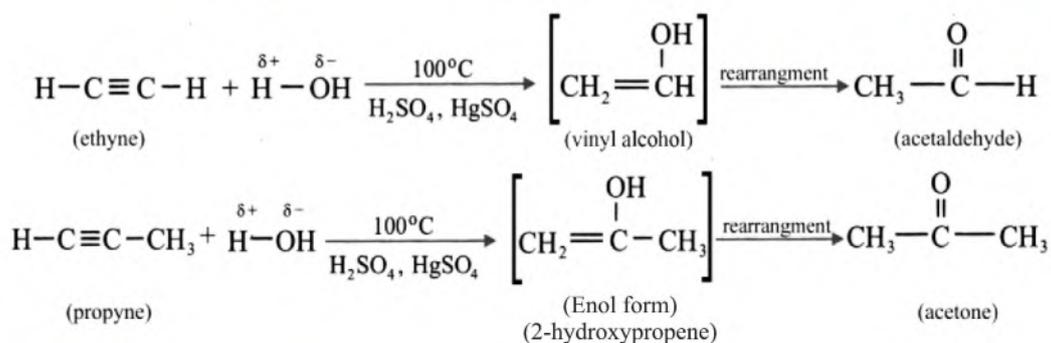
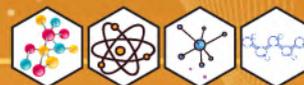
5.5.5.2 Hydrohalogenation

The final product of the reaction of an alkyne with hydrogen halide is a dihaloalkane, however, the reaction completes in two steps. The second step involves the Markovnikov's rule.



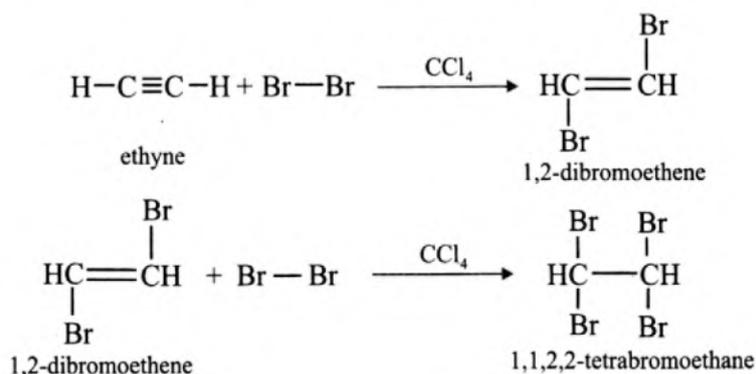
5.5.5.3 Hydration

When an alkyl halide undergoes reaction with water in the presence of mercurous sulphate and sulphuric acid, it forms an enol. This enol subsequently undergoes rearrangement, resulting in the formation of an aldehyde or ketone.



5.5.5.4 Bromination

The addition of bromine to an alkyne molecule gives a dibromo alkene which then absorbs another bromine molecule to produce tetrabromo alkane.



5.5.5.5 Ozonolysis

Ozonolysis is a reaction in which the pi bonds between carbon-carbon atoms are broken down by the addition of ozone (O_3). The ozonolysis of an alkyne initially gives an ozonide, which subsequently undergoes oxidation with hydrogen peroxide. This oxidation results in the formation of glyoxal.

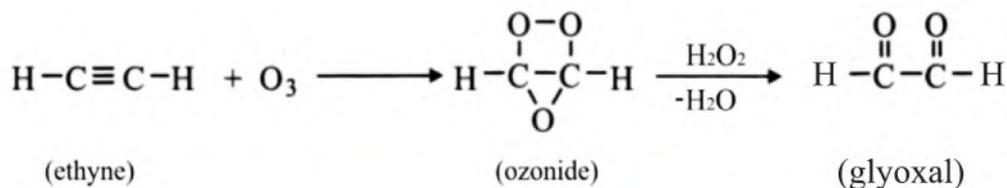




Table 5.2 Comparison of the reactivity of alkanes, alkenes and alkynes

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 .

5.6 ISOMERISM

“A wide range of organic compounds studied in organic chemistry exhibit the same molecular formula, yet differ in their structure or stereochemistry. 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

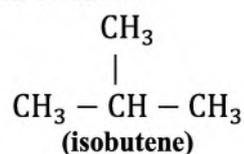
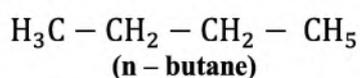
5.6.1 Structural Isomerism

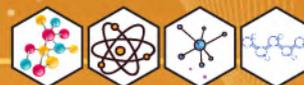
Organic molecules having the same molecular formula but differing in the way their atoms are connected to each other are called as structural isomers. These are further classified into the following types.

Chain isomers

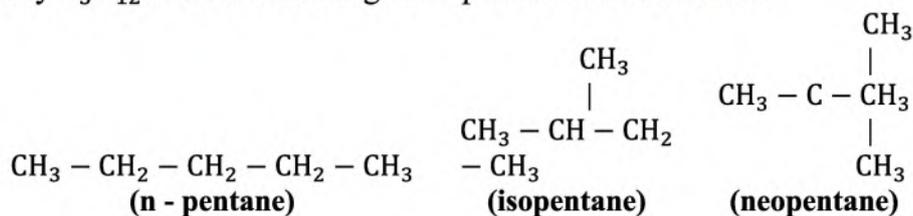
“It is a type of structural isomer in which the molecules differ from each other with respect to carbon skeleton”.

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





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



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.



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



Functional group isomers

“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.



Another example of molecule exhibiting functional group isomerism is C_3H_6O .

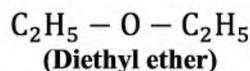
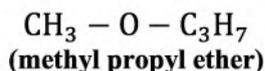


Metamerism

“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.



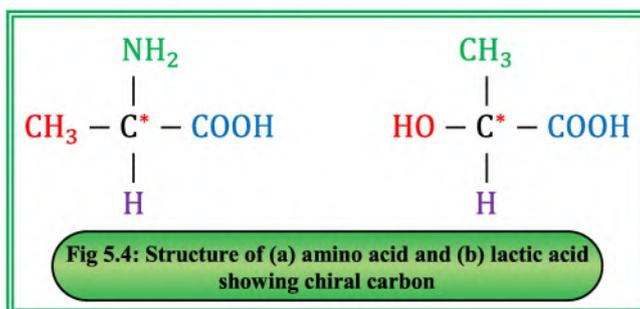
Self-Assessment

- 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.

5.6.2 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.

For example, in the molecules of amino acid and lactic acid four different groups are attached with the α -carbon as given in figure 5.4.



5.6.3 Optical Activity

Light is composed of waves that vibrate in multiple planes, however when this light passes through a polarizer, the waves are restricted to a single plane of vibration and this is now called as plane of polarized light.

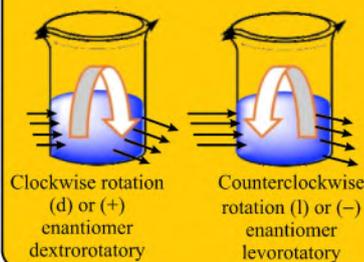
When a plane of polarized light is passed

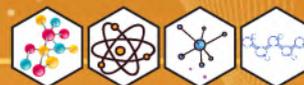


DO YOU KNOW?

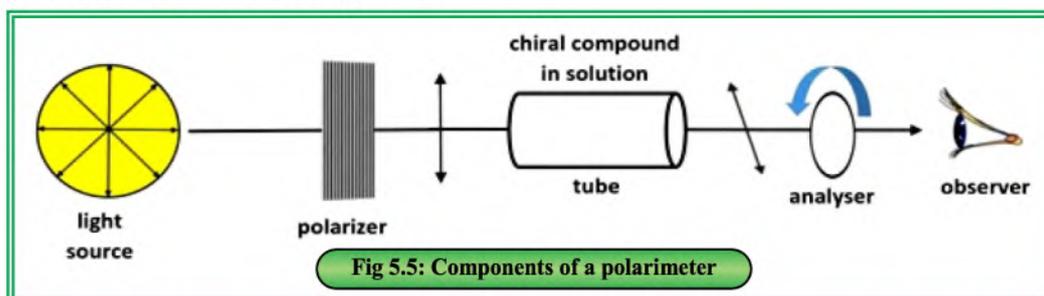
A racemic mixture is formed if both D and L isomers of a compound are present in equal amounts within a solution. The solution exhibits no rotation of polarized light.

A pair of enantiomer



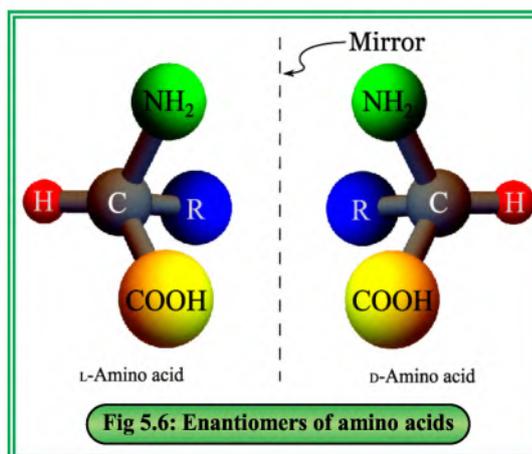


through a solution of organic compound that contain chiral carbon, the light is rotated either clockwise or anticlockwise direction at a certain degree. **“This property of rotating plane of polarized light when passes through a solution of a compound is known optical activity”**. The device used to measure the optical activity is known as polarimeter. The components of a polarimeter is shown in figure 5.5.



5.6.4 Optical Isomers

“Two compounds having the same molecular formula, same structure but differing from each other by the optical rotation of plane of polarized light are called optical isomers or enantiomers”. The compound that rotates 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 referred as levorotatory or L-isomer. These two optical isomers are mirror images to each other but not superimposable and are known as enantiomers (Fig:5.6).



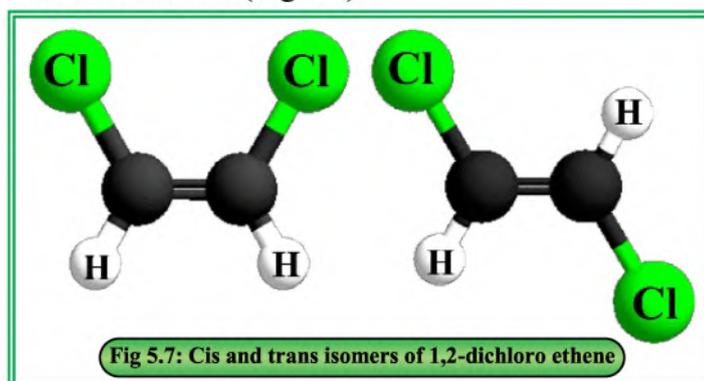
5.6.5 Stereoisomerism (Geometrical isomers)

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 or 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 whereas if the same groups lie on opposite direction in the molecule, this is referred as trans-isomer (Fig:5.7).



5.7 BENZENE AND ITS DERIVATIVES

Benzene is the simplest aromatic compound. It is a colourless, carcinogenic and highly inflammable liquid. It burns with black flames due to the presence of high carbon contents in the molecule. Its molecular formula is C_6H_6 . It was first isolated by Michael Faraday in 1825. The structure of benzene was suggested by Kekule in 1865. According to him **“benzene is a cyclic hexagonal molecule with alternative double bonds”**.

Huckel and certain other chemists studied on Kekule structures of benzene and introduced the term “resonance” within the benzene molecule. Hence the additional stability shown by benzene arises from the presence of delocalized pi electrons.

5.7.1 Physical Properties

- Benzene is a colourless liquid having molecular mass 78 g/mol.
- The melting point of benzene is $5.5^\circ C$ and boiling point is $80^\circ C$.
- The density of benzene is 0.88 g/cm^3 .
- Benzene is insoluble in water but soluble in organic solvents such as ether, acetone and chloroform.



5.7.2 Molecular orbital structure of benzene

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

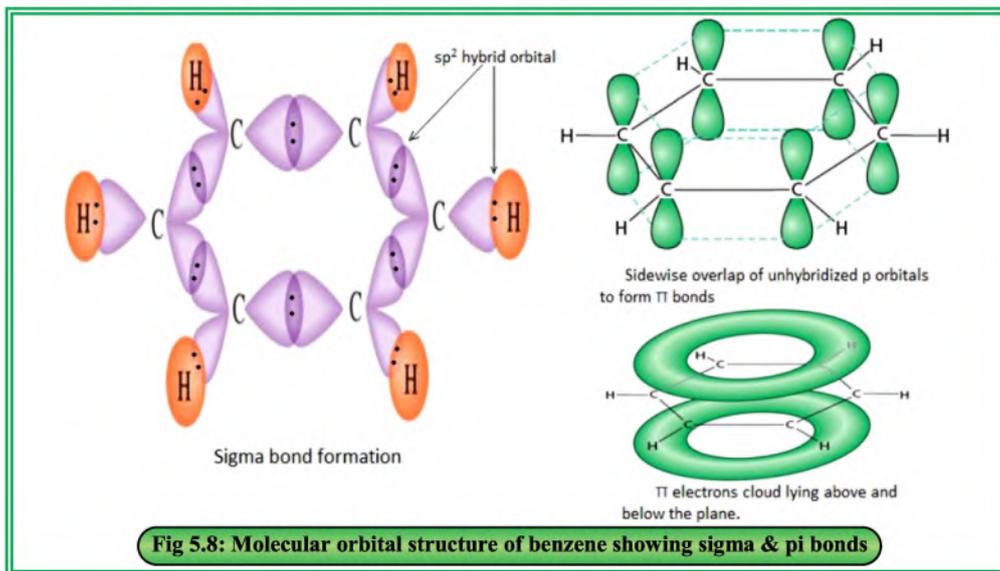
Two hybrid orbitals of each carbon atoms are used to make sigma bond with the adjacent carbon atom, through $sp^2 - sp^2$ overlapping. The third sp^2 hybrid orbital is involved in sigma bonding with hydrogen atoms through $sp^2 - s$ overlapping. All sigma bonds in benzene are coplanar and have bond angle of 120° . In benzene, the carbon-carbon (C-C) bond length as well as carbon-carbon double bond (C=C) length is approximately 1.39 \AA .



DO YOU KNOW?

Delocalized pi electrons are not confined to a specific bond but instead spread out over a larger region of a molecule. Delocalized pi electrons are commonly found in molecules with alternate single and double bonds like benzene.

The six carbon atoms in benzene possess six non hybridized p orbitals that are oriented perpendicular to the sigma bonds. The side wise overlapping of these p orbitals gives six delocalized pi molecular orbitals where half of them are 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 the molecule (Fig:5.8).

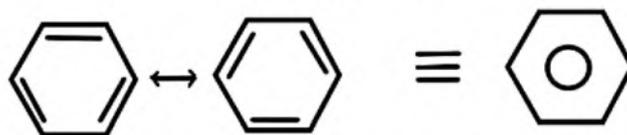




The molecular orbital structure of benzene provides the following information.

- (i) Benzene is a planar hexagonal molecule.
- (ii) Pi electrons of benzene are delocalized and responsible for the extra stability of molecule.
- (iii) Actual structure of benzene is a hybrid of two resonating structures described by Kekule.

Kekule Structures



Two equivalent resonating structures of benzene

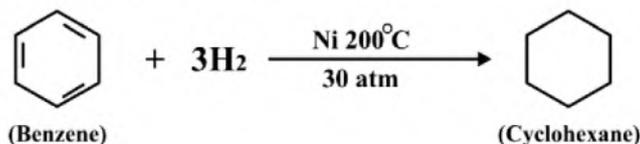
Resonance hybrid

5.7.3 Addition reactions of benzene

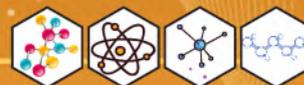
Benzene, being an aromatic compound, is highly resistant to addition reactions due to its stability. However, under specific conditions, it can undergo addition reactions. So far only the addition of hydrogen and chlorine to benzene has been observed.

Addition of Hydrogen

Benzene undergoes an addition reaction with hydrogen to produce cyclohexane. It is a catalytic hydrogenation carried out in the presence of Nickel at 200°C and 30 atmospheric pressure.

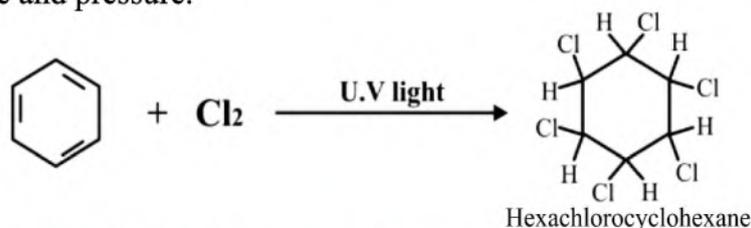


Benzene, despite having six delocalized pi electrons in its six p orbitals, is less susceptible to addition reaction compared to alkenes and alkynes. The reason for this is that pi electrons in alkenes and alkynes are more localized between the two carbon atoms, making them more easily accessible for an electrophilic attack. In contrast, the pi electrons in benzene are highly delocalized, which makes it difficult for incoming electrophile to attack and add on the benzene ring. So far only the addition of hydrogen and chlorine to benzene has been observed.



Addition of Halogen

Chlorine and bromine are added to benzene under sunlight and at high temperature and pressure.



Self-Assessment

Benzene is highly unsaturated but it shows stability towards addition reaction. why?

5.7.4 Electrophilic substitution reactions of benzene

5.7.4.1 General Introduction

Electrophilic substitution reactions are a type of organic reaction in which an electrophile reacts with an electron-rich compound and replaces an electrophile in the compound. The six pi electrons of p orbital of benzene are spread out over all six carbon atoms, this makes benzene less reactive towards addition reactions and more reactive towards Electrophilic substitution reactions.

The proposed general mechanism of Electrophilic substitution reaction of benzene consists of following steps.



DO YOU KNOW?

Electrophile is an electron deficient species that seeks to gain an electron. Some common examples of electrophiles are chloro cation (Cl^+), alkyl cation (R^+), acyl cation (COR^+), nitronium ion (NO_2^+) and sulphonium ion (SO_3H^+).

Step-1: Generation of an electrophile

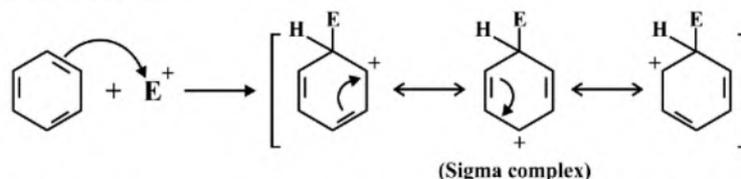
An electrophile (E^+) is generated by reaction of catalyst with the reagent.





Step-2: Formation of Arenium ion

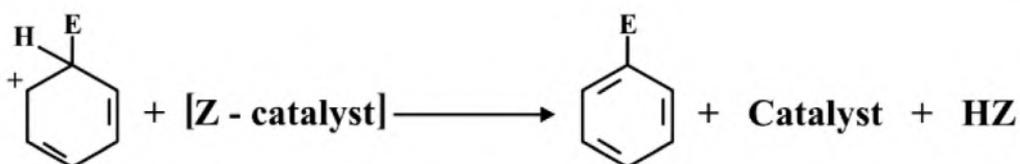
The electrophile attacks on pi system of benzene and forms a carbocation known as arenium ion.



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

Step-3: Abstraction of proton

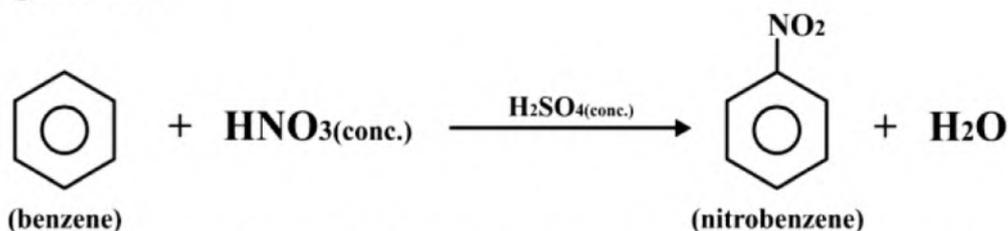
The unstable non aromatic arenium ion then loses a proton and changes into the product.



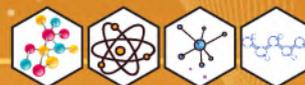
In this stage aromaticity of benzene is restored. Benzene undergoes following types of Electrophilic substitution reactions.

5.7.4.2 Nitration

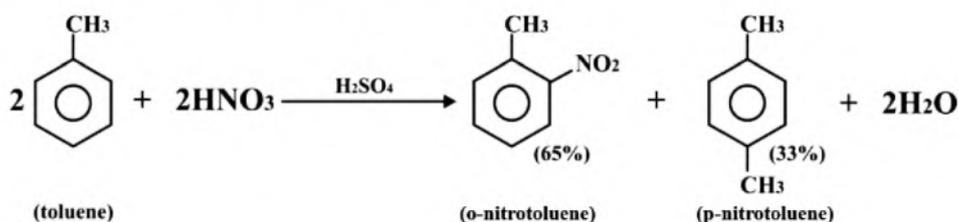
The reaction of benzene with conc. nitric acid to produce nitrobenzene is known as nitration. This reaction is carried out at 50°C in the presence of conc. sulphuric acid.



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

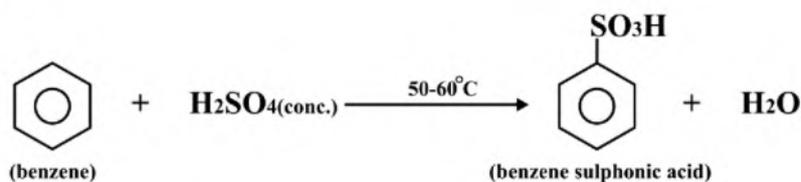


Similar to benzene, toluene also undergoes nitration, but the product is a mixture of ortho and para nitro toluene.

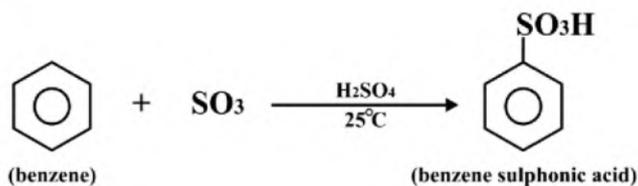


5.7.4.3 Sulphonation

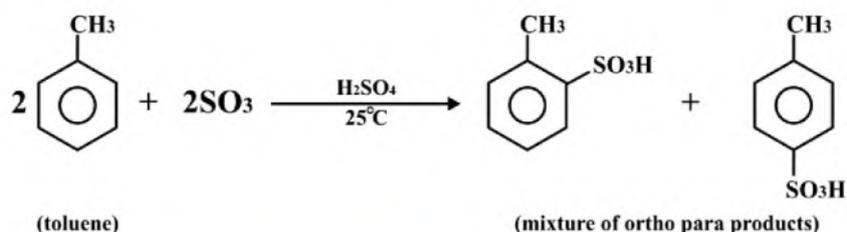
Benzene reacts with conc. sulphuric acid at 50 to 60°C to give benzene sulphonic acid.



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



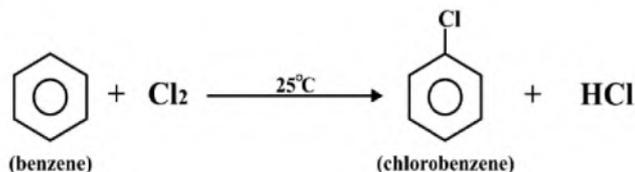
Sulphonation of toluene gives a mixture of ortho, para methyl benzene sulphonate.



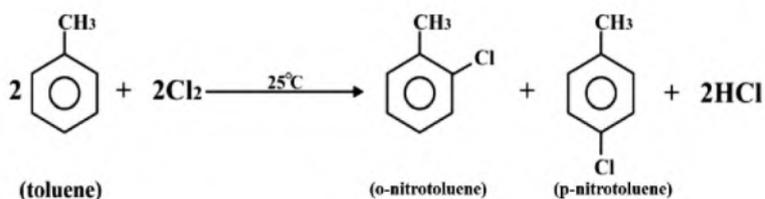


5.7.4.4 Halogenation

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

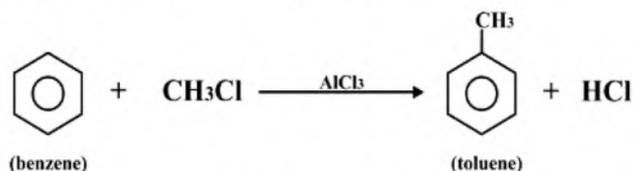


If toluene is allowed to undergo halogenations, it give a mixture of ortho, para chlorotoluene.

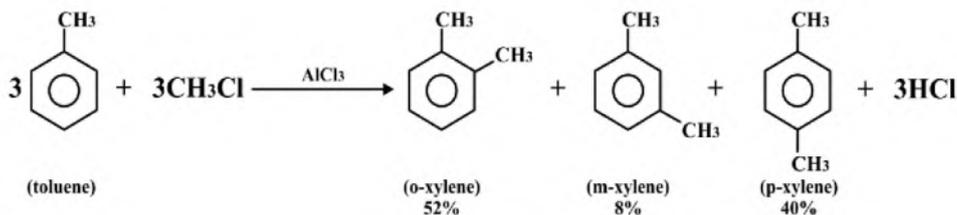


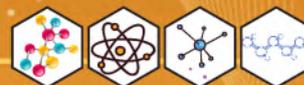
5.7.4.5 Friedal Craft Alkylation

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



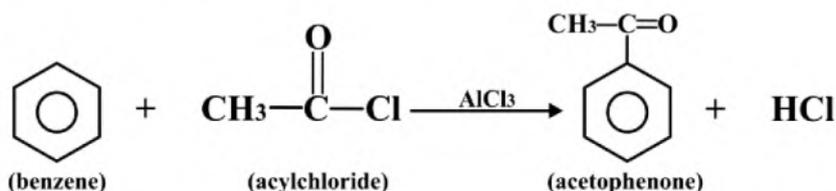
The reaction of toluene with an alkyl halide gives a mixture of ortho, para and meta products.



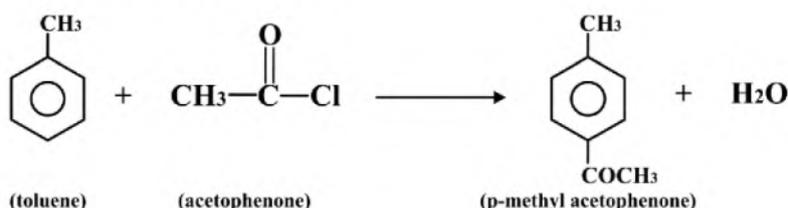


5.7.4.6 Friedal Craft Acylation

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



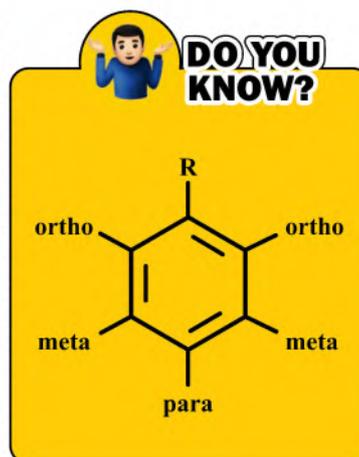
The attacking electrophile in this reaction is acyl cation (RCO^+) which is produced by the reaction of acyl chloride with Lewis acid (AlCl_3). Acylation of toluene give only the para product.



5.7.4.7 Substituent Effect

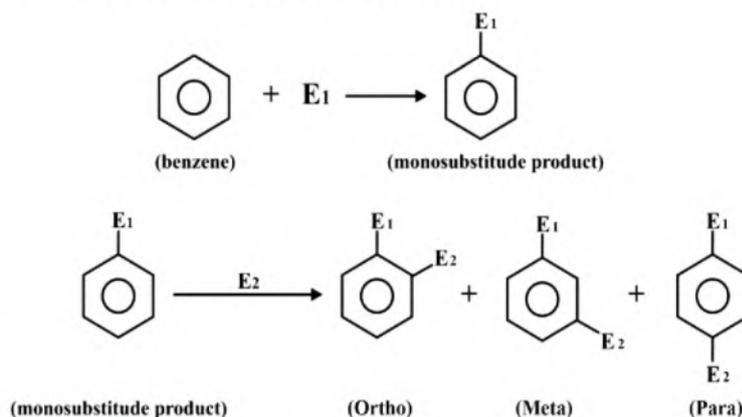
When an Electrophilic reagent reacts with benzene, a monosubstituted product is obtained because all the hydrogen atoms in benzene are equivalent and any one of them can be replaced by an external electrophile. However, if a second substituent is introduced into the benzene ring, it can be substituted at any one of the remaining hydrogen atoms and occupy one of three isomeric positions (ortho, para, meta) while it might be expected that the three isomers would be formed in approximately equal proportion, in reality, the percentage of each disubstituted product is quite different.

It is because the first substituent influences the position occupied by incoming Electrophilic reagent. **“The effect of the first substituent on the**





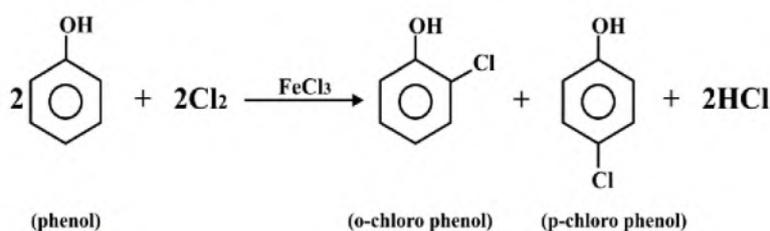
incoming electrophilic reagent is known as substitution effect or orientation of benzene". Generally the substituent of mono substituted benzene provides a direction towards ortho-para or meta positions.



(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 and when reacted with chlorine in presence of ferric chloride (FeCl₃), it gives a mixture of ortho para chloro phenol.



(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 $-\text{COOH}$ part of benzoic acid is meta directing. Thus, when benzoic acid reacts with nitric acid, it produces a meta product.

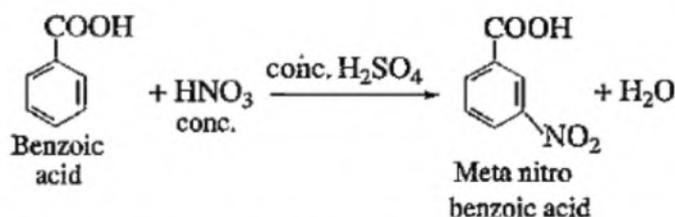


Table 5.3 Comparative studies of ortho, para and meta directing group

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 $-\text{R}$, $-\text{RCO}$, $-\text{OR}$ $-\text{Cl}$, $-\text{Br}$, $-\text{CH}_3$, $-\text{OH}$ etc	Examples are $-\text{COOR}$, $-\text{CHO}$ $-\text{COOH}$, $-\text{NO}_2$, $-\text{COCH}_3$, $-\text{SO}_3\text{H}$ etc

5.7.4.8 Preparation of poly substituted benzene

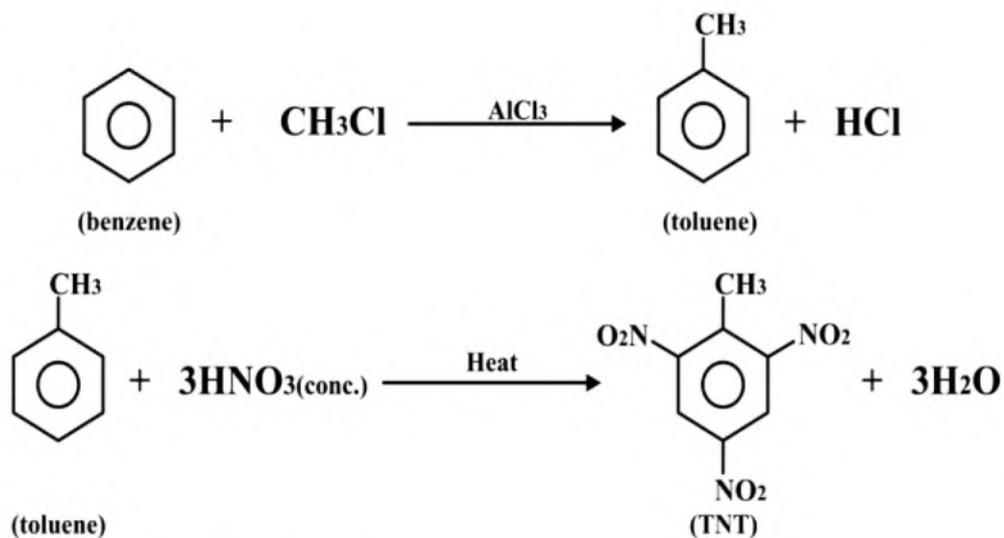
Poly substituted benzene is formed by the replacement of two or more hydrogen atoms of benzene ring with Electrophilic reagents. These are also called derivatives of benzene. When synthesizing a derivative of benzene, it is important to consider whether the electrophile already attached to the mono substituted benzene is meta directing or ortho para directing.

Preparation of trinitro toluene (TNT)

Trinitro toluene is an explosive organic material. During its preparation from benzene, the benzene is first converted into toluene and then toluene is treated with hot concentrated nitric acid. Since $-\text{CH}_3$ group of toluene is ortho

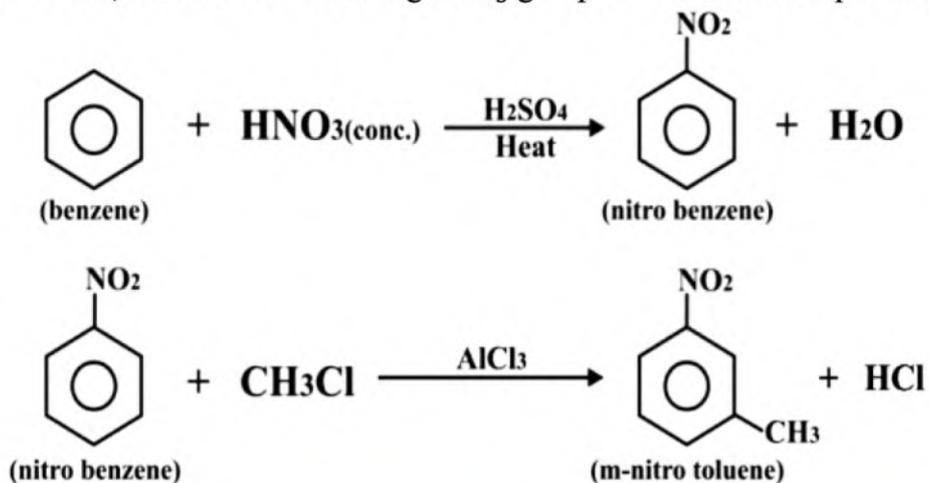


para directing, it invites the NO_2^+ group of nitric acid towards ortho and para positions.



Preparation of m-nitro toluene

In order to synthesize m-nitro toluene, the first step is to transform benzene into nitrobenzene. Due to the meta directing nature of nitro group of nitro benzene, it directs the incoming $-\text{CH}_3$ group towards the meta position.





SOCIETY, TECHNOLOGY AND SCIENCE

Biofuel as energy need of Pakistan

The rising energy demand in Pakistan has led to a growing interest in exploring domestic and low cost alternatives. Biofuel is a type of renewable energy derived from organic material known as biomass. There are three main biofuels manufacturing in Pakistan.

- (i) Bio diesel: It is produced by animal fats and vegetable oils by special chemical process.
- (ii) Bio gas: It is produced from cow dung and other organic wastes.
- (iii) Bio ethanol: It is produced by the fermentation of starch or sugar.



SUMMARY

- Organic compounds which are made up of hydrogen and carbon atoms are known as hydrocarbons.
- In saturated hydrocarbons all carbon atoms are attached with each other by single bond only.
- In unsaturated hydrocarbons one or more double or triple bonds are present in the carbon chain.
- Aromatic compounds are characterized by a cyclic arrangement of atoms that are connected by alternating double bonds.
- The boiling point of straight chain alkanes is higher than branched chain alkanes.
- Cyclopropane is the smallest and simplest cycloalkanes with a ring composed of three carbon atoms and six hydrogen atoms.
- The cleavage of chemical bond takes place in the organic molecule either by homolytic fission or heterolytic fission.



- Alkenes are mostly prepared by dehydration of alcohol and dehydrohalogenation of alkyl halides.
- The higher reactivity of alkene as compared to alkane is attributed to the presence of a pi bond between the carbon atoms.
- Markovnikov's rule 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.
- The addition of oxygen to the double bond of alkene is known as epoxidation.
- Ozonolysis is a chemical reaction that involves the cleavage of an alkene or alkyne by ozone in the presence of reducing agent such as zinc.
- Polymerization of alkene involves the joining of many alkene monomers together to produce a polymer chain.
- All those alkynes which contain terminal hydrogen possess an acidic character.
- Organic molecules having the same molecular formula but differing in the way their atoms are connected to each other are called as structural isomers.
- A chiral centre is formed in a molecule when a carbon atom is bonded to four different atoms or groups.
- Two compounds having the same molecular formula and same structure but differing from each other by the optical rotation of plane polarized light are called optical isomers.
- Benzene, despite having six pi electrons in its six p orbitals, is less susceptible to addition reactions compared to alkenes and alkynes.



EXERCISE

Multiple Choice Questions

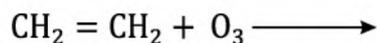
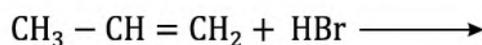
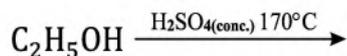
- (i) The final product obtained when hydrogen bromide (HBr) is added to an ethyne molecule:
- (a) Bromo ethene
(b) 1, 1-dibromo ethane
(c) 1,2-bromo ethane
(d) 1,1,2,2 tetra bromoethane
- (ii) The formula of a saturated hydrocarbon is C_3H_6 , it should be:
- (a) Propane
(b) Propene
(c) Propyne
(d) 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) -CH₃
(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 $AgNO_3$



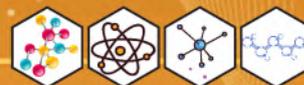
- (ix) Meta directing group among the following is:
(a) – OH (b) – NH₂
(c) – CH₃ (d) – NO₂
- (x) Acylation of benzene in the presence of AlCl₃ gives:
(a) Toluene (b) Acetophenone
(c) Phenol (d) Xylene

Short Questions

1. Give three differences between aliphatic and aromatic hydrocarbons?
2. Give the mechanism of free radical reaction between methane and chlorine in the presence of sunlight.
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.
5. Write the equations with all required conditions for the reaction of benzene with the following:
(i) H₂ (ii) CH₃COCl (iii) HNO₃(conc.) (iv) H₂SO₄(conc.)
6. Bring about the following conversions.
(i) Toluene to ortho-para nitro benzoic acid
(ii) Benzene to m-nitro toluene
7. How can you prepare ethene from dehydration of ethanol and ethyne from dehydro halogenations of ethyl chloride?
8. Alkanes are generally referred as paraffins due to their less reactivity, why are they stable towards chemical reactions?



Descriptive Questions

1. Draw the orbital structures of the following hydrocarbons.
(i) Ethane (ii) Ethylene (iii) Acetylene
2. Write the equations of the following chemical processes.
(i) Ethylene is heated at high temperature and pressure.
(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.
(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?
4. What is meant by isomerism? Explain four different types of structural isomers and give one example of each.
5. Explain the following with suitable examples.
(a) Optical isomers (b) Geometrical isomers
6. Describe the molecular orbital structure of benzene.
7. Give the mechanism of following Electrophilic substitution reaction of benzene.
(a) Nitration (b) Acylation (c) Chlorination
8. What is meant by ortho, para and meta directing groups. Explain the influence of substituent of benzene to the incoming Electrophile.
9. Why ethyne terminal hydrogen is acidic in nature? Give two reactions of ethyne to show their acidic behavior.

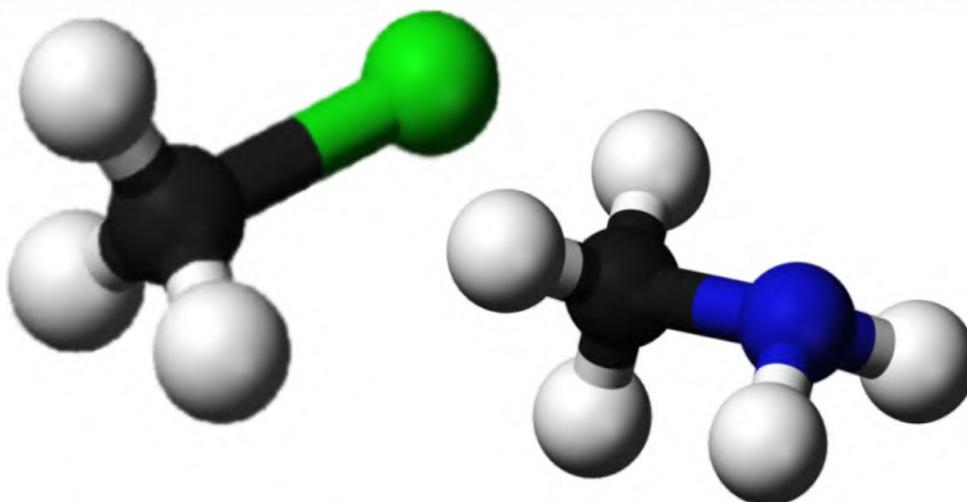


CHAPTER 6

ALKYL HALIDES & AMINES

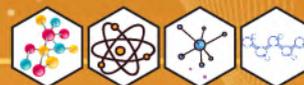


Teaching Periods	10	Assessment	01	Weightage %	08
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Students will be able to:

- ✓ Discuss the physical properties, structure and reactivity of RX. (Understanding)
- ✓ Describe the preparation of RX by the reaction of alcohols with HX, SOCl₂ and PX₃ and by halogenation of alkanes. (Understanding)
- ✓ Explain the mechanism and types of nucleophilic substitution reactions. (Applying)
- ✓ Explain the mechanism and types of elimination reactions. (Applying)
- ✓ Compare the nucleophilic substitution versus elimination reaction. (Analyzing)
- ✓ Explain the preparation and reactivity of Grignard's Reagents. (Applying)
- ✓ Applications of Grignard's reagent (Water, esters and carbon dioxide and amines). (Applying)
- ✓ Explain the structure and basicity of amines. (Applying)
- ✓ Describe the preparation of amines by alkylation of ammonia to RX and reduction of nitriles, nitro and amide functional groups. (Understanding)
- ✓ Explain the reactions of amines (RX, aldehydes, and ketones) and preparation of amides and diazonium salts. (Understanding)
- ✓ Enlist the important compounds of Alkyl Halides and Amines with their applications. (Applying)
- ✓ Explain the reactivity of alkyl halide with respect to polarity of C- X bond. (Understanding)
- ✓ Explain why primary alkyl halide favors S_N² reactions and tertiary alkyl halide S_N¹. (Understanding)



INTRODUCTION

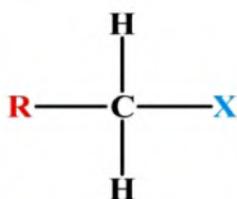
“Organic compounds that contain at least one halogen atom (fluorine, chlorine, bromine, or iodine) bonded to an alkyl group are called haloalkanes”. These compounds are classified on the basis of number of halogen atoms attached to alkyl group. Monohaloalkanes have only one halogen atom, dihaloalkanes have two halogen atoms and trihaloalkanes have three halogen atoms.

Monohaloalkanes are usually called alkylhalides and represented by a formula R-X, where R is an alkyl group and X is halogen atom (functional group). The general formula of monohaloalkanes is $C_nH_{2n+1}X$ where n, represents the number of carbon atoms.

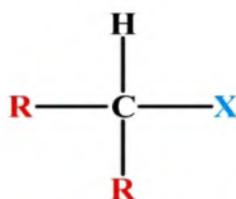
Alkyl halides are widely used in the synthesis of organic compounds as they are versatile compounds that can undergo a wide variety of reactions. They are also used as solvents and in the production of plastics, pharmaceuticals and agrochemicals.

6.1 ALKYL HALIDES

Alkyl halides can be classified according to the carbon atom to which the halogen atom is attached. A primary (1°) alkyl halide refers to an alkyl halide where the halogen-bearing carbon is bonded to only one other carbon atom. When two carbon atoms are attached to the halogen-bearing carbon, it is known as a secondary (2°) alkyl halide. Finally, a tertiary (3°) alkyl halide is characterized by the halogen-bearing carbon being bonded to three carbon atoms.



(1° - Alkyl halide)



(2° - Alkyl halide)



(3° - Alkyl halide)

Examples of alkyl halides are given below

Primary alkyl halide: 1-Bromopropane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$)

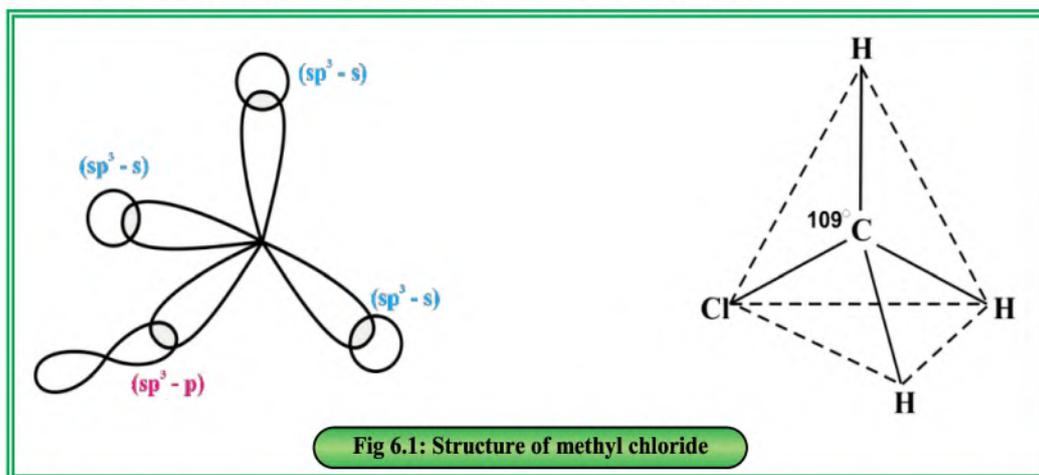
Secondary alkyl halide: 2-Bromopropane ($\text{CH}_3\text{CHBrCH}_3$)

Tertiary alkyl halide: 2-Bromo-2-methylpropane ($\text{CH}_3\text{C}(\text{CH}_3)_2\text{Br}$)



6.1.1 Structure of Alkyl Halide

Let us consider methyl chloride ($\text{CH}_3\text{-Cl}$) 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).



6.1.2 Physical Properties of Alkyl Halides

(i) Physical state

Alkyl halides with lower number of carbon atoms and different halogen atoms exist as gas or liquid at room temperature, whereas alkyl halides with higher carbon atoms i.e. beyond 18-carbon atoms are colourless solids.

(ii) Solubility

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.

(iii) Melting and boiling points

Alkyl halides possess higher melting and boiling points than alkanes of comparable molecular weight, this is due to increasing strength of intermolecular forces.

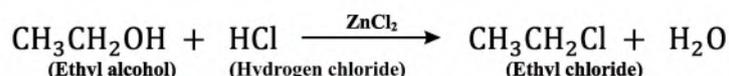


6.1.3 Preparation of Alkyl Halides

Alkyl halides can be prepared by various methods. Some of which are given below:

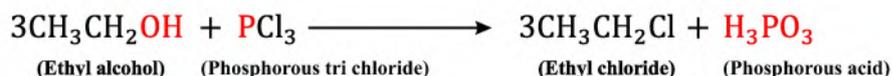
6.1.3.1. Reaction of Alcohol with Hydrogen Halides:

Alcohols can be converted to alkyl halides by the reaction with hydrogen halides. The reactivity of an alcohol with halogen acid follows the trend $\text{HI} > \text{HBr} > \text{HCl}$. When producing an alkyl halide from hydrogen chloride, anhydrous zinc chloride (ZnCl_2) is used as a catalyst.

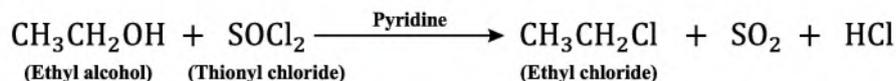


6.1.3.2. Reaction of Alcohols with other halogenated agents

Alcohols react with phosphorous trihalide (PCl_3 , PBr_3 , PI_3) to form alkylhalides. Since phosphorus trichloride is more easily available, the reaction is generally carried out by using this reagent.



Alcohols reacts with thionyl halide (SOX_2) in the presence of pyridine as catalyst to produce an alkyl halides. This is preferred method for the preparation of alkyl halide because both the by products are in gaseous state.

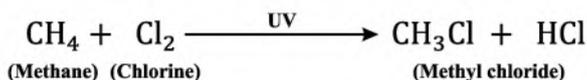


6.1.3.3 By the halogenation of alkane

The reaction between alkanes and halogens in the presence of sun light or high temperature produces alkyl halides. This reaction involves the substitution of one or more hydrogen atoms in alkanes by halogen atoms,



resulting in the formation of a mixture of different haloalkanes. However, due to the production of a mixture of different halogenated alkanes, this method is not considered efficient for the preparation of alkyl halides.



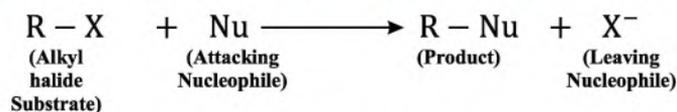
6.1.4. Reactivity

Alkyl halides are highly reactive than their corresponding alkanes. **“The high reactivity of alkyl halides is attributed to the polarity of carbon halogen bond”**. Alkyl halides contain halogen atoms (F, Cl, Br, I), which have high electronegativity than carbon atom and thus make them electrophilic reagents.

The electrophilic center makes alkyl halides susceptible to nucleophilic attacks, which results in nucleophilic substitution reactions. Furthermore, the β -hydrogen atom in the molecule becomes acidic due to the shifting of electron density of C-H bond towards the halogen, making it exposed to elimination reactions.

6.1.4.1. 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”.



When alkyl halides are reacted with an aqueous solution of sodium hydroxide (NaOH) or



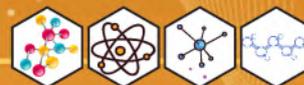
DO YOU KNOW?

Alkyl halides are considered as precursors of many organic compounds due to their ability to undergo various types of chemical reactions and functional group transformations. Chloroethane ($\text{CH}_3\text{CH}_2\text{Cl}$) can be transformed into ethanol (ethyl alcohol) by replacing the chlorine atom with a hydroxyl group ($-\text{OH}$), showcasing the versatility of alkyl halides in organic synthesis.



DO YOU KNOW?

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.



potassium hydroxide (KOH), the hydroxide ion (OH^-) acts as strong nucleophile which attacks the partially electropositive carbon atom of alkyl halide, as a result, new bond is formed between carbon and attacking nucleophile.

Different strong nucleophilic can produce a variety of organic compounds when treated with an alkyl halide.

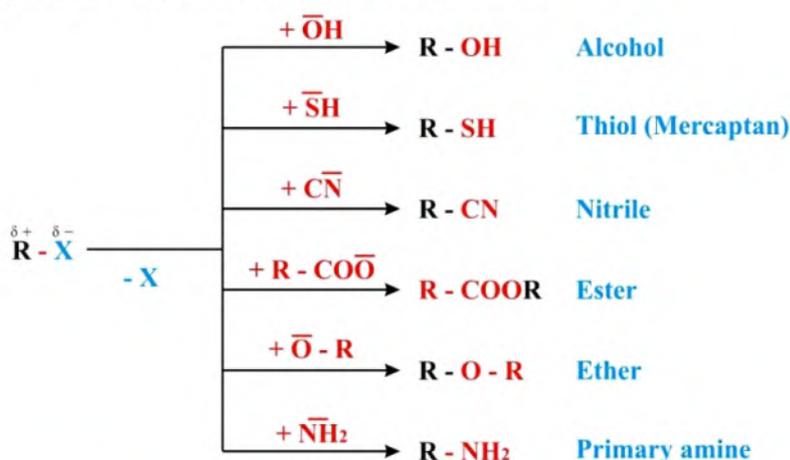


Table 6.1 Some common strong Nucleophiles along with their typical reagents.

Nucleophiles	Typical Reagent
OH^-	NaOH, KOH
SH^-	KSH
CN^-	NaCN
$\text{CH}_3\text{-COO}^-$	$\text{CH}_3\text{-COONa}$
$\text{CH}_3\text{-CH}_2\text{-O}^-$	$\text{CH}_3\text{-CH}_2\text{-ONa}$
NH_2^-	NaNH_2



Self-Assessment

Why alkyl halide undergoes nucleophilic substitution reaction? Which reagent is required to convert a methyl iodide into:

- (i) Methanol (ii) Methyl cyanide (iii) Dimethyl ether (iv) Thiol



Mechanism of nucleophilic substitution reactions

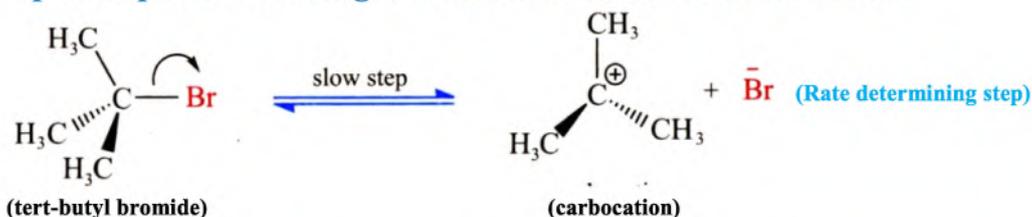
The mechanism of nucleophilic substitution reaction is divided into:

- (i) S_N^1 Reactions
- (ii) S_N^2 Reactions

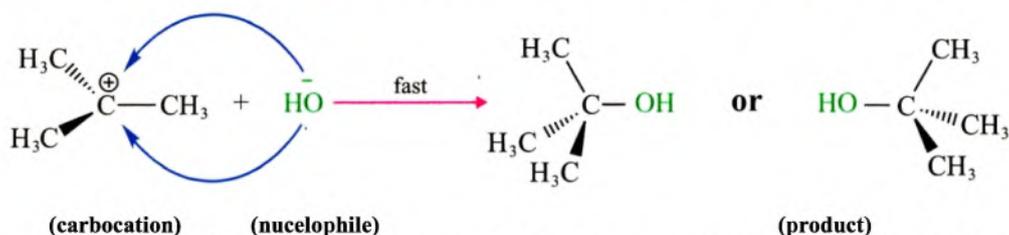
S_N^1 mechanism

It is unimolecular bi-step S_N reaction. "The S_N1 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



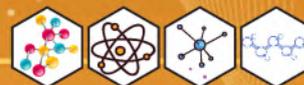
Step-2: Attack of strong nucleophile on carbocation to form product



Tertiary alkyl halides undergo S_N1 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 S_N1 reaction.

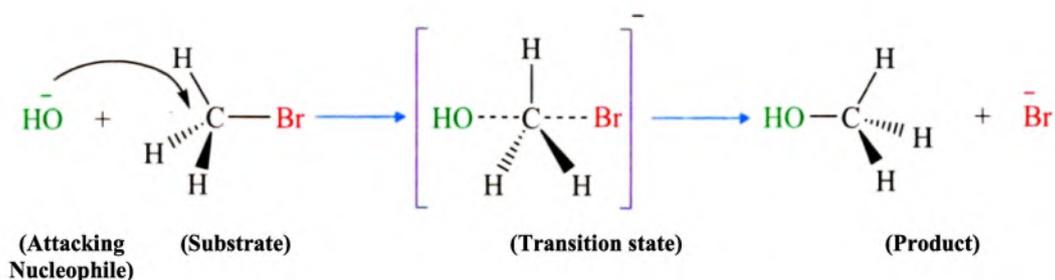
Chemical reactions that processed via the S_N1 mechanism exhibit first-order Kinetics, and the rate of the reaction is dependent on the concentration of the substrate, not on the nucleophile involved in the reaction.

$$R = K [\text{Substrate}]$$



SN² 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.



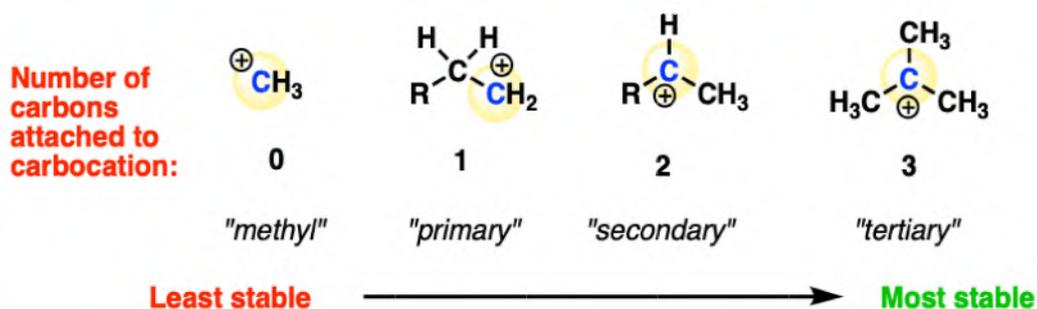
The SN² mechanism is typically observed in primary alkyl halides and methyl halides because primary carbocation and methyl carbocation are highly unstable due to the lack of electron donating alkyl groups.

The SN² mechanism is followed by second order kinetics which means that the reaction rate is dependent upon the concentration of both substrate and attacking nucleophile.

$$R = K [\text{Substrate}] [\text{Nu}^-]$$

Carbocations and their stability

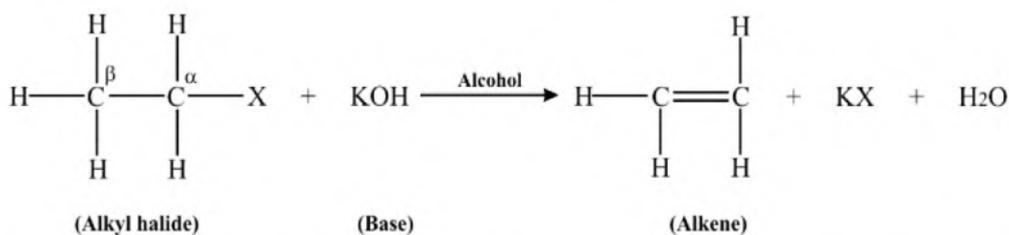
“Carbocations are organic ions that have a positively charged carbon atom. They are formed when a carbon atom loses a pair of electrons”. Carbocations are classified into primary, secondary and tertiary depending upon the number of carbon atoms bonded to positively charged carbon atom. Carbocations are highly reactive species, they can be formed as intermediates during a chemical reaction. Tertiary carbocations are more stable than secondary and primary carbocation because of electron donating tendency of alkyl group.



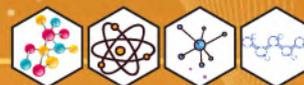
6.1.5. Elimination Reactions

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.

In β -elimination reaction, base initiates the reaction by abstracting a proton from substrate. It leads to the formation of carbocation intermediate, which then eliminated a halogen atom from the adjacent carbon to form a new Pi bond.



There are two common types of β -elimination reactions named as E_1 and E_2 .



Self-Assessment

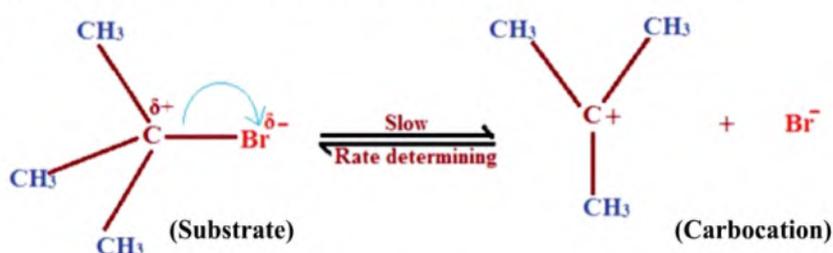
Explain the following:

- Why β -elimination reactions are not possible in methyl halides?
- Why S_N2 reaction is not favourable in tertiary alkyl halides?
- Why tertiary carbocation is more stable than secondary and primary carbocations?

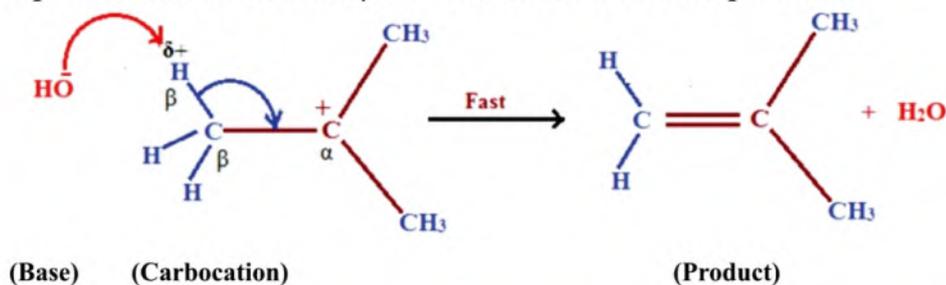
6.1.5.1 Mechanism of E_1 Reaction

E_1 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



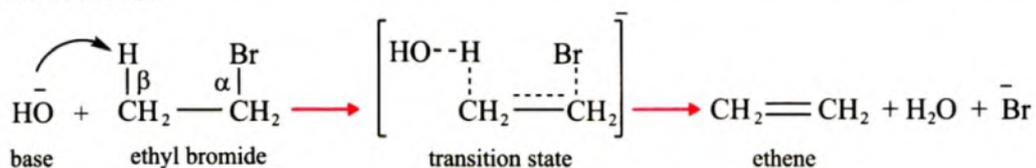


The rate determining step in E^1 mechanism involves the unimolecular ionization of the substrate molecule. Therefore, the rate of the reaction depends only on the concentration of reactant, and not on the concentration of base.

$$R = K [\text{Substrate}]$$

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.



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 α -carbon and the lone pair of electrons is shifted between α and β carbon to give an ethene.

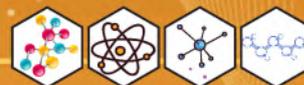
Therefore, as far as kinetics of E_2 reaction is concerned, the rate of this reaction depends upon the concentration of both substrate and attacking base, the rate law may be written as

$$R = K [\text{Sub}] [\text{base}]$$

6.1.6. Substitution Versus Elimination Reactions

Nucleophile substitution reactions can occur alongside the elimination reactions because nucleophile can also act as a base. However, nucleophilic substitution reactions occur when the nucleophile attacks on the α -carbon atom where as elimination reaction occurs when the nucleophile attacks on the β -hydrogen. Several factors can influence the formation of products via either substitution or elimination mechanisms.

- **Solvent effect:** Substitution reactions are favoured in polar solvents while elimination reaction are favoured in non polar solvents.



- **Base effect:** A strong base promotes elimination reaction and hinders substitution reaction.
- **Temperature effect:** The rise in temperature encourages elimination reaction over substitution reaction.
- **Substrate effect:** If the substrate molecule is a tertiary alkyl halide, it favours elimination reaction while if it is primary alkyl halide, it favours substitution reaction. Secondary alkyl halide is consented to both substitution and elimination.

6.2 GRIGNARD'S REAGENTS (ORGANOMETALLIC COMPOUNDS)

Organometallic compounds are defined as **“organic compound that possess at least one bond between a carbon atom and a metal atom”**.

Some common examples of organometallic compounds are given as:

- Grignard reagent: It is a highly reactive organic compound and used in organic synthesis.
- Methylcobalamine: It is a derivative of vitamin B-12.
- Dimethyl Zinc: It is used as insecticide.
- Tetraethyl lead: It is used as knock inhibitor in petroleum industry.



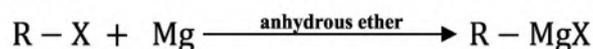
DO YOU KNOW?

Organometallic compounds are being studied as a potential therapeutic agents for a variety of diseases including cancer, HIV and tuberculosis. They are also used as contrasting agents in magnetic resonance imaging (MRI).

6.2.1 Preparation of Grignard Reagent

“Grignard reagent is an organometallic compound that contains a carbon-magnesium (C-Mg) bond”. Grignard reagents are well-known organometallic compounds. The name Grignard is derived from a French chemist Victor Grignard, who first synthesized this compound and was subsequently awarded the Noble Prize in Chemistry in 1912.

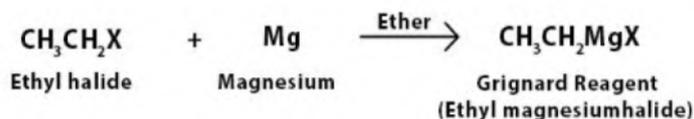
Grignard reagents are prepared in the laboratory by the reaction of an alkyl halide with magnesium metal in the presence of anhydrous ether.



Where R = alkyl group, for example $-\text{CH}_3$, $-\text{C}_2\text{H}_5$ etc



X = halogen, for example - Cl, -Br, -I



The formation of Grignard reagent depends on two factors that determine its ease of production.

- (i) **Size of alkyl group:** The larger the size of alkyl group, the more difficult is the formation of Grignard reagent.
- (ii) **Nature of halogen atom:** The ease of formation of Grignard reagent also depends upon nature of halogen atom attached to an alkyl group of alkyl halide. The order is $\text{I} > \text{Br} > \text{Cl}$ because the bond between iodine and carbon is weaker than corresponding bond with other halogens.



Self-Assessment

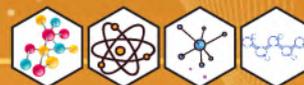
- How are Grignard reagents prepared?
- What are the key properties of organometallic compounds?

6.2.1 Reactivity

In Grignard reagent the carbon-magnesium bond is covalent and highly polar due to high electronegativity of carbon atom than magnesium metal, which creates more electron density on carbon of alkyl group. As a result the carbon atom bears a partial negative charge and acts as nucleophile. Due to this nucleophilic nature of alkyl parts, Grignard reagent reacts with polarized molecules either by nucleophilic substitution or nucleophilic addition.

6.2.3 Reactions of Grignard Reagent

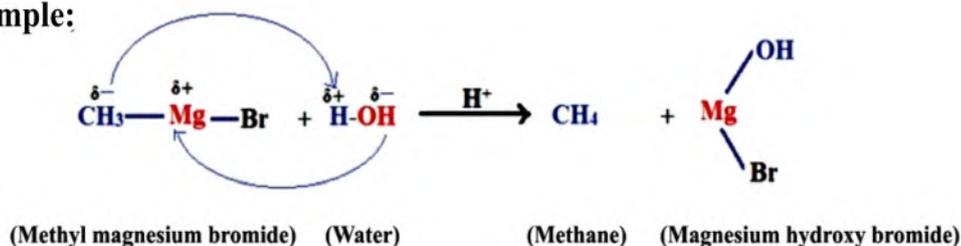
Grignard reagent is a versatile chemical; it is used as starting material for the synthesis of various organic compounds such as alkanes, alcohols, carboxylic acids and ketones.



6.2.1 Reaction with Water

When Grignard reagent reacts with water in an acidic medium, it yields alkanes.

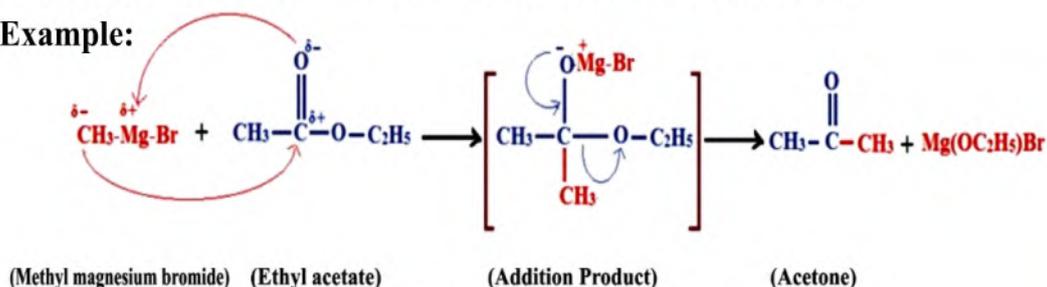
Example:



6.2.3.2. Reaction with ester

Grignard reagent when reacts with ester, it first forms unstable addition product which is later on stabilized with the formation of ketone.

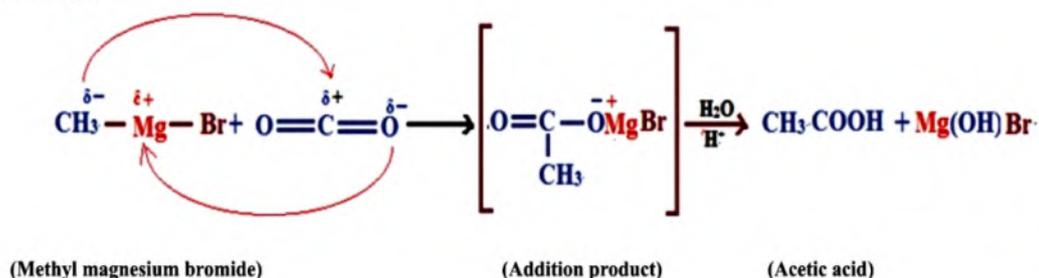
Example:



6.2.3.3. Reaction with carbon dioxide

Grignard reagent when reacts with carbon dioxide, it gives unstable addition product, later on hydrolysis in an acidic medium produces carboxylic acid.

Example:



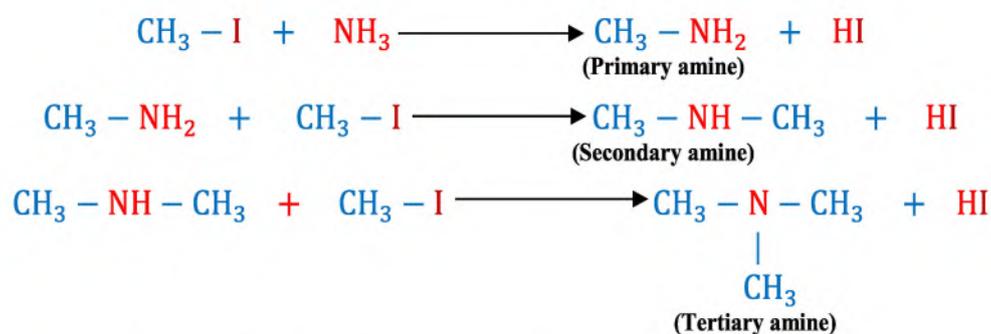


6.3.4. Preparation of Amines

Amines are prepared by different methods:

6.3.4.1. Alkylation of Ammonia by Alkyl Halides

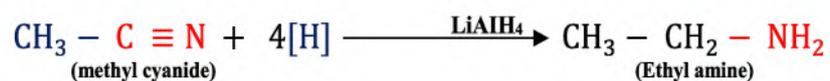
When alkyl halides are heated with alcoholic ammonia in a sealed tube, a mixture of primary, secondary and tertiary amines are obtained.



6.3.4.2. Reduction of Nitrogen Containing Functional Group

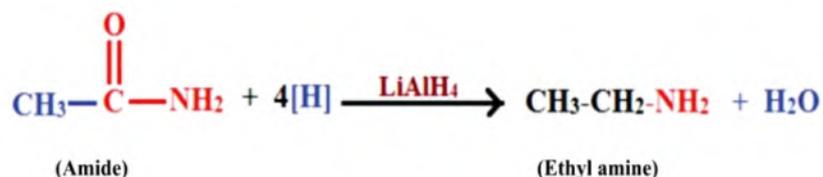
6.3.4.2.1. Reduction of Nitriles:

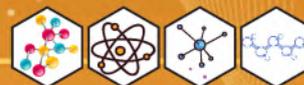
Methyl cyanide (Nitrile) on catalytic hydrogenation can produce ethyl amine.



6.3.4.2.2 Reduction of Amides:

Primary amines can be produced by the reduction of amides with lithium aluminum hydrides.





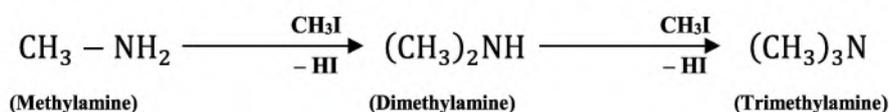
6.3.5. Reactivity

Amines are reactive due to the presence of lone pair of electrons on nitrogen atom and behave as nucleophile or a base. However, the reactivity of amines can be influenced by the nature and number of alkyl groups attached to nitrogen atom.

6.3.6. Reactions of Amines

6.3.6.1 Alkylation of Amines by Alkyl halides

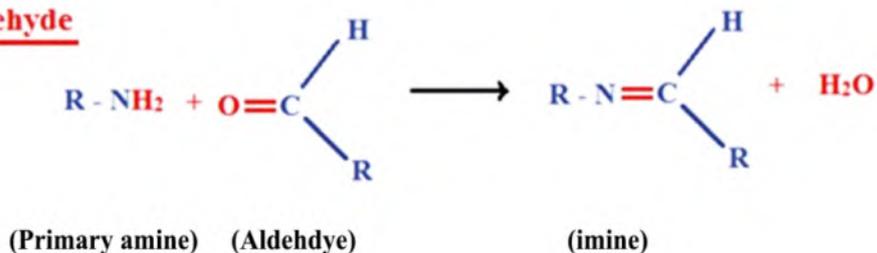
Primary amines react with alkyl halides to form secondary and tertiary amines. In this reaction hydrogen atoms of amines are replaced by alkyl groups.



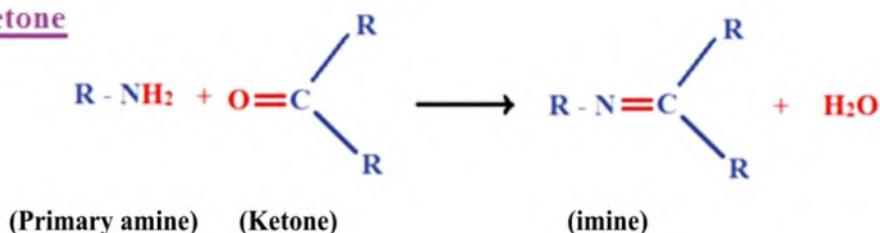
6.3.6.2. Reactions of amine with Aldehydes & Ketones

Primary amines can react with aldehydes and ketones to produce “imines” which also referred as Schiff bases.

with Aldehyde



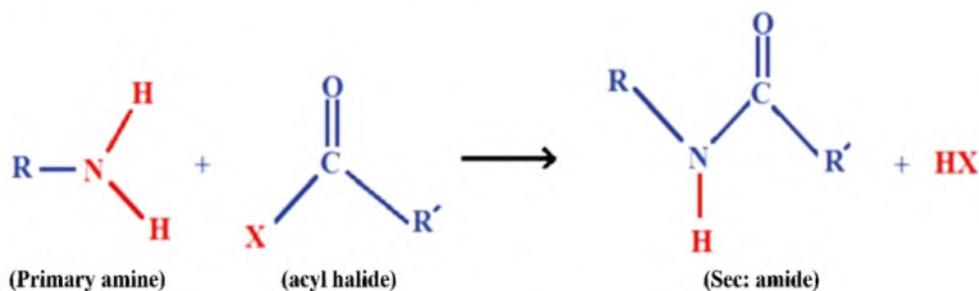
with ketone



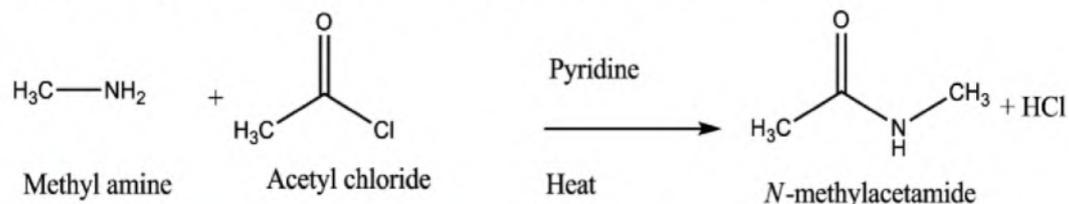


6.3.6.3. Preparation of Amides

When primary amines are reacted with Acyl halide or Acid anhydride, they form amides.

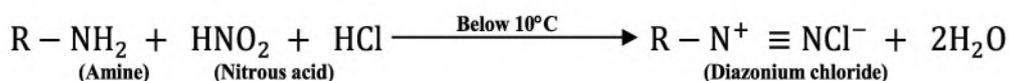


When methyl amine reacts with acetyl chloride to form:

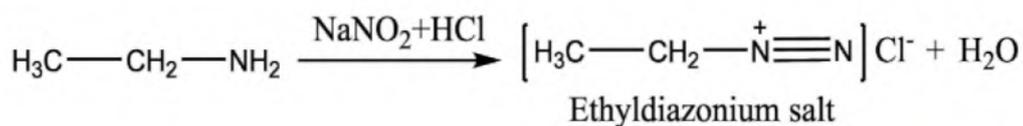


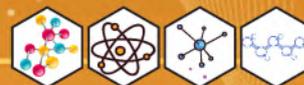
6.3.6.4 Preparation of Diazonium Salt

When amines react with nitrous acid in the presence of hydrochloric acid at below 10°C, a diazonium salt will be obtained.



The reaction of ethylamine with nitrous acid in the presence of hydrochloric acid forms ethyl diazonium, as shown below:





SOCIETY, TECHNOLOGY AND SCIENCE

Haemoglobin and Chlorophyll

Haemoglobin and chlorophyll are coloured organometallic compounds found in animals and plants respectively.

Haemoglobin is a protein, made up of four subunits each containing a heme group with an iron atom that binds to oxygen.

Chlorophyll on the other hand is a large molecule with porphyrin ring structure containing a magnesium atom.

Haemoglobin is involved in the transport of oxygen from lungs to the all body cells, while chlorophyll is responsible for capturing light energy in plants for photosynthesis.



SUMMARY

- Alkyl halides are derivatives of alkanes, they are formed by the replacement of hydrogen of alkanes by halogens.
- Alkyl halides are classified as primary, secondary and tertiary depending upon the nature of carbon to which halogen is bonded.
- Structure of methyl halides is tetrahedral in which carbon atom is bonded to three hydrogen atoms by sp^3 -s sigma bonds and one halogen atom by sp^3 -p sigma bond.
- Alkyl halides are soluble in organic solvents but insoluble in water, this is due to their inability to form hydrogen bonds with water.
- Alkyl halides are reactive due to polar nature of carbon-halogen bond.
- Alkyl halides undergo nucleophilic substitution (S_N) and elimination (E) reactions.
- Grignard reagent is an organometallic compound prepared by the reaction between an alkyl halide and magnesium metal.
- Grignard reagent is very reactive and is used to synthesize many organic compounds like alkanes, carboxylic acids and alcohols etc.

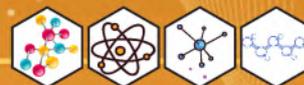


- Amines are derivatives of ammonia, formed by the replacement of one or more hydrogens by alkyl or aryl groups.
- Amines are classified as primary, secondary and tertiary depending upon the number of alkyl groups attached to nitrogen atom.
- Amines serve as bases; due to the presence of lone pair of electrons on nitrogen atom and have ability to accept proton from acids.
- Amines are prepared by alkylation of ammonia, also prepared by reduction of nitriles and amides.

EXERCISE

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

- How are alkyl halides prepared by the reaction of alcohol with (i) HX (ii) PX_3 (iii) SOCl_2 . Give the equations.
- How are amines prepared from nitriles, give the equations.
- Why are secondary and tertiary amines more alkaline than primary amines?
- Why the alkyl part of Grignard reagent is nucleophilic in nature?
- Convert the followings:
 - Methyl magnesium bromide into acetone
 - Ethylchloride into ethyl amine
 - Ethyl chloride into ethyl alcohol
 - Ethylamine into imine
- How is primary amine converted into secondary and tertiary amines, give the equations.
- Give an account on the basicity of amines.
- How can you justify the fact that alkyl halides are water insoluble?
- How can you define a nucleophile? Write the names of four nucleophiles along with their typical reagents.
- Why the mechanism of 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.
2. What is β -elimination? Discuss the mechanisms of E_1 and E_2 reactions.
3. What are organometallic compounds? How is Grignard reagent prepared? Write down the reactions of Grignard reagent with water, carbon dioxide, ester and amines.
4. What are alkyl halides? Define primary, secondary and tertiary alkyl halides.
5. Draw the orbital structure of methyl iodide and explain the type of hybridization in it.
6. Give a comparative study between nucleophilic substitution reactions and elimination reactions of alkyl halides.



CHAPTER 7

Alcohols, Phenols and Ethers



Teaching Periods

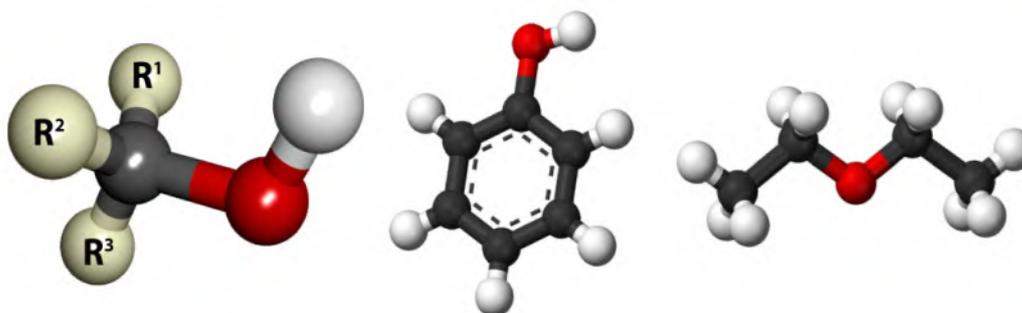
09

Assessment

01

Weightage %

07



Students will be able to:

- ✓ Describe the physical properties and structure of alcohol. (Understanding)
- ✓ Explain the preparation of alcohols by reduction of aldehydes, ketones, carboxylic acids and esters. (Applying)
- ✓ Explain the preparation of alcohols by hydrolysis of alkyl halide and Grignard reagent with aldehyde and ketone. (Applying)
- ✓ Describe reactivity of alcohols (Understanding)
- ✓ Describe the preparation of ether and ester by alcohol and oxidative cleavage of 1, 2- diols. (Understanding)
- ✓ Discuss the physical properties and structure of phenols. (Applying)
- ✓ Explain the preparation of phenol from chlorobenzene and hydrolysis of diazonium salts. (Applying)
- ✓ Explain the reactions of phenol. (Applying)
- ✓ Differentiate between alcohol and phenol. (Understanding)
- ✓ Enlist the important compounds of Alcohols, Phenols and Ethers with their application (Applying)
- ✓ Explain identification test of alcohol and phenol. (Understanding)



INTRODUCTION

Alcohols, Phenols and Ethers are three classes of oxygen containing organic compounds. Alcohols and Phenols are derived by replacing one hydrogen atom of water with an alkyl and aryl group respectively but ethers are formed by replacing both hydrogen atoms of water with alkyl or aryl groups.

Alcohols, phenols and ethers have a wide range of industrial as well as pharmaceutical applications. Methanol and Ethanol are good car fuels with high octane rating, Isopropyl alcohol is a common sanitizer, Ethylene glycol is frequently used as automotive antifreeze, Phenol is the oldest mild antiseptic agent and ethers are known for their anaesthetic properties.

Ethanol has been used by humans since prehistory, however it was first prepared synthetically in early eighteenth century by Michael Faraday. Phenol was isolated from coaltar in the mid eighteenth century whereas ether was first synthesized by distillation of sulphuric acid with ethanol in the mid fifteenth century.

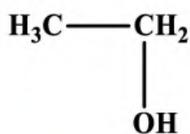
7.1 ALCOHOL

Alcohol is a class of organic compounds in which hydroxyl group (-OH) is attached to an aliphatic carbon atom. They are classified according to the number of hydroxyl groups present in the molecule. Monohydric alcohols contain one hydroxyl group. If two or more hydroxyl groups (-OH) are present in the molecule, these are identified as dihydric and polyhydric alcohols respectively.

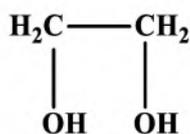


DO YOU KNOW?

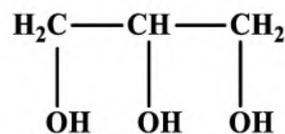
Wood spirit is a term used to refer to methanol, which was traditionally obtained by heating wood through a process known as destructive distillation.



Ethanol
(monohydric alcohol)



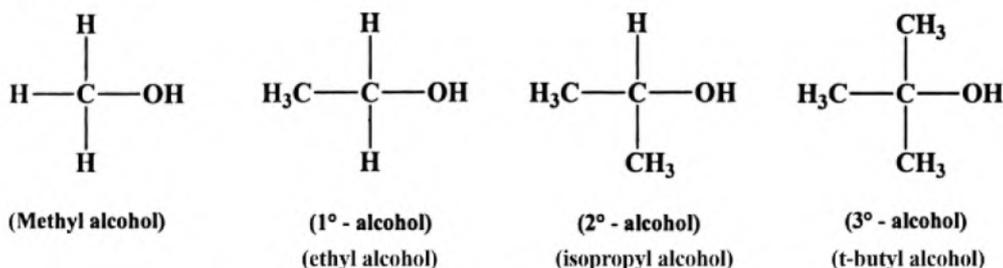
Ethylene glycol
(Dihydric alcohol)



Glycerol
(Trihydric alcohol)

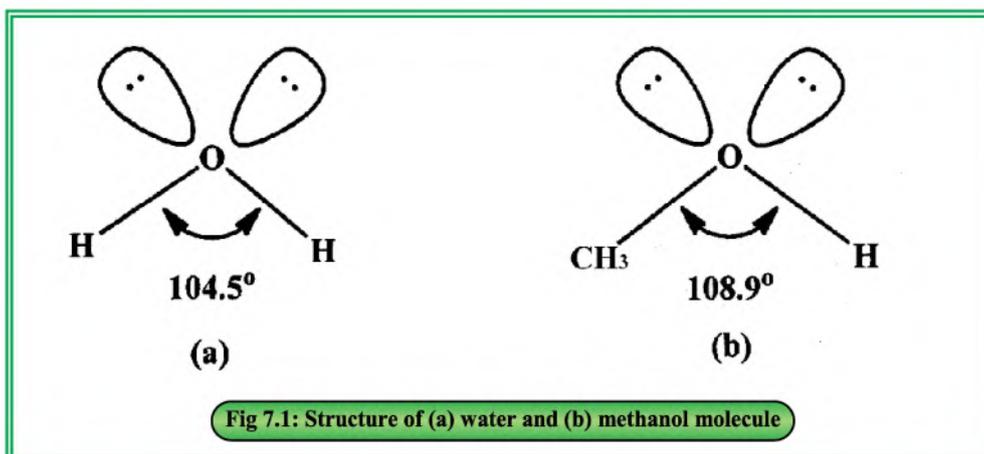


Monohydric alcohols are represented by a general formula R-OH or $C_nH_{2n+1}OH$. Monohydric alcohols are further classified into primary (1° -alcohol), secondary (2° -alcohol) and tertiary (3° -alcohol) depending upon whether the hydroxyl group is attached to primary, secondary or tertiary carbon atom.



7.1.1 Structure of Alcohol

The structure of an alcohol molecule is similar to that of water molecule as shown in figure Fig.7.1. The carbon atom which is bonded 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 atoms while the remaining two sp^3 hybrid orbitals of oxygen contain lone pairs of electrons. The C-O-H bond angle is 108.9° , which is slightly higher than exists in water molecule (104.5°).





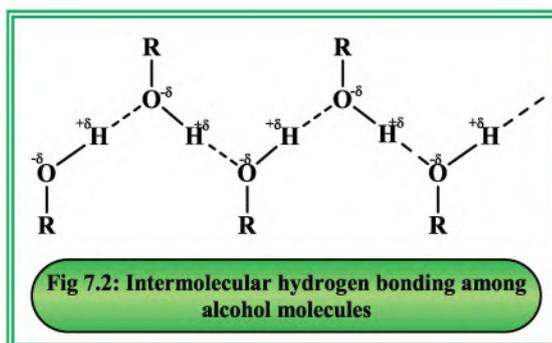
7.1.2 Physical Properties

Physical State: Alcohols of lower molecular mass (up to butanol) are colorless liquids with characteristic sweet smell. Higher members are waxy solids.

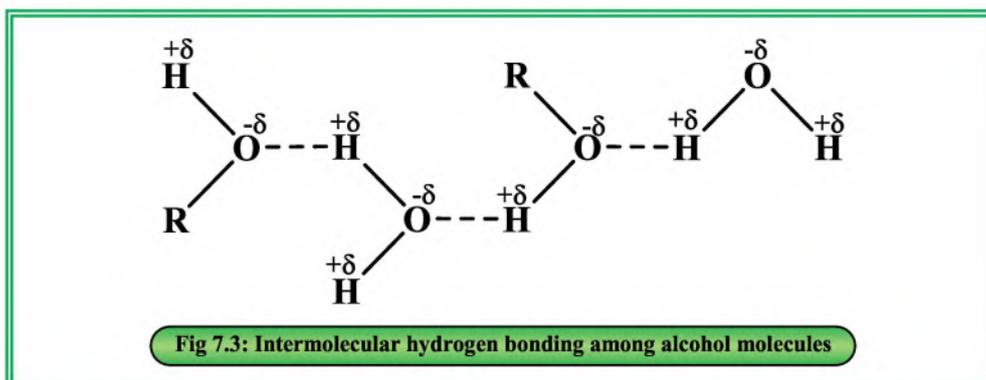
Boiling Point: Boiling point of alcohol is much higher than that of alkanes and ethers of comparable molecular mass. This is because of the existence of intermolecular hydrogen bonding. The greater the number of carbons in the molecule, the higher the boiling point of alcohol. Further, the boiling point of straight chain alcohol is higher than branch chain (Fig.7.2).

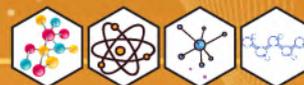
Table 7.1 Boiling points of straight chain and branch chain alcohols

Compound	Boiling Point (°C)
Ethanol	78.37
Propanol	97.2
Isopropanol	82.6
n-Butanol	117.7
Isobutanol	107.89



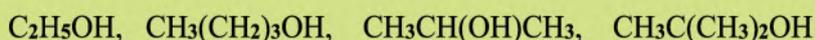
Solubility: Alcohols are generally soluble in water since they form hydrogen bonds with water molecules. However, solubility decreases with increasing the number of alkyl groups in the molecule (Fig.7.3).





Self-Assessment

Arrange the following alcohol molecules in increasing order of their boiling point.



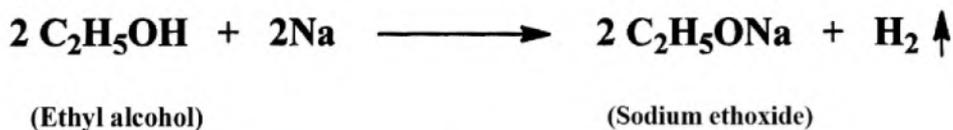
Acidity of Alcohol

Alcohols are generally classified as weak acids due to their ability to donate a proton to a strong base. The acidity of alcohol is determined by the stability of resulting alkoxide ion after the alcohol donates a proton. Compared to tertiary and secondary alcohols, primary alcohols generate more stable alkoxide ions making them relatively more acidic (Table.7.2).

Table 7.2 pka values of comparative alcohol compounds

Types of Alcohols	Structural formula	pka
Methyl alcohol	CH_3OH	15.5
Ethyl alcohol	$\text{C}_2\text{H}_5\text{OH}$	15.9
Sec. Propyl alcohol	$\text{CH}_3\text{CH}(\text{CH}_3)\text{OH}$	16.3
Tert. Butyl Alcohol	$\text{CH}_3\text{C}(\text{CH}_3)_2\text{OH}$	17

Acidic behavior of alcohol can be observed by the evolution of hydrogen gas when a piece of active metal (Sodium or Potassium) is put into anhydrous alcohol.



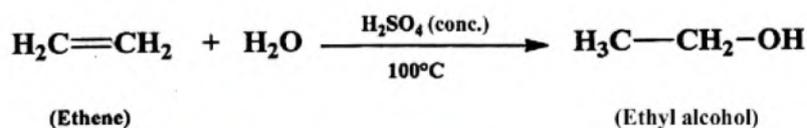
7.1.3 Preparations of Alcohols

There are several methods for the preparation of alcohols. Below are some commonly used methods.



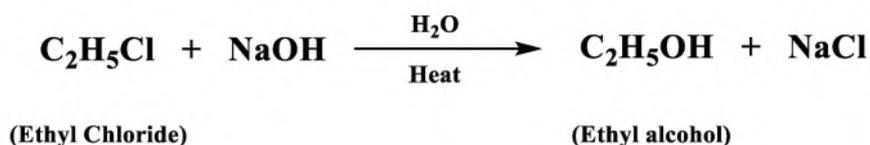
7.1.3.1 Hydration of an Alkene

Alkene when boils with water in the presence of concentrated sulphuric acid to give corresponding alcohol.



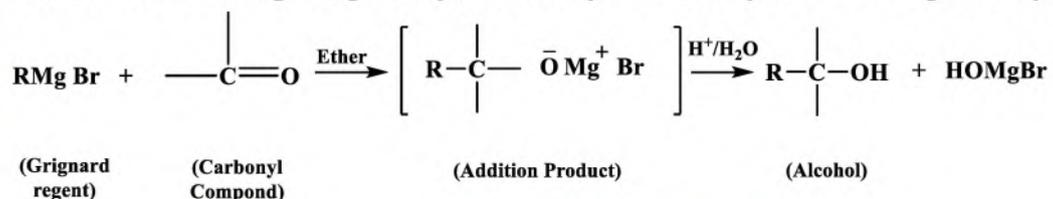
7.1.3.2 Hydrolysis of an Alkyl halide

When an alkyl halide is heated with aqueous alkali (NaOH, KOH), it gives corresponding alcohol.



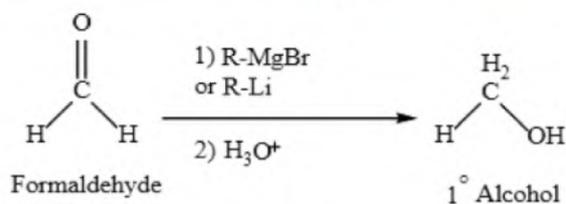
7.1.3.3 Reaction of Grignard reagent with Aldehyde and Ketone

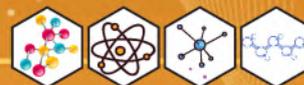
Grignard reagent when reacts with a formaldehyde, acetaldehyde and acetone molecule, it gives primary, secondary and tertiary alcohols respectively.



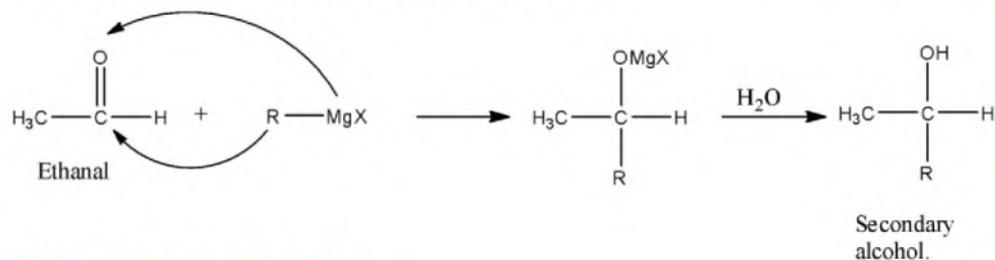
Preparation of primary, secondary and tertiary alcohol

(i) Reaction with formaldehyde

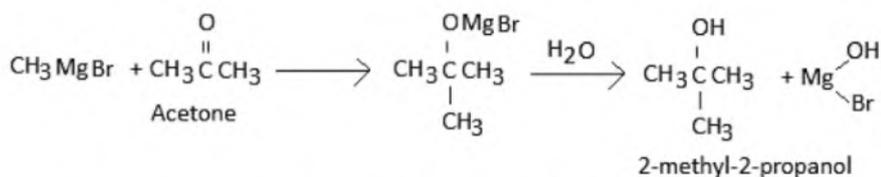




(ii) Reaction with acetaldehyde (ethanal)



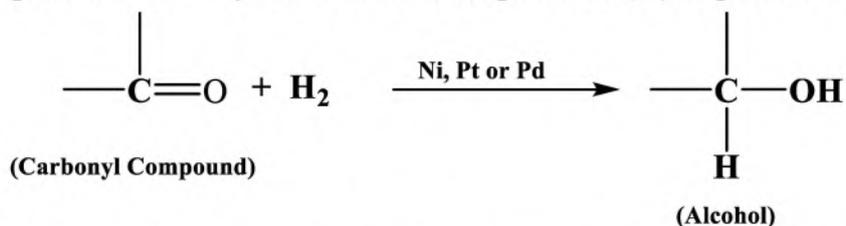
(iii) Reaction with acetone



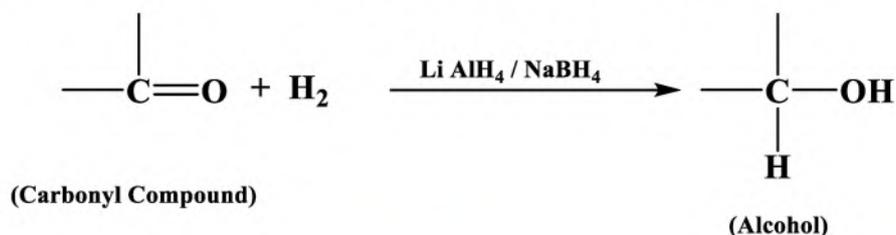
7.1.3.4 Reduction of Aldehydes and Ketones

Aldehydes and Ketones can be reduced to alcohols by using any one of the following two methods:

- (a) Hydrogenation of aldehyde and ketone at high temperature and pressure in the presence of catalyst like nickel (Ni), platinum (Pt) or palladium (Pd).



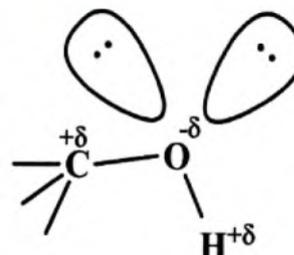
- (b) Reaction of aldehyde and ketone with a reducing agent like lithium aluminum hydride (LiAlH₄) or sodium borohydride (NaBH₄).





7.1.4 Reactivity of Alcohol

The oxygen atom in the alcohol molecule (R-OH) is more electronegative than the carbon and hydrogen atoms that are bonded to it. This creates a polarity in C-O and O-H bonds. In addition, oxygen has two unshared electron pairs which cause it to act as an electron rich centre.



Thus, the reactivity of alcohol can be attributed to the breaking of either C – OH bond with the removal of –OH group or by the breaking O – H bond with the removal of hydrogen (H). The common reactions of alcohol are substitution, elimination and oxidation.

7.1.5 Reactions of Alcohols

A variety of reactions can occur with alcohols, including dehydration, oxidation, reduction, esterification, as well as reactions involving halogens and metals. During reactions with other reagents, alcohol can experience cleavage of either the C-O or O-H bonds (Table.7.3).

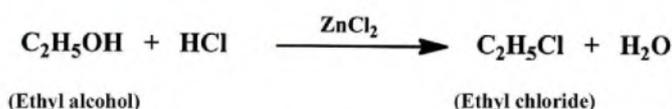
- (i) The C-O bond in an alcohol molecule breaks when it is attacked by a nucleophile.
- (ii) The H-O bond in an alcohol molecule breaks when it is attacked by an electrophile.

Table 7.3 Types of reactions of alcohols and their order of reactivity

Type of Bond Breaking	Type of Attacking Reagent	Order of reactivity of alcohols
O – H	Electrophile	$1^\circ > 2^\circ > 3^\circ$
C – O	Nucleophile	$3^\circ > 2^\circ > 1^\circ$

7.1.5.1 Reaction with Halogen acids (HX)

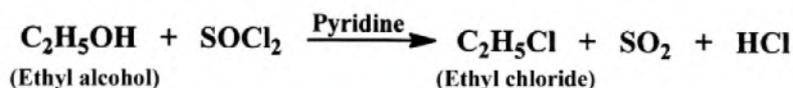
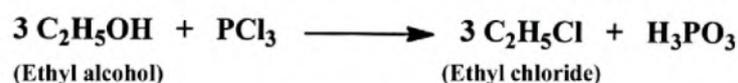
In the presence of a catalyst, zinc chloride (ZnCl_2), ethyl alcohol reacts with hydrochloric acid (HCl) to produce ethyl chloride.



The mixture of concentrated HCl and ZnCl₂ is called “Lucas reagent” and used to distinguish between primary, secondary and tertiary alcohol.

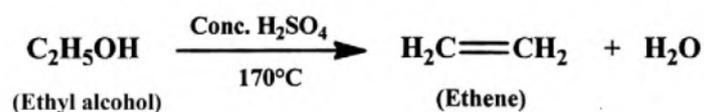
7.1.5.2 Reaction with SOCl₂ and PX₃

When alcohol is treated with Phosphorus tri halide (PX₃) or thionyl chloride (SOCl₂), it gives corresponding alkyl halide (Discussed in chap. 18).



7.1.5.3 Acid Catalyzed Dehydration

When an alcohol is heated with concentrated sulphuric acid at 170°C, it undergoes a dehydration process, resulting in the formation of an alkene. In this process, a water molecule is eliminated.



The ease of acid catalyzed dehydration of alcohol is given as
3°-alcohol > 2°-alcohol > 1°-alcohol

7.1.5.4 Oxidation Reaction

Primary and secondary alcohols oxidize in the presence of strong oxidizing agents such as acidified potassium dichromate (K₂Cr₂O₇) or potassium permanganate (KMnO₄) to give carboxylic acid through an aldehyde

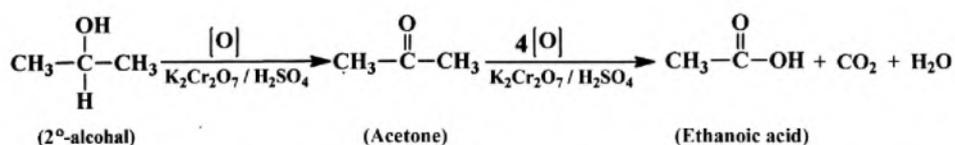
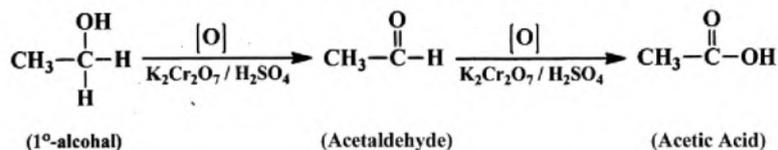


DO YOU KNOW?

In the Lucas test, primary alcohols show no immediate reaction, secondary alcohols form turbidity within a few minutes, and tertiary alcohols produce an immediate and vigorous formation of a cloudy precipitate (alkyl chloride) with Lucas reagent (conc. HCl and ZnCl₂).



or ketone intermediate. Tertiary alcohol cannot be oxidized due to the unavailability of hydrogen on its hydroxyl-bearing carbon.



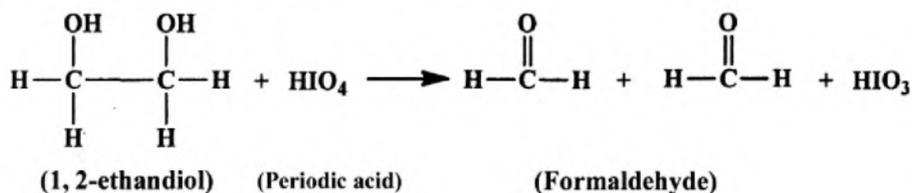
Since the oxidation of ketone involves the breaking of carbon-carbon sigma bond, it is a relatively slow process.

7.1.5.5 Cleavage of 1, 2-diols

An alcohol molecule in which two hydroxyl groups (-OH) are attached on position 1 and 2 is called as 1, 2 -diol or vicinal diol.

When a 1, 2-diol molecule is treated with per iodic acid (HIO₄), an oxidative cleavage occurs between carbon 1 and carbon 2 atoms resulting in the formation of two carbonyl molecules. These carbonyl molecules may be aldehyde or Ketone depending upon the number of alkyl groups attached to the carbon atom bearing hydroxyl groups. In this reaction periodic acid (HIO₄) is reduced into iodic acid (HIO₃).

For example, ethylene glycol (1, 2- ethanediol) is broken down into two formaldehydes molecules if treated with per iodic acid.



DO YOU KNOW?

Periodic acid is a white crystalline solid that dissolves in water and possesses high oxidizing potential owing to the presence of iodine in its composition. Apart from its use in organic chemistry as an oxidizing agent, it is also utilized for staining biological specimens.



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

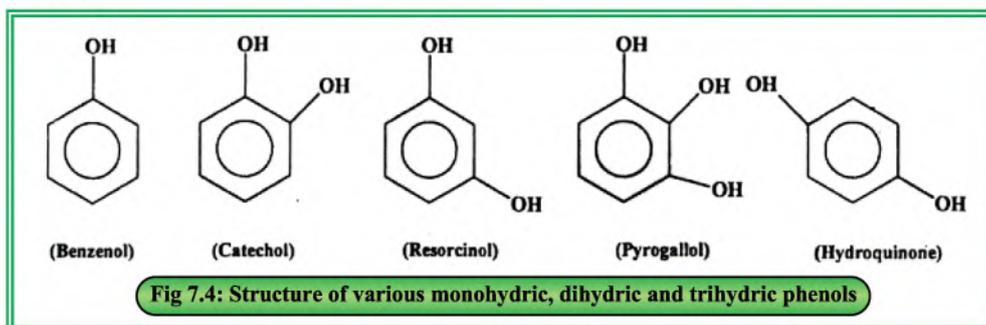
Uses of Alcohol

- (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).

7.2 PHENOLS

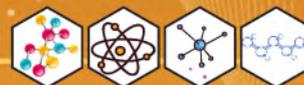
Organic compounds in which hydroxyl group (-OH) is directly attached to benzene ring are called Phenols. The parent compound of this family is monohydroxy benzene which is also known as carbolic acid or benzenol.

On the basis of number of hydroxyl groups (-OH) attached to aromatic ring, Phenols are classified into monohydric, dihydric and trihydric Phenols (Fig.7.4).



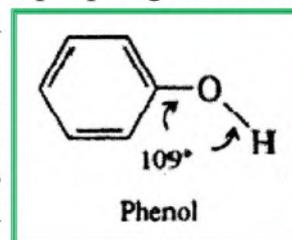
7.2.1 Structure of Phenol

In the molecule of phenol the carbon atom of aromatic ring is attached to an -OH group. The oxygen atom in the -OH group is sp^3 hybridized, while the



carbon atoms in the aromatic ring are sp^2 hybridized. An sp^3-sp^2 sigma bond is formed between oxygen atom of $-OH$ group and carbon atom of aromatic ring.

The $C-O-H$ bond angle is set at 109° which is almost the same as the bond angle of tetrahedral geometry (109.5°) but due to two non-bonded electron pairs of oxygen atom, the geometry is slightly distorted from a normal tetrahedron and exists in a bent shape.

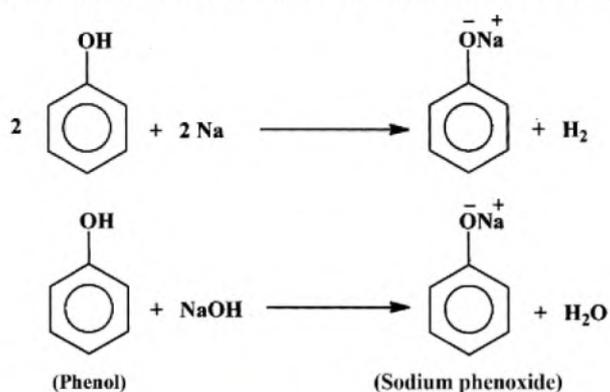


7.2.2 Physical Properties

- (i) **Physical State:** Pure phenol is a white crystalline solid at room temperature however it may appear in red colour due to the presence of some oxidized products as impurities.
- (ii) **Boiling Point:** The boiling point of phenol is higher than that of other compounds of comparable size because the presence of $-OH$ group enables a phenol molecule to form hydrogen bond with other phenol molecules.
- (iii) **Toxicity:** Phenol is toxic and corrosive in nature. When it comes into contact with skin it can lead to a severe burns and tissue damage.
- (iv) **Solubility:** The hydroxyl group attached to the aromatic ring allows phenol to make hydrogen bond with water molecules that is why it is soluble in water.

7.2.3 Acidity of Phenol

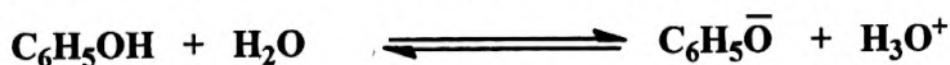
Phenol is fairly acidic since it reacts with an alkali or alkali metal to form salt.





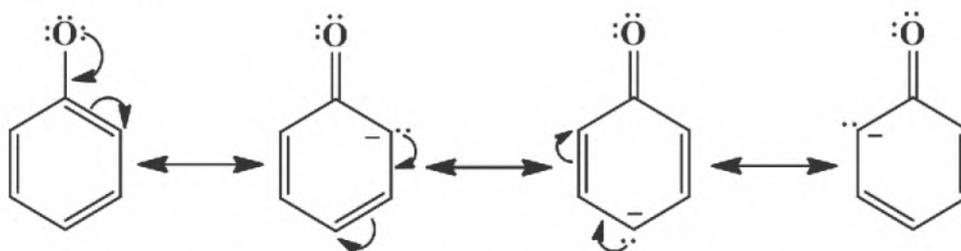
The pka value of phenol is approximately 10, which is far less than carboxylic acid (pka \approx 5) but much higher than alcohol (pka = 15 – 18) that is why phenol is much weaker acid than carboxylic acid but stronger than alcohol.

Comparing phenoxide ion with ethoxide ion, it is noted that the negative charge on oxygen atom of phenoxide ion is delocalized over the entire ring through a process called as resonance and make the phenoxide ion stable.

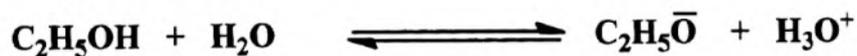


(Phenol)

(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.



(Ethanol)

(Ethoxide ion)

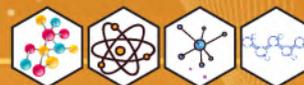


Self-Assessment

Compare the relative acid strength and water solubility of Phenol with Ethanol.

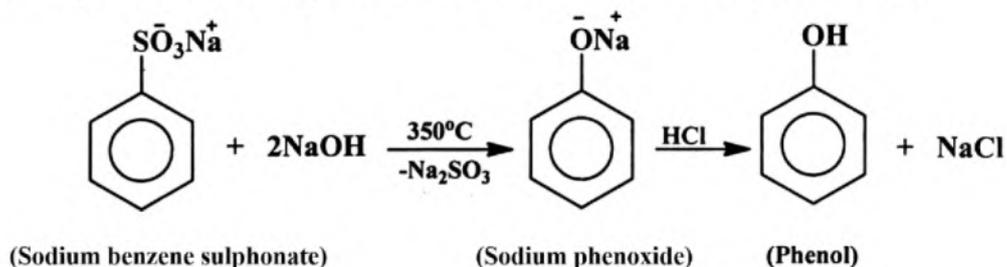
7.2.4 Preparation of Phenol

Phenol can be prepared by various methods. The two most common methods are described below.



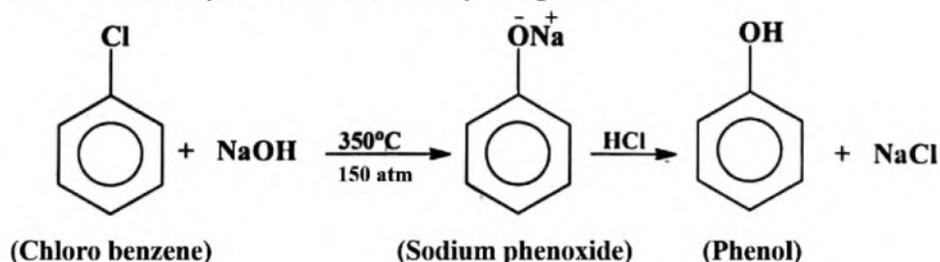
7.2.4.1 From Sodium Benzene Sulphonate

Sodium benzene sulphonate when fused with sodium hydroxide at 300 - 350°C, produces sodium phenoxide which on acidification yield phenol.



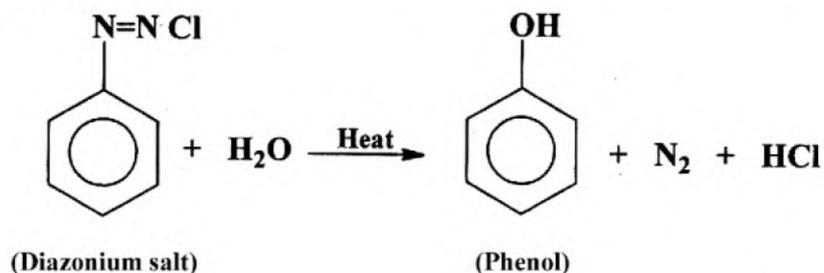
7.2.4.2 From Chlorobenzene (Dow's Process)

Chlorobenzene when fused with aqueous sodium hydroxide (NaOH) at 350°C and 150 atmospheric pressures, it gives sodium phenoxide which then acidified with dilute hydrochloric acid to yield phenol.



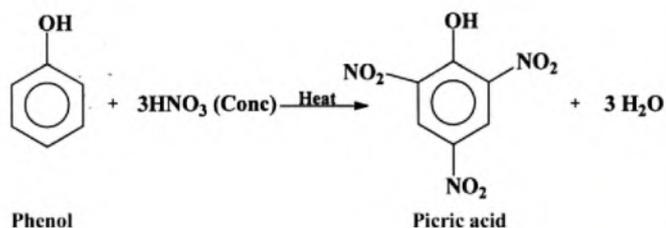
7.2.4.3 Hydrolysis of Diazonium salt

It is a laboratory method for the preparation of phenol. Benzene diazonium chloride on heating with water, changes into phenol with the release of nitrogen gas.





When phenol heated with concentrated nitric acid, it gives 2, 4, 6-trinitrophenol (picric acid).



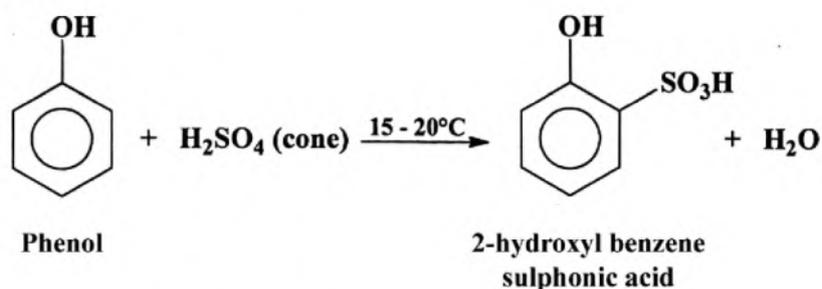
DO YOU KNOW?

Picric acid (2, 4, 6-trinitrophenol) is a yellow colored crystalline solid. It is explosive in dry form that is why it is stored in bottles under a layer of water to reduce the risk of explosion.

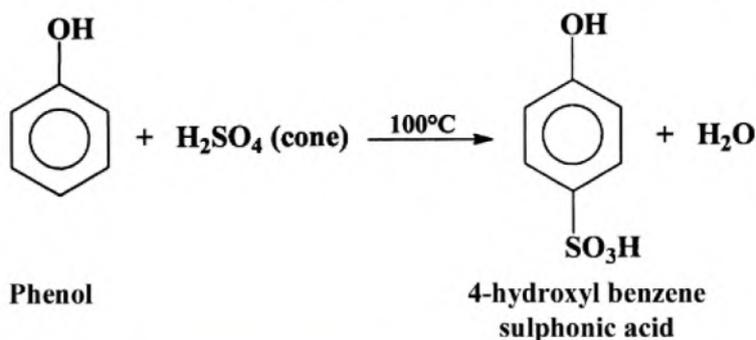
Sulphonation

When phenol is treated with sulphuric acid, it gives Phenol sulphonic acid, however the relative proportion of isomers depends upon temperature.

- (a) On heating at $15^\circ - 20^\circ\text{C}$, ortho phenol sulphonic acid is formed as major proportion.



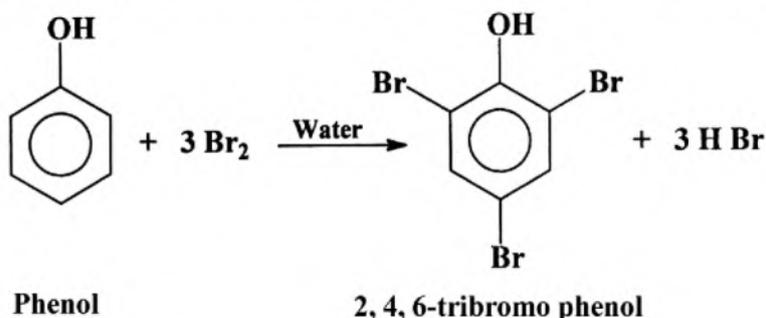
- (b) On heating at 100°C it gives major product of para phenol sulphonic acid.



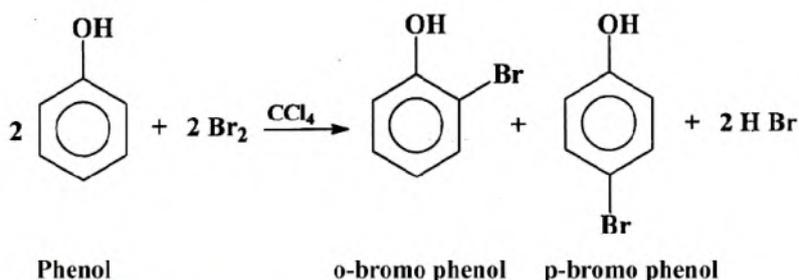


Halogenation

Phenol if reacts with aqueous bromine, it produces 2, 4, 6 – tribromophenol

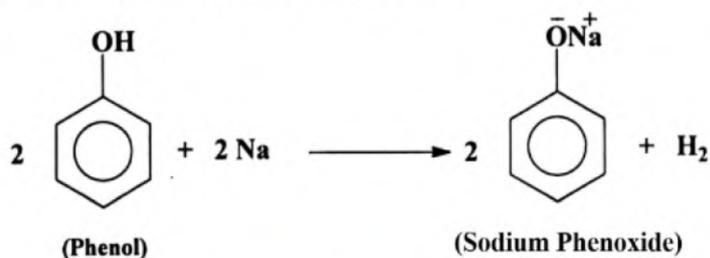


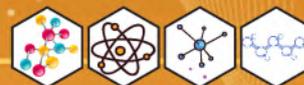
Phenol reacts with Bromine in carbon tetra chloride, it gives a mixture of ortho and para bromophenol.



7.2.6.2 Reaction with Sodium Metal

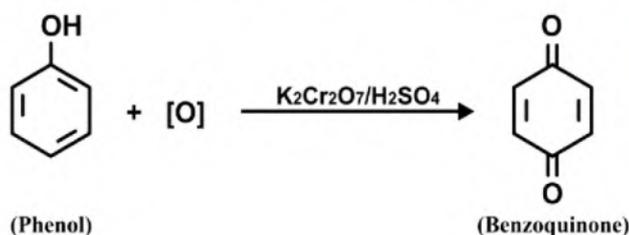
Phenol is an acidic compound. The hydrogen atom of its hydroxyl part (-OH) is ionizable. Thus phenol when reacts with highly active metal such as sodium, the sodium donate an electron to the oxygen atom of the hydroxyl group in phenol forming sodium phenoxide which is an important intermediate in the synthesis of various organic compounds.





7.2.6.3 Oxidation of Phenol

In this reaction potassium dichromate acts as oxidizing agent and the sulphuric acid serves as catalyst. Phenol is oxidized to yellow coloured benzoquinone (conjugated diketone).



DO YOU KNOW?

Benzoquinone has a variety of applications, including its use as a raw material for the production of nylon and polyester polymers. It is also used as a photographic developing agent, and in the production of certain antibiotics.

7.2.7 Difference between Alcohol and Phenol

Table 7.4 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.

7.2.8 Identification tests for Alcohols and Phenols

Tests of identification of Alcohol

(i) Sodium metal test

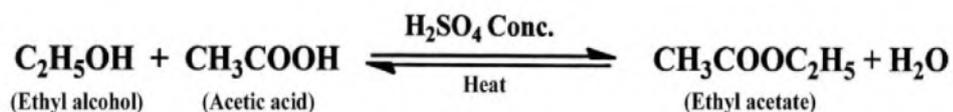
Alcohol readily reacts with sodium metal at room temperature to form sodium alkoxide with the liberation of hydrogen gas.



Brisk effervescence in the solution indicates the presence of alcoholic group in the given organic molecule.

(ii) Ester test

Alcohol when heated with acetic acid in the presence of small amount of concentrated sulphuric acid, it forms an ester.



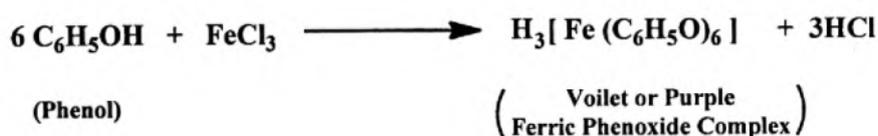
Fruity smell of ester indicates the presence of alcoholic group in the given organic compound.



Tests for identification of Phenol

(i) Ferric chloride test

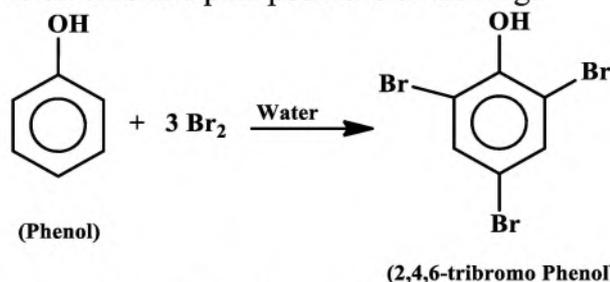
When freshly prepared aqueous solution of ferric chloride (FeCl_3) is added to phenol, it forms a ferric phenoxide complex.



Appearance of violet, blue or purple coloration indicates the formation of complex and identifies the presence of phenol.

(ii) Bromine water test

When bromine water is added to phenol, an electrophilic substitution reaction occurs on orho and para positions of the ring.



Disappearance of brown color of bromine and appearance of white precipitates of 2,4,6-tribromophenol identifies the presence of phenols

7.3 ETHERS

Ethers are an organic compounds having a general formula $\text{R-O-R}'$, characterized by an oxygen atom bonded to two alkyl or aryl groups. It has low reactivity and is commonly used as a solvent in various chemical reactions.

A symmetrical or simple ether is that in which both groups are of same type whereas

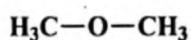


DO YOU KNOW?

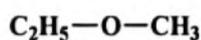
Diethyl ether has been used as anaesthetic in surgery since 1846. It suppresses response to sensory stimulation of brain and produces a temporary local or general anaesthesia.



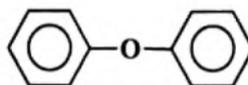
unsymmetrical or mixed ether consists of two different groups.



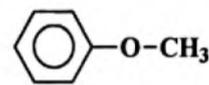
Dimethyl ether
(symmetrical ether)



Ethyl methyl ether
(unsymmetrical ether)



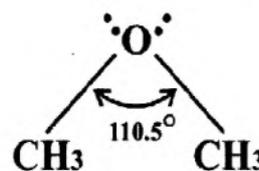
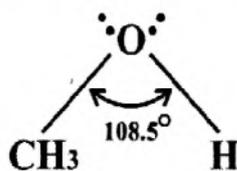
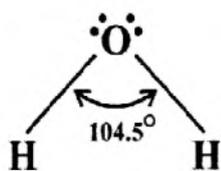
Diphenyl ether
(symmetrical ether)



Phenyl methyl ether
(unsymmetrical ether)

7.3.1 Structure of Ether

The geometry of ether molecule is bent shaped similar to alcohol and water, however the bond angle of C-O-C in ether molecule is 110.5° which is larger than water (104.5°) and alcohol (108.5°). The hybridization of oxygen atom is sp^3 while the hybridization of carbon depends on the nature substituent group (alkyl or aryl) attached to the oxygen atom.

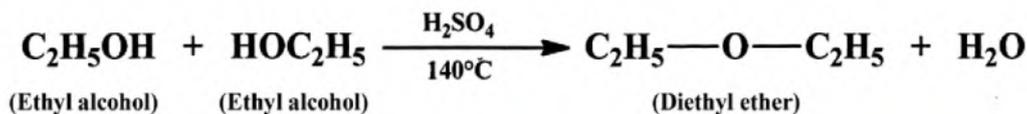


The greater (C-O-C) bond angle in ether is due to greater internal repulsion of hydrocarbon part than the external repulsion of lone pair on oxygen.

7.3.2 Preparation of Ether

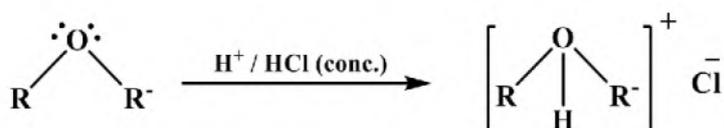
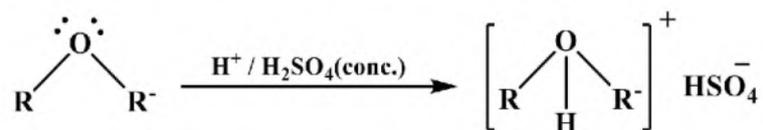
(i) Dehydration of alcohol

Excess of alcohol when heated with concentrated H_2SO_4 at 140°C , an intermolecular dehydration occurs to give ether.





Since oxygen atom of ether possess lone pairs of electrons, they serve as weak base and hence can react with strong acids to form oxonium salt.



The oxonium salt of ether remains stable if acid is concentrated but on dilution with water, it dissociates to reform ether and acid. The reason is that water is stronger Lewis acid than ether.

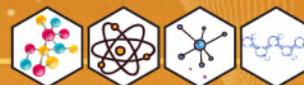


Self-Assessment

- Provide an example of a symmetrical ether.
- Can ethers form hydrogen bonds with water? Why or why not?

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.



SOCIETY, TECHNOLOGY AND SCIENCE

Antiseptics and disinfectants are chemicals used to kill germs such as bacteria, viruses and fungi etc. They are frequently used in our society to reduce the risk of infection.

Although both antiseptic and disinfectant are infection control chemicals, however their applications are different. Antiseptics are substances that are applied on human skin to kill germs whereas disinfectants are used to kill the germs on animate surfaces such as furniture, floors, walls of hospitals, clinics, homes and shopping centres etc. The chemicals used in antiseptics and disinfectants are called 'Biocides'. The concentration of biocides in antiseptics is quite lower than disinfectants to avoid irritation and other toxic effects on the skin. Antiseptics are used for various reasons such as hand sanitizing, infection prevention of minor cut or burn etc.



SUMMARY

- Alcohols are organic compounds in which one or more hydroxyl groups are attached with aliphatic carbon chain. The formula of monohydric alcohol is R-OH.
- Monohydric alcohols are classified into primary alcohol, secondary alcohol and tertiary alcohol depending upon the number of alkyl groups attached to the alpha carbon atom
- Phenols are hydroxyl derivatives of benzene; the simplest phenol is carbolic acid, which has the formula C_6H_5OH
- Methyl alcohol, primary alcohol and secondary alcohol oxidize to carboxylic acids in the presence of hot acidified dichromate or permanganate. Tertiary alcohol does not oxidize due to the unavailability of alpha hydrogen.



- Acidic character of phenol ($pK_a = 10$) is higher than alcohol ($pK_a \approx 16$) because phenoxide ion is more stable than alkoxide ion.
- Boiling points of alcohol and phenol are higher than alkanes and ethers of comparable molecular mass because they form intermolecular hydrogen bonds.
- Both alcohols and phenols are water soluble but solubility of alcohols is higher than phenols.
- The cleavage of ethylene glycol in the presence of periodic acid (HIO_4) gives two formaldehyde molecules.
- Phenols are commercially prepared by Dow's Process during which chlorobenzene is fused with aqueous sodium hydroxide at $350^\circ C$ and 150 atmospheric Pressure.
- The aromatic part of phenol is similar to the benzene which favours electrophilic substitution reaction.
- Phenols are identified by bromine water test as well as ferric chloride test.
- Alcohols are identified by sodium metal test and ester test.
- Ethers are considered as the dialkyl or diaryl derivatives of water. They are represented by a general formula $R-O-R$.
- Boiling point of ethers are much lower than alcohol and phenol since they do not form intermolecular hydrogen bonds.
- Symmetrical ethers are those in which similar alkyl or aryl groups are attached with oxygen atom.
- Ethers are relatively less reactive because $C-O-C$ bond of ether is susceptible for nucleophilic or electrophilic attack.



EXERCISE

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) $\text{K}_2\text{Cr}_2\text{O}_7$ (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

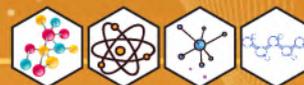
1. Define Phenol? Write the equations for the preparation of Phenol from.
 - (i) Chlorobenzene
 - (ii) Sodium benzene sulphonate
2. Write the equations for the following chemical Process
 - (i) Reduction of acetic acid with LiAlH_4 .



- (ii) Hydration of ethene with hot concentrated H_2SO_4
 - (iii) Oxidation of ethanol with acidified dichromate.
 - (iv) Hydrolysis of diazonium salt
3. Explain the following with scientific reason
- (i) Boiling point of ether is less than alcohol?
 - (ii) Alcohols are soluble in water?
 - (iii) Ethanol is liquid but ethyl chloride is gas at room temperature?
4. Identify each of following with two laboratory tests.
- (i) Phenol
 - (ii) Alcohol
5. What is Lucas reagent? Describe its use to distinguish between primary, secondary and tertiary alcohol.
6. What is oxonium ion? How can ether form oxonium ion?

Descriptive Questions

1. (a) What are alcohols? How alcohols are they classified?
(b) Starting from Grignard reagent how is primary, secondary and tertiary alcohol prepared?
2. Write the equations for the following possible conversions.
- (i) Ethyl alcohol to diethyl ether
 - (ii) Phenol to benzoquinone
 - (iii) Ethyl bromide to ethanol
 - (iv) 2°- alcohol to carboxylic acid
3. Differentiate between alcohol and phenol on the basis of
- (i) Solubility in water
 - (ii) Boiling Point
 - (iii) Acidic character
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
5. Enlist the commercial applications of Alcohol, Phenol and eth

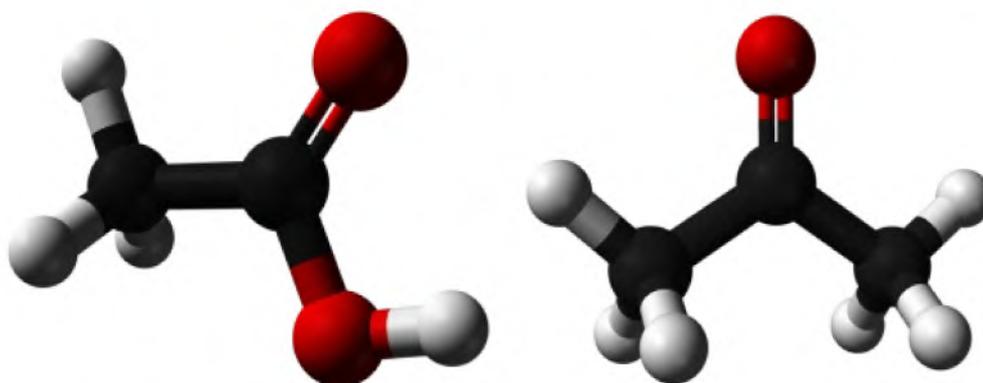


CHAPTER 8

CARBOYNL COMPOUNDS 1: ALDEHYDES AND KETONES



Teaching Periods	04	Assessment	01	Weightage %	03
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Students will be able to:

- ✓ Explain the physical properties and structure of aldehydes and ketones. (Understanding)
- ✓ Explain the preparation of aldehydes and ketones by ozonolysis of alkenes, hydration of alkynes, oxidation of alcohols and Friedel Craft's acylation of aromatics. (Applying)
- ✓ Describe reactivity of aldehydes and ketones. (Understanding)
- ✓ Explain acid and base catalysed nucleophilic addition reactions of aldehydes and ketones. (Applying)
- ✓ Explain reactions of aldehydes and ketones. (Applying)
- ✓ Describe oxidation reactions of aldehydes and ketones. (Applying)
- ✓ Compare the aldehyde and ketone with reference to their laboratory test (tabular form)(Understanding)
- ✓ Enlist the important compounds of Aldehydes and Ketones with their application. (Applying)

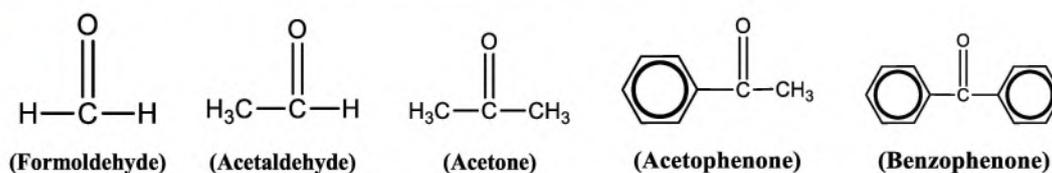


INTRODUCTION

Aldehydes and ketones hold significant importance, with widespread usage in several industries. They are the simplest carbonyl compounds; both contain a carbonyl group, which is a functional group consisting of a carbon atom double-bonded to an oxygen atom.

Aldehyde contain a carbonyl group at the terminal carbon of their carbon chain, whereas ketone have a carbonyl group located on the carbon within their carbon chain. Both types of compounds have unique properties and reactivity due to the presence of the carbonyl group, which makes them useful in a variety of applications.

The typical representatives of this class of compounds are formaldehyde, acetone, benzaldehyde and acetophenone. Formaldehyde is exceptional since it carries two hydrogen atoms instead of alkyl substituents.



Organic chemistry emphasizes the study of aldehyde and ketones due to their significant applications in various industrial sectors.

For example, formaldehyde is used to produce resins, synthetic plastic and urea formaldehyde. Acetone is used in the preparation of iodoform, chloroform and nail polish remover Benzaldehyde is used in the manufacturing of dyes etc.

8.1 PHYSICAL PROPERTIES

Physical State: Methanal and ethanal are gases; the other lower aldehydes and ketones are colourless liquids at room temperature. The higher aldehydes and ketones (more than C₂₀) are solids at room temperature.

Odour: Lower aldehydes have a pungent smell whereas ketones and higher aldehydes have a pleasant smell.



Boiling Point: Carbonyl compounds have higher boiling points than alkanes of similar molecular weights due to the polar nature of the carbonyl group, enabling intermolecular forces. However, they have lower boiling points compared to alcohols and carboxylic acids due to the absence of intermolecular hydrogen bonding.

Solubility: Carbonyl compounds are generally polar, and they are soluble in polar solvents such as water and ethanol. However, their solubility decreases as the size of the hydrophobic group (hydrocarbon chain) attached to the carbonyl carbon increases.

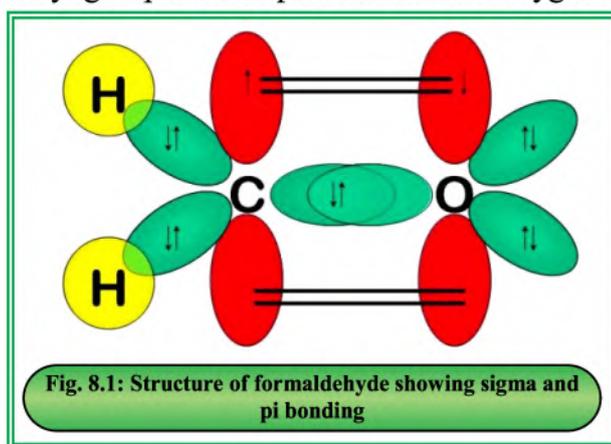


Self-Assessment

Why carbonyl compounds possess low boiling points than alcohols and carboxylic acids?

8.2 STRUCTURE OF ALDEHYDES AND KETONES

In aldehyde and ketone, the carbonyl group comprises a carbon atom that is double bonded to an oxygen atom. The carbon atom in the carbonyl group is sp^2 hybridized, with one of its sp^2 hybrid orbitals participating in sigma bond formation with the oxygen atom, while the other two sp^2 hybrid orbitals form sigma bonds with other atoms. The unhybrid p orbital of the carbon atom in the carbonyl group forms a pi bond with the oxygen atom (Fig.8.1).

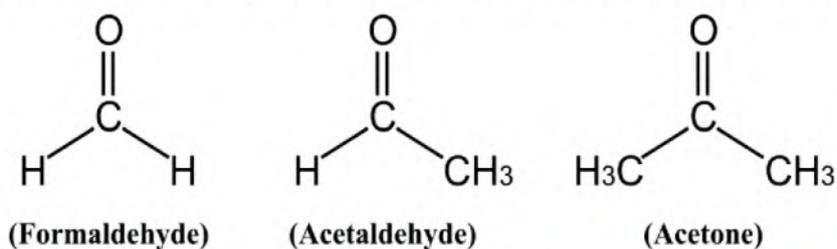


DO YOU KNOW?

Glucose and fructose are simple sugars, chemically known as aldehydextose and ketohexose. They possess aldehyde and ketone functional groups in the molecular structure respectively.



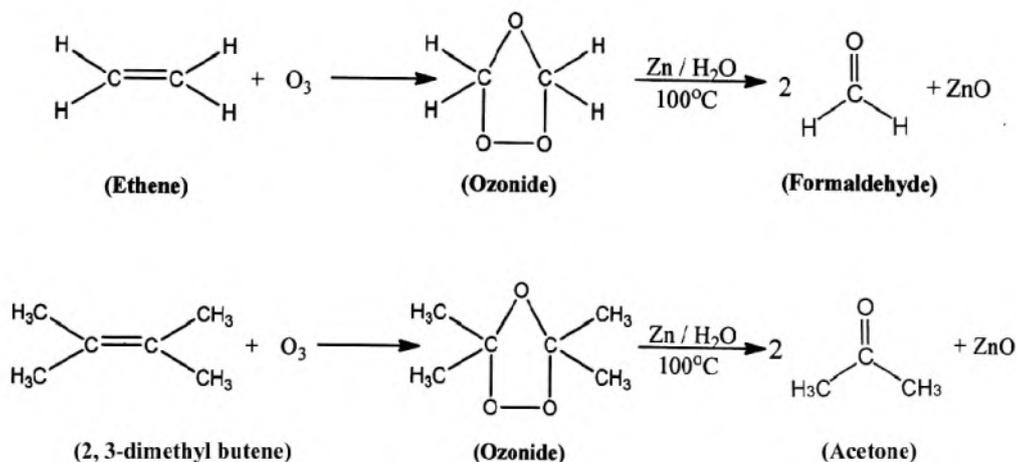
The sp^2 hybridization of the carbon atom in the carbonyl group allows it to acquire a trigonal planar geometry, with bond angles of approximately 120° .



8.3 PREPARATION OF ALDEHYDES AND KETONES

8.3.1 Ozonolysis of Alkenes

Alkenes can be ozonolyzed to yield aldehydes and ketones. This reaction involves the breaking of $C=C$ of alkene by the use of ozone and reducing agent such as zinc.



Self-Assessment

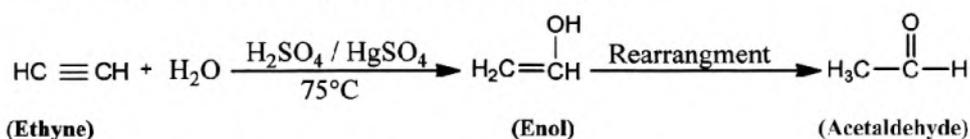
What is ozonolysis of alkenes and what are the main types of products that can be obtained from this reaction?



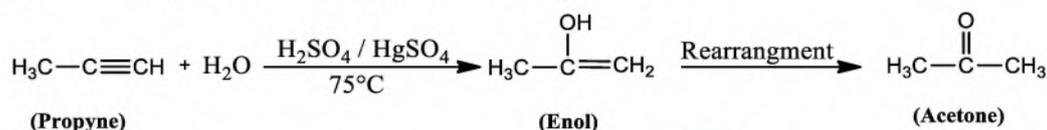
8.3.2 Hydration of Alkyne

Alkynes when heated with water in the presence of H_2SO_4 and HgSO_4 , an acid catalysed addition reaction occur on $\text{C} \equiv \text{C}$ to form an unstable enol which then on tautomerization, gives aldehyde or Ketone.

(i) The hydration of ethyne gives acetaldehyde



(ii) The hydration of propyne gives propanone



8.3.3 Oxidation of Alcohol

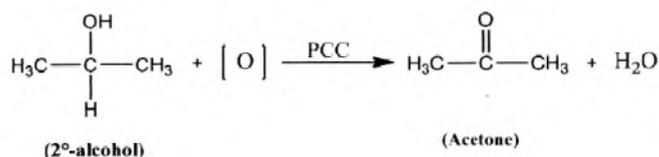
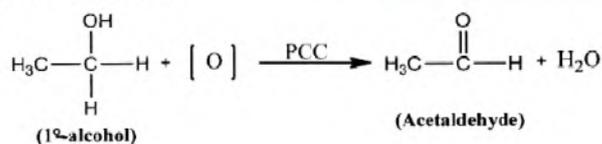
In the oxidation of alcohols, the $-\text{OH}$ functional groups are converted to carbonyl groups ($\text{C}=\text{O}$). Primary alcohols are oxidized to aldehydes, and secondary alcohols are oxidized to ketones, which can be achieved using pyridinium chlorochromate (PCC) as an oxidizing agent. However, tertiary alcohols do not undergo oxidation. This controlled process is valuable in obtaining specific carbonyl compounds in organic synthesis.



DO YOU KNOW?

Formalin is an aqueous solution of formaldehyde, typically containing 37-40% formaldehyde by weight. It is used as a disinfectant and preservative for biological specimens.

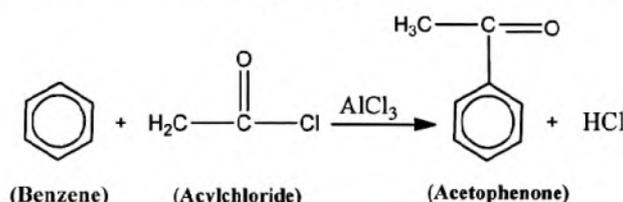
However, it is a known carcinogen and can cause skin and respiratory irritation and should be handled with cautions and appropriate protective measures.





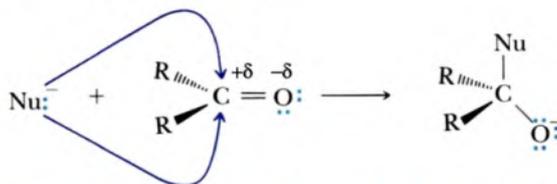
8.3.4 Friedel-Craft Acylation of Aromatic Compounds

Aromatic ketones can be synthesized through the Friedel Craft acylation method. In this reaction, an acyl chloride reacts with benzene or its derivatives in the presence of a Lewis acid catalyst, typically aluminum chloride (AlCl_3).



8.4 REACTIVITY OF CARBONYL COMPOUNDS

The carbon-oxygen bond ($\text{C}=\text{O}$) in the carbonyl group is highly polar due to the electronegativity difference between carbon and oxygen. It creates partially negative charge on oxygen and partially positive charge on carbon, making the carbon and oxygen atoms in aldehydes and ketones act as electrophiles and nucleophiles. Aldehydes are more reactive than ketones due to less steric hindrance (having one alkyl group) and a greater electron-withdrawing effect of the aldehyde's hydrogen, which enhances the electrophilicity of its carbonyl carbon, making it more attractive to nucleophiles.



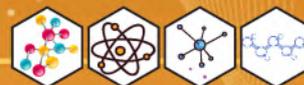
8.5 REACTIONS OF ALDEHYDE AND KETONES

Aldehyde and ketone undergo following types of reactions.

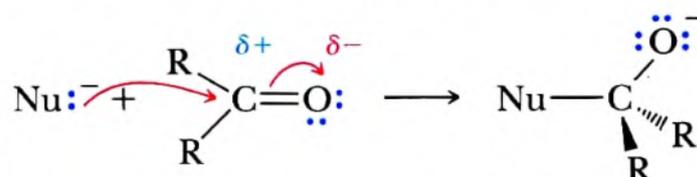
- (i) Nucleophilic addition reactions
- (ii) Reduction reaction
- (iii) Oxidation reaction

8.5.1 Nucleophilic addition reaction

In these reactions, nucleophiles attack the carbonyl carbon of aldehydes and ketones, leading to a change in the hybridization of the carbon atom from sp^2 to



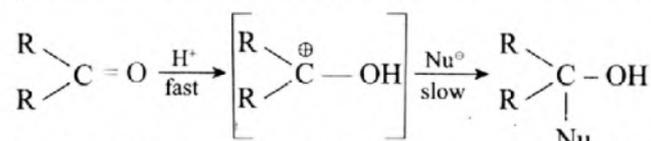
sp^3 . The pi electron pair of C=O shifts towards the oxygen atom, forming an alkoxide intermediate, which is subsequently protonated to yield the addition product.



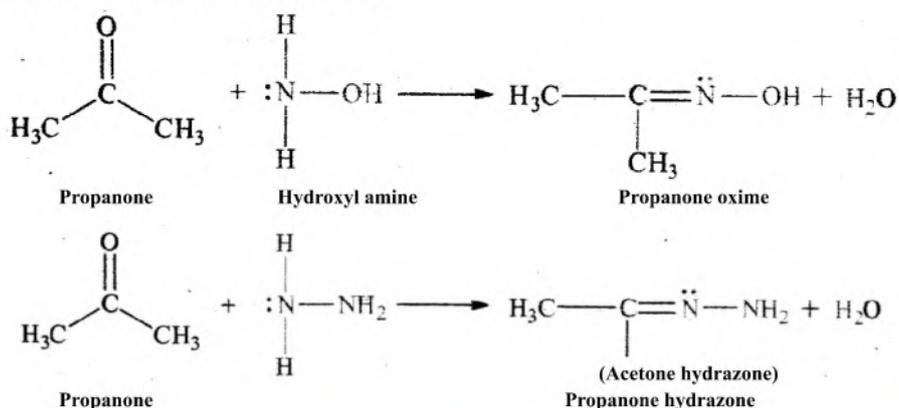
Nucleophilic addition reactions can be either acid-catalyzed or base-catalyzed, depending on the nature of reactants and the reaction conditions.

(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 nucleophile. 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.



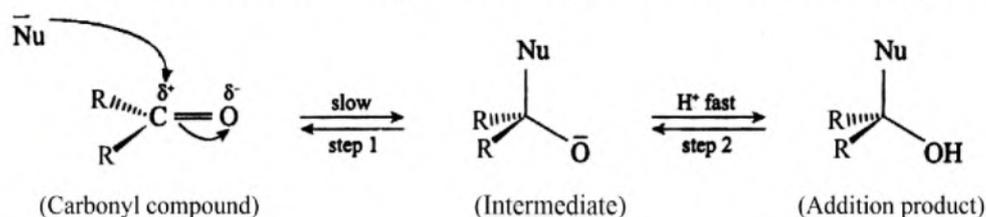
Addition of hydrazine ($\text{NH}_2\text{-NH}_2$) and hydroxyl amine (NH_2OH) on aldehyde and ketone is catalysed by an acid.



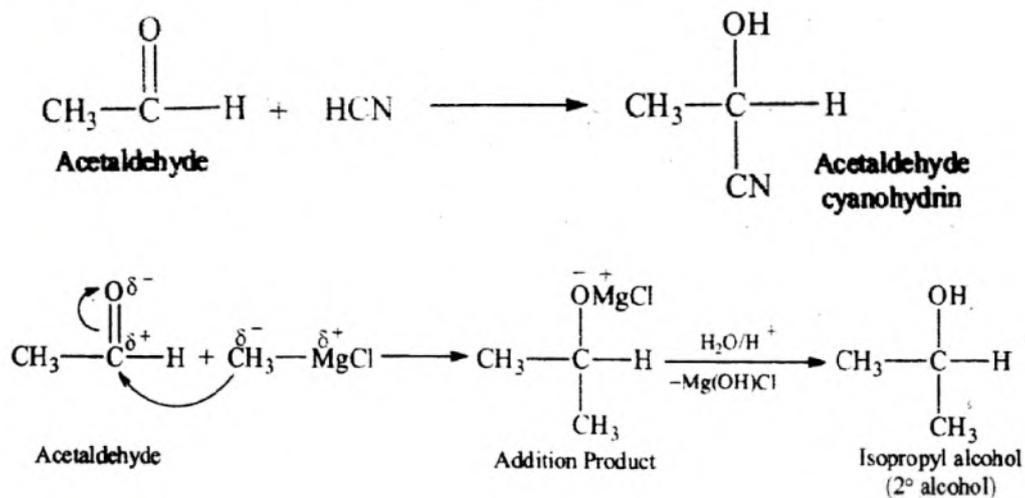


(ii) Base catalysed Nucleophilic addition reaction

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.



Addition of HCN and Grignard reagent is catalysed by base.



Self-Assessment

Give equations for the reactions of propanone with the following reagents
 (a) Hydrazine (b) Hydroxylamine

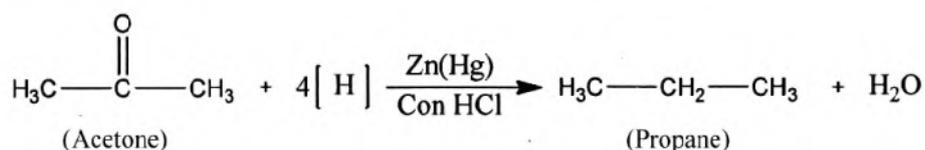
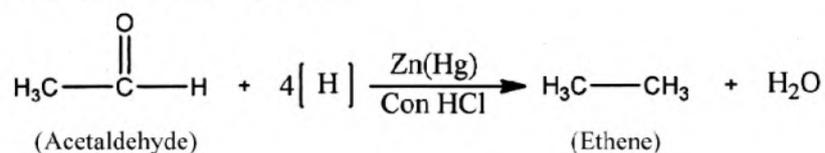


8.5.2 Reduction of Aldehyde and Ketone

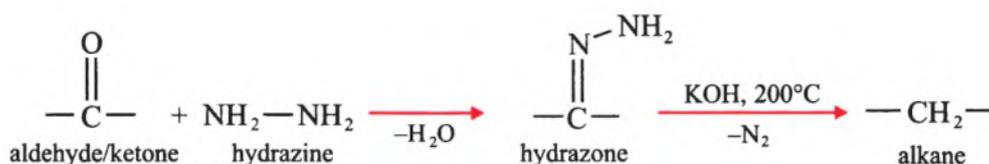
The reduction of aldehydes and ketones involves the addition of hydrogen to the carbonyl group resulting in the formation of an alkane or alcohol depending upon the suitable reducing agent used in the reaction.

8.5.2.1 Reduction to Hydrocarbon

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.

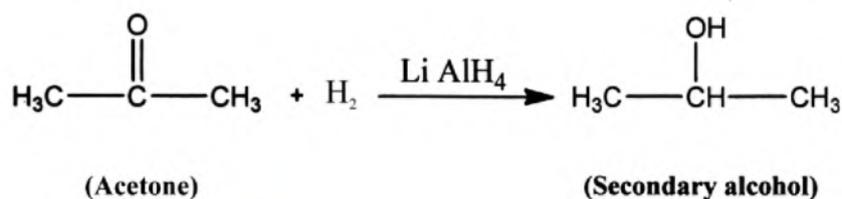
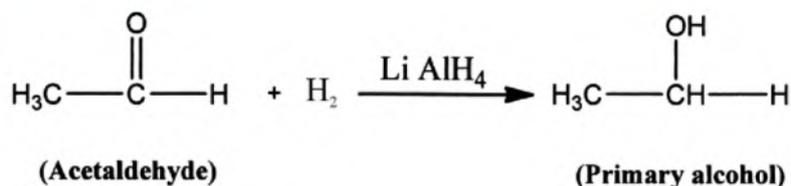


Aldehyde and ketone can also be converted into alkane by using hydrazine (NH₂-NH₂) and potassium hydroxide. This is known as Wolf Kishner reaction.



8.5.2.2 Reduction to Alcohol

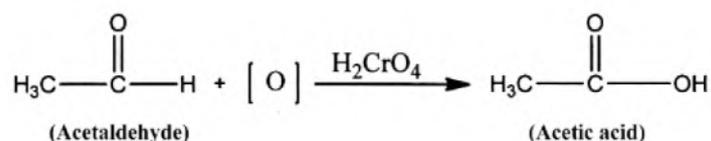
Aldehyde and ketone when treated with strong reducing agents such as NaBH₄ or LiAlH₄, they reduce into primary and secondary alcohols respectively.



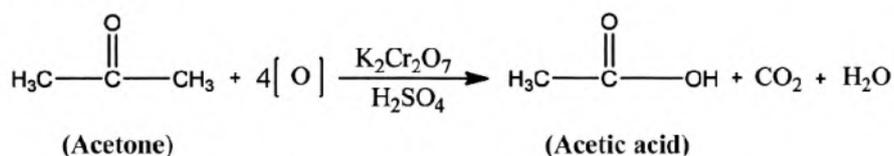
8.5.3 Oxidation Reaction

Aldehydes and ketones undergo oxidation with an oxidizing agent to give carboxylic acid. However, the reactivity of aldehyde towards oxidation reaction is quite easy due to the availability of active hydrogen atom at the carbonyl position, thus

- i. A variety of mild oxidizing agents such as chromic acid (H_2CrO_4), Tollen's reagent, Fehling reagent and Benedict reagent can be used to convert aldehyde into corresponding carboxylic acid. Aldehydes can also be oxidized by strong oxidizing agents.



- ii. Oxidation of ketone is relatively slow and it involves the breaking of carbon-carbon sigma bond and it happens only in the presence of strong oxidizing agent.





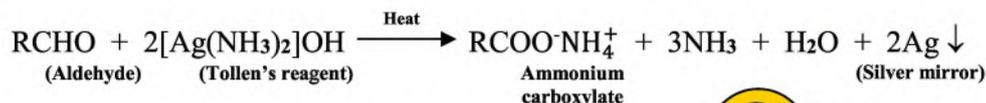
Self-Assessment

What reagent can be used to convert an alcohol to aldehydes or ketones without the formation of carboxylic acid?

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.

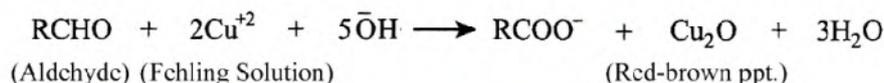


While performing the test, Tollen's reagent is mixed with the given carbonyl compound and heated to boiling. If aldehyde is present, a silver mirror will form on the inside of the test tube.

(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) with sodium potassium tartarate.

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 colour of Fehling solution (Cu^{+2}) changes to red precipitates (ppt) of copper (I) oxide.



DO YOU KNOW?

Tollen's reagent, Fehling solution and Benedict solution are three commonly used chemical reagents for a laboratory test to distinguish between an aldehyde and ketones.

- Silver nitrate and ammonium hydroxide are the components of Tollen's reagent.
- Copper sulphate, sodium hydroxide and tartaric acid are the components of Fehling solution.
- Copper sulphate, sodium hydroxide and citric acid are the components of Benedict solution.



8.5.4 Difference between Aldehyde and Ketone

Basic Structure: Both aldehydes and ketones are carbonyl compounds but in aldehydes, the carbonyl carbon is attached with at least one alkyl or aryl group while in ketones, carbonyl carbon is attached with two alkyl or aryl groups.

Physics Properties: The boiling point of ketones is relatively higher than aldehydes since carbonyl group of ketones is more polarized than aldehydes.

Reactivity: The reactivity of aldehydes towards nucleophilic addition is greater than ketones because of less steric hindrance and less electronic effect.

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.

Reduction into alcohol: Reduction of aldehydes in the presence of strong reducing agents such as lithium aluminum hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$) gives primary alcohol while the reduction of ketones gives secondary alcohol.

Table 8.1 Some applications of aldehydes and ketones

Application	Aldehydes	Ketones
Organic Synthesis	Used as key intermediates in various organic reactions.	Important starting materials for creating complex organic compounds.
Flavor and Fragrance	Provide characteristic aroma and taste to many natural and synthetic products, e.g., vanillin and benzaldehyde.	Used as flavoring agents and fragrances in the food, cosmetic, and perfume industries.
Pharmaceuticals	Serve as building blocks for various pharmaceuticals, such as anti-inflammatory drugs and antihistamines.	Some ketones are used as active pharmaceutical ingredients in medicines.
Solvents	Formaldehyde is used as a solvent for certain reactions.	Acetone is a widely used solvent for chemical reactions and as a nail polish remover.



SOCIETY, TECHNOLOGY AND SCIENCE

Role of Ozonolysis in drinking water

Ozone is a powerful oxidizing agent, it is successfully used in the treatment of drinking water in the following manners.

- (i) It serves as biocides since it ozonolyses the organic substances present in the cell membrane of microorganisms such as bacteria, viruses and the protozoa and hence killed them.
- (ii) It oxidizes certain metals (Cu, Fe, Mn, etc.) which are present in the excess amount in water that can be easily separated by filtration.



SUMMARY

- Aldehydes and ketones are organic compounds that contain carbonyl functional group ($>C=O$).
- The boiling point of aldehydes and ketones is lower than alcohols since they do not form intermolecular hydrogen bond.
- The boiling point of aldehydes and ketones is higher than alkanes because of molecular polarity and dipole-dipole attractive forces among their molecules.
- The chemical reactivity of aldehydes and ketones is attributed to the polar carbonyl group they contain.
- The geometry of aldehydes and ketones molecules is trigonal planar since carbon atom of carbonyl group ($C=O$) is sp^2 hybridized.
- Preparation of aldehydes and ketones is mostly carried out by ozonolysis of alkene and hydration of alkyne.
- Reduction of aldehydes and ketones with $LiAlH_4$ or $NaBH_4$ gives primary and secondary alcohol respectively.
- Aldehydes can be oxidized into carboxylic acid with mild oxidizing agent such as chromic acid (H_2CrO_4), Tollen's reagent and Fehling solution etc.



- Ketones can be oxidized into carboxylic acid in presence of strong oxidizing agent.
- Nucleophilic addition reactions of aldehydes and ketones are catalysed by acid or base depending upon the availability of either weak or strong nucleophilic reagent.
- Water, alcohol, and ammonia can undergo nucleophilic addition reactions with aldehydes and ketones, and these reactions are catalyzed by acids.
- Hydrogen cyanide (HCN) and Grignard reagent (RMgX) can react with aldehydes and ketones in the presence of a base catalyst.
- Identification of aldehydes in a laboratory can be carried out by Tollen's reagents or by Fehling solution.

? EXERCISE

Multiple Choice Questions

- (i) Ketones when treated with LiAlH_4 , they reduce to:

(a) Primary alcohol	(b) Secondary alcohol
(c) Tertiary alcohol	(d) Dihydric alcohol
- (ii) The reagent used to oxidizes ketones into carboxylic acids is:

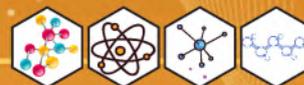
(a) Ammoniacal silver nitrate	(b) Potassium dichromate
(c) Fehling solution	(d) Benedict solution
- (iii) The carbonyl carbon of aldehydes and ketones is:

(a) Sp hybridized	(b) Sp^2 hybridized
(c) Sp^3 hybridized	(d) dsp^3 hybridized
- (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
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- (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) $\text{CH}_3\text{-O-CH}_3$
(c) $\text{C}_2\text{H}_5\text{OH}$ (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

- Give reasons for the following:
 - The boiling point of aldehydes and ketones is lower than alcohol.
 - Formaldehyde is highly soluble in water as compared to other aldehydes.
 - Oxidation of aldehydes is faster than ketones.
- Write the equation for the reaction of acetaldehyde with the following:
 - Chromic acid (H_2CrO_4)
 - Lithium Aluminum hydride (LiAlH_4)
 - Zinc mercury amalgam
- How is formaldehyde prepared by ozonolysis?
- Why is formaldehyde more reactive towards Nucleophilic addition reactions compared with ketones.
- How does the oxidation of ketones differ from the oxidation of aldehydes?
- Why are ethers considered as good solvents in organic reactions?

Descriptive Questions

- What are aldehydes and ketones? Describe the structure and type of hybridization in them.
- Explain the acid-catalyzed and base-catalyzed nucleophilic addition reactions in aldehydes and ketones.



3. Describe how aldehydes are distinguished from ketones by the following laboratory test.
 - (i) Tollen's reagents
 - (ii) Fehling solution
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 $AlCl_3$.
5. Give four differences between aldehydes and ketones.
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
7. Explain the factors that influence the reactivity of carbonyl compounds towards nucleophilic addition reaction.

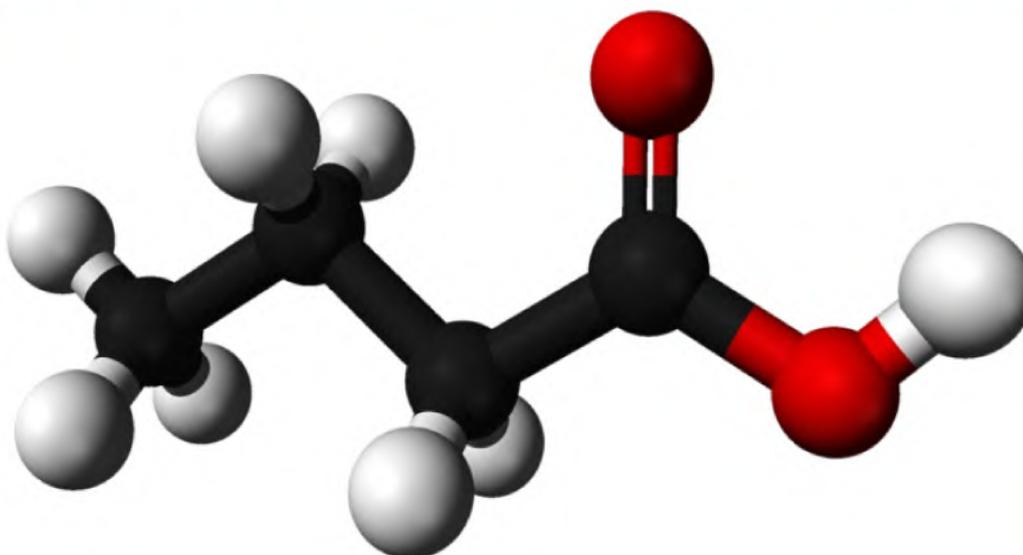


CHAPTER 9

CARBONYL COMPOUNDS II: CARBOXYLIC ACID AND FUNCTIONAL DERIVATIVES



Teaching Periods	07	Assessment	01	Weightage %	06
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Students will be able to:

- ✓ Discuss the physical properties and acidity of carboxylic acid. (Understanding)
- ✓ Describe preparation of carboxylic acids by carbonation of Grignard's Reagent, hydrolysis of nitriles, oxidation of primary alcohols, oxidation of aldehydes and oxidation of alkyl benzenes. (Applying)
- ✓ Conversion of carboxylic acids into their derivatives (acyl halides, acid anhydrides, esters, amides) without mechanism. (Applying)
- ✓ Enlist the important compounds of carboxylic acids and their derivatives with their application. (Applying)



INTRODUCTION

“Organic compounds which contain carbonyl group ($C = O$) attached to hydroxyl group ($-OH$) are referred as carboxylic acid”. In these compounds one or two carboxyl groups ($-COOH$) are directly attached with the alkyl or aryl carbon chain.

Carboxylic acids are versatile compounds. They have many important applications in various fields. In food industry they are used as preservatives, flavouring and acidity regulators. They are used in the manufacturing of many pharmaceuticals such as aspirin, ibuprofen and penicillin. Carboxylic acids are essential for many biological processes, including the breakdown of fat and carbohydrates. Carboxylic acids are used as starting materials in the manufacturing of polymers such as nylon, polyester etc.

9.1 PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS

i) Colour and odour

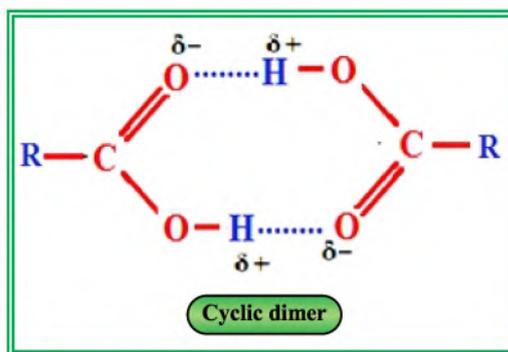
Aliphatic monocarboxylic acids are generally colourless. They have a pungent odour. However, the intensity of odour decreases with the length of chain.

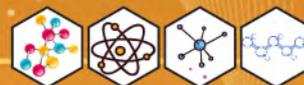
ii) Solubility

Carboxylic acids are soluble in polar solvents such as water and alcohols, due to their ability to form hydrogen bonds with these solvents. However, as the length of carbon chain increases, their solubility in water decreases.

iii) Boiling points

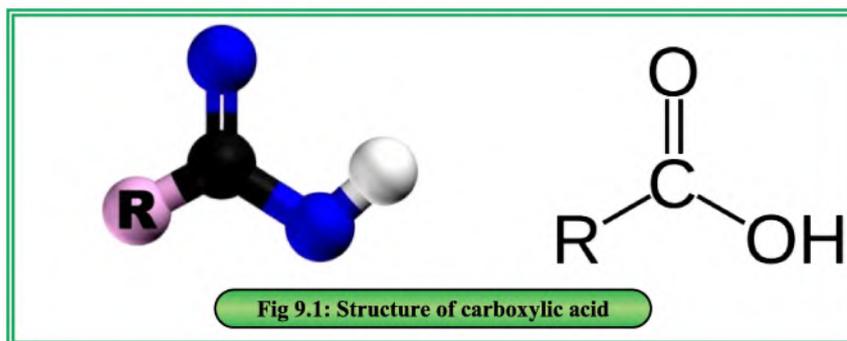
Compared to alcohols, carboxylic acids are more polar and have a high tendency to form hydrogen bonds among themselves. As a result, carboxylic acids generally have higher boiling points than their corresponding alcohols. The hydrogen bonding in carboxylic acids mostly exists in cyclic dimer form.





9.2 STRUCTURE OF CARBOXYLIC ACID

Structure of carboxylic acid is explained by the hybrid orbital theory (Fig.9.1). 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.



9.3 ACIDITY OF CARBOXYLIC ACID

“Carboxylic acids are considerably stronger acids than alcohols, phenols and water. However, they are weaker acids compared to mineral acids”.

Table 9.1 Comparative acid strength of carboxylic acid with alcohol, phenol and water		
Name of Compound	Molecular Formula	pKa Value
Acetic acid	CH ₃ COOH	5
Phenol	C ₆ H ₅ OH	10
Ethyl alcohol	C ₂ H ₅ OH	16
Water	H ₂ O	15.7

When carboxylic acids are dissolved in water, they undergo dissociation to produce carboxylate ions. This dissociation occurs because the carbon atom in the carboxyl group is electron withdrawing group, which leads to a weakening of hydrogen oxygen bond. Consequently, the carboxyl group is able to lose a proton in aqueous medium which makes it an acid.



Self-Assessment

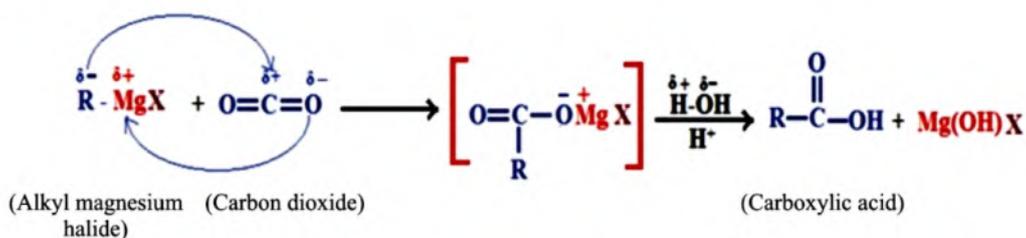
Carboxylic acids are more acidic than alcohol and explain on the basis of their pKa values.

9.4 PREPARATION OF CARBOXYLIC ACIDS AND THEIR DERIVATIVES

Carboxylic acids are prepared by the following different methods.

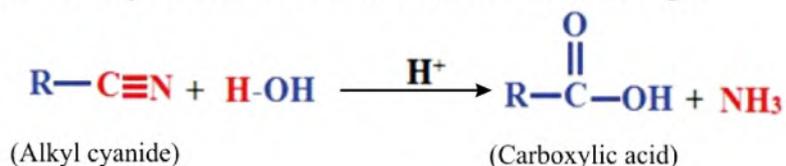
9.4.1 By the Carbonation of Grignard Reagent

When Grignard reagent reacts with carbon dioxide, it changes into an addition product which on hydrolysis in acidic medium produce carboxylic acid.



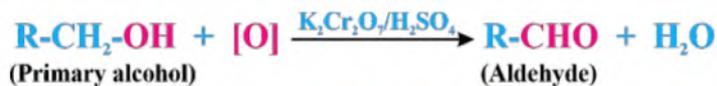
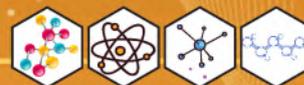
9.4.2 By the Hydrolysis of Nitriles

Alkyl cyanide (nitrile) when reacts with water in the presence of acid, it changes into carboxylic acid with the liberation of ammonia gas.



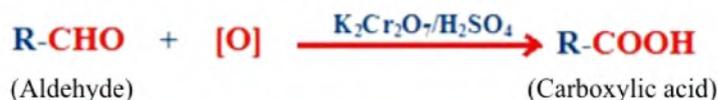
9.4.3 By the Oxidation of Primary Alcohols

By using acidified oxidizing agents such as $\text{K}_2\text{Cr}_2\text{O}_7$ or KMnO_4 primary alcohols can be oxidized to form carboxylic acids. This process occurs through an intermediate stage where the alcohol is converted into an aldehyde.



9.4.4 By the Oxidation of Aldehyde

Aldehydes oxidized when mixed with Potassium dichromate and sulphuric acid to produce carboxylic acid.



9.4.5 By the Oxidation of Alkyl Benzene

When an alkyl benzene reacts with potassium permanganate (KMnO_4) under acidic conditions, the alkyl group is oxidized to $-\text{COOH}$ group.



9.5 REACTIONS OF CARBOXYLIC ACIDS AND THEIR DERIVATIVES

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 hydroxyl group of carboxylic acid with an alkyl or aryl group. Their general formula is R-COOR e.g. Ethyl acetate ($\text{CH}_3\text{COOCH}_2\text{CH}_3$), Methyl propionate ($\text{CH}_3\text{CH}_2\text{COOCH}_3$).



DO YOU KNOW?

Esters are mostly found in fruits. An ester named as ethyl butanoate ($\text{C}_3\text{H}_7\text{COOC}_2\text{H}_5$) is specifically found in pineapple which contributes its specific aroma and as flavour.



(ii) **Acid halides:** They are formed by replacing the hydroxyl group of carboxylic acid with a halogen (X) atom. Their general formula is RCOX e.g. Acetyl chloride (CH_3COCl), Propionyl chloride ($\text{CH}_3\text{CH}_2\text{COCl}$).

(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 ($\text{C}_6\text{H}_5\text{CONH}_2$).

(iv) **Anhydrides:** They are formed by removing a water molecule from two carboxylic acid molecules. Their general formula is $(\text{RCO})_2\text{O}$ e.g. Acetic anhydride ($(\text{CH}_3\text{CO})_2\text{O}$), Maleic anhydride ($\text{C}_4\text{H}_2\text{O}_3$).

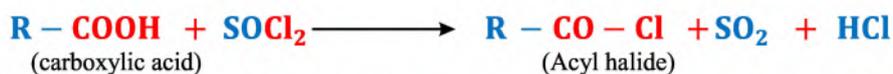
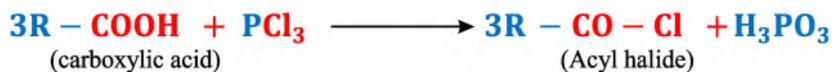


DO YOU KNOW?

Acetic anhydride is a corrosive and hazardous chemical but widely used in organic chemistry such as in the manufacturing of cellulose acetates pigments dyes and pharmaceuticals.

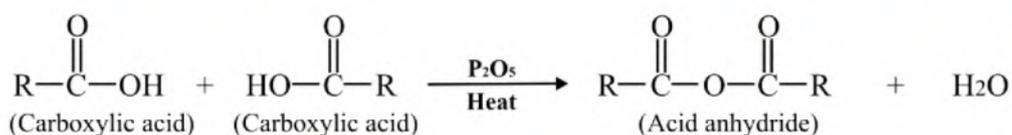
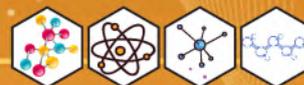
9.5.1 Conversion of carboxylic acids into acyl halides

Like alcohols, the hydroxyl groups of carboxylic acids are easily replaced by halogen atom on heating with PCl_5 , PCl_3 or SOCl_2 . However, the thionyl chloride (SOCl_2) is generally preferred because the by-products obtained are in the gaseous state which are escaped out from reaction mixture to get pure acyl halides.



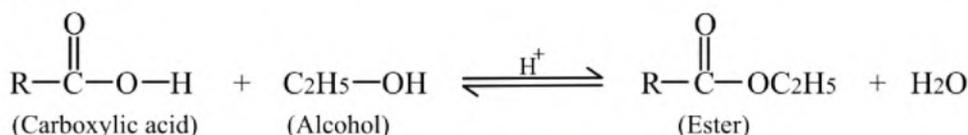
9.5.2 Conversion of Carboxylic Acids into Acid Anhydrides

The formation of an acid anhydride involves a condensation reaction between two carboxylic acid molecules. This reaction is typically conducted in the presence of a dehydrating agent like phosphorus pentoxide (P_2O_5).



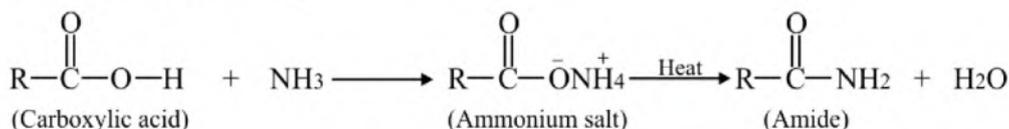
9.5.3 Conversion of Carboxylic Acids into Ester

Esters are produced from carboxylic acids through a reaction called esterification. In this reaction carboxylic acid reacts with an alcohol in the presence of a catalyst usually concentrated sulphuric acid to produce an ester and water.



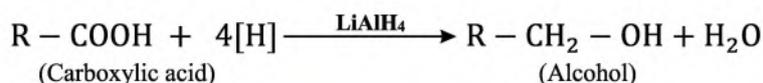
9.5.4 Conversion of Carboxylic Acids into Amides

Amides can be produced by the reaction between carboxylic acid and ammonia, where an ammonium salt is formed, which upon heating yields the corresponding acid amide.



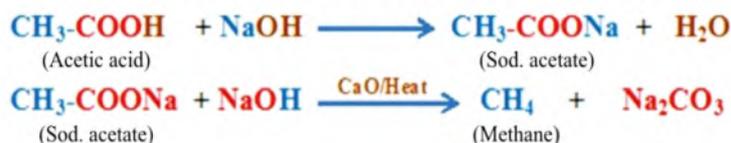
9.5.5 Conversion of Carboxylic Acids into Alcohols

Carboxylic acids upon catalytic reduction with lithium aluminum hydrides produce primary alcohols.



9.5.6 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.





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

Uses of some common carboxylic acids and their derivatives

Citric Acid ($C_6H_8O_7$)

It is used as a preservative, flavor enhancer and acidity regulator.

Malic Acid ($C_4H_6O_5$)

It is used as a food additive and pH control agent.

Tartaric Acid ($C_4H_6O_6$)

It is commonly used in food and beverage industry.

Acetic Acid (CH_3COOH)

It is used as a preservative and as a raw material of various chemicals.

Salicylic Acid (HOC_6H_4COOH)

It is used in the preparation of skin care products and in the production of aspirin.

Benzoic Acid (C_6H_5COOH)

It is used in the production of dyes, perfumes and plastics.

Acetamide (CH_3CONH_2)

It is used as a raw material in pharmaceuticals and drug synthesis.

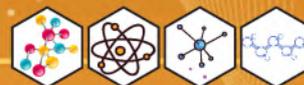
Acetic anhydride ($C_4H_6O_3$)

It is used in making cellulose acetate and in the manufacturing of dyes.



DO YOU KNOW?

Butyric acid is a short chain fatty acid with the formula C_3H_7COOH . It is found in dairy products like butter, cheese and milk. It is responsible for distinct aroma and flavor of these products.



The important compounds of carboxylic acids and their derivatives with their applications:

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	$\text{CH}_3\text{CH}_2\text{COOH}$	Milk, butter and cheese (Greek Protos, First; pion, fat)	Animal feed additive for preventing mold growth
Butyric acid	$\text{CH}_3(\text{CH}_2)_2\text{COOH}$	Butter (Latin; Butyrum)	Flavoring agent in food products
Valeric acid	$\text{CH}_3(\text{CH}_2)_3\text{COOH}$	Valerian root (Latin; Valere, to be strong)	Manufacture of valerate esters used in perfumes
Caproic acid	$\text{CH}_3(\text{CH}_2)_4\text{COOH}$	Goat (Latin; Caper)	Pharmaceuticals and plasticizers



SOCIETY, TECHNOLOGY AND SCIENCE

Carboxylic Acids as food preservative

Carboxylic acids, such as benzoic acid, sorbic acid and propanoic acid, are commonly used as food preservatives due to their antimicrobial properties. These acids can prevent the growth of bacteria, yeast and molds that can cause the spoilage and food born illness. When added to food, carboxylic acids dissociate into their corresponding anions, which penetrate microbial cell membranes and inhibit the growth and metabolism of microorganisms. They also disrupt enzymes and cellular functions essential for microbial survival, leading to their death.



SUMMARY

- Organic compounds which contain carbonyl group ($>C = O$) attached to a hydroxyl group ($-OH$) are called carboxylic acid.
- Carboxylic acids are water soluble since they have ability to form hydrogen bonds with water.
- Boiling point of carboxylic acids are higher than their corresponding alcohols because they form hydrogen bonds themselves in a cyclic dimer form.
- The shape of carboxylic acid molecule is planar triangular in which carbonyl carbon is sp^2 hybridized.
- Carboxylic acids are stronger acids than alcohols, phenols and water. However, weaker than mineral acids.
- Carboxylic acids can be prepared by the oxidation of alcohols. The suitable oxidizing agents in this conversion are potassium dichromate ($K_2Cr_2O_7$) or potassium permanganate ($KMnO_4$).
- There are four derivatives of carboxylic acid named as Ester, Acyl halide, Acetic anhydride and Acid amide.



- Carboxylic acids can be converted into acyl chloride, if they are treated with PCl_3 , PCl_5 or SOCl_2 .
- Carboxylic acids can be converted into esters, if they are heated with an alcohol in the presence of concentrated sulphuric acid.
- Carboxylic acids can be converted into amide, if they are treated with ammonia.

EXERCISE

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) $\text{C}_2\text{H}_5\text{OH}$ (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?
 - ii) The structure of carboxylic acid is trigonal planar?
2. What happens when:
 - i) Formaldehyde reacts with a mixture of Potassium dichromate & sulphuric acid.
 - ii) Carboxylic acid reacts with thionyl chloride
 - iii) Carboxylic acid reacts with ammonia
 - iv) Ethyl magnesium bromide reacts with carbon dioxide
3. Write down the commercial applications of carboxylic acids.
4. Write the natural sources of following carboxylic acids.
(a) Formic acid (b) Acetic acid (c) Valeric acid (d) Caproic acid



Descriptive Questions

- How is carboxylic acid prepared by:
 - Carbonation of Grignard reagent
 - Hydrolysis of alkyl nitriles
 - Oxidation of primary alcohols
- Explain the structure of carboxylic acid.
- Discuss the acidic nature of carboxylic acid. How is it stronger than other organic compounds and weaker than mineral acids?
- Convert the followings:
 - Carboxylic acid into acid anhydride
 - Ester into carboxylic acid
 - Toluene into benzoic acid
- Explain the following physical properties of carboxylic acids:
 - Solubility
 - Boiling point
- Write the names of four derivatives of carboxylic acids and give the equation for their preparation from acetic acid.

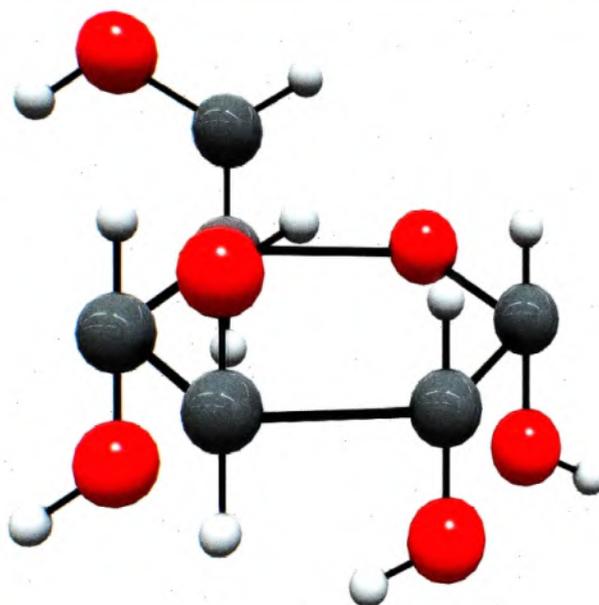


CHAPTER 10

BIOCHEMISTRY



Teaching Periods	06	Assessment	01	Weightage %	05
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Students will be able to:

- ✓ Discuss the natural sources of Carbohydrates and classification based on structure. (understanding)
- ✓ Enlist the role of various Carbohydrates in health and diseases. (Applying)
- ✓ Identify the nutritional importance and their role as energy storage (Applying)
- ✓ Explain the classification of protein on the basis of structure and their functions. (Applying)
- ✓ Explain classification and Functions of Lipids. (Applying)
- ✓ Enlist sources and the role of Iron, Calcium, Phosphorous and Zinc in nutrition. (Applying)



INTRODUCTION

“Biochemistry is the branch of science that deals with the chemical processes taking place in the organisms”. It focuses on the study of structure, function and interaction of biological macromolecules such as proteins, carbohydrates and lipids as well as the chemical reactions and pathways that occur within cells.

Biochemistry aims to investigate the structure, function and interaction of biological molecules. It describes the metabolic pathways that regulate cellular energy production, biosynthesis and degradation of molecules. It plays a vital role in understanding the molecular basis of disease and the impact of drugs on the biological molecules.

10.1 CARBOHYDRATES

Carbohydrate is an essential group of foods in human and animal diets. It is more realistic to define a carbohydrate as **“polyhydroxy aldehydes and ketones or the substances that yield such compounds when they react with water on hydrolysis.”** Carbohydrates are the main source of energy for, tissues, and organs of our body. They are components of DNA and RNA (that transmit and store genetic information). Rice, potatoes, wheat and barley are some natural sources of carbohydrates.

10.1.1 Classification based on structure

“Carbohydrates are classified as monosaccharides, disaccharides, oligosaccharide and polysaccharides”. This classification is based on the number of sugar unit present in carbohydrates.

Monosaccharides contain a single sugar unit for example glucose, fructose, and galactose. Disaccharides contain two sugar units, examples are sucrose, lactose and maltose. Oligosaccharide are carbohydrates that are made up of 3 to 10 sugar units, for example kestose (glucose-fructose-fructose) and melezitose (glucose-fructose-glucose). Polysaccharides Contain more than 10 sugar units, Cellulose, starch and glycogen are examples of polysaccharides.

Monosaccharides are classified on the basis of the number of carbons present in the molecule. In this classification prefix is used to indicate number of carbon atoms in the molecule and the suffix *-ose*, is used to indicate carbohydrate as a class of biomolecule.

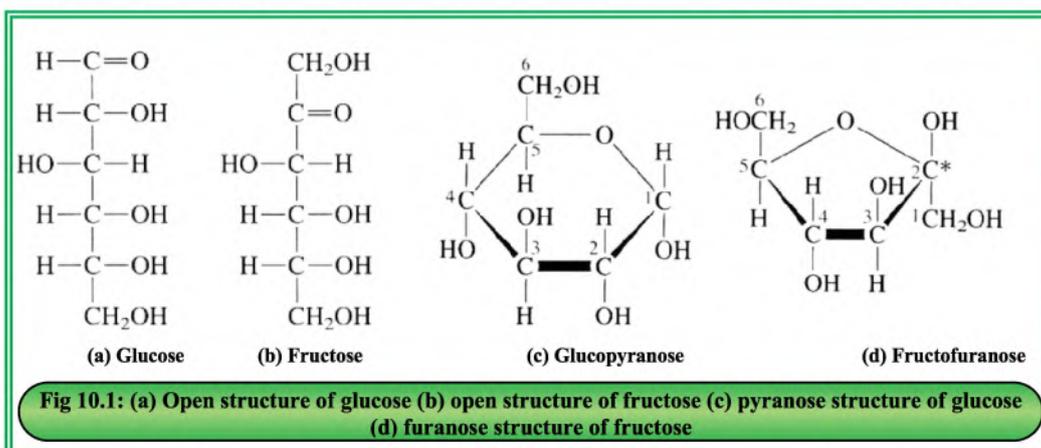


Table 10.1 Examples of some monosaccharide sugar

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

Among these monosaccharide, hexose sugar is important since it plays a crucial role in biological system. Hexose sugars are classified into aldohexose and ketohexose. An example of aldohexose is glucose where as ketohexose is fructose.

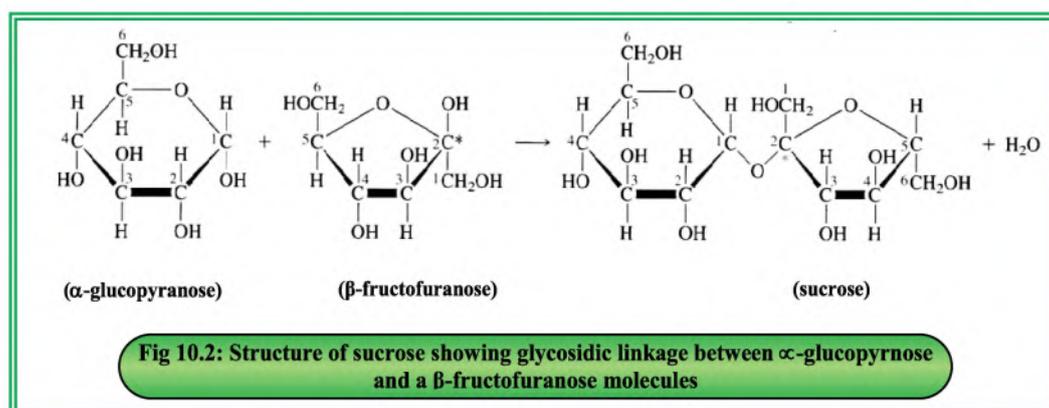
Glucose and fructose exist in both open chain and close chain form however, the open chain form is relatively unstable. The close chain form of glucose is called pyranose since it resembles with pyran where as the close chain form of fructose is known a furanose since it resembles with furan .



Disaccharides are carbohydrates consisting of two monosaccharide units join together through glycosidic bond. **“A glycosidic bond (O-C-O) is a type of covalent bond that join two monosaccharide units together to form a larger carbohydrate molecule”**. It is formed through a condensation reaction



with the elimination of water molecule (Fig.10.2). Disaccharides are water soluble crystalline solids and represented by molecular formula $C_{12}H_{22}O_{11}$.



“Polysaccharides are macro bio molecules. They are amorphous, water insoluble and made up of more than ten hexose sugars”. These hexose molecules are associated with each other through glycosidic linkage. Polysaccharides are further classified into animal polysaccharides and plant polysaccharides. Example of animal polysaccharide is glycogen, which is found in the muscles and liver of animals. It is a storage carbohydrate and commonly known as animal starch.

Plant polysaccharide are the reserved carbohydrates of plants. Example of plant polysaccharides are starch and cellulose which are composed of thousands glucose units. Starch is a main component of our carbohydrate intake. It is found in potato, wheat, burley etc. cellulose is found in the cell wall of plant. It is used in making cotton, cellulose fiber and paper etc.



DO YOU KNOW?

In carbohydrates, "alpha" and "beta" refer to the position of the hydroxyl group attached to the anomeric carbon (the carbon bearing the carbonyl group). "+ (plus)" denotes the configuration when the hydroxyl group is below the plane of the ring, and "- (minus)" denotes the configuration when the hydroxyl group is above the plane of the ring.



Self-Assessment

What is glycosidic linkage? Draw the structure of maltose and show glycosidic linkage in it.

10.1.2 Importance of Carbohydrates

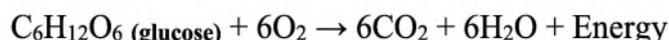
Carbohydrates are nutritionally significant bio molecules and are essential part of our balanced diet.

Carbohydrates such as starch, sucrose, maltose etc convert into glucose in our digestive system which is then absorbed into the bloodstream and transported to the various cells where it is utilized for the energy production for maintaining the biological processes.



DO YOU KNOW?

Complex carbohydrates are important as they provide a slow and steady release of energy, aiding in maintaining stable blood sugar levels. For example, starch found in foods, supporting prolonged physical and mental activities without sudden spikes in blood glucose levels.

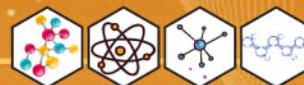


Glucose plays a vital role in energy storage within the body. The extra glucose of the bloodstream is converted into glycogen which serves as a primary form of energy storage in animals including humans. Glycogen is stored in muscles and liver. Another way glucose can be stored by converting it into triglycerides which are then stored as body fat.

Glucose serves as fuel for the brain. The adequate intake of carbohydrate ensures normal brain function. Certain carbohydrates like dietary fibers are not digested by human enzymes and pass through the digestive system. However, they regulate bowel movements and promote the digestive health. Certain non-digestible carbohydrates (fibers) help promoting growth and activity of good bacteria in digestive gut.

Role of Common Carbohydrates in Health and Disease

Glucose: It is a vital component of our blood. Typically, the normal range of glucose in blood ranges between 70 to 110mg per 100 dl. However, if glucose



level exceeds this range, it can lead to the Diabetes which can be managed through insulin control.

Fructose: Fructose is a simple sugar that found in many fruits and honey. It is the sweetest among all other carbohydrates. Its main function is to provide energy during metabolism in the body. However, a high intake of fructose has been associated with weight gain and obesity.

Lactose: It is a disaccharide. It is found in milk and hence also known as milk sugar. During intake, it is broken down into glucose and galactose in the alimentary canal by the enzymatic activity. Lactose is difficult to digest by adult human because they lack the enzyme needed to break down lactose into glucose and galactose. Lactose provides energy. In infants, it is very important for the growth and development. In some adult humans where lactase enzyme is not produced by the body, its intake causes indigestion which is symptomized by bloating gas, abdominal pain and diarrhea.



DO YOU KNOW?

Lactose is present from 5 to 8 percent in human milk, 4 to 6 percent in cow milk and 3 to 4 percent in goat milk that is why goat milk is relatively easily digestible in adult human.

Sucrose: It is also a disaccharide and made up of a glucose and a fructose sugar. It is known as table sugar or cane sugar. An excess amount of sucrose in our diet can cause the development of gum disease such as fatness, plaque formation in the teeth, and even tooth decay.



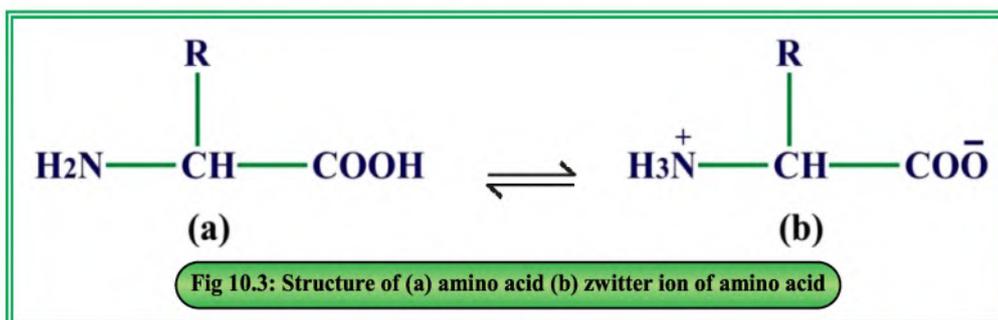
Self-Assessment

What do plant and animal starch means? What is the role of animal starch for energy storage in the body.

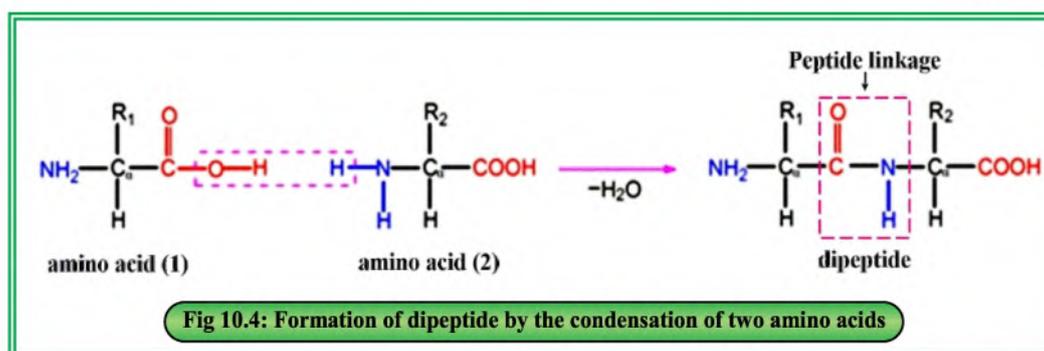


10.2 PROTEINS

Proteins are naturally occurring macromolecules made up of long chain of amino acids that fold into precise three dimensional configurations (Fig.10.3). All living organisms including plants, animals and bacteria contain proteins and their presence is vital for the life.

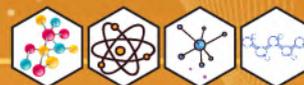


There are twenty two (22) different types of alpha amino acids that can be used to build proteins. Each amino acid consists of an amino group as well as a carboxyl group. These amino acids are associated with each other through poly peptide linkage (CONH). The specific arrangement and sequence of these amino acids determine the structure and function of the protein (Fig.10.4).



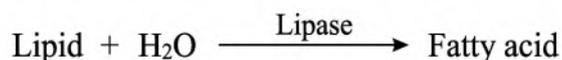
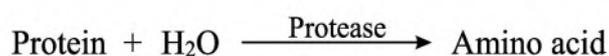
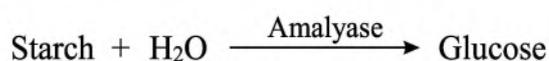
10.2.1 Classification of proteins

Proteins may be classified into several groups based on their functions and structures. 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.



(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 membranes and in the blood stream. For example, haemoglobin.

(iv) Regulatory or hormonal proteins:

These proteins play a critical role in regulating the function of body by transmitting signals between the cells.



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.

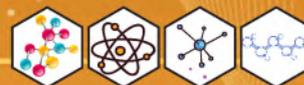
10.2.2 Classification of proteins on the basis of their structure

Proteins are essential macromolecules classified into four main types based on their structure.



Table 10.2 Classification of proteins

Classification	Description	Structure
Primary	<ul style="list-style-type: none"> ➤ 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	<ul style="list-style-type: none"> ➤ 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	<ul style="list-style-type: none"> ➤ 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; <ul style="list-style-type: none"> • Salt bridge (ionic bond) • Disulfide bridge (covalent bond) • Van der Waals forces • Hydrogen bond ➤ Example: Myoglobin exhibits a tertiary structure. 	
Quaternary	<ul style="list-style-type: none"> ➤ 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. 	



10.2.3 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.

10.2.4 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) Hormones 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.



Self-Assessment

Haemoglobin, hormones and antibodies are categorized as proteins. What is the biological role of these proteins in human body.

10.3 LIPIDS

“Lipids are naturally occurring heterogeneous organic compounds that are insoluble in water but soluble in Bloor’s reagent”. The term “lipid” originates from the Greek word “Lipos” meaning “fat like” due to their greasy or oily texture when touched.



DO YOU KNOW?

Bloor's reagent (a mixture of diethyl ether and ethyl alcohol in the ratio of 2:1).



Lipids are vital components of our diet and can be obtained from various sources such as animal fat (e.g. butter, ghee) vegetable oil etc.

10.3.1 Classification of lipids

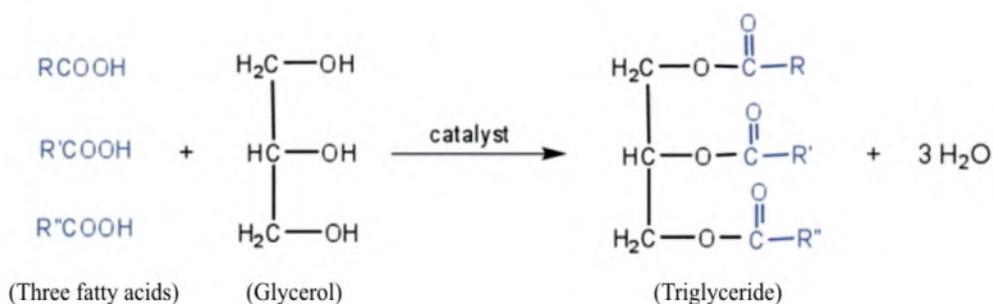
On the basis of chemical composition lipids are classified into three main groups, named as simple lipids, compound lipids and steroids.

Simple Lipids

These lipids are chemically esters, made up of fatty acids and alcohols, mainly serve as energy source to the body. Simple lipids are further classified into fat, oil and waxes.

Fats and Oils

“These lipids are abundantly found in nature and chemically known as **triglycerides or triesters**”. They are formed by the condensation of three fatty acid and a glycerol molecule.



The fatty acid chains in the molecules of fat and oil consists of C₁₂ to C₂₄ carbon atoms which may be saturated or unsaturated. Vegetable oil contains unsaturated fatty acids and are liquid at room temperature. Animals fats are composed of saturated fatty acids and usually solids at room temperature.



DO YOU KNOW?

Most of the lipids hydrolysed with alkalis to form soap, these are known as saponifiable lipids. Lipids of steroid family cannot form soap with an alkali and are called nonsaponifiable lipids.



Table 10.3 Types of 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.

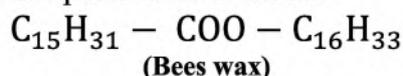


Self-Assessment

Fat and oil are both triacylglycerol how you can differentiate between them?

Waxes

“Waxes are the naturally occurring esters of long-chain fatty acids and long chain alcohols”. Waxes are solids with water repellent nature. In plants they form coating on the surface of leaves, fruits and other parts helping to prevent water loss and protect against environment. Honey bees produce wax to build honey combs for the protection of hives.



Compound lipids

“These are esters of glycerol with two fatty acids and some other compounds such as carbohydrates, amino acids, phosphoric acid etc”.

These are classified into phospho lipids, glyco lipids and lipo proteins on the basis of introduction of additional groups like phosphoric acid, glycogen and protein etc. Example: LDL (low-density lipoprotein).

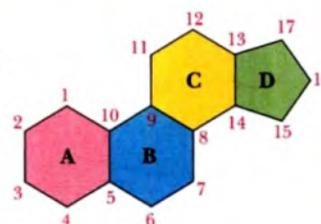
Steroids

These are derived lipids that are composed of specific structure of four interconnected carbon rings (Cyclopentenophenanthrene nucleus). Examples of steroids are cholesterol and cholic acid.



DO YOU KNOW?

Cholic acid is a derivative of cholesterol. It is found in bile juice as sodium salt. It serves as enzyme that participates in the digestion of fat.





10.3.2 Structure of lipids

The structure of lipids varies depending on their classification. However the basic structure consists of a hydrophilic head and a hydrophobic carbon tail.

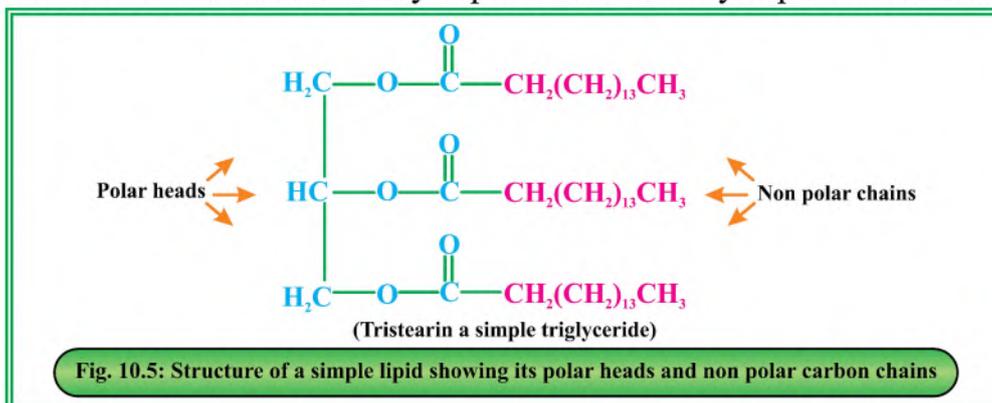


Fig. 10.5: Structure of a simple lipid showing its polar heads and non polar carbon chains

10.3.3 Properties of lipids

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.
- Lipids are poor conductors of heat and electricity therefore serve as insulators for the animal body.

Chemical Properties

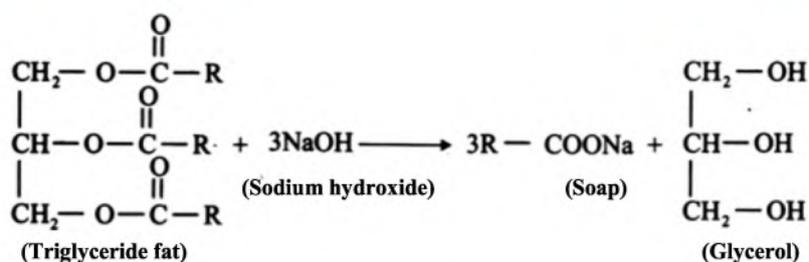
Addition reactions

Oils undergo addition reactions with hydrogen in the presence of nickel (catalyst) to produce fats. In this chemical reaction, unsaturated fatty acids of oil convert into saturated fatty acids.



Saponification

Fat and oil are hydrolysed when heated with an alkali to produce soap and glycerol, this process is known as saponification.



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 odour. This process is commonly referred to as rancidity.

10.3.4 Importance of lipids

Lipids play important role in human body.

- (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.

10.4 MINERALS OF BIOLOGICAL SIGNIFICANCE

“Minerals are inorganic substances that are required to maintain physical health and prevent us from certain diseases”. Although more than twenty five minerals are present in our body but sixteen minerals are recognized as essential for the body health. Some minerals are required in the larger quantity and known as macro minerals while others are needed in small quantity and referred as micro minerals.



DO YOU KNOW?

Minerals and water are smaller sized inorganic substances that are directly absorbed into the blood without being digested through enzymatic process in the alimentary canal.



10.4.1 Sources of important minerals

Minerals are generally found in fruits, vegetables, whole grains, dairy products, meats, sea food and water etc.

Sources of some minerals are listed in the Table 10.4.

Minerals	Sources
Calcium	Milk, Cheese, Yogurt, Leafy greens
Iron	Red meat, Poultry, Sea Food, Bean, Lentils
Zinc	Beef, Chicken, Sea Food, Beans
Phosphorous	Meat, fish, dairy products, nuts, seeds, and whole grains.

10.4.2 Biological Significance of Iron, Calcium, Phosphorous and Zinc

Minerals perform a diverse range of functions in the body such as maintenance of pH, acid-base balance, hormonal control. However; each mineral has its specific role in the body.

Iron:

Iron is crucial for the body because it involves in the oxygen transport, immune function, temperature regulation and the production of red cells.

Calcium:

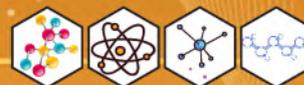
Calcium is used to build strong bones and teeth. It helps muscles contract and relax. It also helps in blood clotting and immune system. Its deficiency causes bone weakness and poor body growth.

Phosphorous:

Phosphorous is important for healthy bones and teeth. Being a part of DNA and RNA, it is important for protein synthesis and transferring genetic information. It is also important for muscular system and to maintain heartbeat.

Zinc:

Zinc is important for normal growth, wound healing and the working of nervous system. 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.



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Insulin and Diabetes

Diabetes is a complex metabolic disorder marked by elevated blood sugar levels. It is triggered by either insufficient production of insulin or the body's inability to effectively use it. Insulin is a protein hormone secreted by pancreas and plays a significant role in controlling blood sugar levels. The glucose level in the blood fluctuates throughout the day, increasing after meals and then gradually returning to normal within approximately two hours. The typical range of normal blood glucose level for adults in a fasting state is 70 to 110 mg/dl.



SUMMARY

- The study of chemical reactions in living things is known as biochemistry.
- Carbohydrate is essential group of foods in human and animal diet.
- Carbohydrates are defined as polyhydroxy aldehydes and ketones or the compounds which give polyhydroxy aldehyde or ketone on hydrolysis.
- Carbohydrates are classified as monosaccharides, disaccharides, oligosaccharides and polysaccharides.
- The basic function of carbohydrates is to supply energy to all cells in the body.
- Body stores excess amount of glucose in the liver and muscles in the form of glycogen.
- Proteins are macro-molecules consist of amino acids linked together through peptide bonds.
- There are four levels of the structures of protein; primary, secondary, tertiary and quaternary.
- Tertiary structure of protein is stabilized by disulfide bridges, Van der Waals' forces, hydrogen bonds and ionic bonds.
- Physical, chemical and biological properties of proteins are temperature and pH dependent.



- Lipids are water insoluble heterogeneous organic compounds, which are chemically ester of fatty acid and alcohols.
- Meat, nuts, cereals, fish, milk and dairy foods, fruits and vegetables, are sources of minerals.
- Saponification is a chemical reaction of fat and oil with an alkali.
- Rancidity involves two simultaneous reactions named as oxidation and hydrolysis which makes the animal fat bad taste and bad odour.

EXERCISE

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

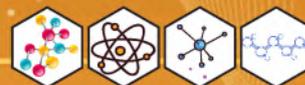
Short Questions

1. Mention the three main functions of lipids.
2. Comparing with other nutrients, why lipids are better source of energy?
3. Carbohydrates are necessary component of our diet. Give two dietary importance of carbohydrates.
4. What is meant by saponification? Give the reaction.
5. What is rancidity which chemical reaction involves in this process?
6. Write three essential functions of protein in the body.
7. Write down the sources from which we intake fructose and lactose.



Descriptive Questions

1. What are Carbohydrates? Give their classification on the basis of structure.
2. Explain the role of glucose, fructose, sucrose and lactose in the health of human being.
3. What are Proteins? Classify various types of proteins on the basis of their function.
4. What are Lipids? Give their classification, properties and biological significance.
5. How can you explain primary, secondary and tertiary structure of proteins?
6. Describe physical properties of proteins.
7. Why minerals are essential for our health? Give the biological significance of Calcium, Iron, Zinc, and phosphorus.



CHAPTER 11

INDUSTRIAL CHEMISTRY



Teaching Periods	08	Assessment	01	Weightage %	07
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Students will be able to:

- ✓ Explain the role of the chemical industries in the economy of Pakistan. (Analyzing)
- ✓ Describe the various pharmaceutical products (Understanding)
- ✓ Enlist different pharmaceutical products with their functions (Applying)
- ✓ Explain the formation and uses of PVC and Nylon. (Applying)
- ✓ Describe the composition and effects of various cosmetics like nail polish, nail polish remover, lipsticks and perfumes (Understanding)
- ✓ Describe the adhesives and their applications. (Understanding)



INTRODUCTION

Industrial chemistry is the branch of chemistry which deals with the conversion of raw materials into useful product through chemical process.

The primary objective of industrial chemistry is to investigate new ways and technologies to enhance the efficiency of chemical processes, reduce expenses and increase product yields.

An industrial chemist plays a crucial role in enhancing productivity through the exploration of novel catalysts and optimizing reaction conditions, while also aiming to reduce production costs by utilizing economical raw materials. Their contributions extend to the development of innovative materials and technologies that benefit various industries. Moreover, industrial chemists ensure safety standards, risk assessment, and proper storage protocols.

This multi-disciplinary field of industrial chemistry intersects with other scientific branches, including agriculture, engineering, and pharmaceuticals.

11.1 INTRODUCTION TO CHEMICAL INDUSTRIES

“The term chemical industries refers to all those companies that manufacture chemicals”. These industries

involves a broad range of activities including, production of chemicals, quality assurance packaging and distribution etc. Several chemical industries are involved in the manufacturing of basic chemicals, including acids, alkalis, salts, gases and more. Chemicals play important role for the production of wide range of products such as dyes, adhesives, cosmetics, synthetic polymers, pesticides, cement, detergents, fertilizers, fibers, glasses, agrochemicals etc.

These industries encompass a wide range of sectors and generate substantial revenue and create employment opportunities. Some well-established chemical industries are given below;

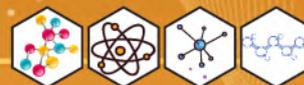
- (i) **Petrochemical Industries:** These industries are primarily focuses on the extraction, refining and processing of petroleum and natural gases.



DO YOU KNOW?

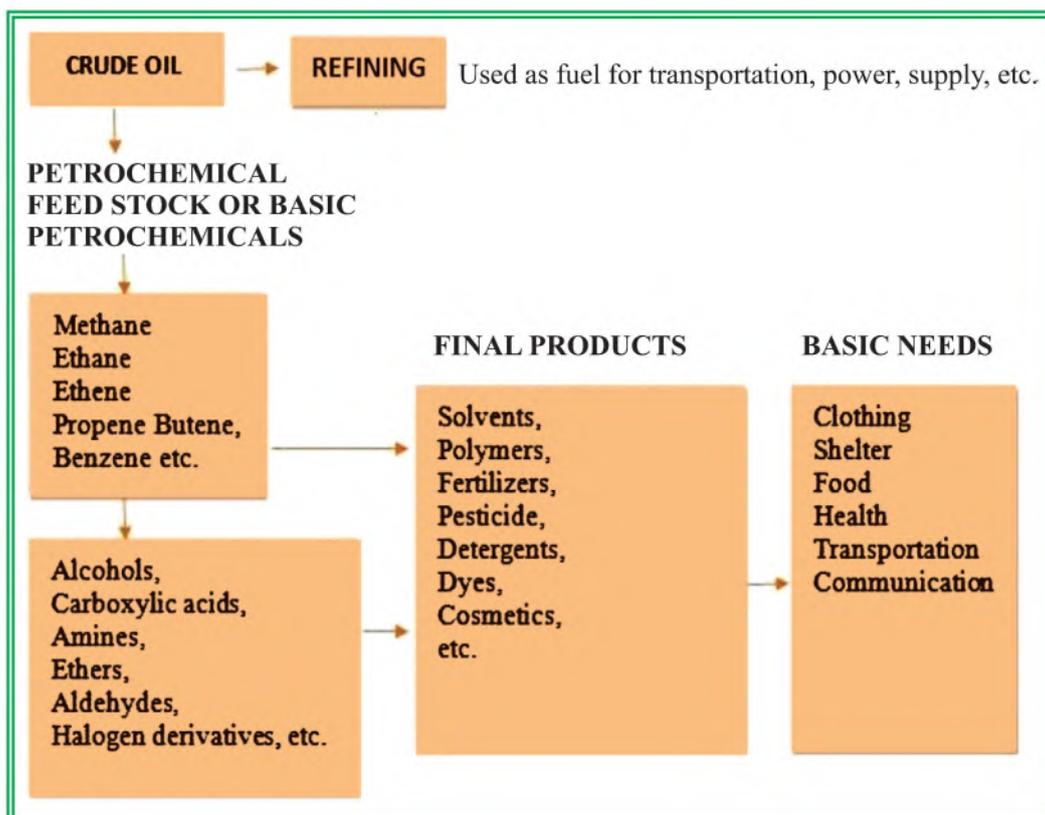
The control and regulation of chemical industries in Pakistan involves a combination of various Government agencies such as:

- Pakistan standard and quality control authority (PSQCA).
- Environmental protection agency (EPA).



They also produce many other chemicals as by products which then sold as a raw materials several useful substances.

Products of crude oil and its uses



(ii) Fertilizer Industries:

Fertilizer industries are responsible for the production of fertilizers, which are substances used to improve soil fertility and promote plant growth. Fertilizers provide essential nutrients to plants, enhancing crop yields and agricultural productivity. There are two main types of fertilizers: organic fertilizers, which are derived from natural sources, and synthetic fertilizers, which are manufactured chemically. Some common synthetic fertilizers are listed in Table 11.1:



Table 11.1 Examples of some synthetic fertilizers and their uses

Synthetic Fertilizer	Chemical Formula	Nutrients Provided	Uses
Ammonium Nitrate	NH_4NO_3	Nitrogen	Development of roots and maintaining pH soil
Urea	$\text{CO}(\text{NH}_2)_2$	Nitrogen	Development of leaf, stem and fruits
Diammonium Phosphate (DAP)	$(\text{NH}_4)_2\text{HPO}_4$	Nitrogen, Phosphorus	Development of early stage of plants growth
Potassium Chloride (MOP)	KCl	Potassium	Help enzyme activities and photosynthesis

(iii) Textile Industries: Textile industries are sectors of the economy that involve the production of fabrics and textiles, including natural fibers like cotton and wool, as well as synthetic materials like polyester and nylon. These industries play a vital role in providing a wide range of products, from clothing and household items to industrial materials (Table.11.2).

Table 11.2 Examples of some synthetic Textiles products and their uses

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,

(iv) Paint Industries: The paint industry is a sector that produces liquid or powdered substances used for coating surfaces, providing protection, decoration, and other functional purposes in various applications such as construction, automotive, and industrial sectors (Table.11.3).

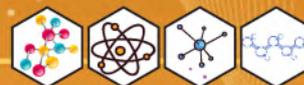


Table 11.3 Examples of some synthetic paints and their uses

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.

(v) Detergent Industries: The detergent industry produces cleaning products, typically containing surfactants and other agents, designed for various applications like laundry, dishwashing, and surface cleaning. These products help to remove dirt, stains, and grease for improved hygiene and cleanliness (Table.11.4).

Table 11.4 Examples of some synthetic detergents and their uses

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



(vi) Cement Industries: The cement industry involves the production of cement, a binding material used in construction, made primarily from limestone, clay, and other raw materials. Cement is a fundamental component of concrete and mortar, essential for building infrastructure and structures worldwide (Table.11.5).

Table 11.5 Examples of some synthetic cement and their uses

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.



Self-Assessment

Some chemically industries operating in Pakistan have been mentioned in section 11.1. Do you know some more industries working in Pakistan?

11.2 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". Pharmaceutical industries provide significant contribution to health care sector. They are not only concerned with the manufacturing of medicines for diseases control but also invest in extensive research and development activities to discover new drugs, therapies and treatment approaches.

Classification of pharmaceutical products is based on various factors, such as chemical structure, mechanism of action, therapeutic use and biological activities. Some common drugs are described below.

Analgesics

"A drug that specifically targeted on central nervous system to provide pain relief without consciousness is known as analgesic drug". "Asprin" is the oldest and the most common analgesic drug.

Antibiotics

This drug is produced from certain chemicals of microorganism. **"It suppress the growth or kills microorganisms"**. "Penicillin" was the first discovered antibiotic. Now a days a range of antibiotics are used depending upon doctors prescription.

Antipyretic medicines

"A drug which lower the body temperature to normal is known as antipyretic". The most widely used antipyretic medicine is "paracetamol".

Anti fungal medicine

"These drugs use to kill fungi that cause infections on skin". The most common skin infections are ringworm and dandruff. Example of antifungal drug is "fluconazole".

Anti inflammatory medicine

"These drugs helps reduce inflammation, and relieve pain". Ibuprofen (Brufen) is an example of anti inflammatory medicine. However many other options are also available.



DO YOU KNOW?

Bayer commercially introduced aspirin in 1899 as pain reliever. Its chemical name is acetyl salicylic acid. However, historically, it was derived from a plant willow bark for medicinal use.



Anti allergic medicine

These are also called antihistamines. Histamine is a chemical produce in the body due to decarboxylation of an amino acid known as histidine. **“The administration of these drugs reduces the histamine level in the body”**. A wide range of anti-allergic medicines are available in the market, one example of anti-allergic medicine is “diphenyl hydramine”.

Anti malarial medicine

Anti protozoal or anti-Malarial drugs are use to treat mosquito bite infectious diseases such as malaria. Most commonly used anti material drug is chloroquine.

There are hundreds of pharmaceutical industries operating in Pakistan. Health ministry of Govt. of Pakistan play important role in the availability and accessibility of drugs in public sector.

11.3 PESTICIDES

“Chemical which are used to control, repel or kill pets or insects or fungus are known as pesticides”.

Pets and insects can cause significant damage to crops, leading to their reduced yields and poor quality. In modern agricultural practices, formers utilize pesticides as a preventive measure to safeguard crops from pets and to ensure the maximum yield (Fig.11.1).



Fig 11.1: Pesticide spray on crops with all safety measures



Although, the term pesticides is commonly associated with crop protection, it also encompasses the chemicals use to destroy community pets including cockroaches, mosquitoes, rats, flies etc.

Types of Pesticides

Pesticides are classified into three major classes named as insecticides, fungicides and herbicides.

Insecticides

“Chemical substances which use to kill insects are called as insecticides”. The best known insecticide is Dichlorodiphenyltrichloroethane (DDT),

Herbicides

Undesirable herbs often co-exist with crops creating problems for the growth and fertility of crops, by taking away their share of nutrient water and sunlight, these types of herbs are known as weeds. **“Herbicides are the chemicals which either destroy or stop growing weeds”**. A very common herbicide which former prefer to use is 2,4-dichlorophenoxyaceticacid (abbreviated as 2, 4-D).

Fungicides

“Fungicides are chemical substances employed to eliminate undesired fungi that develop within crops”. A very common fungicide Mancozeb (Manganese ethylenebis(dithiocarbamate) zinc salt) which is used to control various fungal diseases on crops like potatoes, tomatoes, and grapes.

Toxic effects of pesticides

Despite the prevalent use of pesticides in the modern agriculture, it is crucial to acknowledge and address their harmful impact on health and environment. Pesticides spray on crops can contaminate soil, water and air leading to the toxic effects on human, animals and environment. A high level of pesticides



DO YOU KNOW?

A mosquito repellent, classified as a type of less toxic pesticides provides protection against mosquito bites when a small amount is applied to exposed area of skin.

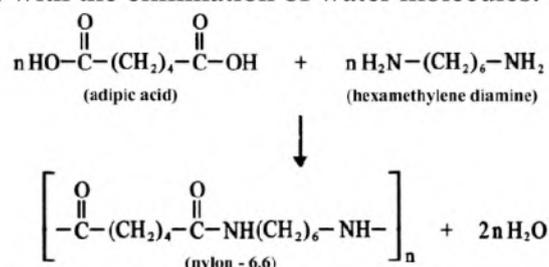


PVC is used in the manufacturing of bottles, pipes, medical tubes, blood bags and insulation material on electric wires.

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.



Nylon 6, 6 is used in making tents, parachutes, ropes, fish net, bristles of brushes and tires etc (Fig.11.2).



Fig 11.2: Product of (a) PVC (b) Nylon 6, 6

11.5 COSMETICS

The word cosmetic is derived from the Greek word “kosmetiko” meaning beautifying complexion of skin.

“Cosmetics are the products that are used to enhance or alter the appearance of face, body, nails or hairs”. Thousands of cosmetic products are manufactured in the industries, few very common are briefly described below.



DO YOU KNOW?

Glycerine is commercial name for glycerol. It is an organic oily liquid. It is widely used in moisturizers and lotions. It is commonly used for healing mouth ulcers.



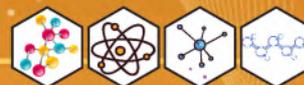
- (i) **Lipstick:** “Lipstick is a chemical used to colour, moisturization and protection of the lips”. It is a type of makeup that usually available in a stick and is applied directly to the lips. Lipstick is typically made from a mixture of oils, waxes, pigments, fragrance and moisturizing agent.
- (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” along with some other ingredients such as scent.
- (iv) **Hair Dyes:** These are chemicals that change the colour of hairs. Hair dyes are classified into temporary and permanent hair dyes. Temporary hair dye last for a short period of time, typically a few washes. It is available in various form such as spray, gels and shampoos.

Permanent hair dye refers to a colouring product that last for long period of time. It mainly consists of colourant and developer. The developer is an oxidizing agent generally, hydrogen per oxide is used as developer.

- (v) **Perfumes:** These are complex mixtures of aromatic compounds, solvents, and fixatives that create pleasant and distinctive scents. They typically consist of top, middle, and base notes, which work together to provide a well-balanced and long-lasting fragrance.



Fig 11.3: Various cosmetics (a) Lipsticks (b) Nail polishes (c) Hair dyes (d) Perfume



11.6 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 easily prepared and low cost. Starch is used as a thickening agent in various food products and as a raw material for the production of biodegradable plastics.

Epoxy Resins

These are strong synthetic adhesives and commonly used for bonding metals, plastics, glasses and ceramic items.

Silicon Resins

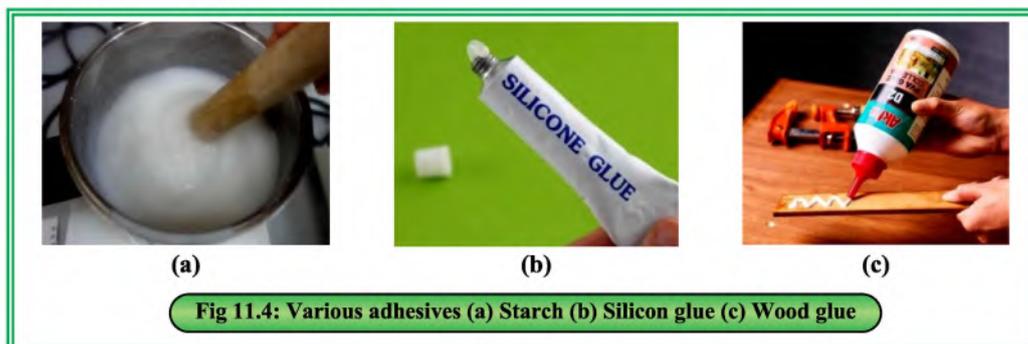
These are known with their high strength, high thermal stability and water repellent ability. These are use in sealing of engines, gasket making, bonding of optical instruments and medical instruments.

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.

Wood Glue

It is chemically named as polyvinyl acetate. It is a water based adhesive. It form a strong and durable bond between pieces of woods when compressed them under high pressure.





SOCIETY, TECHNOLOGY AND SCIENCE

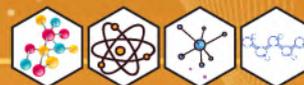
Development and use of synthetic fibers

Polyester is a well-known fiber utilized in fabric production. It is prepared by the reaction between terephthalic acid and ethylene glycol. When polyester is blended with cotton in the ratio of 65% polyester and 35% cotton it makes poly-cotton fiber (tropical fabric) which is known for its light weight nature, ease of ironing and soft texture. Poly-cotton fabric is widely used in the production of all types of clothing, including shirts, trousers, bed sheets etc.



SUMMARY

- Industrial chemistry is the branch of chemistry which deals with the conversion of raw materials into useful product through chemical process.
- Drug is a substance that is used to treat or cure a disease in human or animals.
- A drug that specifically targeted on central nervous system to provide pain relief without consciousness is known as analgesic drug.
- A drug which suppress the growth or kills microorganisms is known as antibiotics.
- A drug which lower the body temperature to normal is known as antipyretic.
- A drug which is used to kill fungi that cause infections on skin is known as anti-fungal.
- Chemical which are used to control, repel or kill pests or insects or fungus are known as pesticides.
- 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.
- Cosmetics are the products that are used to enhance or alter the appearance of face, body, nails or hairs.
- Adhesives or glue are chemical substance that use to stick materials together.



EXERCISE

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) Ibuprofen (b) Chloroquine
(c) Paracetamol (d) Diphenyl hrdramine
- (v) Aspirin 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.
2. What is antihistamine drug? Give the symptoms in which it is used.
3. Write the names of two synthetic and two natural polymers.
4. Write the name of four main components of Nail polish?

Descriptive Questions

1. How can you define Cosmetics? Describe four cosmetics which are commonly used.
2. What are pesticides? Explain various types of pesticides along with their specific use.
3. Describe the preparation, properties and uses of Nylon and polyvinyl chloride.
4. What are adhesives? Explain the significance of super glue and silicon resins.

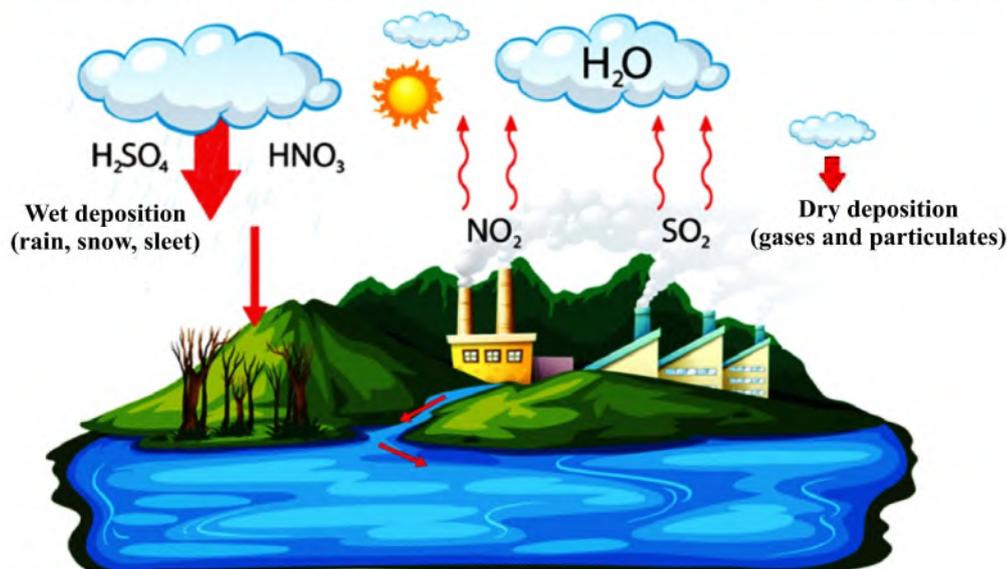


CHAPTER 12

ENVIRONMENTAL CHEMISTRY



Teaching Periods	09	Assessment	01	Weightage %	08
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Students will be able to:

- ✓ Recognize various chemical reactions occurring in the atmosphere. (Understanding)
- ✓ Recognize that the release of CO_x, SO_x, NO_x, VOCs are associated with the combustion of hydrocarbon based fuels. (Applying)
- ✓ Outline problems associated with release of pollutants including acid rain. (Understanding)
- ✓ Describe causes and impacts of smog. (Analyzing)
- ✓ Explain greenhouse effect and global warming as resulting in climate change. (Analyzing)
- ✓ Explain the buildup and the adverse effects of ozone in the troposphere. (Applying)
- ✓ Describe the role of CFCs in destroying ozone in the stratosphere. (Applying)
- ✓ Describe the role of ozone in the stratosphere in reducing the intensity of harmful UV radiation reaching the earth. (Understanding)
- ✓ List possible alternatives of CFCs. (Applying)
- ✓ Recognize and describe various water pollutants. (Applying)
- ✓ Explain the various parameters of drinking water analysis and compare with WHO standard limits. (Applying)
- ✓ List some major products of petrochemicals industry with their uses. (Applying)

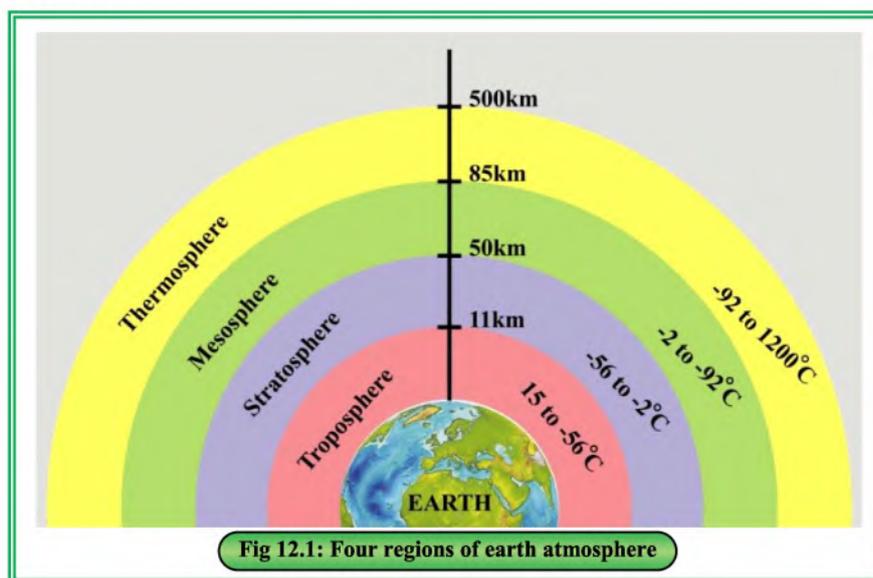


INTRODUCTION

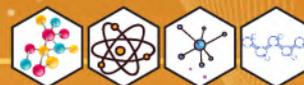
Environmental chemistry is a special area of chemistry that look at how chemicals interact in the environment and effect living things. **“It deals with the study of chemical processes happening in Earth’s environment and their direct or indirect impact on organisms that live on Earth”**.

“The presence of undesirable substances in the environment that harm the natural balance of eco systems is known as environmental pollution”. There are several types of pollution that can negatively impact the environment and human health such as air pollution, water pollution, soil pollution, noise pollution, radioactive pollution etc. Earth’s environment consists of four interconnected parts that work together to sustain life. These parts include;

- **Lithosphere** which comprises Earth crust and soil covering with the rocks.
- **Hydrosphere** which consists of all surface and underground water.
- **Biosphere** which includes the entire living being on the Earth.
- **Atmosphere** which is extended to 500 km above the Earth’s surface and consists of gases.



The Earth’s atmosphere is further divided into four major regions based on variation in the temperature and compositions. These regions are commonly known as atmospheric layers.



Troposphere: It is the lowest layer of atmosphere extending from Earth's surface up to an altitude of 11km.

Stratosphere: It starting from the top of troposphere and extending up to 50km above the Earth's surface.

Mesosphere: It lies above stratosphere stretching from 50km to 85km above the Earth's surface.

Thermosphere: It is the upper most layer of the Earth's atmosphere extending from 85km to 500km.

12.1 CHEMISTRY OF THE TROPOSPHERE

Troposphere is the lowest layer of Earth's atmosphere, where we experience our daily weather conditions such as rain, snow, winds, storms, thunders, clouds. The temperature in this region decreases constantly with increasing altitude from the ground of Earth's surface approximately 15°C to -56°C . The air pressure at sea level is nearly 760 torr but it decreases with increasing the altitude. This region plays a vital role in supporting life on Earth as it holds a significant portion of oxygen, carbon dioxide and water vapours which are essential for the sustenance of living organisms.



DO YOU KNOW?

Thermosphere is the highest temperature region of atmosphere due to the absorption of intense solar radiation. They natural light display known as aurora is occurred in this region.

12.1.1 Reactions of CO_x , NO_x , VOC_s , SO_x and O_3 with the atmosphere

Gases like nitrogen (N_2) and oxygen (O_2) form a protective layer in the Earth's atmosphere. However, certain toxic substances, including nitrogen oxides (NO_x) sulphur oxides (SO_x), volatile organic compounds (VOCs) and ozone (O_3) can cause atmospheric pollution.

Chemistry of oxides of carbon (CO_x)

The oxides of carbon in troposphere are carbon monoxide (CO) and carbon dioxide (CO_2), collectively written as CO_x .

Carbon monoxide is very toxic gas, since it has great affinity for hemoglobin. It is released by the partial combustion of fuel in automobile,



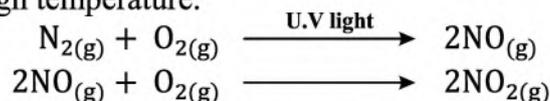
petroleum refining and forest fire etc. Carbon monoxide in troposphere is broken down by U.V radiation into free carbon particles which are responsible for the smog formation.



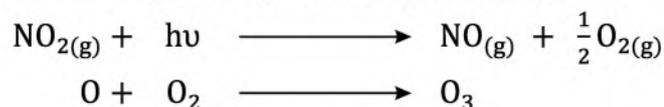
Carbon dioxide is added to atmosphere due to the combustion of fossil fuels such as coal, wood, petroleum. It is also released during the respiration of animals. The increase level of carbon dioxide in atmosphere causes suffocation and respiratory disorders.

Chemistry of Oxides of Nitrogen (NO_x)

There are two main oxides of nitrogen which cause pollution of air. These are nitric oxide (NO) and nitrogen dioxide (NO₂) and are collectively written as NO_x. These oxides produce from the combustion of fuel such as coal, petrol and natural gases at high temperature.



These gases are also formed by photolytic reaction in atmosphere.

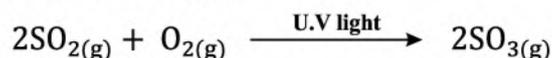


The high concentration of NO and NO₂ gases in air is harmful because they form acid rain and ozone in the atmosphere.

Chemistry of Oxides of Sulphur (SO_x)

There are two oxides of sulphur found in air named as sulphurdioxide (SO₂) and sulphur trioxide (SO₃), these are together abbreviated as SO_x. The pollution of SO_x is equally due to volcanic eruption and the burning of sulphur containing coal in thermal power plants.

In atmosphere SO₃ gas can be produced by photochemical oxidation of SO₂ under the influence of sun light.



The presence of these gases in atmosphere causes cardiac and respiratory diseases and also effect negatively on crops production.



Chemistry of Volatile Organic Compounds (VOCs)

Volatile organic solvents are commonly used in various chemical industries such as paints, varnishes, cosmetics, aerosols, air freshener and gasoline. During the chemical processes taking place in the factories, these chemical evaporates into the Earth's atmosphere and leading to the pollution. **“All those solvents which evaporate into atmosphere and contribute the atmospheric pollution are known as volatile organic compound (VOCs)”**.

Although the presence of volatile organic compounds (VOCs) in the Earth's atmosphere poses a threat to us, their exposure to ultra violet light lead to their decomposition and the formation of ozone which is even more hazardous for health. Examples of VOCs include formaldehyde, benzene, and toluene.



DO YOU KNOW?

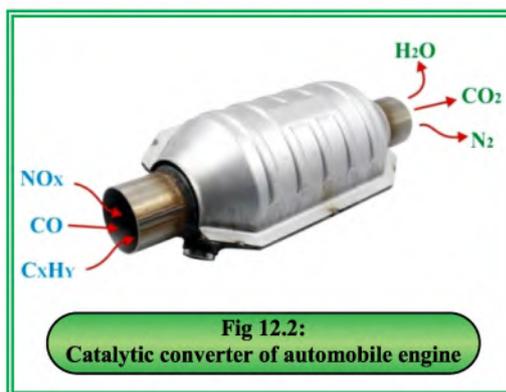
The industrial areas are experiencing severe pollution due to the presence of diverse industrial waste. These wastes are either released into the atmosphere or discharged into the stream, ultimately reaching the sea and causing pollution that impacts negatively on aquatic life.

Chemistry of Ozone (O₃)

Ozone is an allotropic form of oxygen. It is present in a very low concentration in troposphere. Its presence is hazardous to both human health and the environment. Its side effects include respiratory issues, cardiac issues and irrigation of plants and crops.

12.1.2 Automobile Pollutants and the Catalytic Converter

The burning of gasoline in a car engine results in the formation of carbon monoxide (CO), nitric oxide (NO) and various unburnt volatile hydrocarbons. These substances, when released into the air, contribute to atmospheric pollution and have a direct impact on life. To solve this issue, modern car engines are equipped with catalytic converter **“The purpose of catalytic converter is to transform**





the harmful chemicals produced during internal combustion of engine into less harmful or non harmful substances such as carbon dioxide (CO_2), nitrogen (N_2), oxygen (O_2) and water (H_2O)". Catalytic converter contain a mixture metals such as platinum and palladium which serves as catalyst.



Self-Assessment

- (i) Can a vehicle run without catalytic converter?
- (ii) How does catalytic converter contribute to reducing air pollution.

12.1.3 Industrial Smog

Smog is a type of air pollution. This term is the combination of smoke and fog.

In the industrial zones of a country, numerous industries are operational, manufacturing various valuable commercial products. However, during the chemical processes involved, a significant number of harmful by-products are emitted into the atmosphere. Some industries release sulphurdioxide (SO_2) when burning coal and oil while other introduce harmful solid particles like metal oxides, salt particles and even soil into the air (Fig.12.3). The mixing of these harmful

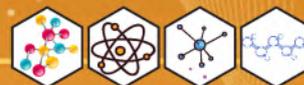


Fig 12.3 Atmospheric pollution due to industrial smog

substances contributes to the formation of smog "**Smog is a mixture of SO_2 , aerosols and volatile organic compounds**". It forms a brown-yellow layer usually in industrial areas. Smog has many harmful side effects on human health, plant growth and overall a major contributor of environmental pollution.

12.1.4 Global warming and Climate Change

"**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 worldwide atmosphere.



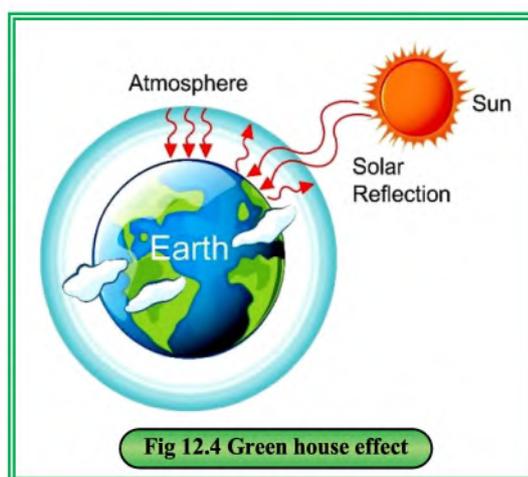
“The temperature of our earth is regulated by certain gases present in the atmosphere such as CH_4 , CO_2 , N_2O and H_2O known as green house gases”. The change in concentration of these gases can lead to alterations in the Earth’s climate.

To prevent global warming, we need to reduce greenhouse gas emissions by alternating to renewable energy sources, promoting energy efficiency, and implementing sustainable practices in sectors like transportation and agriculture.

Green House Effect

It is an essential natural process that helps in regulating the Earth’s temperature enabling the existence of life on our planet (Fig.12.4).

Sun release energy in the form of sunlight, which then reaches the earth atmosphere and a portion of it (UV and visible radiation) is absorbed by the earth which makes the earth warm. The warm surface of earth is then emitting radiation of IR frequency.



The green house gases in the atmosphere (CH_4 , H_2O , CO_2 etc) absorbs some of IR radiations emitted by the Earth’s surface. The absorption of heat by green house gases prevents the escaping of heat into the space. The absorbed heat energy by green house gases is reemitted toward the earth surface and warms it.

Global warming causes a widespread rise in temperature all around the world. This has a significant impact on climate change leading to various consequences such as the melting of glaciers, rising sea levels, acid rain, irregular crop pattern and even changes in human life style.



Self-Assessment

- Why climate change occurs?
- What measures can be taken to mitigate climate change?



12.1.5 Acid Rain

The term acid 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, sulphuric 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 depending upon the concentration of acidic components present in it.

Pollutants like oxides of carbon, nitrogen and sulphur are present in the atmosphere. These oxides may undergo chemical reaction with atmospheric water to produce sulphuric acid (H_2SO_4), nitric acid (HNO_3) and carbonic acid (H_2CO_3). These acidic components mixed with rainwater and fall to the earth as acid rain (Fig. 12.5).

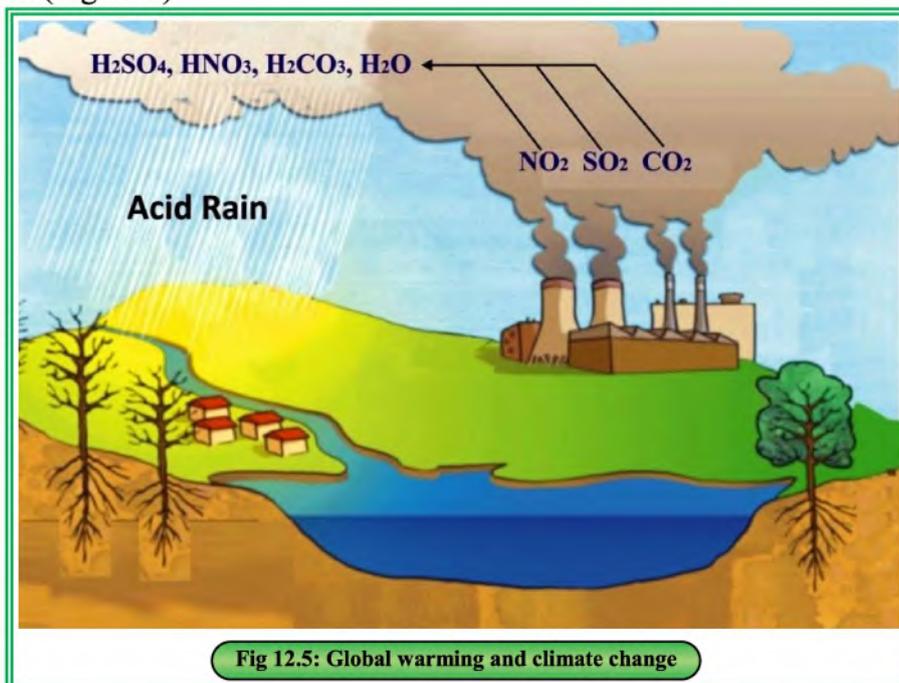
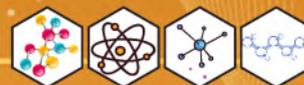


Fig 12.5: Global warming and climate change

Acid rain has several adverse effects on the environment and human life style for example.

- (i) Acid rain increases the acidity of rivers, which affect negatively on aquatic animals and plants causing a disturbance of eco system.
- (ii) Acid rain reduces soil fertility due to lowering in soil pH from their normal range and ultimately effect on crops production.



- (iii) Acid rain causes corrosion of buildings, bridges and other concrete and metal made things.
- (iv) Acid rain makes the underground water toxic and undrinkable.



Self-Assessment

What is acid rain? Explain the primary causes of acid rain and its environmental impacts.

24.2 CHEMISTRY OF STRATOSPHERE

The region from 11km to 50km above the Earth's surface is referred as stratosphere. This region is distinguished by the remarkable presence of ozone (O_3) layer. This layer plays a vital role in blocking and absorbing maximum portion of sun harmful radiations (Fig.12.6). The life on the Earth's would not be possible without the protection of this layer.

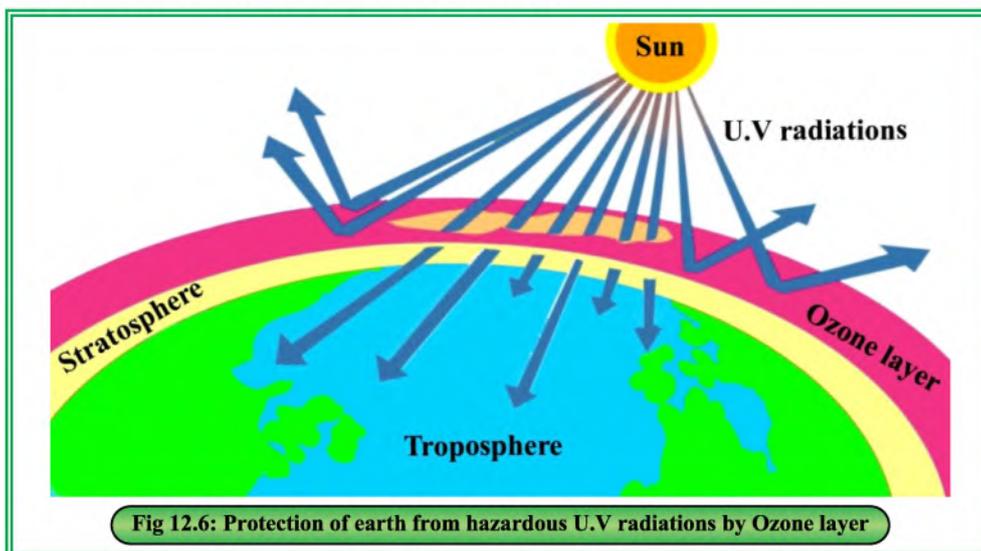
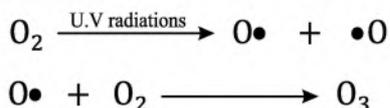


Fig 12.6: Protection of earth from hazardous U.V radiations by Ozone layer

12.2.1 Production and destruction of ozone

Ozone is produced in stratosphere region due to photochemical reaction of sun rays and oxygen gas. Ultra-violet radiations of sunlight breaks oxygen molecule (O_2) into free radicals. The oxygen free radicals are then combine with another oxygen molecule to produce ozone.

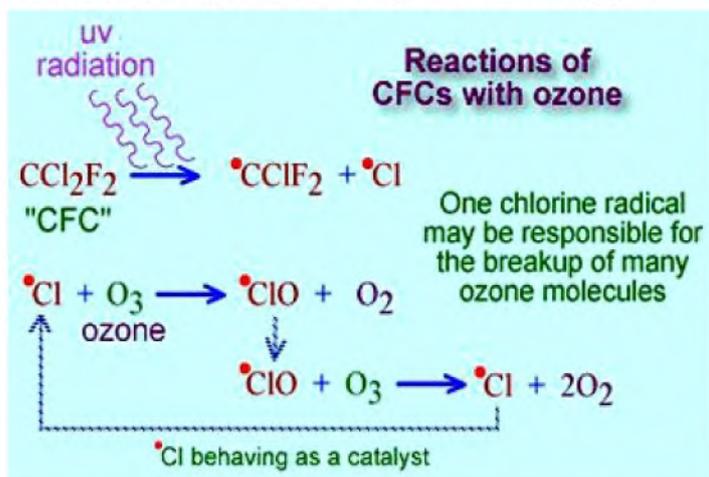


Ozone in stratosphere also destroyed by solar energy but the two phenomena are in equilibrium and hence the thickness of ozone layer remain undisturbed.

Human activities can contribute 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 Carbon (CFCs)

Chlorofluoro carbons is a highly stable gas used as coolant in refrigeration and also as repellent in aerosol spray. When (CFCs) reaches into stratosphere region, it breakdown into free chlorine and fluorine atoms which then react with ozone in U.V light and decompose it into oxygen.



DO YOU KNOW?

An ozone meter is a device used to measure and monitor the concentration of ozone (O_3) in the air, providing valuable data for assessing air quality and potential health risks associated with high ozone levels.

To address the problem of (CFCs) causing ozone depletion, scientists have been working on developing alternatives to (CFCs) in order to prevent further damage to the ozone layer. The best alternative is hydrofluoro carbons (HFCs) which do not have chlorine and do not contribute to ozone depletion.



Self-Assessment

What is the process of ozone formation in the stratosphere? How does the ozone layer provide protection for life?

12.3 WATER POLLUTION AND WATER ANALYSIS

About 75% of the Earth's is covered with water. Population explosion, industrialization, urbanization and many other human activities made the water polluted. **“Any undesirable change in the quality of water which affect the life adversely is known as water pollution”**.

12.3.1 Types of Water Pollution

The addition of pollutant substances alter the physical, chemical or biological properties of water and makes it unfit for the health of human. The substance which causes water pollution is classified into following three groups.

12.3.1.1 Suspended Solids and Sediments

“Small solid particles such as dust, coal microscopic organisms etc which remain suspended in the water are called colloids and the particles such as sand, clay which settle down to the bottom are called sediments”. These are the common pollutants of rivers, lakes and streams which produce turbidity in water and reduce the amount of sun light available to aquatic animals .

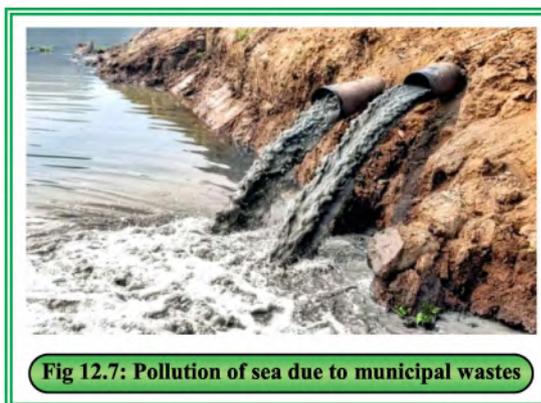


Fig 12.7: Pollution of sea due to municipal wastes

12.3.1.2 Dissolved Solids

Various organic and inorganic compound found in water. Inorganic solids consists of minerals, salts, metal cations like calcium, magnesium, sodium, potassium and anions such as chlorides, carbonates, bicarbonates, sulphates.



The organic solids originate from organic sources such as decomposition of animals, plants and microorganisms. Both inorganic and organic solids have very small particle size and hence soluble in water. They come from industrial water and sewage. When they fall into the river or oceans, they have a negative effect on aquatic life.

12.3.1.3 Waste Water Analysis

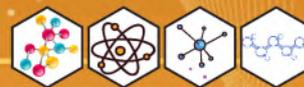
Samples of waste water are collected from different areas and analysed through a series of tests.

- (i) Physical test: These include estimation of odour, colour and taste.
- (ii) Chemical test: These involve the checking of pH, presence of biocides and toxic chemicals.
- (iii) Microbiological test: These tests involve checking for the presence of harmful bacteria and other microorganisms.
- (iv) Organic test: These tests are performed for the presence of pesticides and volatile organic solvents such as petrol, benzene, toluene etc.

Parameter of drinking water analysis

To ensure the safety and quality of drinking water, a variety of parameters are examined. Some essential parameters generally assessed during drinking water analysis along with their corresponding standard set by WHO are given below:

- (i) pH: It is an indicator of acidity or alkalinity of water. The WHO recommended pH range for drinking water is 6.5 to 8.5.
- (ii) Turbidity: It refers to the cloudiness of water due to suspended particles. The WHO recommendation for turbidity is less than 5 turbidity units.
- (iii) Total dissolved solids (TDS): All inorganic and organic solid particles suspended in the water are collectively known as total dissolved solids (TDS). The WHO guideline for TDS is below 600 mg/l.
- (iv) Chlorine residue: Chlorine residue means the chlorine remaining present in the water after the chlorination process. WHO recommends less than 0.2 mg/l in drinking water.
- (v) For freshwater bodies used for drinking water purposes, the WHO recommends BOD levels to be below 5 mg/L and COD levels to be below 10 mg/L.



12.4 GREEN CHEMISTRY

“The design and development of processes that minimize or eliminate the use of hazardous chemicals is known as green chemistry”. Green chemistry aims to create safer chemicals and processes to make the environment friendly. There are twelve rules of green chemistry.

- (i) **Prevent waste:** Design chemical synthesis to avoid waste. There should be no waste material left for treatment or clean up.
- (ii) **Maximize atom economy:** Design syntheses to get the maximum product out of the starting materials. Avoid un-reacted material.
- (iii) **Design less hazardous chemical syntheses:** Design synthetic techniques for the use and production of substances that are of little or no toxicity to humans and the environment.
- (iv) **Design safer chemicals and products:** Develop chemical products that are completely effective, yet have little or no toxicity.
- (v) **Use safer solvents and reaction conditions:** Avoid the use of solvents and other supporting chemicals. If any is unavoidable, use the safer ones.
- (vi) **Increase energy efficiency:** Design chemical reactions that can be carried out at room temperature and pressure.
- (vii) **Use renewable feedstock:** Use renewable raw materials in chemical industry rather depletable. The source of renewable raw materials is often agricultural products or by-product of industrial processes. Sources of depleting resources are often fossil fuels (oil, natural gas, or coal).
- (viii) **Use catalysts, not stoichiometric reagents:** Use catalytic reactions to minimize waste. The catalyst is effective in small amount and can carry out same reaction multiple times. They are preferred over stoichiometric reagents used in larger quantity and are carried out only once.
- (ix) **Design chemicals and products to degrade after use:** Design chemical products which decompose into harmless substances and do not accumulate in the environment.
- (x) **Analyze in real time to prevent pollution:** Include in-process, real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.
- (xi) **Minimize the potential for accidents:** Design safer techniques for chemicals and their physical forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.



SOCIETY, TECHNOLOGY AND SCIENCE

Three ways of water purification

- (i) Distillation:** It involves the heating of water to its boiling point to vapourize it and then condensing the vapours back into liquid form which left the impurities behind.
- (ii) Filtration:** Filter paper or other filter devices consists of small pores. They allow the passage of water while capturing larger particles.
- (iii) Reverse Osmosis:** In this method water is subjected to high pressure and forced through a semi permeable membrane from the impure side to pure side. Tiny pores of semi permeable membrane prevent impurities and allow to pass water molecules thereby producing purified water.



SUMMARY

- Environmental chemistry deals with the study of chemical processes happening in Earth's environment and their direct or indirect impact on organisms that live on Earth.
- Troposphere is the lowest layer of atmosphere extending from Earth's surface up to an altitude of 11km.
- Stratosphere starting from the top of troposphere and extending up to 50km above the Earth's surface.
- Mesosphere lies above stratosphere stretching from 50km to 85km above the Earth's surface.
- Thermosphere is the upper most layer of the Earth's atmosphere extending from 85km to 500km.
- Certain toxic substances, including nitrogen oxides (NO_x) sulphur oxides (SO_x), volatile organic compounds (VOCs) and ozone (O₃) can cause atmospheric pollution.



- All those solvents which evaporates into atmosphere and contribute the atmospheric pollution are known as volatile organic compound (VOCs).
- Catalytic converter is a device use in automobile for the conversion of harmful chemicals produced during internal combustion of engine into less harmful or non harmful substances.
- Catalytic converter contains a mixture metals such as platinum and palladium which serves as catalyst.
- Smog is a mixture of SO_2 , aerosols and volatile organic compounds.
- Global warming refers to the gradual rise in Earth's average surface temperature.
- Green house effect is an essential natural process that helps regulating the Earth's temperature enabling the existence of life on our planet.
- Acid rain refers to rainfall that has acidic components such as nitric acid, sulphuric acid and carbonic acid.
- Ozone is produced in stratosphere region due to photochemical reaction of U.V rays of sunlight and oxygen gas.
- Human activities can contribute the depletion of ozone layer through the emission of certain chemicals known as ozone-depletion substances (ODS).
- The chemical which is the most effective for ozone depletion is chlorofluorocarbons (CFCs) which are released from cooling devices.
- Any undesirable change in the quality of water which affect the life adversely is known as water pollution.
- Waste water analysis can be done by a series of methods such as physical methods, chemical methods, microbiological methods and organic methods.
- The design and development of processes that minimize or eliminate the use of hazardous chemicals is known as green chemistry.



EXERCISE

Multiple Choice Questions

- (i) The greenhouse gas is:
(a) Oxygen (O_2) (b) Nitrogen (N_2)
(c) Argon (Ar) (d) Carbon dioxide (CO_2)
- (ii) The pH of acid rain is:
(a) Between 7 to 8 (b) Between 6 to 7
(c) Below 5 (d) Above 8
- (iii) Ozone depletion in upper atmosphere is mainly caused by:
(a) Sulphur dioxide (SO_2) (b) Nitrogen oxides (NO_x)
(c) Carbon monoxide (CO) (d) Chlorofluorocarbons (CFCs)
- (iv) The region of sphere which extend from 11km to 50km from our Earth's is known as:
(a) Troposphere (b) Stratosphere
(c) Mesosphere (d) Thermosphere
- (v) The increase in global average temperatures is primarily attributed to:
(a) Solar radiations (b) Oxides of sulphur (SO_x)
(c) Green house gases emission (d) Natural climate variations
- (vi) The primary goal of green chemistry is:
(a) Maximizing industrial production
(b) Minimizing waste generation
(c) Reducing energy consumption
(d) Developing environmentally friendly chemicals
- (vii) Smog is word used for the combination of:
(a) Water vapours and fog (b) Smoke and fog
(c) Sediments and colloids (d) Oxides of nitrogen and sulphur
- (viii) The catalyst used in automobile catalytic converter is a mixture of:
(a) Pt and Pd (b) Ni and Fe
(c) Cu and Cr (d) Pb and Hg



- (ix) Ozone layer is present in which of the following region of atmosphere:
- | | |
|-----------------|------------------|
| (a) Troposphere | (b) Stratosphere |
| (c) Mesosphere | (d) Thermosphere |
- (x) The major source of water pollution is:
- | | |
|---------------------------|------------------------------|
| (a) Organic farming | (b) Global warming |
| (c) Industrial activities | (d) Renewable energy sources |

Short Questions

1. Write the name of four segments of atmosphere and mention in which segment we live.
2. Explain the causes of depletion of ozone layer.
3. What is industrial smog and how is it formed?
4. What are the main gases responsible for green house effect?
5. Explain four fundamental methods for the testing of waste water.

Descriptive Questions

1. What is the effect of acid rain on human health and what measures can be taken to prevent acid rain?
2. What is the main cause of Global warming? How does it effect on weather pattern?
3. Describe the chemistry involves due to the presence of oxides of nitrogen and sulphur in the troposphere.
4. What is Green house effect? How does human activities contributes to the enhancement of the green house effect?
5. What are ozone depletion substances (ODS)? What human activities have contributed to ozone depletion in the stratosphere?
6. What is a catalytic converter? What are the main pollution targeted by catalytic converter?

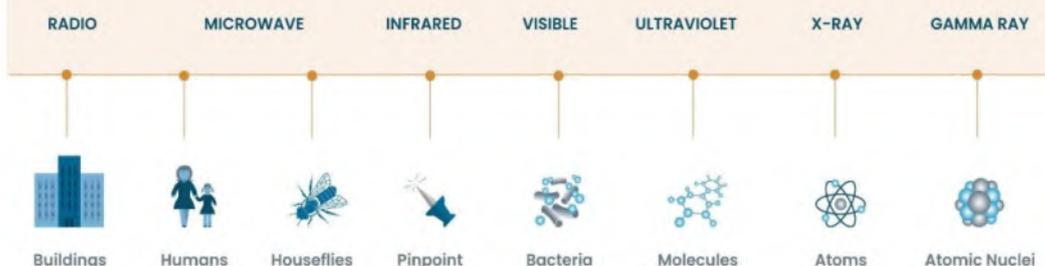
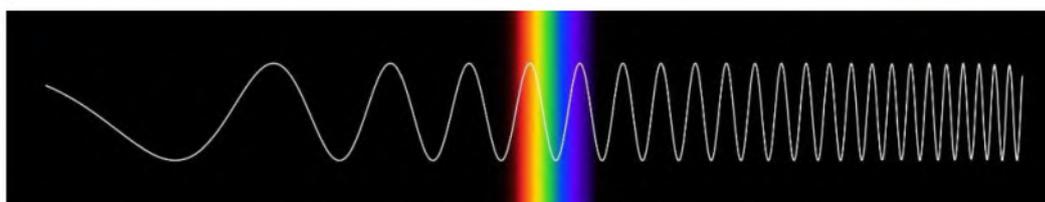


CHAPTER 13

SPECTROSCOPY



Teaching Periods	11	Assessment	02	Weightage %	09
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Students will be able to:

- ✓ Define spectroscopy and discuss its applications in different fields (Understanding)
- ✓ Enlist the regions of electromagnetic spectrum used in IR and UV/Vis spectroscopy (Applying)
- ✓ Identify Ethanol by using different techniques of Spectroscopy. (Applying)
- ✓ Explain atomic emission and atomic absorption spectrum. (Understanding)
- ✓ Describe the application of NMR, UV, IR and Mass Spectroscopy in different fields. (Understanding)



INTRODUCTION

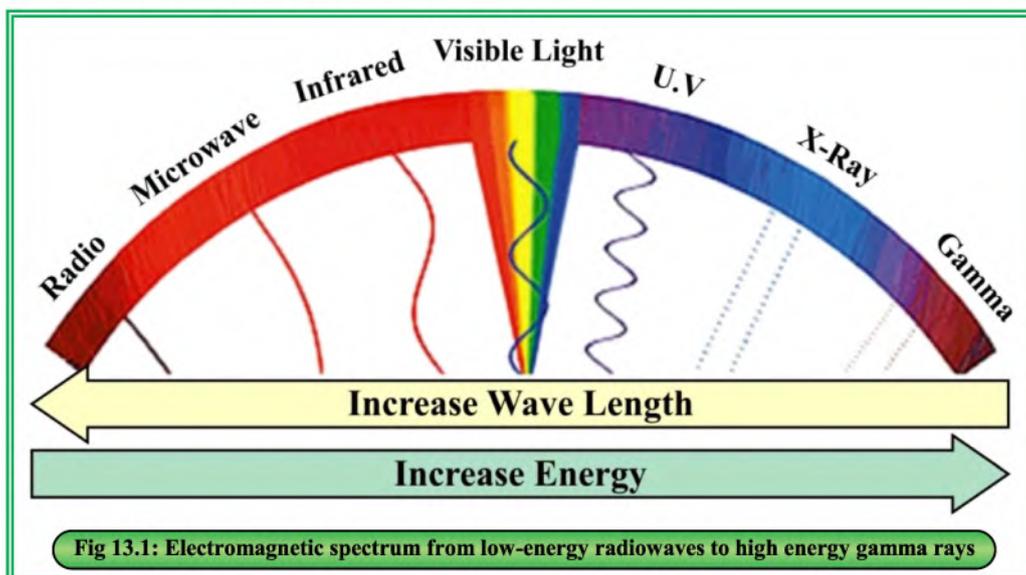
Billions of the compounds have been synthesized to date, each differing from one another based on the arrangement of atoms, bond positions and the type of functional groups present in their structures. Traditionally, the identification of compounds relied on a series of chemical tests. However, spectroscopy has now superseded the conventional methods for various reasons **“Spectroscopy is the study of interaction of electromagnetic radiation of light with matter”**. It is a powerful analytical technique for the determination of structure of molecules.

Spectroscopy has a wide scope of applications in various fields of science and technology and significantly favoured over conventional methods because;

- It is easier and takes very little time to analyze a sample.
- It requires a very small amount of substance which is to be analyzed.
- It provides more reliable information about chemical molecule.

Some applications of spectroscopy are given as:

- Analysis of chemical compounds
- Quality control of drugs syntheses
- Analysis of water pollution
- Determination of protein structure
- Analysis of forensic materials
- It helps in structure analysis





13.1 METHODS OF SPECTROSCOPY

Sunlight consists of a wide range of electromagnetic waves including radiowaves, microwaves, infrared radiations, visible radiations, ultra-violet radiations, etc. When electromagnetic radiations interact with molecule, some of the rays are absorbed by the molecules while other are transmitted. The wave length and frequency of absorbed light can provide valuable information about the structure of molecule. Various methods of spectroscopy are commonly used to analyze and characterize the compounds.



DO YOU KNOW?

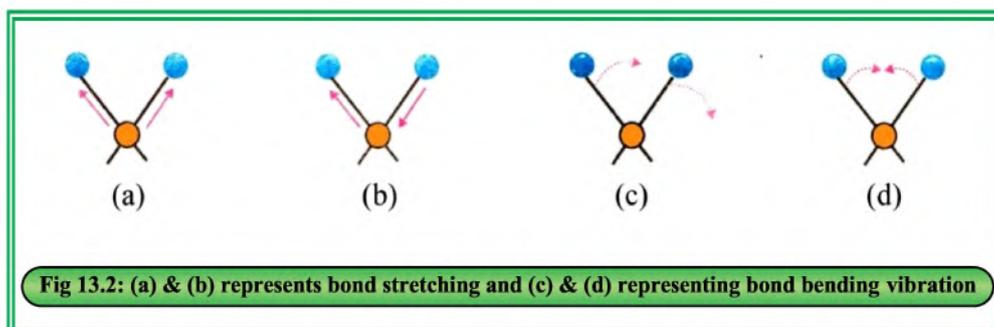
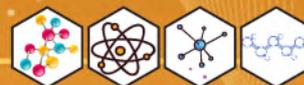
After manufacturing, food, drugs and other pharmaceutical products are sent to the quality control department of the factory. In this department, various spectroscopic techniques are applied to these products to assess their purity, quality and ensure consumer safety.

13.1.1 Infrared (IR) Spectroscopy

“Infrared spectroscopy is used to detect the type of bonds and the functional groups present in molecule”. I.R frequency is expressed in the unit of wave number (cm^{-1}). The most useful IR range lies between $4000\text{-}670\text{ cm}^{-1}$.

Region	Wavenumber range (cm^{-1})
Near IR	12000-4000
Middle IR	4000-200
Far IR	200-10

The atoms in a molecule already undergo vibration and rotation, in their normal routine, however when the molecule absorbs I.R 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 change.

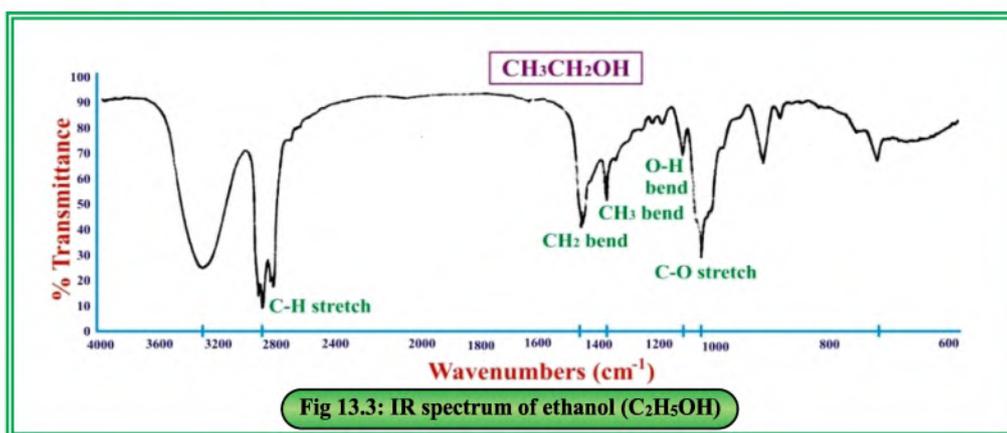


The bending and stretching of each type of bond present in the molecule occurs at a particular frequency of IR spectrum and show the signals at a particular region. There are two regions in IR spectrum;

- i. Finger print region ($1500\text{-}500\text{ cm}^{-1}$)
- ii. Functional group region ($4000\text{-}1500\text{ cm}^{-1}$)

For example if we want to identify ethanol ($\text{C}_2\text{H}_5\text{OH}$) by I.R spectroscopy. We should note the region of absorption bands, in I.R finger print and functional group regions.

- A peak around $1150\text{-}1200\text{ cm}^{-1}$ shows OH in bond bending.
- A carbon-oxygen bond stretching peak is appeared at $1050\text{-}1100\text{ cm}^{-1}$.
- A carbon-hydrogen bond bending of CH_2 and CH_3 groups are observed at $1400\text{ }1500\text{ cm}^{-1}$





Applications of IR Spectroscopy

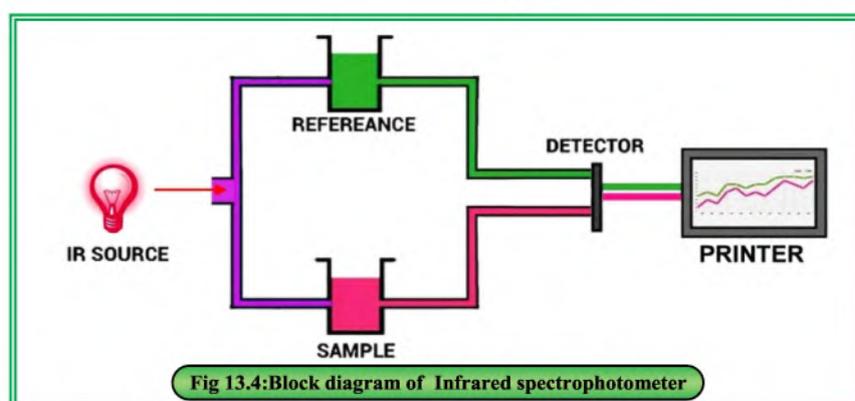
- (i) I.R spectroscopy provides information for the presence of different functional groups in the organic molecules.
- (ii) I.R spectroscopy is also useful for identifying the impurities present in the sample to be analyzed.



DO YOU KNOW?

Chemical instruments and technology are closely inter connected.

- > Chemical instruments are the tools used to analyze or measure chemical processes.
- > Technology refers to the application of scientific knowledge for practical purpose.

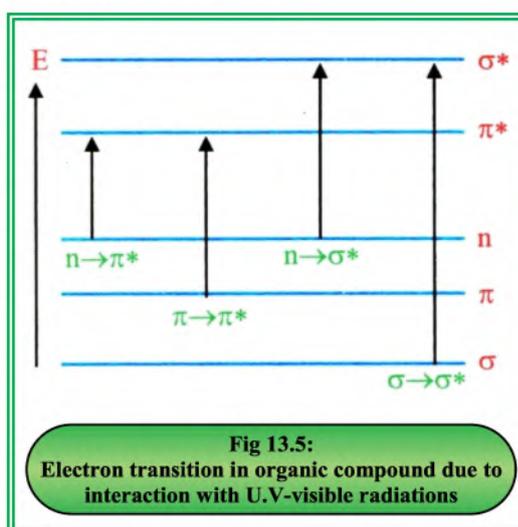


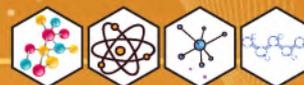
13.1.2 Ultra-violet/Visible (UV-Vis) Spectroscopy

“Ultra-violet-visible spectroscopy is used to determine the presence of double and triple bonds as well as conjugated system in the molecule”.

The U.V region of electromagnetic spectrum extends from 200nm to 400nm and the visible region extends from 400nm to 800nm.

When a molecule absorbs electromagnetic radiations of U.V-visible range (200nm-800nm) electronic transitions occur. Its electrons are promoted from lower





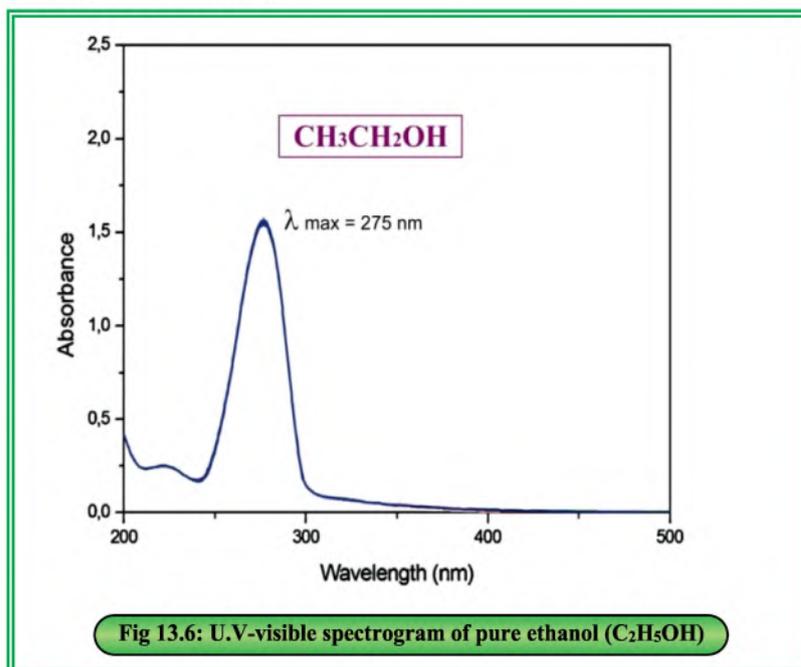
energy level to higher energy level. The transition of electrons may be of the following types.

(i) $\sigma - \sigma^*$ transition: It requires very high energy which is beyond the range of U.V-visible radiations therefore carbon-carbon single bond do not absorb U.V-visible radiations and cannot be detected.

(ii) $\pi - \pi^*$ transition: This transition occurs in the molecule that contain double or triple bonds or aromatic rings. The range of wavelength for the absorption of $\pi - \pi^*$ transition is 180-320 nm.

(iii) $n - \pi^*$ transition: This transition is associated with the molecules in which double or triple bond is connected with a hetero atom (N, O, S) for example aldehyde and ketone, etc. The range of wavelength of $n - \pi^*$ transition can vary depending upon the specific molecular system, however it is approximately 200-500nm.

(iv) $n - \sigma^*$ transition: This transition is concerned with the saturated molecule with hetero atoms like alkyl halide, alcohol etc. The range of $n - \sigma^*$ transition roughly falls around 150-300nm.





Application of U.V-visible spectroscopy

- (i) U.V spectroscopy can provide valuable information regarding the structure of a compound particularly in relation to the presence of double bond, triple bond, aromatic system and hetero atoms.
- (ii) U.V spectroscopy is extensively used for determining the concentration of unknown compounds in a solution by using Beer-Lambert's law.



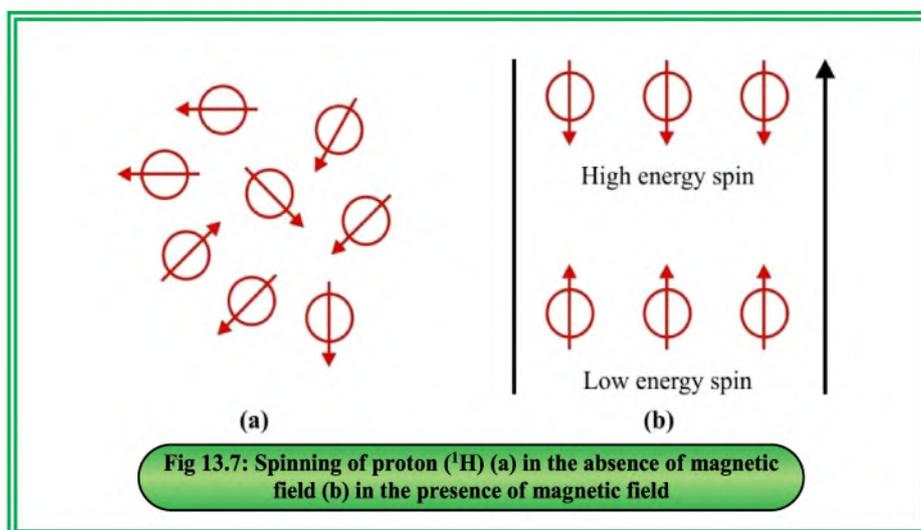
Self-Assessment

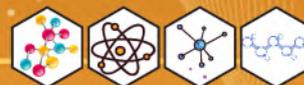
What is the range of wave length typically used in U.V-visible spectroscopy?

13.1.3 Nuclear Magnetic Resonance (NMR) Spectroscopy

The nucleus of certain elements like ^1H (proton) 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 in the opposite direction of the applied magnetic field and said to be high energy spin state.





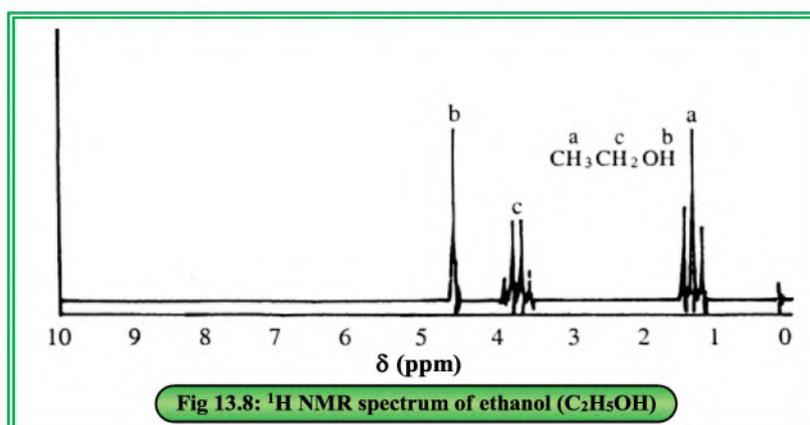
When a sample of a compound is placed in a strong magnetic field and subjected to radio frequency radiation, the nuclei with specific spin state absorb energy and flip into a high energy state, this absorption of energy is detected as signals in the NMR spectrum. The solvent used in NMR spectroscopy is usually D_2O or $DMSO$, since it does not interfere with NMR of the sample but with the conditions that compound is soluble in both solvents.

The graph of 1H NMR consists of following parameters.

- (i) x-axis represents chemical shift which shows position of proton signals relative to TMS (tetramethylsilane).
- (ii) y-axis represents absorption which shows the intensity of NMR-signals.
- (iii) Peaks represent splitting pattern (singlet, doublet, triplet, quartet) due to neighboring protons.

To understand 1H NMR spectrum let us consider the example of ethanol. 1H NMR spectrum of ethanol has three types of protons.

- Methyl (CH_3) protons appear as triplet at around 1.1 to 1.3 ppm.
- Methylene protons (CH_2) appear as a quartet around 3.5 to 4 ppm.
- The hydroxyl proton appears as a broad singlet around 4 to 5 ppm.



DO YOU KNOW?

Magnetic resonance imaging (MRI) is a medical imaging technique that uses strong magnetic field and radio waves to generate detailed images of the internal structure of the body.



DO YOU KNOW?

The position of signal along the x-axis of an NMR spectrum is called chemical shift. Most of the protons in compound have chemical shift values between 0-12 ppm relative to TMS. TMS is internal standard assigned 0 ppm value.



Applications of NMR Spectroscopy

NMR spectroscopy is a powerful analytical technique, it 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. This technique is successfully applied in drug analysis, material science, forensic analysis and many other fields.

13.1.4 Atomic Absorption and Emission Spectroscopy

Atomic absorption and emission spectroscopy are established techniques used to identify elements in various samples including metal compounds. Within an atom, electrons are distributed in different energy levels, when atoms receive energy from an external source like heat or an electric discharge, electrons can be promoted to a higher energy level. These excited electrons then undergo transition involving the absorption or emission of electromagnetic radiations.

Atomic absorption spectroscopy

In atomic absorption spectroscopy, the sample is exposed to a wide range of light, the atom selectively absorbs specific wavelengths of light that align with the energy needed to elevate electrons to a higher energy level. The absorbed wavelengths of light appear as dark lines in a unique pattern specific for that element. By examining the absorbed wavelength, a chemist can identify the presence of a specific element in the given sample.

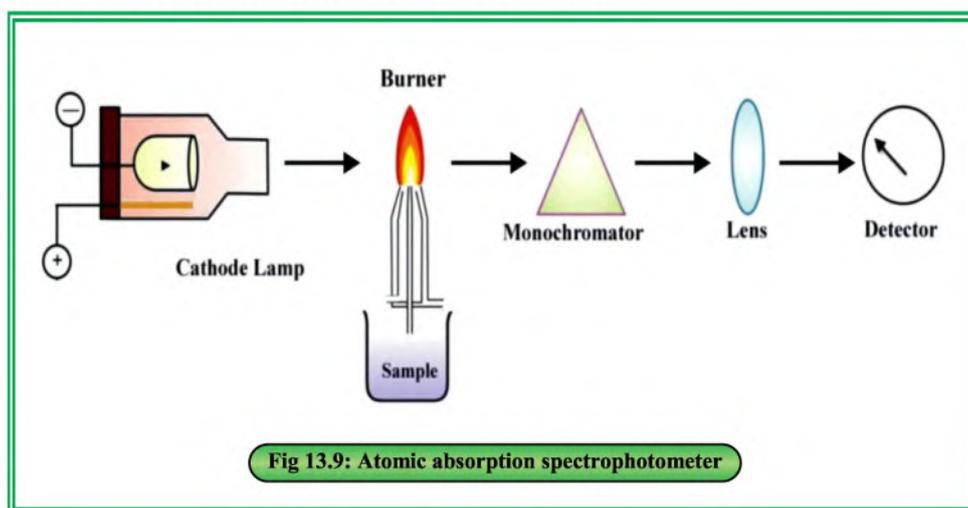
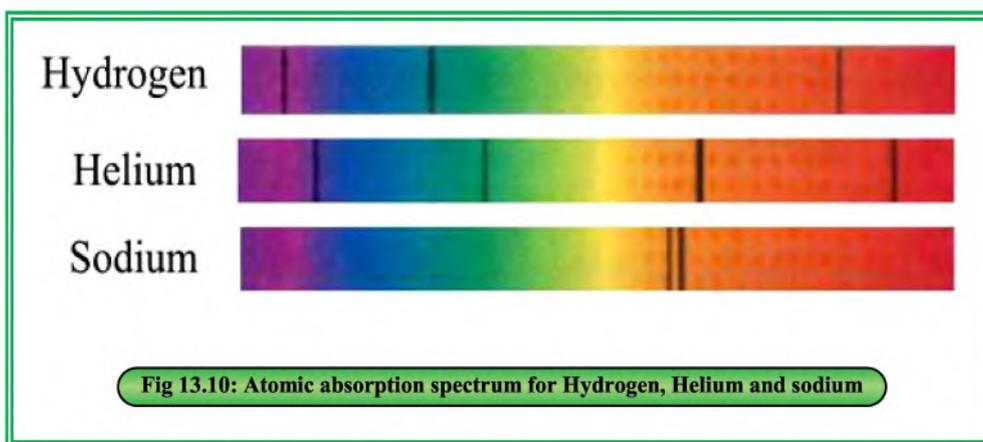
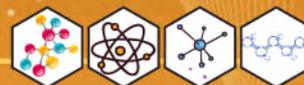
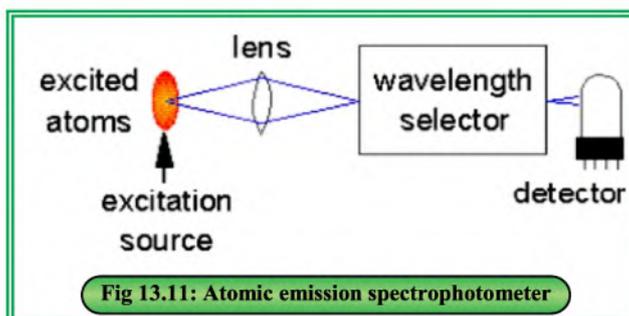


Fig 13.9: Atomic absorption spectrophotometer

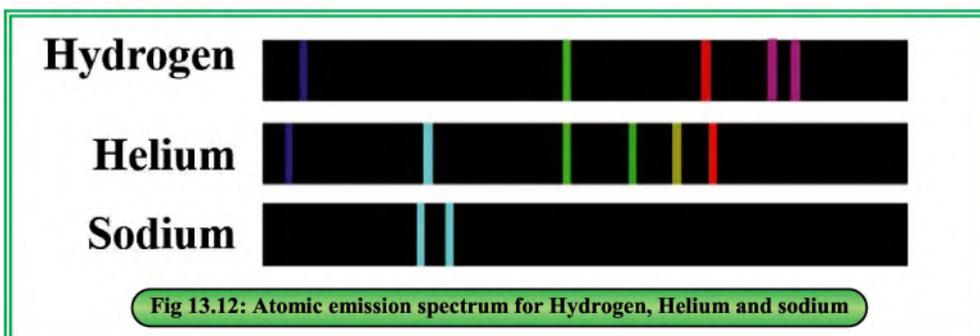


Atomic emission spectroscopy

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 commonly found U.V visible or rarely in IR range. 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.



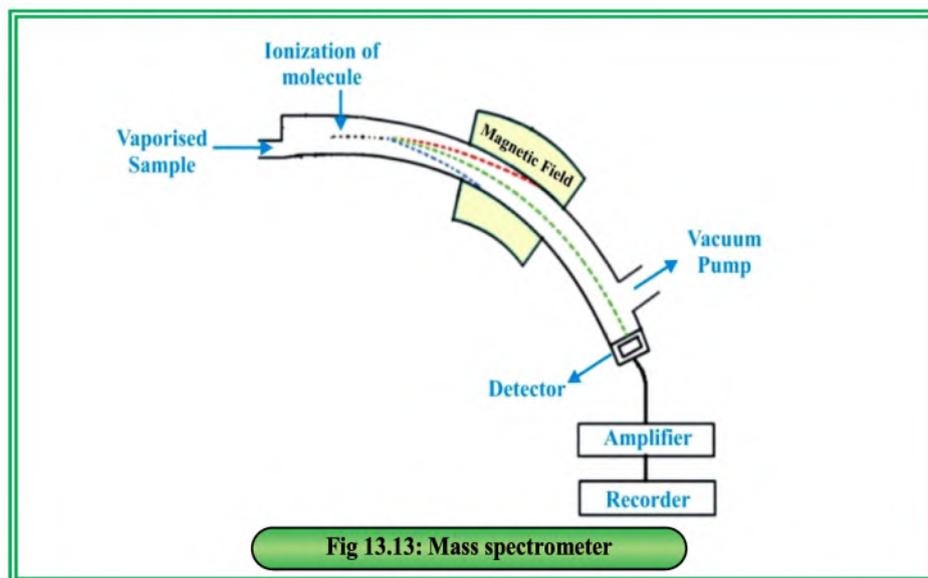


Self-Assessment

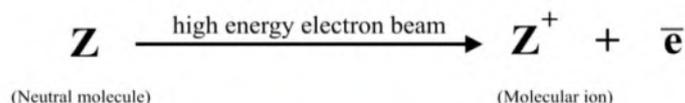
What is the principle behind atomic emission spectroscopy?

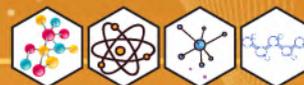
13.1.5 Mass Spectrometry

“Mass spectrometry is 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 and play an important role in the structure elucidation of molecule.

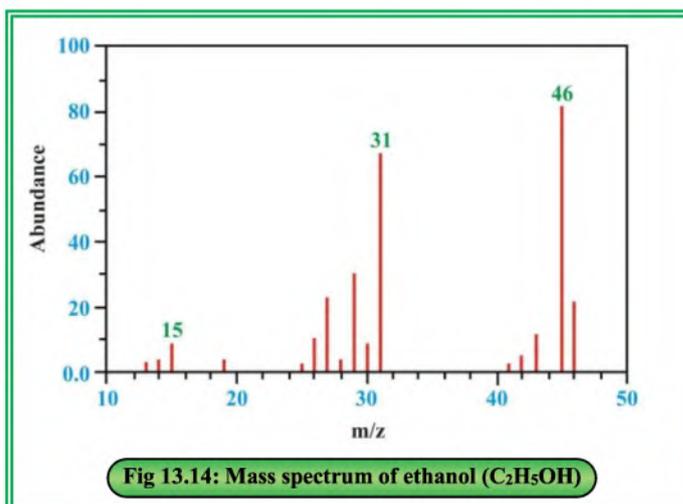


In mass spectrometry, the vapours of compounds are bombarded with beam of high energy electrons from electron gun that makes the neutral molecule loose an electron and change into molecular ion. These molecular ions further break into smaller possible fragments of specific charge to mass ratio (m/z).





These molecular ions then pass through 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.



Self-Assessment

What is mass spectrum? What is the role of detector in mass spectrometer?

Applications of mass spectroscopy

- (i) It is used to determine the molecular mass of unknown compounds on the basis of mass to charge ratio.
- (ii) It is used for the identification and purification of drugs and other pharmaceutical products.



SOCIETY, TECHNOLOGY AND SCIENCE

Use of MS in forensic test

Mass spectrometry provides precise and reliable data for the identification, analysis and interpretation of evidence found at crime scenes such as hairs, blood, illegal drugs, harmful substances, explosive residues, DNA analysis etc. Use of MS help forensic scientists to determine the nature of substance involved in crime and assisting forensic investigators in solving crimes and presenting scientific evidence in court.



SUMMARY

- Spectroscopy is the study of interaction of electromagnetic radiation of light with matter.
- Sunlight consists of a wide range of electromagnetic waves including radio waves, microwaves, infrared radiations, visible radiations, ultra-violet radiations etc.
- Infrared spectroscopy is used to detect the type of bonds and functional groups present in the molecule.
- Ultra violet-visible spectroscopy is used to determine the presence of double and triple bonds as well as conjugated system in the molecule.
- The U.V region of electromagnetic spectrum extends from 200 nm o 400 nm and the visible region extends from 400 nm to 800 nm.
- ^1H NMR spectroscopy is carried out when the sample of compound is placed in a strong magnetic field and subjected to radio frequency waves.
- In atomic absorption spectroscopy absorbed wavelength of light appears as dark lines with bright background.
- In atomic emission spectroscopy absorbed wavelength of light appears as bright lines with dark background.
- Mass spectroscopy is technique used to determine the mass to charge ratio (m/z) of ions in a sample.



EXERCISE

Multiple Choice Questions

- (i) The energy of IR radiations is:
- (a) Higher than radio waves (b) Higher than U.V waves
(c) Lower than micro waves (d) Higher than x-rays
- (ii) The fingerprint region of an IR spectrum typically found in the range of:
- (a) $1500\text{-}4000\text{cm}^{-1}$ (b) $2000\text{-}4000\text{cm}^{-1}$
(c) $1500\text{-}500\text{cm}^{-1}$ (d) $4000\text{-}8000\text{cm}^{-1}$
- (iii) Which unit of measurement is used for the wave number of IR spectrum:
- (a) Nanometer (nm) (b) Angstrom (\AA)
(c) Centimeter $^{-1}$ (cm^{-1}) (d) Hertz (Hz)
- (iv) Electronic excitation occurs in electromagnetic spectrum if the molecule absorbs:
- (a) I.R radiations (b) U.V-visible radiations
(c) Radio waves (d) Micro waves
- (v) In NMR spectroscopy, the hydroxyl proton of $\text{C}_2\text{H}_5\text{OH}$ appears as a broad singlet around:
- (a) 1 – 2 ppm (b) 2 – 3 ppm
(c) 4 – 5 ppm (d) 6 – 7 ppm
- (vi) Atomic absorption spectrum is represented by:
- (a) Dark lines against bright background
(b) Bright lines against dark background
(c) Bright lines against bright background
(d) Dark lines against dark background
- (vii) Infrared spectroscopy is a technique use to determine _____ in the given organic molecule:
- (a) Double and triple bonds (b) Mass to charge ratio
(c) Functional group (d) Conjugated system



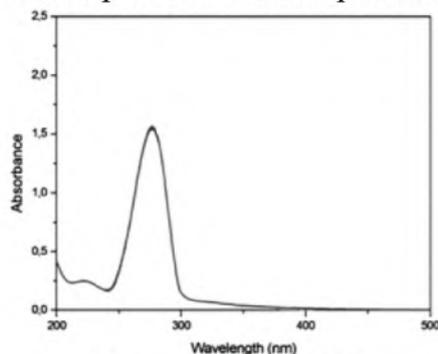
- (viii) Highest U.V-visible absorption energy require for the transition of:
- (a) σ to σ^* (b) π to π^*
(c) n to σ^* (d) n to π^*
- (ix) NMR spectroscopy is carried out if radiations interact with molecules in high magnetic field:
- (a) U.V-visible rays (b) Radio rays
(c) X-rays (d) Infrared rays
- (x) In which of the following spectroscopy technique D_2O can be used as solvent:
- (a) Mass spectroscopy (b) NMR spectroscopy
(c) Atomic absorption spectroscopy (d) I.R spectroscopy

Short Questions

1. What types of nuclei are detected in proton NMR spectroscopy?
2. Name the components which represents x-axis and y-axis of a proton NMR spectrum.
3. Differentiate between atomic absorption and emission spectroscopy.
4. What is the purpose of U.V-visible spectroscopy? What is its applications in chemistry and biology?

Descriptive Questions

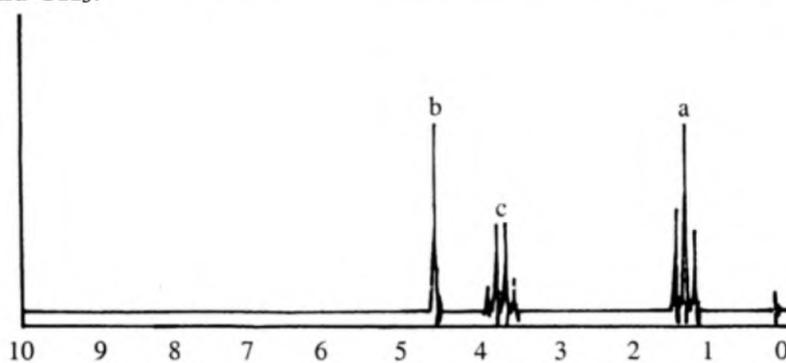
1. What information about the structure of a molecule we can get from mass spectroscopy? Give the applications of mass spectroscopy.
2. What is proton NMR spectroscopy? How does it work? Give its applications.
3. Explain λ_{\max} with the help of U.V-visible spectrum of ethanol (C_2H_5OH).



Spectrum of ethanol



4. Explain the graph of proton NMR of ethanol (C_2H_5OH) proton peaks of OH, CH_2 and CH_3 .





APPENDIX - 1

Some IR Absorptions for Common Functional Groups

Bond	Type of Compound	Frequency (cm ⁻¹)
$\begin{array}{c} \\ -\text{C}-\text{H} \\ \end{array}$	alkanes	2800-3000
$\begin{array}{c} \\ =\text{C}-\text{H} \end{array}$	alkenes, aromatics	3000-3100
$\equiv\text{C}-\text{H}$	alkynes	3300
$-\text{O}-\text{H}$	alcohols, phenols	3600-3650 (free)
$-\text{O}-\text{H}$	carboxylic acids	3600-3650 (H-bonded) (broad) 2500-3300
$\begin{array}{c} \\ -\text{N}-\text{H} \end{array}$	amines	3300-3500 (doublet for NH ₂)
$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{H} \end{array}$	aldehydes	2720 and 2820
$\begin{array}{c} \quad \\ -\text{C}=\text{C}- \\ \quad \end{array}$	alkenes	1600-1680
$\begin{array}{c} \quad \\ -\text{C}=\text{C}- \\ \quad \end{array}$	aromatics	1500-1600
$-\text{C}\equiv\text{C}-\text{H}$	alkynes	2100-2270
$\begin{array}{c} \text{O} \\ \\ -\text{C}- \end{array}$	aldehydes, ketones, carboxylic acids	1680-1740
$-\text{C}\equiv\text{N}$	nitriles	2220-2260



APPENDIX - 2

MCQS ANSWER KEYS

Chap #	MCQs No.									
	(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)	(ix)	(x)
1	a	c	d	a	c	c	b	a	b	a
2	c	c	b	b	c	d	d	a	c	d
3	d	d	d	a	c	c	b	d	a	c
4	a	c	c	b	b	d	d	c	c	d
5	b	d	b	b	a	b	b	d	d	b
6	b	a	c	c	b	c	a	a	d	a
7	b	c	c	b	d	c	d	c	b	c
8	b	b	b	c	a	a	c	a	a	c
9	d	d	c	c	b	c	b	c	b	a
10	c	c	b	a	a	d	a	b	b	c
11	a	a	b	b	c	b	c	b	b	d
12	d	c	d	b	c	d	b	a	b	c
13	a	c	a	b	c	a	c	a	b	b



APPENDIX - 3

PHYSICAL PROPERTIES OF ORGANIC COMPOUNDS

Name	Melting Point °C	Boiling Point °C
Methane	-182	-162
Ethane	-183	-88
Ethene	-169	-104
Ethyne	-82	-84
Cyclopropane	-128	-33
Cyclohexane	6.5	81
Benzene	5.5	80
Phenol	43	182
Toluene	-95	110
Benzoic acid	122	249
Chlorobenzene	-45	132
Nitrobenzene	5.7	210
Methanol	-98	64
Ethanol	-115	78
Dimethyl ether	-141	-25
Diethyl ether	-116	34
Methyl amine	-93	-6.3
Ethyl amine	-81	17
Formic acid	8.4	101
Acetic acid	16.6	118
Acetyl chloride	-112	51
Acetic anhydride	-73	140
Methyl formate	-100	32
Ethyl acetate	-84	77
Formaldehyde	-92	-21
Acetaldehyde	-121	21
Acetone	-95	56



APPENDIX - 4

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