CHEMISTRY

For Class XII

SINDH TEXTBOOK BOARD, JAMSHORO

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

CHEMISTRY

FOR CLASS - XII

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SINDH TEXTBOOK BOARD,
JAMSHORO.

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PREFACE

This chemistry textbook for class XII is based on the revised curriculum which is being introduced in the province of Sindh from 1991. It aims to make the study of chemistry easy and interesting for the students of intermediate classes.

This book gives comprehensive knowledge and will, therefore, be beneficial for students, parents and teachers. All the topics of inorganic and organic chemistry have been arranged systematically. Special emphasis has been made to include fundamental definitions which are explained in simple language. Exprimental verifications have been added where necessary, labelled diagrams have been given so that the students can understand topics thoroughly. In addition to this, organic chemistry has been introduced with special and due attention.

Chemistry is a very rapidly progressing science and its scope has grown beyond all recognition during recent years. It is hoped that the present book will open up the vast fields of chemistry to create curiosity to acquire more knowledge and gain sufficient understanding of chemistry. Chemistry is a science which plays a major role in the development of Pakistan.

Editors feel that lapses, errors and omissions might be present in the body of the book. It is hoped that teachers, students and parents would not hesitate in bringing these to the notice of the Sindh Text book Board authorities. With the co-operation of all users of this book, it would be possible to bringout improved new edition.

Editors

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PART 1

INORGANIC CHEMISTRY

CHAPTER 1

PERIODIC CLASSIFICATION

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1.1 INTRODUCTION

The aim of the classification of elements is to group together those elements which resemble each other in some respect and to separate those elements which differ. The best classification will clearly be that which brings together elements which resemble one another in the greatest number of ways.

1.2 DOBEREINER'S TRIADS

After the acceptance of atomic mass values universally, attempts were made to find out relations between properties of various elements and their atomic masses. In 1829, J.W Dobereiner discovered that within a group of elements of three closely related in chemical

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properties, the atomic masses are either nearly the same (eg. Iron, cobalt and nickel) or the atomic mass of the middle element is approximately the arithmetic mean of other two elements. These are called Dobereiner's triads.

TRIADS

Elements		Atomic Mass	Arithmetic Mean
Triads →	Lithium Sodium Potassium	7 23 39	$\frac{7+39}{2} = 23$
Triads →	Chlorine Bromine Iodine	35.5 80 126.5	$\frac{35.5+126.5}{2} = 81$
Triads →	Calcium Strontium Barium	40 87 137	$\frac{137+40}{2} = 88$

1.3 NEWLAND'S LAW OF OCTAVES

The next attempt was made by an English chemist Newland between 1864–1869. He arranged the elements in the ascending order of their atomic weights. He observed that the properties of every eighth element were similar to those of the first one. He called this regularity of elements as the "Law of Octaves" and arranged most of the elements then known accordingly.

Newland's arrangement of elements.

Li=7	Be=9.4	B=11	C=12	N=14	O=16	F=19
Na=23	Mg=24	Al=27.3	Si=28	P=31	S=32	Cl=35.5

In this classification, Li and Na; Be and Mg; B and Al; C and Si; N and P, O and S; and F and Cl resemble in chemical properties.

Advantages and Disadvantages of Law of Octaves.

(i) This law provided a basis for the classification of elements into groups of elements having similar properties.

(ii) This law provided a wider scope to arrange all known elements into a tabular form.

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(iii) The periodic arrangement of elements did not include Noble gases because they were not discovered then, and the heavier elements could also not be accommodated.

1.4 LOTHAR MEYER'S CLASSIFICATION

Lothar Meyer, a German chemist published an incomplete periodic table in a book in 1864 and he extended it in 1869 to include 56 elements arranged in groups from I to VIII. Further to bring in light the concept of chemical periodicity, Lothar Meyer plotted the values of certain physical properties such as atomic volumes, against atomic weights, and obtained different curves. He observed that elements with similar physical properties occupied similar position in the curve. For example, alkali metals occupy the peaks of the curves, and the halogens and elements forming acidic oxides occur on the ascending portion of the curves.

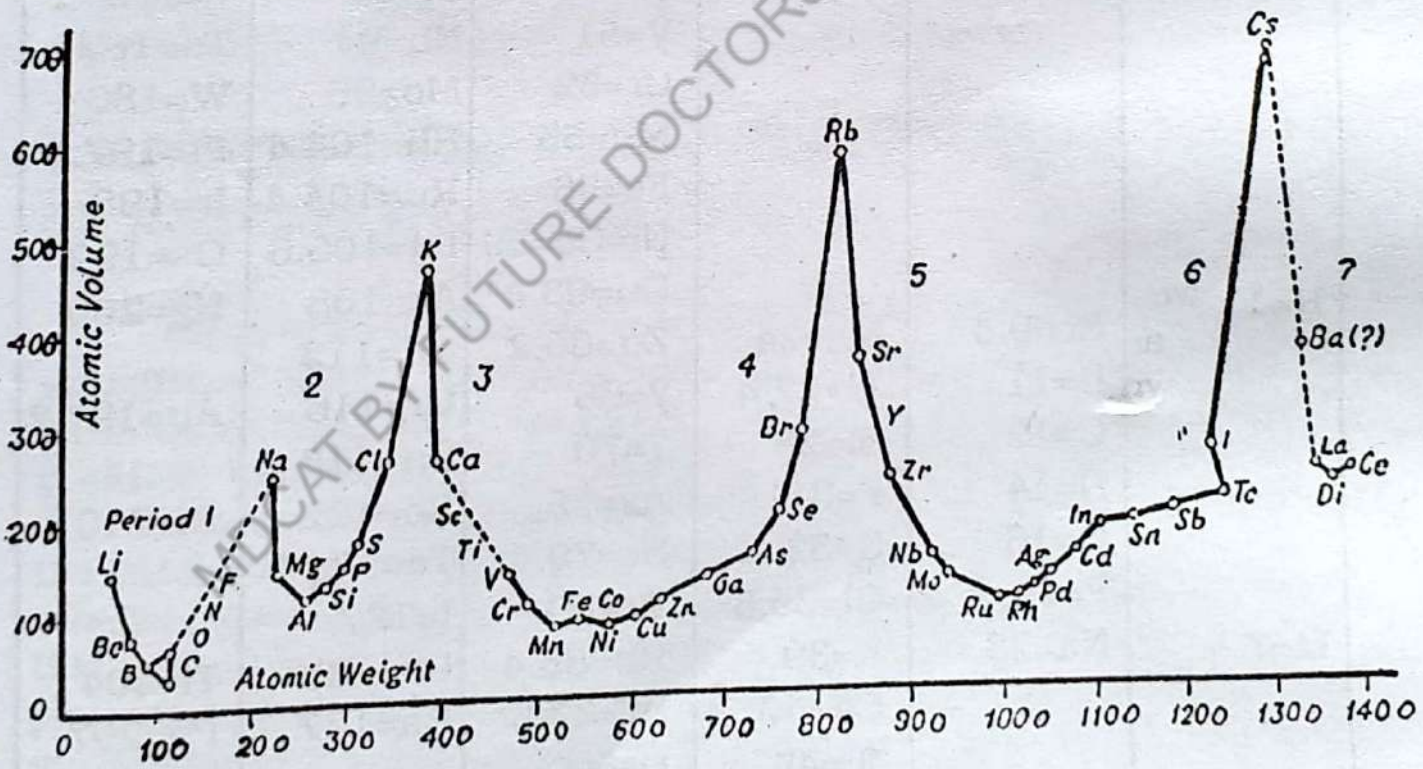

Fig: 1.1— Lothar Meyer's Atomic Volume Curve.

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Lothar Meyer's periodic classification could not receive proper attention. There may be two reasons for this;

(i) Meyer's periodic table was incomplete compared with Mendeleev's periodic table which was published in the same year with remarkable predictions of discoveries of certain elements.

(ii) Meyer's classification was supported by a study of various physical properties such as atomic volumes, malleability, brittleness, and electro chemical behaviour related with atomic weights with no empirical or logical basis for classification, as we find in Mendeleev's periodic classification which is entirely based on periodic law.

1.5 MENDELEEV'S PERIODIC TABLE AND PERIODIC LAW–1869

In the year 1869 Mendeleev mainly on the basis of physical and chemical properties discovered empirically a law known as periodic law which he stated as "The properties of the elements are a periodic function of their atomic weights".

Mendeleev's periodic table

			Ti=50	Zr=90	?=180
			V=51	Nb=94	Ta=182
			Cr=52	Mo=96	W=186
			Mn=55	Rh=104.4	Pt=197.4
			Fe=56	Ru=104.4	Ir=198
			Ni=Co=59	Pd=106.6	Os=199
			Cu=63.4	Ag=108	Hg=200
H=1			Zn=65.2	Cd=112	
	Be=9.4	Mg=24	?=68	Ur=116	Au=197 ?
	B=11	Al=27.4	?=70	Sn=118	
	C=12	Si=28	As=75	Sb=122	Bi=210
	N=14	P=31	Se=79.4	Te=128 ?	
	O=16	S=32	Br=80	I=127	
	F=19	Cl=35.5	Rb=85.4	Cs=133	Tl=204
Li=7	Na=23	K=39	Sr=87.6	Ba=137	Pb=207
		Ca=40	Ce=92		
		? =45	La=94		
		?Er=56	Di=95		
		?Yt=60	Th=118?		
		?In=75.6			

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Mendeleev's law is an extension of Newland's law of octaves. Although there was no fundamental basis for the periodic law, due to lack of knowledge about the atomic structure or atomic numbers, yet the classification of elements on the basis of periodic law proved useful for predicting unknown elements and for establishing a relation between chemical properties and atomic weights. Mendeleev arranged all the then known elements in order of their increasing atomic weights in seven horizontal lines, called periods, and in eight vertical columns, called groups. It is felt that in certain cases Mendeleev himself disregarded the periodic law. For instance he placed Ar(39.9) before K (39) and Te (127.6) before I (126.9). This fulfilled the real objective of classification i.e. to put together those elements which resemble and to separate which differ in properties.

Mendeleev left certain gaps in his periodic table for the elements to be discovered. According to his prediction he named them as Eka–Boron; Eka–Aluminium and Eka–Silicon. He also predicted the atomic weights and properties of the undiscovered elements. These elements were discovered in the life of Mendeleev and were named Scandium, Gallium, and Germanium. Further, these elements were found to possess properties as were predicted by Mendeleev.

1.6 MODERN PERIODIC LAW–PERIODIC TABLE BASED ON MOSELEY'S CONTRIBUTION

From 1904 to 1913 various attempts were made to explore the structure of atom. Lord Rutherford's experiment of the deviation of α–particles striking a thin metal foil revealed the existence of a dense positively charged nucleus wrapped in a thin cloud of electrons. In 1913 Moseley, a British physicist established that atomic number is the fundamental property of the elements. He succeeded to reveal a relation between properties and atomic numbers of the elements. On this ground he modified Mendeleev's periodic law to the form, "The properties of the elements are the periodic functions of their atomic numbers and not the atomic weights".

The modern periodic law provided logical and scientific ground for the classification of elements. This law also provided justification for correcting the position of some elements wrongly placed in Mendeleev's periodic table.

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This periodic table was not of much use because the representative and the transition elements were placed in the same group side by side dividing each group as sub groups A and B.

The periodic laws and the periodic tables were developed empirically but they did not diminish the usefulness of the periodic table. Both contributed to the development of chemistry.

Periodic law was originally an empirical approach to express periodicity of the elements with increasing atomic masses or atomic numbers; but with further development in atomic structure, periodic law may be restated as: "The physical and chemical properties of the elements are a function of the electronic configuration of their atoms which vary with increasing atomic numbers in a periodic manner".

1.7 CLASSIFICATION AND LONG FORM OF PERIODIC TABLE ON THE BASIS OF ELECTRONIC CONFIGURATION

The electronic configuration of elements provided a sound fundamental basis to the classification of elements. The properties of elements change in a periodic manner as the atomic numbers increase from one inert gas to the next higher inert gas. Thus it would be better to select inert gas family for studying the correlation between electronic configuration and periodicity.

The basic concept of Aufbau principle of building up of electronic shells is that every electron goes to the available lowest energy level.

The energy sequence of orbitals is 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p.

The periodicity of elements is closely related with this sequence of energy levels. The similarities among elements leading to the formation of various groups from I to VIII clearly correspond to similarities in electronic configurations and particularly in the resemblance of valence electrons. On the basis of electronic configuration the elements can be divided as:

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Long Form of Periodic Table

This table also contains the complete and valance shell ground state electronic Configurations of the atoms of the elements. Here [He], [Ne], [Ar], [Kr], [Xe], and [Rn] indicate the complete configurations of helium, neon, argon, krypton, xenon and radon respectively which are as: [He] (Atomic number, Z = 2) → 2; [Ne] (Z = 10) → 2, 8; [Ar] (Z = 18) → 2, 8, 8; [Kr] (Z = 36) → 2, 8, 18, 8; [Xe] (Z = 54) → 2, 8, 18, 18, 8; and [Rn] (Z = 86) 2, 8, 18, 32, 18, 8.

Metals — Non-metals and Metalloids

s-Block Elements — p-Block Elements — d-Block Elements (Transition Elements) — f-Block Elements (Inner-transition Elements)

	IA	IIA	IIIB	IVB	VB	VIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	Noble Gases Zero
1 [He]+	1 H $1s^1$ Hydrogen																2 He $1s^2$ Helium
2	3 Li $2s^1$ Lithium	4 Be $2s^2$ Beryllium										[He]+ 5 B $2s^2p^1$ Boron	6 C $2s^2p^2$ Carbon	7 N $2s^2p^3$ Nitrogen	8 O $2s^2p^4$ Oxygen	9 F $2s^2p^5$ Fluorine	10 Ne $2s^2p^6$ Neon
3 [Ne]+	11 Na $3s^1$ Sodium	12 Mg $3s^2$ Magnesium										[Ne]+ 13 Al $3s^2p^1$ Aluminium	14 Si $3s^2p^2$ Silicon	15 P $3s^2p^3$ Phosphorus	16 S $3s^2p^4$ Sulphur	17 Cl $3s^2p^5$ Chlorine	18 Ar $3s^2p^6$ Argon
4 [Ar]+	19 K $4s^1$ Potassium	20 Ca $4s^2$ Calcium	21 Sc $3d^14s^2$ Scandium	22 Ti $3d^24s^2$ Titanium	23 V $3d^34s^2$ Vanadium	24 Cr $3d^54s^1$ Chromium	25 Mn $3d^54s^2$ Manganese	26 Fe $3d^64s^2$ Iron	27 Co $3d^74s^2$ Cobalt	28 Ni $3d^84s^2$ Nickel	29 Cu $3d^{10}4s^1$ Copper	30 Zn $3d^{10}4s^2$ Zinc	31 Ga $3d^{10}4s^2p^1$ Gallium	32 Ge $3d^{10}4s^2p^2$ Germanium	33 As $3d^{10}4s^2p^3$ Arsenic	34 Se $3d^{10}4s^2p^4$ Selenium	35 Br $3d^{10}4s^2p^5$ Bromine	36 Kr $3d^{10}4s^2p^6$ Krypton
5 [Kr]+	37 Rb $5s^1$ Rubidium	38 Sr $5s^2$ Strontium	39 Y $4d^15s^2$ Yttrium	40 Zr $4d^25s^2$ Zirconium	41 Nb $4d^45s^1$ Niobium	42 Mo $4d^55s^1$ Molybdenum	43 Tc $4d^55s^2$ Technetium	44 Ru $4d^75s^1$ Ruthenium	45 Rh $4d^85s^1$ Rhodium	46 Pd $4d^{10}5s^0$ Palladium	47 Ag $4d^{10}5s^1$ Silver	48 Cd $4d^{10}5s^2$ Cadmium	49 In $4d^{10}5s^2p^1$ Indium	50 Sn $4d^{10}5s^2p^2$ Tin	51 Sb $4d^{10}5s^2p^3$ Antimony	52 Te $4d^{10}5s^2p^4$ Tellurium	53 I $4d^{10}5s^2p^5$ Iodine	54 Xe $4d^{10}5s^2p^6$ Xenon
6 [Xe]+	55 Cs $6s^1$ Cesium	56 Ba $6s^2$ Barium	57 La $5d^16s^2$ Lanthanum	72 Hf $4f^{14}5d^26s^2$ Hafnium	73 Ta $4f^{14}5d^36s^2$ Tantalum	74 W $4f^{14}5d^46s^2$ Tungsten	75 Re $4f^{14}5d^56s^2$ Rhenium	76 Os $4f^{14}5d^66s^2$ Osmium	77 Ir $4f^{14}5d^76s^2$ Iridium	78 Pt $4f^{14}5d^96s^1$ Platinum	79 Au $4f^{14}5d^{10}6s^1$ Gold	80 Hg $4f^{14}5d^{10}6s^2$ Mercury	81 Tl $4f^{14}5d^{10}6s^26p^1$ Thallium	82 Pb $4f^{14}5d^{10}6s^26p^2$ Lead	83 Bi $4f^{14}5d^{10}6s^26p^3$ Bismuth	84 Po $4f^{14}5d^{10}6s^26p^4$ Polonium	85 At $4f^{14}5d^{10}6s^26p^5$ Astatine	86 Rn $4f^{14}5d^{10}6s^26p^6$ Radon
7 [Rn]+	87 Fr $7s^1$ Francium	88 Ra $7s^2$ Radium	89 Ac $6d^17s^2$ Actinium	104 Ku $5f^{14}6d^27s^2$ Kurchatovium	105 Ha $5f^{14}6d^37s^2$ Hahnium													

Lanthanides (4f-Block Elements) 6 [Xe]+	58 Ce $4f^25d^06s^2$ Cerium	59 Pr $4f^35d^06s^2$ Praseodymium	60 Nd $4f^45d^06s^2$ Neodymium	61 Pm $4f^55d^06s^2$ Promethium	62 Sm $4f^65d^06s^2$ Samarium	63 Eu $4f^75d^06s^2$ Europium	64 Gd $4f^75d^16s^2$ Gadolinium	65 Tb $4f^95d^06s^2$ Terbium	66 Dy $4f^{10}5d^06s^2$ Dysprosium	67 Ho $4f^{11}5d^06s^2$ Holmium	68 Er $4f^{12}5d^06s^2$ Erbium	69 Tm $4f^{13}5d^06s^2$ Thulium	70 Yb $4f^{14}5d^06s^2$ Ytterbium	71 Lu $4f^{14}5d^16s^2$ Lutetium	
Actinides (5f-block Elements) 7 [Rn]+	90 Th $5f^06d^27s^2$ Thorium	91 Pa $5f^26d^17s^2$ Protactinium	92 U $5f^36d^17s^2$ Uranium	93 Np $5f^46d^17s^2$ Neptunium	94 Pu $5f^66d^07s^2$ Plutonium	95 Am $5f^76d^07s^2$ Americium	96 Cm $5f^76d^17s^2$ Curium	97 Bk $5f^86d^17s^2$ Berkelium	98 Cf $5f^{10}6d^07s^2$ Californium	99 Es $5f^{11}6d^07s^2$ Einsteinium	100 Fm $5f^{12}6d^07s^2$ Fermium	101 Md $5f^{13}6d^07s^2$ Mendelevium	102 No $5f^{14}6d^07s^2$ Nobelium	103 Lw $5f^{14}6d^17s^2$ Lawrencium	

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Electronic configuration (Valence Orbit)	Group and sub-group	Types of elements
ns^1 ns^2	I A II A	s-block elements
$ns^2\ np^1 - ns^2\ np^5$	III A to VII A	p-block active elements
$ns^2\ np^6$	VIII A or 0	p-block inert elements as reference point
$(n-1)d^1\ ns^2 - (n-1)d^{10}\ ns^2$	III B to VIII B and I B; II B	d-block outer transition elements or elements between s and p-blocks
$(n-2)f^1\ (n-1)d^1\ ns^2 - (n-2)f^{14}\ (n-1)d^{10}\ ns^2$	III B	f-block or inner transition elements

The period number (numbers of horizontal rows) is given by the quantum number of the outermost orbit.

The tabular arrangement following Aufbau principle is called long form of periodic table. Periodic table is built up as follows on the basis of electronic configuration:

Period-1: This period corresponds to filling up of K-shell. It is the shortest period and contains only 2 elements H and He with electronic configuration $1s^1$ and $1s^2$.

Period-2: This period corresponds to filling up of L-shell. In this period electrons occupy 2s and 2p orbitals. Therefore, it contains 8 elements from lithium $(1s^2, 2s^1)$ to Neon $(1s^2, 2s^2, 2p^6)$. It is called first short period.

Period-3: This period corresponds to the filling up of M-shell. In this period 3s and 3p orbitals are being filled. It starts from Na and ends at Ar. This period also contains 8 elements and is called second short period.

Period-4: This period corresponds to the filling up of N-shell. It starts with the filling of 4s orbital followed by 3d and 4p orbitals. It contains 18 elements. It is called first long period.

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Period-5: This period corresponds to the filling up of O-shell. It starts with the filling of 5s orbital followed by 4d and 5p. It contains 18 elements. It is called second long period.

Period-6: This period includes 2 elements of s-block with configuration $6s^1$ and $6s^2$, 10 elements of d-block with configuration $6s^2,5d^1$ to $6s^2,5d^{10}$ and 14 elements of f-block with configuration $6s^2,5d^1,4f^1$ to $6s^2,5d^1,4f^{14}$(Lanthanides). This is an exceptional case where electrons start filling 4f orbitals after 5d accommodates one electron.

Period-7: This period includes 2 elements of s-block with configuration $7s^1$ and $7s^2$, 10 elements of d-block with configuration $7s^2,6d^1$ to $7s^2,6d^{10}$and 14 elements of f-block with configuration $7s^2,6d^1,4f^1$ to $7s^2,6d^1,5f^{14}$(Actinides). This is also an exceptional example where electrons are accommodated in 5f orbitals after 6d acquires one electron.

1.8 TYPES OF ELEMENTS BASED ON ELECTRONIC CONFIGURATION

The periodic table has been divided into s, p, d and f-blocks on the basis of electronic configuration:

(i) The Noble gases:- In the periodic table, the noble gases are found at the end of each period in zero group. They are colourless gases upto some extent chemically unreactive and diamagnetic.

The electronic arrangement of $ns^2,np^0$is exceptionally stable. Discontinuities in energy level diagram occur after these configurations are attained. With the exception of helium (Z=2), all the noble gases have outer electronic configuration of $2s^2,2p^0$. No atom has a complete outer shell with the exception of helium and noble gases.

(ii) Representative elements or typical elements:- All elements of A sub-groups of the periodic table are called representative or typical elements. They include metals, non-metals and metalloids. Some of the elements are paramagnetic and some are diamagnetic. These include elements of s and p-blocks.

(a) s-block elements:- In these elements the last electron enters ns orbital which is being progressively filled. The elements of I A and II A belong to s-block. The valence shell configuration varies from ns^1 to ns^2 where 'n' is the period in which the element is present.

(b) p-block elements:- The elements in which p orbitals are being progressively filled are called p-block elements. The elements of

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the groups III A, IV A, V A, VI A, VII A and zero groups are members of p-block. The valence shell configuration of these elements ranges from ns^2, np^1 to $ns^2, 2p^6$.

(iii) d-block elements (outer transition elements):- The elements in which the last electron enters (n-1)d orbitals are called d-block elements. These elements are also called outer transition elements. The valence shell configuration of these elements ranges from $ns^2, (n-1)d^1$ to $ns^2, (n-1)d^{10}$. There are four series of outer transition elements, the 4th is incomplete.

(iv) f-block elements (Inner transition elements):- The elements in which the last electron enters (n-2)f orbital are called f-block elements or inner transition elements. They have outer electronic configuration: $ns^2, (n-1)d^1, (n-2)f^{1-14}$

ASSIGNMENT

1. Complete the following table:

Symbol	Atomic number	Mass number	Protons	Neutrons	Electrons
Zr	40	91			
Zn	30			35	
		108			47
				117	78
Cs		133		78	
Pb^+				125	81
		80			36

2. Explain the following with examples:
   (a) s-block elements
   (b) p-block elements
   (c) d-block elements
   (d) f-block elements
3. Identify the groups of the periodic table that have following groundstate electronic configurations in their outer shells:
   (a) $3s^2, 3p^6, 4s^1$
   (b) $3s^2, 3p^5$
   (c) $4s^2, 4p^6$
   (d) $6s^2, 5d^1, 4f^3$

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4. How is the atomic number related to:
   (a) The number of protons
   (b) The number of electrons

5. Explain the periodic system of classification of elements proposed by Mendeleev and discuss its advantages and anomalies.
6. State the Periodic Law and explain how it was arrived at. In what various ways does it help the chemists?
7. What are the main features of the periodic classification of the elements? Explain some of its important applications.
8. Give the characteristic valence shell configuration of the following:
   (a) Noble gases (b) Representative elements
   (c) Transition elements.

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CHAPTER 2

HYDROGEN

2.1 INTRODUCTION

Laboratory methods of preparation, properties and uses of hydrogen have already been discussed at secondary level. Here some more aspects of study of hydrogen will be considered.

2.2 POSITION OF HYDROGEN IN THE PERIODIC TABLE

Elements are arranged in the periodic table on the basis of their electronic configuration and to some extent on the basis of their properties. Electronic configuration and properties of hydrogen partially resemble with the elements of group IA (Alkali metals), group IVA (carbon family) and with group VIIA (halogens) but does not resemble completely with the members of any one of the groups. This can be seen from the following discussions:

Hydrogen resembles with alkali metals only in possessing one electron in the s–orbital of the outermost shell (valence shell) but it differs from them in many respects. It is a gas at ordinary temperature and is also a non–metal. It does not lose its valence electron and does not form H^+ ion like Na^+ because the valence electron in hydrogen is strongly attracted by the positively charged nucleus. Although it forms compounds with non–metals such as HF, HCl etc and their aqueous solutions, ionize to form hydrogen cation ($HCl \rightleftharpoons \overset{+}{H} + \overset{-}{Cl}$) but these $\overset{+}{H}$ ions or protons unlike $\overset{+}{Na}$ do not exist free in water except in the solvated form such as $\overset{+}{H}_3O$.

It resembles with carbon and its family members (group IVA) in that the valence shell of hydrogen is half filled. Some thermodynamic properties such as ionization potential, electron affinity values etc of hydrogen are also similar to that of carbon and other members of its family. However hydrogen differs in many respects from the members of carbon family. It is a gas. It shows monovalency

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and its valence shell consists of "s" orbital where as members of carbon family are solids. They show tetra valency and their valence shell consists of s and p orbitals.

Hydrogen also resembles with halogens in that it is a non – metal and forms H^- ion by gaining electron from strong electro – positive metals. Thus Na^+H^- and Na^+Cl^- are comparable. It is also a gas consisting of diatomic molecules (H_2) like F_2 and Cl_2. However, it differs from halogens in that unlike Cl^-, H^- is incapable of existence in water since H_2 is formed immediately and there is no stabilization due to solvation. Electron affinity of hydrogen is also much less than halogens.

In the light of above facts, hydrogen does not completely resembie with members of any one of the groups mentioned. Therefore, some authors place hydrogen at the top of group IA, others place it at the top of group VIIA. Its exact position still remains undecided. The different behaviour of hydrogen is because of its simplest atom which possesses a singly positive charged nucleus and one electron moving around the nucleus.

2.3 INDUSTRIAL PREPARATIONS OF HYDROGEN

In industry, hydrogen is manufactured from water, natural gas and ammonia. Methods are arranged in the order of their importance:

(i) Electrolysis of Water: When electricity is passed through water containing a small quantity of an electrolyte (an acid, a base or a salt), water decomposes into hydrogen and oxygen. Hydrogen collects at cathode and oxygen gas, a by – product, is collected at anode.

$$2H_2O \xrightarrow{\text{Electricity}} 2H_{2(g)} + O_{2(g)}$$

The gases produced are in the purest form. This process is expensive and is used to produce hydrogen where electricity is available at cheaper rates.

(ii) Steam and Hydrocarbon Process: A mixture of steam and natural gas when passed over nickel catalyst at 900°C, produces a mixture of hydrogen and carbon monoxide commonly known as Water gas. Natural gas contains about 94.60% methane.

$$CH_{4(g)} + H_2O_{(g)} \xrightarrow[900^\circ C]{Ni} \underbrace{3H_{2(g)} + CO_{(g)}}_{\text{Water gas}}$$

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(iii) **By the action of Steam on Coal:** When steam is passed over red hot coke at about 1000°C, a mixture of hydrogen and carbon monoxide (Water gas) is formed.

$$C_{(s)} + H_2O_{(g)} \xrightarrow{1000^\circ C} \underbrace{H_{2(g)} + CO_{(g)}}_{\text{Water gas}}$$

Hydrogen is obtained in free state by removing carbon monoxide from water gas. It is done by heating the mixture of two gases with more steam at 500°C in the presence of catalyst (Iron oxide or cobalt oxide). As a result carbon monoxide is changed to carbon dioxide which can easily be separated by dissolving in water under high pressure leaving behind free hydrogen gas.

$$CO_{(g)} + H_2 + H_2O_{(g)} \xrightarrow[500^\circ C]{FeO} CO_{2(g)} + 2H_{2(g)}$$

Carbon monoxide can also be removed by cooling water gas at-200°C, with the help of liquid air. Carbon monoxide becomes liquid and free hydrogen gas is separated. Traces of carbon monoxide are further removed by passing the contaminated hydrogen through sodium hydroxide solution which absorbs carbon monoxide to form sodium formate.

$$CO_{(g)} + NaOH_{(l)} \longrightarrow HCOONa_{(l)} \text{ (Sodium formate)}$$

(iv) **Steam Methanol Process:** A mixture of steam and vapours of methanol when heated at 250°C produces a mixture of hydrogen and carbon dioxide.

$$CH_3OH_{(g)} + H_2O_{(g)} \xrightarrow{250^\circ C} CO_{2(g)} + 3H_{2(g)}$$

Carbon dioxide is separated by passing the mixture through water under high pressure where by CO_2 will dissolve in water and free hydrogen gas is obtained.

(v) **Thermal Decomposition of Hydrocarbons:** Methane (a major constituent of natural gas) when heated in the absence of oxygen, is decomposed into its constituent elements.

$$CH_{4(g)} \xrightarrow{700^\circ C} C_{(s)} + 2H_{2(g)}$$

Carbon thus obtained is known as "Carbon black" which is a by—product and is used in rubber industry, specially as fillers for tyres. It is also used as a pigment for inks, plastics, paints, type writer carbon papers etc.

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(vi) Thermal Decomposition of Ammonia: This process consists of vaporizing the liquid ammonia from cylinders, heating at 1000°C and passing over an active catalyst.

$$2NH_{3(g)} \xrightarrow[\text{Catalyst}]{1000^\circ C} N_{2(g)} + 3H_{2(g)}$$

The mixture of nitrogen and hydrogen is cooled to − 196°C when nitrogen becomes liquid and free hydrogen gas is obtained.

2.4 ATOMIC HYDROGEN

Ordinary hydrogen exists as diatomic molecules (H_2), therefore, it is also called as molecular hydrogen. The two atoms in a molecule of hydrogen are held together by a shared pair of electrons known as covalent bond having very high bond energy (104 K cal. mol^{-1}). The molecules are very stable and dissociate into atoms only under extreme conditions. The product obtained as a result of dissociation of molecular hydrogen is known as atomic hydrogen. These atoms have very short life and quickly combine together to form molecules again.

Preparation of Atomic Hydrogen: Atomic hydrogen is prepared by thermal decomposition of ordinary hydrogen or by electrical dissociation under reduced pressure.

$$\text{(i)}\ H_{2(g)} + 104\ K.cal \xrightarrow{5000^\circ C} 2H$$

$$\text{(ii)}\ H_{2(g)} \xrightarrow[1mm-0.1mm\ pressure]{\text{Electric discharge}} 2H$$

Properties of Atomic Hydrogen: Atomic hydrogen is more reactive than molecular hydrogen. Expected reactions of molecular hydrogen are only those in which more than 104 K.cals per mole are evolved per two gram atoms of hydrogen. Reactions producing less than this energy will not take place spontaneously. For the reactions of atomic hydrogen, there is no such condition. Most of the reactions take place at ordinary temperature and some even below room temperature. Some reactions of atomic hydrogen are given below:—

$$P + 3H \longrightarrow PH_3$$

$$O_2 + 2H \longrightarrow H_2O_2$$

$$S + 2H \longrightarrow H_2S$$

$$Cl_2 + 2H \longrightarrow 2HCl$$

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$$CuO + 2H \longrightarrow Cu + H_2O$$

$$AgCl + H \longrightarrow Ag + HCl$$

Uses: Atomic hydrogen is used to produce atomic hydrogen torch to attain a temperature of 4000 – 5000°C which is employed in welding aluminium alloys, high chromium and nickel steels. It is based on the fact that when a jet of hydrogen is passed through an electric arc set up between the tungsten rods, atomic hydrogen is produced which at once recombines to give a flame having a temperature between 4000 – 5000°C. The heat is not produced by burning of hydrogen but from recombination of hydrogen atoms.

$$H + H \longrightarrow H_{2(g)} + 104 \text{ K. cal. mol}^{-1}$$

It is worth to note that hydrogen set free at the time of its preparation from its compounds is also in atomic form and is commonly known as nascent hydrogen. If a substance capable of reacting with these atoms is present, the reaction will take place before any H_2 molecules are formed but if such a substance is not present then hydrogen atoms unite together and form H_2 molecules. That is why nascent hydrogen is more reactive than ordinary molecular hydrogen.

2.5 BINARY COMPOUNDS OF HYDROGEN

Hydrogen combines with other elements and forms binary compounds which are called hydrides. Hydrogen forms binary compounds with all types of elements, metals and non-metals excluding zero group gases. Hydrides, therefore, have also varied structures and properties. So hydrides may be classified into the following major groups according to the nature of bonding and properties:

(i) Ionic or salt like hydrides

(ii) Covalent hydrides

(iii) Complex hydrides

(iv) Metallic hydrides

(v) Polymeric hydrides

(vi) Border line hydrides

(i) **Ionic Hydrides:** These type of hydrides are formed by the metals of group IA (alkali metals) and group IIA (alkaline earth metals) except Be and Mg. In these hydrides, metal atoms form positive ion by losing valence electrons and

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hydrogen forms negative ion by gaining that electron in order to complete its shell. They have general formula $\overset{+}{M}\overset{-}{H}$ in case of group IA and $\overset{+2}{M}\overset{(-1)}{H_2}{}^{2}$ in case of metals of group IIA. Therefore, these hydrides are known as ionic hydrides. Also they possess salt like characters. Therefore, they are called salt like or saline hydrides. They are prepared by passing hydrogen gas over hot alkali metals or alkaline earth metals.

$$2Na + H_2 \xrightarrow[200^oC]{Heat} 2NaH_{(s)}$$
Sodium hydride

$$Ca + H_2 \xrightarrow[200^oC]{Heat} CaH_2$$
Calcium hydride

They are colourless nonvolatile salt like solids having high melting points. They are sufficiently stable towards heat. Stability decreases with increasing atomic masses. They are insoluble in organic solvents but soluble in water with which they react and produce hydrogen. They also produce hydrogen on reaction with acids and alcohols.

$$\overset{+}{Na}\overset{-}{H} + H_2O \longrightarrow NaOH + H_{2(g)}$$
$$\overset{+}{Na}\overset{-}{H} + HCl \longrightarrow NaCl + H_{2(g)}$$
$$\overset{+}{Na}\overset{-}{H} + C_2H_5OH \longrightarrow C_2H_5ONa + H_{2(g)}$$
$$\overset{++}{Ca}\overset{2(-1)}{H_2} + 2H_2O \longrightarrow Ca(OH)_2 + 2H_{2(g)}$$

Such reactions are vigorous with hydrides of alkali metals and moderate with hydrides of alkaline earth metals. Generally CaH_2 is used to prepare hydrogen.

They are used as a source for producing hydrogen, as reducing agents in metallurgical processes and as dehydrating agents for organic solvents.

(ii) **Covalent Hydrides:** Elements from group IIIA to group VIIA form binary compounds with hydrogen. They contain covalent bonds, therefore, they are called "Covalent hydrides". They can be prepared by direct or indirect methods as shown in the following examples:

$$H_2 + Cl_2 \xrightarrow{Sunlight} 2HCl$$
$$2H + O_2 \xrightarrow{Ignition} 2H_2O$$
$$H_2 + S \xrightarrow{450^oC} H_2S$$
$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

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$$Al_4C_3 + 6H_2O \longrightarrow 2Al_2O_3 + 3CH_4$$

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

They are colourless gases or volatile liquids having low boiling points except water which has high boiling point (100 °C) due to polarity of molecule and presence of inter–molecular hydrogen bonds.

Hydrides of group IIIA and IVA are neutral. Hydrides of group VA are basic while those of group VIA and VIIA are generally acidic. Acidic strength increases from group VIA to VIIA and from top to bottom.

(iii) **Complex hydrides:** Members of group IIIA do not form stable binary compounds except boron. However, hydrides of these elements combine with alkali metal hydrides to form compound of complex nature possessing all the three types of chemical bonds. These compounds are called complex hydrides and have general formula ABH_4 where A is univalent metal ion such as Li^+, Na^+ etc and B is trivalent positive ion of elements of group IIIA such as B^{3+}, Al^{3+} etc.

$$LiH + AlH_3 \longrightarrow Li^{1+}Al^{3+}H_4^{1-}$$

$$NaH + BH_3 \longrightarrow Na^{1+}B^{3+}H_4^{1-}$$

These compounds are salt like white solids, stable upto 300°C. They are soluble in water in which they ionize to give Li^+ and AlH_4^- ions, the latter ion immediately reacts with water to produce hydrogen.

$$Na^+AlH_4^- + 4H_2O \longrightarrow Al(OH)_3 + NaOH + 4H_{2\,(g)}$$

(iv) **Metallic Hydrides:** With transition metals, hydrogen forms hydrides of intermediate composition by penetrating the crystal lattice structure of these metals. Properties of these hydrides are apparently those of pure metals, therefore, they are named as metallic hydrides. In these hydrides hydrogen occupies interstitial spaces (empty spaces between atoms), therefore, they are also called interstitial hydrides. These hydrides on heating release hydrogen in atomic state. For this reason transition metals such as platinum, nickel etc.are used as catalysts in hydrogenation reactions.

(v) **Polymeric Hydrides:** First two members of group IIA i.e beryllium and magnesium form hydrides having formulae $(BeH_2)_n$ and $(MgH_2)_n$. Because

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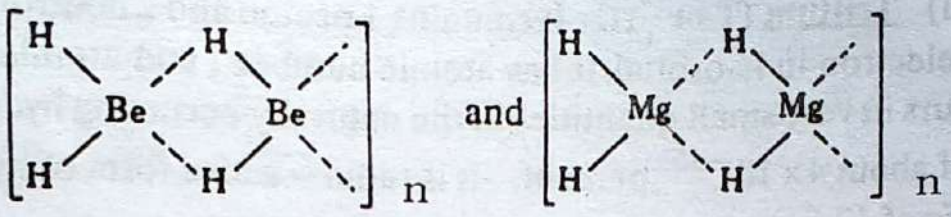
large number of BeH_2 and MgH_2 molecules are polymerized, therefore, they are known as "Polymeric hydrides". Their structures are given below:



Their properties are intermediate between ionic hydrides and covalent hydrides.

(vi) <u>Border Line Hydrides:</u> These hydrides are formed by metals of group IB, IIB and few metals of group IIIA such as indium and thallium e.g CuH_2, ZnH_2 and TlH_2. These hydrides are intermediate between metallic hydrides and covalent hydrides.

2.6 ISOTOPES OF HYDROGEN

The existence of isotopes of elements was first discovered by J.J. Thomson in 1912–1913 while working on the properties of neon. The isotopes may be defined as <u>"Atoms of the same elements having same atomic number but different mass numbers".</u>

It may also be defined as "Atoms that have the same number of protons but different number of neutrons in their respective nuclei."

Nearly all elements found in nature are mixture of several isotopes. Isotopes of hydrogen are given special names while isotopes of other elements are not given any special name.

There are three isotopes of hydrogen, namely:

(i) Protium (ii) Deuterium (iii) Tritium

(i) <u>Protium</u> ($^{1}_{1}H$): It is also known as ordinary hydrogen. It contains one proton in the nucleus and there is one electron in 1s orbital(First shell). It has atomic number 1 and atomic mass number 1. Naturally free occurring hydrogen or in the form of compounds contains about 99.98 percent protium.

(ii) <u>Deuterium</u> (D or $^{2}_{1}H$): It is also called "Heavy hydrogen" although this name is inappropriate because there is another isotope of hydrogen namely "Tritium" which is even heavier than deuterium.

It contains one proton and one neutron in the nucleus and one electron in 1s orbital. It has atomic number 1 and atomic mass number 2. It is present in

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naturally occurring hydrogen to the extent of about 0.0156 percent. i.e in the ratio 1:15000

(iii) **Tritium** (T or $^{3}_{1}H$): It contains 1 proton and 2 neutrons in the nucleus and 1 electron in 1s orbital. It has atomic number 1 and atomic mass number 3. It occurs in very small quantities in the naturally occurring hydrogen to the extent of about 4×10^{-15} percent. It is radio – active form of hydrogen and has half life of 12.5 years.

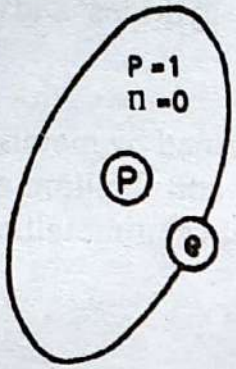

Fig. 2.1
Atomic composition of protium

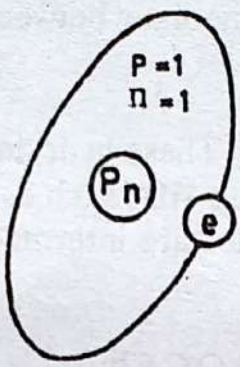

Fig. 2.2
Atomic composition of deuterium

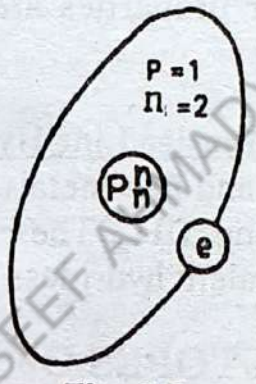

Fig. 2.3
Atomic composition of tritium

ASSIGNMENT

1. With the help of balanced chemical equation, explain what happens when:
   (i) Zinc is put in dilute hydrochloric acid
   (ii) Zinc is put in concentrated sodium hydroxide
   (iii) Hydrogen is passed over hot tungsten oxide.
   (iv) Hydrogen is reacted with carbon monoxide in presence of a catalyst.
2. What do you understand by the term isotope? Define various isotopes of hydrogen.
3. What is water gas and how is it prepared?
4. Are the reactions of ordinary molecular hydrogen slow or rapid? Why? What is atomic hydrogen?
5. Write notes on the following:
   (i) Position of hydrogen in the periodic table
   (ii) Binary compounds of hydrogen

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CHAPTER 3

S – BLOCK ELEMENTS

3.1 INTRODUCTION

The elements of IA and IIA groups of the periodic table are referred to as "s-Block Elements" because they are associated with ns^1 and ns^2 valence shell electronic configuration respectively as shown in table 3.1

Table 3.1 Electronic Configuration of s – block elements

Elements of Group IA	Symbol	Atomic Number	Electronic Configuration	Principal Oxidation State
Lithium	Li	3	$[He]2s^1$	1^+
Sodium	Na	11	$[Ne]3s^1$	1^+
Potassium	K	19	$[Ar]4s^1$	1^+
Rubidium	Rb	37	$[Kr]5s^1$	1^+
Caesium	Cs	55	$[Xe]6s^1$	1^+

Elements of Group IIA	Symbol	Atomic Number	Electronic Configuration	Principal Oxidation State
Beryllium	Be	4	$[He]2s^2$	2^+
Magnesium	Mg	12	$[Ne]3s^2$	2^+
Calcium	Ca	20	$[Ar]4s^2$	2^+
Strontium	Sr	38	$[Kr]5s^2$	2^+
Barium	Ba	56	$[Xe]6s^2$	2^+

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The elements Francium–87 and Radium–88 are radioactive and have been omitted from respective groups. The IA group elements are called alkali metals because they form soluble hydroxides which are alkaline. While IIA group elements are known as alkaline earth metals. Their hydroxides are also alkaline but they are sparingly soluble in water and these metals exists as their oxides in the earth.

The elements of both these groups with the exception of Be which gives many distinctly covalent compounds, form colourless ionic compounds. $KMnO_4$ is pink colour due to the colour of MnO_4^- ions. In these compounds, they exhibit fixed oxidation state of 1^+ and 2^+ respectively. The compounds of IA group and IIA group elements differ markedly in their solubility and thermal stability. These differences in properties arise mainly from differences in ionic size and charge densities.

The lightest elements (Li and Be) of these groups are unique in many ways, because their small sizes result in a high charge densities on the ions which produce strong polarizing effects and high heats of hydration. Lithium and beryllium differ markedly from their heavier congeners. Lithium has many similarities to its diagonal neighbour magnesium in Be group. Be shows resemblance to aluminium which is its diagonal neighbour in boron group.

3.2 GROUP TRENDS IN ALKALI AND ALKALINE EARTH METALS

In this section, the group trends in properties such as electronegativity, ionization potential, heat of hydration, sizes of atoms and ions and other physical properties are discussed.

(i) Electronegativity:– The elements have very small electronegativity values and are generally called electropositive elements. Electronegativity decreases from Li through Cs as one moves down the group. Pauling's electronegativity values for IA and IIA group elements are summarized in table 3.2

Table 3.2 The electronegativity values of s–block elements

Elements of Group IA	Li	Na	K	Rb	Cs
Electronegativity	1.0	0.9	0.8	0.8	0.7
Elements of Group IIA	Be	Mg	Ca	Sr	Ba
Electronegativity	1.5	1.2	1.0	1.0	0.9

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(ii) **Ionization Potential:–** s–Block elements in general have low first ionization enthalpies because the outer's – electron is shielded very effectively from the nucleus by the inner electrons. The first ionization enthalpy of each of the alkali metal is lower than corresponding alkaline earth element in the same period, because the latter has an extra nuclear proton which causes an increase in the electrostatic attractive force between the nucleus and the outermost electrons. Secondly there is a progressive decrease in ionization enthalpies in each series as the outer most electron is less firmly held as the group is descended. These generalizations can be seen by comparing the ionization enthalpy values of s – block elements given in table 3.3

Table 3.3 First and second Ionization enthalpies of s – block elements

Elements of Group IA	First Ionization Enthalpy ΔH–KJ mol^{-1}	Second Ionization Enthalpy ΔH–KJ mol^{-1}
Li	+ 525	+ 7304
Na	+ 500	+ 4563
K	+ 424	+ 3068
Rb	+ 408	+ 2644
Cs	+ 308	+ 2257

Elements of Group IIA	First Ionization Enthalpy ΔH–KJ mol^{-1}	Second Ionization Enthalpy ΔH–KJ mol^{-1}
Be	+ 906	+ 1760
Mg	+ 742	+ 1450
Ca	+ 596	+ 1150
Sr	+ 554	+ 1060
Ba	+ 508	+ 1000

The ionization enthalpies of elements that is the firmness with which outer s – electrons are held, is also related to the sizes of the atoms (See table 3.4). The ionization enthalpies decrease with increasing size of the atom down the group.

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(iii) **Radii Sizes of Atoms and Cations of s – Block Elements:–** The alkali metals have the largest covalent radii of all the elements in their respective periods because they possess the smallest nuclear charge which exerts the weakest electrostatic attractive force on the outer most electrons. The elements of Be family have the next largest atoms because of the same reasons. The covalent radii of these elements are listed in table 3.4.

Table 3.4 Covalent radii of s–block elements

IA Group elements	Li	Na	K	Rb	Cs
Covalent radius (nm)	0.123	0.157	0.203	0.216	0.236
IIA Group elements	Be	Mg	Ca	Sr	Ba
Covalent radius (nm)	0.089	0.089	0.174	0.191	0.198

(iv) **Radii (Sizes) of Cations:–** Since the elements of IA and IIA groups have large sizes. Low ionization enthalpy, low electron affinity values, these elements readily lose their valence electrons to form cations with a positive charge of 1^+ and 2^+ respectively. In the process of forming M^{1+} and M^{2+} ions, alkali and alkaline earth metals acquire the configurations of the respective inert gases in the previous period. e.g.

$$Na \longrightarrow Na^{1+} + e^{-1}$$

$$[Na]\ 3s^1 \qquad [Na]$$

$$\text{and } Mg \longrightarrow Mg^{2+} + 2e^{-1}$$

$$[Ne]\ 3s^2 \qquad [Ne]$$

In Na^+ ions the outer electronic level now being empty, the number of protons in the cation exceeds the number of electrons. The size of the cation is relatively much smaller than the parent atom. The alkaline earth metal cations are even smaller than corresponding alkali metal counterpart in the same period. The sizes of cations are summarized in table 3.5.

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Table 3.5 Ionic sizes of s – block elements.

IA Group ions	Li^+	Na^+	K^+	Rb^+	Cs^+
Cation radius (nm)	0.060	0.095	0.133	0.148	0.169
IIA Group ions	Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Cation radius (nm)	0.031	0.065	0.099	0.113	0.135

(v) **Hydration Energy of Ions:–** The alkali and alkaline earth metals require considerable amount of energy to form $M^{1+}_{(g)}$ and $M^{2+}_{(g)}$ ions respectively (See table 3.3). But when these ions are formed in solution, $M^{1+}_{(g)}$ and $M^{2+}_{(g)}$, the energy required in the formation of gaseous ions is off set by the high negative values for the enthalpies of hydration of the ions listed in the table 3.6.

Table 3.6 Enthalpies of Hydration for s – block elements in K J mol^{-1}.

Li^+	Na^+	K^+	Rb^+	Cs^+
-499	-390	-306	-281	-248
Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
-2425	-1891	-1562	-1414	-1273

The alkaline earth metal ions (M^{2+}) are more strongly hydrated than alkali metal ions (M^{1+}) because M^{2+} ions have a stronger electric field than M^{1+} ions. Hydration enthalpy increases with decreasing size of the ion and it is true both for M^{1+} and M^{2+} ions. Thus Li^{1+} is the most readily hydrated of the alkali metal ions as shown by its high negative value and small ionic size for the enthalpy of hydration. The same is true for the Be^{2+} ions in the IIA group ions. The ease of hydration falls down the group with increasing size of the ion.

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(vi) **Electrode Potentials:–** The s–block elements are powerful reducing agents and this is evident from their high negative aqueous electrode potentials (reduction) e.g. $Li^{1+}_{(aq)}/Li_{(s)}$ couple has exceptionally high negative electrode potential because of its large value for the hydration enthalpy which promotes oxidation of $Li_{(s)}$ to form $Li^{1+}_{(aq)}$ ion. The electrode potential values are used to predict the ease of the formation of $M^{2+}_{(aq)}$ ions from the respective metal atoms. Table 3.7 shows the electrode potential values of s–block elements.

Table 3.7 Electrode potentials (Reduction) of s–block elements

IA Group elements	E^o(V)	IIA Group elements	E^o(V)
Li^+/Li	-3.05	Be^{2+}/Be	-1.85
Na^+/Na	-2.71	Mg^{2+}/Mg	-2.37
K^+/K	-2.93	Ca^{2+}/Ca	-2.87
Rb^+/Rb	-2.93	Sr^{2+}/Sr	-2.89
Cs^+/Cs	-2.92	Ba^{2+}/Ba	-2.90

These values immediately point out that the alkali and alkaline earth metals cannot be used in voltaic cells based on water as the solvent because of their rapid oxidation by that solvent.

(vii) **Densities, Melting and Boiling Points of s–Block Elements:–** The IA and IIA group elements have relatively large volumes and smaller nuclear masses than the other elements in their respective periods, hence they tend to be less dense and have lower melting and boiling points.

Lithium, sodium and potassium of IA group are less denser than water and are very soft owing to a relatively weak interatomic forces in their crystals. All the alkali metals have body centered cubic structure. In comparison the densities of first transition series metals are more than s–block elements. Densities of s–block elements are listed in table 3.8.

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Table 3.8 Densities of s – block elements

IA Group elements	Li	Na	K	Rb	Cs
Density ($g.cm^{-3}$)	0.53	0.67	0.86	1.53	1.90
IIA group elements	Be	Mg	Ca	Sr	Ba
Density ($g.cm^{-3}$)	1.85	1.74	2.54	2.62	3.35

The densities of elements increase as the groups are descended. Alkaline earth metals are, however, denser than corresponding alkali metals in the given period.

The IA group metals have very low melting and boiling points. The general decrease in melting and boiling points is seen as the group is descended.

The IIA group metals are appreciably harder than alkali metals because the presence of divalent cations in their metallic structure produce greater binding forces. Thus they also have larger values for their melting and boiling points as shown in table 3.9

Table 3.9 Melting and boiling points of s – block elements

IA Group elements	Li	Na	K	Rb	Cs
Melting point (°C)	180	98	64	39	29
Boiling point (°C)	1330	890	774	688	690
IIA group elements	Be	Mg	Ca	Sr	Ba
Melting point (°C)	1280	650	850	768	714
Boiling point (°C)	2477	2110	1487	1380	1640

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3.3 CHEMICAL PROPERTIES OF s – BLOCK ELEMENTS

All the s – block elements of the periodic table except Be and Mg are highly reactive elements. The reactivity increases down each group and elements of lithium group are more reactive than corresponding members of beryllium family. Thus metallic caesium (Cs) is the most reactive of all the s – block elements.

The chemistry of s-block elements is dominated by their tendency to loose s–valence electrons and to attain the stable inert gas configuration. This tendency is supported by low ionization enthalpy and high negative electrode potential values for these elements. They are among the most powerful reducing agents and combine directly with most non – metals yielding binary ionic salts.

Reactions with Halogens:–

$2M + X_2 \longrightarrow 2MX$ (M = Li, Na, etc)

$M + X_2 \longrightarrow MX_2$ (M = Be, Mg, etc)

Reactions with Hydrogen: –

$2M + H_2 \longrightarrow 2MH$ (All alkali metals)

$M + H_2 \longrightarrow MH_2$ (M = Ca, Sr, Ba).

Reactions with Nitrogen: –

$6M + N_2 \longrightarrow 2M_3N$ (All alkali metal nitrides)

$3M + N_2 \longrightarrow M_3N_2$ (All alkaline earth metal nitrides except Be).

Reactions with Oxygen: The alkali and alkaline earth metals directly combine with oxygen producing variety of compounds, e.g, normal oxides (O^{2-}), peroxides (O_2^{1-}) and super oxides ($O_2^{-\frac{1}{2}}$). The type of the product depends upon the metal and conditions.

$4Li + O_2 \longrightarrow 2Li_2O$ (Lithium oxide)

$2Na + O_2 \longrightarrow Na_2O_2$ (Sodium peroxide)

$M + O_2 \longrightarrow MO_2$ (Super oxide M = K, Rb, Cs)

$2M + O_2 \longrightarrow 2MO$ (M = Be, Mg, Ca)

$M + O_2 \longrightarrow MO_2$ (Peroxides M = Sr, Ba)

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Reactions with water:– Most of the alkali and alkaline earth metals react with water violently and explosively. Be and Mg form a protective coating of hydrated metal oxide on their surface by the action of water and are protected from extensive corrosion by water. Magnesium reacts more extensively with boiling water.

$$\underset{\text{(Alkali metals)}}{2M + 2H_2O} \longrightarrow 2M^+OH^-_{(aq)} + H_{2(g)}$$

$$\underset{\text{(Alkaline metals)}}{M + 2H_2O} \longrightarrow M^{2+}(OH^-)_{2(aq)} + H_{2(g)}$$

$$Mg + 2H_2O \xrightarrow{\text{Boil}} Mg(OH)_2 + H_{2(g)}$$

3.4 OCCURRENCE AND EXTRACTION OF METALS

(a) **The Alkali Metals:–** The IA group metals are very reactive and do not occur free in nature but are found in variety of compounds which are very stable. The alkali metals sodium and potassium are most abundant. Caesium is rather rare and Francium exists only in trace quantities as the product of radioactive decay. Fr is itself radioactive. The metals can be obtained in the free state by electrolysis of fused salts such as chlorides. The following discussion gives the extraction of sodium as an example.

Manufacture of Sodium by Down's Process:

The electrolysis of molten sodium chloride for industrial production of sodium metal involves the reduction of Na^+ ions at the cathode. This is carried out in Downs cell shown in fig.3.1.

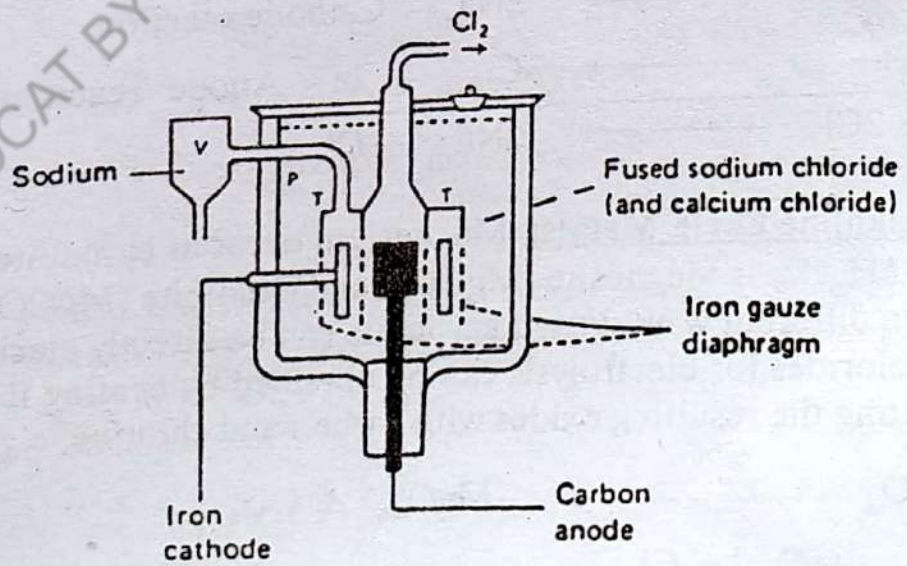

Fig. 3.1
Electrolysis of fused NaCl.

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In this process a mixture of sodium chloride and calcium chloride is electrolyzed in a cylindrical outer iron cell lined with fire–bricks. Calcium chloride is added to sodium chloride to decrease the fusion temperature to about 600°C (The melting point of pure sodium chloride is 801°C). This lowering in melting temperature makes the process feasible. The cell is fitted with a central graphite anode and a surrounding iron cathode. The two electrodes are separated by a cylindrical iron gauze diaphragm which screens the graphite anode from the ring–shaped iron cathode. This keeps away the molten sodium metal which floats to the top of the cathode compartment from gaseous chlorine formed at the anode. The sodium metal collects in the inverted trough (T) placed over the cathode, rises up the pipe (P) and is tapped off through the iron vessel (V).

Some of the calcium ions are also reduced at the cathode to give calcium metal but calcium being much denser than sodium, does not mix with it and can easily be separated. During electrolysis of molten salts Na^+ and Cl^- are free to move to the respective electrodes and the following reactions occur:

Cathode	Anode
Na^+ ions migrate to the cathode and are reduced by the gain of electrons.	Cl^- ions migrate to the anode and are oxidized by the loss of electrons.
$Na^+ + e^- \longrightarrow Na_{(l)}$	$2Cl^- \longrightarrow Cl_{2(g)} + 2e^-$

Over all reaction will be as illustrated below:

$$2Na^+ + 2e^- \longrightarrow 2Na_{(l)} \quad \text{Cathode reaction}$$

$$2Cl^- \longrightarrow Cl_{2(g)} + 2e^- \quad \text{Anode reaction}$$

$$2Na^+ + 2Cl^- \longrightarrow 2Na_{(l)} + Cl_{2(g)}$$

(b)**<u>The Alkaline Earth Metals:</u>** Magnesium occur as carnallite double salt ($MgCl_2.KCl.6H_2O$), as Magnesite ($MgCO_3$) and Dolomite ($MgCO_3 CaCO_3$). It is extracted in different ways. Fused carnallite can be directly electrolyzed or a mixture of chlorides for electrolysis can be obtained by heating the carbonate ores and heating the resulting oxides with carbon and chlorine, e.g.

$$MgCO_3 \longrightarrow MgO_{(s)} + CO_{2(g)}$$

$$MgO_{(s)} + C_{(s)} + Cl_{2(g)} \longrightarrow MgCl_{2(s)} + CO_{(g)}$$

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Alternately, magnesium chloride in sea water can be precipitated as magnesium hydroxide by adding slaked lime.

$$MgCl_{2(aq)} + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaCl_{2(aq)}$$

Magnesium hydroxide is heated to obtain magnesium oxide which is converted to chloride as above.

Calcium metal is obtained by electrolysis of a fused mixture of calcium chloride and calcium fluoride, the latter lowers the melting point.

Barium occurs as Barytés ($BaSO_4$) and Whiterite ($BaCO_3$). The carbonate is converted into the chloride by reaction with hydrochloric acid and barium is obtained by electrolysis of fused chloride.

3.5 INDUSTRIALLY IMPORTANT COMPOUNDS OF S–BLOCK ELEMENTS

(i) <u>Sodium Chloride (NaCl):–</u> Sodium chloride (i.e common salt or table salt) occurs in nature as "Rock salt". Large deposits of rock salt are found in Pakistan at Khewra. It also occurs in sea water to the extent of about 3 percent. The salt is mined as solid or pumped from under ground deposit as a saturated solution known as "Brine" by flooding underground salt beds with water by boring. Most of the brine is used in industry for the production of sodium carbonate and sodium hydroxide.

In tropical regions, sodium chloride is obtained by the solar evaporation of sea–water, the impurities such as calcium and magnesium are removed by treating brine with sodium carbonate and sodium hydroxide to precipitate these metals.

$$Ca^{2+}Cl^{-}_{2(aq)} + Na^{+}_{2}CO^{2-}_{3(aq)} \longrightarrow CaCO_{3(s)} + 2Na^{+}Cl^{-}$$

$$Mg^{2+}Cl^{-}_{2(aq)} + 2Na^{+}OH^{-}_{(aq)} \longrightarrow Mg(OH)_2 + 2Na^{+}Cl^{-}_{(aq)}$$

Soluble barium chloride is used to precipitate sulphate. This purified product is suitable for industrial use but requires further purification for its use as table salt.

Sodium chloride is an essential part of our daily diet. It is also used as food preservative. In chemical industry, it is used in the manufacture of sodium metal, chlorine gas, sodium hydroxide, sodium carbonate, sodium hypochlorite (I)

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sodium chlorate (V), etc. The other chemical uses of sodium chloride are in glazing earthen ware, regeneration of water softeners and in salting out of soap.

(ii) Sodium Carbonate (Na_2CO_3):– Sodium carbonate is manufactured by Ammonia–solvay process. The raw materials used are sodium chloride, lime stone and ammonia gas. The process involves three important steps and its flow–sheet diagram is shown in Fig 3.2.

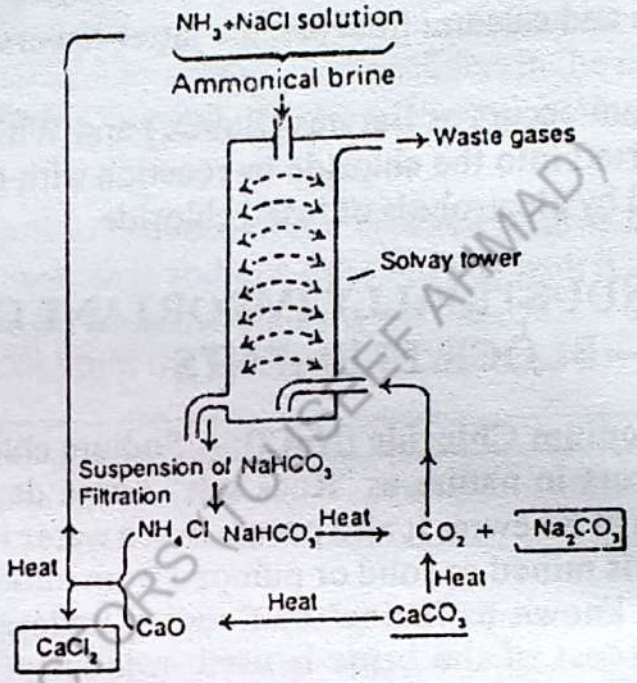

Fig. 3.2
Ammonia-Solvay process

Step I – Ammoniation of Brine: In this step a saturated solution of sodium chloride (about 28 percent by mass) or brine is allowed to flow down an ammoniating tower. The tower consists of mushroom–shaped baffles at short intervals which control the flow of brine and ensures proper saturation with ammonia passing up the tower.

Step II – Carbonation of Ammoniated Brine: In this step ammoniated brine is allowed to trickle down a carbonating tower, called SOLVAY TOWER fitted with baffle–plates and meets an upward current of carbon dioxide gas obtained by heating lime stone. The baffle–plates check the flow of liquid and break up the carbon dioxide into small bubbles to ensure good conditions for the reaction. The carbon dioxide and ammonia react to give NH_4^+ and HCO_3^- ions.

$$2NH_{3(g)} + CO_{2(g)} + H_2O_{(l)} \longrightarrow 2NH^+_{4(aq)} + CO^{2-}_{3(aq)}$$

$$CO^{2-}_{3(aq)} + CO_{2(g)} + H_2O_{(l)} \longrightarrow 2HCO^-_{3(aq)}$$

Hydrogen carbonate ion
(Bi carbonate ion)

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i.e.

$$\text{I} \cdot 2NH_3 + CO_2 + H_2O \longrightarrow (NH_4)_2^{+1} CO^{-2}_{3(aq)}$$

$$\text{II} \cdot (NH_4)_2^{+1}CO^{-2}_{3(aq)} + CO_{2(g)} + H_2O_{(l)} \longrightarrow 2NH_4^{+1} HCO^{-1}_{3(aq)}$$

The NH_4^+ and HCO_3^- ions then react with Na^+ and Cl^- ions of brine to precipitate less soluble sodium hydrogen carbonate leaving ions of ammonium and chloride (NH_4^+ and Cl^-) in solution.

$$Na^{+1}Cl^{-1}_{(aq)} + NH_4^{+1}HCO^{-1}_{3(aq)} \longrightarrow NaHCO_{3(s)} + NH_4^+Cl^-_{(aq)}$$

Sodium bicarbonate

Since the overall effect of these reactions is exothermic, the temperature of the material rises. This tends to increase the solubility of sodium hydrogen carbonate and thereby inhibits its precipitation. To counter this adverse effect the lower part of the tower is cooled. The precipitated product ($NaHCO_3$) is removed by vacuum filtration and washed to free of ammonium salts.

<u>Step III – Conversion to Sodium Carbonate:–</u> The sodium hydrogen carbonate is heated to give anhydrous sodium carbonate (Soda ash).

$$2NaHCO_{3(s)} \longrightarrow Na_2CO_{3(s)} + H_2O_{(l)} + CO_{2(g)}$$

The CO_2 liberated by this reaction is recycled to the carbonating tower. Soda ash is re–crystallized from hot aqueous solution and yields sodium carbonate deca hydrate ($Na_2CO_3.10H_2O$) which is known as washing soda.

<u>Sources of Materials:–</u>

(i) Brine is obtained from natural sources of common salt.

(ii) Carbon dioxide is obtained by heating limestone; large deposits of which are found in nature.

$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$$

lime stone — Quick lime

(iii) Ammonia is recovered from the solution of ammonium chloride left after the removal of $NaHCO_3$ by vacuum filtration. This is done by steam–heating the solution with quick lime-obtained above.

$$CaO_{(s)} + H_2O_{(l)} \longrightarrow Ca(OH)_{2(s)}$$

$$2NH_4^+Cl^-_{(aq)} + Ca(OH)_{2(s)} \longrightarrow CaCl_{2(aq)} + 2H_2O_{(l)} + 2NH_{3(g)}$$

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Uses of Sodium Carbonate:– Sodium carbonate has extensive uses: e.g.

(1) In the manufacture of glass and water glass. water glass is made by fusing sodium carbonate with sand.

$$Na_2CO_3 + \underset{\text{sand or silica}}{SiO_2} \longrightarrow \underset{\text{water glass}}{Na_2SiO_3} + CO_{2(g)}$$

The ordinary soda glass is manufactured by fusing a mixture of sand, calcium carbonate and anhydrous sodium carbonate.

(2) Washing soda is used as water–softener as it precipitates calcium ions from water as carbonate.

$$Ca^{2+}_{(aq)} + Na_2CO_{3(aq)} \longrightarrow CaCO_{3(s)} + 2Na^{+}_{(aq)}$$

(3) Sodium carbonate is used in the making of soap, paper, detergents and chemicals such as NaOH.

(iii) **Sodium Hydrogen Carbonate ($NaHCO_3$):** Sodium hydrogen carbonate commonly known as baking soda can be obtained as precipitate by ammonia–solvay process but it is all converted to sodium carbonate. However, sodium hydrogen carbonate is commercially produced by treating saturated sodium carbonate solution with carbon dioxide:

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$$

Uses:– Sodium hydrogen carbonate is used as baking powder, in medicines and as an antiacid.

(iv) **Sodium Hydroxide or caustic soda (NaOH):–** Sodium hydroxide is one of the most important chemicals of industrial use. This must be handled carefully because it is caustic to touch and causes painful burns. It is commonly known as caustic soda.

Sodium hydroxide is now manufactured by an electrolytic process, known as Castner – Kellner's process.

Castner–Kellner's process :- This process is used for the preparation of sodium hydroxide.

Construction and working of Castner–Kellner's cell:- This cell is diagrammetically shown in figure 3.3. The electrolyte is 25% w/w solution of sodium chloride containing Na^+ and Cl^- ions as:

$$2NaCl \xrightarrow{\text{water}} 2Na^+ + 2Cl^-.$$

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The anode consists of a number of titanium plates where chlorine is liberated.

$$2C\bar{l} \longrightarrow Cl_2 + 2\bar{e} \quad \text{(Oxidation)}$$

The cathode is a steam of flowing mercury. In ordinary process of electrolysis of acqueous solution of sodium chloride, H_2 and Cl_2 are liberated at cathode and anode respectively as H^+ ions are more easily discharged as compared to $N\overset{+}{a}$ ions.

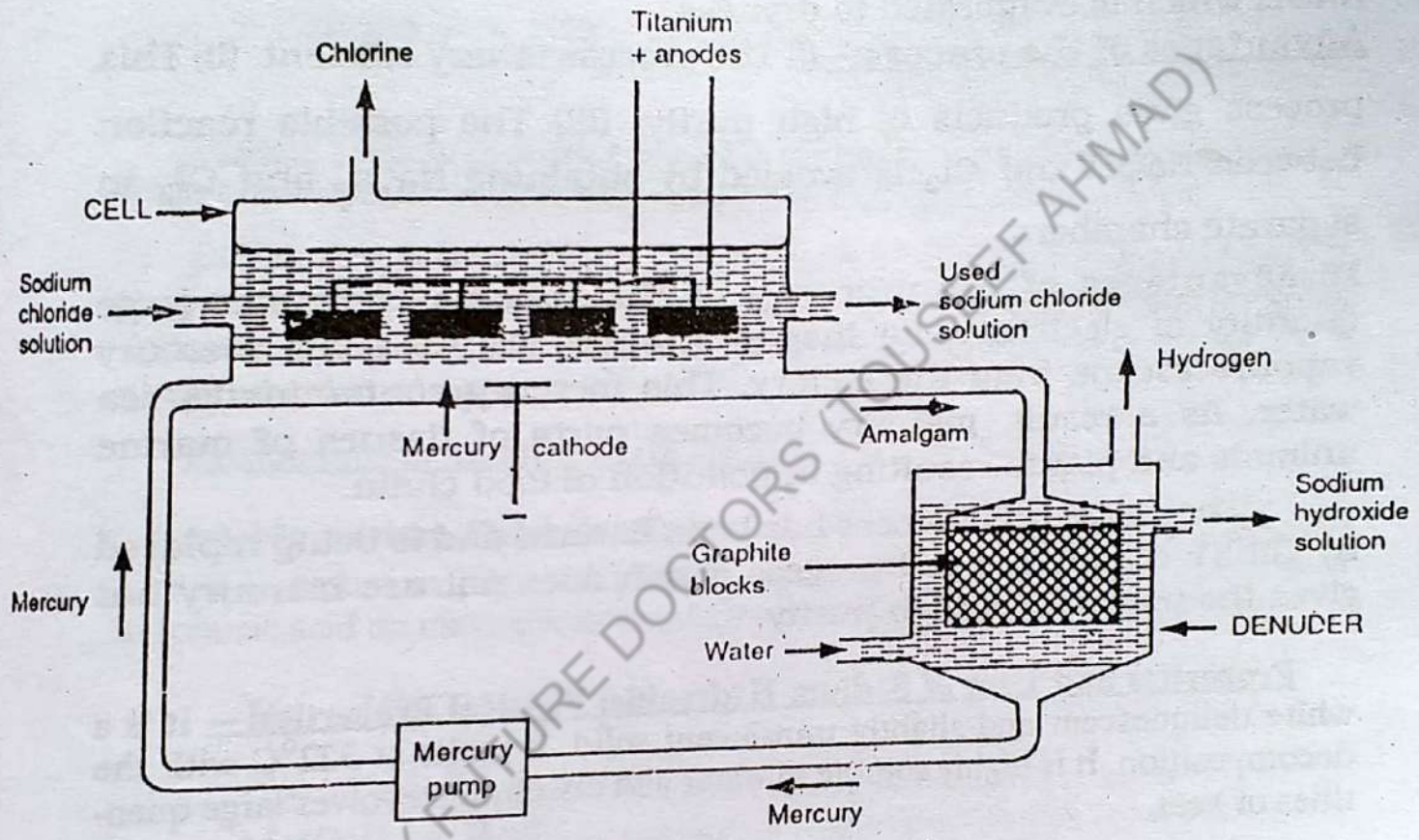

Fig: 3.3 Electrolytic manufacture of sodium hydroxide

In castner – Kellner's process, H^+ ions are not easily discharged due to high voltage of H^+ ions, on the contrary $N\overset{+}{a}$ ions are easily discharged over mercury surface. The sodium, thus liberated dissolves in mercury forming an amalgam.

$$2N\overset{+}{a} + 2\bar{e} \longrightarrow 2Na \quad \text{(Reduction)}$$

$$Na + Hg \longrightarrow Na/Hg \quad \text{(Amalgam)}$$

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The mercury containing dissolved sodium is sent to another chamber called denuder where sodium reacts with water forming sodium hydroxide and hydrogen.

$$2Na / Hg + 2H_2O \longrightarrow 2NaOH + H_2 + Hg_{(l)}$$

The mercury is recycled to dissolve more of sodium. Denuder is packed with graphite blocks as hydrogen is easily liberated over graphite surface.

The solution which flows out from denuder, is a solution of NaOH which is evaporated to dryness.

Advantages of the process:- (i) The process is very efficient. (ii) This process gives products of high purity. (iii) The possible reaction between NaOH and Cl_2 is avoided by obtaining NaOH and Cl_2 in separate chambers.

Disadvantages of the process:- (i) This process consumes large quantity of electricity. (ii) Inspite of strict control some mercury vapours escape from the factory. This mercury contaminates sea water. As a result, mercury becomes parts of tissues of marine animals and plants resulting in pollution of food chain.

The use of this process has been banned and is being replaced by Gibb's diaphragm cell process which does not use mercury but gives the products of high purity.

Properties and Uses of Sodium Hydroxide: Physical Properties:– It is a white deliquescent and slightly translucent solid. It melts at 322°C with the decomposition. It is highly soluble in water and dissolution evolves large quantities of heat.

Chemical Properties of Sodium Hydroxide:

(i) Sodium hydroxide is a strong alkali and ionizes fully as Na^+ and OH^- ions in solution. Its characteristic alkaline properties include its action on indicators (Litmus turns blue) and neutralization reactions, e.g.,

$$Na^+OH^-_{(aq)} + H^+Cl^-_{(aq)} \longrightarrow Na^+Cl^-_{(aq)} + H_2O_{(l)}$$

(ii) Sodium hydroxide reacts with ammonium salts on warming and liberates ammonia:

$$NaOH + NH_4Cl \longrightarrow NH_4^{+1}OH^{-1} + NaCl$$

$$NH^{+1}_{4\,(aq)}\ OH^{-1}_{(aq)} \longrightarrow NH_{3\,(g)} + H_2O_{(l)}$$

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(iii) It precipitates in soluble metal hydroxides from their salts:

$$Fe^{3+}_{(aq)} + 3OH^-_{(aq)} \longrightarrow Fe(OH)_{3\,(s)}$$

However, when precipitated hydroxides are amphoteric, they redissolve in excess of sodium hydroxide forming complex anions, e.g.,

$$Zn^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Zn(OH)_{2\,(s)}$$

$$Zn(OH)_{2\,(s)} + 2OH^-_{(aq)} \longrightarrow [Zn(OH)_4]^{2-}_{(aq)}$$

Tetrahydroxo – Zincate (II) ion

Uses:– Sodium hydroxide is used in the preparation of variety of chemicals such as phosphine, sodium chlorate (I) and sodium chlorate (V), etc.

In industry, it is used in the manufacture of soap, purification of bauxite, paper making and the manufacture of petroleum products. In textile industry, it is used in bleaching and dyeing process in mercerizing cotton and in the production of rayon.

Compounds of Alkaline Earth Metals:

(v) Magnesium Sulphate (Epsom = $MgSO_4$):– Magnesium – sulphate occurs in nature as Kieserite ($MgSO_4.H_2O$). It is prepared by the reaction of sulphuric acid on magnesium metal, its oxide, hydroxide or carbonate e.g.

$$Mg + H_2SO_4 \longrightarrow MgSO_4 + H_2$$

$$MgO + H_2SO_4 \longrightarrow MgSO_4 + H_2O$$

$$Mg(OH)_2 + H_2SO_4 \longrightarrow MgSO_4 + 2H_2O$$

$$MgCO_3 + H_2SO_4 \longrightarrow MgSO_4 + H_2O + CO_2$$

The hepta hydrate ($MgSO_4.7H_2O$) is the best known form of magnesium sulphate and is commonly known as "Epsom salt". It is used as a mild purgative. It is soluble in water. When heated crystalline Epsom loses water forming anhydrous magnesium sulphate.

(vi) Calcium Sulphate ($CaSO_4$): Calcium sulphate occurs in nature as anhydride. It also occurs as dihydrate ($CaSO_4.2H_2O$). Calcium sulphate is sparingly soluble solid and produces permanent hardness in water.

When gypsum ($CaSO_4.2H_2O$) is heated to about 100°C, it loses some water of crystallization and is converted to calcium sulphate hemihydrate

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($CaSO_4 \frac{1}{2} H_2O$). This product is commonly known as plaster of paris. The reaction is:

$$\underset{\text{Gypsum}}{2CaSO_4.2H_2O_{(s)}} \xrightarrow{100^oC} \underset{\text{Plaster of paris}}{(CaSO_4)_2.H_2O} + 3H_2O$$

At higher temperatures gypsum loses all the water of crystallization to give anhydrous calcium sulphate.

Anhydrous calcium sulphate and gypsum being the sources of sulphur dioxide are used in the manufacture of sulphuric acid. Gypsum is also used in the making of cement.

$CaSO_4 \cdot \frac{1}{2} H_2O$ when mixed with water, sets in about 5 minutes to a hard mass. This setting takesplace with expansion. This property permits to use in the preparation of moulds used in surgery and castings.

(vii) Bleaching Powder:- Professor Odling suggested the formula of bleaching powder as $Ca(OCl)Cl$ or $CaOCl_2$ on the basis of available percentage of chlorine.

It is prepared on a large scale by Hasen Clever process. The plant consists of a number of iron cylinders in which chlorine is brought in contact with slaked lime $[Ca(OH)_2]$. It is formed according to the reaction.

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

The bleaching powder so formed is collected.

It is a white amorphous powder with smell of chlorine.

Reactions:- (i) Bleaching powder is generally used with reasonable quantity of water. In aqueous solution, it liberates chlorine.

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

(ii) When it reacts with acids, chlorine is set free.

$$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$$

(iii) It liberates HOCl on reaction with atmospheric CO_2 and moisture.

$$2CaOCl_2 + CO_2 + H_2O \longrightarrow CaCO_3 + CaCl_2 + 2HOCl$$

Uses:- (i) It is used for sterlization of drinking water. (ii) It is used for bleaching of cotton, linen and paper pulp. (iii) It is used for the preparation of Cl_2 gas and chloroform ($CHCl_3$).

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ASSIGNMENT

1. Explain the following:

(i) Lithium and beryllium markedly differ from other members of their respective groups.

(ii) The first ionization enthalpies of alkali and alkaline earth metals are generally low. However, ionization enthalpies of IIA group elements are higher than IA group elements.

(iii) Ionization potential decreases from Li to Cs.

(iv) Alkali metals have largest covalent radii.

(v) Alkali and alkaline earth metals easily form cations.

(vi) Na^+ ions are smaller than sodium atoms.

(vii) Alkaline earth metal ions are more strongly hydrated than alkali metal ions.

(viii) Li^+ ions are more readily hydrated than K^+ ions.

(ix) Alkali metals are powerful reducing agents.

(x) Li^+/Li couple has exceptionally high negative electrode potential.

(xi) Alkali metals cannot be used in voltaic cells.

(xii) Alkaline earth metals are harder than alkali metals.

(xiii) In manufacture of sodium, the two electrodes are separated by iron–gauze diaphragm.

(xiv) Alkali metals are highly reactive.

(xv) How the given reaction is avoided during the preparation of sodium hydroxide.

$$6OH^-_{(aq)} + Cl_{2(g)} \longrightarrow Cl^-_{(aq)} + ClO^-_{3(aq)} + 3H_2O_{(l)}$$

(xvi) Na^+ ions are discharged at the cathode in preference to H^+ in the manufacture of NaOH.

(xvii) Zinc hydroxide is soluble in excess of sodium hydroxide solution.

(xviii) Plaster of Paris is used in making plaster coats and moulds.

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2. Describe the extraction of sodium from common salt. How and under what conditions sodium reacts with: (a) Water, (b) Nitrogen, (c) Chlorine, (d) Hydrogen and (e) Oxygen.

3. Describe the physiochemical principles involved in the manufacture of sodium carbonate by Ammonia – solvay process. How sodium carbonate reacts with:

(i) Carbon dioxide, (ii) Silica, (iii) Calcium Hydroxide.

4. How sodium hydroxide is manufactured by electrolysis of sodium chloride? Describe uses of sodium hydroxide.

5. What happens when sodium hydroxide reacts with:

(i) Ferric chloride, (ii) Carbon dioxide, (iii) Sulphuric acid, (iv) Zinc hydroxide,(v) Chlorine gas and (vi) Ammonium chloride

6. Write brief account and uses of the following: –

(i) Sodium chloride, (ii) Calcium sulphate, (iii) Bleaching powder (iv) Magnesium sulphate. (v) Sodium hydrogen carbonate.

7. Compare the properties of alkali and alkaline earth metals with respect to their first ionization enthalpies, electrode potentials, melting and boiling points and hydration enthalpies.

8. Alkali and alkaline earth metals form only 1^+ and 2^+ ions respectively. Explain.

9. Discuss the variations in electronegativity values and sizes of s – block elements.

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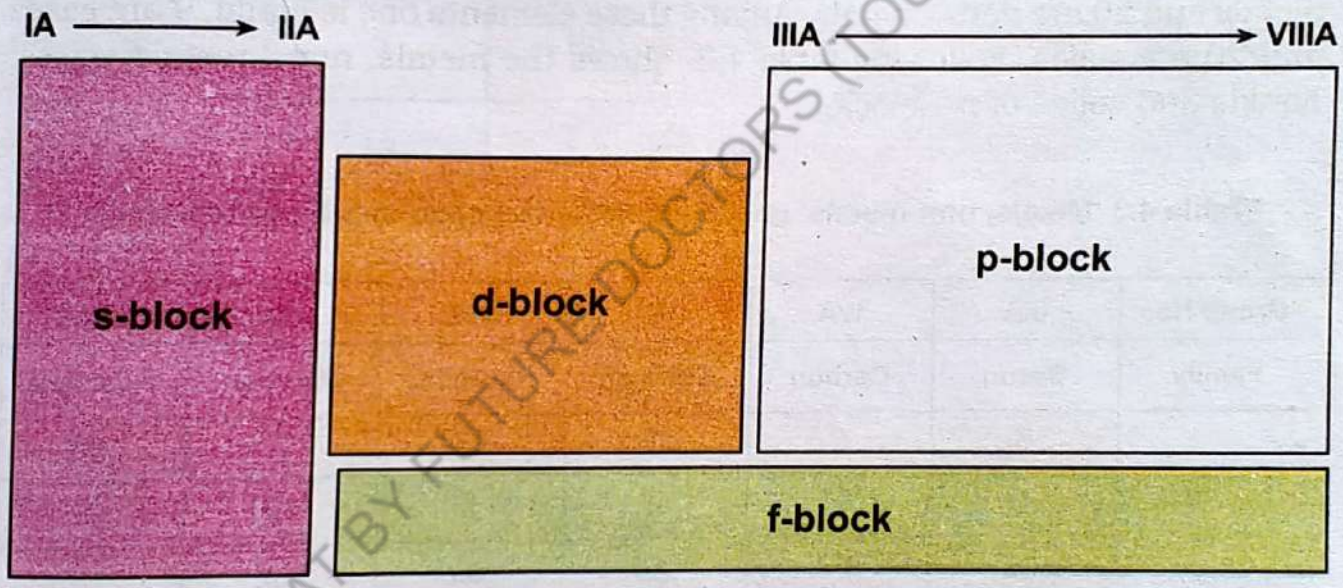
CHAPTER 4

p – BLOCK ELEMENTS

4.1 INTRODUCTION

The periodic chart has been divided into s, p, d and f blocks on the basis of electronic configuration. The table 4.1 shows the division of s, p, d and f-block elements:

Table 4.1 Division of s, p, d and f – Block elements



s – Block consists of the elements of IA and IIA groups, which has ns^1 and ns^2 valence configuration. p–Block elements occur in the groups IIIA to VIIIA, they have atoms in which the outer most p–orbital consists of one to six electrons (np^1 to np^6). The general valence configuration of p–block elements ns^2, np^1 to ns^2, np^6. As it is clear from the configuration that the total number of electrons in the outer most shell of p–block, rises from three (3) for IIIA to eight (8) for VIIIA group (except He). Thus the elements in which the filling of electrons occur in p–orbitals, are called as p–block elements.

For example: – $6C^{12} = 1s^2, 2s^2, 2p^2$ is the p – block element.

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It may be pointed out that the position of elements in periodic table depends upon the total number of electrons in their valence shells. The group number corresponds to the total number of electrons in their valence shells, as shown in table 4.2.

Table 4.2 Valence shell electrons

Group No.	Element	Configuration	Total no: of valence electrons
IIIA	Boron	$1s^2, 2s^2, 2p^1$	3
IVA	Carbon	$1s^2, 2s^2, 2p^2$	4
VA	Nitrogen	$1s^2, 2s^2, 2p^3$	5
VIA	Oxygen	$1s^2, 2s^2, 2p^4$	6
VIIA	Fluorine	$1s^2, 2s^2, 2p^5$	7

There are 30 elements in six sub–groups of p–block. Out of which 10 are metals and 20 are non–metals. Among these elements one is liquid, 9 are gases and 20 are solids. Following table 4.3, shows the metals, non–metals, gases, liquids and solids of p–block.

Table 4.3 Metals, non-metals, gases, liquids and solids in p-block elements.

Group No.	IIIA	IVA	VA	VIA	VIIA	VIIIA
Family	Boron	Carbon	Nitrogen	Oxygen	Halogen	Noblegas
	B	C	N	O	F	Ne
	Al	Si	P	S	Cl	Ar
	Ga	Ge	As	Se	Br	Kr
	In	Sn	Sb	Te	I	Xe
	Tl	Pb	Bi	Po	At	Rn

= Non-metals

= Metals

= Gases

= Liquid

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Group – Trends:– The properties of elements depend upon the number and arrangements of electrons in valence shells. Atoms with the same number of valence electrons would be expected to be chemically similar. Though the elements of the same group are chemically similar but show gradual change in their physical properties, due to different number of total electrons in inner shells. For example, in the elements of IIIA group (boron family), the number of valence electrons are these (ns^2, np^1) but number of inner electrons are different, this difference is given in table 4.4.

Table 4.4 Difference in inner electrons

Element	At.No.	Inner electrons	Valence electrons
B	5	$1s^2$	$2s^2$, $2p^1$
Al	13	$1s^2$, $2s^2$, $2p^6$	$3s^2$, $3p^1$
Ga	31	$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$	$4s^2$, $4p^1$

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It means B, A1 and Ga possess 2, 10 and 28 inner electrons respectively. Due to this reason, we do not only observe in a group a simple repetition of properties but also more or less marked and regular variations. The regular variations in the properties are known as Group – trends. For example, the atomic size, ionic size, metallic character increase from top to bottom in each group; where as electronegativity and ionization potential decrease down the group. The group trends in physical properties are discussed below:

(i) Atomic Radii: The atomic radii increase down the group in all "p – block" elements. In each group, with the rise of atomic numbers, the number of energy levels increase. Due to the increase in the number of energy levels, the atomic radii increase down each group of "p – block" elements. It means that the size of first element in each group is smallest and last element is largest. The trend in atomic radii is shown in table 4.5

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Table 4.5 Trend in atomic radii in p – block elements in Angstrom unit (A^o)

IIIA	IVA	VA	VIA	VIIA	VIIIA
B 0.80	C 0.77	N 0.74	O 0.74	F 0.72	Ne 1.60
Al 1.25	Si 1.17	P 1.10	S 1.04	Cl 0.99	A 1.91
Ga 1.25	Ge 1.22	As 1.21	Se 1.17	Br 1.14	Kr 2.0
In 1.50	Sn 1.40	Sb 1.41	Te 1.37	I 1.33	Xe 2.2
Tl 1.55	Pb 1.46	Bi 1.52	Po 1.52	At –	Rn –

(ii) Ionic Radii:– Ions are formed by gain or loss of electrons. p – Block elements include metals and non–metals, so they form positive as well as negative ions. It may be pointed out that positive ion is smaller than its parent atom and negative ion is bigger than its parent atom.

Ionic radii increase from top to bottom in each group of p – block elements due to increasing atomic – radii. The values of ionic radii are given in table 4.6.

Table 4.6 Trend in Ionic radii in p – block elements in Angstrom unit (A^o)

IIIA E^{+3}	IVA E^{+4}	VA E^{-3}	VIA E^{-2}	VIIA (E^-)
B 0.20	C 0.15	N 1.71	O 1.40	F 1.36
Al 0.50	Si 0.41	P 2.12	S 1.84	Cl 1.81
Ga 0.62	Ge 0.53	As 2.22	Se 1.98	Br 1.95
In 0.81	Sn 0.71	Sb 2.45	Te 2.21	I 2.16
Tl 0.95	Pb 0.84	Bi	Po	At

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(iii) Electronegativity:- The relative tendency of an atom to attract the shared pair of electrons to itself is known as electronegativity. It decreases down the group in all p – block elements (except – IIIA). The electro negativity is inversely proportional to the atomic size. The atomic size increases in each group from top to bottom, hence electronegativity decreases down each group in p – block elements. It means the electronegativity of first element of each group is highest and last element is lowest. The trend in electronegativity is shown in Table 4.7.

Table 4.7 Electronegativity trend in p – block elements (No unit)

IIIA	IVA	VA	VIA	VIIA	VIIIA
B 2.0	C 2.5	N 3.1	O 3.5	F 4.0	Ne –
Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar –
Ga 1.6	Ge 1.7	As 2.0	Se 2.4	Br 2.8	Kr –
In 1.7	Sn 1.7	Sb 1.8	Te 2.1	I 2.5	Xe –
Tl 1.8	Pb 1.7	Bi 1.7	Po 2.0	At 2.2	Rn –

(iv) Ionization Potential:- The amount of energy required to remove the outer most electron from a gaseous atom, is called as ionization potential. It decreases down the group in all p – block elements – (except IIIA) where there is no regular change.

The ionization potential depends upon atomic size and shielding effect of inner energy levels. It is inversely proportional to the atomic size as well as shielding effect i.e. smaller the size and lower is the shielding effect, the greater will be the attraction and hence greater will be the ionization potential.

The atomic size and shielding effect increase down the group, hence ionization potential decreases down the group. The trend in ionization potential is shown in table 4.8.

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Table 4.8 Ionization potential trend in p – block elements (Electron Volt) (i.e. v = 95 KJ) approximately.

IIIA	IVA	VA	VIA	VIIA	VIIIA
B 8.29	C 11.26	N 14.54	O 13.61	F 17.42	Ne 21.55
Al 5.98	Si 8.14	P 11.0	S 10.35	Cl 13.01	Ar 15.75
Ga 6.0	Ge 6.13	As 10.0	Se 9.75	Br 11.84	Kr 13.99
In 5.78	Sn 7.32	Sb 8.64	Te 9.01	I 10.44	Xe 12.12
Tl 6.1	Pb 7.41	Bi 8.0	Po 8.43	At –	Rn 10.5

(v) Electropositivity or Metallic Character:– The tendency of an atom to give out electrons is known as electropositivity. This tendency decides the metallic character, greater the tendency to give out electrons, more is the metallic character.

The metallic character increases down the group in all "p – block" elements. Metallic character depends upon ionization potential and electron population of outer most shells. Metallic character is inversely proportional to both these factors. The ionization potential and electron population of outer most shells decrease down the group, hence metallic character as well as electropositivity increases from top to bottom.

The explanation of metallic character on the basis of electron population of outer most shells is explained as under:

The maximum capacity of electron accommodation of boron in its outer most shell is eight electrons and that of aluminium is eighteen electrons.

e.g. B = 5 = $1s^2, 2s^2, 2p^1$ (outer most shell is L. The ratio is 3:8)

Al = 13 = $1s^2, 2s^2, 2p^6, 3s^2, 3p^1$ (outer most shell is M. The ratio is 3:18)

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It means the electron population of aluminium is less than boron. Due to less electron population, the number of neighbouring atoms in the lattice increases, that is why metallic character of aluminium is greater than boron.

(vi) Melting and Boiling Points:- Trend in melting and boiling points in the groups of p – block elements is not similar. For example, in IIIA group, there is no regular trend, in IVA group, there is decrease, where as from VA to VIIIA melting and boiling points increase down the group. This is because, the melting and boiling points depend upon various factors, such as:

(a) Inter atomic forces (b) Inter molecular forces (c) Structure or state

Melting and boiling points decrease in IVA group because the strength of inter atomic bond decreases down the group. The increase in melting and boiling points from VA to VIIA may be explained on the basis of structure and inter molecular forces. In these groups the structure gradually changes from discrete state to aggregated state (gas to solid). As a result of this change, the inter molecular forces increase and melting and boiling points increase down the groups. In VIIIA group, the increase in melting and boiling points is due to increase in inter molecular forces of attraction (all are gases). The trends in melting and boiling points are shown in table 4.9.

Table 4.9 Trend in Melting and Boiling Points in p – block Elements.

Group No.	IIIA	IVA	VA	VIA	VIIA	VIIIA
Element m.p°C b.p°C	B 2300 2550	C – 3840	N -210 -195.8	O -219 -183	F -223 -188	Ne – -246
Element m.p°C b.p°C	Al 658 1800	Si 1410 2680	P 44.1 280	S 119 444.6	Cl -102 -35	Ar – -186
Element m.p°C b.p°C	Ga 29.75 1700	Ge 937 2830	As 814 633	Se 217.4 685	Br -7.0 59	Kr – -153
Element m.p°C b.p°C	In 155 1450	Sn 232 2687	Sb 630 1325	Te 450 1390	I 114 184	Xe – -107
Element m.p°C b.p°C	Tl 303 1650	Pb 327 1751	Bi 271 1560	Po – –	At – –	Rn – -65

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4.2 BORIC ACID (H_3BO_3)

Preparation:-

(i) From Borax:- Boric acid is prepared by the action of **sulphuric acid** on hot solution of borax. The resulting solution on cooling **gives crystals of** boric acid.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow 4H_3BO_3 + Na_2SO_4$$

(ii) From Boron Nitride:- Boric acid is also obtained by the **action of** super heated water on boron nitride.

$$BN + 3H_2O \longrightarrow H_3BO_3 + NH_3$$

Properties:- It forms soft, silky and white crystals. It is greasy in feel due to the gliding of sheets over one another. It is sparingly soluble in cold water but readily soluble in hot water. It is very weak acid and exclusively monobasic acid, because it is beleived that it does not only act as a proton donor but also a lewis acid i.e. acceptor of OH^- ion.

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^{1+}$$

The aqueous solution of acid acts as a mild antiseptic and it is also employed as an eye – wash.

Boric acid on heating forms different products. At 100°C, it loses water molecule and forms metaboric acid (HBO_2). At 140°C meta–boric acid changes to pyroboric acid ($H_2B_4O_7$) and on further heating it forms boric oxide.

i) $H_3BO_3 \xrightarrow[-H_2O]{100^oC} HBO_2$ Metaboric acid

ii) $4HBO_2 \xrightarrow[-H_2O]{140^oC} H_2B_4O_7$ (Pyroboric acid)

iii) $H_2B_4O_7 \xrightarrow[-H_2O]{abov240^oC} 2B_2O_3$

Structure:- Boric acid forms white needle like crystals in which $B(OH)_3$ units are linked together by hydrogen bonding to form infinite layers. These layers lie 3.18°A apart from one another and held together by weak Vender Waal's forces of attraction, due to this reason, they glide easily over one another and hence it is soft.

Borax = $Na_2B_4O_7.10H_2O$ (Suhaga):

Borax is also known as sodium tetraborate decahydrate or tincal.

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Preparation:– (i)Borax is prepared by the action of NaOH or Na_2CO_3 on orthoboric acid.

$$4H_3BO_3 + 2NaOH \longrightarrow Na_2B_4O_7 + 7H_2O$$

$$4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2$$

(ii) Borax is obtained from colemanite ($Ca_2B_6O_{11}.5H_2O$) when boiled with concentrated solution of Na_2CO_3.

$$Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2$$

Properties of Borax:– It is a white crystalline solid. It is soluble in water and forms an alkaline solution due to hydrolysis.

$$Na_2B_4O_7 + 7H_2O \longrightarrow 2NaOH + 4H_3BO_3$$

It is used as flux in soldering and welding. It is used in tiles and pottery glazes and in manufacture of optical and hard glass (Pyrex and jena).

4.3 METALLURGY OF METALS

Metallurgy of Aluminium: Occurrence: Aluminium does not occur free in nature, but it is widely distributed in combined state. It comes third in abundance after oxygen and silicon in nature. It forms about 7.3% of the earth's crust. Its important ores are given below:–

(a) **Silicates:–**
- (i) Kaolin = $Al_2O_3.2SiO_2.2H_2O$
- (ii) Potash felspar = $K_2O.Al_2O_3.6SiO_2$
- (iii) Potash–mica = $K_2O.3Al_2O_3.6SiO_2.2H_2O$

(b) **Fluoride:–**
- (i) Cryolite = Na_3AlF_6

(c) **Sulphate:–**
- (i) Alunite = $K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$

(d) **Oxides:–**
- (i) Bauxite = $Al_2O_3.nH_2O$
- (ii) Gibbisite = $Al_2O_3.3H_2O$
- (iii) Diaspore = $Al_2O_3.H_2O$
- (iv) Coruhdum = Al_2O_3

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Bauxite: It occurs near village Khilla of Muzaffarabad; Village Gian and Salhan of Tehsil Kotli ; Margilla hills of Rawalpindi ; surge of Attock district as well as in Tharparkar and Dadu districts.

Corundum:– The varieties of corundum occur in Pakistan some of which are described below:

(a) Emerald (green = Panna):– It occurs in Mangora of Swat state and Mohmand agency as well as in Dir State.

(b) Ruby (red = chuni):– It occurs in Hunza, higher regions of Gilgit and Azad Kashmir.

(c) Sapphire (blue = Neelum):– It occurs near Mochel in Pador district of Kashmir.

(d) Topaz (yellow = Pukhraj):– It occurs at Gobar–o–Bach in Lutkho valley of Chitral.

Extraction of Aluminium

Aluminium is extracted from its ore bauxite ($Al_2O_3.nH_2O$). The extraction involves two steps:

(a) Purification of bauxite to alumina.

(b) Electrolysis of Pure alumina.

Purification of Bauxite:–

Bauxite usually contains oxides of iron (Fe_2O_3) and silica (SiO_2) as chief impurities. These impurities must be removed in order to get aluminium of good quality because these impurities make the metal brittle and liable to corrosion. The bauxite may be purified by any one of the following methods depending upon the nature of impurities present in it:

(i) **Hall's method:–** This method is used for the purification of bauxite containing Fe_2O_3 and silica (SiO_2) as impurities. When finely divided bauxite is fused with sodium carbonate (Na_2CO_3), it dissolves to form sodium – aluminate, while the impurities Fe_2O_3 and SiO_2 are left unaffected.

$$Al_2O_3.nH_2O + Na_2CO_3 \longrightarrow 2NaAlO_2 + CO_2 + nH_2O$$

The fused mass is extracted with water leaving behind both impurities. By heating the so obtained sodium aluminate ($NaAlO_2$) upto $50^oC - 60^oC$ in

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presence of CO_2, the precipitates of aluminium hydroxide $[Al(OH)_3]$ are formed.

$$2NaAlO_2 + 3H_2O + CO_2 \longrightarrow 2Al(OH)_3 + Na_2CO_3$$

The precipitates of $Al(OH)_3$ are washed to remove Na_2CO_3, dried and ignited at about 1500°C to get pure alumina.

$$2Al(OH)_3 \xrightarrow[1500^oC]{Heat} \underset{Alumina}{Al_2O_3} + \uparrow 3H_2O_{(g)}$$

(ii) **Baeyer's method:–** This method is used for the purification of ore containing excess of Fe_2O_3. When finely divided bauxite is treated with strong caustic soda (45%), then the bauxite goes into solution as sodium aluminate

$$Al_2O_3.nH_2O + 2NaOH \longrightarrow 2NaAlO_2 + 2(n)H_2O$$

The solution is filtered to remove Fe_2O_3, remaining part is same as described in first method.

(iii) **Serpek's method:–** This method is used for the purification of bauxite containing excess of silica (SiO_2). The powdered bauxite is mixed with carbon and heated up to 1800°C in the current of nitrogen, when aluminium nitride is formed.

$$Al_2O_3.nH_2O + 3C + N_2 \longrightarrow 2AlN + 3CO + nH_2O$$

$$SiO_2 + 2C \longrightarrow Si + 2CO$$

Aluminium nitride on hydrolysis with hot water, produces precipitates of $Al(OH)_3$ and NH_3

$$AlN + 3H_2O \longrightarrow Al(OH)_3 + \uparrow NH_{3(g)}$$

Aluminium hydroxide is filtered, dried and ignited, to get pure alumina.

$$2Al(OH)_3 \xrightarrow{Heat} \underset{Alumina}{Al_2O_3} + 3H_2O$$

(iv) **Electrolysis of pure alumina:–** The electrolysis is carried out in a steel tank lined with carbon (graphite). The carbon lining serves as cathode, where as anode is carbon rods hanging in the molten mass as given in fig.4.1

The electrolyte consists of alumina dissolved in fused cryolite and fluorspar. Cryolite lowers the melting point of alumina i.e about 950°C and fluorspar

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increases the fluidity of the melt, so that the liberated aluminium may sink at the bottom of electrolytic cell. When electric current is passed through this mixture, then aluminium is obtained at cathode in liquid state, so it sinks to bottom from where it is drawn periodically through the tapping hole.

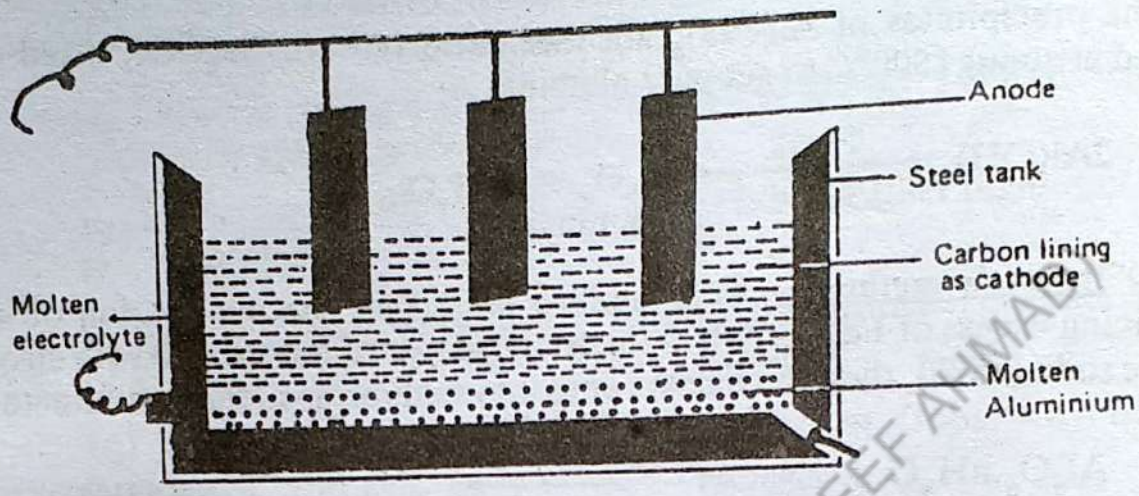

Fig. 4.1(a) Electrolysis of pure Alumina

(v) Refining of Aluminium by Hoope's Electrolytic method:- The Aluminium obtained by electrolysis of Alumina, is 99% pure. It is further refined by electrolysis. The electrolysis is carried out in iron box which is lined with carbon at the bottom. It contains three layers of fused mass. The lower layer consists of an alloy of impure aluminium with copper. This layer serves as anode. The middle layer consists of a solution of cryolite $Na_3Al\ F_6$ and $Ba\ F_2$. The upper layer consists of pure Aluminium and serves as cathode. The three layers remain separated due to the difference in specific gravity.

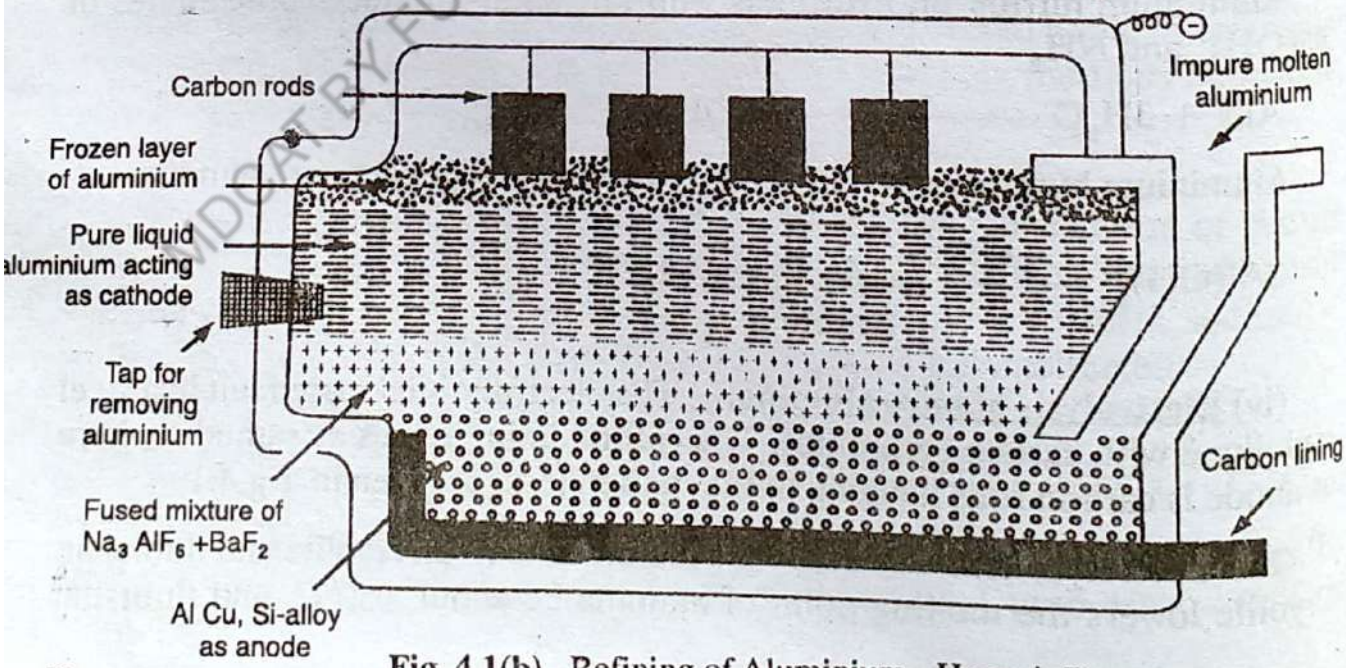

Fig. 4.1(b) Refining of Aluminium - Hoope's Process

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On electrolysis Al^{3+} ions from the middle layer migrate to the upper layer where they are reduced to aluminium. Equal number of Al^{3+} ions are produced in the lower layer. These Al^{3+} ions migrate to the middle layer. Pure aluminium is tapped off from time to time. In this way 99.99% pure aluminium is obtained.

$$Na_3AlF_6 \xrightarrow{950-1000^{\circ}C} 3NaF + AlF_3$$

$$AlF_3 \rightleftharpoons Al^{3+} + 3F^-$$

At cathode $Al^{3+} + 3e^- \longrightarrow Al_{(s)}$

At anode $Al \longrightarrow Al^{3+} + 3e^-$
(goes to molten cryolite)

Overall reaction

$$Al^{3+} + Al_{(s)} \longrightarrow Al_{(s)} + Al^{3+}$$

Properties of Aluminium

(a) **Physical Properties:** It is bluish white metal with brilliant silvery lusture which is soon destroyed by the layer of oxide formation. It is light and cheap and thus used in making the house hold utensils. It is malleable and ductile. It is resistant to corrosion. Its density is about 2.7 gm/ml. It melts at 658°C and boils at 1800°C. It is good conductor of heat and electricity. It is used in the manufacture of electrical transmission wires. Aluminium foil is used for wrapping chocolates, medicines, cigarettes and photographic films. The mixture of aluminium powder and aluminium nitrate, known as "ammonal", is used in explosive bombs. It is used in the preparation of some important alloys, namely:

(i) Aluminium bronze : It contains 10% of Al and 90% of Cu.

This alloy is light, tough resistant to corrosion and golden in colour. It is used in the manufacture of imitation jewellery, coins and statues etc.

(ii) Dura lumin:— It is composed of 95% of Al, 4% of Cu, 0.5% of Mg and 0.5% of Ni. This alloy is light, tough, ductile, tensile and resistant to corrosion. It is used in making aeroplanes etc.

(b) **Chemical Properties**

(i) **Action of Air:—** Aluminium is not affected by dry air at ordinary temperature but moist air forms a thin film of oxide on its surface. This film protects the

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metal from further oxidation, hence aluminium is a self – protected metal. If aluminium is heated strongly in air, it burns with a brilliant white light to form aluminium oxide.

$$4Al + 3O_2 \longrightarrow 2Al_2O_3 \quad \Delta H = -798.18 \text{ K cal / mol}$$

(ii) **Action of Acids:–** Aluminium reacts (dissolves) with HCl and dil. H_2SO_4 to form H_2 gas.

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$$

$$2Al + 3H_2SO_4 \xrightarrow{\text{dil:}} Al_2(SO_4)_3 + 3H_2$$

Concentrated and hot H_2SO_4 reacts with aluminium to form SO_2 and $Al_2(SO_4)_3$.

$$2Al + 6H_2SO_4 \xrightarrow{\text{conc:}} Al_2(SO_4)_3 + 6H_2O + 3SO_2$$

Aluminium is made passive by nitric acid.

(iii) **Action of Halogens:–** Aluminium reacts with halogens during heating and forms corresponding halides:

e.g.

$$2Al + 3X_2 \longrightarrow \underset{\text{Aluminium trihalide}}{2AlX_3}$$

$$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$

$$2Al + 3Br_2 \longrightarrow 2AlBr_3$$

(iv) **Action of Alkalis:–** Aluminium reacts with alkalis and forms aluminates and liberates H_2 gas:

e.g.

$$2Al + 2NaOH + 2H_2O \longrightarrow \underset{\text{Sodium aluminate}}{2NaAlO_2} + 3H_2$$

$$2Al + 2KOH + 2H_2O \longrightarrow 2KAlO_2 + 3H_2$$

(v) **Action of Nitrogen:–** When aluminium is heated with nitrogen up to 700^oC, it forms aluminium nitride:

e.g.

$$2Al + N_2 \longrightarrow 2AlN$$

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(vi) **Action of Carbon:–** When aluminium is heated with carbon up to 2000°C, it forms aluminium carbide:

e.g.

$$4Al + 3C \longrightarrow Al_4C_3$$

Aluminium carbide

(vii) **Aluminium as Reducing Agent:–** Aluminium is a powerful reducing agent. It readily reduces the oxides of most of the other metals just like Fe, Mn, Cr etc:

e.g.

$$Fe_2\overset{3+}{O_3} + 2Al \longrightarrow 2Fe^{o} + Al_2O_3$$

This is exothermic reaction and great amount of energy is released so that the temperature increases upto 3500°C. Due to this reason, this process is used for welding purposes. The reduction of metal oxides involving aluminium as reducing agent is termed as "thermite process".

Alum (Phit kari) The series of double sulphates of monovalent and trivalent metals containing 24 molecules of water of crystallization are known as alums. There are various compositions of alums. The alums are usually the sulphates of sodium, potassium or ammonium with aluminium, iron or chromium.

Examples.

$$K_2SO_4.Al_2(SO_4)_3.24H_2O$$
$$K_2SO_4.Cr_2(SO_4)_3.24H_2O$$
$$(NH_4)_2SO_4.Cr_2(SO_4)_3.24H_2O$$
$$(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$$

Out of these alums, the ordinary is potash–alum ($K_2SO_4.Al_2(SO_4)_3.24H_2O$). It is commonly known as phitkari.

Preparation:– It is prepared by mixing the solutions of K_2SO_4 and $Al_2(SO_4)_3$ in equimoleculer quantities. The solution is evaporated to saturation and allowed to cool when crystals of alum are formed.

Properties:– It is white crystallization solid, readily soluble in water and used in purification of water. It is used for tanning leather, sizing paper and in

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foam type fire extinguishers. When alum is heated, it melts at 92°C and swells up, loses the whole of its water of crystallization at 200°C to form porous mass called burnt alum or "phul – Phitkari".

Occurrence of Alum:– It occurs in Gajbeds of Maki–Nai in Ranikot Dadu and Shah Hassan near Trimuhi in Khairpur, Shaidmena in Khyber agency; Jatta and near Dozha Banda in Kohat district; Sani in Kalat, Koh–i–Sultan, north Nokkunda as well as in salt range in KalaBagh Chi chali pass near Kotki.

4.4 ALLOTROPY

The existence of an element in more than one forms in known as allotropy. The different forms are called as allotropic modifications or allotropes. The allotropic forms of a particular element possesses similar chemical properties but different physical properties. The difference in physical properties is due to arrangement of atoms in the lattice.

Allotropic Modifications of Carbon: There are two allotropic forms of carbon:

(a) Crystalline and (b) Amorphous

(a) Crystalline forms:– There are two crystalline forms namely:

(i) Diamond and (ii) Graphite.

(b) Amorphous forms:– There are various amorphous allotropic forms of carbon namely coal, coke, charcoal, lamp black etc.

(i) Diamond:

Properties of Diamond :– In pure state, it is crystalline solid. It is hardest natural substance known. Its density is about 3.51 g/cm^3. Diamond possesses high refractive index i.e 2.45, due to which, it acquires great brilliance. It is a bad conductor of electricity and melts at 3500°C. Pure Diamond is transparent to X–Rays, hence X–Ray is used to distinguish between imitation and pure diamond. The value of diamond depends upon its size and colour. Usually pure diamonds are colourless but due to presence of impurities, they are also blue, green, yellow, red or black. The black diamonds (Bort and carbonado) are used for drilling and boring rocks etc because they are not suitable as gem–stones. The well known diamonds are Koh–i–noor, Regent, Excelsior, Victoria, Hope, Star of South and Cullinan etc.

Structure of Diamond. In diamond each carbon atom is covalently linked with four other carbon atoms to give basic tetrahedral unit. The tetrahedral unit is shown in figure 4.2.

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These basic tetrahedral units unite with one another and produce the cubic unit cell of diamond as shown in figure 4.3.

The lattice pictured in figure 4.3 continues indefinitely in three dimensions and form over all structure of diamond.

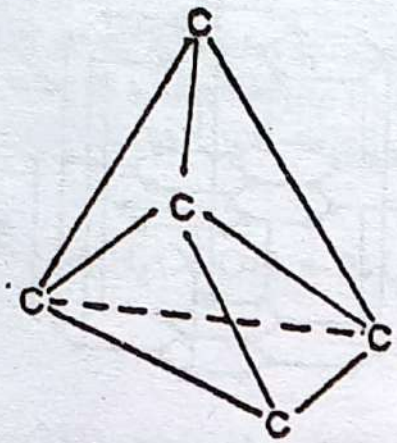

Fig. 4.2

Basic tetrahedral unit

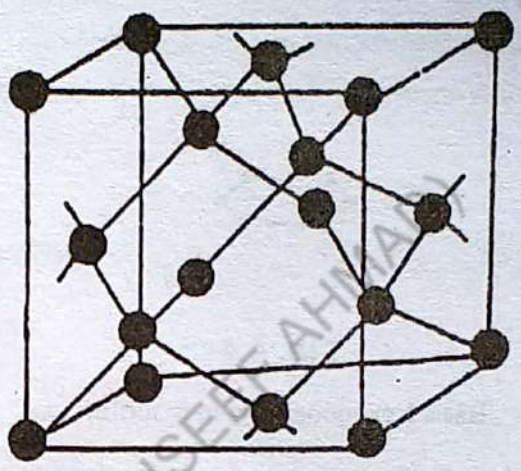

Fig. 4.3

Cubic unit cell of diamond

In diamond each carbon atom utilizes its four unpaired electrons in the formation of four covalent bonds. These bonding electrons pairs are localized between specific pair of carbon atoms. Due to this reason diamond is bad conductor of electric current.

In diamond each carbon atom is bonded strongly to four other carbon atoms which are located at the corner of regular tetrahedron. Each carbon at the corner of one tetrahedron is at the centre of another tetrahedron. It means all carbon – carbon bonds in entire crystal are covalent, strong and definite. The carbon – carbon bond length is 1.54°A and bond energy for each carbon – carbon bond is 347 KJ mol^{-1}. This is because diamond is hard and possesses high melting point.

(ii) <u>Graphite:</u>

Properties:– It is dark grey crystalline solid and possesses dull metallic lustre. It is soft and greasy to feel. It is used as lubricant. Its density is about 2.2 g/cm^3 and lighter than diamond. It is good conductor of electricity and hence used in the preparation of electrodes. It leaves black mark on paper, so it is used in making pencils. It possesses high melting point and it is used as moderator in nuclear reactors.

<u>Structure:–</u> In graphite each carbon atom is trigonally (sp^2) hybridized and covalently linked with three other C atoms to give basic hexagonal ring.

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The hexagonal rings then form different layers in graphite. These layers are 3.35°A away from one another and held together by weak Vander Waal's forces of attraction. The inter layer binding energy is very low and it is about 3.99 Kcal/mol. The arrangement of different layers in graphite is shown in fig 4.5.

Fig. 4.4

Basic hexagonal ring in graphite

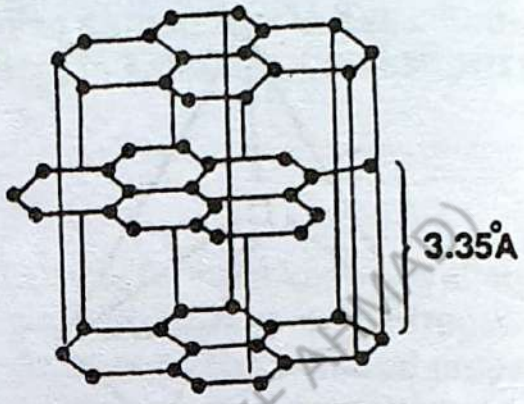

Fig. 4.5

Structure of graphite

In hexagonal rings C−C bond distance is 1.42°A. The fourth electron of each carbon forms the delocalized π −bonds which spread uniformly over all carbon atoms. Due to delocalized π − bonds, graphite conducts electricity parallel to the plane of its layers.

Due to large inter planner distance (3.35°A), the layers slide easily over one another that is why it is soft and used as lubricant.

4.5 LEAD PIGMENTS

Lead forms various types of pigments which are used to give the proper colour to paints etc. Some of them are described below:

(i) White lead pigment

(ii) Red lead pigment

(iii) Chrome yellow pigment

(iv) Chrome red pigment

(v) Turner's yellow pigment

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(i) **White lead pigment:–** It is basic lead carbonate and has approximately composition as $[2PbCO_3.Pb(OH)_2]$ or $Pb_3(OH)_2.(CO_3)_2$

Preparation:–

Chamber process or Duch process:– When a mixture of the vapours of acetic acid and steam is passed into the chambers containing lead sheets (buckets) about 2–3 days, until the corrosion of lead is complete. By passing the mixture of CO_2 and vapours of acetic acid through this corroded lead for about 3–4 weeks, the "White Lead" is formed on the surface of lead sheets. This product is then scratched, dried and packed.

$$2Pb + 2CH_3COOH + 2H_2O \longrightarrow [Pb(OH)_2.Pb(CH_3COO)_2] + 2H_2$$

$$3[Pb(OH)_2.Pb(CH_3COO)_2] + 2H_2O + 2CO_2 \longrightarrow \underbrace{2[2PbCO_3.Pb(OH)_2]}_{\text{White lead}} + 6CH_3COOH$$

A better "White Lead" is obtained by passing CO_2 into the suspension of lead oxide in water containing little amount of lead acetate.

$$2PbO_2 + 2CO_2 + 2H_2O + Pb(CH_3COO)_2 \longrightarrow [2PbCO_3.Pb(OH)_2] + 2CH_3COOH + O_2$$

It is used as white pigment for paints, but it gradually darkens due to the formation of PbS with atmospheric H_2S. It is also poisonous hence in recent years, white–lead has been replaced by titanium–dioxide.

(ii) **Red lead pigment (Sandhur):–** It is called as triplumbic tetraoxide or lead–sesqui oxide and its composition is Pb_3O_4 or $(2PbO.PbO_2)$.

Preparation:– It is prepared by heating lead monoxide (litharge) in a revolving furnace with excess of air at about 450°C.

$$6PbO + O_2 \xrightarrow{450^\circ C} \underset{\text{Red lead}}{2Pb_3O_4}$$

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It is used as red coloured pigment. Actually the colour of this pigment varies from orange red to brick red due to particle size and impurities. It is insoluble in water but soluble in acids.

(iii) **Chrome yellow pigment:–** It is lead chromate with composition ($PbCrO_4$). It occurs in nature as crocoite.

Preparation:– (1) It is prepared by adding the solution of potassium chromate to the solution of lead nitrate, then fine yellow precipitates of lead chromate (chrome yellow) are obtained.

$$Pb(NO_3)_2 + K_2CrO_4 \longrightarrow \underbrace{PbCrO_4}_{\text{Chrome yellow}} + 2KNO_3$$

(2) It is also prepared by the action of K_2CrO_4 on lead acetate.

$$Pb(CH_3COO)_2 + K_2CrO_4 \longrightarrow PbCrO_4 + 2CH_3COOK$$

It is yellow coloured pigment, insoluble in water but soluble in nitric acid and caustic alkalis.

(iv) **Chrome red pigment:–** It is basic lead chromate and its composition is $PbCrO_4.PbO$ or Pb_2CrO_5.

Preparation:– It is prepared by digesting lead chromate with NaOH.

$$2PbCrO_4 + 2NaOH \longrightarrow Na_2CrO_4 + \underset{\text{Chrome red}}{Pb_2CrO_5} + H_2O$$

It is dark red pigment and is used in paints.

(v) **Turner's yellow pigment:–** Its composition is $PbCl_2.4PbO$.

Preparation:– It is prepared by boiling the solution of sodium chloride with litharge (PbO) and then heating to solid product.

$$5PbO + H_2O + 2NaCl \longrightarrow 2NaOH + \underbrace{PbCl_2.4PbO}_{\text{Turner's yellow}}$$

It is also used as lead pigment in paints.

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Except above pigments, yellow lead monoxide (massicot) and red lead monoxide (Litharge or Murda – Sang) also used in paints.

4.6 NITRIC ACID (HNO_3)

Nitric acid is prepared commercially by the oxidation of ammonia by Ostwald's method. In this method ammonia is oxidised to NO in the presence of platinum as catalyst at 600°C. NO then combines with oxygen of air forming NO_2 which is dissolved in water to produce HNO_3.

$$4NH_3 + 5O_2 \underset{600^\circ C}{\overset{pt}{\rightleftharpoons}} 4NO + 6H_2O \qquad \Delta H = -24.8 \text{ kcal}$$

$$2NO + O_2 \rightleftharpoons 2NO_2$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

Details of the process:- (i) Oxidation of ammonia: 1 part by volume of NH_3 is mixed with 8 parts by volume of air. The mixture is allowed to enter the converter which contains platinum gauge heated to a temperature of 600°C in the beginning, the temperature is then maintained due to exothermic reaction of oxidation of NH_3.

About 95% of NH_3 is oxidised to NO. The gases from the converter are led by iron pipe which passes through a boiler. Steam is produced by the absorption of heat from the gases and the temperature is lowered to 150°C.

(ii) Oxidation of NO to NO_2:- NO and air enter the oxidation chamber where the temperature is further lowered to 50°C and NO is oxidised to NO_2.

(iii) Formation of HNO_3:- NO_2 gas from the oxidation chamber is allowed to enter the absorption tower packed with acid proof stones. The gas is absorbed by the water sprayed from the top of the tower. The nitric acid formed is very dilute in the beginning. It is recycled to absorb more and more NO_2 gas till maximum saturation is obtained. The nitric acid obtained by this process is 68%. Further concentration is achieved by passing vapours of HNO_3 over sulphuric acid.

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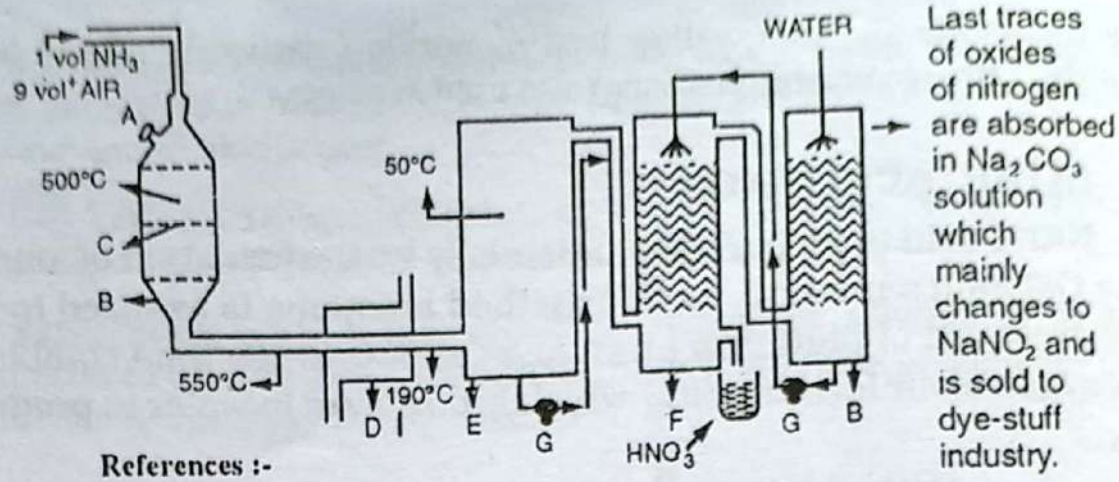

References :-

A. Slight window to check temperature.
B. Ammonia Oxidation Converter.
C. Electrically heated platinum guaze to start
D. Boiler
E. Oxidation Chamber
F. Absorption towers
G. Pumps

Fig. 4.6 Preparation of Nitric acid

Physical Properties of HNO_3

In pure state, it is colourless fuming liquid with choking smell and has a sour taste. It boils at 83°C and freezes at −41.6°C. It is available in market in following forms:

(a) Ordinary nitric acid containing 65% HNO_3 and density is about 1.4 g/l.

(b) Concentrated nitric acid containing 98% HNO_3 and density is 1.51 g/l.

(c) Fuming nitric acid containing dissolved oxides of nitrogen (NO_2) and reddish–yellow liquid.

Structure of HNO_3 :–

In vapour phase, the nitric acid molecule is planar in which atoms are arranged as given in fig.4.7.

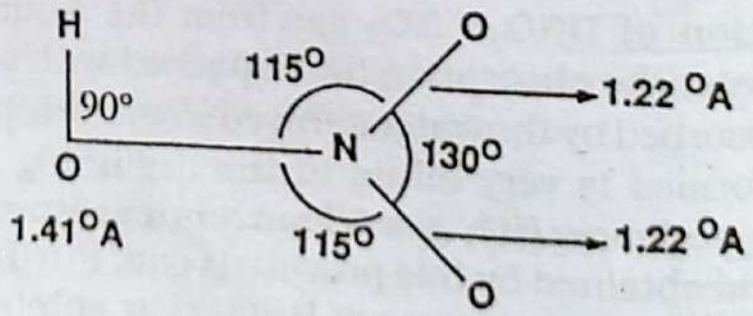

Fig. 4.7 Structure of Nitric acid in vapour phase

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The structure of nitric acid crystal in solid state at about $-42^{o}C$ is given in figure 4.8.

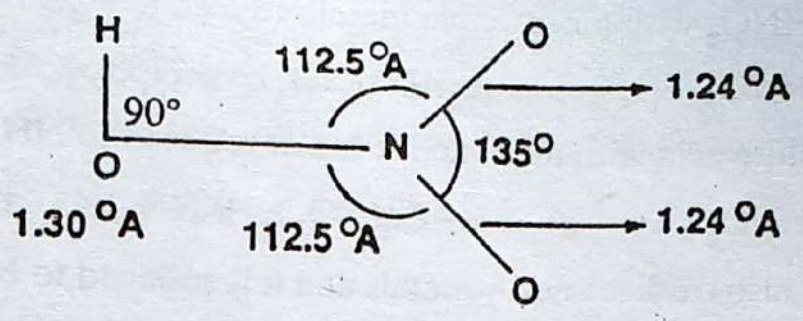

Fig. 4.8 Structure of Nitric acid in solid state

Chemical properties:– The chemical properties of HNO_3 are divided into following sets:

(i) Acidic properties

(ii) Oxidizing properties

(iii) Nitrating properties

(i) **Acidic properties:–** It is strong acid because it reacts easily with water to form hydronium ion H_3O^+ (i.e it provides H^+ ion). It is monoprotic acid, because it loses only one H^+ ion. At the same time it neutralizes bases, hence it acts as an acid.

(a) $HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^{-1}$

(b) $HNO_3 + NaOH \longrightarrow NaNO_3 + H_2O$

(ii) **Oxidizing properties:–** Nitric acid is strong oxidizing agent. The oxidizing properties of nitric acid are due to the instability of its molecule and presence of nitrogen in its highest oxidation state of +5. During oxidation nitrogen changes from +5 oxidation state to −3. The degree of oxidation depends upon the concentration of acid and nature of element. Lower the concentration of acid and higher the reactivity of element, then greater would be the degree of oxidation. For example:

(a) Concentrated HNO_3 is reduced to NO_2.

$$Cu + 4HNO_3 \xrightarrow{conc} Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

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(b) Dilute HNO_3 is reduced to NO.

$$3Cu + 8HNO_3 \xrightarrow{dil} 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

(c) Dilute HNO_3 with more active metal reduced to N_2O

$$4Mg + 10HNO_3 \longrightarrow 4Mg(NO_3)_2 + N_2O + 5H_2O$$

(d) Very dilute acid with more active metal reduced to NH_4NO_3.

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O.$$

Nitric acid also oxidizes non – metals and it is reduced to NO_2.

$$S + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$$

$$P + 5HNO_3 \longrightarrow H_3PO_4 + 5NO_2 + H_2O$$

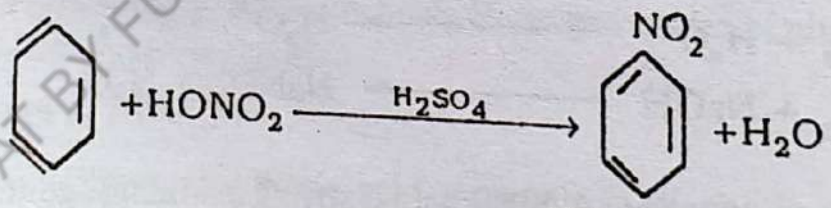
$$Si + 4HNO_3 \longrightarrow SiO_2 + 4NO_2 + 2H_2O$$

(iii) Nitrating properties (Agent):- HNO_3 replaecs one or more hydrogen atoms of organic compounds with nitro group and acts as a nitrating agent .e.g.

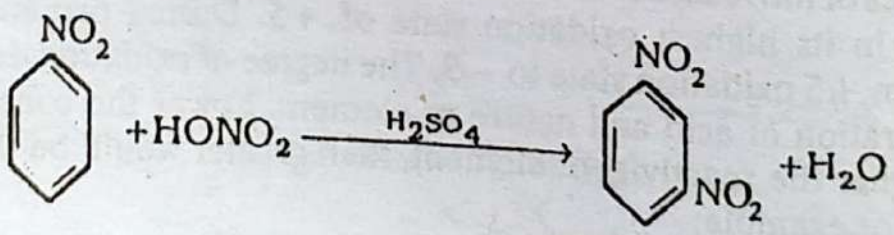
(a) When vapours of HNO_3 and alkane are passed through copper tube at 450°C, nitro alkane is formed.

$$CH_4 + HONO_2 \xrightarrow[450°C]{Cu} CH_3NO_2 + H_2O$$

(b) It reacts with benzene in the presence of H_2SO_4 (Conc.) and forms nitro benzene.



Nitro benzene



meta-di-nitrobenzene

Importance:– It is an important chemical compound. Large amounts of HNO_3 are used in the manufacture of fertilizers, just like ammonium nitrate and sodium nitrate. It is used in Glyceryl – trinitrate (nitro – glycerine). Nitro –

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glycerine is an explosive which detonates violently even with slight shock. Dynamite is prepared by absorbing nitro glycerine in Kieselguhr. Dynamite is also an explosive but it is much safer to handle. It is also used in the manufacture of nitro cellulose lacquers and smokeless gun–powder.

(iv) Aqua Regia:– A mixture containing 1 part by volume of HNO_3 (Conc) and 3 parts by volume of HCl (Conc) is called aqua regia which means royal water. It can dissolve gold and other noble metals due to liberation of chlorine.

$$HNO_3 + 3HCl \longrightarrow 2H_2O + \underset{\text{Nitrosyl-chloride}}{NOCl} + 2Cl$$

$$Au + 3Cl \longrightarrow AuCl_3$$

$$AuCl_3 + HCl \longrightarrow \underset{\text{Hydroauric chloride}}{\overset{+}{H}[AuCl_4]^-}$$

4.7 ALLOTROPIC FORMS OF SULPHUR

There are various allotropic forms of sulphur which exist in solid, liquid and gaseous states. Here we discuss some of them in detail:

(i) Crystalline sulphur
(ii) Plastic sulphur

(i) Crystalline sulphur:– Important crystalline forms of sulphur are following:–

(a) Rhombic, Octahedral or α – sulphur
(b) Monoclinic, prismatic or β – sulphur

(a) Rhombic sulphur:– It is stable crystalline form at ordinary temperature. It is prepared by slow evaporation of solution of ordinary sulphur in carbon disulphide.

Properties:– It is ordinary form of sulphur. It is in the form of pale yellow crystals, giving lemon-yellow powder. It is the only stable form at ordinary conditions and most of the other forms pass into it on standing. It melts at 112.8°C. Its density is about 2.1 gm/cm^3 at 20°C. It is soluble in carbon disulphide (CS_2), petroleum, S_2Cl_2, benzene and turpentine. It is non–conductor of heat and electricity.

Structure:– Rhombic sulphur consists of sulphur atoms in S_8 molecules giving eight membered rings. Each S_8 molecule has the form of puckered rings. The different views of rings are given below in figure 4.9

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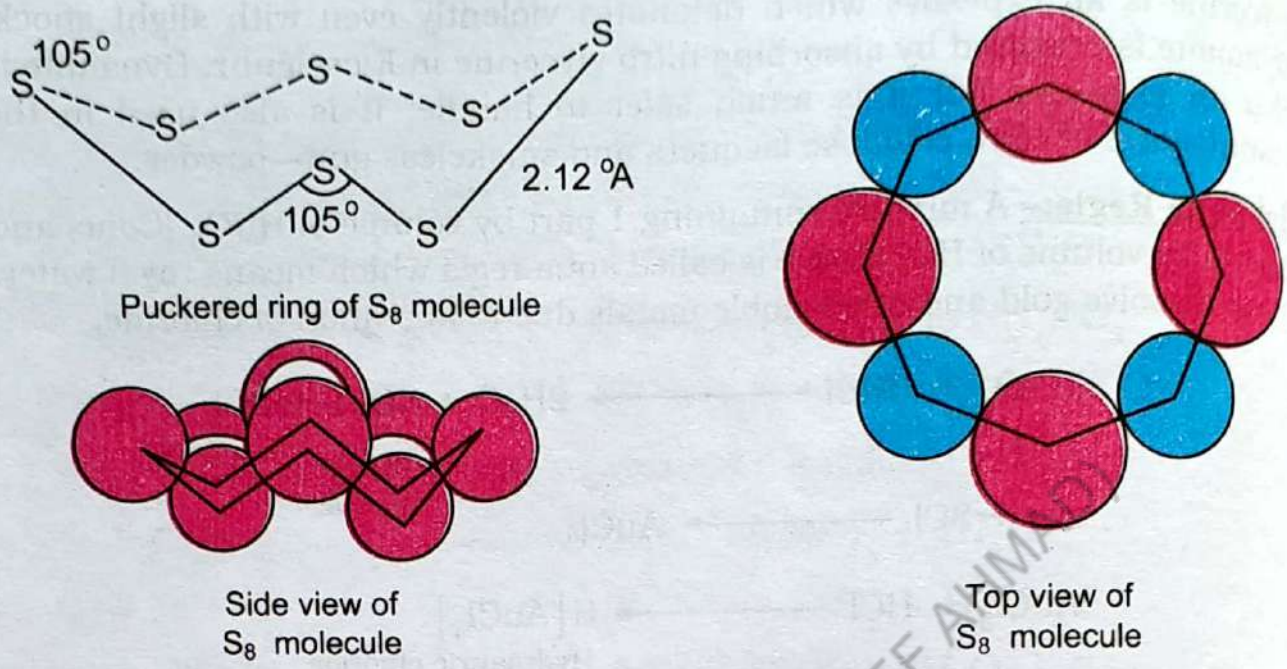

Fig. 4.9 The different views of rings in Rhombic sulphur

In each puckered ring, four sulphur atoms lie in one plane and other four atoms lie in another plane as described in above figures. Each sulphur is linked to another sulphur by a single bond in same ring. The sulphur – sulphur bond distance is 2.12°A and S – S – S bond angle is 105°. These puckered rings unite with one another and form the crystal of rhombic sulphur. These rings are held together by Vander Waal's forces of attraction. The shape of rhombic crystal is given below in figure 4.10

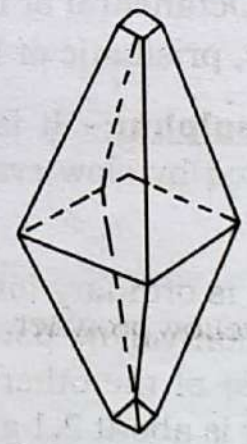

Fig. 4.10 Crystal of rhombic sulphur

(b) Monoclinic sulphur:– It is dark yellow transparent needle like crystal, on standing the crystals become opaque, brittle and Lemon – yellow in colour. It melts at 119.25°C. It is soluble in carbon disulphide (CS_2) but insoluble in water. It is stable between 95.5°C and 119.25°C. The transformation of monoclinic sulphur to rhombic sulphur is reversible. Below 95.5°C, the rhombic

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sulphur is stable and above 95.5°C monoclinic sulphur is stable. This temperature at which both forms of sulphur are in equilibrium is called as transition temperature i.e is about 95.5°C.

$$\text{Rhombic sulphur} \xrightleftharpoons{95.5^{\circ}C} \text{Monoclinic sulphur}$$

Structure of Monoclinic sulphur:– Monoclinic sulphur consists of sulphur atoms in S_8 molecules giving eight membered puckered rings just like rhombic sulphur. The only difference is the difference in the shapes of their crystals. The crystal of monoclinic sulphur is needle shaped as given in figure 4.11.

Fig. 4.11
Crystal of monoclinic sulphur

(ii) **Plastic Sulphur or γ – sulphur:–** When molten sulphur is heated up to boiling and then poured with a thin stream into cold water, it turns into elastic rubber like material which is called plastic sulphur.

Properties:– It is soft, sticky rubber like material. Its specific gravity is 1.92. It is soluble in CS_2. It on standing, is converted into opaque brittle solid containing some rhombic sulphur.

Structure:– The plastic sulphur is composed of long chains of sulphur atoms coiled up as given in figure 4.12. The elasticity of plastic sulphur is due to uncoiling of long sulphur chains and then recoiling of chains by the release of tension.

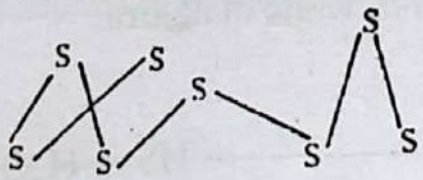

Fig. 4.12 Chains of sulphur atoms

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4.8 HYDROGEN SULPHIDE

(A) Preparation of Hydrogen sulphide (H_2S)

(i) **From Sulphur:–** When sulphur is heated with hydrogen up to 600°C–650°C, it forms H_2S.

$$H_2 + S \longrightarrow H_2S$$

(ii) **From stibnite:–** Pure hydrogen sulphide is prepared by heating antimony trisulphide (Stibnite) with concentrated HCl.

$$Sb_2S_3 + 6HCl \longrightarrow 2SbCl_3 + 3H_2S$$

(iii) **From ZnS:–** When ZnS is treated with HCl, it forms H_2S

$$ZnS + 2HCl \longrightarrow ZnCl_2 + H_2S$$

(iv) **Laboratory method:–** In laboratory H_2S is prepared in Kipp's apparatus by the action of HCl or H_2SO_4 on ferrous sulphide (FeS)

$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$$
$$FeS + 2HCl \longrightarrow FeCl_2 + H_2S$$

Properties:– It is a colourless gas with unpleasant smell just like that of rotten eggs. It is little heavier than air i.e 1.2 times heavier than air. It liquifies at – 60.8°C and solidifies at – 85.7°C. It is very toxic gas and prolonged inhalation of air containing H_2S gas even in small quantities causes serious poisoning. The best antidote in the case of H_2S poisoning in very dilute chlorine. It is soluble in water and solution of H_2S in water is called as "hydrogen sulphide water". Its solution in water is acidic in nature.

$$H_2S + H_2O \longrightarrow H\bar{S} + H_3O^+ \quad (K_1 = 1.0 \times 10^{-7})$$

$$H\bar{S} + H_2O \longrightarrow S^{-2} + H_3O^+ \quad (K_2 = 1.0 \times 10^{-14})$$

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It burns with blue flame in air to form SO_2 and H_2O

$$2H_2S + 3O_2 \longrightarrow 2H_2O + 2SO_2$$

It is strong reducing agent. This is because the S^{2-} ion loses its electrons readily to form sulphur atom and hence reduces other substances.

$$H_2S^{2-} + \overset{0}{Br_2} \rightarrow 2H\overset{1-}{Br} + S^0$$

$$2\overset{3+}{Fe}Cl_3 + H_2S^{2-} \rightarrow 2\overset{2+}{Fe}Cl_2 + S^0 + 2HCl$$

$$2H\overset{5+}{N}O_3 + H_2S^{2-} \rightarrow 2\overset{4+}{N}O_2 + S^0 + 2H_2O$$

$$H_2\overset{6+}{S}O_4 + H_2S^{2-} \rightarrow \overset{4+}{S}O_2 + S^0 + 2H_2O$$

<u>Structure:–</u> The molecule of H_2S is non–linear. The angle between HSH is 92.2° and the bond distance between S and H is 1.34°A

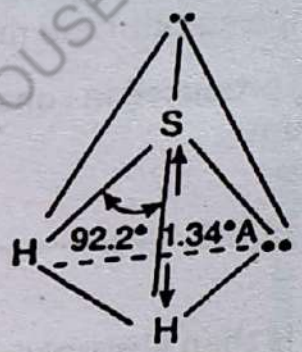

Fig. 4.13 Structure of hydrogen sulphide

4.9 SULPHURIC ACID (H_2SO_4)

<u>Manufacture of sulphuric acid by Contact–method:–</u>

The present day method which produces pure sulphuric acid, is the contact method. It actually began to be used only at the end of last century.

In this method SO_2 is produced by burning sulphur or iron pyrites in pyrite burners.

$$S + O_2 \longrightarrow SO_2$$

or

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_{3(s)} + 8SO_{2(g)}$$

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It is very important in contact method that SO_2 and air mixture should be free from impurities, which poison the catalyst. For this reason the mixture of SO_2 and air is passed through special filters, washing and drying towers. This washed, dried and purified mixture of SO_2 and air is passed through contact tower. In this tower SO_2 is oxidized to SO_3 in presence of catalyst vanadium pentaoxide (V_2O_5).

$$\underset{\text{2 volumes}}{2SO_2} + \underset{\text{1 volume}}{O_2} \rightleftharpoons \underset{\text{2 volumes}}{2SO_3} \quad \Delta H = -45 \text{ Kcal}$$

Since the reaction is reversible and exothermic, the favourable conditions for obtaining maximum yield of SO_3 are (a) low temperature (b) high pressure and (c) excess of O_2. In actual practical, however a temperature of 450 – 500°C appears to be optimum temperature in the presence of catalyst and pressure of 1.5 to 1.7 atmosphere is applied. This temperature is low enough to permit most of the sulphur and oxygen to react rapidly if catalyst is present. Under these conditions, the equilibrium mixture contains 98% of SO_3.

The SO_3 produced in contact tower is absorbed first by H_2SO_4 concentrated to form oleum.

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7 \text{ (Oleum)}$$

Oleum is then absorbed in calculated amount of water in order to get the acid of desired concentration.

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

The continuous nature of this process is shown diagrammatically in figure 4.14

It should be mentioned that the heat produced during this process

$$2SO_2 + O_2 \longrightarrow 2SO_3 \quad \Delta H = -45 \text{ Kcal}$$

is used in the process to generate steam from water which supply power for all the activities of the plant. For example, pump to move the acid from one tower to other and fans to move gases from one reaction tower to another. Practically all the operations are done by automatic machinery, hence a plant that turns out 100 tons of acid per day may be manned by only a few workers.

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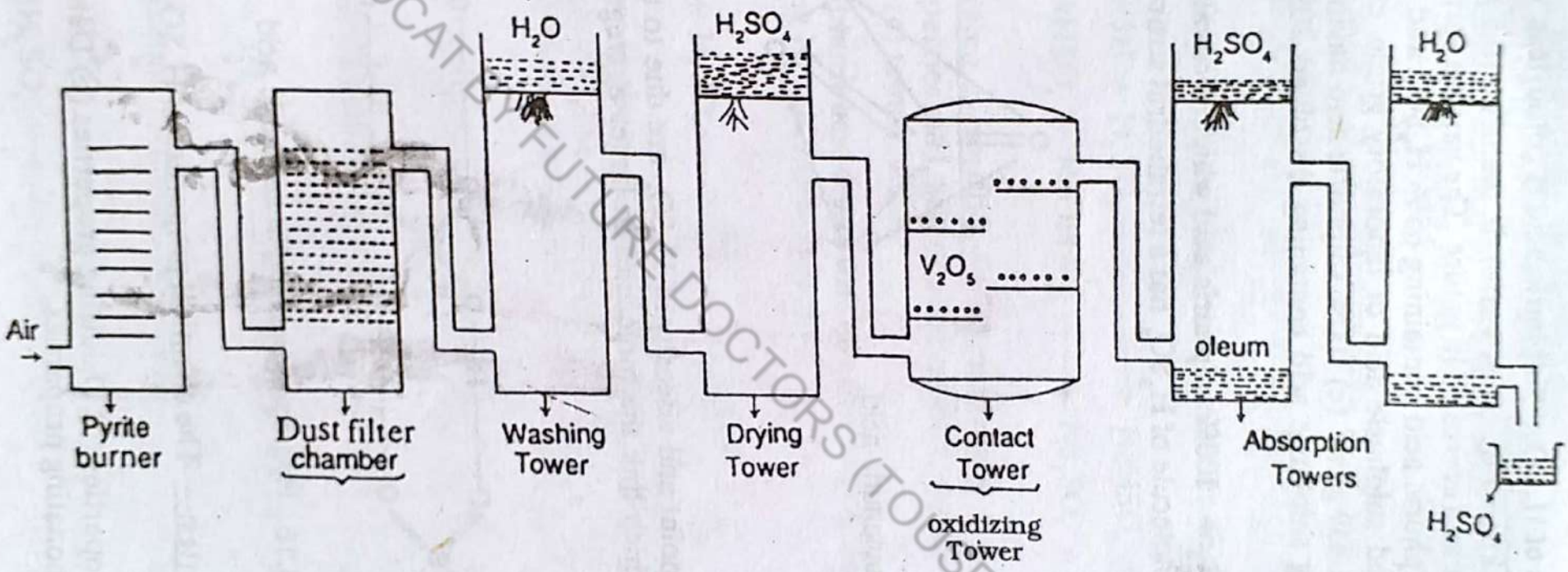

Fig. 4.14 Manufacture of sulphuric acid by contact process.

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Physical properties of H_2SO_4: Sulphuric acid is colourless, odourless, viscous oily liquid, often known as oil of vitriol. It melts at 10.5°C and boils at 290°C. It is hygroscopic and corrosive in nature. The various forms of sulphuric acid are (a) Dilute sulphuric acid containing 65% H_2SO_4 and density is 1.55 g/cm³ (b) Concentrated sulphuric acid of laboratory grade containing 98% H_2SO_4 and density is 1.839 g/cm³ (c) 100% sulphuric acid having density 1.838 g/cm³ and (d) Fuming sulphuric acid contaning dissolved 20% SO_3 having density 1.929 g/cm³.

Structure of H_2SO_4:– 100% sulphuric acid which is covalent compound, like sulphate ion, the molecule of H_2SO_4 has a tetrahedral structure as given in figure 4.15.

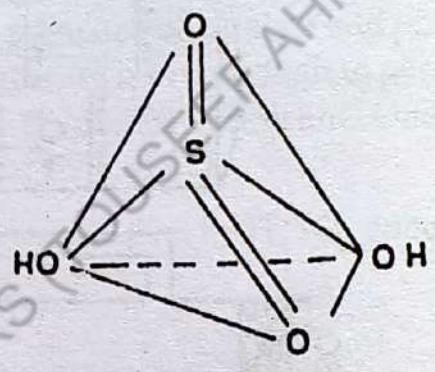

Fig. 4.15
Structure of sulphuric acid

The high boiling point and viscosity of H_2SO_4 are due to the presence of hydrogen bonding, which link the molecules in larger aggregates as given in figure 4.16.

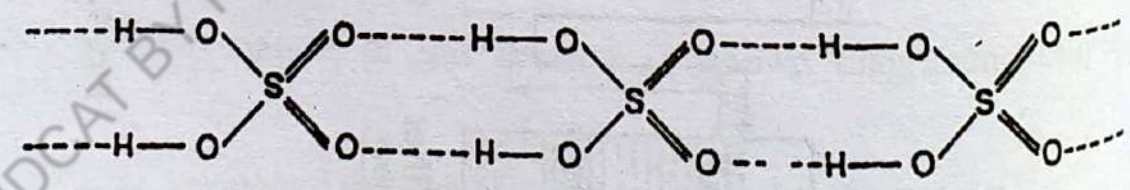

Fig. 4.16 Hydrogen bonding in sulphuric acid

Chemical properties:– The chemical properties of H_2SO_4 are divided into following sets:

(a) Acidic properties (b) Oxidizing properties (c) Dehydrating properties (d) Sulphonating properties

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(a) **Acidic properties:–** It is strong acid, because it reacts with water to form hydronium ion (i.e it provides H^+ ion). It is diprotic acid because it loses second H^+ ion after the loss of first H^+ ion. Due to loss of two H^+ ions, it forms two ionic species and acts as diprotic acid.

$$\text{(i)}\ H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$$

$$\text{(ii)}\ HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{-2}$$

It also neutralizes bases and forms two series of salts.

$$\text{(i)}\ NaOH + H_2SO_4 \longrightarrow NaHSO_4 + H_2O$$

$$\text{(ii)}\ NaHSO_4 + NaOH \longrightarrow Na_2SO_4 + H_2O$$

(b) **Oxidizing properties:–** Sulphuric acid acts as oxidizing agent. The oxidizing properties of H_2SO_4 depend upon: (a) concentration of acid (b) nature of metal and (c) temperature.

Dilute sulphuric acid reacts with metals standing high in the electrochemical series, yielding H_2 and metal sulphates.

$$Zn + H_2SO_4 \xrightarrow{\text{dil:}} ZnSO_4 + H_2$$

Metals low in the electrochemical series, such as Cu, Pb and Hg are not oxidized by dilute H_2SO_4 but concentrated and hot H_2SO_4 oxidizes these metals to form SO_2 and metal sulphates.

$$Cu + 2H_2SO_4 \xrightarrow[\text{hot}]{\text{conc:}} CuSO_4 + SO_2 + 2H_2O$$

Reactive metals with concentrated acid form different products, such as

$$4Zn + 5H_2SO_4 \xrightarrow{\text{90\% conc:}} 4ZnSO_4 + H_2S + 4H_2O$$

It also oxidizes non – metals, for example:

$$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

$$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$

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(c) **Dehydrating properties:–** Sulphuric acid has great affinity for water, hence it extracts the elements of water from other compounds. This type of reaction is called as dehydration reaction. It extracts water molecules from different compounds and forms different products.

$$\underset{\text{sugar}}{C_{12}H_{22}O_{11}} + H_2SO_4 \xrightarrow{\text{conc.}} 12C + 11H_2O + H_2SO_4$$

$$\underset{\text{Oxalic acid}}{H_2C_2O_4} + H_2SO_4 \xrightarrow{\text{conc.}} CO + CO_2 + H_2O + H_2SO_4$$

$$\underset{\text{Formic acid}}{HCOOH} + H_2SO_4 \xrightarrow{\text{conc.}} CO + H_2O + H_2SO_4$$

(d) Sulphonating properties :- Sulphuric acid on reaction with organic compounds replaces one or more hydrogen atoms and acts as a sulphonating agent e.g.

(i) It reacts with hexane and higher members forming alkane sulphonic acid.

$$C_6H_{14} + HO.SO_2.OH \longrightarrow \underset{\text{Hexane sulphonic-acid}}{C_6H_{13}.SO_2.OH} + H_2O$$

(ii) It reacts with benzene and forms benzene sulphonic acid.

$$C_6H_6 + HO.SO_2.OH \longrightarrow \underset{\text{Benzene sulphonic - acid}}{C_6H_5.SO_2.OH} + H_2O$$

Importance of sulphuric acid:– Sulphuric acid is so important chemical compound that it is called "King of Compounds", because only few industries could operate without its use. Progress and prosperity of any nation can be measured in terms of amount of sulphuric acid that its industries consume annually.

It is used in the manufacture of fertilizers just like "Supper phosphates and Ammonium nitrate", as well as "Rayon" and Plastics. It is also used in the production of HCl and HF and used in pickling of steel. It is also used in the preparation of detergents eg sodium benzene dodecyl sulphate ($C_{18}H_{29}SO_3^-Na^+$), which is main active constituent of tide and surf. It is also used as dehydrating, nitrating and drying agents.

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4.10 CHLORINE

Electrolytic method:– Chlorine is manufactured by the electrolysis of aqueous solutions of sodium chloride. For this purpose two cells are used which are described below:

(a) **Nelson's cell:-** This cell consists of U–shaped perforated steel vessel which acts as cathode and carbon rod as anode. This U–tube is separated from anode by asbestos layer deposited on the inner wall of the U–tube as shown in figure 4.17

The U–tube is filled by aqueous solution of sodium chloride. On passing the electric current, chlorine is obtained at anode reaction:

(i) Ionization $NaCl \longrightarrow Na^+ + Cl^-$

(ii) Reaction at anode $2Cl^- - 2e \longrightarrow Cl_2$

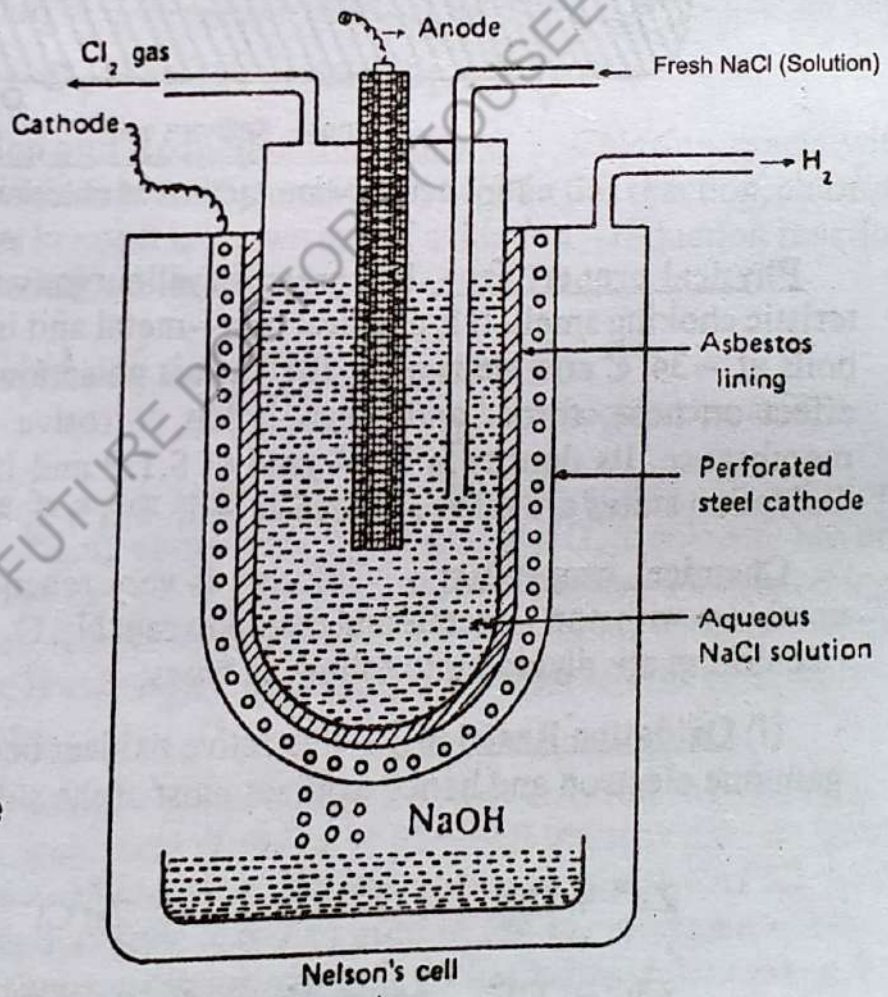

Fig. 4.17

Manufacture of chlorine

(b) **Castner–Kellner's cell:-** This cell has a cathode consisting of layer of mercury at the bottom of cell which flows from right to left. Saturated solution of sodium chloride also flows slowly through the cell in same direction as the mercury. The anode rods are of graphite which dip into the solution of sodium chloride as given in figure 4.18.

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On electrolysis chlorine is liberated at anode and passes out of the cell through a tube at the top. Sodium is liberated at cathode where it dissolves in the mercury and is removed from the cell.

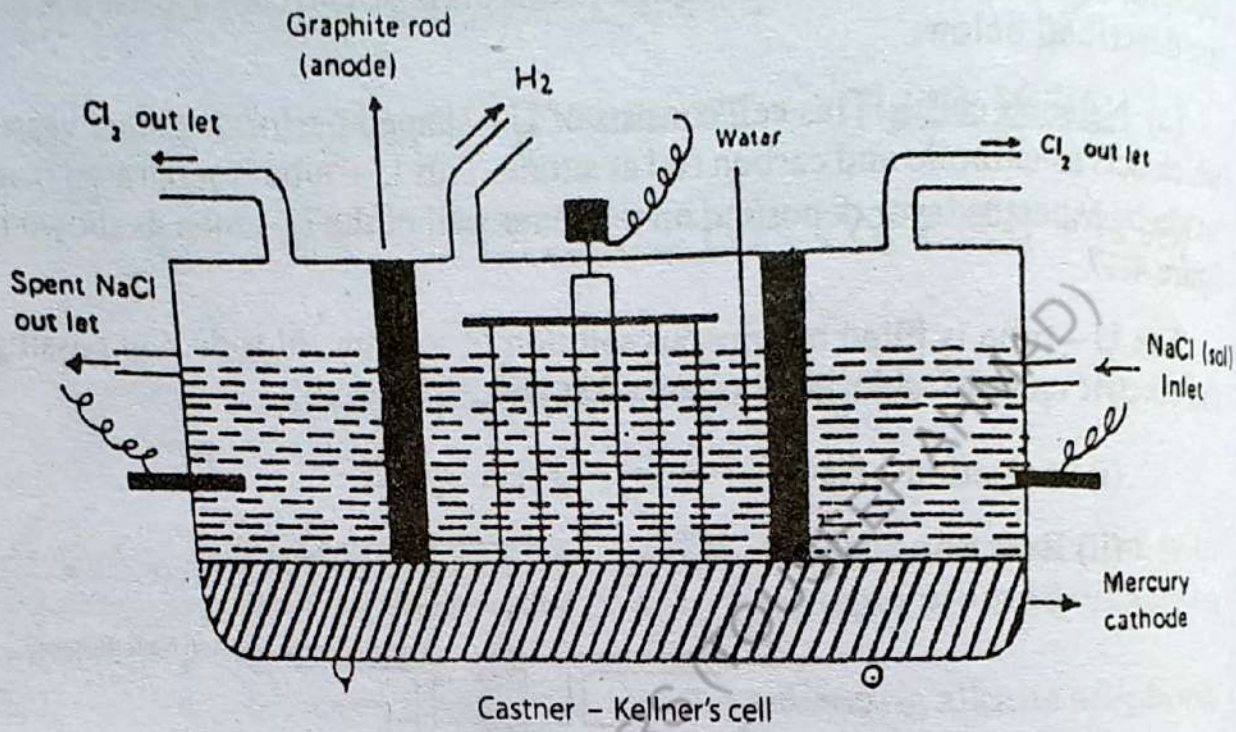

Fig. 4.18 Manufacture of chlorine

Physical properties:– It is greenish yellow gas with a pungent and characteristic choking smell. It is a typical non–metal and is fairly soluble in water. It boils at $-34^{o}C$ and melts at $-101^{o}C$. It is poisonous gas which has irritating effect on nose, throat and lungs. It has corrosive action on the mucous-membrance. Its density is 3.214 gm/l at S.T.P and its electronegativity is 3.0. Oxidation states are different such as -1, $+1$, $+3$, $+5$ and $+7$.

Chemical properties:– Chlorine is very reactive element and it readily combines with non–metals and metals except N_2, O_2 and carbon. The reactions of chlorine are divided into following types:

(i) **Oxidation Reactions:–** It is active oxidant because it has the capacity to gain one electron and hence oxidizes most of the substances.

$$Zn^{o} + Cl_2^{o} \longrightarrow Zn^{+2}Cl^{-1}$$

$$Cu^{o} + Cl_2^{o} \longrightarrow Cu^{+2}Cl_2^{(-1)_2}$$

$$P^{o} + 5Cl_2^{o} \longrightarrow 2P^{+5}Cl_5^{(-1)_5}$$

$$H_2^{o} + Cl_2^{o} \longrightarrow 2H^{+1}Cl^{-1}$$

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(ii) **Addition Reactions:–** Chlorine directly combines with certain compounds to form addition products such reactions are called as addition reactions.

$$CH_2 = CH_2 + Cl_2 \longrightarrow \underset{Cl}{CH_2} - \underset{Cl}{CH_2}$$

$$CO + Cl_2 \longrightarrow COCl_2$$

$$SO_2 + Cl_2 \longrightarrow SO_2Cl_2$$

(iii) **Substitution Reactions:–** Chlorine replaces one or more atoms from other compounds such reactions are called as substitution reactions.

$$H_2S + Cl_2 \longrightarrow 2HCl + S$$

$$2KI + Cl_2 \longrightarrow 2KCl + I_2$$

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$$

(iv) **Auto–Oxidation and Reduction Reactions:–** Chlorine reacts with water to form hydrochloric acid and hypochlorous acid. In this reaction, chlorine oxidizes as well reduces hence it is known as self oxidation–reduction reaction or auto–oxidation–reduction reaction.

$$Cl_2^0 + H_2^{+1}O^{-2} \longrightarrow H^{+1}Cl^{-1} + H^{+1}O^{-2}Cl^{+1}$$

Hypochlorous acid

Solution of chlorine in water is strong oxidizing agent and in this solution HOCl usually acts as oxidizing agent. This is because in HOCl, chlorine has an oxidation number +1 and has a strong attraction for electrons. The bleaching action of chlorine is also due to same reason, i.e first of all chlorine forms hypochlorous acid (HOCl) with water which then oxidizes coloured compounds to colourless compounds.

Importance:– The production and consumption of chlorine on large scale, make it one of the most important products of chemical industry and national economy. It is used in the manufacture of Organic compounds just like CCl_4 and $CHCl_3$ which are organic solvents. It is also used in the manufacture of vinyl chloride which is used in the preparation of plastic PVC. Chloro carbon preparations, such as DDT and hexa chloro–cyclohexane are effective pesticides and various synthetic products such as rubber etc.

Chlorine is also used as bleaching agent for cotton, rayon, wood–pulp etc. It is used in sterilizing of drinking water and disinfecting drainage. It is also used in layer test for detection of Br and I.

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ASSIGNMENT

1. How many blocks of elements are there? Define p – block elements.

2. Explain why physical properties change down the group and what are group trends?

3. How many metals, nonmetals, gases, liquids and solids are there in "p – block"? Name at least two gases of this block?

4. Describe the group trends of following properties in "p – block"

   (i) Atomic radii (ii) Ionic radii (iii) Electronegativity (iv) Ionization potential (v) Electro positivity.

5. What is allotropy? Describe the different allotropic forms of carbon and sulphur.

6. Describe the structure of diamond and graphite?

7. What is rhombic sulphur? Show its structure with different views.

8. What is plastic sulphur? Why is it elastic?

9. Describe the chemistry of Aluminium

10. In what forms, the corundum occurs in Pakistan? Also mention the different localities of its occurrence.

11. How is bauxite purified ? Give at least three methods for the purification of bauxite.

12. Write short notes on:

    (i) H_2S (ii) Boric acid (iii) Borax (iv) Alum

13. Describe the commercial preparation of chlorine.

14. Explain the working of Nelson and Castner – Kellner cells.

15. Explain the auto – oxidation and reduction of chlorine.

16. Discuss the importance of following:

    (i) Cl_2 (ii) HNO_3 (iii) H_2SO_4

17. How sulphuric acid is obtained by contact method?

18. Show that H_2SO_4 acts as:

    (i) Acid (ii) Oxidizing agent (iii) Dehydrating agent

19. Prove that HNO_3 is a strong oxidant.

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20. Write down the structures of HNO_3 and H_2SO_4 in different states.
21. What are lead pigments? Describe them in detail.
22. Explain the following:

(i) Ionization potential decreases from top to bottom in a group.

(ii) Electropositivity increases from top to bottom in a group.

(iii) Diamond is hardest substance.

(iv) Graphite is a good conductor of electricity.

(v) Atomic size of S is bigger than O.

(vi) Boiling point and viscosity of H_2SO_4 are high.

23. What happens when:

(i) Carbon monoxide is treated with chlorine.

(ii) Nitric acid is treated with sodium hydroxide.

(iii) Carbon is treated with conc: H_2SO_4.

(iv) Litharge is heated with excess of air.

(v) Hydrogen sulphide is treated with bromine.

(vi) Aluminium is reacted with sodium hydroxide.

24. Complete the following equations:

(i) $Al + H_2SO_4 \xrightarrow{dil} Al_2(SO_4)_3 + ------$

(ii) $Al + H_2SO_4 \xrightarrow{conc} Al_2(SO_4)_3 + ---- + ------$

(iii) $H_3BO_3 + NaOH \longrightarrow -------- + H_2O$

(iv) $SO_2 + Cl_2 \longrightarrow ----------$

(v) $Cu + HNO_3 \xrightarrow{conc} ------ + ------ + ------$

(vi) $Cu + HNO_3 \xrightarrow{dil} ------ + ------ + -------$

(vii) $Zn + H_2SO_4 \xrightarrow{dil} ------ + --------$

(viii) $Zn + H_2SO_4 \xrightarrow{90\%} ------- + ---- + ----$

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CHAPTER 5

d – BLOCK ELEMENTS (TRANSITION ELEMENTS)

5.1 INTRODUCTION

The elements which have partially filled d – orbitals either in the ground state of the free atom or in one or more of their ions, are called d – block elements. They are also called transition elements because they show their properties which are transitional between highly reactive and strong electro-positive elements of s – block elements which form ionic – compounds and p – block elements which form largely covalent compounds.

The transition elements do not only include d – block elements but also the f – block, in which f – orbitals are partially filled. The d – block elements consist of the following three series of ten elements each:

(i) From scandium, Sc (z = 21) to zinc, Zn (z = 30);

(ii) From yttrium, Y (z = 39) to cadmium, Cd (Z = 48); and

(iii) From lanthanum, La (z = 57) to mercury, Hg (z = 80) omitting lanthanides (rare – earth elements).

The f – block elements constitute two series which are:

(i) From cerium, Ce (Z = 58) to Lutetium, Lu (z = 71) which are called lanthanides; and

(ii) From Actinium, Ac (z = 89) to lawrencium, Lr (z = 103) which are called actinides.

The d – block elements are some times called the outer transition elements and the f – block elements, the inner transition elements. In this chapter we shall study only the first series of d – block elements.

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5.2 OCCURRENCE OF THE TRANSITION ELEMENTS IN PAKISTAN

A number of minerals containing iron, chromium, manganese and copper have been found in Pakistan especially in the provinces of Khyber Pakhtunkhuwah and Baluchistan.

The deposits of haematite (an iron ore) are found in Kohat district at Mazari Tang and in Hazara district at Langrial. Magnetite deposits are found in Chagai district in Baluchistan and in Chitral state, and sedimentary iron deposits are found in Kalabagh area. Chromium ore, the chromite has been found in Baluchistan. Large deposits of copper ores are found in Zhob Pishin, Loralai, Chagai districts, in North Waziristan agency, Gilgit, Dir and Chitral.

5.3 GENERAL CHARACTERISTICS

(i) <u>Electronic Configuration:–</u> The electronic configuration of the first series of the d–block elements consisting of ten elements is shown below:

Scandium, Sc, $z=21=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^1, 4s^2$

Titanium, Ti, $z=22=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^2, 4s^2$

Vanadium, V, $z=23=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^3, 4s^2$

Chromium, Cr, $z=24=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$

Manganese, Mn, $z=25=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^2$

Iron, Fe, $z=26=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6, 4s^2$

Cobalt, Co, $z=27=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^7, 4s^2$

Nickel, Ni, $z=28=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^8, 4s^2$

Copper, Cu, $z=29=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^1$

Zinc, Zn, $z=30=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2$

From the electronic configuration of the first series of the d–block (Transition) elements, it is learnt that the differentiating electron enters 3d orbital of the penultimate orbit, and therefore, the outer most orbit (4s) remains with the same number of electrons in their atoms except Cr and Cu. In Cr and Cu atoms, the 4s electron jumps to 3d orbital, which is due to the additional stability when d-orbitals are either half–filled or completely filled.

Since the outer most shell of these elements contains the same number of electrons in general, one can expect that these elements may have most of their

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physical and chemical properties in common. Thus all the transition elements are typical metals. They are brittle and good conductor of heat and electricity. Some of the physical properties are shown in table 5.1

Table 5.1
Physical properties of the first series of 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 °A (covalent radii)	1.44	1.32	1.22	1.17	1.17	1.17	1.16	1.15	1.17	1.25
First ionization potential (ev)	6.56	6.83	6.74	6.76	7.43	7.89	7.86	7.63	7.72	9.4
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

(ii) Size (Atomic or Covalent Radii):– The atomic or covalent radii of the transition elements decrease to a small extent from Sc to Zn as their atomic number increases. It is because there is a continuous increase of the nuclear charge without increasing the number of shells. The result of this gives greater attraction of electrons towards the nucleus and a contraction in size occurs. These elements are smaller than s – block elements.

(iii) Ionization Potential:– The ionization potential values (i.e., the amount of energy required to remove an electron from an isolated atom in its gaseous state) of the transition elements are intermediate between those of s – block and p – block elements. This suggests that these elements are less reactive than Groups I and II (i.e s – block) elements and are more electropositive or more reactive than p – block elements. This property also suggests that these elements may form either ionic or covalent compounds depending on the conditions. Generally, their compounds are ionic in their lower oxidation states and covalent in higher oxidation states.

(iv) Melting And Boiling Points:– Both the melting and boiling points of the elements are very high, except zinc, where the d – orbitals are completely filled. These higher values are due to small atomic radii of the elements which give strong inter atomic attraction. Thus the first series of d – block elements are hard and have high melting and boiling points.

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(v) **Variable Oxidation States:–** The transition elements show variable oxidation states in their compounds. This variation is due to the very small energy difference in between 3d and 4s orbitals. As a result, electrons of 3d as well as of 4s take part in the bond formation. The oxidation states of the elements are shown in the Table 5.2. The oxidation states of the elements are related to their electronic configuration. The higher oxidation of +7 is shown by Mn in $KMnO_4$ where it is using two s, and five d electrons for bonding.

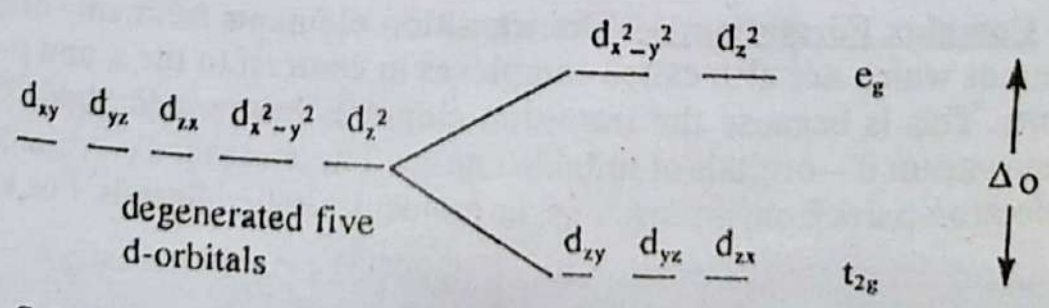
Table 5.2 Oxidation states

Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Electronic structure	d^1s^2	d^2s^2	d^3s^2	d^5s^1	d^5s^2	d^6s^2	d^7s^2	d^8s^2	$d^{10}s^1$	$d^{10}s^2$
Oxidation states				+1					+1	
		+2	+2	+2	+2	+2	+2	+2	+2	+2
	+3	+3	+3	+3	+3	+3	+3	+3		
		+4	+4	+4	+4					
			+5	+5						
				+6	+6	+6				
					+7					

(vi) **Colour:-** The transition metal complex ions are coloured (except those of zinc which are white). Crystal Field Theory explains fully the colour of the complex ions. According to Crystal Field Theory (C.F.T) the bonding between ligands and a metal ion is electrostatic. The ligands surrounding the metal ion create an electrostatic field around its d-orbitals. This field splits five degenerated d-orbitals into two sets with different energies:

(i) a higher energy pair, $d_{x^2-y^2}$ and d_{z^2} designated as e_g; and

(ii) a lower energy trio, d_{xy}, d_{yz} and d_{zx} designated as t_{2g}



Splitting of five degenerated d-orbitals into two sets e_g and t_{2g}.

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In many cases, the energy difference Δ_O between two sets (e_g and t_{2g}) of d-orbitals is equivalent to a wave length in the visible region. Thus by absorbing visible light, an electron may be able to move from lower energy set (t_{2g}) to higher energy set e_g of d-orbitals. In doing so, some of the component wave length of white light is removed, so the remaining component wave length of the light reflected or transmitted shows the colour to the viewers. For example copper, cu^{2+} ions absorb red light, hence the transmitted light gives blue colour.

(vii) **Magnetic properties:–** Many compounds of the transition elements are paramagnetic, i.e., they are attracted into a magnetic field. Paramagnetism is generally caused by the presence of unpaired electron spins in the ions and atoms of the elements.

Elements such as Fe, Co and Ni are ferromagnetic i.e., they can be magnetized.

(viii) **Catalytic Properties:–** Transition elements and some of their compounds are commonly used as catalysts in the chemical industry. Catalysts are the substances which accelerate or retard the rate of a chemical reaction. The transition elements as catalysts, in some cases, may form unstable intermediate compounds, and in other cases they provide a suitable surface areas where gases are absorbed. For example, Ni is used for the hydrogenation of vegetable oils; Fe in the manufacture of ammonia (NH_3), V_2O_5 to convert SO_2 into SO_3.

(ix) **Interstitial (Non–stoichiometric) Compounds:–** The transition elements form compounds of indefinite structure and proportion which are called interstitial or non–stoichiometric compounds. This non–stoichiometry is shown due to the variable oxidation state of the d–block elements, and also to the defects in their solid structures. Small atoms such as H,B,C and N can reside within the holes present in the crystal lattice of these elements and bear no stoichiometric composition. For example $TiH_{1.73}$. Alloys (Substances containing two or more metals) are also considered as the interstitial compounds. Examples are brass (Cu–Zn), bronze (Cu–Zn–Sn) etc.

(x) **Complex Formation:–** The transition elements form co–ordination compounds which are also called complexes in contrast to the s, and p–block elements. This is because the transition elements have small, highly charged ions, and vacant d–orbitals of suitable energy. These vacant d–orbitals accept lone electron pairs from atoms, ions, or molecules called ligands. For example

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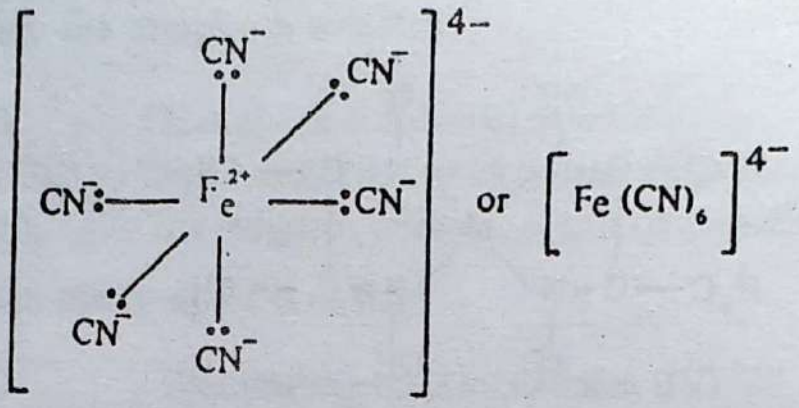
ferrocyanide which is a complex ion containing six cyanide (CN^-) ions donating their lone electron pair to the central ferrous (Fe^{2+}) ion.



(xi) **Transition Metal Complexes:–** A compound containing the complex ion or complex molecule in which the central metal atom or ion is surrounded by a number of oppositely charged ions or neutral molecules called ligands, is known a co–ordination compound or a complex. The central atom is always a transition element. The number of ligands bonded to the central atom or ion is called its co–ordination number. For example diammine cuprous $(Cu(NH_3)_2)^+$ ion, in which central atom is cuprous (Cu^+) ion and the ligand is ammonia (NH_3). The two NH_3 molecules are co–ordinating with cuprous (Cu^+) ion, hence the co–ordination number of the ion is 2.

Co–ordinating groups or ligands generally called Lewis bases, are sub-divided into two main groups – mono–or unidentate containing only one co–ordinating atom e.g., H_2O, NH_3, CN^-; NO_2^- and halides. The second group is known as poly–or multidentate containing two or more electron pair donor atoms in a molecule or an ion. Examples:

(a) COO^- – COO^-
Oxalate ion

(b) $H_2\ddot{N} - CH_2 - CH_2 - \ddot{N}H_2$
Ethylene diamine

are bidentate and the tridentate

$$H_2\ddot{N} - CH_2 - CH_2 - \ddot{N}H - CH_2 - CH_2 - \ddot{N}H_2$$

Diethylene triamine and

$$^-OOC - H_2C \diagdown \ddot{N} - CH_2 - CH_2 - \ddot{N} \diagup CH_2 - COO^-$$
$$^-OOC - H_2C \diagup \qquad\qquad \diagdown CH_2 - COO^-$$

Ethylene diamine tetra acetate (EDTA) ion is an example of a hexadentate.

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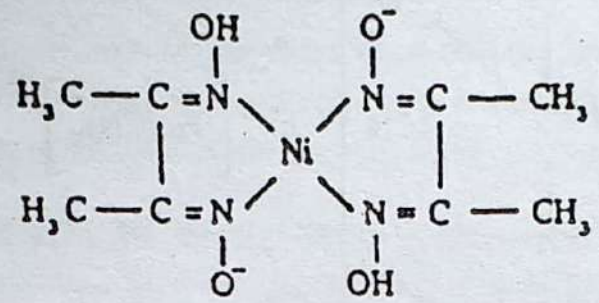
The poly or multidentates are also called chelating agents. The chelating agent on co—ordination with a central atom forms a ring structure called chelates, a Greek word meaning Crab's claw. Example is nickel dimethyl glyoximate



NOMENCLATURE OF COORDINATION COMPOUNDS (IUPAC Names of Transition Metal Complexes)

International Union of Pure and Applied Chemistry (IUPAC) recommended following rules in naming the coordination compounds:

1. As in simple ionic compounds, the cation is named first and then the anion.

2. In naming a complex ion, the names of negative ligands are written first, neutral ligands next and finally metal atom. The prefixes di-, tri-, tetra-, penta-, etc (or some times bis-, tris-, tetrakis-, pentakis-, etc for organic ligands) are used with the name of the ligand when more then one ligand of the same kind occurs within the complex ion.

3. The names of the anionic ligands are modified to end in -O. For example fluoro (F^-), chloro (Cl^-), bromo (Br^-), iodo (I^-), cyano (CN^-), nitro (NO_2^-), nitrato (NO_3^-), hydroxo (OH^-), amido (NH_2^-), oxalato ($C_2O_4^{2-}$), carbonato (CO_3^{2-}).

The names of neutral ligands usually remain unchanged. Two exceptions are water and ammonia

H_2O aquo NH_3 amine.

4. The charge of the central metal ion is indicated by a Roman numeral (I,II,III,IV etc) following the name of the metal. When the complex is either a cation or a neutral molecule, the central metal ion is written in its English name followed by the oxidation state (the charge number) in Roman numerals in parenthesis e.g., nickel (o), iron (II), copper (I) etc. When the complex ion is anionic, the

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suffix-ate is added, often to the stem of the Latin name for the metal e.g., cuperate, ferrate, stannate etc. The formal oxidation state is again shown by Roman numerals in parentheses.

Examples in which the complex is a cation:

$[Co(NH_3)_6]\ Cl_3$	Hexa amine cobalt (III) chloride.
$[Cr(NH_3)_4Cl_2]\ Cl$,	Dichlorotetra amine chromium (III) chloride.
$[Co(en)_3]\ (NO_3)_3$,	Tris (ethylene diamine) cobalt (III) nitrate.

Examples in which the complex is neutral

$[Pt\ (NH_3)_2\ Cl_4)$	Diamine tetra chloro platinum (IV)
$[Co\ (NH_3)_3\ (NO_2)_3]$	Triamine trinitro cobalt (III)

Examples in which the complex is an anion

$K_3\ [Fe(CN)_6)]$	Potassium hexacyano ferrate (III)
$K_4[Fe(CN)_6]$	Potassium hexacyano ferrate (II)
$K_3[Co(NO_2)_6]$	Potassium hexanitro cobaltate (III)

5.4 METALLURGY OF COPPER

Copper occurs both in free as well as in combined states. In combined state, it occurs mainly as the sulphide and oxide ores. The chief ores of copper are copper pyrite or chaleopyrite ($CuFeS_2$), chalocite (Cu_2S) and malachite [$CuCO_3.Cu(OH)_2$] green and azurite [$2CuCO_3\ Cu(OH)_2$] blue.

Extraction

Copper is mostly extracted from sulphide ores which contain about 6% Cu. The sulphide ore is first roasted (i.e., heated strongly in a current of air) on the hearth of a large flat furnace whereby the following changes occur:

(i) Large amount of sulphur burns to sulphur dioxide (SO_2).

(ii) Iron present oxidizes to ferrous oxide (FeO); and

(iii) Copper changes into cuprous sulphide (Cu_2S).

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

The roasted material is then mixed with sand (SiO_2) to remove iron as ferrous silicate ($FeSiO_3$) a slag which floats on the surface of the molten matte of copper. The liquid copper matte containing cuprous sulphide (Cu_2S) with

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some unreacted ferrous sulphide (FeS) and silica is oxidized in a Bessemer converter (Fig 5.1) by blowing air through. FeS is oxidized to FeO and SO_2. Ferrous oxide reacts with sand to give ferrous silicate and the blast of air converts Cu_2S partly into Cu_2O which reacts with the remaining Cu_2S to give metallic copper in its molten state:

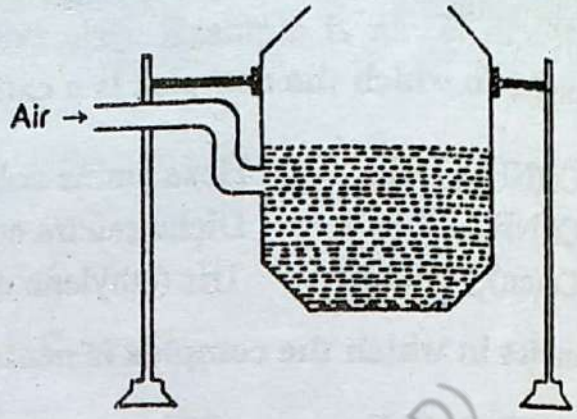

Fig. 5.1 Bessemer converter.

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

$$FeO + SiO_2 \longrightarrow FeSiO_3$$

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

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

The copper thus produced is called blister copper because, as it solidifies hidden sulphur dioxide gas and 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 may also be present. As such, the copper is not suitable particularly for electrical work so it is thus refined.

Refining of Copper:– Copper is refined by electrolysis, in which blocks of blister copper are used as anodes and thin sheets of pure copper as cathodes. The cathode plates or sheets are coated with graphite in order to remove depositing copper easily. The electrolyte is copper sulphate ($CuSO_4$), acidified with sulphuric acid (H_2SO_4). The current of 1.3 volts is used for electrolysis which helps to deposit copper only on the cathode leaving impurities which are soluble and fall to the bottom of the cell as a sludge or anode mud. The chemical reactions which occur are given as under:–

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

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

The electrolytically refined copper is 100% pure.

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5.5 CHEMISTRY OF SILVER NITRATE ($AgNO_3$)

Silver nitrate or Lunar caustic is prepared by dissolving silver metal in dilute nitric acid. On crystallization, the long crystals or sticks are formed.

$$3Ag + 4HNO_3 \longrightarrow 3AgNO_3 + NO + 2H_2O$$

Silver nitrate is readily soluble in water. It is also soluble in organic solvents such as, ethyl alcohol, pyridine etc. It decomposes at 450°C, giving out nitrogen dioxide and oxygen leaving silver as metal.

$$2AgNO_3 \xrightarrow{450^\circ C} 2Ag + 2NO_2 + O_2$$

With sodium hydroxide (NaOH), silver nitrate first forms unstable silver hydroxide (AgOH) which changes into a dark brown silver oxide (Ag_2O).

$$AgNO_3 + NaOH \longrightarrow AgOH + NaNO_3$$

$$2AgOH \longrightarrow Ag_2O + H_2O$$

With ammonia in water, silver nitrate first forms precipitates of silver oxide which in excess dissolves forming silver–ammonia complex (Diammine silver nitrate).

$$AgNO_3 + 2NH_3 \longrightarrow [Ag(NH_3)_2]NO_3$$

Diamine silver nitrate

Silver nitrate produces black spots when it comes in contact with organic substances such as skin and cellulose.

Silver nitrate is used in laboratory as a reagent for the detection and determination of halides. It produces white precipitates of AgCl with chloride ions (Cl^-), light yellow precipitates of AgBr with bromide ions (Br^-) and yellow precipitates of AgI with iodide ions (I^-)

It is also widely used in photography and medicines.

5.6 COPPER SULPHATE ($CuSO_4.5H_2O$)

Cupric sulphate or copper sulphate which is also called blue vitriol or blue stone, is prepared by reacting metallic copper with dilute sulphuric acid in the presence of air.

$$2Cu + 2H_2SO_4 + O_2 \longrightarrow 2CuSO_4 + 2H_2O$$

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It is also prepared by dissolving copper oxide (CuO) or copper carbonate ($CuCO_3$) in dilute sulphuric acid and crystallizing.

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

$$CuCO_3 + H_2SO_4 \longrightarrow CuSO_4 + CO_2 + H_2O$$

Copper sulphate crystalline is blue in colour which on heating loses all its water of crystallization slowly changing into colourless form (anhydrous).

$$\underset{\text{Blue(hydrated)}}{CuSO_4.5H_2O} \xrightarrow{230^oC} \underset{\text{White(anhydrous)}}{CuSO_4} + 5H_2O$$

Copper sulphate is very soluble in water but insoluble in alcohol and is precipitated in small crystals from its aqueous solutions by the addition of ethyl alcohol.

It liberates iodine precipitating white cuprous iodide (Cu_2I_2) on addition to potassium iodide solution.

$$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$$

With aqueous ammonia, copper sulphate forms a pale blue gelatinous precipitate of cupric hydroxide [$Cu(OH)_2$], the latter dissolves very readily in excess aqueous ammonia (NH_4OH). forming the deep – blue complex $Cu(NH_3)_4$

$$CuSO_4 + 2NH_3 + 2H_2O \xrightarrow{\text{small}} Cu(OH)_2 + (NH_4)_2SO_4$$

$$CuSO_4 + 4NH_3 \xrightarrow{\text{excess}} \underset{\text{Cuperic tetramine solution}}{[Cu(NH_3)_4]SO_4}$$

Copper sulphate is used in copper plating, in electric cells, in making green pigments, as a mordant in dyeing and with milk of lime to kill fungus and molds.

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5.7 POTASSIUM CHROMATE, (K_2CrO_4)

Potassium chromate can be prepared by strongly heating a mixture of powdered chromite ore ($FeO.Cr_2O_3$) and potassium carbonate in air.

$$4FeO.Cr_2O_3 + 8K_2CO_3 + 7O_2 \longrightarrow 2Fe_2O_3 + 8K_2CrO_4 + 8CO_2$$

It can also be prepared by boiling chromium oxide with potassium hydroxide and bromine water when a yellow solution of potassium chromate is formed. It is then crystallized out on evaporation.

$$Cr_2O_3 + 10KOH + 3Br_2 \longrightarrow 2K_2CrO_4 + 6KBr + 5H_2O$$

Potassium chromate is a lemon – yellow crystalline solid substance. It is very soluble in water and gives a yellow coloured solution. The yellow colour of the potassium chromate solution changes into red on addition of an acid such as sulphuric acid due to the formation of dichromate ion ($Cr_2O_7^{2-}$).

$$\underset{\text{Chromate ion}}{2CrO_4^{-2}} + 2H^+ \rightleftharpoons \underset{\text{Dichromate ion}}{Cr_2O_7^{2-}} + H_2O$$

5.8 POTASSIUM DICHROMATE ($K_2Cr_2O_7$)

Potassium dichromate is prepared from potassium chromate (K_2CrO_4) by adding a calculated amount of sulphuric acid into its saturated solution. It is then crystallized out on evaporation.

$$2K_2CrO_4 + H_2SO_4 \longrightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$$

It can also be prepared by treating the saturated solution of sodium dichromate with the calculated quantity of potassium chloride. Potassium dichromate being less soluble, separates out from the solution as orange – red crystals.

$$Na_2Cr_2O_7 + 2KCl \longrightarrow 2NaCl + K_2Cr_2O_7$$

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Potassium dichromate is moderately soluble in water and gives an orange colour in solution. The colour changes to yellow on the addition of an alkali due to the formation of potassium chromate

$$K_2Cr_2O_7 + 2KOH \longrightarrow 2K_2CrO_4 + H_2O.$$

On addition of conc. H_2SO_4 to the cold solution of potassium dichromate, red crystals of chromic oxide (CrO_3) separate out.

$$K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2CrO_3 + H_2O$$

It acts as a strong oxidizing agent. It oxidizes ferrous (Fe^{2+}) salts to ferric salts and liberates iodine from potassium iodide in the presence of dil H_2SO_4

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$$

$$6KI + K_2Cr_2O_7 + 7H_2SO_4 \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O$$

On heating potassium dichromate with solid potassium chloride (KCl) in the presence of concentrated sulphuric acid, it gives reddish brown vapours of chromyl chloride (CrO_2Cl_2).

$$K_2Cr_2O_7 + 4KCl + 6H_2SO_4 \longrightarrow 6KHSO_4 + 2CrO_2Cl_2 + 3H_2O$$

Potassium dichromate is used as a powerful oxidizing agent in the volumetric determination of ferrous iron, in preparation of chromium compounds such as chrome alum, chrome yellow, chrome red etc., which are used as pigments and in the preparation of certain organic compounds such as acetaldehyde and ethyl alcohol.

5.9 POTASSIUM PERMANGANATE ($KMnO_4$)

Potassium permanganate is prepared on large scale from manganese dioxide (MnO_2). Manganese dioxide is fused with potassium hydroxide in the presence of air to produce the green coloured potassium manganate (K_2MnO_4).

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

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Potassium manganate is extracted with water and the solution is treated either with chlorine or ozone to get the oxidized product potassium permanganate

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$$

$$2K_2MnO_4 + H_2O + O_3 \longrightarrow 2KMnO_4 + 2KOH + O_2$$

Potassium permanganate can also be prepared from potassium manganate by electrolytic oxidation

$$2K_2MnO_4 + 2H_2O \longrightarrow 2KMnO_4 + 2KOH + H_2$$

Potassium permanganate is the most important chemical compound of manganese. It is a deep purple crystalline solid and is readily soluble in water giving deep pink colour. On heating, it liberates oxygen and forms potassium manganate and manganese dioxide.

$$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$$

Potassium permanganate is a powerful oxidizing agent and is used for this purpose in acidic, alkaline or neutral solutions. In acidic solution permanganate ion accepts five electrons to form manganese (Mn^{2+}) ion, whereas in alkaline or neutral solutions, it accepts three electrons to form manganese dioxide (MnO_2).

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

Basic or neutral medium

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

Potassium permanganate oxidizes ferrous (Fe^{2+}) salts to ferric (Fe^{3+}) salts, nitrites (NO_2^-) to nitrates (NO_3^-), oxalic acid ($H_2C_2O_4$) to carbon dioxide, hydrogen peroxide (H_2O_2) to oxygen and potassium iodide (KI) to iodine (I_2) in acidic medium.

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

$$2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$$

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$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

$$2MnO_4^- + 5H_2O_2 + 6H^+ \longrightarrow 2Mn^{2+} + 5O_2 + 8H_2O$$

$$2MnO_4^- + 10KI + 16H^+ \longrightarrow 2Mn^{2+} + 10K^+ + 5I_2 + 8H_2O$$

In neutral or alkaline medium permanganate oxidizes potassium iodide to potassium iodate (KIO_3) and hydrogen peroxide to oxygen and itself reduces to manganese dioxide.

$$2KMnO_4 + H_2O + KI \xrightarrow[\text{medium}]{\text{Alkaline}} 2KOH + 2MnO_2 + KIO_3$$

$$2KMnO_4 + 3H_2O_2 \xrightarrow[\text{medium}]{\text{Neutral}} 2MnO_2 + 2KOH + 3O_2 + 2H_2O$$

Potassium permanganate is used as an oxidizing agent and as a disinfectant.

5.10 CORROSION AND ITS PREVENTION

The term corrosion is defined as a harmful and an undesirable reaction of a metal material as a result of exposure to atmosphere or any chemical agent. Almost all metals except noble metals, such as Ag, Au, and Pt., show great tendency to corrode with different rates when exposed to atmosphere or water or any reactive liquid. For example iron acquires brown flaky surface called rust, copper surfaces become covered with a layer of green coloured substances, cells made of zinc get white powder deposits on their surface often leading to holes in the zinc case.

When corrosion in a metal is due to the action of atmosphere, it is known as atmospheric corrosion, and when the corrosion is due to the reaction of a liquid on a metal, it is termed as corrosion in liquid. Different metals corrode at different rates as for example, sodium and potassium metals tarnish immediately on exposure to air, calcium corrodes quickly, iron corrodes slowly and tin, lead and copper corrode very slowly.

It has been learnt through experiments that due to corrosion one – fifth of the iron in use is lost annually and it also reduces very much the strength of iron structure. Since iron and steel are very widely used metals, number of various

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methods have been used to prevent the corrosion. Below are enlisted some of the methods:

(i) **Protective Metallic Coating:–** The iron or steel can be protected from corrosion by coating with another metal as in galvanized iron i.e., covering with zinc, tin plating (Tin covered).

(ii) **Electroplating:–** Noble and bare metals are used for electroplating on any desired metal.

(iii) **Alloying of Metals:–** One of the most important way of protection of a metal from corrosion is by mixing of it with another metal i.e., alloy formation e.g., stainless steel is an alloy of Fe, Cr and Ni.

(iv) **Coating with Non–Metallic Material:** Metals can be protected from corrision by using various kinds of non–metallic materials such as paints, oils, grease, plastic emulsion etc.

5.11 STAINLESS STEEL

The term stainless steel is used to those iron–based alloys which show resistance to corrosion. They are formed by the addition of chromium or chromium and nickel in steel.

There are three main types of stainless steel which have different percentages of base metals and are listed below:

(i) Stainless steel containing 13% Cr and 0.1 to 0.4% C

(ii) Stainless steel containing 17% Cr and 2% Ni and

(iii) Stainless steel containing 18% Cr and 6% Ni

All the types of stainless steel are corrosion resistant alloys and are oxidizable only to such a slight degree that a very fine film of oxide is formed on the material surface which resist further corrosion. This fine coating of oxide is so thin that the colour and appearance of the basic material look like unchanged.

Stainless steels are used in the production of house hold utensils, cutlery, articles for decoration and its application in industry is unlimited.

5.12 SILVERING OF MIRRORS

The term silvering was formerly applied to the formation of coating of an amalgam (an alloy of tin and mercury) on a glass for giving it the properties of a mirror. Now a days, mostly a pure silver metal is deposited on the glass by reduction instead of old amalgamation process.

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The silvering of mirror was originated by Liebig in 1938 when he heated an aldehyde with an ammoniacal solution of silver nitrate in a glass tube and observed a brilliant deposit of metallic silver on the surface of the glass. A method for glass mirroring with silver is given below:

Clean the glass sheet with ammonia and wipe with a wet chamois. Then prepare a solution of silver nitrate in distilled water to which add dilute aqueous ammonia slowly until the brown precipitate of silver oxide is redissolved. In another beaker prepare solution of Rochelle salt (Sodium potassium tartrate) in water. This solution is called ammonical $AgNO_3$ solution. To this solution add glucose which acts as a reducing agent and immediately pour the solution on the middle of the glass to be silvered. It will spread itself over the surface of the glass sheet. The reduction immediately begins as follows:

$$AgNO_3 + NH_4OH \longrightarrow \underset{\text{White precipitate}}{AgOH} + NH_4NO_3$$

$$AgOH + 2NH_4OH \longrightarrow \underset{\text{Diamine silver (I) hydroxide}}{[Ag(NH_3)_2]OH} + 2H_2O$$

$$[2Ag(NH_3)_2]OH \longrightarrow Ag_2O + H_2O + 4NH_3\uparrow$$

$$\begin{array}{l} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ CHO \end{array} + Ag_2O \longrightarrow \begin{array}{l} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ COOH \end{array} + 2Ag$$

Photography:– The art of developing a picture on a photographic plate or film by means of exposure to light is called photography.

A photographic film or a plate consists of an emulsion of silver bromide and silver iodide suspended in gelatin coated to a cellulose acetate sheet. Silver bromide (AgBr), is sensitive to light and undergoes a photochemical decomposition. Sulphur, which is a constituent of gelatin increases the sensitivity of silver bromide.

On exposure to light some of the grains of silver bromide in the photographic plate undergo reduction to metallic silver. This film can then be developed by organic reducing agents such as metal hydroquinone or pyrogallol, called

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developer. This reduces the sensitized silver bromide to silver metal, whereas the unsensistized silver bromide grains remain unchanged. By this technique the developed film reproduces the pattern of the light that exposed it. This film is called the negative because it is blackened with metallic silver where the light in the original image was most intense.

The negative film is then fixed by immersing it in the fixing bath containing the solution of sodium thiosulphate ($Na_2S_2O_3 5H_2O$) called 'hypo' which removes the excess of undeveloped silver salts forming soluble silver thiosulphate complex.

$$AgBr + 2Na_2S_2O_3 \longrightarrow Ag(S_2O_3)_2^{3-} + Br^{-1} + 4Na^{+1}$$

A positive print can be made by exposing photographic paper containing a coat of silver—bromide and silver iodide emulsion, to light that passes through the superimposed negative print. The exposed paper is finally developed and fixed in a similar manner.

5.13 TIN PLATING

Tin plating is an art of making a coat of metallic tin on baser metals such as iron and copper for their protection from corrosion and poisoning. Tin plated iron sheets are thus used extensively for making cooking oil containers and all types of containers. The household utensils of copper and brass are protected from poisoning by tin plating. The process of tinning may be carried by mechanical or electrolytic method.

In the mechanical process the iron sheets or mild steel are first thoroughly cleaned by dipping in warm dilute sulphuric acid to remove the oxide film. The sheets are then washed with water and after drying, dipped in the bath containing molten tin. The sheets are then rolled to remove superfluous tin. The copper and brass utensils are first heated and then rubbed with some quantity of ammonium chloride (NH_4Cl), to remove the oxide film. A little of tin metal is rubbed over the hot surface and after sprinkling some ammonium chloride, the surface of the utensils are polished with a rag until a uniform layer of tin is obtained.

In the electrolytic process, the iron sheets after cleaning, washing and drying are suspended into a bath containing a mixture of stannous chloride and hydrochloric acid. Pure tin is made the anode and the iron sheets are made the cathode. On passing the current through the bath, tin starts depositing on the iron sheets in amounts corresponding to the tin going into the solution. Thus iron sheets are tinned electrolytically.

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ASSIGNMENT

1. Give the electronic configuration of the following elements:

   (a) Scandium (21) (b) Vanadium (23) (c) Manganese (25) (d) Iron (26)

2. Give the general characteristics of the transition elements.

3. Name the following compounds and give the oxidation number of chromium and manganese in each:

   (i) $CrCl_3$ (ii) H_2CrO_4 (iii) $Cr_2(SO_4)_3$ (iv) MnO_2 (v) MnS (vi) $KMnO_4$

4. Name the following compounds:

   $K_4[Fe(CN)_6]$; $Na_3[Co(NO\ )_6]$; $[Cr(NH_3)_3Cl_3]$;

   $[Co(H_2O)_6]SO_4$; $[Cu(NH_3)_4]SO_4$

5. Water and ammonia molecules act as ligands but H_3O^+ and NH_4^+ do not act as ligands, explain.

6. Give the conditions favouring the rusting of iron. How can corrosion be prevented?

7. Describe the metallurgy of copper.

8. What do you know about the chemistry of the following compounds:

   (i) $AgNO_3$ (ii) $CuSO_4 . 5H_2O$ (iii) K_2CrO_4, (iv) $K_2Cr_2O_7$

9. Write short notes on:

   (i) Silvering of mirrors (ii) Photography (iii) Tin plating

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PART II

ORGANIC CHEMISTRY

CHAPTER 6

INTRODUCTION TO ORGANIC CHEMISTRY

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Organic chemistry is the study of properties and structure of compounds which contain carbon hydrogen bonds. Previously the term "Organic" was used only for those substances which were obtained from animal or plant sources and could not be prepared in the laboratory. It was thought that a vital force was required for their production. This theory was rejected in 19th century by experimental observations of a number of scientists.

For example in Germany, a young chemist Wohler in 1828, prepared urea in the laboratory from inorganic material, ammonium cyanate by boiling it with water. Urea is a waste product of metabolism and is excreted through urine and hence it is a typical organic compound.

$$NH_4CNO \xrightarrow[\text{(boil)}]{H_2O} H_2N - \overset{\overset{\displaystyle O}{\|}}{C} - NH_2$$

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Thus the vital force theory (vital = life) i.e. organic compounds could not be made without living cells was discarded. Now a days many organic compounds are made from inorganic materials. A vast number of organic compounds previously isolated from plant and animal sources have been synthesized. For example, rubber was isolated in the form of latex from rubber plant. Today rubber is manufactured largely from synthetic materials

Kekule in 1865 proved that the valency of carbon is four in carbon compounds. He also established chain structures of the carbon compounds and ring structures of benzene, a typical organic compound. The vast number of organic compounds prepared over a short period and unique nature of such compounds necessitated treatments made the study of organic compounds separately from necessitated the study of organic compounds separately from compounds derived from rest of the elements.

In view of the unique properties of carbon compounds, these are studied separately from inorganic materials. However, some oxides of carbon eg: carbon monoxide, carbon dioxide and those complex compounds which contain metal, are excluded from this branch. Although the earth's crust contains only 0.027% carbon, millions of organic compounds are known because of the ability of carbon atoms to bond itself to other carbon atoms forming long chains, branched chains, rings and compounds with chains and rings together. This property is called catenation i.e: the ability of an element to bond itself with its own atoms. Other elements also exhibit the property of catenation but carbon does it to a greater extent. Silicon has same tendency to catenate, but it is insignificant as compared to catenation ability of carbon.

6.1 NATURAL SOURCES OF ORGANIC COMPOUNDS

The mineral sources of organic compounds are coal, natural gas and petroleum. Plants are also among natural sources of important organic compounds.

Coal:– The bituminous or soft coal is a very important source of organic compounds. This when subjected to destructive distillation, products of industrial importance are obtained.

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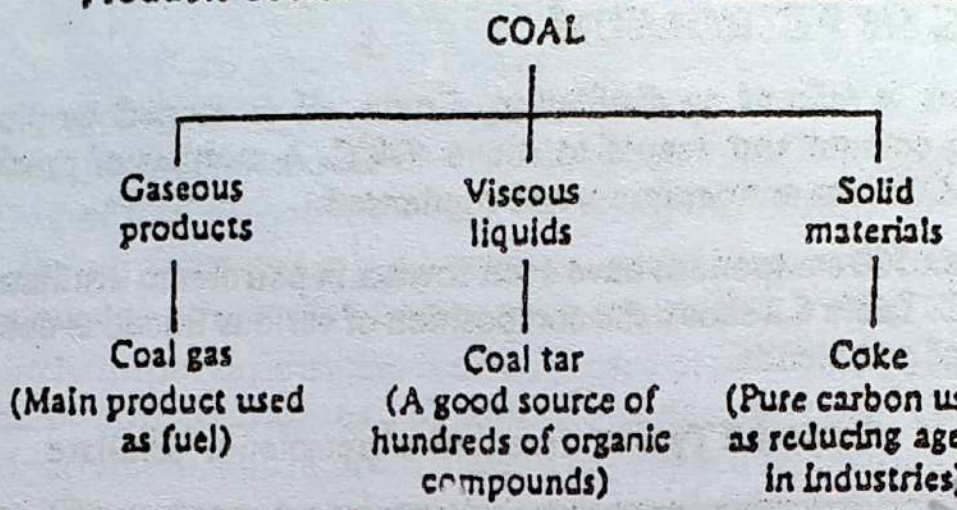
Table 6.1

Products obtained from destructive distillation of coal



Fractional Distillation Of Coal–Tar:– When coal is destructively distilled, four principal fractions are obtained, viz: coal gas, coal tar, coke and ammonical liquors. Of these coal gas which consists mainly of methane and hydrogen is used as a fuel, while coke a form of carbon, is used in the manufacture of iron and steel industry. The composition of coal tar varies depending on the nature of the coal. However, coal is composed of various aromatic hydrocarbons.

These components are separated by fractional distillation of coal tar. It has been calculated that 100 Kg of coal tar yield 1–2 Kg of benzene.

Natural Gas:– Natural gas is also one of the important sources of simple organic compounds specially like methane. It is found at Sui in Pakistan and known as Sui Gas. It is also found at other places.

Composition of Sui Gas

Methane	94.60%
Ethane	1.05%
Propane	0.28%
Butane	0.17%
Nitrogen	3.88%
Carbon dioxide	0.02%

6.2 Petroleum: Petroleum means rock oil in Latin. It is usually found below the surface of earth. It is a viscous liquid comprising of components with different boiling points. It contains alkanes, alkenes, cyclo-alkanes, aromatic hydrocarbons, besides, some inorganic compounds. It is also called crude oil. When subjected to fractional

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distillation, several groups of products are obtained. This is known as refining of petroleum.

REFINING OF PETROLEUM

Petroleum is refined by distillation. Crude oil is carried by pipes to a fractionating column and heated to above 400°C. A number of products are obtained at different temperatures and condensed.

More than 500 compounds have been found in petroleum distillate boiling below 200°C. Table 6.2 shows the composition of various fractions obtained by distillation of petroleum.

Table 6.2 Typical fractions of petroleum distillate

Boiling range of fraction	No. of C–atoms	Nature and use
Below 20°C	C_1-C_4	Natural gas, bottled gas, petrochemicals
20–60°C	C_3-C_6	Petroleum ether, solvents
60–120°C	C_6-C_7	Ligroin, solvents (Naptha)
40–200°C	C_5-C_{10}	Gasoline
175–325°C	$C_{12}-C_{18}$	Kerosene and jet fuel
250–400°C	C_{12}–higher	Gas oil, fuel oil, diesel oil
Nonvolatile liquids	C_{20}–higher	Refine mineral/ lubricating oil, grease
Nonvolatile solids	C_{20}–higher	Paraffin wax, asphalt and tar

Gasoline or petrol is a mixture of hexane (C_6H_{14}) and heptane (C_7H_{16}). Since the demand of gasoline is increasing due to its increased use as a fuel for automobiles, airplanes etc. The cracking is employed to obtain increased quantities of petrol from crude oil.

REFORMING OF PETROLEUM

Knocking is a sharp metallic sound produced in the internal combustion engine. Its cause is gasoline of low octane number. The

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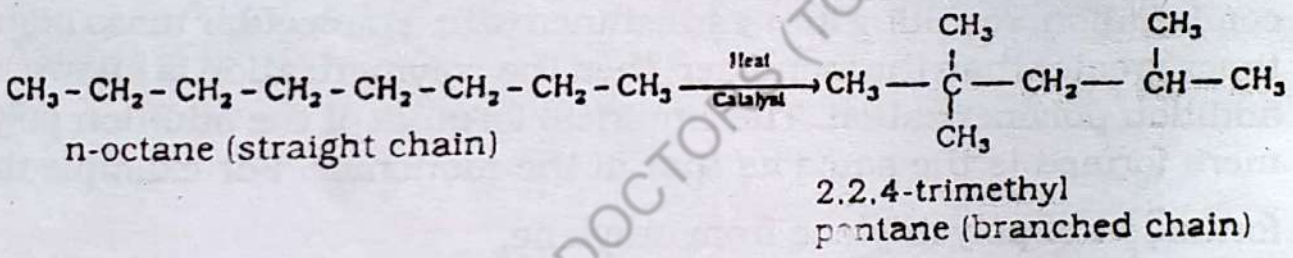
octane number of gasoline is improved by reforming, a process somewhat similar to cracking, which again brings about the conversion of straight chain alkanes into branched chain alkanes. If the petrol used is of such quality that its vapour mixed with air can ignite prior to high compression on passing of firing spark, the energy produced by burning of fuel is not utilized in moving the piston. By the use of catalyst, the straight chain hydrocarbon molecules may be reformed to other molecules which give better performance as motor fuels. This is particularly important in the manufacture of aviation gasoline. In the presence of compounds called antiknock compounds, the knocking can be decreased. Value of the fuel is expressed in terms of its octane number. The octane number of gasoline may also be increased by adding tetraethyl lead $Pb(C_2H_5)_4$ as knock inhibitor, which moderates the explosions in the cylinders of the engine. But fuels containing $Pb(C_2H_5)_4$, pollute the atmosphere with lead.

Example:



6.3 CRACKING

The fractional distillation of petroleum yields only about 20% petrol. Additional quantities of petrol are obtained by cracking of higher boiling fractions. Cracking involves splitting the larger molecules of the less volatile fractions into smaller molecules of greater volatility by subjecting them to high temperatures and pressures in the presence of catalyst. Besides increasing the yield of petrol from petroleum, cracking also yields large amounts of useful by products such as ethene, propene, butene and benzene. These are used for making drugs, plastics, detergents, synthetic fibers, synthetic rubber, fertilizers, weed killers and important chemicals like ethanol, phenol and acetone.

Example: When propane is heated to temperature between 700–800°C in the absence of air, it is cracked to give propene, ethene, methane and some hydrogen gas.

$$\underset{\text{Propane}}{2(CH_3-CH_2-CH_3)} \xrightarrow[\text{absence of air}]{700\text{-}800^\circ C} \underset{\text{Propene}}{CH_3-CH=CH_2} + \underset{\text{Ethene}}{CH_2=CH_2} + \underset{\text{Methane}}{CH_4} + H_2$$

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With high members of alkane, the cracking reaction becomes complex. Consider for example the cracking of heavy gas oil in the presence of zeolite as catalyst.

$$\underset{\text{Heavy gas oil}}{C_7H_{15}(C_{15}H_{30})C_7H_{15}} \xrightarrow[\text{zeolite}]{500-550^\circ C} \underset{\text{n-heptane}}{C_7H_{16}} + \underset{\text{1-heptene}}{C_7H_{14}} + \underset{\text{This further cracks into smaller molecules.}}{C_{15}H_{30}}$$

6.4 POLYMERIZATION

Polymerization is defined as the process in which many small molecules join together to form very large molecules. It is a self addition reaction.

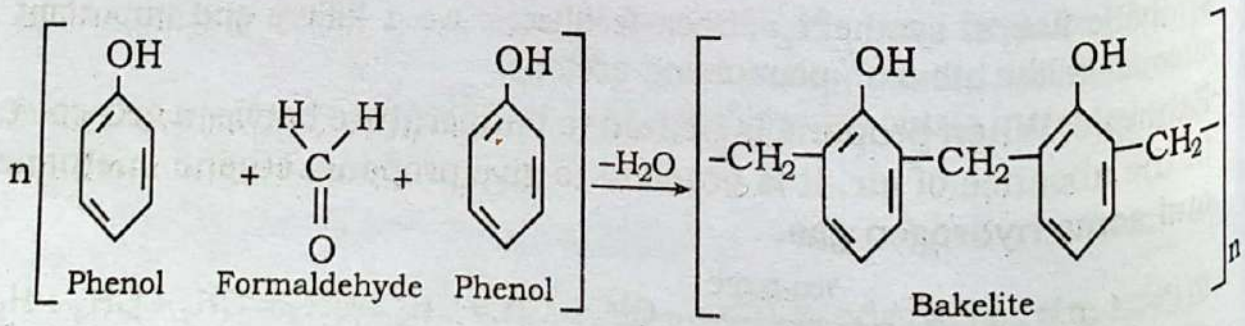
Types of polymerization:- There are two types of polymerization.

1. Addition polymerization and
2. Condensation polymerization

1. Addition polymerization:- When many monomers undergo self combination, resulting into a substance with a molecular mass many times greater than the monomer, then the polymerization is known as addition polymerization. The empirical formula of the addition polymers formed is the same as that of the monomer. For example the formation of polyethylene from ethylene.

$$\underset{\text{Ethylene}}{n(CH_2 = CH_2)} \xrightarrow[0.01\%\ O_2]{200^\circ C,\ 100\ atm} \underset{\text{Polyethylene}}{(-CH_2 - CH_2 - CH_2 - CH_2 -)_n}$$

2. Condensation polymerization:- In condensation polymerization, there is an elimination of a by-product usually water. Bakelite is an example of a polymer formed by the condensation process, involving phenol and formaldehyde as monomers.



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6.5 CLASSIFICATION OF ORGANIC COMPOUNDS OR TYPES OF ORGANIC COMPOUNDS.

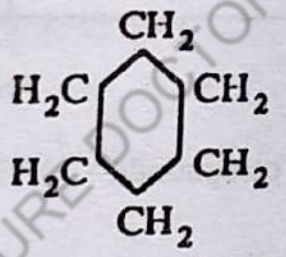
Organic compounds are divided into two major groups:
(1) Open-chain or acyclic compounds or Aliphatic compounds
(2) Closed-chain or cyclic compounds

Open-chain compounds have open chain structures and are generally called as Aliphatic compounds.

The organic compounds containing closed ring are called cyclic compounds. The cyclic compounds are further divided into two types: (a) Homocyclic or carbocyclic compounds, when the ring consists of carbon atoms only and (b) Heterocyclic compounds, when the ring contains in addition to carbon atoms, other atoms like O, S, N etc.

Homocyclic compounds may further be divided into two types: (i) Alicyclic compounds. (ii) Aromatic compounds.

Alicyclic compounds are carbocyclic or homocyclic compounds which resemble aliphatic compounds in many ways and do not contain benzene ring e.g. cyclohexane.

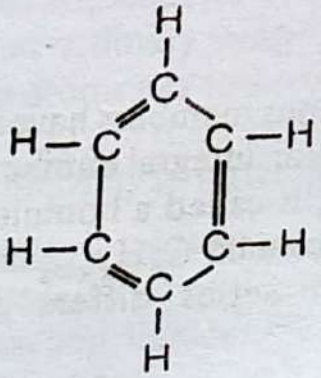


Cyclohexane (Alicyclic)

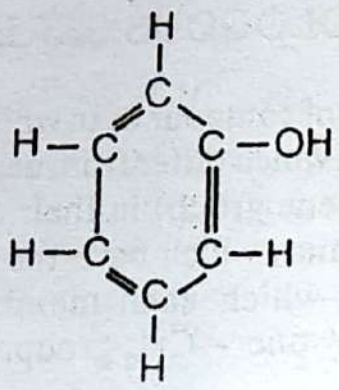
Alicyclic compounds are also called non-benzenoids.

Aromatic compounds are also carbocyclic or homocyclic compounds, containing atleast one benzene ring. A benzene ring is a hexagonal ring of six carbon atoms with three alternating double and single bonds.

Example:



aromatic benzene



aromatic phenol

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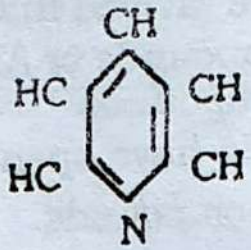
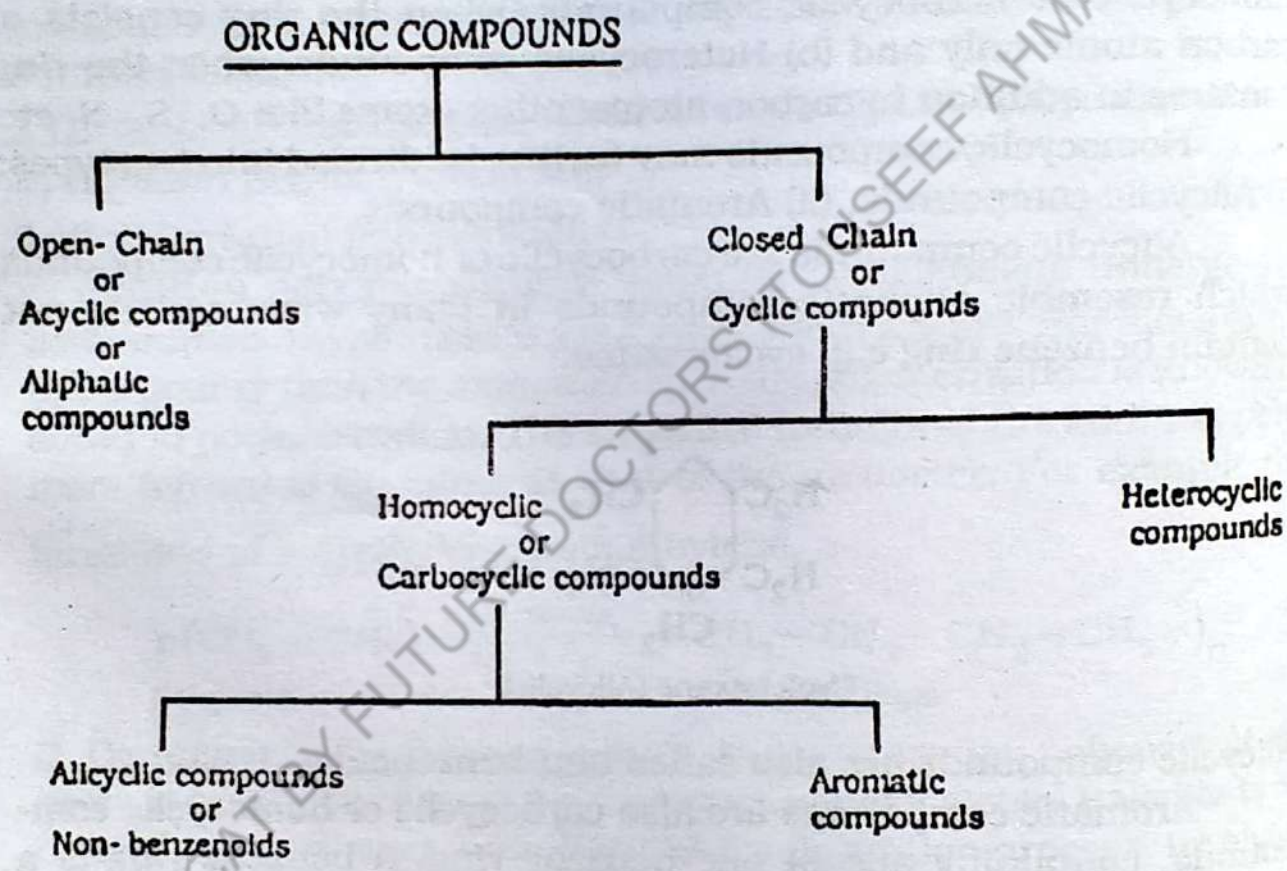
Heterocyclic compounds are cyclic compounds containing other elements besides carbon on the ring. e.g.



Pyridine



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6.6 HOMOLOGOUS SERIES

A series of compounds in which the various members have similar structural features but which differ from each other by an integral number of $-CH_2$ group (the methylene group) in their structures, is called a homologous series. The normal alkanes which have the general formula C_nH_{2n+2} are a homologous series, in which each member of the series differs from adjascent member by one $-CH_2$ group.

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The members of the homologous series have similar chemical properties and there is a smooth gradation in the physical properties of the compounds. For example melting and boiling points tend to increase with the increasing molecular weight in a homologous series (The first member of the series is sometimes an exception to this rule since its properties are somewhat different from the properties of other members).

1. All members of the homologous series have similar structures.

2. Physical properties of homologous series change progressively and more or less with the number of carbon atoms.

3. The composition of all members of a homologous series can be expressed by a general formula. Thus alkanes can be represented by the general formula C_nH_{2n+2}, alkenes by C_nH_{2n} and alkynes by C_nH_{2n-2}, where 'n' is the number of carbon atoms in a compound.

4. Successive members of the series always differ in composition by $-CH_2$ (molecular weight 14). Any two members of the series, therefore, differ by some multiple of $-CH_2$.

Homologous series of saturated hydrocarbons i.e. alkanes.

CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}
Methane	Ethane	Propane	Butane	Pentane	Hexane

General Molecular Formula:– All members of homologous series share a general molecular formula. e.g. C_nH_{2n+2} for the alkanes, each successive member in such a series differs on its molecular formula by the addition of a $-CH_2$ group and in its molecular weight by an increase of 14.

Physical Properties:– The physical properties of the members change gradually as the number of carbon atoms per molecule increases. For example, the boiling points of the alkanes increase along the series, so that first four members are gases at ordinary temperatures and pressures, member with five to seventeen carbon atoms per molecule are liquids while the higher members are wax like solids. Similarly the melting points and densities of the alkanes also increase while the solubility in water decreases along the series.

Chemical properties:– All members show similar chemical properties, e.g. all the alkanes are generally fairly unreactive under ordinary conditions. They burn in air forming carbon dioxide and water and undergo substitution reactions with halogens.

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General methods of preparation:– All the members can easily be prepared by using the same general method e.g alkanes can be prepared by the reduction of alkyl halides.

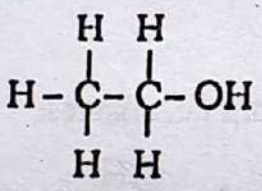
$$Zn + 2HCl \rightarrow ZnCl_2 + 2[H]$$

$$C_2H_5I + 2[H] \xrightarrow{Zn/HCl} C_2H_6 + HI$$

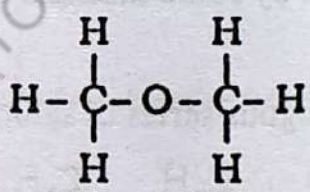
Ethane

6.7 ISOMERISM.

Compounds having same molecular formulas but differing in structural formula due to different arrangement of atoms or groups, are called isomers (iso=same; mers=units means same units) and the phenomenon is called isomerism e.g;
C_2H_6O is the molecular formula of two isomers namely; ethyl alcohol and dimethyl ether.



Ethyl alcohol
(Ethanol)



Dimethyl ether
(Methoxy methane)

This means isomers are different compounds which have same molecular formula but different structural formulas.

Types of Isomerism:- There are various types of isomerism but out of which some are given below:

(1) Chain Isomerism (skeletal Isomerism):- Different compounds which have same molecular formula but differ in chain of carbon atoms i.e skeletals are called chain isomers and the phenomenon is termed as chain isomerism. e.g; pentane (C_5H_{12}) has the following three isomers:-

(i) $CH_3 - CH_2 - CH_2 - CH_2 - CH_3$ n-pentane

(ii) $CH_3 - CH_2 - CH(CH_3) - CH_3$ Iso-pentane

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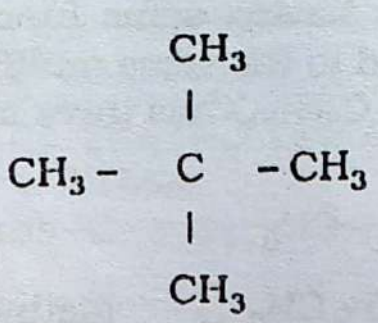
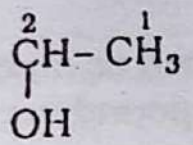
(iii)  neo–pentane

(2) Position Isomerism:- Isomerism caused by the difference in position of the functional group in the same chain is termed as position isomerism e.g; propyl alcohol (C_3H_7OH) has two position isomers:

i) $CH_3 - CH_2 - CH_2 - OH$ n-propyl alcohol or 1-propanol

ii)  Iso-propyl alcohol or 2- propanol

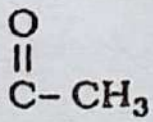
Similarly butene (C_4H_8) has two position isomers:

(i) $\overset{4}{C}H_3 - \overset{3}{C}H_2 - \overset{2}{C}H = \overset{1}{C}H_2$ 1-butene

(ii) $\overset{4}{C}H_3 - \overset{3}{C}H = \overset{2}{C}H - \overset{1}{C}H_2$ 2-butene

(3) Functional group Isomerism:- Functional group isomerism is exhibited by the compounds which have same molecular formula but diffreent functional groups e.g. C_3H_6O is the molecular formula of two functional group isomers which are given below:

(i) Propion aldehyde or propanal

(ii)  Acetone or 2- propanone

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(4) Metamerism:- Metamerism is a type of isomerism which is exhibited by the compounds having same functional groups but different alkyl groups attached to the same multivalent atom .e.g. A ether with molecular formula $C_4H_{10}O$ has three metamers.

(i) $CH_3-CH_2-O-CH_2-CH_3$ Di-ethyl ether

(ii) $CH_3-CH_2-CH_2-O-CH_3$ Methyl-n- propyl ether

(iii) $(CH_3)_2CH-O-CH_3$ Methyl-iso-propyl ether

Functional groups:- The properties of organic compounds depend on the presence of an atom or group of atoms that is substituted in the chain of carbon atoms in place of a hydrogen atom which is termed as functional group. Each functional group has its own characteristic properties.

Thus functional group is defined as an atom or group of atoms whose presence in an organic compound confers the properties to organic compound unique to that atom or group of atoms. Functional group also defines the structure of a particular family of organic compounds.

In alkyl halides (R–X), halogen atom (–X) is the functional group and in alcohols (R–OH), the hydroxyl group (–OH) is the functional group.

A large part of organic chemistry deals with the chemistry of functional groups. The orgainc compounds on which functional groups are present, can be considered as derivatives of hydrocarbons in which one or more than one hydrogen is replaced by the functional group. The functional group determines the basic chemistry of an organic compound while the alkyl group has an effect on its physical properties. For instance, the polar hydroxyl group (–OH) in alcohols, promotes the solubility in water but the non-polar alkyl group opposes it. For all alkyl groups larger than C_4H_9 (Butyl), this opposing effect is sufficiently greater to limit the solubility of a compound in water.

Table 6.3, Names of some common functional groups and structures of organic compounds containing them.

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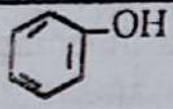
TABLE 6.3

HOMOLOGOUS SERIES	GENERAL MOLECULAR FORMULA	FUNCTIONAL GROUP AND ITS NAME
i. ALKANES	C_nH_{2n+2} or R – H	——
ii. ALKENES	C_nH_{2n}	$>C=C<$ Double bond
iii. ALKYNES	C_nH_{2n-2}	$-C \equiv C-$ Triple bond
iv. HALOALKANES	R–X (where x=F,Cl,Br,I) or $C_nH_{2n+1}X$	–X (Halide group)
v. ALCOHOLS	R–OH or $C_n H_{2n+1}$ OH	–OH (Hydroxyl group)
vi. PHENOLS	 or C_6H_5OH	–OH (Hydroxyl group)
vii. ETHERS	R–O–R' or $C_nH_{2n+2}O$	–OR' (Alkoxyl group)
viii. ALDEHYDES	$H>C=O$ (R)	$H>C=O$ (Carbonyl group) or –CHO
ix. KETONES	$R>C=O$ (R')	$>C=O$ (Carbonyl group)
x. CARBOXYLIC ACIDS	$R-\overset{O}{\overset{\|\|}{C}}-OH$ or R–COOH	$-\overset{O}{\overset{\|\|}{C}}-OH$ (Carboxyl group)
xi. ESTERS	$R-\overset{O}{\overset{\|\|}{C}}-OR'$	$-\overset{O}{\overset{\|\|}{C}}-OR'$ (Alkoxy carbonyl group) or Ester group.

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HOMOLOGOUS SERIES	GENERAL MOLECULAR FORMULA	FUNCTIONAL GROUP AND ITS NAME
xii.ACID HALIDES	$R-\overset{\overset{\large O}{\|}}{C}-X$	$-\overset{\overset{\large O}{\|}}{C}-X$ (Acyl group)
xiii.ACID AMIDES	$R-\overset{\overset{\large O}{\|}}{C}-NH_2$	$-\overset{\overset{\large O}{\|}}{C}-NH_2$ (Amido group)
xiv.PRIMARY AMINES	$R-NH_2$	$-NH_2$ (Amino group).

6.8 NOMENCLATURE

In early days organic compounds were named on the basis of their origins. For example, methane as marsh gas, methyl alcohol as wood, spirit, similarly acetic acid from vinegar (Latin: accteum=vinegar). These names are called, as Trivial or common names.

A increase in the number of organic compounds due to their rapid growth, caused a problem in naming the compounds. To overcome the problem, th leading chemists held a meeting in Geneva in 1882 and formulated a system of nomenclature, called as Geneva system. This system later on was modified by the International Union of Chemistry (I.U.C) at Liege in 1930. The I.U.C system was further imporved by International Union of Pure and applied chemistry in 1960 and termed as I.U.P.A.C system of nomenclature .

The basis of IUPAC system is the alkanes.

ALKANES (SATURATED ALIPHATIC HYDROCARBONS)

The first four straight chain saturated aliphatic hydrocarbons (methane, ethane, propane and butane) have long established names. The higher members of the series are named from Greek numerals indicating the number of carbon atoms in the molecule wih the suffix- "ane" added, e.g pentane, hexane etc.

The general molecular formula for alkanes is $C_n H_{2n+2}$ where 'n' is the number of carbon atoms present in a molecule.

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The names of first ten alkanes are given below:

Table:

n	n
1. Methane (CH_4)	6. Hexane (C_6H_{14})
2. Ethane (C_2H_6)	7. Heptane (C_7H_{16})
3. Propane (C_3H_8)	8. Octane (C_8H_{18})
4. Butane (C_4H_{10})	9. Nonane (C_9H_{20})
5. Pentane (C_5H_{12})	10. Decane ($C_{10}H_{22}$)

Univalent alkyl radicals are derived from alkanes by the removal of a hydrogen atom and are represented by the general formula C_nH_{2n+1}. They derive their names from alkanes by changing the suffix-"ane" to-yl

Example:

$-CH_3$ (methyl radical) from CH_4 (Methane) and CH_3-CH_2- (Ethyl radical) from CH_3-CH_3 (Ethane).

On the basis of arrangement of carbon atoms, alkyl radicals may be n (normal), Iso– and Neo–.

$CH_3-CH_2-CH_2-$ (Propyl or n-propyl radical) from $CH_3-CH_2-CH_3$ (propane) and $CH_3-\underset{|}{CH}-CH_3$ (isopropyl radical) from $CH_3-CH_2-CH_3$ (propane)

Other examples:

$$\underset{\text{n-Butyl}}{CH_3-CH_2-CH_2-CH_2-}, \qquad \underset{\text{Iso-butyl}}{CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-}$$

$$\underset{\text{Neo-pentyl}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-}$$

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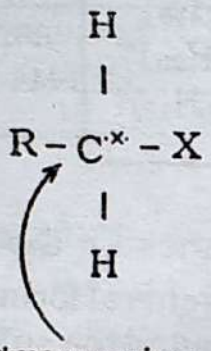
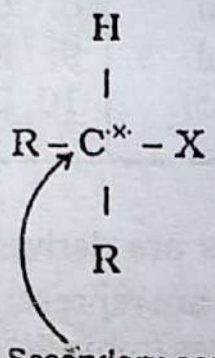
Primary, Secondary and Tertiary carbon:-

The carbon atom to which a functional group is attached may be classified as primary, secondary or tertiary.

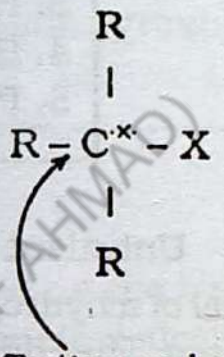
A carbon atom bonded to functional group when attached one, two or three other carbon atoms is called primary, secondary or tertiary carbon atom.



Primary carbon

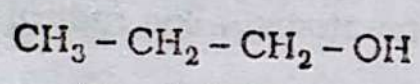


Secondary carbon

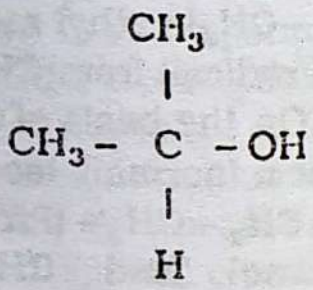


Tertiary carbon

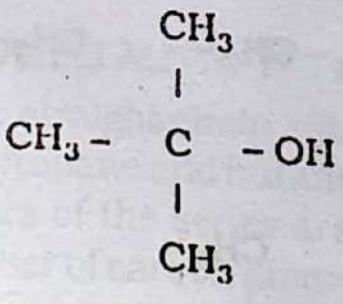
Examples:



Propyl alcohol
(primary or 1° alcohol)



Isopropyl alcohol (sec. or 2° propyl alcohol)



Ter.butyl alcohol (tertiary or 3° alcohol).

IUPAC NOMENCLATURE OF ALKANES

Rules for naming Alkanes:-

1. Select the longest continuous chain of carbon atoms whether straight or branched and consider it as the parent alkane.

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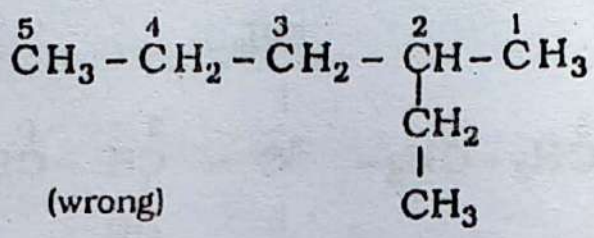
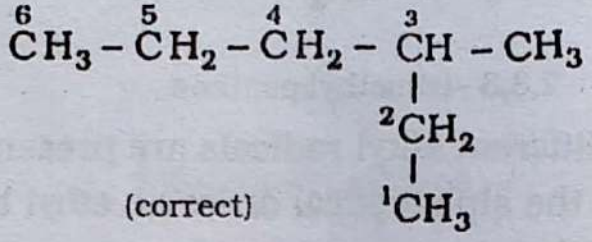
Example:



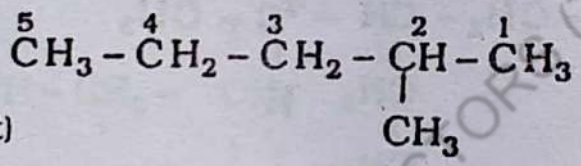
(wrong)



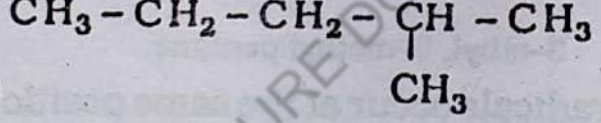
(correct)

2. Number the carbon atoms of the longest chain selected in which direction gives the nearest branching for the location of all branches.

Example:



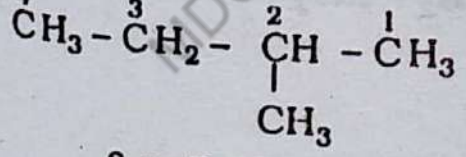
(correct)



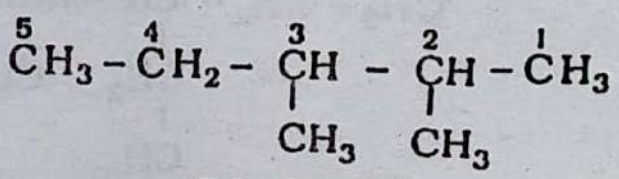
(wrong)

3. Position of each alkyl radical is designated by number of carbon atom to which it is attached

Example:



2-methyl butane



2,3- dimethyl pentane

4. If identical radicals appear more than once in the chain then the number of alkyl radicals is represented by adding prefixes di, tri, tetra, penta etc with the name of alkyl radical.

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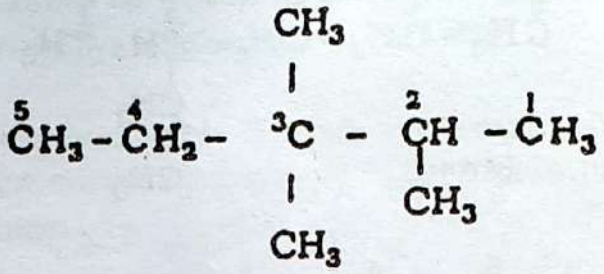
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

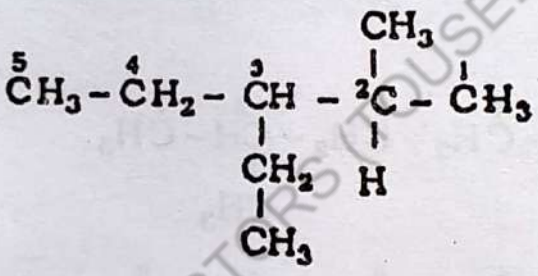
Example:



2,3,3 -trimethyl pentane.

5. When two or more different alkyl radicals are present in the chain then they are named in the alphabetical order i.e ethyl before methyl, and methyl before propyl etc.

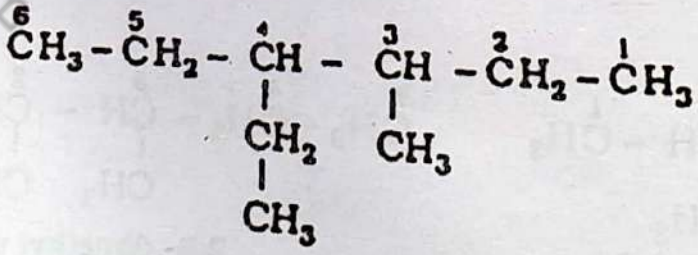
Example:



3-ethyl, 2-methyl pentane.

6. When different alkyl radicals occur at the same position on a carbon atom from either end of the chain then the carbon chain is numbered from that end where the smaller radical is attached.

Example:



4-ethyl, 3-methyl hexane

7. The radicals are always mentioned with their positions before the actual compound i.e before the base name of alkane.

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Other examples:

(i) $CH_3-C(CH_3)_2-(CH_2)_2-CH_3$

or
$$\overset{1}{C}H_3-\overset{2}{C}(CH_3)_2-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}H_3$$

2,2-dimethyl pentane

(ii) $(CH_3)_3CH$ or $\overset{1}{C}H_3-\overset{2}{C}H(CH_3)-\overset{3}{C}H_3$

2-methyl propane

(iii) $(CH_3)_2CH-CH_2-CH(C_2H_5)$ or

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

2,4 -dimethyl hexane

(iv) $(CH_3)_2CH-CH(C_2H_5)-C(CH_3)_3$ or

$$\overset{5}{C}H_3-\overset{4}{C}H(CH_3)-\overset{3}{C}H(CH_2CH_3)-\overset{2}{C}(CH_3)_3-\overset{1}{C}H_3$$

3-ethyl -2,2,4-trimethyl pentane

(Note: Use hyphens)

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MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

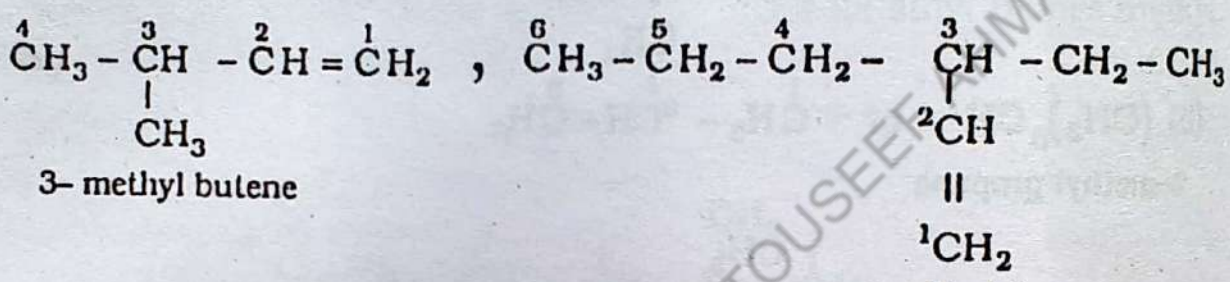
IUPAC NOMENCLATURE OF ALKENES.

Rules for naming alkenes:-

1. Select the longest continuous chain of carbon atoms which must include both the carbon atoms containing double bond.

2. The numbering of the longest chain starts from that end nearest to the carbon–carbon double bond, irrespective of the location of alkyl radicals .

Example:

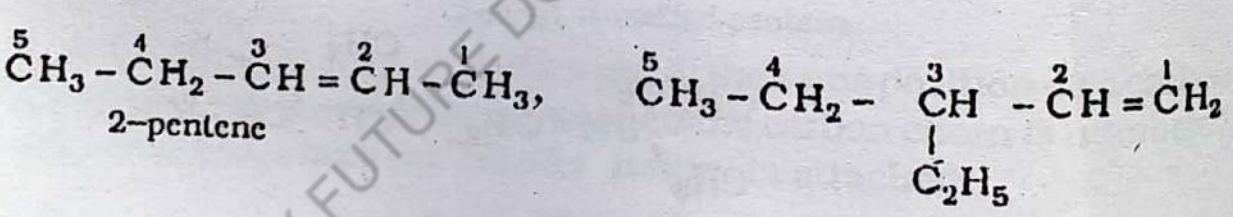


3– methyl butene

3–ethyl hexene

3. The double bond in the compound is indicated by changing the suffix– "ane" of the corresponding alkane by –"ene" and the position of double bond in the chain should also be mentioned .

Examples:

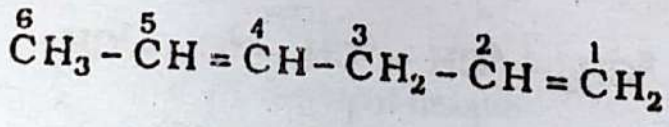


2–pentene

3– ethyl –1–pentene

4. If two or more double bonds are present in lthe chain then they are indicated by adding the prefixes di, tri, tetra etc before the suffix "ene".

Example:



1,4– hexadiene

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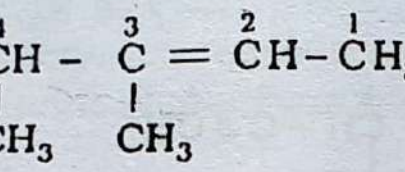
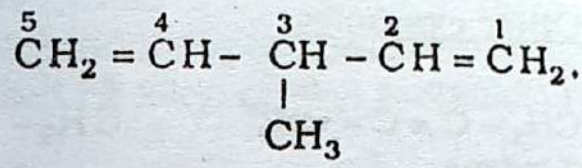
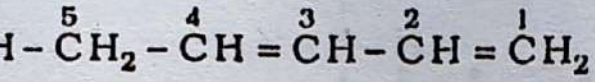
Other examples:



3,4 –dimethyl –2–pentene



3–methyl–1,4 –pentadiene



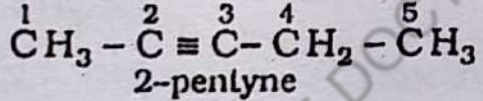
1,3,6– heptatriene or hepta-1,3,6–triene.

IUPAC NOMENCLATURE OF ALKYNES

Rules for naming alkynes:-

1. Select the longest continuous chain of cabon atoms which must include both the carbon atoms containing triple bond.
2. The numbering of the longest chain of carbon atoms starts from that end nearest to carbon–carbon triple bond, irrespective of the location of alkyl radical.

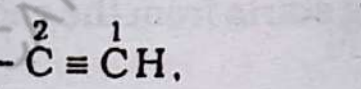
Example :



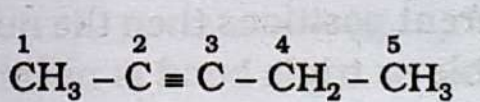
2–pentyne

3. The position of triple bond is indicated by the number of that carbon atom which has lower number .
4. The triple bond in the compound is indicated by changing the suffix–"ane" of the corresponding alkane to –"yne".

Example:



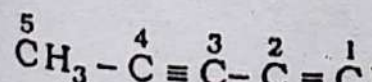
1–butyne



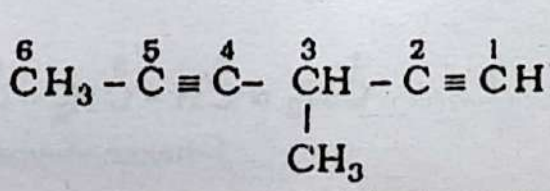
2-pentyne

5. If two or more triple bonds are presented in the chain then they are indicated by adding the prefixes di,tri etc before the suffix–"yne"

Example:



1,3–pentadiyne



3–methyl–1,4 –hexadiyne

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6. Other rules remain same as usual.

Other examples:

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

2-butyne

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

3,4 – dimethyl-1-pentyne

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

4-ethyl-5-methyl -2-hexyne

Compounds that contain double and triple bonds:-

Rules:

1. When double and triple bonds both are present in a molecule at equal positions then the preference of numbering is given to the double bond

Example:

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

1- penten-4-yne

$\overset{1}{C}H_3 - \overset{2}{C}H = \overset{3}{C}H - \overset{4}{C}H_2 - \overset{5}{C} \equiv \overset{6}{C} - \overset{7}{C}H_3$

2-hepten-5-yne

2. In case of a chain containing both double and triple bonds at different positions then the numbering starts from the end where the double or triple bond is nearest.

Example:

$\overset{6}{C}H_3 - \overset{5}{C}H = \overset{4}{C}H - \overset{3}{C}H_2 - \overset{2}{C} \equiv \overset{1}{C}H$

4-hexen-1-yne

$\overset{1}{C}H_2 = \overset{2}{C}H - \overset{3}{C}H_2 - \overset{4}{C} \equiv \overset{5}{C} - \overset{6}{C}H_3$

1-hexen-4-yne

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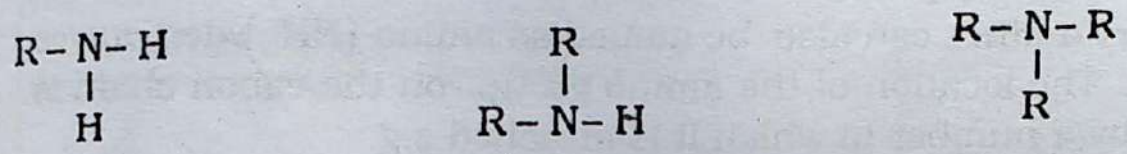
NOMENCLATURE OF AMINES:

Alkyl or aryl derivatives of ammonia are called amines. They may be primary, secondary or tertiary depending upon the number of hydrogen atoms of ammonia are replaced by alkyl or aryl radicals.



Primary amine Secondary amine Tertiary amine

Trivial or common nomenclature of amines:- Amines are commonly named by adding the suffix amine to the name of alkyl radical. In secondary and tertiary amines, the prefix di–or tri– is used before the name of alkyl radical e.g.

(i) $CH_3 - NH_2$ Methyl amine

(ii) $C_2H_5NH_2$ Ethyl amine

(iii) $CH_3 - NH - CH_3$ Dimethyl amine

(iv) $CH_3 - N(CH_3) - CH_3$ Trimethyl amine

(v) $CH_3 - N(C_2H_5) - CH_3$ Dimethyl ethyl amine

(vi) $C_6H_5NH_2$ (Aniline) Phenyl amine

(vii) $C_6H_5 - N(C_6H_5) - H$ Di–phenyl amine

(viii) $C_6H_5 - N(C_6H_5) - C_6H_5$ Triphenyl amine

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IUPAC NOMENCLATURE OF PRIMARY AMINES:

In this system amine is named by replacing "–e" of the parent alkane with suffix–amine, e.g.

(i) CH_3NH_2 Methanamine

(ii) $CH_3 - CH_2 - NH_2$ Ethanamine

The primary amines can also be named as amino (NH_2) derivatives of alkanes. The location of the amino group on the cabon chain is indicated by a number to which it is attached e.g.

(i) CH_3NH_2 Amino methane

(ii) $CH_3 - CH_2NH_2$ Amino ethane

(iii) $\overset{3}{C}H_3 - \overset{2}{C}H_2 - \overset{1}{C}H_2NH_2$ 1– amino propane

(iv) $\overset{3}{C}H_3 - \overset{2}{C}H(NH_2) - \overset{1}{C}H_3$ 2– amino propane

I.U.P.A.C NAMES OF ORGANIC COMPOUNDS CONTAINING FUNCTIONAL GROUPS

If a functional group is present then the final "e" from the name of hydrocarbons (Alkane, alkene or alkyne) is dropped and the suffix is added.

The table 6.4 explains the naming together with the names of functional groups when they are used as suffixes or prefixes.

TABLE 6.4

Functional group with family	IUPAC name as suffix	Name of the functional group as prefix
(i) – OH (ALCOHOLS)	–ol	hydroxy–
(ii) $-\overset{O}{\overset{\|\|}{C}}-H$ (ALDEHYDES)	–al	oxo–

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Functional group with family	IUPAC name as suffix	Name of the functional group as prefix
(iii) $-\overset{\overset{O}{\|}}{C}-$ (KETONES)	–one	oxo–
(iv) $-\overset{\overset{O}{\|}}{C}-OH$ (CARBOXYLIC ACIDS)	–oic acid	carboxy–
(v) $-\overset{\overset{O}{\|}}{C}-OR$ (ESTERS)	alkyl –oate	alkoxy carbonyl–
(vi) R–O–R' (ETHERS)	alkoxy–alkane	alkoxy–
(vii) $-NH_2$ (PRIMARY AMINE)	– amine	amino
(viii) —X (ALKYL HALIDES)	Haloalkanes	halo–
(ix) C=C (ALKENES)	– ene	—
(x) C≡C (ALKYNES)	– yne	—

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

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MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

ASSIGNMENT

1. Define Organic chemistry and discuss its development as a separate branch of chemistry.

2. Briefly describe the natural sources of Organic compounds.

3. What is meant by each of the following:

   (a) Catenation (b) Homologous series (c) Isomerism

4. Name the following compounds according to IUPAC system:-

   (i) $(CH_3)_2CH-CH_2-CH_3$

   (ii) $(CH_3)_3C-CH(CH_3)-CH_2-CH_3$

   (iii) $CH_3-\underset{\underset{C_2H_5}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

   (iv) $C_2H_5-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH\begin{matrix}/CH_3\\ \backslash CH_3\end{matrix}$

   (v) $(CH_3)_2CH-(CH_2)_3-CH(CH_3)_2$

   (vi) $CH_3-CH=CH-CH_3$

   (vii) $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2$

   (viii) $CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_3$

   (ix) $CH_3-CH_2-\underset{\underset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{C}-CH(CH_3)_2$

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(x) $CH_2 = C(CH_3) - CH = CH - CH_3$

(xi) $CH_3 - CH_2 - C \equiv C - CH_3$

(xii) $(CH_3)_2CH - CH_2 - C \equiv CH$

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

(xiv) $CH_3 - CH(CH_3) - C \equiv C - CH_2 - CH_3$

(xv) $CH \equiv C - CH_2 - C \equiv C - CH_3$

(xvi) $CH \equiv C - CH_2 - C(CH_3)(C_2H_5) - CH_3$

5- Write the structural formulas of the followings:

(i) 3-methyl hexane

(ii) 2,3- dimethyl pentane

(iii) 2,3,4-trimethyl heptane

(iv) 3-ethyl -2-methyl pentane

(v) 3-heptene

(vi) 2-methyl-1-butene

(vii) 1,3 -pentadiene

(viii) 1-hexen-3-yne

(ix) 1,3-pentadiyne

(x) 4-hexen-1-yne

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CHAPTER 7

CHEMISTRY OF HYDROCARBONS

The compounds containing only carbon and hydrogen are called hydrocarbons. On the basis of structure, the hydrocarbons are divided into two main classes i.e Aliphatic and Aromatic – hydrocarbons.

7.1 OPEN CHAIN AND CLOSED CHAIN HYDROCARBONS

In aliphatic hydrocarbons, the carbon atoms are attached to another carbon to form chains. These chains may be either open or closed (rings) chains. The open chains on the basis of saturation of valence are classified as saturated and unsaturated hydrocarbons.

(i) **Saturated Hydrocarbons:–** The compounds in which all the valencies of carbon atoms are fully satisfied by single bonds,are called saturated hydrocarbons. The examples of saturated hydrocarbons are alkanes.

(i) CH_4 Methane (ii) C_2H_6 Ethane

(ii) **Unsaturated Hydrocarbons:–** The compounds in which all the valencies of carbon atoms are not fully utilized,are called unsaturated hydrocarbons. Alkenes and alkynes are the examples of unsaturated open chain hydrocarbons. The examples of unsaturated hydrocarbons are:

(i) C_2H_4 or $\begin{matrix} H \\ H \end{matrix}\rangle C = C \langle \begin{matrix} H \\ H \end{matrix}$ Ethylene or ethene

(ii) C_2H_4 or $H - C \equiv C - H$ Acetylene or ethyne

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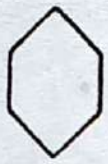
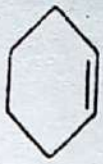
The hydrocarbons which contain closed chain of carbon atoms are called cyclic hydrocarbons and examples are cyclo alkanes and cyclo alkenes.

(i) 

Cyclo – alkanes

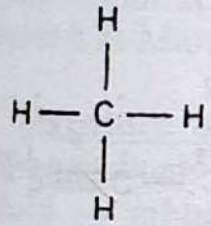
(ii) 

Cyclo – alkenes

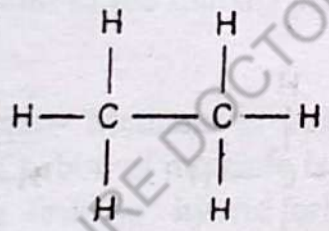
Aromatic compounds are benzene and its homologs. These compounds are further divided into homonuclear and hetero – nuclear aromatic compounds.

Some Important Terms

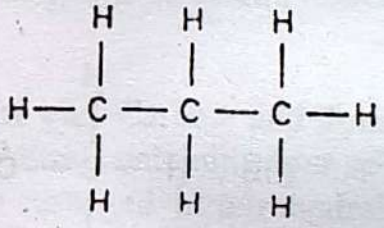
Alkanes:– Alkanes are the open chain saturated hydrocarbons in which all bonds are single covalent bonds. Each carbon atom is tetrahedrally surrounded by hydrogen atoms and other carbon atoms. The names of alkanes end with "–ane" and general formula is C_nH_{2n+2}. The structural formulas of few alkanes are given below:

(i) 

Methane(CH_4)

(ii) 

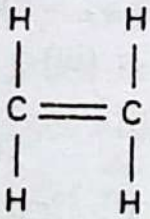
Ethane(C_2H_6)

(iii) 

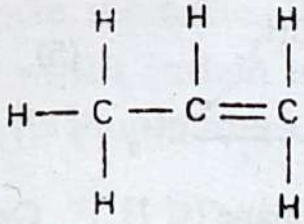
Propane(C_3H_8)

In actual molecular structures, the carbon chains are not in straightlines but they are three dimensional in nature.

Alkenes:– Alkenes are unsaturated open chain hydrocarbons in which two carbon atoms are connected by a double bond (>C=C<). The names of alkenes end with "–ene" and general formula is C_nH_{2n} where n is a whole number which is equal to 2 or greater than 2. The structural formulas of few alkenes are given below:–

(i) 

Ethene(C_2H_4)

(ii) 

Propene(C_3H_6).

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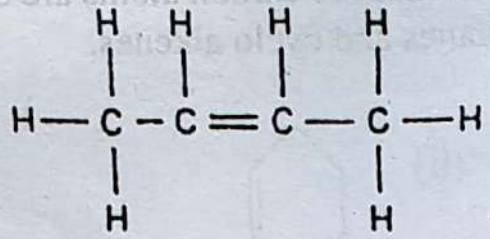
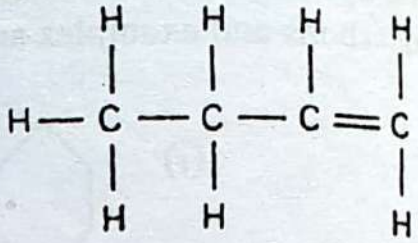
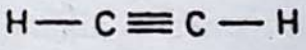
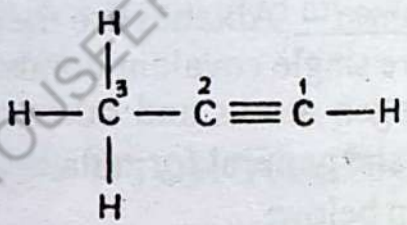
(iii)  or 

2 – butene (C_4H_8) 1–butene

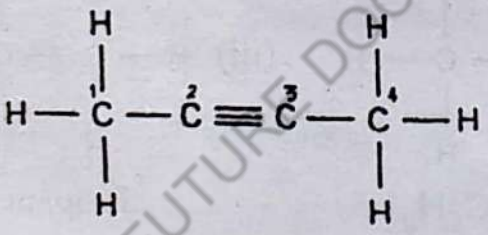
Alkynes:– Alkynes are unsaturated open chain hydrocarbons in which two carbon atoms are connected by a triple bond (–C ≡ C–). The names of alkynes end with "-yne" and general formula is C_nH_{2n-2} where n is a whole number which is equal to 2 or greater than 2. The structural formulas of few alkynes are given below.

(i) 

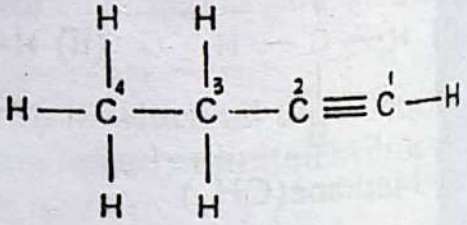
Ethyne(C_2H_2)

(ii) 

1 – propyne(C_3H_4)

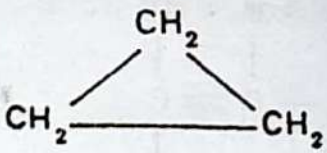
(iii) 

2 – butyne

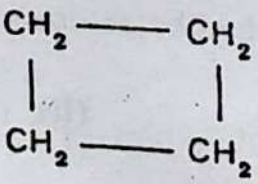


1 – butyne (C_4H_6)

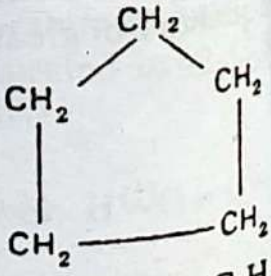
Cyclic–Hydrocarbons:– The ali cyclic aliphatic hydrocarbons are closed chain hydrocarbons. The cyclic hydrocarbons are named by prefixing the word cyclo to the name of the corresponding open chain hydrocarbon. The general formula is C_nH_{2n}. Where n is a whole no.which is equal to 3 or greater than 3. The structural formulas of few cyclo alkanes are given below: –

(i) 

Cyclo–propane (C_3H_6)

(ii) 

Cyclo–butane(C_4H_8)

(iii) 

Cyclo–pentane(C_5H_{10})

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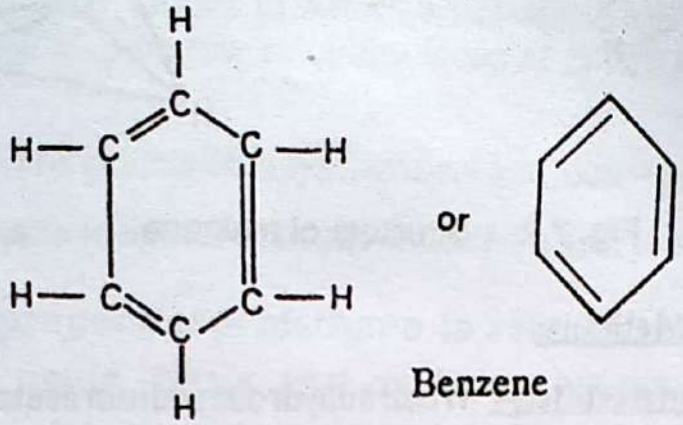
Aromatic–Hydrocarbons:– Aromatic hydrocarbons are special class of cyclic compounds containing benzene ring. Benzene ring is a six–membered ring of carbon atoms with alternate double bonds. Other aromatic hydrocarbons are the derivatives of benzene.



Benzene

7.2 CHEMISTRY OF METHANE

Methane is the first and simplest member of alkane family with molecular formula CH_4. It is the major constituent of natural gas which contains 94% of Methane. In Pakistan natural gas occurs in the form of sui gas found at Sui in Baluchistan. It is also found in the marshy places and stagnant pond and hence named as Marsh gas.

Structure of Methane:– Methane is composed of one Carbon and four hydrogen atoms i.e. CH_4. Carbon of methane is sp^3 hybridized containing four sp^3 hybrid — orbitals. These four sp^3 hybrid orbitals are arranged in tetrahedral fashion with an angle of 109.5° as given in figure 7.1.

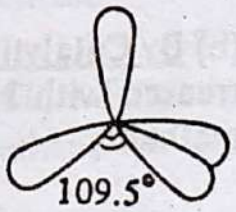


Fig. 7.1 Shape of sp^3 hybridized C-atom.

Four sp^3 hybrid orbitals of carbon over lap with four s orbitals of four hydrogen atoms to form methane. It means the structure of methane is tetrahedral in which carbon is situated at centre and hydrogen atoms are lying at its four corners of a tetrahedron as given in fig.7.2.

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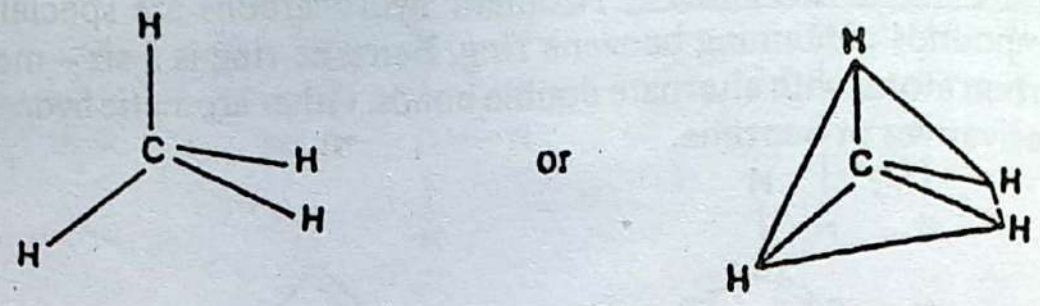

Fig. 7.2 Structure of methane

Preparation of Methane:

(1) **From Sodium Acetate:–** When anhydrous sodium acetate is heated with soda lime, it forms methane. Soda lime is quick lime shaked with concentrated solution of sodium hydroxide.

$$CH_3COONa_{(s)} + NaOH_{(s)} \longrightarrow CH_{4(g)} + Na_2CO_{3(s)}$$

This is the most convenient method for the preparation of methane.

(2) **By the reduction of methyl iodide:–** Methyl iodide may be converted into methane by various methods, some of them are given below:

(a) **Reduction of Methyl Iodide With Nascent Hydrogen:–** When methyl iodide is treated with nascent hydrogen [H], it produces methane. The nascent hydrogen is obtained by the action of HCl with Zn.

$$CH_3I + 2[H] \xrightarrow{Zn/HCl} CH_4 + HI$$

(b) **By Catalytic Reduction of Methyl Iodide:–** When methyl iodide is treated with H_2 in the presence of palladium catalyst, it produces methane.

$$CH_3I + H_2 \xrightarrow{Pd} CH_4 + HI$$

(3) **From Methyl Magnesium Iodide (Grignard Reagent):–** Methyl magnesium iodide on hydrolysis produces methane.

$$CH_3-Mg-I + H-OH \longrightarrow CH_4 + Mg\begin{matrix}OH\\I\end{matrix}$$

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Physical Properties:–

(i) Methane is a colourless, odourless and non – poisonous gas.

(ii) It is slightly soluble in water i.e 100 mls of water dissolve only 5 mls of methane at 20°C. The low solubility in water is due to non–polar nature of methane.

(iii) Methane molecule is symmetrical and non–polar.

(iv) Methane is lighter than air. When liquified, it is less denser than water.

Chemical properties:- Methane is relatively unreactive. It is not affected by acids, basis and oxidizing agents such as potassium permegnate and potassium dichromate at ordinary conditions. Important reactions of methane are halogination and combustion reactions.

(a) Halogenation Reaction:– The replacement of one or more hydrogen atoms of methane with halogen atom is called halogenation and it is an example of substitution reaction. The halogenation is carried out, when methane is treated with halogen in the presence of sun light, heat as a catalyst.

For example when methane is treated with chlorine in presence of sun light, the one hydrogen of methane is replaced by one chlorine and produce following products.

$$CH_4 + Cl_2 \xrightarrow{\text{sunlight}} CH_3Cl + HCl$$

Chloromethane

$$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$$

Dichloromethane

$$CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$$

Tri chloro methane (Chloroform)

$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$

Tetra chloro methane
(Carbon tetra Chloride)

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Mechanism of Reaction:– The mechanism of chlorination is free radical chain reaction. The reaction starts by photo chemical dissociation of chlorine molecule into chlorine free radical (odd electron species) because Cl – Cl bond is weaker than C–H bond. The chlorine free radical then attacks methane molecule and forms methyl free radical. This methyl free radical then removes a chlorine atom from another chlorine molecule and form chloro-methane and chlorine free radical. This chlorine free radical (atom) repeats same sequence. This is shown below:

(i) $Cl_2 \xrightarrow{h\nu} 2\ :\ddot{\underset{..}{Cl}}\cdot$

Chlorine free radical

(ii) $CH_4 + :\ddot{\underset{..}{Cl}}\cdot \longrightarrow \dot{C}H_3 + HCl$

(iii) $\dot{C}H_3 + Cl_2 \longrightarrow CH_3Cl + :\ddot{\underset{..}{Cl}}\cdot$

Methyl free radical

(b) Combustion Reaction:- When methane burns in oxygen, it produces carbon dioxide (CO_2), steam and lot of heat. Combustion reaction is highly exothermic and a lot of heat is given out.

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)} \quad \Delta H = -45.93\ K.J/mole$$

$$= -2.85\ K.J/g \text{ of methane}$$

Burning of methane takes place at high temperature i.e either by flame or a spark. Once started, the reaction gives off heat. This heat is sufficient to maintain the high temperature and to permit burning to continue.

Uses of methane:– (i) Methane is used as a domestic fuel (ii) It is used in the manufacture of methanol, carbon black, polishes etc.

7.3 CHEMISTRY OF ETHANE

Ethane is the second member of alkane with molecular formula C_2H_6. It occurs along with methane in natural gas and gases from oil – wells. In very small quantities, it is also present in coal gas.

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Structure of Ethane:– Ethane is composed of two carbon atoms and six hydrogen atoms i.e C_2H_6. Each C–atom of ethane is sp^3 hybridized containing four sp^3 hybrid orbitals. These four sp^3 hybrid orbitals are arranged in tetrahedral fashion. Out of four sp^3 hybrid orbitals of each C–atom, three hybrid orbitals are utilized in the formation of sigma bonds with three hydrogen atoms, where as remaining sp^3 hybrid orbital of one C–atom overlaps with sp^3 hybrid orbital of other carbon atom to form a sigma orbital between carbon atoms, giving ethane molecule, as shown in figure 7.3:

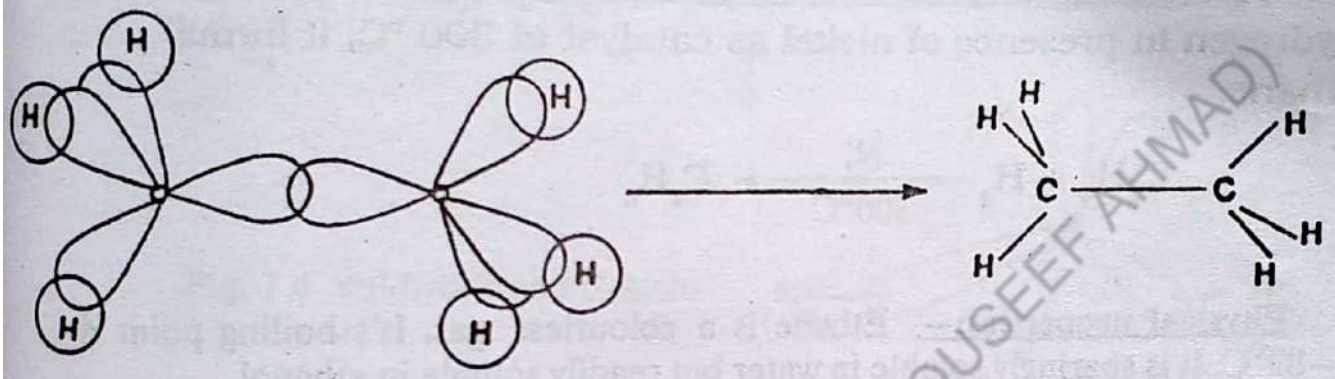

Fig. 7.3 Structure of ethane

Preparations of Ethane:

(1) **From Ethyl Iodide:–** Ethyl iodide on the reduction with nascent hydrogen produces ethane. In this condition,nascent hydrogen is obtained from zinc-copper couple and ethanol.

$$Zn/Cu + 2C_2H_5OH \longrightarrow (C_2H_5O)_2Zn + 2[H] + Cu$$

$$C_2H_5I + \underset{\text{Nascent hydrogen}}{2[H]} \longrightarrow C_2H_6 + HI$$

(2) **By Wurtz Reaction:–** When methyl iodide is treated with sodium metal, ethane is formed.

$$2CH_3I + 2Na \xrightarrow[\text{Solvent}]{\text{Ether}} C_2H_6 + 2NaI$$

In this reaction other products are also formed.

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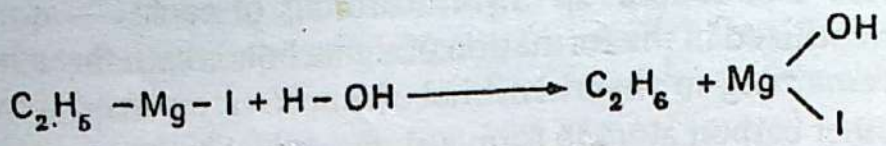
(3) **From Ethyl Magnesium Iodide (Grignard Reagent)** Pure ethane may be obtained by the hydrolysis of ethyl magnesium iodide.



(4) **Catalytic Hydrogenation of Ethene:–** When ethene is treated with hydrogen in presence of nickel as catalyst at 300 °C, it forms ethane.

$$C_2H_4 + H_2 \xrightarrow[300^\circ C]{Ni} C_2H_6$$

Physical properties:– Ethane is a colourless gas. It's boiling point is $-89^\circ C$. It is sparingly soluble in water but readily soluble in ethanol.

Chemical properties:– (i) It burns in air or oxygen with a non–luminous flame to form carbon dioxide and water with the evolution of heat.

$$2C_2H_6 + 7O_2 \longrightarrow 4CO_2 + 6H_2O + \text{Heat}$$

(ii) Halogenation:– It reacts with halogens in a similar manner to methane to form substitution products. The resultant reaction products are, however, much more and these are 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.

$$CH_3-CH_3 \xrightarrow{Cl_2} CH_3-CH_2Cl \xrightarrow{Cl_2} \underset{\text{1.1–dichloro ethane}}{CH_3-CHCl_2} + \underset{\text{1.2–dichloro ethane}}{ClCH_2-CH_2Cl}$$

7.4 CHEMISTRY OF ETHENE (ETHYLENE C_2H_4)

It is the first member of alkenes with molecular formula C_2H_4. It is unsaturated compound containing double bond between two carbon atoms

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$\left(\begin{matrix}H\\H\end{matrix}\!>C=C<\!\begin{matrix}H\\H\end{matrix}\right)$. It occurs in coal gas upto 9%. It is also produced during the destructive distillation of coal.

Structure of Ethene: It is the fist member of alkenes and is composed of two atoms of carbon and four atoms of hydrogen i. e C_2H_4. Each carbon of ethene is sp^2 hybridized containing three sp^2 hybrid orbitals and one unhybridized p_z atomic orbital. Three sp^2 hybrid orbitals are arranged in trigonal fashion with an angle of 120° where as p_z is lying perpendicualr to the plane of sp^2 hybrid orbitals as shown in fig. 7.4.

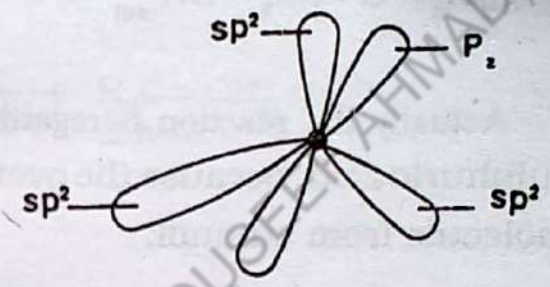

Fig. 7.4 sp^2-hybridized C-atom

Out of three sp^2 hybrid orbitals, two orbitals of each carbon-atom are utilized in the formation of 2 σ– bonds with two hydrogen – atoms, third sp^2 hybridized orbital of one carbon overlaps with sp^2 hybridized orbital of second carbon and forms sigma bond between two carbon–atoms. The remaining p_z orbital of each carbon atom undergoes parallel overlapping with one another and form second bond between two carbon atoms and this is π– bond as given in figure 7.5

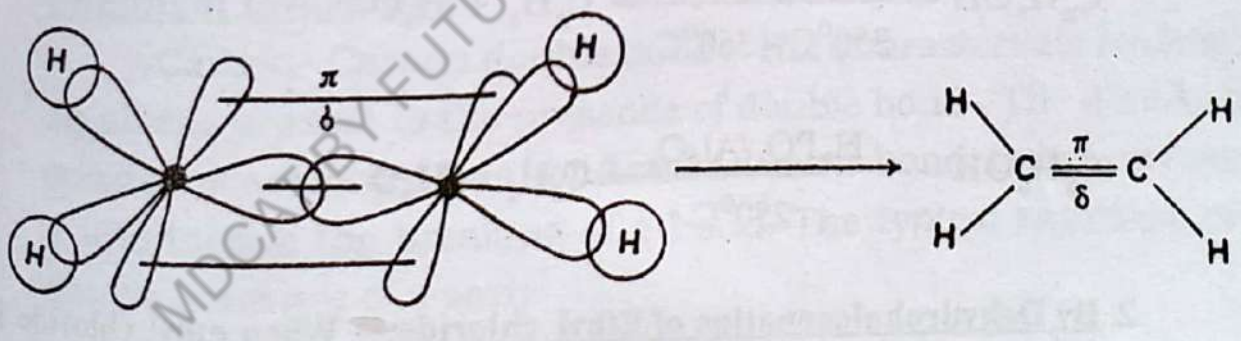

Fig. 7.5

Preparations of Ethene:–

1–(a) **By the Dehydration of Alcohols:–** When ethanol is heated with concentrated H_2SO_4 at 170°C, it produces ethene. The reaction is taking place

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in two stages. On mixing ethanol and sulphuric acid in ratio of 1:2 by volume. Ethyl hydrogen sulphate is formed in cold

$$C_2H_5OH_{(aq)} + H_2SO_{4(aq)} \longrightarrow \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5 \cdot O \cdot SO_2 \cdot OH_{(aq)}} + H_2O_{(l)}$$

On heating ethyl hydrogen sulphate, it decomposes into ethene

$$C_2H_5-O-SO_2-OH_{(aq)} \xrightarrow{\text{Heat}} C_2H_{4(g)} + H_2SO_{4(aq)}$$

Actually the reaction is regarded as the dehydration of ethanol by hot sulphuric acid, because the over all change is the removal of one water molecule from ethanol.

$$C_2H_5OH_{(aq)} \xrightarrow[170\ ^\circ C]{\text{Conc. } H_2SO_4} C_2H_{4(g)} + H_2O_{(l)}$$

(b) Ethanol may be converted to ethene by passing the vapours of ethanol over catalyst just like Al_2O_3, H_3PO_4/Al_2O_3

$$C_2H_5OH \xrightarrow[350^\circ C-360^\circ C]{Al_2O_3} C_2H_4 + H_2O$$

$$C_2H_5OH \xrightarrow[250^\circ C]{H_3PO_4/Al_2O_3} C_2H_4 + H_2O$$

2. **By Dehydrohalogenation of Ethyl chloride:--** When ethyl chloride is treated with alcoholic potassium hydroxide, it produces ethene. This reaction is the example of elimination reaction in which hydrogen is lost by one carbon atom and chlorine from the other carbon atom.

$$CH_3-CH_2-Cl + \underset{\text{Alcohol}}{KOH} \xrightarrow{\text{Heat}} \underset{\text{Ethene}}{CH_2=CH_2} + KCl + H_2O$$

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3. **Dehalogenation of 1,2 – dichloroethane (Vicinal dichloride):–** When vicinal dichloroethane is treated with zinc metal powder, it loses one molecule of halogen and forms ethene.

$$\underset{\underset{Cl}{|}}{CH_2} - \underset{\underset{Cl}{|}}{CH_2} + \underset{(dust)}{Zn} \xrightarrow{Heat} CH_2 = CH_2 + ZnCl_2$$

4. **By Reduction of Ethyne:–** Ethyne on hydrogenation under limited conditions using Ni as a catalyst, adds one molecule of hydrogen to form ethene.

$$\underset{Ethyne}{H - C \equiv C - H} \xrightarrow[Ni/200\ ^{\circ}C]{H_2} \underset{Ethene}{H_2C = CH_2}$$

Physical properties

(i) It is a colourless gas with sweet smell.

(ii) It produces anaesthesia on inhalation

(iii) It is sparingly soluble in water but soluble in organic solvent just like alcohol and ether.

(iv) It is less denser than air.

Chemical properties

Carbon– Carbon double bond:- The characteristic reactions of an alkene are due to the presence of double bond . The double bond consists of a strong sigma bond and a weak π–bond, therefore reaction would involve the breaking of π–bond. The typical reactions of the double bond are of a sort:

$$\rangle C = C \langle + AB \longrightarrow - \underset{\underset{A}{|}}{\overset{\overset{|}{}}{C}} - \underset{\underset{B}{|}}{\overset{\overset{|}{}}{C}} - \quad \text{Addition reaction}$$

In this reaction π bond is broken and two strong δ bonds are formed in its place. A reaction in which two molecules combine to yield a single molecule as product is called addition reaction.

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In these reactions π–bond provides electron to the reagent that is seeking electrons. These reagents are called electrophilic reagents, hence the reaction is called electrophilic addition reaction.

Addition Reactions:-

(1) Addition of hydrogen (2) Addition of halogen (3) Addition of hydrogen halides (4) Addition of sulphuric acid (5) Addition of hypohalous acid. (6) Addition of water.

1-Addition of H_2 (Hydrogenation):- Ethene adds one molecule of hydrogen to form ethane in the presence of nickel catalyst.

$$CH_2 = CH_2 + H_2 \xrightarrow{Ni/300^\circ C} CH_3 - CH_3$$

Ethene reacts rapidly and completely with hydrogen at low temperature and pressure in the presence of metal catalyst such as nickel, platinum and palladium. For maximum catalytic effect, the metal is usually obtained in a finely divided state. This is achieved for platinum and palladium by reducing the metal oxide with hydrogen.

An specially active form of Raney nickel is prepared from a nickel– aluminium alloy; sodium hydroxide is added to dissolve the aluminium and nickel remains as black or nickel catalysts can be prepared by reducing metal salts with sodium hydroxide.

2 - <u>Addition of Halogen:–</u> Ethene adds one molecule of halogen and forms 1,2–dihalo ethane. The order of reactivity of the addition of halogens is $Cl_2 > Br_2 > I_2$ for example Cl_2 and Br_2 add at room temperature where as iodine adds in the presence of ethanol.

$$CH_2 = CH_2 + Cl_2 \xrightarrow{\text{Room temp.}} \underset{Cl}{CH_2} - \underset{Cl}{CH_2}$$

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$$CH_2 = CH_2 + Br_2 \xrightarrow{\text{Room temp.}} \underset{Br}{CH_2} - \underset{Br}{CH_2}$$

$$CH_2 = CH_2 + I_2 \xrightarrow{\text{Ethanol}} \underset{I}{CH_2} - \underset{I}{CH_2}$$

3- **Addition of Hydrogen Halides:–** Ethene adds one molecule of hydrogen halide and forms halo – ethane, the order of the reactivity is HI > HBr > HCl. for example HCl and HBr react slowly than HI.

$$CH_2 = CH_2 + HCl \longrightarrow CH_3 - \underset{Cl}{CH_2}$$

Chloro ethane

4- **Addition of H_2SO_4 :–** Ethene reacts with cold conc: H_2SO_4 (88%) and forms ethyl – hydrogen sulphate.

$$CH_2 = CH_2 + H - O - \overset{O}{\underset{O}{S}} - OH \longrightarrow \underset{H}{CH_2} - \underset{OSO_3H}{CH_2}$$

This reaction is important because ethyl hydrogen sulphate on boiling with water yields ethyl alcohol.

$$CH_3\text{-}CH_2\text{-}OSO_3H + H_2O \longrightarrow CH_3\text{-}CH_2\text{-}OH + H_2SO_4$$

5- **Addition of Hypohalous acid:–** Ethene adds hypohalous acid and forms ethane halo hydrin

$$CH_2 = CH_2 + \overset{\delta-}{HO} - \overset{\delta+}{X} \longrightarrow \underset{OH}{CH_2} - \underset{X}{CH_2}$$

In hypohalousacids (HO – X), the OH^- group is the negative ends of hypohalous acids.

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Reaction with chlorine water and bromine water:– Chlorine water containing HCl and HOCl, combines with ethene and forms a mixture of chloroethanol (chlorohydrin) and chloroethane.

$$Cl_2 + H_2O \rightarrow HCl + HOCl$$

$$CH_2 = CH_2 + H\overset{\delta-}{O}C\overset{\delta+}{l} \rightarrow \underset{OH}{C}H_2 - \underset{Cl}{C}H_2$$

$$CH_2 = CH_2 + \overset{\delta+}{H}-\overset{\delta-}{Cl} \rightarrow CH_2 - CH_2Cl$$

6 – **Reaction with $KMnO_4$:–** When ethene is added in dilute and alkaline solution of $KMnO_4$, ethene is oxidized to ethane 1 – 2 diol (ethylene glycol) and purple colour of $KMnO_4$ is decolourized.

$$CH_2 = CH_2 + H_2O + [O] \xrightarrow[\text{From } KMnO_4]{} \underset{OH}{CH_2} - \underset{OH}{CH_2}$$

Ethylene glycol

7 – **Addition of water (Hydration):–** Water adds with ethene under the catalytic action of acid. It is reversible reaction because dehydration (loss of water) is also acid catalyzed reaction.

$$CH_2 = CH_2 + H_2O \overset{H^+}{\rightleftharpoons} \underset{H}{CH_2} - \underset{OH}{CH_2} \quad \text{or} \quad CH_3 - CH_2 - OH$$

8- Formation of Mustard gas:- Ethene on treatment with sulphur monochloride forms mustard gas which is highly poisonous. It attacks especially to skin. It was used in first World War.

$$2CH_2 = CH_2 + S_2Cl_2 \longrightarrow S\left\langle \begin{matrix} CH_2 - CH_2 - Cl \\ CH_2 - CH_2 - Cl \end{matrix} \right. + S$$

β, β' –dichloro di-ethyl sulphide (Mustard gas)

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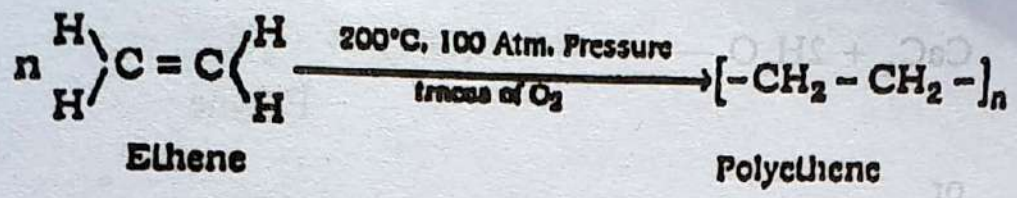
9- Formation of polyethene:- Ethene polymerizes at 200°C and under 100 atmospheric pressure in the presence of traces of oxygen to form polyethene.



Uses:– Ethylene or ethene is used as anaesthetic and in the manufacture of mustard gas $Cl_2(CH_2-CH_2)_2S$, plastic etc. It is also used for ripening of fruits.

7.5 CHEMISTRY OF ETHYNE (ACETYLENE)

It is the first member of alkynes with molecular formula C_2H_2. It is unsaturated compound containing triple bond between two carbon atoms (H–C≡C–H).

It is present in oil gas and coal gas upto 10%. It is commonly called as acetylene.

Structure of Ethyne:– Each carbon atom in acetylene is attached to one hydrogen atom by a single covalent bond (σ–bond) and to another carbon atom by a triple bond. Thus each carbon uses sp^1 hybridized orbitals and two unhybridized 2p orbitals (p_y and p_z) to form its pi–bonds (π–bond). It is shown in the figure 7.6

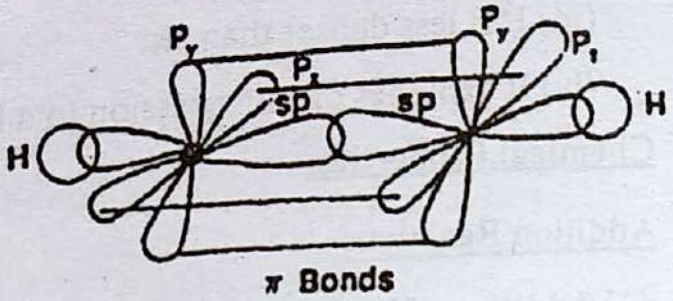


Fig. 7.6 Structure of ethyne

Electron diffraction studies have shown that acetylene is a linear structure. The H–C–C or C–C–H bond angle is 180°. The C–H bond length is 1.09°A and C≡C bond length is 1.20°A.

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Preparations of Ethyne:–

(1) **From calcium carbide:–** It is obtained by the action of cold water on calcium carbide.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Ethyne}}{C_2H_2}$$

or

$$\overset{Ca}{\diagup\diagdown}C \equiv C + 2H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Ethyne}}{HC \equiv CH}$$

(2) From dibromo ethane:– Dibromoethane on boiling with alcoholic KOH produces acetylene.

$$\underset{Br}{\underset{|}{CH_2}} - \underset{Br}{\underset{|}{CH_2}} + 2KOH \xrightarrow{\text{Alcoholic}} CH \equiv CH + 2KBr + 2H_2O$$

Physical Properties:–

(i) It is a colourless gas with sweet smell.

(ii) It is sparingly soluble in water.

(iii) It is less denser than air.

(iv) It explodes on compression to a liquid because of unstable nature.

Chemical Properties:

Addition Reactions

(1) **Addition of Hydrogen (Hydrogenations):–** Ethyne adds two molecules of H_2 in presence of catalyst, (Ni) at about 200°C to ethene and then to ethane.

$$\underset{\text{Ethyne}}{HC \equiv CH} \xrightarrow[200°C]{H_2/Ni} \underset{\text{Ethene}}{CH_2 = CH_2} \xrightarrow[300°C]{H_2/Ni} \underset{\text{Ethane}}{CH_3 - CH_3}$$

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(2) **Addition of Halogens:–** Ethyne reacts with Cl_2 and Br_2 in the presence of a catalyst even in dark and forms chloro and bromo derivatives. The reaction rate is slower as compared to ethene.

(i) $$CH \equiv CH + Cl_2 \longrightarrow \begin{array}{c} CH = CH \\ | \quad\quad | \\ Cl \quad\quad Cl \end{array}$$

(ii) $$\begin{array}{c} CH = CH \\ | \quad\quad | \\ Cl \quad\quad Cl \end{array} + Cl_2 \longrightarrow \begin{array}{c} Cl \quad\quad Cl \\ | \quad\quad\quad | \\ CH - CH \\ | \quad\quad\quad | \\ Cl \quad\quad Cl \end{array}$$

Ethyne adds I_2 with difficulty but in the presence of ethanol, di–iodide is formed.

$$CH \equiv CH + I_2 \xrightarrow{\text{Ethanol}} \begin{array}{c} CH = CH \\ | \quad\quad | \\ I \quad\quad I \end{array}$$

(3) **Addition of Hydrogen Halides:–** Ethyne adds one or two molecules of hydrogen halides.

$$CH \equiv CH + HBr \longrightarrow \begin{array}{c} CH = CH \\ | \quad\quad | \\ H \quad\quad Br \end{array} + HBr \longrightarrow \begin{array}{c} H \quad\quad Br \\ | \quad\quad\quad | \\ CH - CH \\ | \quad\quad\quad | \\ H \quad\quad Br \end{array}$$

Vinyl bromide 1.1-Dibromo ethane

The addition of second molecule of HBr to vinyl bromide, takes place according to Markownikoff's rule. This rule states that the negative part of HBr adds with carbon of the compound which contains the least number of hydrogen atoms.

Ethyne combines with hydrogen iodide at room temperature, with hydrogen bromide at 100°C and the reaction with hydrochloric acid is very slow.

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(4) **Addition of HCN:–** Ethyne adds HCN in the presence of cuperous chloride and NH_4Cl to form acrylonitrile (Vinyl cyanide).

$$HC \equiv CH + HCN \xrightarrow{Cu_2Cl_2/NH_4Cl} \underset{CN}{HC} = \underset{H}{CH}$$

Vinyl cyanide

Acrylonitrile is used in the manufacture of polymers.

(5) **Addition of Water:–** Ethyne reacts with water in presence of mercuric sulphate and sulphuric acid at 75°C to produce unstable intermediate vinyl alcohol which on rearrangement forms ethanal (aldehyde).

$$CH \equiv CH + H_2O \xrightarrow[75\,^{o}C]{HgSO_4/H_2SO_4} \left[CH_2 = \underset{OH}{CH} \right] \xrightarrow{\text{Rearrangement}} CH_3 - \overset{O}{\overset{\|}{C}} - H$$

Intermediate vinyl alcohol

Ethanal

(6) **Combustion of Ethyne:–** The complete combustion of ethyne is exothermic and releases 312 KJ/mole heat. Due to evolution of this high amount of heat, the oxyacetylene flame can attain a temperature upto 3000°C which is used in gas weldings.

$$CH \equiv CH + \frac{5}{2}O_2 \longrightarrow 2CO_2 + H_2O \quad \Delta H = -312\ KJ/mole$$

(7) **Oxidation of Ethyne:–** When ethyne is treated with hot aqueous $KMnO_4$, two molecules of acid are formed.

$$CH \equiv CH + H_2O + 3[O] \xrightarrow[Cold]{KMnO_4} 2HCOOH$$

Formic acid

$$CH \equiv CH + 4[O] \xrightarrow[Hot]{KMnO_4} O = \overset{OH}{\overset{|}{C}} - \overset{OH}{\overset{|}{C}} = O$$

Oxalic acid

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Substitution Reaction or Acidility of Ethyne

(1) **Replacement by Na:–** When acetylene is passed over heated sodium, both the monosubstituted, and disubstituted acetylides are formed.

$$HC \equiv CH \xrightarrow[\text{heat}]{\text{Na}} \underset{\text{Mono sodium acetylide}}{CH \equiv CNa} \xrightarrow[\text{heat}]{\text{Na}} \underset{\text{Di - sodium acetylide}}{NaC \equiv CNa}$$

If di-sodium acetylide is treated with an acid, acetylene is reformed.

$$NaC \equiv CNa + 2HCl \longrightarrow HC \equiv CH + 2NaCl$$

(2) **Replacement of Heavy Metals:–** When acetylene is heated with $AgNO_3$ or cuprous chloride in Ammonia cuprous acetylide or silver acetylide is formed.

$$CH \equiv CH + 2AgNO_{3(aq)} \xrightarrow{\text{Ammonia}} \underset{\substack{\text{Silver acetylide} \\ \text{(White solid)}}}{AgC \equiv CAg} + 2HNO_3$$

$$CH \equiv CH + 2CuCl_{(aq)} \xrightarrow{\text{Ammonia}} \underset{\substack{\text{Copper acetylide} \\ \text{(Red solid)}}}{Cu - C \equiv C - Cu} + 2HCl$$

In these reactions, acetylene shows acidic properties.

Uses:– Acetylene is used for the preparation of oxyacetylene flame which has a temperature of 3000°C. It is also used in welding purposes. It is used for the preparation of acetaldehyde, acetic acid and ethanol for the manufacture of PVC i.e polyvinyl chloride.

7.6 BENZENE

In the early nineteenth century, when organic chemistry was still developing, organic compounds were classified as either aliphatic or aromatic. Aliphatic compounds are open chain or acyclic compounds and were so named because

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of the fact that the first compounds of this class to be studied were fatty acids (Greek : aliphos = fat). Besides aliphatic compounds, large number of compounds were obtained from natural sources e.g. resins, balsams and "aromatic" oils from plants, whose structures at that time were unknown but had one thing in common, a pleasant smell and were thus classified as aromatic (Greek : aroma = pleasant smell). Careful investigations of these compounds showed that they contained a much higher percentage of carbon content than corresponding aliphatic hydrocarbons and majority of simple aromatic compounds contained at least six carbon atoms. It was also discovered that when these compounds were subjected to various treatment they often yielded benzene or its derivatives. It was thus concluded that aromatic compounds were related to benzene whose molecular formula was found to be C_6H_6. Benzene was first isolated by Faraday in 1825 and was found to be one of the constituents of coal tar by Hofmann in 1845. Coal tar and petroleum are the two main sources of obtaining benzene and its derivative on industrial and commercial scale.

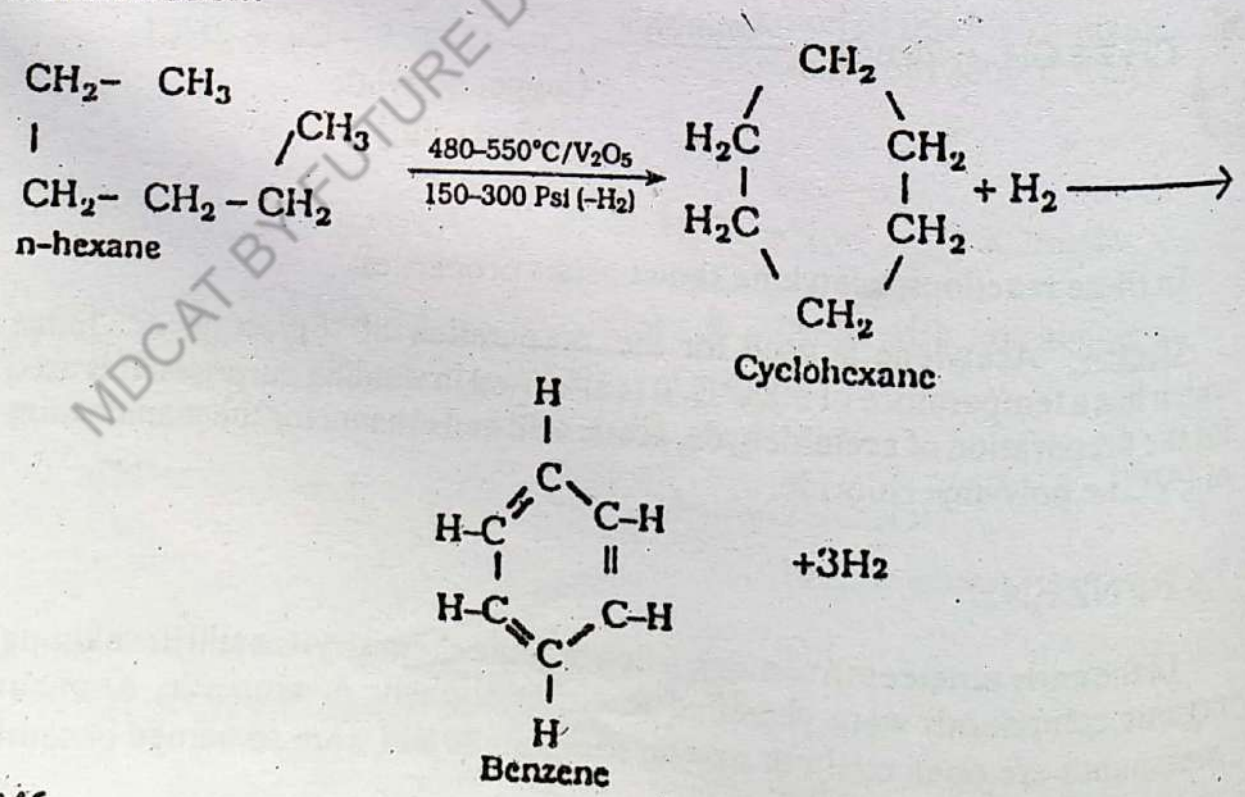
Extraction of benzene (Isolation)

Benzene is prepared by different methods as under:

(i) From Petroleum (n-hexane) (Hydro forming process):-

n-hexane on heating at 480–550°C and under pressure of 150–300 pounds per square inch and in presence of catalyst such as oxides of chromium, molybdenum, vanadium forms benzene.

This method is based on dehydrogenation, cyclisation and isomerization.



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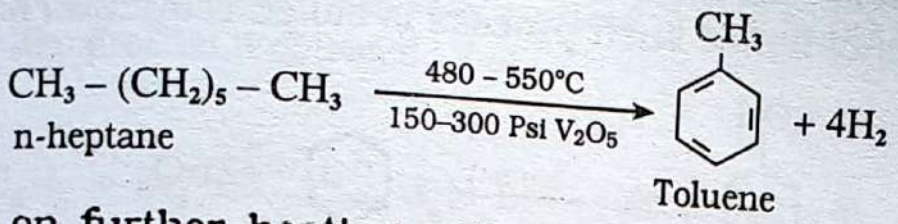
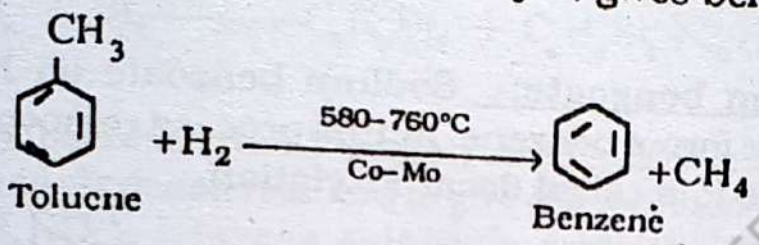
(ii) From n-heptane:- When n-heptane is heated at high temperature and under high pressure and in presence of catalyst, gives toluene.



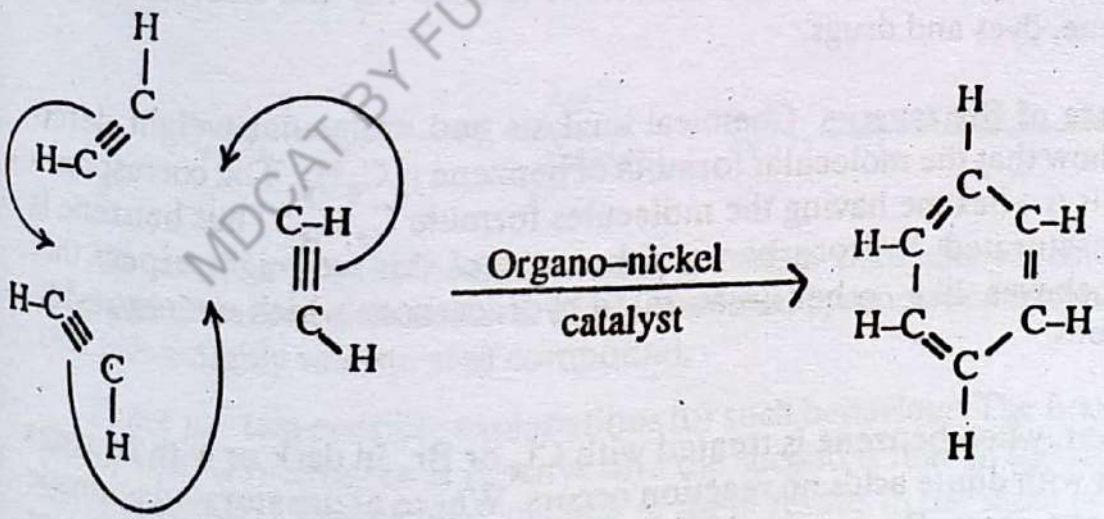
Toluene on further heating with hydrogen at 580–760°C and in presence of cobalt–molybdenum catalyst, gives benzene.



(iii) From Coal:- One thousand kilograms of bituminous–coal on heating in absence of air, gives 50 kg. of coal tar (along with coal gas and coke) which by further fractional distillation produces 0.5 to 1.0 kg. benzene.

Bituminous Coal (1000 kg) $\xrightarrow{\text{Heated in absence of air}}$ Coal tar (50Kg) $\xrightarrow[\text{distillation}]{\text{fractional}}$ Benzene (0.5–1.0 kg)

(iv) From Acetylene:- Acetylene on passing through red hot tube in presence of organo nickel catalyst, forms benzene by polymerization.



or

$$\underset{\text{Acetylene}}{3(H-C\equiv C-H)} \longrightarrow \underset{\text{Benzene}}{C_6H_6}$$

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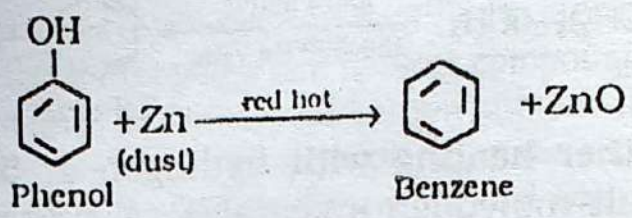
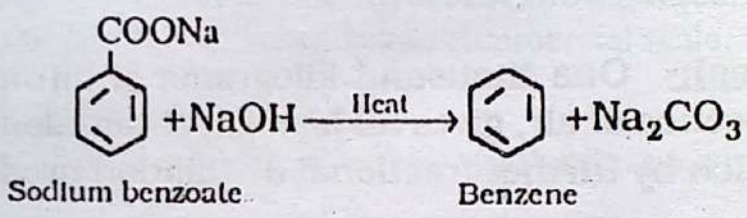
(v) From phenol:- When vapours of phenol are passed over red hot zinc dust then it is converted into benzene. As removal of oxygen takes place from phenol hence such process is called reduction of phenol.



(vi) From sodium benzoate:- Sodium benzoate on heating with sodium hydroxide forms benzene. In this process removal of carboxyl takes place hence it is called decarboxylation.



Physical Properties of Benzene:– Benzene is a colourless liquid having m.p. 5.5°C, b.p. 80°C with a peculiar smell. It is highly inflammable as aromatic compounds contain more carbon and less hydrogen. Benzene burns with a smoky flame as it contains 93.6% carbon. It is immiscible in water. It is however miscible in ethanol and ether and dissolves fats, resins, sulphur, iodine etc. It is toxic compound and causes blood cancer. It is used for the manufacture of nitrobenzene, dyes and drugs.

Structure of Benzene:– Chemical analysis and molecular weight determination show that the molecular formula of benzene is C_6H_6. The corresponding alkane is n–hexane having the molecules formula C_6H_{14}. Thus benzene is a highly unsaturated hydrocarbon and because of this we might expect that benzene behaves like other unsaturated hydrocarbons which undergo addition reactions.

However, when benzene is treated with Cl_2 or Br_2 in dark or with aqueous $KMnO_4$ or with dilute acids,no reaction occurs. Where as unsaturated aliphatic hydrocarbons react. Benzene reacts with these reagents but under different conditions and undergoes substitution reaction. Substitution reaction is the most common kind of reaction of the aromatic ring i.e replacement of hydrogen by another atom or group of atoms.

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For instance, benzene will react with bromine in presence of Lewis acid catalyst ferric bromide. The product obtained is bromobenzene,(C_6H_5Br) in which one hydrogen atom has been replaced or substituted by bromine atom. No addition product is obtained ; thus

$$\text{(i)}\ C_6H_6 + Br_2 \xrightarrow{FeBr_3} C_6H_5Br + HBr\ \text{(Observed)}$$

$$\text{(ii)}\ C_6H_6 + Br_2 \longrightarrow C_6H_6Br_2 + C_6H_6Br_4 + C_6H_6Br_6\ \text{(Not observed)}$$

Similarly, benzene (aromatic rings) undergoes chlorination, nitration, sulphonation and alkylation reactions to give chlorobenzene (C_6H_5Cl), nitrobenzene ($C_6H_5NO_2$), benzene sulphonic acid ($C_6H_5SO_3H$) and toluene ($C_6H_5CH_3$) respectively.

$$C_6H_6 + Cl_2 \xrightarrow[\text{catalyst}]{\text{iron as}} C_6H_5Cl + HCl$$

$$C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} C_6H_5NO_2 + H_2O$$

$$C_6H_6 + H_2SO_4 \longrightarrow C_6H_5SO_3H + H_2O$$

$$C_6H_6 + CH_3 - Cl \xrightarrow[\text{catalyst}]{AlCl_3} C_6H_5CH_3 + HCl$$

All these are substitution products rather than the expected addition products. Benzene thus behaves like a saturated hydrocarbon in spite of the fact that it is a highly unsaturated compound.

There are two possible explanations for such behaviour. The first is that only one of the six hydrogens is reactive and the second is that all the six hydrogens are equivalent and replacing any one of them results in the same product.

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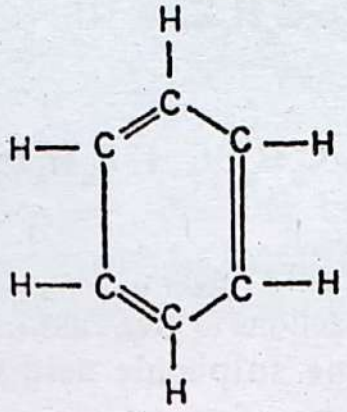
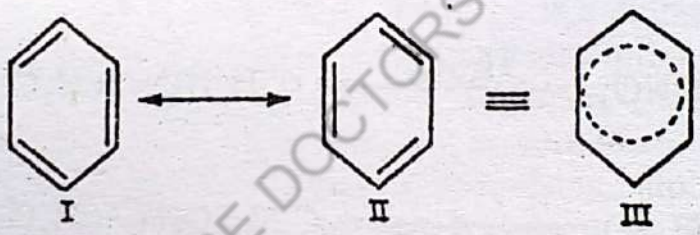
The second explanation appears to be more acceptable and as we will soon learn to be the correct one.

To explain such unusual behaviour of benzene several structures were proposed. Kekule in 1865 proposed a ring structure (I) for benzene with alternate carbon – carbon double bonds.

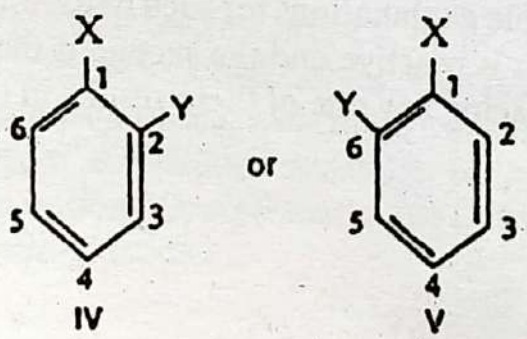


According to Kekule, formula of benzene should give addition products. The structure of benzene is equally represented by structures I and II and that these structures are equivalent and can result by shifting of double bond.



The structure would amount to a structure some what similar to III above. It would appear that the double bond is not fixed and that all C – C positions have a partial double bond character.

The structure and bonding in benzene ring was debated for about 30 years. One objection to Kekule formula was that it would give two disubstituted (IV or V) ortho – products (in which the substituents are on adjacent carbons) whereas in practice only one was isolated



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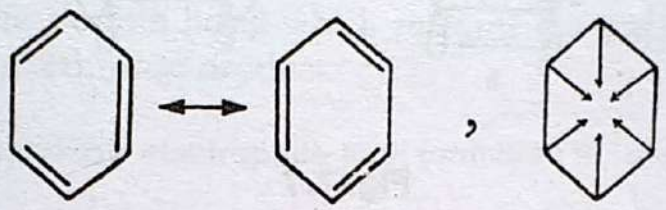
In IV the substituents (X and Y) are on carbons containing a single bond while in V the substituents are on carbons containing a double bond. To explain why only one product is obtained, Kekule in 1872 forwarded his theory that the carbon atoms in benzene were in a state of vibration and due to this vibration, each carbon – carbon pair had a single bond half of the time and a double bond the other half. This results in oscillation of double and single bond resulting in form VI and VII.



VI VII VIII

Following the suggestion of Armstrong in 1887, Bayer in 1892 proposed the Armstrong – Bayer centric formula VIII in which the fourth valence of each carbon is directed towards the centre. This, however, did not find much support.

7.7 THE MOLECULAR ORBITAL TREATMENT OF BENZENE

The fact that benzene molecule is a regular flat hexagon, with all the six hydrogen atoms lying in the plane of the ring and that the bond angles of the carbon atoms (C–C–C) in the ring and carbon – carbon – hydrogen (C–C–H) atoms are all 120°, strongly indicates that each carbon atom forms a hybrid orbital by mixing of 2s and two 2p orbitals which are called sp^2 hybrid orbital. The sp^2 orbitals of adjacent carbon atoms overlap with each other linearly ($sp^2 - sp^2$) and form sigma bonds.

The third electron of each carbon atom forms another sigma bond with 1s orbital of hydrogen atom ($sp^2 - s$). Like this there are twelve sigma bonds, six between two carbon atoms and six between carbon and hydrogen atoms. The fourth electron of $2p_z^1$ remains with the carbon atom in the form of lobes. The $2p_z^1$ of the two adjacent carbon atoms are shared forming a π orbital. These π orbitals are parallel to each other. There are six $2p_z^1$ electrons one on each

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carbon atom. These six $2p_z$ electrons or orbitals on each carbon atoms are perpendicular to the plane of the ring and parallel to each other as shown in figure 7.7 (a).

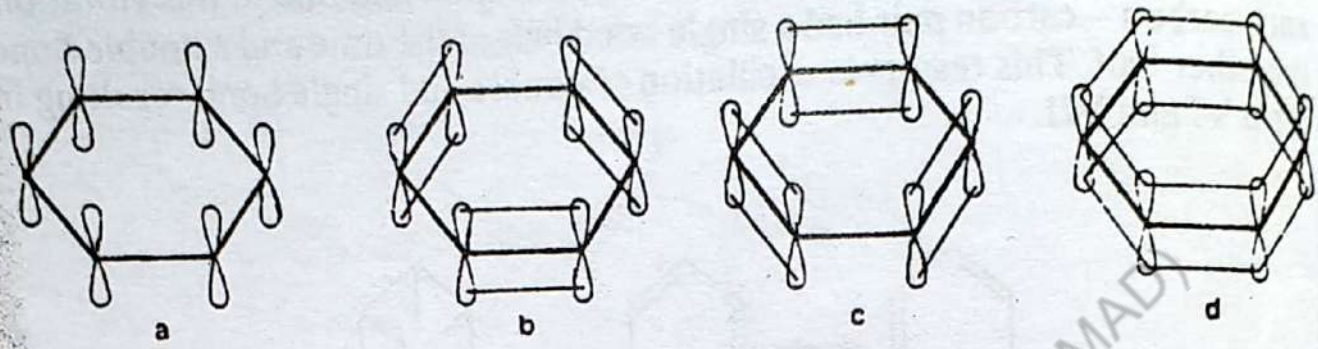

Fig. 7.7

The electrons in these p – orbitals can be paired in two ways (as shown in figure 7. 7 b,c) and since the carbon – carbon bond lengths are all 1.39 °A, each orbital overlaps its neighbour equally and, therefore, all the six can be regarded as forming a single molecular orbital (M O) embracing all the six carbon atoms as shown in figure 7.7 d.

Modern Representation of Benzene Structure:– The molecular orbital representation of benzene as shown in figure 7. 7 a and d are useful for understanding the high stability of the benzene ring but inconvenient for normal use. Two symbols are at present commonly used to represent the benzene molecule. These are: (1) A regular hexagonal with an inscribed circle and (2) A hexagonal with alternate single and double bonds. These are shown in Figure 7.8 .

Fig. 7.8

The first symbol is useful to describe the delocalisation of π electrons in the aromatic system; while the second which is similar to Kekule structure is a simple and accurate way of representing the movement of electrons.

Reaction of Benzene:– The principal reactions of benzene are electrophilic substitution reactions. However, under special conditions, benzene undergoes addition and oxidation reactions.

Electrophilic Substitution Reactions:– If we look again at the figure 7.7 a, d we will observe that there is a cloud of π – electrons above and below the

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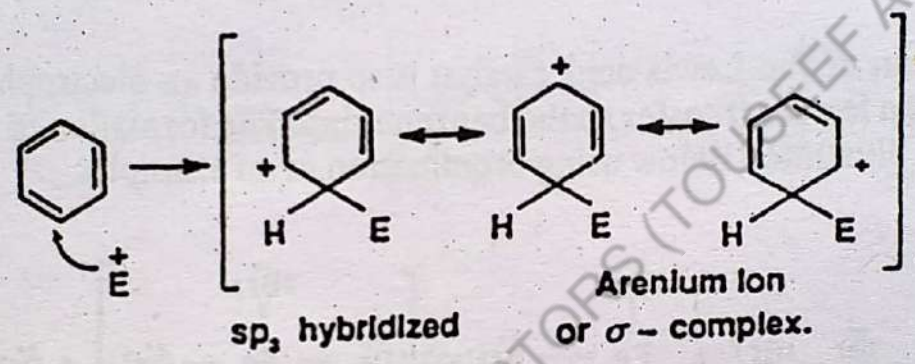
plane of benzene molecule. It is these π – electrons that are responsible for electrophilic substitution reactions of benzene. In these types of reactions, an electrophile attacks the π – system of benzene to yield a delocalized carbocation known as arenium ion or a σ – complex. The electrophile does this by taking two electrons of the p_z – system to form a σ – bond between it and one carbon of the benzene ring. This breaks the cyclic system of π(Pi) electrons, because when arenium ion is formed, one carbon (the carbon that is attacked by the electrophile) becomes sp^3 – hybridized. This causes instability and to overcome this instability the arenium ion loses a proton from the carbon that bears the electrophile as shown below in step (1) and (2). The loss of proton results in the regeneration of the double bond which restores the stability of the ring and formation of the substitution product.

Step 1 Attack by electrophile and formation of σ - complex.



Step 2 Loss of proton, formation of substitution Product.

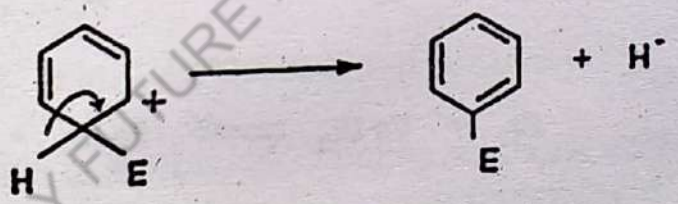


Fig. 7. 9

Important electrophilic reactions of benzene are the following:

(i) Halogenation

(ii) Nitration

(iii) Sulphonation

(iv) Alkylation and acylation by Friedel-Crafts reaction

These reactions are important since the substitution products they form, are used as starting raw materials for a multitude of organic compounds.

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(i) Halogenation Of Benzene:– In the presence of Lewis acids catalyst, benzene reacts with bromine and chlorine to yield bromobenzene and chlorobenzene. Iodination does not give good yield and fluorination is too vigorous to control.

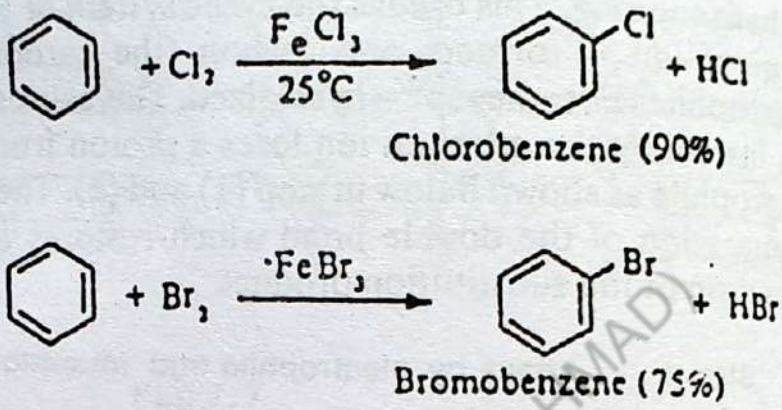

Fig. 7.10 Halogenation of benzene.

The function of the Lewis acid catalyst is to provide an electrophile i.e a positive halogen ion for transfer to the benzene ring. The formation of positive halogen ion is illustrated below using bromination as an example.

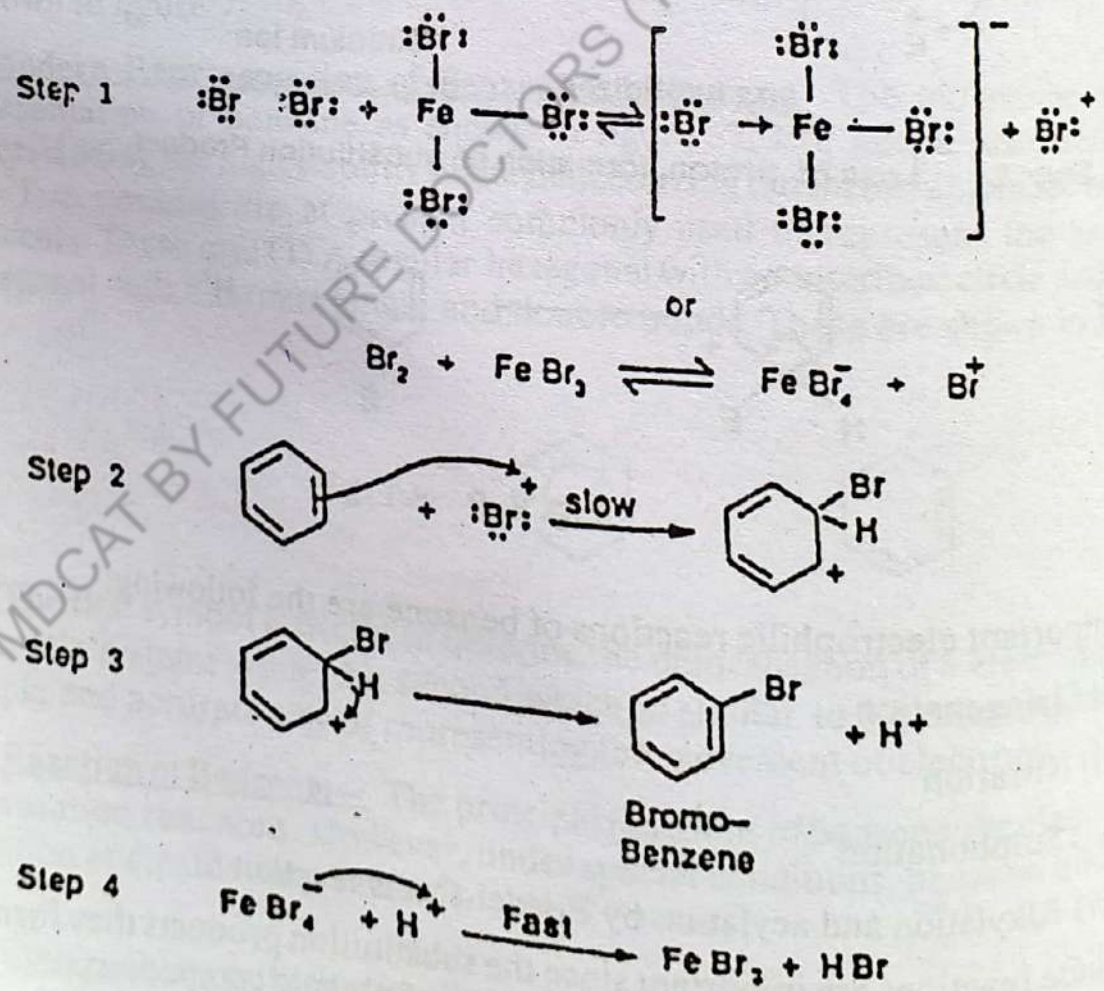

Fig. 7.11

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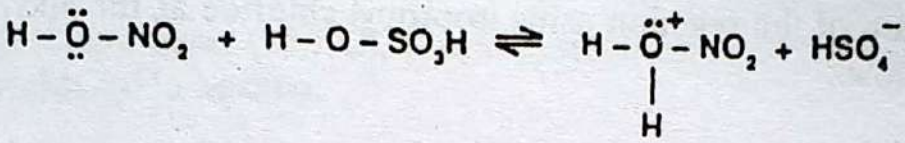
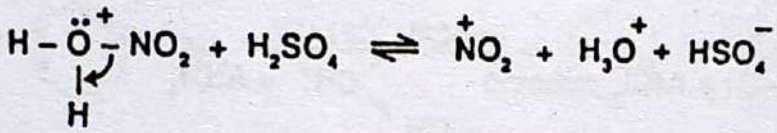
(ii) Nitration of Benzene:– The nitration of benzene is carried out using a mixture of concentrated HNO_3 and conc.H_2SO_4 in the ratio 1:1. The function of conc. H_2SO_4 is to increase the rate of reaction by increasing the concentration of the electrophile – the nitronium ion, NO_2^+ . The various steps of the reactions are as follows:

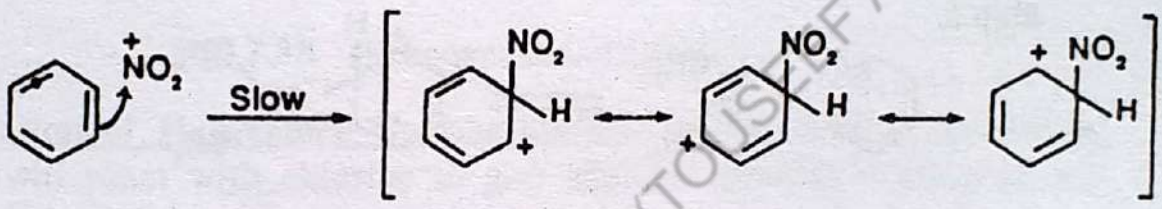
Step 1.



Step 2.



Step 3.



Step 4.

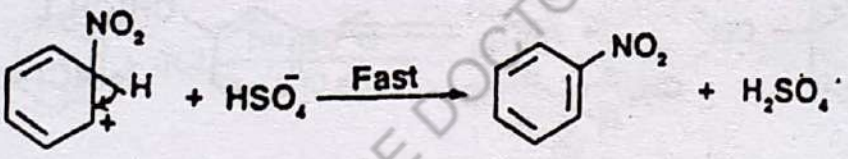


Fig. 7.12 (Nitration of benzene)

(iii) Sulphonation of Benzene:– Fuming sulphuric acid at room temperature reacts with benzene to produce benzene sulphonic acid. Fuming sulphuric acid contains sulphur trioxide (SO_3) which is the sulphonating reagent.

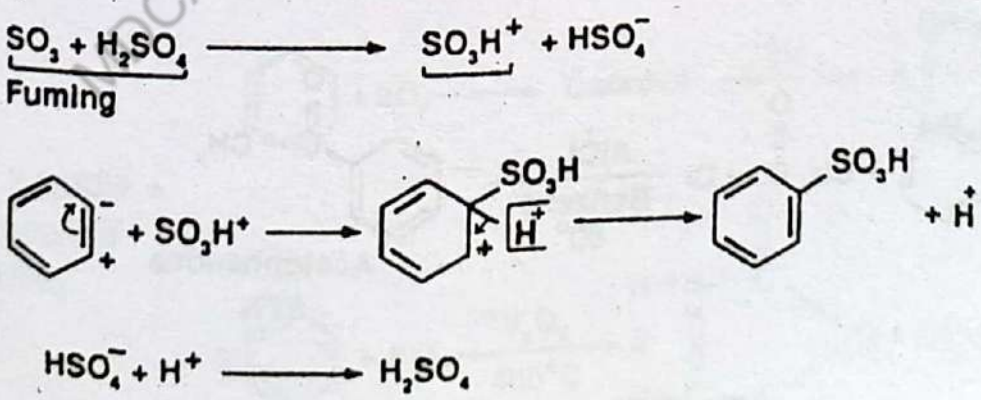


Fig. 7.13 Sulphonation of benzene

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(iv) Alkylation and Acylation by Friedel-Crafts Reaction:- The introduction of the alkyl group (R –) and acyl group (R – C = O) in the benzene ring is generally achieved with the help of Lewis acid catalysts such as $AlCl_3$. The reaction is known as Friedel — Crafts reaction after a French chemist, Friedel and his American collaborator, Craft.

Alkylation of benzene is affected by alkyl halide using $AlCl_3$ as Lewis acids. The mechanism of the reaction using isopropyl chloride as the alkyl halide is illustrated below:

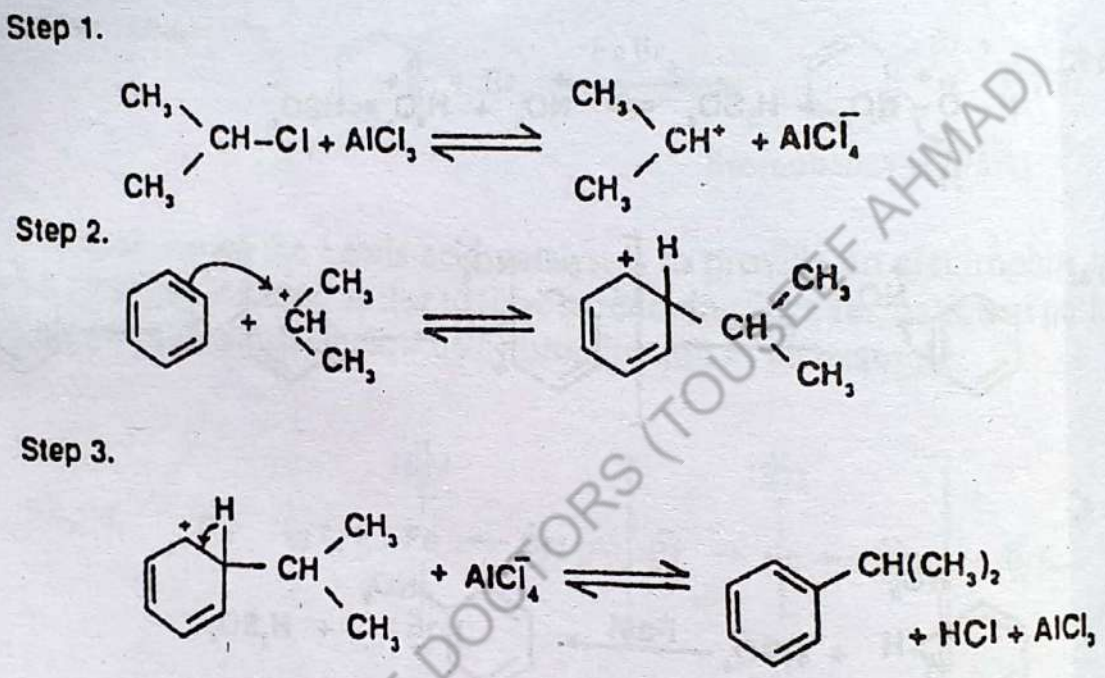

Fig. 7.14 Friedel Crafts alkylation and acylation

Friedel-Crafts Acylation is achieved by using a suitable acyl halide in presence of lewis acid catalyst ($AlCl_3$) for example:

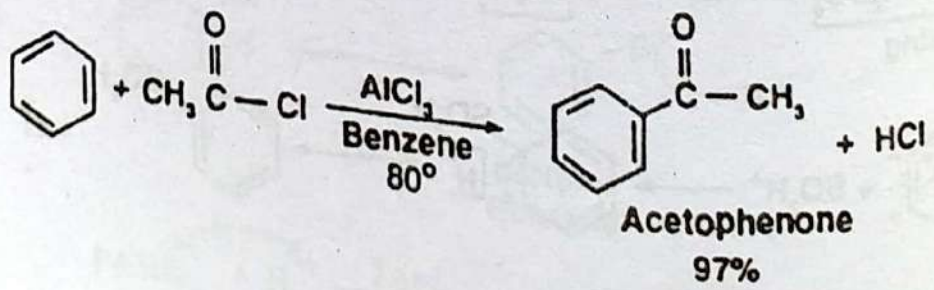

Fig. 7.15 Acylation of benzene

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Addition Reaction of Benzene:– Under rigorous conditions benzene undergoes addition reaction like hydrogenation and halogenation. In both cases the aromatic character of the ring is lost and benzene is reduced successively to an unsaturated and saturated cyclic compounds.

Hydrogenation of Benzene

At high temperature (150°C), 10 atm. pressure and in presence of Ni catalyst, benzene yields cyclo hexane.

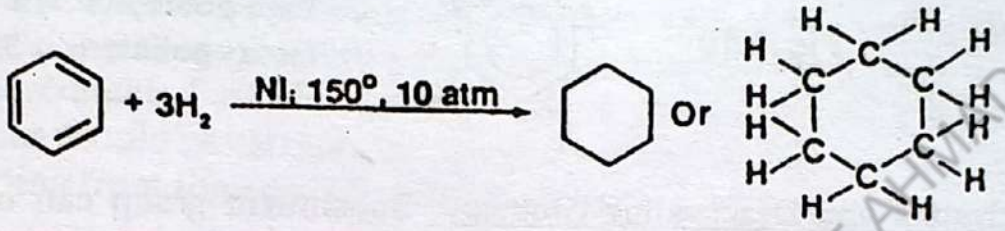


Fig. 7.16 Hydrogenation of benzene

Formation of Hexachloro Cyclohexane :– Under suitable conditions, benzene will react with chlorine to give addition product — Hexa chloro cyclohexane.

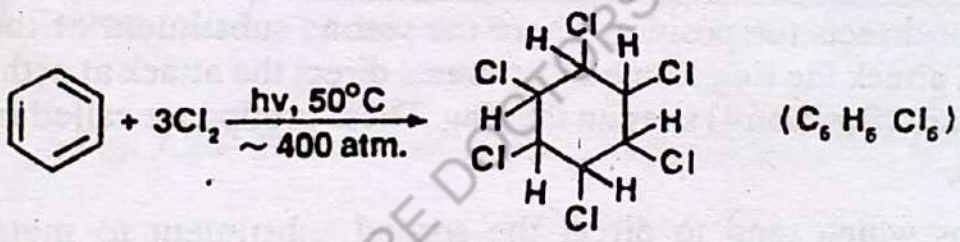


Fig. 7.17

Oxidation of Benzene:– Benzene is not affected by common oxidizing reagent such as $KMnO_4$ or $K_2Cr_2O_7$. It however, forms an ozonide with ozone and may be oxidized to maleic anhydride under proper conditions.

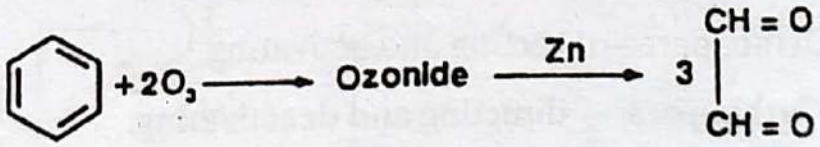
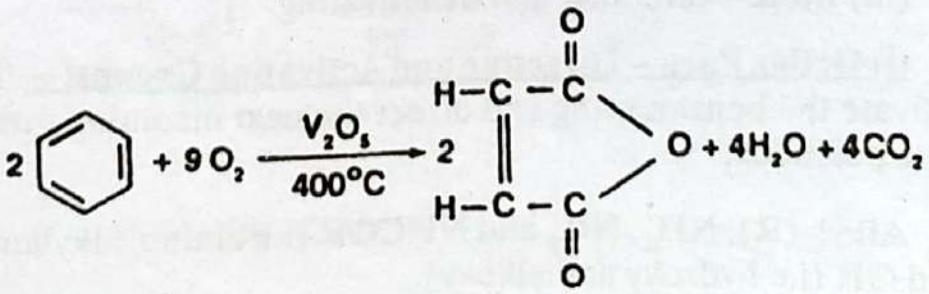


Fig. 7.18 Oxidation of benzene.



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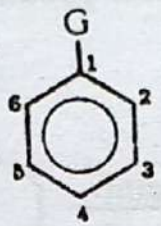
The Electrophilic Substitution Reactions of Monosubstituted Benzenes:

When monosubstituted benzene (C_6H_5-G) undergoes electrophilic attack, the substituent (G) already present on the ring affects both the rate of the reaction and site of the attack. The numbering of the ring of substituted benzene is shown below:

Fig. 7.19



Ortho positions 2, 6
Para positions 4
Meta - positions 3, 5

Activating and Deactivating Groups:– Substituent group can be classified into two main groups according to their influence on the reactivity of the ring. Groups that cause the ring to be more reactive than benzene, are termed activating groups. Those groups that make the ring less reactive are called deactivating groups.

Ortho-Para Directors and Meta Directors:– The substituent G, also influences or directs the position where the second substituent or the incoming group will attack the ring. Some substituents direct the attack at ortho (Position 2,6) and para (Position 4) sites on the ring. These groups are called ortho–para directors.

Groups which tend to direct the second substituent to meta–position (positions 3,5) are called **Meta–Directors**

It is useful and convincing to remember the following classification of the substituent groups into three different classes with regard to whether they are activating or deactivating and whether they are ortho, para directing or meta–directing.

(i) Ortho, para – directing and activating.

(ii) Ortho, para – directing and deactivating.

(iii) Meta – directing and deactivating.

(i) Ortho, Para – Directing and Activating Groups:– The following groups activate the benzene ring and direct the next incoming substituent to ortho and para positions:

Alkyl (R); NH_2, NR_2 and NHCOR (i.e amino, alkylamino and amide), OH and OR (i.e hydroxy and alkoxy).

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(ii) Ortho, Para directing and de – activating groups:– The halogens: F, Cl, Br and I are moderate de – activating groups and direct the incoming groups to ortho – para position.

(iii) Meta – directing and de – activating groups:– The following are included in this group NO_2 (nitro); SO_3H (Sulphonic acid) and all carbonyl compounds: COOH, COOR, CHO and COR (carboxylic acids, esters, aldehydes and ketones).

Preparation of Benzene Derivative:– The knowledge of substitution reactions of aromatic rings and the nature of substitution already present on the ring together, provides a chemist a very powerful tool to synthesize a large number of benzene derivatives. Part of the art of synthesis lies in deciding the order in which reactions should be carried out. Suppose we wish to make m – Nitrobenzoic acid starting from toluene. We will follow the following route.

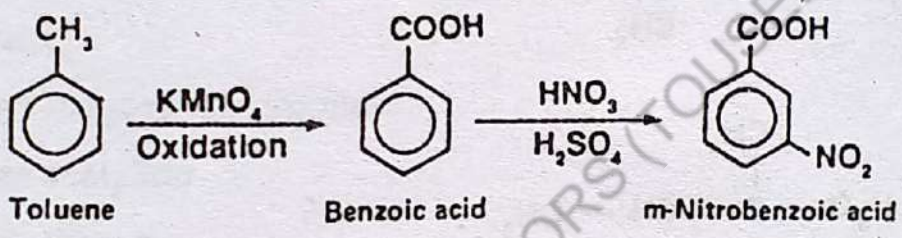

Fig. 7.20 Preparation of benzene derivative

If we wish to make ortho or para – nitrobenzoic acid, we will simply reverse the order of reaction; thus: –

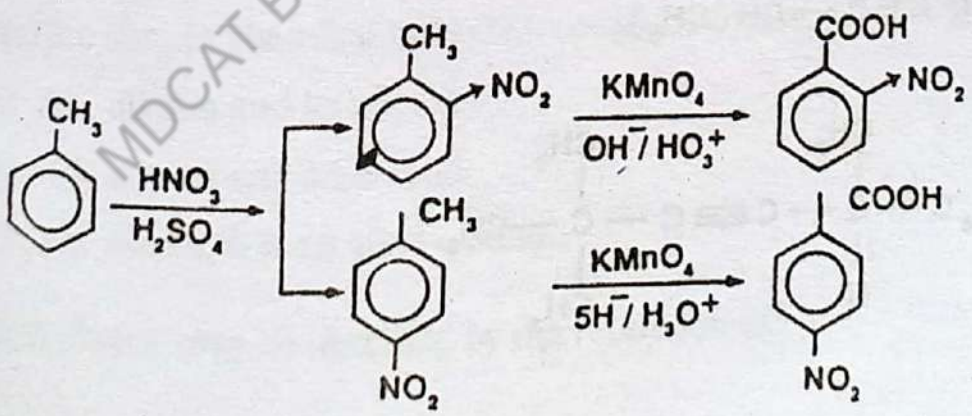

Fig. 7.21

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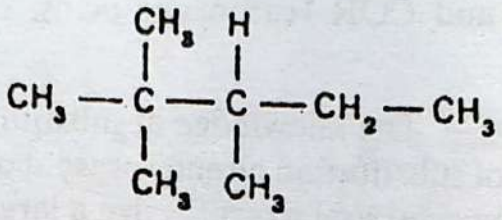
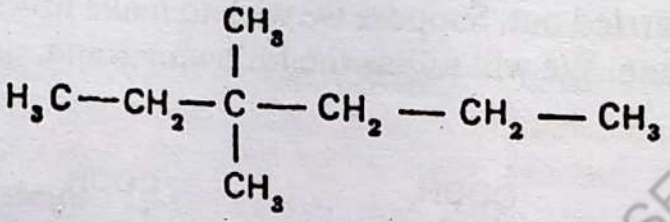
ASSIGNMENT

1. Name the following by I.U.P.A.C system:

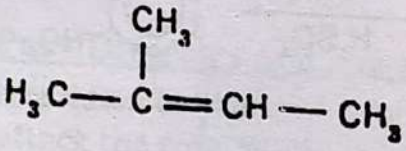
(i)



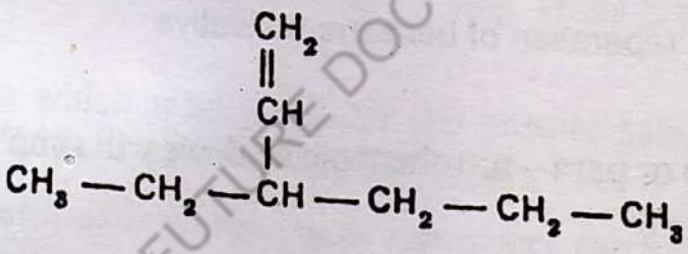
(ii)



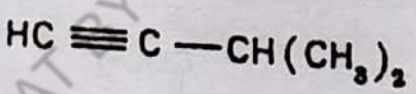
(iii)



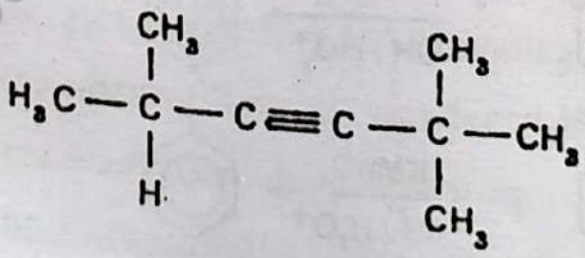
(iv)



(v)



(vi)



2. Give the structural formulas of:

(i) 2,2,3,3-tetramethyl pentane.

(ii) 1,2-dibromo – 2 – methyl propane.

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(iii) Diethyl Acetylene

(iv) 3 – bromo – 4 – methyl – 3 – hexene

(v) 3,3 dimethyl – 1 – butyne

(vi) 1 – chloro – 2 – methyl – 2 – butene.

(vii) 3 – ethyl – 1 – heptyne

3. (a) Derive the structure of all isomers of pentane (C_5H_{12}) and name them by the I.U.P.A.C. system.

(b) Write the structural formulas for the five isomeric hexanes and three isomeric pentynes and name them by I.U.P.A.C system.

4. Write electronic structures for the following simple organic molecules

(i) Acetone

(ii) Phenyl magnesium bromide

(iii) Silver acetylide

(iv) Nitro ethane.

5. What alkyl halide would yield each of the following pure alkenes upon dehydrohalogenation by strong base.

(a) 1 – pentene, (b) 2 – pentene.

(c) 2 – methyl – 1 – butene. (d) 2 – methyl – 2 – butene

(e) 1 – butene

6. Describe simple chemical tests that would distinguish between:

(a) An alkene and an alkane

(b) An alkene and an alkyne

(c) An alkane and an alkyl – halide

7. Which alkane may be obtained by the reduction of:

(a) 2 – bromo propane

(b) Sec – butyl bromide

(c) Isopropyl bromide

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8. Write equations for the formation of hydrocarbon by the action of Na metal on:

(i) Ethyl chloride

(ii) 2 – bromo butane

(iii) Methyl iodide

9. A hydrocarbon, C_4H_6 absorbs two moles of hydrogen in the presence of platinum as a catalyst. The reduction product is inert towards bromine and potassium permanganate. Draw possible structures for C_4H_6. What further information is necessary in order to establish the identity of the hydrocarbon?

10. What are the principal sources of benzene and its homologues?

11. Draw the structures of the following compounds:

(i) Benzene
(ii) Toluene
(iii) Ethyl benzene
(iv) Nitrobenzene
(v) P – bromobenzoic acid
(vi) O – dichlorobenzene

12. (a) What do you understand by the term "Aromaticity" and how will you explain the stability of benzene molecule?

(b) Draw resonance structures for benzene.

13. What would be the major monochloro product (or products) formed when each of the following compounds react with chlorine in presence of ferric chloride?

(i) Ethyl benzene, $C_6H_5CH_2CH_3$

(ii) Trifluoromethyl benzene, $C_6H_5CF_3$

(iii) Methyl benzoate, $C_6H_5COOCH_3$

14. Starting from benzene how will you prepare the following:

(i) Acetophenone
(ii) m–nitrotoluene
(iii) p–nitrobenzoic acid

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CHAPTER 8

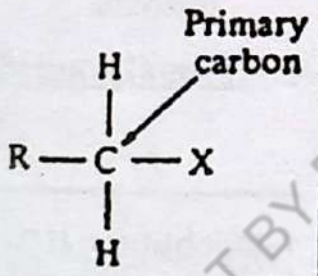
ALKYL HALIDES

These compounds are supposed to be derived from alkanes by replacing a hydrogen atom with a halogen atom. Their general formula is $C_nH_{2n}+1X$ or simply R–X, where R represents an alkyl group and X, any halogen atom like Cl, Br or I.

$$RH \xrightarrow[+X]{-H} RX$$

8.1 CLASSIFICATION OF ALKYL HALIDES

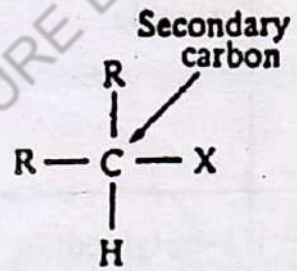
Alkyl halides are classified as primary (1°),Secondary (2°) and Tertiary (3°), depending on the kind of carbon atom that bears the halogen (x) atom.



Primary (1°) alkyl halide

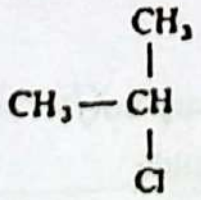
e.g. chloroethane or ethylchloride

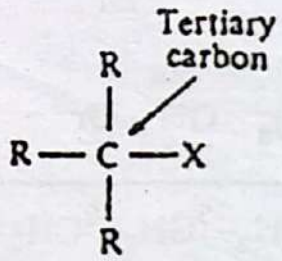
CH_3CH_2Cl



Secondary (2°) alkyl halide

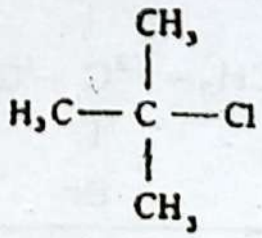
e.g. 2–chloropropane or sec–propyl chloride





Tertiary (3°) alkyl halide

e.g 2–chloro–2–methyl propane or Ter–butyl chloride



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8.2 NOMENCLATURE

Common names of alkyl halides are obtained by first writing the name of the alkyl group to which the halogen (x) is attached and then writing the name of the halide ion (Chloride, bromide or iodide). For secondary and tertiary alkyl halides, prefix Sec– and Ter– are respectively used.

According to the I.U.P.A.C. system, these compounds are named as haloalkanes. The substituents are indicated by numbers of the carbon atoms to which they are attached and the halogen bearing carbon is given the lowest possible number. For example:

Structural formula	Common name	I.U.P.A.C name
(i) CH_3Cl	Methyl chloride	Chloromethane
(ii) CH_3CH_2Br	Ethyl bromide	Bromoethane (1°)
(iii) $CH_3 - CH_2 - CH_2 - I$	Propyl iodide	1-Iodopropane (1°)
(iv) $^3CH_3 - {}^2C(H)(Br) - {}^1CH_3$ or $(CH_3)_2\ CH - Br$	Isopropyl bromide or secondary propyl bromide	2-bromo propane(2°)
(v) $^4CH_3 - {}^3CH_2 - {}^2CH_2 - {}^1CH_2 - I$	1-butyl iodide	1-Iodobutane (1°)
(vi) $^4CH_3 - {}^3CH_2 - {}^2CH(Cl) - {}^1CH_3$	Secondary butyl-chloride	2-chlorobutane(2°)
(vii) $^3CH_3 - {}^2C(CH_3)(Br) - {}^1CH_3$	Tertiary butyl-bromide	2-bromo-2-methyl-propane

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Preparations:–

(1) **From Alcohols:–** The –OH group of alcohols (R–OH) can be replaced by halogen atom, by the reaction of alcohols with halogen acids (HX) or with reagents like PCl_3, PBr_3, PCl_5, $SOCl_2$ (thionyl chloride) etc.

(i) $CH_3-CH_2-OH + HBr \longrightarrow CH_3-CH_2-Br + H_2O$

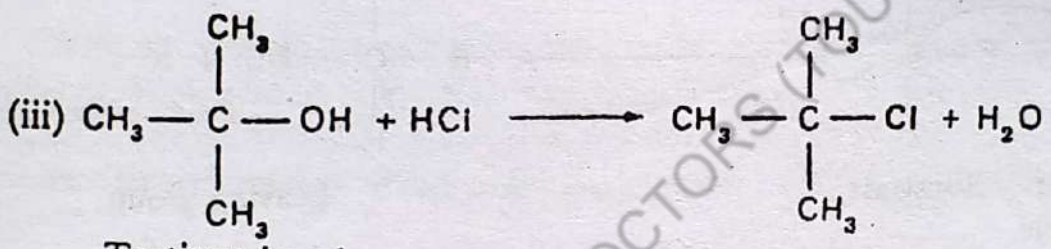
Ethyl bromide

(ii) $CH_3-CH_2-CH_2-OH + SOCl_2 \xrightarrow{\text{Pyridine}} \overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2-Cl + SO_2 + HCl$

Primary Propyl alcohol

Propyl chloride or 1–chloropropane

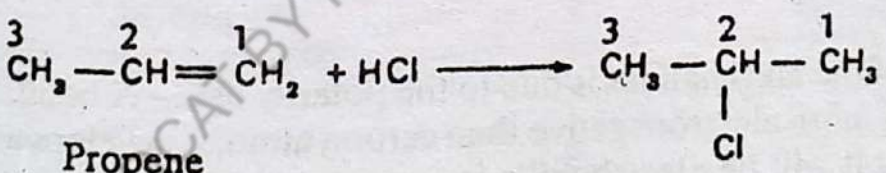
(iii)



Tertiary butyl alcohol

Ter–butyl chloride

(2) **From Alkenes:–** Alkenes react with halogen acids (HX) to give an alkyl halides.



Propene

2–chloropropane

(3) **From Alkanes:–** Alkyl halides can also be obtained by halogenation of alkanes.

$$RH \xrightarrow{X_2} RX + HX$$

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

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8.3 REACTIONS

Alkyl halides are highly reactive compounds and show a variety of reactions, however, only the following two types of reactions will be discussed here:

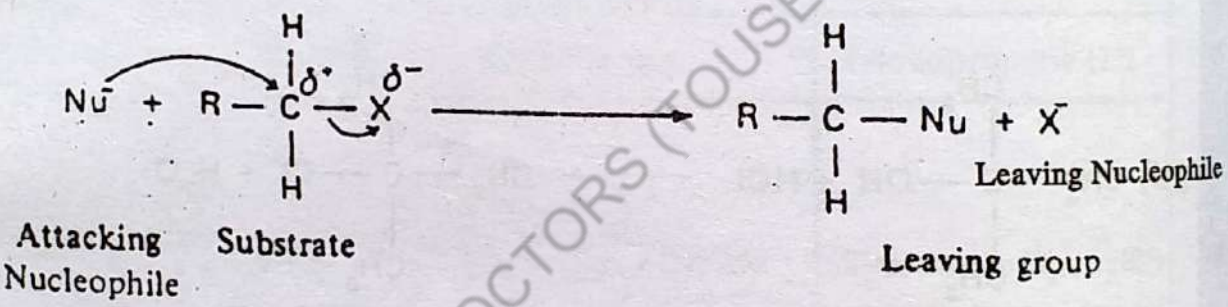
(i) Nucleophilic Substitution Reactions (S_N reactions)

(ii) Formation of Grignard Reagent and its applications.

(iii) Elimination Reactions.

(i) <u>Nucleophilic Substitution Reactions</u> (S_N reaction: where S stands for substitution and N for Nucleophilic).

In these reactions a nucleophilic (Nu^-) an electronegative ion substitutes the halogen atom of the alkyl halide:



$Nu^- = OH^-, OR^-, SH^-, CN^-, NH_3, NH_2^-, R-\overset{O}{\overset{\|}{C}}-O^-$ etc.

The reactivity of the alkyl halides is due to the polarity of C – X bond. Since the halogen atom is more electronegative than carbon atom, it develops a small positive charge, i.e, it will be electrophilic in nature and can accept a pair of electrons from a nucleophilic reagent (Nu^-) to form a new carbon – nucleophile bond, while the halide ion leaves with the electron pair of the Carbon–halogen bond.

The reagent Nu^-, is called an attacking nucleophile, the alkyl halide $R-CH_2-X$, is the substrate and X^- (the halide ion, which is also a nucleophile) is called the leaving group.

Following examples show how different types of organic compounds can be obtained as a result of nucleophilic substitution reaction of alkyl halides:

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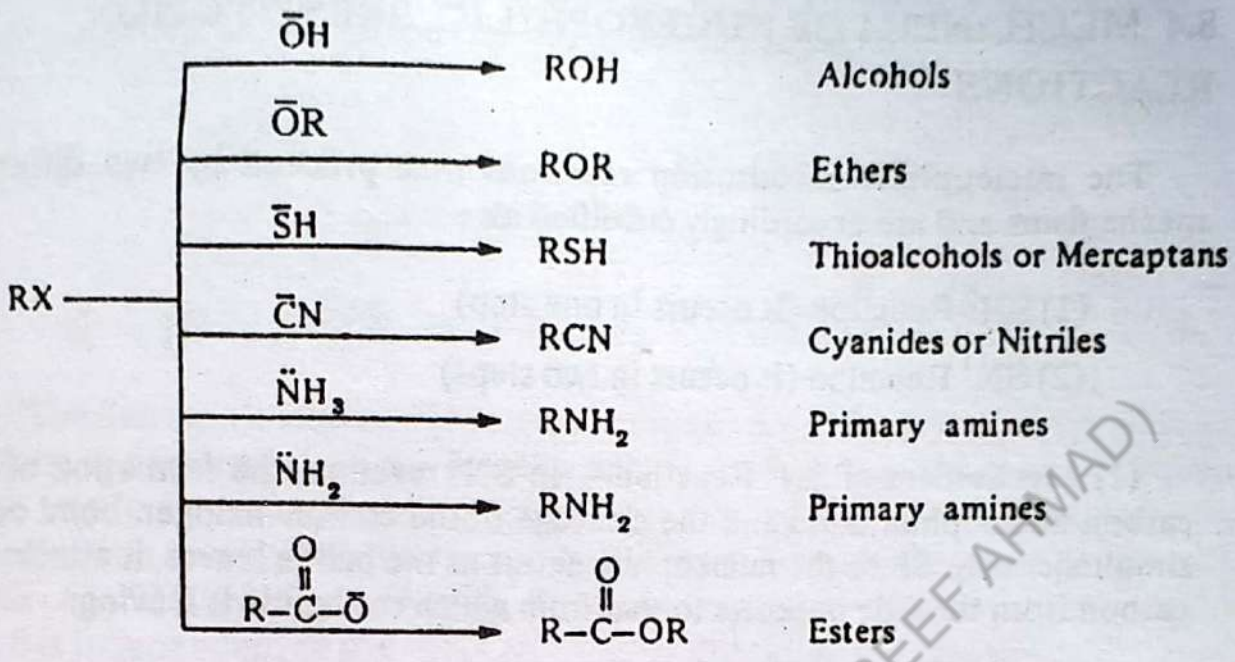

To be an effective nucleophile in a nucleophilic substitution reaction, the nucleophile should be a stronger base than the leaving group. For example OH^- displaces weaker base Cl^-, but the reverse is not true (Cl^- will not displace OH^-). A few nucleophiles that are stronger bases than the halide ions are listed in table 8.1.

Table 8.1 Some Nucleophiles that can displace X from RX

Nucleophile	Typical Reagent
$\bar{O}H$	NaOH
$\bar{O}R$	C_2H_5ONa
$\bar{S}H$	KSH
$\bar{C}N$	NaCN
$\ddot{N}H_2$	$NaNH_2$
$R-\overset{O}{\overset{\|}{C}}-\bar{O}$	$CH_3-\overset{O}{\overset{\|}{C}}-ONa$

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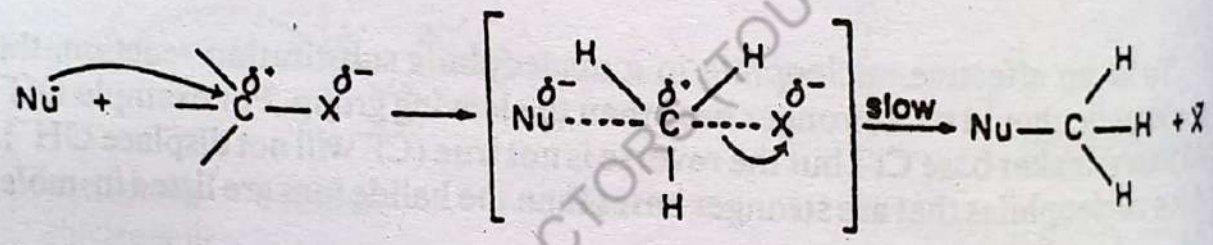
8.4 MECHANISM OF NUCLEOPHILIC SUBSTITUTION REACTIONS

The nucleophilic substitution reactions may proceed by two different mechanisms and are accordingly classified as:

(1) SN^2 Reaction (It occurs in one step)

(2) SN^1 Reaction (It occurs in two steps)

(1) Mechanism of SN^2 Reaction:– In SN^2 reaction, the formation of the carbon nucleophile bond and the cleavage of the carbon–halogen bond occur simultaneously. Since the nucleophile enters as the halide leaves, it attacks the carbon from the side opposite to that from which the halide is leaving:



Transition state
(Dotted lines indicate bonds that
are being formed and broken simultaneously)

As the bond making and bond breaking processes occur simultaneously, it is also the "Rate determining or Slow Step" of the reaction, i.e it determines the overall rate of the reaction. Such a reaction in which two molecules participate in the rate determining step is called a bimolecular reaction. This mechanism is called SN^2 mechanism , which stands for substitution Nucleophilic bimolecular. The transition state drawing (shown above) is an illustration to visualize, what is happening.

The rate of an SN^2 reaction depends on the concentrations of both the attacking nucleophile (Nu^-) and the alkyl halide (RX).

$$r \propto [Rx]\,[N\bar{u}]$$

(2)Mechanism Of SN^1 Reaction:– SN^1 reaction occurs in two steps. In the first step the C–X bond splits reversibly to give a positively charged ion (Species with positive charge on a carbon atom are known as carbonium ion) and a halide

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ion. In the second step the attacking nucleophile reacts with the positively charged ion (Carbonium ion) to give the final product:

$$R\text{–}X \xrightleftharpoons{\text{Slow}} \underset{\text{(Carbonium ion)}}{\overset{+}{R}} + \overset{-}{X} \quad \text{(First Step)}$$

$$\overset{+}{R} + N\bar{u} \xrightarrow{\text{Fast}} R - Nu \quad \text{(Second Step)}$$

The first step is slow and hence rate determining. Therefore in such reactions the rate of formation of the product will depend on the first step and since in this step only one molecule participates, it is said to be unimolecular. This mechanism is known as SN^1 mechanism, where 1 stands for unimolecular. The rate of an SN^1 reaction depends only on the concentration of the substrate (RX) and is independent of the concentration of attacking nucleophile.

$$\gamma \propto [Rx]$$

The stability of the various types of carbonium ions which may be formed during SN^1 reaction is as under:

$R_3\overset{+}{C}$	>	$R_2\overset{+}{C}H$	>	$RC\overset{+}{H}_2$	>	$\overset{+}{C}H_3$
Tertiary(3°)		Secondary (2°)		Primary(1°)		Methyl radical

Stability decreases →

3°–alkyl halides, therefore, generally react by SN^1 mechanism and 1° alkyl halides by SN^2 mechanism, 2° alkyl halides may react by SN^1 or SN^2 mechanism depending on the nature of solvent in which the reaction is carried out. Polar solvents help ionization, so they favour SN^1 mechanism, whereas non–polar solvents favour SN^2 mechanism.

Alkyl halides	R_3CX 3°	R_2CHX 2°	RCH_2X 1°	CH_3X
Mechanism generally observed	SN^1	Mixed SN^1 and SN^2	SN^2	SN^2

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Formation of Grignard's Reagents:– Alkyl halides react with magnesium metal in anhydrous ether to give alkyl magnesium halides or Grignard's reagents:

$$RX + Mg \xrightarrow[\text{Anhydrous}]{\text{Ether}} RMgX$$

$$CH_3I + Mg \xrightarrow[\text{Anhydrous}]{\text{Ether}} CH_3MgI \text{ Methyl Magnesium Iodide}$$

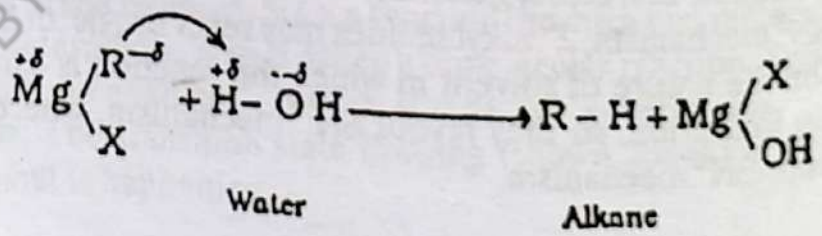
Reactions of Grignard reagent are explained on the basis that Carbon - Magnesium bond is polarized due to the electrophilic nature of the metal. As a result the carbon atom bonded to magnesium bears a partial negative charge

$$\overset{\delta^-}{R} - \overset{\delta^+}{Mg} - X$$

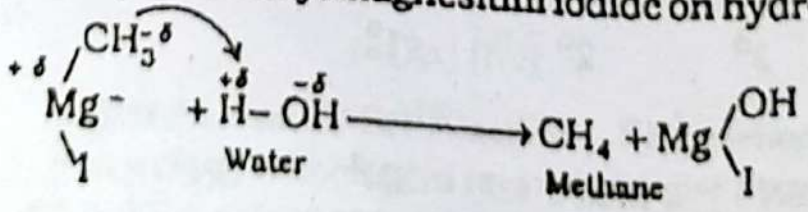
and hence behaves as a nucleophile, i.e. it will react with electrophilic reagents to make new bond. This makes Grignard Reagents as one of the important synthetic reagents, i.e. they can be used to prepare a variety of organic compounds. Some reactions and important applications of Grignard reagents are given below:

1. Hydrolysis of Grignard's reagent (Formation of alkane):-

Grignard's reagent on hydrolysis gives alkane.



For example:- Methyl magnesium iodide on hydrolysis gives methane.



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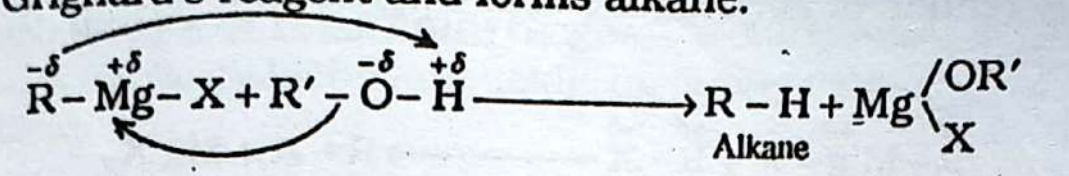
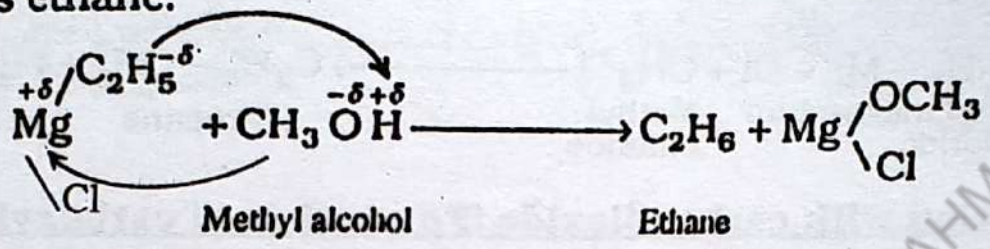
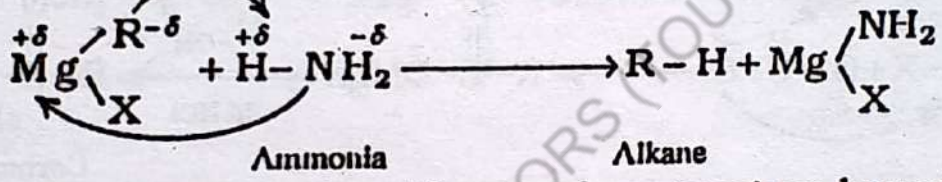
2. Reaction with alcohol (Formation of alkane):- Alcohol reacts with Grignard's reagent and forms alkane.



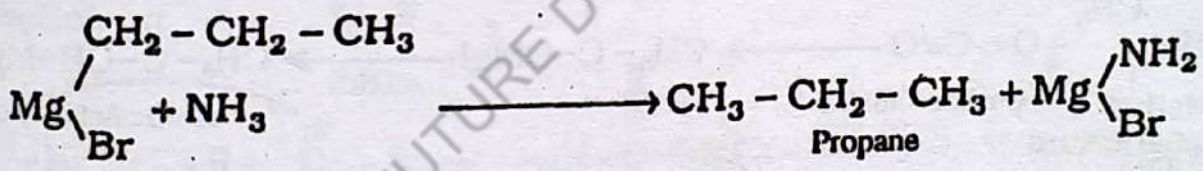
For example: Ethyl magnesium chloride reacts with methyl alcohol and gives ethane.



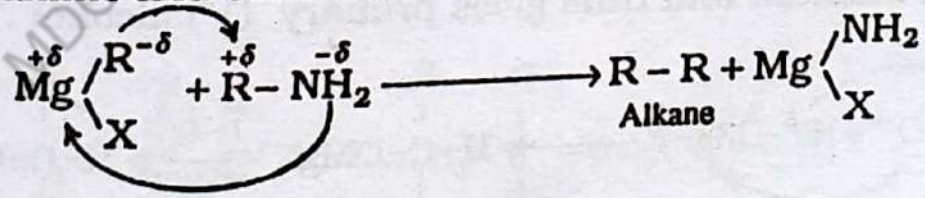
3. Reaction with ammonia (Formation of alkane):- Alkanes are formed by the action of ammonia wih Grignard's reagent.



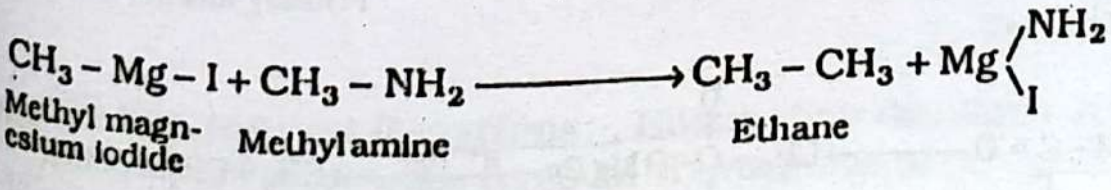
For example: Ammonia reacts with propyl magnesium bromide and forms propane.



4. Reaction with amine (Formation of alkane):- Grignard's reagent reacts with amine and thus forms alkane.



Example:



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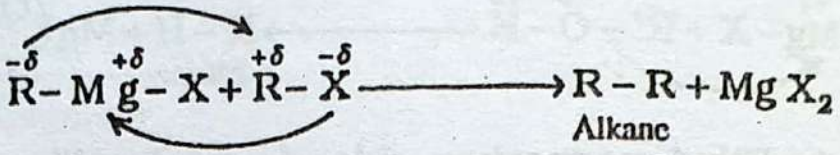
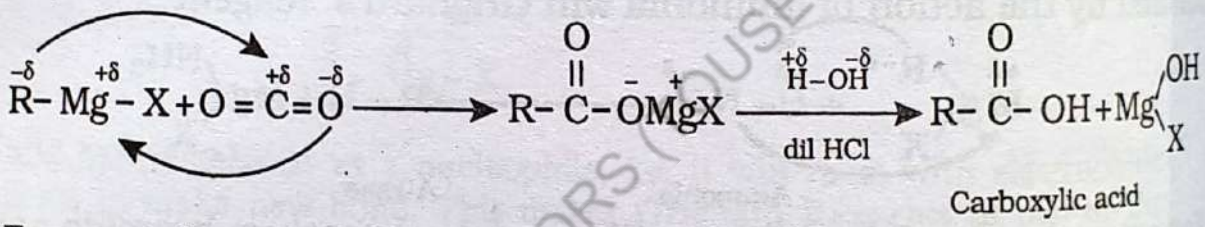
5. Reaction with alkyl halide (Formation of alkane):- Alkanes are formed by reation of alkyl halide with Grignard's reagent.

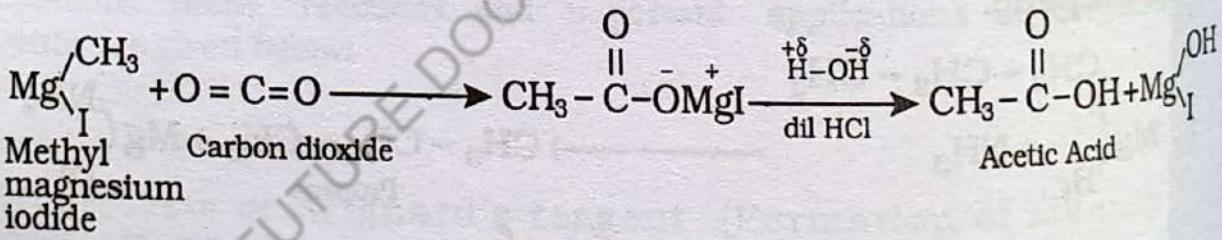


For example:

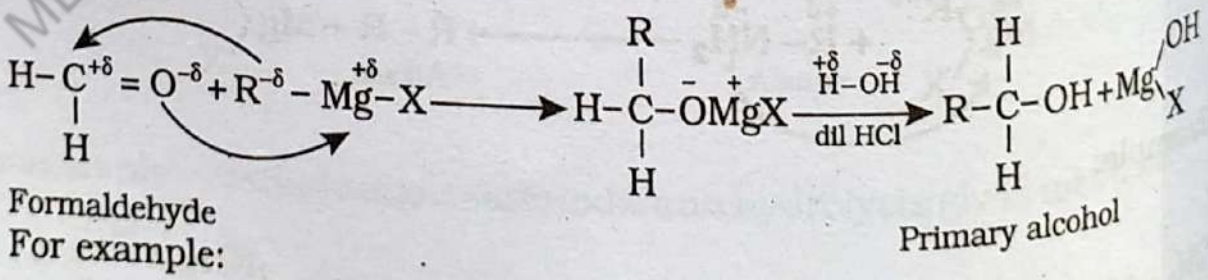
6. Reaction with carbondioxide (Formation of carboxylic acid):- Grignard's reagent reacts with carbon dioxide and forms addition product which on hydrolysis in acidic medium gives carboxylic acid.



For example:-



7. Reaction with formaldehyde (Formation of primary alcohol):- Formaldehyde reacts with Grignard's reagent followed by hydrolysis in acidic medium and thus gives primary (1°) alcohol .



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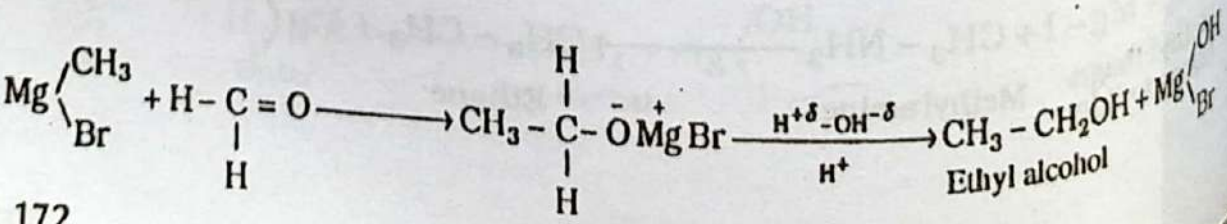

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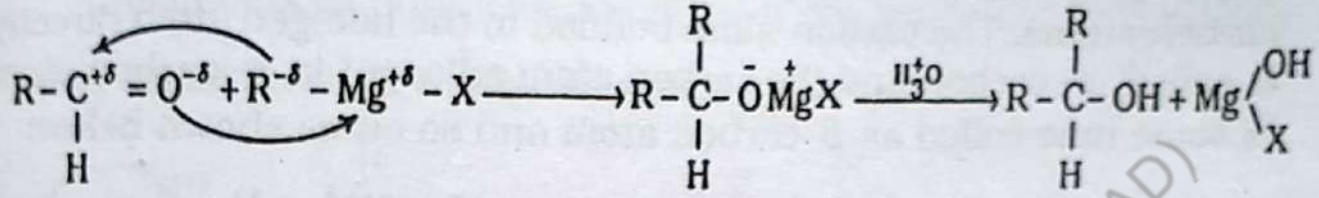
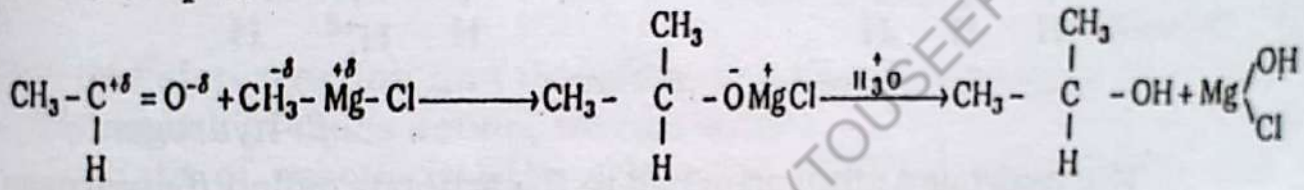
8. Reaction with aldehydes other than formaldehyde (Formation of secondary (2°) alcohol):- Grignard's reagent reacts with aldehyde other than formaldehyde in acidic medium and thus forms secondary alcohol.



Sec.alcohol

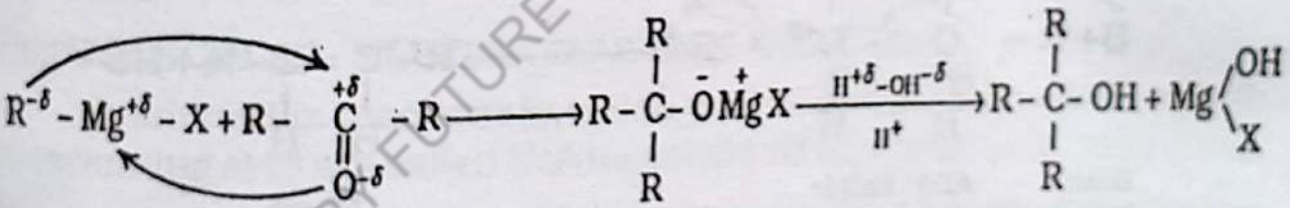
For example:



Acetaldehyde

Isopropyl alcohol

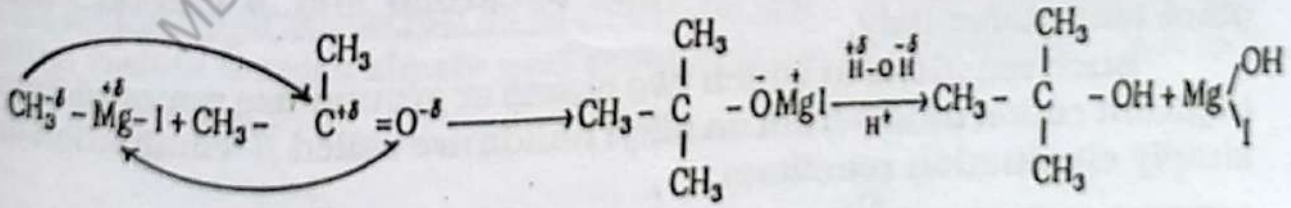
9. Reaction wih ketone (Formation of tertiary alcohol):- Ketone reacts with Grignard's reagent in acidic medium forming tertiary (3°) alcohol.



Ketone

Tertiary alcohol

For example:



Ter: butyl alcohol

(iii) Elimination Reactions:- Elimination reactions are those reactions which involve the removal of two atoms or groups from adjacent carbon atoms of the molecule to form a multiple bond.

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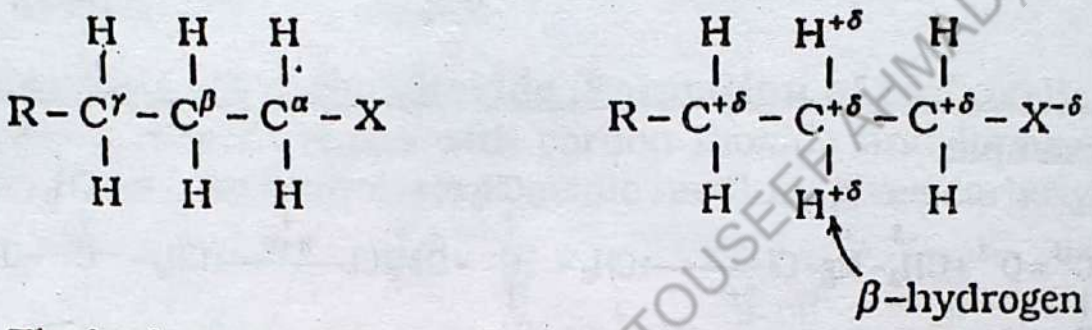
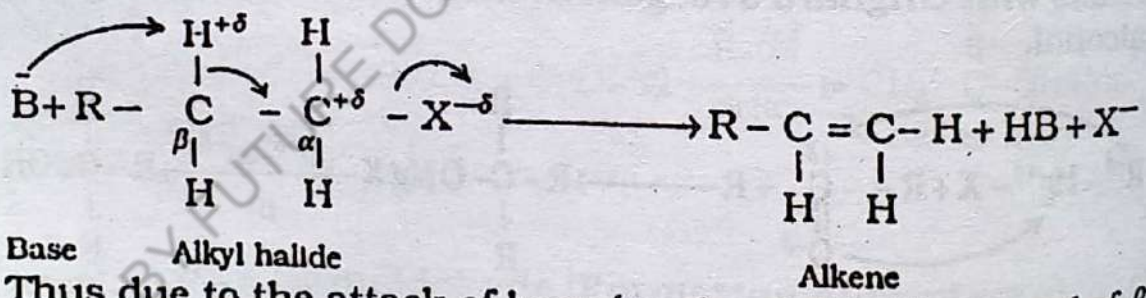
When alkyl halide is heated with alcoholic potash, a molecule of halogen acid (HX) is eliminated to form alkene (dehydrohalogenation), e.g. ethyl chloride gives ethene.

$$CH_3-CH_2Cl + \underset{\text{Alcoholic}}{KOH} \longrightarrow \underset{\text{Ethene}}{CH_2=CH_2} + KCl + H_2O$$

Explanation:- Consider an alkyl halide having two or more than two carbon atoms. The carbon atom bonded to the halogen atom directly is called α– carbon and the carbon atom adjacent to α–carbon atom is some time called as β-carbon atom and so on as shown below:



The hydrogen atom attached to β-carbon is called β-hydrogen. It is slightly acidic in nature due to high electronegativity of helogen atom when a base is allowed to react with alkyl halide containing β-hydrogen . The elimination reaction can proceed as:



Thus due to the attack of base (nucleophile) (i) removal of β-hydrogen, (ii) removal of halogen atom as halide ion (X^-) and (iii) formation of double bond between α–carbon and β-carbon takes place simultaneously.

Such reactions in which two atoms or groups are removed from adjacent cabon atoms from an alkyl halide are called β-elimination or simply elimination reactions.

MECHANISM OF ELIMINATION REACTION:

According to Hughes and Ingold (1941), the elimination reaction between alkyl halide and strong base occurs by two mechanisms namely:

(i) Bimolecular elimination (E_2) reaction and

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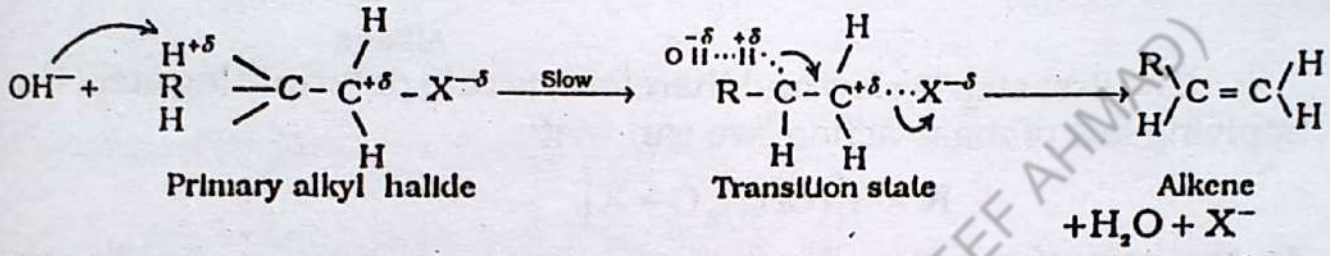
(ii) Unimolecular eliminaion (E_1) reaction

Bimolecular elimination (E_2) reaction:-

Elimination reactions in which substrate (alkyl habide) and attacking nucleophile or base such as OH^- are involvd in rate determining step are called bimolecular elimination or E_2 reaction.

Reactions of primary alkyl halides are generally E_2 reactions which occur through transition state.



It is one step reaction and therefore, is a rate determining step. On applying law of mass action, we can write :

Rate of reaction $= K[R-CH_2-CH_2X][OH^-]$ where K is the specific rate constant and [ ] denotes the concentraion of species in moles/dm^3.

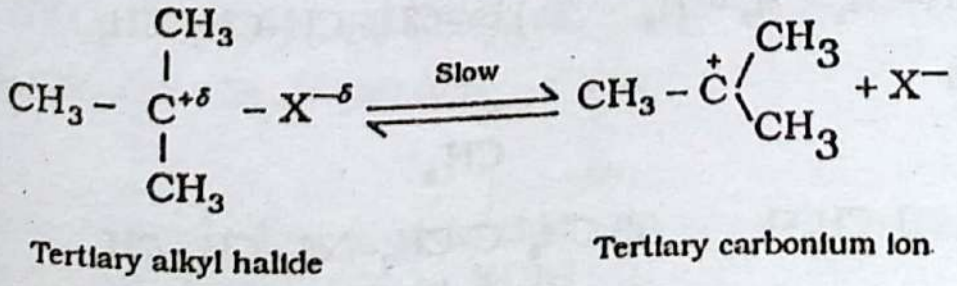
Such reations in which rate of reation depends on the oncentration of two molecules are called bimolecular elimination or E_2 reacions.

UNIMOLECULAR ELIMINATION (E_1) REACTION.

Elimination reactions in which only substrate is involved in rate determining step are called Unimolecular elimination or E_1 reactions.

Reactions of tertiary alkyl halides are E_1 reactions which occur in two steps:

(i) First step -Formation of carbonium ion:- In this step the tertiary alkyl halide ionises slowly and reversibly to give carbonium ion (R^+) and halide ion (X^-).



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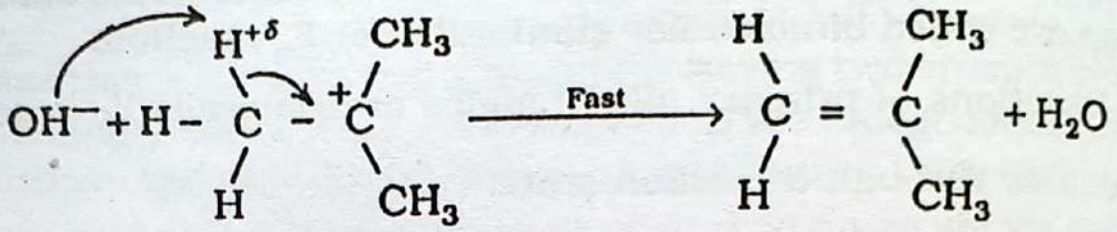
(ii) Second step-Formation of double bond (Alkene):- In this step, the attacking base (OH^-) removes a proton (H^+) from the β-carbon atom with the simultaneous formation of double bond between α-carbon and β-carbon (alkene). This is a fast reaction.



The first step is slow and therefore, is rate determining step. On applying law of mass action, we can write.

$$R = K[(CH_3)_3C-X]$$

As the rate of reaction depends on the concentration of only one molecule i.e substrate hence it is unimolecular elimination (E_1) reaction.

Secondary alkyl halides give both E_2 and E_1 reactions but that depend on the nature of solvent. For E_2 reaction the solvent should be non-polar where as E_1 reaction requires polar solvent.

ASSIGNMENT

1. Outline the structure of each of the following compounds:

   (a) Isobutyliodide (b) 1–chloro–2–methylpentane

   (c) 2–bromo–3–methylbutane (d) 1–iodo–4–methylheptane

   (e) 2–chloro–2–methylbutane (f) Ter–butyliodide

2. Name the following by I.U.P.A.C. system:

   (a) $CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_2-CH_3$ (b) $Br-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_3$

   (c) $(CH_3)_2CH-CH_2-I$ (d) $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-CH_2-CH_2-CH_2-CH_3$

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3. Classify the following alkyl halides as 1°, 2° or 3°:

(a) $(CH_3)_2CH-CH_2Cl$ (b) $(CH_3-CH_2)_3CBr$ (c) $CH_3-\overset{|}{\underset{|}{CH}}-CH_3$

4. Outline the structures of the isomeric alkyl halides with molecular formula. C_4H_9Cl.

5. Explain the following terms:

(i) SN^2 Reactions (ii) SN^1 Reactions

6. Give equations for the following reactions:

(a) 2– iodohexane with sodium methoxide

(b) 1– chlorobutane with sodium ethoxide

(c) Ter–butyl chloride with sodium cyanide

(d) 1– bromopropane with potassium hydrogen sulphide

(e) Ethyl magnesium iodide with formaldehyde

(f) Isopropyl magnesium bromide with water

(g) Methyl magnesium iodide with carbondioxide

(h) 1–iodo–butane and magnesium in presence of anhydrons ether.

7. Outline stepwise reaction mechanism for the following reactions:

(a) SN^2 reaction between bromomethane and NaOH

(b) SN^1 reaction between 2– chloro –2–methylpropane and NaCN.

8. Name the following compounds by I.U.P.A.C. system:

(i) $(CH_3)_2.CBr.CH_3$ (ii) $(CH_3)_2HC.C.Cl_3$

(iii) $CH_3-\underset{|}{\underset{I}{CH}}-CH_2Br$ (iv) $(CH_3)_3.C.\underset{|}{\underset{Br}{CH_2}}$

9. Give the structure and name of the chief organic product expected from the reaction of n – butyl bromide with aq. KOH?

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CHAPTER 9

CARBON COMPOUNDS WITH OXYGEN CONTAINING FUNCTIONAL GROUPS

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A list of compounds with oxygen containing functional groups is as under:

(i) Alcohols
(ii) Phenols } Hydroxyl group (– OH)

(iii) Ethers (R–O–R)

(iv) Aldehydes $\left(\begin{matrix} R \\ H \end{matrix}\!\!>C=O\right)$

(v) Ketones $\left(\begin{matrix} R \\ R \end{matrix}\!\!>C=O\right)$

(vi) Carboxylic acids (R–COOH) and

(vii) Esters (R–COO–R)

In this chapter, the classification and nomenclature of each of the above class of compounds will be discussed along with uses of typical members.

9.1 ALCOHOLS

Aliphatic compounds containing hydroxyl group (–OH) attached to a carbon atom are called alcohols. They are classified according to the number of hydroxyl groups present in the compound. Monohydric alcohols contain one hydroxyl

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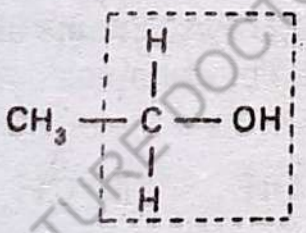
group; dihydric (two OH^-), trihydric (three OH^-), etc. When the alcohols contain four or more hydroxyl groups, they are usually called polyhydric alcohols:

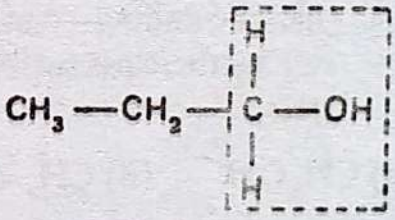
Monohydric alcohols: CH_3OH , C_2H_5OH
Methyl alcohol Ethyl alcohol

Dihydric alcohols : $HO-CH_2-CH_2-OH$, $HO-CH_2-CH_2-CH_2-OH$
1.2 ethan diol 1.3 propan diol

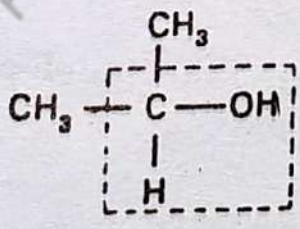
Trihydric alcohols : $HOCH_2-CH(OH)-CH_2-OH$, $CH_3-CH(OH)-CH(OH)-CH_2OH$
1.2.3–propan triol. 1.2.3–butan triol

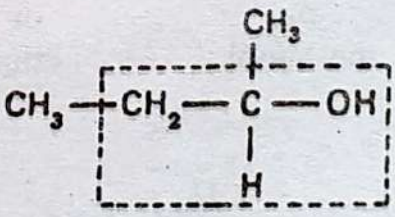
The monohydric alcohols form a homologous series with the general formula $C_nH_{2n+1}OH$ or simply ROH. They are further classified into primary (1°) alcohol, Secondary (2°) alcohol or tertiary (3°) alcohol, depending on whether the hydroxy group is attached to a primary, secondary or a tertiary carbo- atom.

Primary alcohol (1°) : 

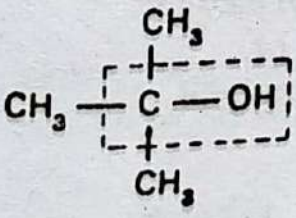
; 

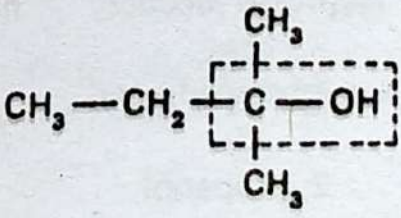
Ethyl alcohol n-propyl alcohol

Secondary alcohol (2°): 

; 

Sec. propyl alcohol

Tertiary alcohol (3°) 

; 

Tertiary butyl alcohol

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It will be observed from the above examples that characteristic group of primary alcohols is $-CH_2OH$, that of secondary alcohols is $>C<^{OH}_{H}$ and that of tertiary alcohols is $\geq C-OH$.

Nomenclature Of Monohydric Alcohols:

1. **Common Names:–** The simpler alcohols are commonly known by their common names. In this system alcohols are named after the alkyl group to which –OH group is attached. The prefix sec–or ter– is added before the name of the alkyl group where necessary.

2. **IUPAC Names:–** Following rules are observed while giving I.U.P.A.C. names to alcohols:

(i) The longest carbon chain containing the hydroxyl group is chosen as the parent alkane.

(ii) Position of side chains and hydroxyl group are indicated by number of the carbon atoms to which they are attached. Lowest possible number being given to the carbon atom to which the –OH group is attached.

(iii) The ending – e of the I.U.P.A.C. name of the parent alkane is replaced by the class suffix –ol. For example:

(i) CH_3OH
Methyl alcohol
or
methanol

(ii) CH_3-CH_2OH
Ethyl alcohol
or
ethanol

(iii) $\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2OH$
n–propyl alcohol
or
1–propanol

(iv) $\overset{3}{C}H_3-\overset{2}{C}H(\overset{1}{C}H_3)-OH$
Isopropyl alcohol
or
sec–propyl alcohol
or
2–propanol

(v) $\overset{4}{C}H_3-(\overset{3}{C}H_2)_2-\overset{1}{C}H_2OH$
n–butyl alcohol
or
1–butanol

(vi) $\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H(OH)-\overset{1}{C}H_3$
Sec–butyl alcohol
or
2–butanol

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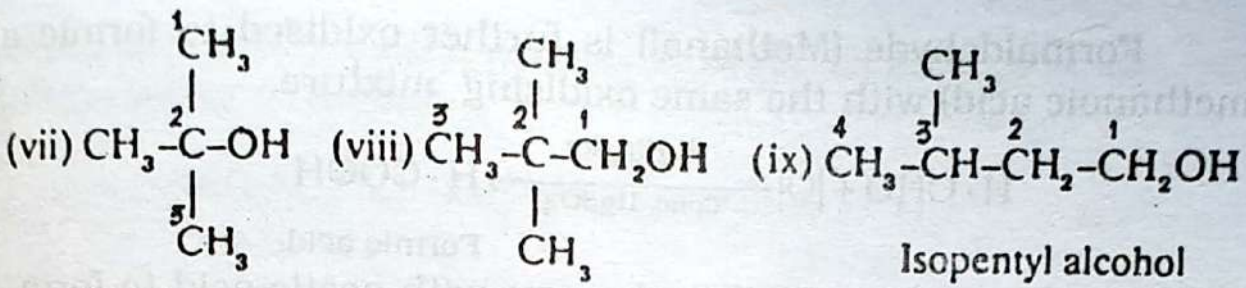

(vii) Ter-butyl alcohol or 2-methyl-2-propanol

(viii) Neopentyl alcohol or 2-2 dimethyl-1-propanol

(ix) Isopentyl alcohol or 3-methyl-1-butanol

1. METHYL ALCOHOL (Methanol, CH_3OH)

Methanol is also called Wood spirit because formerly it was obtained by destructive distillation of Wood which yielded:

(i) Volatile inflammable gases

(ii) Strongly acidic liquid distillate called pyroligneous acid which contains methanol, acetone, acetic acid, methyl acetate and other organic compounds.

Methanol was separated by fractional distillation of this liquid.

(iii) The residue is wood charcoal.

Recent Industrial preparation:- These days methanol is produced synthetically from a mixture of water gas and hydrogen or a mixture of carbon monoxide and hydrogen. The gaseous mixture is subjected to 200 atmospheric pressure and then passed over heated catalyst mixture of ZnO and Cr_2O_3 kept heated to 400 to 450°C.

The resulting methanol vapours are condensed.

Reaction:

$$\underset{\text{Water gas}}{\left[CO_{(g)} + 2H_{2(g)}\right]} \xrightarrow[400-450^0C/200\ atom]{ZnO/Cr_2O_3} \underset{\text{Methanol}}{CH_3OH}$$

Properties:

Physical properties:- Methanol is a colourless, volatile, thin liquid with specific gravity 0.796 at 15°C. It boils at 64.7°C. It is more toxic and poisonous. It is miscible with water.

Chemical properties:-

(i) Oxidation to formaldehyde:- Methanol is oxidised to formaldehyde (H.CHO) when heated with a mixture of $K_2Cr_2O_7$ and conc. H_2SO_4.

$$CH_3OH + |O| \xrightarrow[Conc.\ H_2SO_4]{K_2Cr_2O_7} \underset{\text{Formaldehyde}}{H-CHO} + H_2O$$

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Formaldehyde (Methanal) is further oxidised to formic acid (methanoic acid) with the same oxidising mixture.

$$H \cdot CHO + |O| \xrightarrow[\text{Conc. } H_2SO_4]{K_2Cr_2O_7} H \cdot COOH$$

Formic acid

(ii) Ester formation:- Methanol reacts with acetic acid to form an ester.

$$CH_3OH + CH_3COOH \rightleftharpoons CH_3 - COO - CH_3 + H_2O$$

Dimethyl ester
or methyl acetate

(iii) Reaction with halogen acid:- Methanol reacts with halogen acid like HCl to form methyl chloride. This reaction is catalysed by $ZnCl_2$.

$$CH_3OH + HCl \xrightarrow{ZnCl_2} CH_3 - Cl + H_2O$$

Uses of Methyl alcohol:-

(i) Methyl alcohol is used as a solvent in lacquers and varnishes.
(ii) It is mixed with ethyl alcohol to render it unfit for human use. The mixture is called methylated spirit.
(iii) It is used to produce formaldehyde and formalin which is used as preservative for life specimen.
(iv) It is used to prepare antifreeze solution .
(v) It is also used in the preparation of some drugs, dyes and perfumes.

2. Ethyl Alcohol (Ethanol, C_2H_5OH):-

Ethyl alcohol, commonly known as alcohol, is produced on large scale by fermentation process of starch or molasses by catalytic action of enzymes produced by micro-organism such as yeast.

(a) Fermentation of Starch:- The alcohol for beverages is derived by the fermentation of starch present in rice or potato. For this purpose the grain is cooked to form a pulp and then to this is added malt (germinated barley). The enzyme diastase present in malt hydrolyses starch to sugar maltose. Further action is carried out by yeast which secrets two enzymes maltase; converting maltose into glucose and zymase which converts glucose into ethanol. Since CO_2 escapes in

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the form of bubbles so the process is called fermentation meaning gentle bubbling or boiling.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)} + H_2O \xrightarrow[\text{In malt}]{\text{Diastase}} \underset{\text{Maltose}}{C_{12}H_{22}O_{11}}$$

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{In yeast}]{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow[\text{In yeast}]{\text{Zymase}} \underset{\substack{\text{Ethanol}\\ \text{(b.p. 78.5 °C)}}}{2C_2H_5OH} + 2CO_2\uparrow$$

(b) Formentation of molasses:- The thick dark brown coloured syrup left after isolation of crystalline cane sugar is treated with yeast which contains enzyme sucrase which converts sugar in molasses to glucose and fructose, which further react with zymase present in the yeast. The fermentation gives ethanol.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{In yeast}]{\text{Sucrase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow[\text{In yeast}]{\text{Zymase}} \underset{\substack{\text{Ethanol}\\ \text{(b.p. 78.5 °C)}}}{2C_2H_5OH} + 2CO_2\uparrow$$

Ethanol is separated by distillation.
Rectified spirit contains 92-95% ethanol by weight.
Absolute Alcohol is 99.9% pure which is obtained by absorbing water of rectified spirit with CaO and then distilling alcohol at 78 °C.
Denatured alcohol:- Ethanol 85%, water 11% and methanol 4% known as methylated spirit.
Beverages contain ethanol in varying percentages.
Properties:
Physical properties:- Ethyl alcohol is a thin colourless liquid of specific gravity 0.79 at 15 °C. It boils at 78.5 °C at 1 atmospheric

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pressure. It solidifies at −112 °C. It is highly miscible with water. Its structure resembles the structure of H_2O.

Chemical Properties:-

(i) Oxidation to Acetaldehyde:- Ethanol is oxidised to acetaldehyde with $K_2Cr_2O_7$/conc. H_2SO_4.

$$\underset{\text{Ethanol}}{CH_3 \cdot CH_2 \cdot OH} + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Acetaldehyde (Ethanal)}}{CH_3 \cdot CHO} + H_2O$$

(ii) Reaction with Halogen acid:- Ethanol (1° alcohol) reacts with HCl in presence of $ZnCl_2$ as catalyst to form ethyl chloride.

$$C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5 - Cl + H_2O$$

Note: In this reaction alcohol loses its hydroxyl group.

(iii) Reaction with sodium:- Ethanol reacts with sodium metal. The H-atom of hydroxyl group is replaced by sodium to produce sodium ethoxide liberating hydrogen gas.

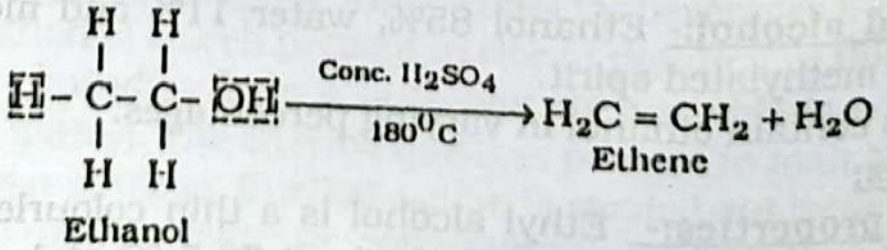
$$C_2H_5OH + Na \longrightarrow C_2H_5\bar{O}\overset{+}{Na} + \frac{1}{2}H_{2(g)}$$

Ethoxide ($C_2H_5\bar{O}$) is used as a strong nucleophile. This reaction shows the acidic nature of ethanol.

(iv) Esterification:- Ethanol reacts with acetic acid in the presence of H_2SO_4 forming ester. In this reaction ethanol loses hydrogen and acetic acid loses hydroxide (OH).

$$C_2H_5O\boxed{H + HO} - \underset{\underset{O}{\|}}{C} - CH_3 \xrightarrow{H_2SO_4} \underset{\text{Ethyl acetate}}{C_2H_5 - O - \underset{\underset{O}{\|}}{C} - CH_3} + H_2O$$

(v) Dehydration of Ethanol:- Ethanol when heated with conc. H_2SO_4, loses water (H_2O) forming ethene.



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(vi) Ether formation:- Ethanol in excess when treated with conc. H_2SO_4 at low temperature, yields ether in two steps:

$$CH_3 \cdot CH_2 \cdot OH + HO \cdot SO_2 \cdot OH\ (conc) \longrightarrow CH_3 \cdot CH_2 \cdot OSO_3H + H_2O$$

Ethyl hydrogen sulphate

$$CH_3 \cdot CH_2 \cdot O\boxed{SO_3H} + CH_3 \cdot CH_2 \cdot \boxed{OH} \longrightarrow CH_3 \cdot CH_2 - O - CH_2 - CH_3 + H_2SO_4$$

(Excess) Diethylether

(vii) Reaction with PCl_3, PCl_5 and $SOCl_2$:- Ethyl alcohol reacts with acid chlorides like PCl_3, or PCl_5 or $SOCl_2$ to produce ethyl chloride.

$$3C_2H_5OH + PCl_3 \longrightarrow 3C_2H_5Cl + H_3PO_3.$$

Ethylchloride

$$C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + POCl_3 + HCl.$$

$$C_2H_5OH + SOCl_2 \longrightarrow C_2H_5Cl + SO_2 + HCl.$$

(viii) Dehydrogenation of ethanol:- Ethanol vapours lose hydrogen (H_2) to form acetaldehyde when passed over Cu-Ni couple.

$$CH_3 \cdot CH_2OH \xrightarrow[180°C]{Cu-Ni} CH_3 \cdot CHO + H_{2(g)}$$

Acetaldehyde

Uses of Ethanol:

(i) Ethanol is used as a solvent. It dissolves a large variety of organic substances such as gums, resins, tinctures and varnishes.

(ii) It is being extensively used in the form of different beverages. For this ethanol obtained by fermentation of grains or fruit is used.

(iii) It is used as a raw material for the preparation of other organic compounds such as $CHCl_3$, ether and esters. Deodorised ethanol is used as base for perfumes.

(iv) It is used for low temperature thermometer and as fuel substitute.

(v) Ethanol is used as an inert solvent for certain organic reactions and recrystallisation of many organic compounds .

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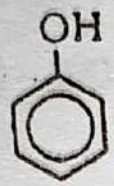
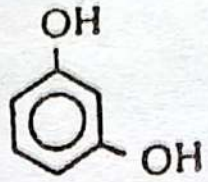
9.2 PHENOL (CARBOLIC ACID C_6H_5OH)

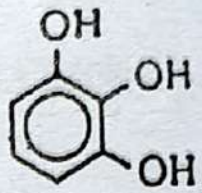
Phenols are aromatic compounds containing hydroxyl group directly attached to a aromatic ring of carbon atoms. They are classified as monohydric, dihydric, trihydric phenols, etc., according to the number of hydroxyl groups present on aromatic carbon ring.

(i) 

Phenol
(Monohydric)

(ii) 

Resorcinol
(Dihydric)

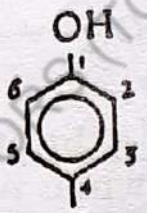
(iii) 

Pyrogallol
(Trihydric)

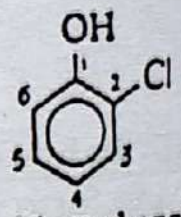
<u>Nomenclature:-</u> Some well known phenols have trivial names, eg, catechol, Resorcinol, p–cresol, etc. Substituted phenols are generally named as derivatives of phenol. Position of substituents and –OH group are indicated by number of the carbon atoms to which they are attached. Number one is assigned to the carbon bearing the –OH group. For example:

(i)

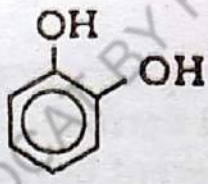
Phenol
(Commonly known as carbolic acid

(ii) 

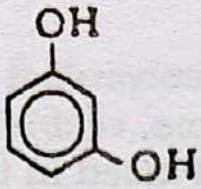
P–cresol
or
4–methylphenol

(iii) 

2–chlorophenol

(iv) 

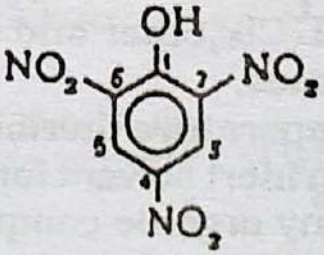
Catechol

(v) 

Resorcinol

(vi)

Hydroquinone

(vii) 

2,4,6–trinitrophenol
or Picric acid

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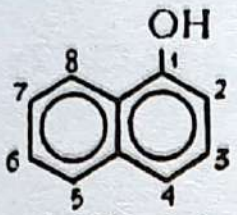
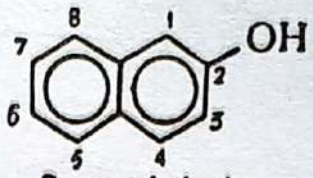
Compounds having –OH group linked to a naphthalene ring, are also phenols but they are called naphthols:



1– Naphthol
or
α–naphthol

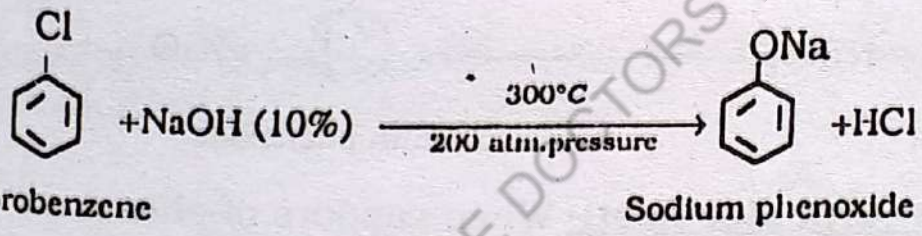
(ii)

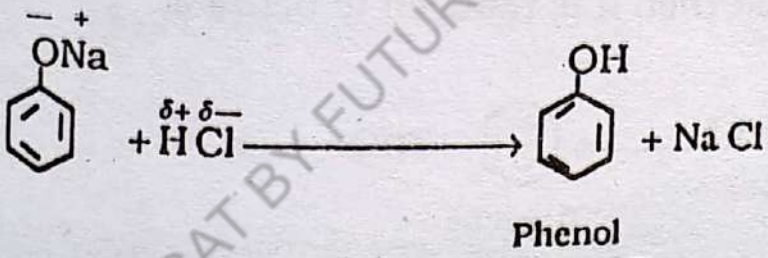


2– naphthol
or
β–naphthol

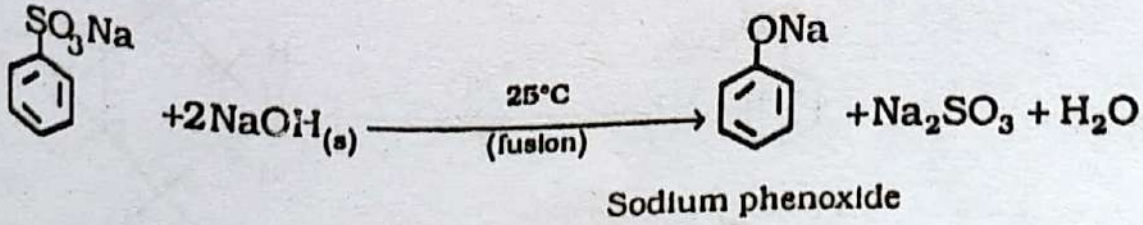
Methods of preparation.

(i) From chlorobenzene (Down's process):- Chlorobenzene on heating with 10% NaOH at 300°C and under 200 atmospheric pressure, forms sodium-phenoxide which on further heating with hydrochloric acid gives phenol.





(ii) From benzene sulphonate:- Benzene sulphonate is fused with solid sodium hydroxide at 25°C in nickel crucible and gives sodium phenoxide



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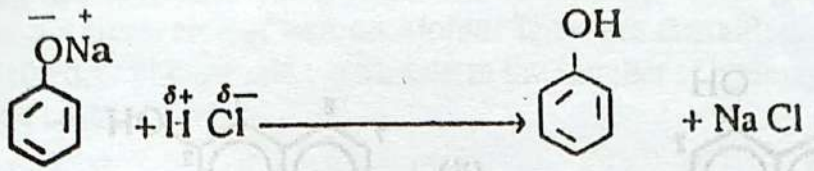
Sodium phenoxide on further treating with hydrochloric acid gives phenol.

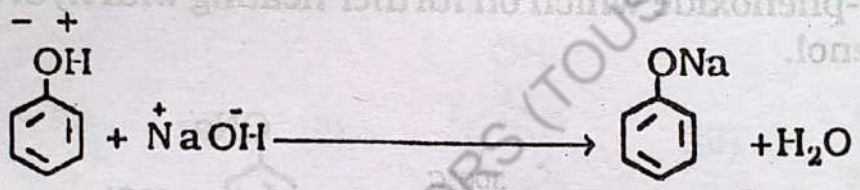


Phenol

Physical Properties:- Phenol is colourless crystalline solid. It has peculiar odour. It is poisonous. Its melting point is 43°C and boiling point is 182°C. It is miscible with water above 68.5°C in all proportions.

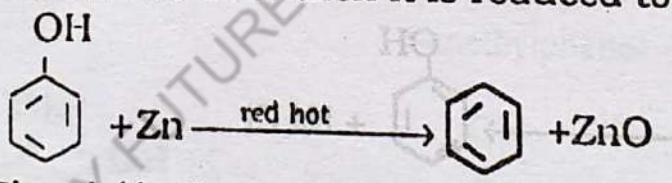
Chemical reactions:

(i) Reaction with sodium hydroxide:- Phenol is fairly acidic in nature and reacts with strong base like sodium hydroxide, yielding sodium phenoxide.



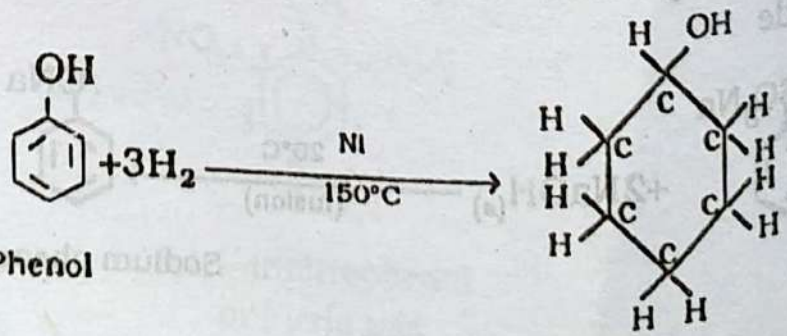
Phenol Sodium phenoxide

(ii) Reaction with zinc dust:- When vapours of phenol are passed over red hot zinc dust then it is reduced to benzene.



Phenol (dust) Benzene

(iii) Hydrogenation (Reaction with hydrogen gas):- Hydrogen gas is bubbled through phenol at 150°C and in presence of finely divided nickel, then cyclohexanol is obtained.



Phenol Cyclohexanol

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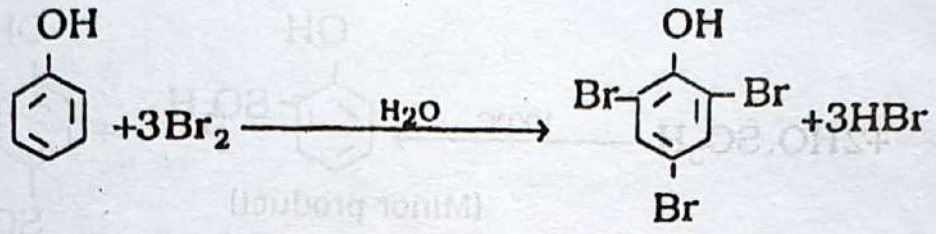
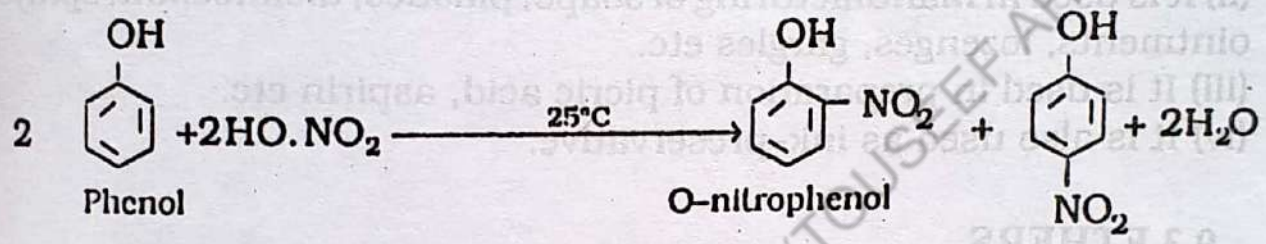
(iv) Halogenation (Reaction with bromine water):- Phenol reacts rapidly with bromine water and produces 2,4,6–tri bromo phenol.



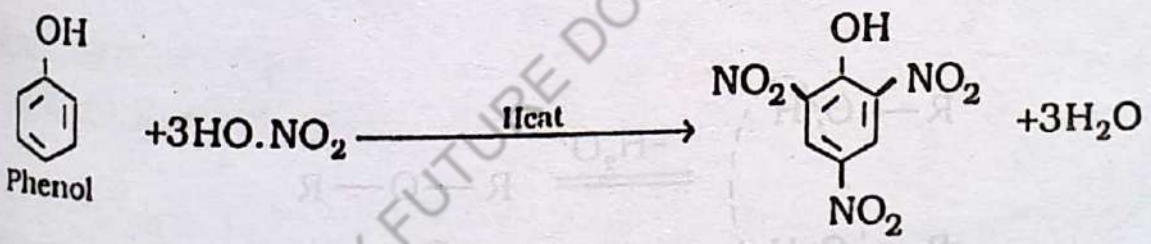
Phenol 2,4,6– tri bromo phenol.

(v) Nitration (a) Reaction with dilute Nitric acid:- Phenol on treating with dilute nitric acid at 25°C, gives O–nitrophenol and P–nitrophenol because hydroxyl (–OH) group is ortho and para directing group.



Phenol O–nitrophenol P–nitrophenol

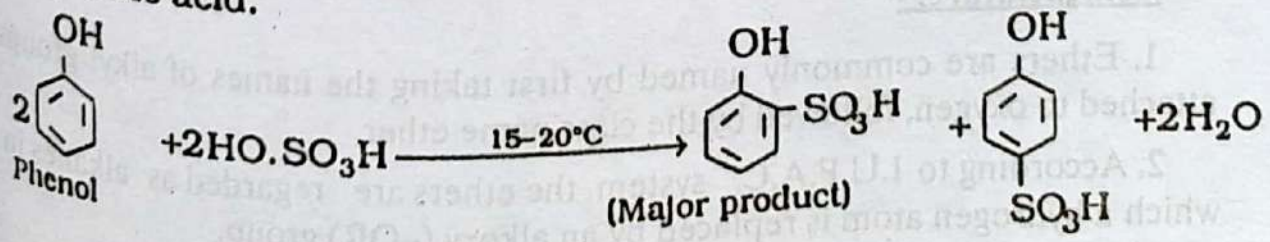
(b) Reaction with conc. Nitric acid:- Phenol on heating with conc. nitric acid, gives 2,4,6–trinitrophenol.



Phenol 2,4,6– tri nitrophenol.

(vi) Sulphonation (Reaction with sulphuric acid):- When phenol is treated with sulphuric acid, it gives relative proportion of both Ortho and para isomers of phenol sulphonic acid depending upon temperature.

(a) on heating at 15–20°C, it gives major ratio of ortho–phenol sulphonic acid.



Phenol (Major product) (Minor product)

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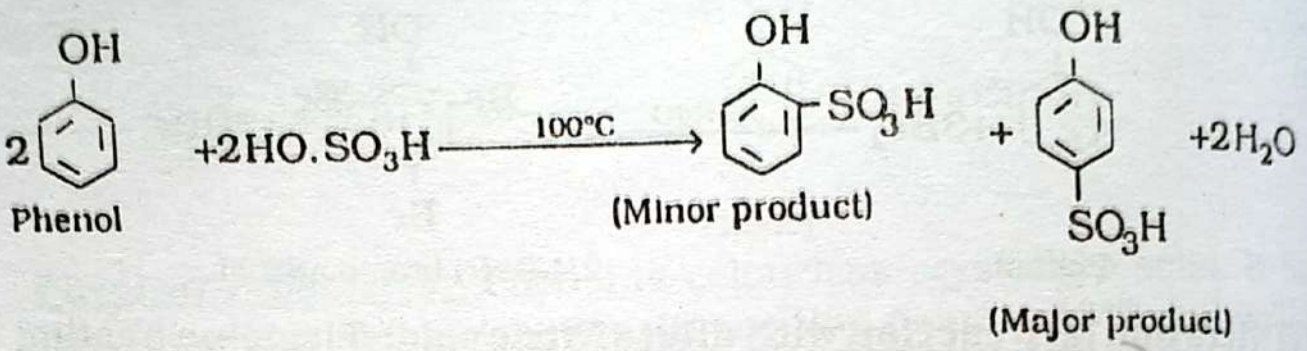
(b) On heating at 100° C, it gives major product of para-phenol sulphonic acid.



Uses:

(i) It is used as antiseptic and disinfectant.

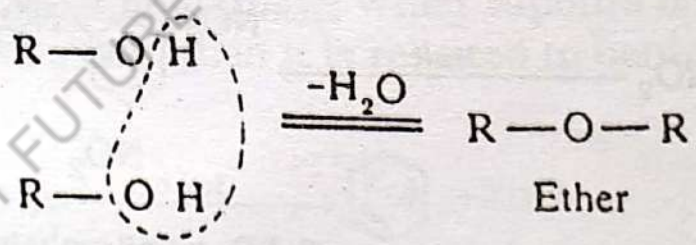
(ii) It is used in manufacturing of soaps, plastics, disinfectant, sprays, ointments, lozenges, gargles etc.

(iii) It is used in preparation of picric acid, aspirin etc.

(iv) It is also used as ink-preservative.

9.3 ETHERS

Ethers are compounds with the general formula $C_n H_{2n+2} O$, which is the same as that for monohydric alcohols and since their general structure is R–O–R, they may be regarded as alkyl oxides or the anhydride of alcohols.



2- molecules of alcohol

If the two alkyl groups in an ether are same. The ether is said to be symmetrical or simple, e.g., C_2H_5–O–C_2H_5. When the two alkyl groups are different, the ether is said to be unsymmetrical or mixed, e.g., CH_3–O–C_2H_5.

Nomenclature:-

1. Ethers are commonly named by first taking the names of alkyl groups attached to oxygen, followed by the class name ether.

2. According to I.U.P.A.C. system, the ethers are regarded as alkanes in which a hydrogen atom is replaced by an alkoxy (–OR) group.

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In mixed ethers, the larger alkyl group is chosen as the alkane:

(a) CH_3-O-CH_3
Dimethyl ether
or
Methoxymethane

(b) $CH_3-O-C_2H_5$
Ethyl methyl ether
or
Methoxyethane

(c) $C_2H_5-O-C_2H_5$
Diethyl ether
or
Ethoxyethane

(d) $CH_3-O-CH_2-CH_2-CH_3$
Methyl propyl ether
or
Methoxypropane

(e) $\overset{5}{C}H_3-\overset{2}{C}H(\overset{1}{C}H_3)-O-CH_3$
Isopropyl methyl ether
or
2-methoxy propane

(f) $C_2H_5-O-\overset{2}{C}(\overset{1}{C}H_3)(\overset{3}{C}H_3)-CH_3$
Ethyl ter-butyl ether
or
2-methyl-2-ethoxypropane

DIETHYL ETHER

Methods of preparation:-

(i) From ethyl alcohol:- William Son prepared diethyl ether from ethyl alcohol called as William Son synthesis. He used sodium metal and sulphuric acid.

(a) From ethyl alcohol using sodium metal:-

(i) Ethyl alcohol on treating with metallic sodium, forms sodium ethoxide.

$$2CH_3-CH_2-OH + 2Na \longrightarrow \underset{\text{Sodium ethoxide}}{2CH_3-CH_2-O.Na} + H_2$$

(ii) Sodium ethoxide on further treating with ethyl bromide, forms diethyl ether.

$$CH_3-CH_2-\overset{-}{O}.\overset{+}{N}a + CH_3-\overset{+}{C}H_2-\overset{-}{Br} \longrightarrow \underset{\text{Diethyl ether}}{CH_3-CH_2-O-CH_2-CH_3} + NaBr$$

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(b) From ethyl alcohol using sulphuric acid:- Diethyl ether is prepared by reaction of ethyl alcohol with sulphuric acid.

$$CH_3-\overset{+}{C}H_2\boxed{-\overset{-}{O}H+\overset{+}{H}}\overset{-}{O}-CH_2-CH_3 \xrightarrow{H_2SO_4} CH_3-CH_2-O-CH_2-CH_3+H_2O$$

Diethyl ether

(ii) From ethyl chloride using silver oxide:- Ethyl chloride on heating with dry silver oxide, produces diethyl ether.

$$2CH_3-\overset{+}{C}H_2-\overset{-}{C}l+\overset{+}{A}g_2\overset{-}{O} \xrightarrow{Heat} CH_3-CH_2-O-CH_2-CH_3+2AgCl$$

Ethyl chloride — Diethyl ether

Physical properties:- It is colourless liquid. It is highly inflammable. It has low boiling point. It is a good solvent. It is soluble in concentrated sulphuric acid like organic compounds containing oxygen.

Chemical reactions:- Diethyl ether is relatively un-reactive because of greater stability.

1. Oxygen of diethyl ether possesses two electron pair free (un-shared) which react with strong acid like hydrogen iodide to form oxonium ion by accepting proton.

$$C_2H_5-\ddot{O}-C_2H_5+\overset{+}{H}-\overset{-}{I} \longrightarrow C_2H_5-\underset{H}{\overset{+}{\ddot{O}}}-C_2H_5+\overset{-}{I}$$

Oxonium ion

Iodide ion (I^-) being strong nucleophile reacts with oxonium ion forming ethyl alcohol and ethyl iodide by breaking carbon-oxygen bond.

$$C_2H_5-\underset{H}{\overset{+}{\ddot{O}}}-C_2H_5+\overset{-}{I} \longrightarrow C_2H_5OH+C_2H_5I$$

Ethyl alcohol thus formed further reacts with hydrogen iodide under same conditions and forms more ethyl iodide.

$$C_2H_5OH+HI \longrightarrow C_2H_5I+H_2O$$

Oxonium ion:- When oxygen is positively charged and is bonded with three other atoms or group of atoms then it is called oxonium ion.

Example: $R-\underset{H}{\overset{+}{O}}-R$, $H-\underset{H}{\overset{+}{O}}-H$, $H_3\overset{+}{O}$

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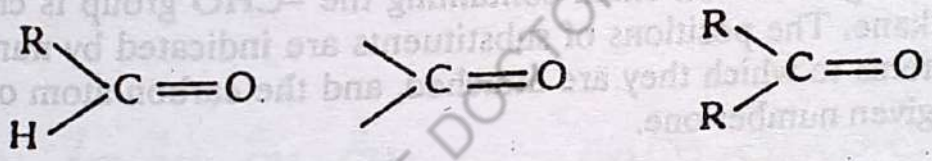
Uses:

It is used as solvent for facts, waxes, gums, resins and other organic material. It is used as solvent in Wurtz reaction. It is used in preparation of Grignard's reagent. It has been used as general anaesthetic. It is used in manufacture of smokeless powder and artificial silk collodion. It explodes due to low boiling point and highly inflammable nature.

9.4 ALDEHYDES AND KETONES

Aldehydes and ketones both have the general formula $C_nH_{2n}O$, and since both contain the carbonyl group $\left(>C=O\right)$, they are also known as carbonyl compounds. In aldehydes one of the two available valencies of the carbonyl carbon is satisfied by a hydrogen atom and the other by a alkyl group., whereas in ketones both the valances are satisfied by alkyl groups.



Aldehyde Carbonyl group Ketone

In aldehydes the functional group is $-CHO$ $\left({}_{H}>C=O\right)$ and in ketones the functional group is $>C=O$.

Nomenclature Of Aldehydes:-

1. The common names of aldehydes are derived from the name of carboxylic acids that they form on oxidation. The suffix–ic acid is replaced by–aldehyde:

(i) $HCHO \xrightarrow{[O]} HCOOH$
Formaldehyde → Formic Acid

(ii) $CH_3CHO \xrightarrow{[O]} CH_3COOH$
Acetaldehyde → Acetic Acid

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(iii) $CH_3 - CH_2 - CHO \xrightarrow{[O]} CH_3\,CH_2\,COOH$

Propionaldehyde → Propionic acid

The position of substituent is indicated by Greek letters, $\alpha, \beta, \gamma, \delta$, etc; the α–carbon being the one to which the –CHO group is attached:

(i) $\overset{\delta}{-C}\ \overset{\gamma}{C}-\overset{\beta}{C}-\overset{\alpha}{C}-CHO$

(ii) $\underset{\beta}{CH_3}-\underset{\alpha}{CH}(CH_3)-CHO$

α–methyl propion aldehyde

(iii) $\underset{\gamma}{CH_3}-\underset{\beta}{CH}(CH_3)-\underset{\alpha}{CH_2}-CHO$

β–methylbutyraldehyde

2. **I.U.P.A.C. Names:–** In this system aldehydes are named after the name of the corresponding alkane. The ending "–e" of alkane being replaced by suffix – al. The longest carbon chain containing the –CHO group is chosen as the parent alkane. The positions of substituents are indicated by numbers of the carbon atoms to which they are attached, and the carbon atom of the –CHO group is given number one.

(i) HCHO

Methanal or Formaldehyde

(ii) $\overset{2}{C}H_3\overset{1}{C}HO$

Ethanal or Acetaldehyde

(iii) $\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}HO$

Propanal

(iv) $\overset{5}{C}H_3-(\overset{4}{C}H_2)_{\overset{3}{2}}-\overset{2}{C}H_2\overset{1}{C}HO$

Pentanal or valeraldehyde

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

2–methylbutanal

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

4–methylpentanal

Nomenclature of Ketones:

1. **Common Names:–** Simple ketones are usually named after the name of alkyl groups attached to the carbonyl group, followed by the word Ketone.

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If the two alkyl groups in a ketone are same, the ketone is said to be simple or symmetrical; if the two alkyl groups are different, then it is said to be mixed or unsymmetrical ketone.

2. I.U.P.A.C. Names:- In this system the longest carbon chain having the carbonyl group is chosen as the parent alkane and the ketone is named by replacing –e of the parent alkane with suffix –one. The position of substituents is indicated by numbers of the carbon atoms to which they are attached and the carbon of carbonyl group is given the lowest possible number:

(i) $\overset{1}{C}H_3-\overset{2}{\overset{O}{\overset{\|}{C}}}-\overset{3}{C}H_3$

Dimethyl ketone
(commonly known as acetone)
or
2–propanone
or
propan–2–one

(ii) $\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{\overset{O}{\overset{\|}{C}}}-\overset{1}{C}H_3$

Methyl ethyl ketone
or
2 – butanone
or
butan –2–one

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

Methyl propyl ketone
or
pentan–2–one

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

2,4–dimethylhexan–3–one

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

Diethyl ketone
or
pentan–3–one

(vi) $\overset{6}{C}H_3-\overset{5}{\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}}-\overset{4}{C}H_2-\overset{3}{C}O-\overset{2}{C}H_2-\overset{1}{C}H_3$

5,5-dimethylhexan – 3–one

FORM ALDEHYDE (METHANAL, $H-\overset{O}{\overset{\|}{C}}-H$)

Methanal is commonly available as a 40% aqueous solution. It is the first and the most important member of aldehyde series which is widely used in synthetic industry.

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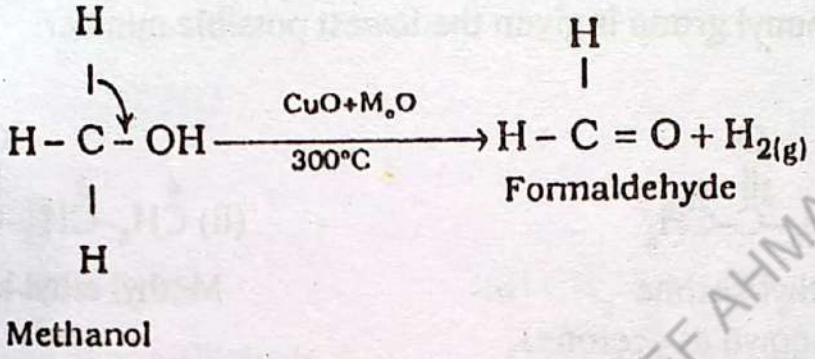
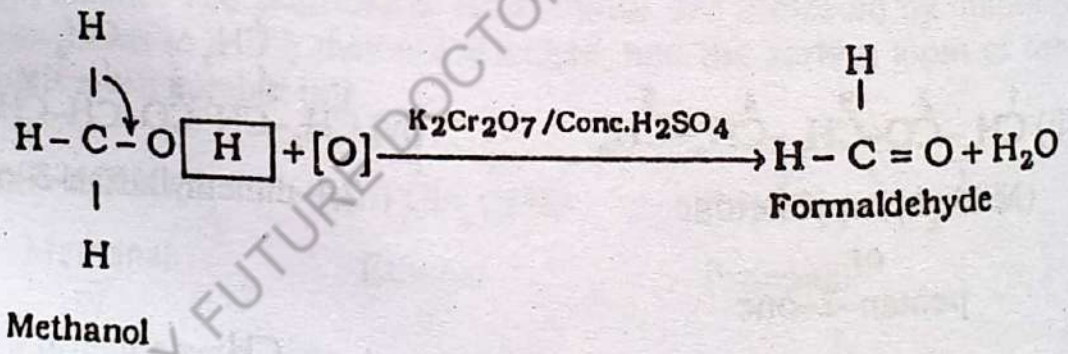
Methods of preparation:-

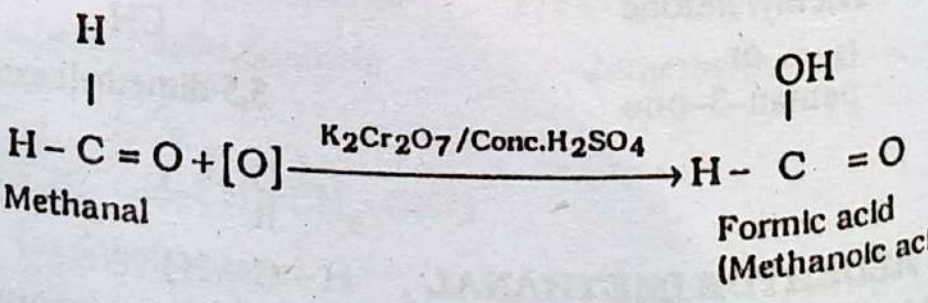
1. By the dehydrogenation of methyl alcohol:- On large scale, methanal is obtained by passing a mixture of methanol (CH_3-OH) vapours and air over heated catalyst . In this reaction methanol loses hydrogen to produce methanal i.e. Formaldehyde. Formaldehyde is absorbed in water to get its aqueous solution.



2. By the oxidation of methyl alcohol:- Methyl alcohol is oxidised to formaldehyde by heating methyl alcohol with a mixture of $K_2Cr_2O_7$ / conc.H_2SO_4. The first step oxidaion gives formaldehyde, as



If this oxidation continues then methanal further oxidised to formic acid, as



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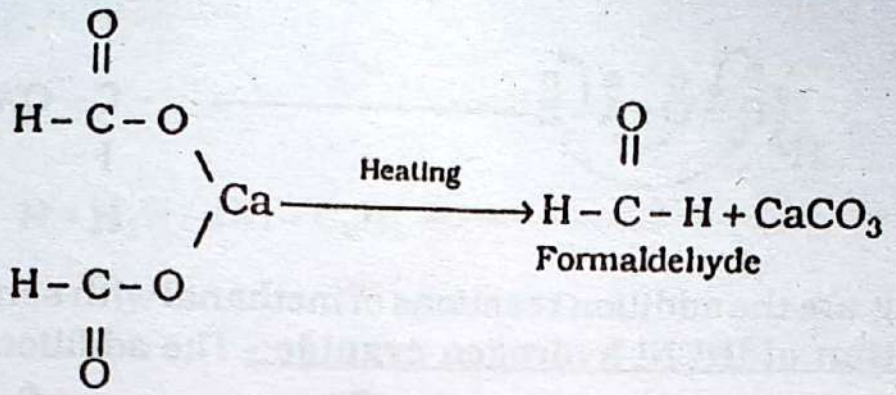
3. By dry distillation of calcium formate:- Calcium formate on dry distillation, gives vapours of formaldehyde.



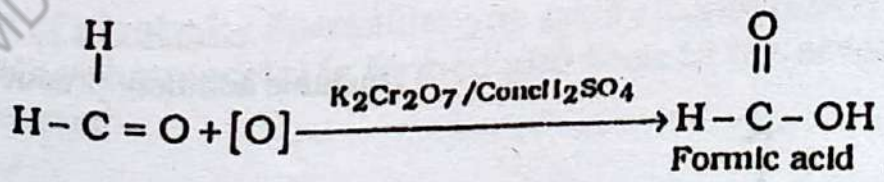
Properties:

(a) Physical properties:-

(i) Formaldehyde is a gas at ordinary condition.
(ii) It may condense to liquid at-21°C
(iii) It is readily soluble in water and the aqueous solution has penetrating suffocating odour.
(iv) On evaporating aqueous solution,a crystalline solid known as para-formaldehyde $(HCHO)_n H_2O$ is obtained.

(b) Chemical properties:-

(1) Oxidation of aldehyde group:- Like all aldehydes, formaldehyde possesses active H-atom attached to carbonyl group which is easily oxidised when formaldehyde is treated with oxidising mixture ($K_2Cr_2O_7$.+conc. H_2SO_4) to form formic acid



2. Addition at carbonyl, >C=O:- The carbonyl bond ($\overset{+\delta}{C}=\overset{-\delta}{O}$) is polarised in all carbonyl compounds and the addition of various reagents across the carbon – to–oxygen double bond of cabonyl group is characterised by active hydrogen.

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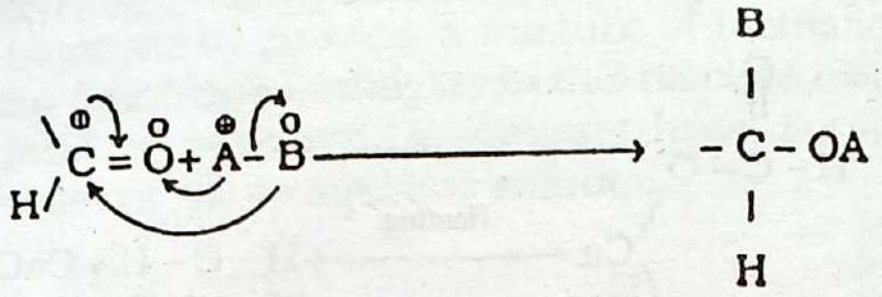
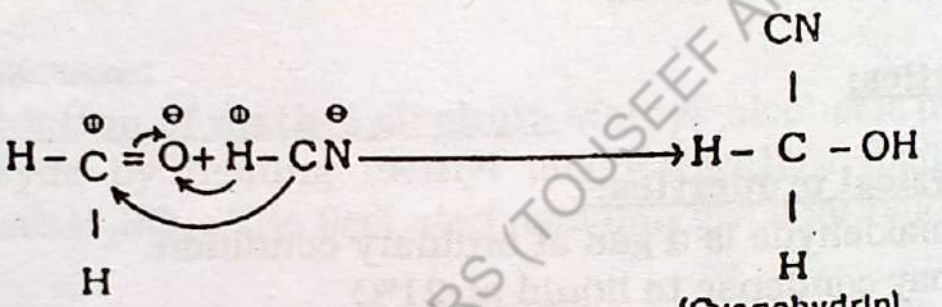
General reaction of this type may be represented as:



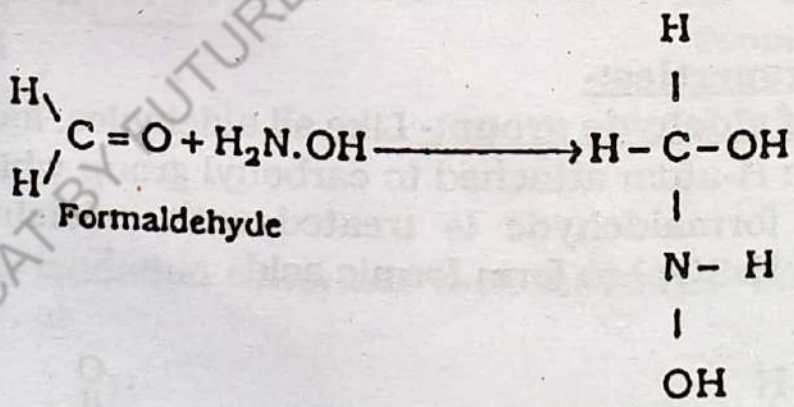
Following are the addition reactions of methanal with some reagents.

(a) Addition of (HCN) hydrogen cyanide:- The addition reaction is initiated by nucleophilic attack of $C^{\ominus}N$ at electrophilic $\overset{\oplus}{C}$.



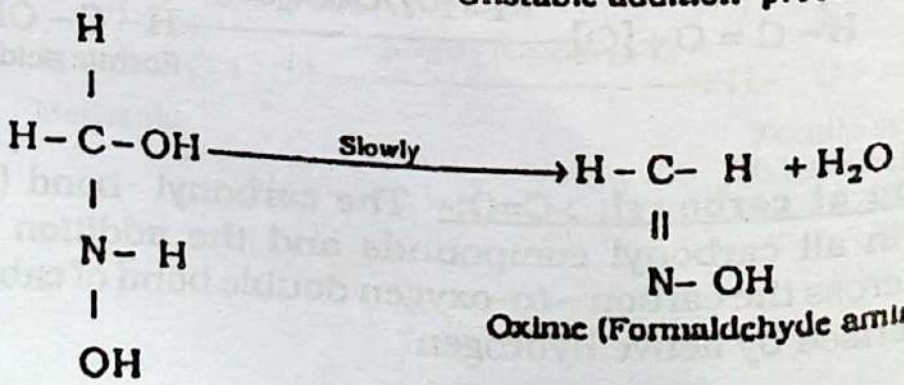
(Cyanohydrin) addition product

(b) Addition of hydroxalamine (NH_2OH):- Formaldehyde adds hydroxalamine (NH_2OH) to form a stable product called "Oxime".



Formaldehyde

Unstable addition product



Oxime (Formaldehyde amine)

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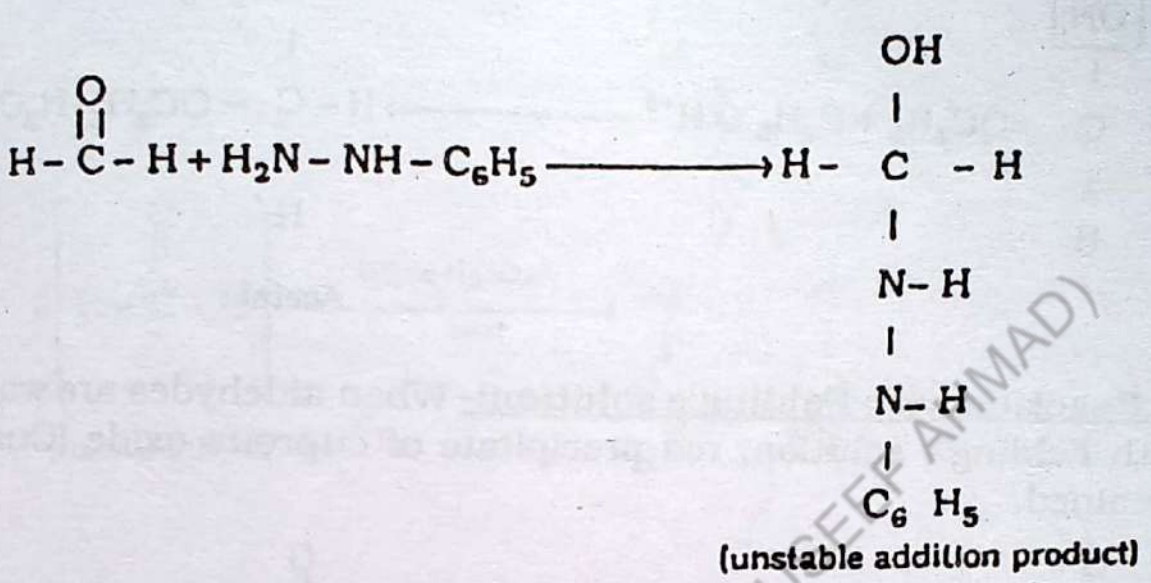
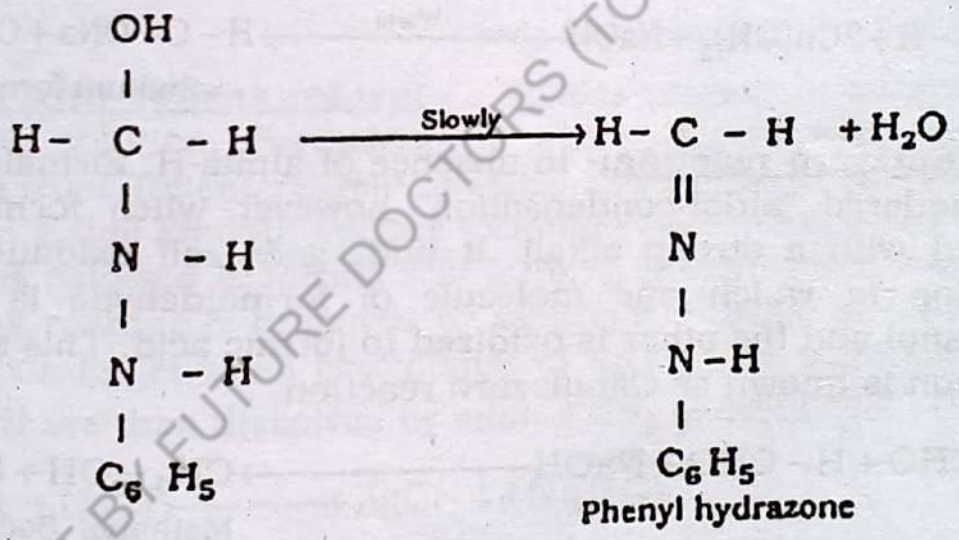
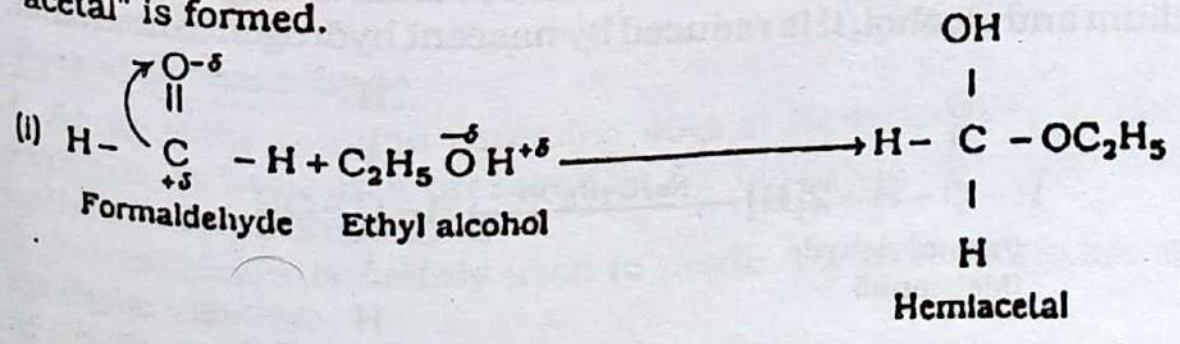
(C) Addition Of Phenylhydrazine (H_2N-NH-C_6H_5):- Fromaldehyde adds phenyl hydrazine in normal manner to form stable product called phenyl hydrazone.





(d) Addition of alcohol:- Formaldehyde adds alcohol (Ethyl alcohol). In the first stage hemiacetal is formed and then in the second stage "acetal" is formed.



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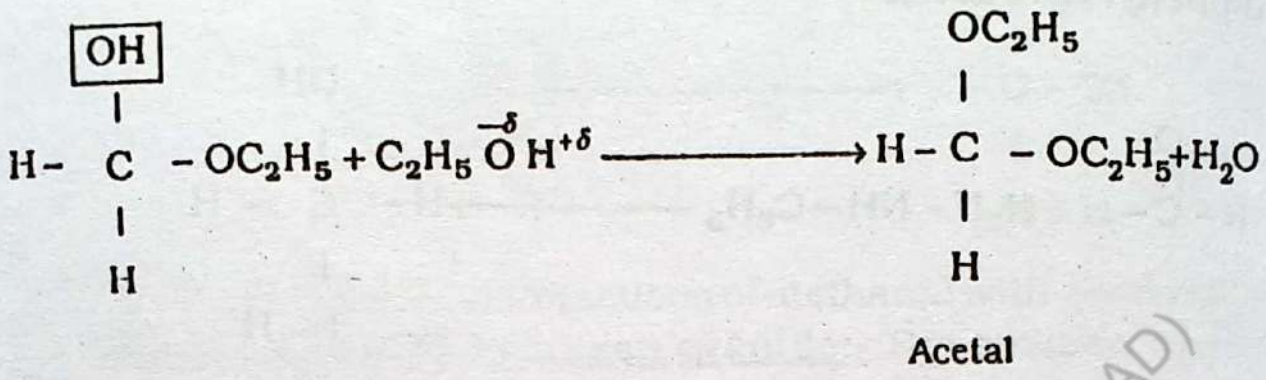
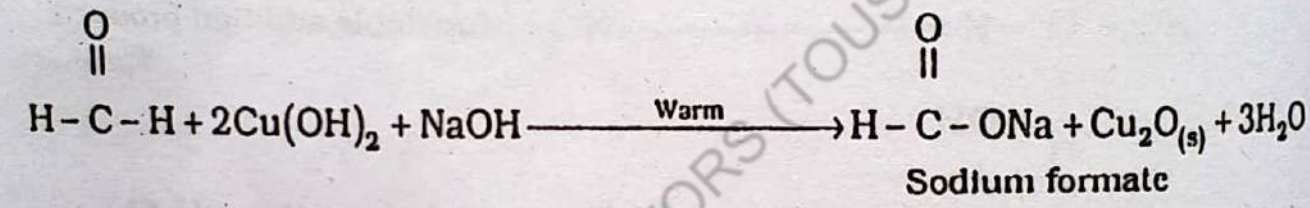
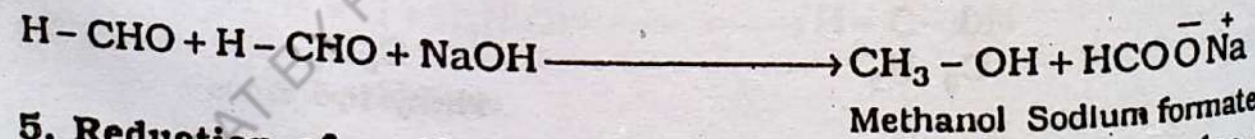
(ii)



3. Reaction with Fehling's solution:- When aldehydes are warmed with Fehling's solution, red precipitate of cuprous oxide (Cu_2O) is obtained.

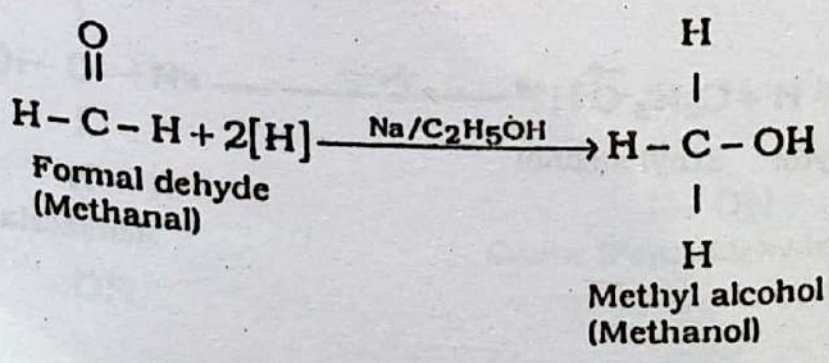


4. Cannizzaro reaction:- In absence of alpha-H, formaldehyde does not undergo "aldol-condensation" however when formaldehyde is treated with a strong alkali, it undergoes self oxidation-reduction reaction in which one molecule of formaldehyde is reduced to methanol and the other is oxidized to formic acid. This self addition-reaction is known as Cannizzaro reaction.



5. Reduction of methanal to methanol:- Hydrogen may also be added in the carbonyl group of an aldehyde by using some reagent which liberates nascent hydrogen.

When formaldehyde is reacted with sodium amalgam and water or sodium and alcohol, it is reduced by nascent hydrogen to methanol.



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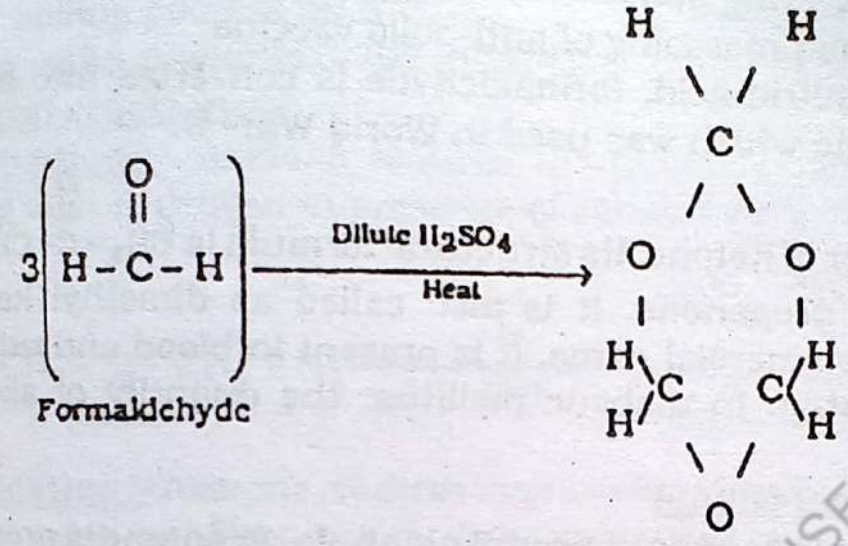
6. Polymerisation:- Formaldehyde polymerises in the presence of dilute H_2SO_4. on heating to form a trimer known as meta formaldehyde which melts at 62°C.



meta formaldehyde

7. Reaction with Tollens reagent:- Tollens reagent is ammonical silver nitrate solution. Formaldehyde when reacted with Tollens reagent then from Tollens reagent, metallic silver is reduced which is deposited on a fine smooth surface forming silver mirror. The aldehyde group is oxidised to formic acid forming ammonium formate.

Tollens reagent is prepared by adding few drops of NaOH to $AgNO_3$ solution to get white precipitates of AgOH. The white precipitates of AgOH are then dissolved by adding NH_3 or NH_4OH.

$$AgNO_3 + NaOH \longrightarrow AgOH\downarrow + NaNO_3$$

$$AgOH + 2NH_4OH \longrightarrow [Ag(NH_3)_2]OH_{(aq)} + 2H_2O$$

Diamine silver (I) hydroxide

$$H-CHO + 2[Ag(NH_3)_2]OH \xrightarrow{\Delta} 2Ag\downarrow + HCOONH_4 + 3NH_3 + H_2O$$

Formaldehyde

Uses of formaldehyde:

1. An aqueous solution containing 40% of formaldehyde known as foronalin, is used as a preservative for biological specimen and as antiseptic and disinfectant.
2. Formaldehyde is mainly used to produce the following resins or synthetic plastics:
(i) Ureaformaldehyde by condensation of formaldehyde and urea.

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(ii) Bakelite by condensation of formaldehyde and phenol.
(iii) Melamine.
3. It is used to prepare drying oils and dyes.
4. It is used in silvering of mirror.
5. It is used in the processing of anti-polio vaccine.
6. With fuming nitric acid, formaldehyde is converted into highly explosive cyclonite which was used in World War- II.

ACETONE.

It is basic member of Ketone. Its structural formula is $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$. Its IUPAC name is propanone. It is also called as dimethyl ketone. Acetone is the commercial name. It is present in blood and urine in very small quantity. In diabetic mellitus, the quantity of acetone increases.

Methods of preparation:-

(i) By oxidation of secondary propyl alcohol:- Acentone is prepared by oxidation of secondary propyl alcohol with acidified potassium dichromate solution. Due to oxidation, loss of two hydrogen atoms take place.

$$CH_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3+[O]\xrightarrow[H_2SO_4\,(Conc.)]{K_2Cr_2O_7}\underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}+H_2O$$

Sec. propyl alcohol
(2-propanol)

(ii) By pyrolysis of Acetic acid:- When vapours of acetic acid are passed over manganese dioxide at 500°C, it yields acetone.

$$2CH_3-\overset{\overset{O}{\|}}{C}-OH\xrightarrow[500^{o}C]{MnO_2}\underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}+CO_2+H_2O$$

(iii) By distillation of calcium acetate:- Industrially acetone is prepared by dry distillation of calcium acetate.

$$\begin{matrix}CH_3-COO\\ CH_3-COO\end{matrix}\!\!>Ca\xrightarrow{\text{Dry distillation}}\underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}+CaCO_3$$

Calcium acetate

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Physical properties:

(i) It is colourless, inflammable liquid with peculiar smell.
(ii) Due to its characteristic smell, it can be identified.
(iii) It is miscible with alcohol, ether and water.
(iv) Its boiling point is 56.5°C.
(v) Its specific gravity is 0.792 at 20°C.

Chemical reactions:-

(i) Reduction:- Acetone reduces to secondary propyl alcohol on heating with hydrogen in presence of catalyst palladium.

$$\underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + H_2 \xrightarrow[\text{Heat}]{\text{Pd.}} \underset{\text{Sec. propyl alcohol}}{CH_3-\overset{\overset{OH}{|}}{C}H-CH_3}$$

(ii) Oxidation:- Acetone oxidizes in presence of strong oxidizing agent such as mixture of potassium dichromate and conc. sulphuric acid and forms acetic acid.

$$\underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + 4[O] \xrightarrow[H_2SO_4\ (\text{Conc})]{K_2Cr_2O_7} \underset{\text{Acetic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + CO_2 + H_2O$$

(iii) Formation of Iodoform:- Acetone on heating with iodine in presence of sodium carbonate, forms yellow precipitates of iodoform.

$$\underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + 3I_2 + 2Na_2CO_3 \longrightarrow \underset{\text{Iodoform}}{CHI_3} + CH_3-\overset{\overset{O}{\|}}{C}-ONa + 3NaI + 2CO_2 + H_2O$$

Uses:

(i) It is used as solvent for acetylene, cellulose acetate, cellulose nitrate and celluloid.
(ii) It is used for storage of acetylene in solution form.
(iii) It is used in preparation of iodoform, chloroform etc.
(iv) It is used in preparation of artificial scent.
(v) It is used as nail polish remover.
(vi) It is used in preparation of smokeless gun powder and synthetic rubber.

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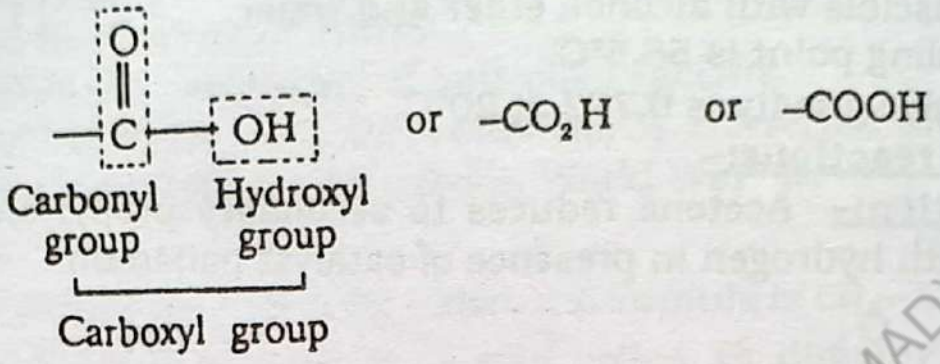
9.5 CARBOXYLIC ACIDS

Organic compounds which contain carboxyl group (–COOH) are called carboxylic acids. The carboxyl group contains a carbonyl group and a hydroxyl group:



Compounds which have only one carboxyl group are called mono carboxylic acids, if there are two or three carboxyl groups in a molecule then it is called as dicarboxylic or tricarboxylic acid. In this chapter only saturated monocarboxylic acids will be discussed.

The saturated mono carboxylic acids are also referred as fatty acids, due to the fact that some higher members (e.g; palmitic and stearic acids) occur in fats. Their general formula is $C_n H_{2n+1} COOH$ or simply RCOOH.

Nomenclature:–

1. **Common Names:–** The common names of monocarboxylic acids refer to their sources rather than to their chemical structures, e.g., Formic acid was so named because it was first obtained by the distillation of ants; latin word for ants is formica; Acetic acid is the chief constituent of vinegar, the Latin word for which is acetum.

Table 9.1 Common Names Of some Carboxylic acid.

Structure	Common name	Occurrence and derivation of name
HCOOH	Formic acid	Ants (L. Formica)
CH_3COOH	Acetic acid	Vinegar (L. Acetum)
CH_3CH_2COOH	Propionic acid	Milk, butter and cheese (Gr. Protos, First; pion, fat)
$CH_3(CH_2)_2COOH$	Butyric acid	Butter (L. Butyrum)
$CH_3(CH_2)_3COOH$	Valeric acid	Valerian root (L. Valere, to be strong)
$CH_3(CH_2)_4COOH$	Caproic acid	Goat (L. Caper)

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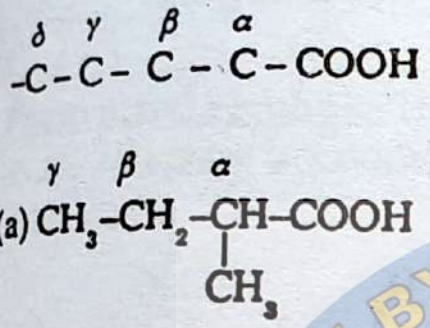
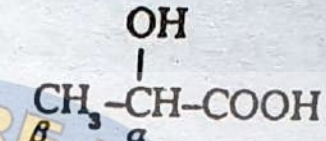
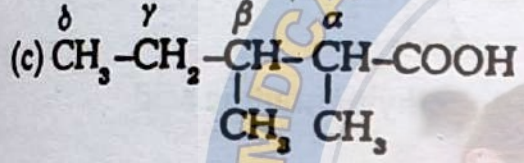
The positions of substituents are indicated by Greek letters $\alpha, \beta, \gamma, \delta$ etc; α-carbon atom is the one linked to the carboxyl group:



α– methylbutyric acid



α– hydroxypropionic acid



α, β dimethylvaleric acid or 2,3 – dimethyl pentanoic acid

I.U.P.A.C. Names:– The IUPAC names follow the usual pattern. The longest continuous carbon chain containing the carboxyl group is considered the parent alkane, and the acid is named by replacing – e of the corresponding alkane with – oic acid.

The common names and I.U.P.A.C. names of some of the common acids are listed in table 9.2.

Table 9.2 Names of some Carboxylic acid

Structure	Common Name	IUPAC Name
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2COOH$	Butyric acid	Butanoic acid
$CH_3(CH_2)_3COOH$	Valeric acid	Pentanoic acid
$CH_3(CH_2)_{14}COOH$	Palmitic acid	Hexadecanoic acid
$CH_3(CH_2)_{16}COOH$	Stearic acid	Octadecanoic acid

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The position of a substituent is indicated as usual by number of the carbon atom to which it is attached. The carbon atom of the carboxyl group is given number one.

$$\overset{5}{-C}-\overset{4}{C}-\overset{3}{C}-\overset{2}{C}-\overset{1}{COOH}$$

(a) $\overset{4}{CH_3}-\overset{3}{\underset{}{CH}}(CH_3)-\overset{2}{CH_2}-\overset{1}{COOH}$ (b) $\overset{5}{CH_3}-\overset{4}{C}(CH_3)_2-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{COOH}$

3–methylbutanoic acid 4,4–dimethylpentanoic acid

(c) $\overset{3}{CH_3}-\overset{2}{CH}(Br)-\overset{1}{COOH}$ (d) $\overset{4}{CH_3}-\overset{3}{CH}(Cl)-\overset{2}{CH_2}-\overset{1}{COOH}$

2–bromopropanoic acid 3– chlorobutanoic acid

ACETIC ACID (Ethanoic acid, $CH_3-\overset{O}{\overset{||}{C}}-OH$ or CH_3COOH).

Acetic acid is the main constituent of vinegar (acetum meaning vinegar) hence the name.

Commercial Production:–

1. From Pyroligneous Acid:- The brown aqueous distillate obtained during destructive distillation of wood was the chief source of acetic acid. This liquid which is called pyroligneous acid contains acetic acid, acetone and mehyl alcohol is subjected to fractional distillation to collect acetic acid.

2. From Ethyne:- These days acetic acid is produced by the oxidation of acetaldehyde which is obtained by passing acetylene (ethyne) through dilute H_2SO_4 solution containing some $HgSO_4$ which acts as a catalyst.

$$HC\equiv CH + H-OH \xrightarrow[95°C]{\text{dil } H_2SO_4/HgSO_4} H_2C=CH(OH)$$

Vinyl alcohol

$$H_2C=CH(OH) \xrightarrow{\text{Molecular rearrangement}} CH_3-CHO$$

Acetaldehyde (ethanal)

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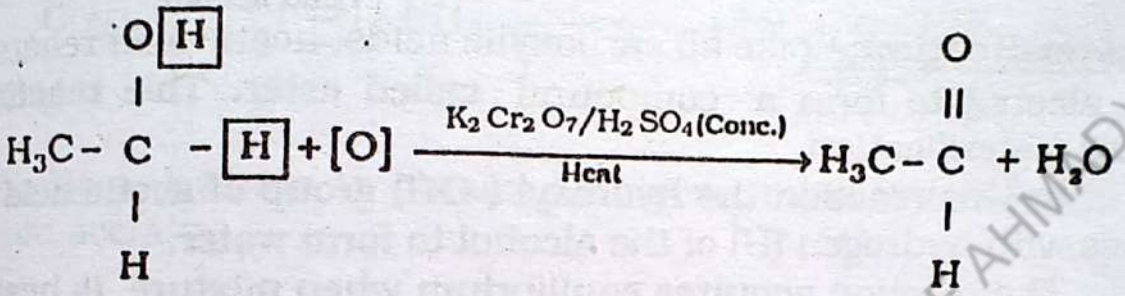
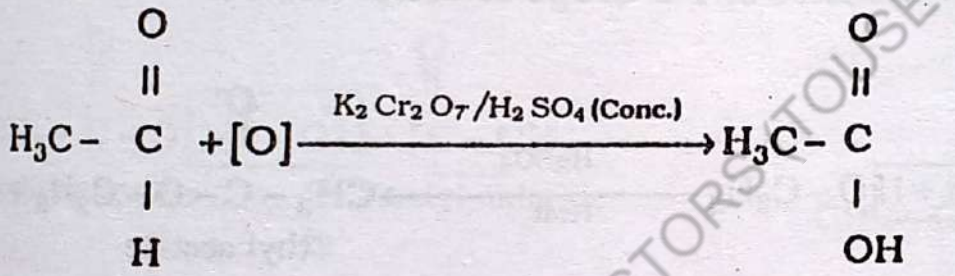
The oxidation of acetaldehyde is carried out with $K_2Cr_2O_7$/conc. H_2SO_4.

$$CH_3CHO + [O] \xrightarrow[(H_2SO_4\ CONC.)]{K_2Cr_2O_7} CH_3COOH$$

Acetic acid

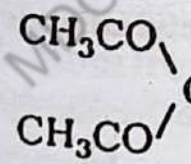
3. From ethyl alcohol:- The oxidation of ethyl alcohol with $K_2Cr_2O_7$/ conc. H_2SO_4 gives acetaldehyde which is oxidised to acetic acid.





Acetaldehyde Acetic acid

Physical properties:- The common acetic acid is a colourless volatile liquid having sharp vinegar smell and a sour taste. An hydrous acetic acid is a crystalline hygroscopic solid. It freezes like glassy mass hence is called glacial acetic acid. It is miscible with water, alcohol and ether. The acetic anhydride has formula:



which is highly hygroscopic

Chemical properties:

1. Acetic acid as a monobasic weak acid:- It ionises in aqueous solution producing one proton(H^+) per molecule.The ionisation constant of acetic acid is $Ka = 1.7 \times 10^{-5}$ which means that it is a very weak monobasic acid as compared to mineral acids for which Ka is about 10^8 order but acetic acid is a stronger acid than carbonic acid

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for which $Ka = 4.3 \times 10^{-7}$. It neutralises alkalies forming salts which are called acetates.

$$CH_3COOH + NaOH \longrightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + H_2O$$

$$2CH_3COOH + PbO \longrightarrow \underset{\text{Lead acetate}}{(CH_3COO)_2Pb} + H_2O$$

2. Esterification:- Like all carboxylic acids, acetic acid reacts with an alcohol to form a compound called ester. This reaction is called esterification.

In this reaction the hydroxyl (–OH) group of acetic acid combines with hydrogen (H) of the alcohol to form water.

The reaction acquires equilibrium when mixture is heated to boiling in the presence of 1-2 drops of conc. H_2SO_4.

$$CH_3-\overset{\overset{O}{||}}{C}-\boxed{OH+H}O-C_2H_5 \xrightarrow[\text{Heat}]{H_2SO_4} \underset{\text{Ethyl acetate}}{CH_3-\overset{\overset{O}{||}}{C}-O-C_2H_5} + H_2O$$

3. Formation of acid halide:- Acetic acid reacts with thionyl chloride ($SOCl_2$) or with phosphorus trihalide (PX_3) or with phosphorus pentahalide (PX_5) to form acid halide such as acetyl chloride or acetyl bromide

$$CH_3-\overset{\overset{O}{||}}{C}-OH + SOCl_2 \longrightarrow \underset{\text{Acetyl chloride}}{CH_3-\overset{\overset{O}{||}}{C}-Cl} + SO_2\uparrow + HCl$$

$$3(CH_3-\overset{\overset{O}{||}}{C}-OH) + PCl_3 \longrightarrow 3CH_3-\overset{\overset{O}{||}}{C}-Cl + H_3PO_3$$

$$CH_3-\overset{\overset{O}{||}}{C}-OH + PBr_5 \longrightarrow \underset{\text{Acetyl bromide}}{CH_3-\overset{\overset{O}{||}}{C}-Br} + POBr_3 + HBr$$

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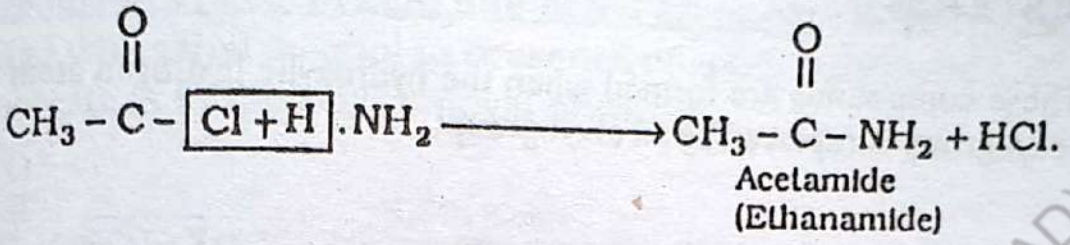
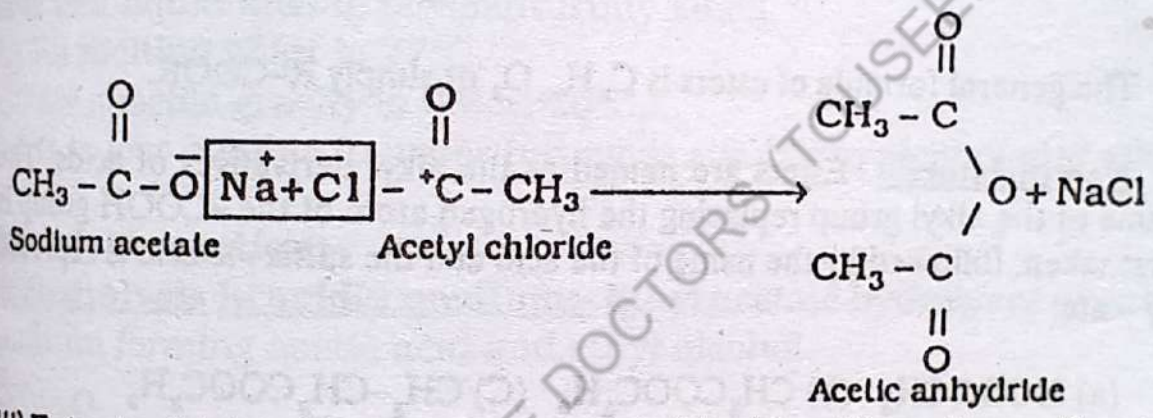
The acid halides are important compounds to be used for the synthesis of other compounds For example:

(i) "Acetamide" is produced by the action of ammonia (NH_3) on acetyl chloride.



(ii) Acetic anhydride is obtained by reacting acetyl chloride with sodium acetate.



(iii) Ester is obtained by reacting acetyl chloride with sodium ethoxide.

4. Decarboxylation:- When sodium acetate is heated with sodalime, it loses one C-atom from the chain as CO_2 which is absorbed by NaOH, the active ingredient of sodalime(CaO+NaOH)

$$CH_3COONa + NaOH \xrightarrow{CaO} CH_4 + Na_2CO_3$$

Uses:

(i) Acetic acid, glacial acetic acid and acetic anhydride are commonly used as laboratory reagents.

(ii) Acetic acid is used as solvent for phosphorus, sulphur, gums and resins.

(iii) It is widely used in artificial leather producion.

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(iv) Acetic acid is used to prepare acetates, esters and celluloscacetate silk.
(v) Acetyl chloride or acetic anhydride is used for acetylation.
(vi) After naturing and colouring, it is used as vinegar.

9.6 ESTERS

These compounds are formed when the hydroxylic hydrogen atom of the carboxyl group is replaced by an alkyl group:

$$\underset{\text{Carboxylic acid}}{R-\overset{O}{\overset{\|}{C}}-OH} \xrightarrow{R'OH/H^+} \underset{\text{Ester}}{R-\overset{O}{\overset{\|}{C}}-OR} + H_2O$$

The general formula of esters is $C_nH_{2n}O_2$ or simply R–COOR.

<u>Nomenclature:–</u> Esters are named as the alkyl derivatives of acids. The name of the alkyl group replacing the hydrogen atom of the –COOH group is first taken, followed by the name of the acid and the suffix –ic acid is replaced by – ate:

(a) $HCOOCH_3$ Methyl formate or methylmethanoate

(b) $CH_3COOC_2H_5$ Ethyl acetate or ethylethanoate

(C) $CH_3-CH_2COOC_2H_5$ Ethyl propionate or ethyl propanoate

(d) $CH_3-COO(CH_2)_3CH_3$ n-butyl acetate or butylethanoate

(e) $CH_3-CH_2COOCH(CH_3)_2$ Isopropyl propionate or isopropyl propanoate

ETHYL ACETATE

It is an ester and is derivative of carboxyl group. When hydrogen atom (H) of carboxylic group is replaced by alkyl group, then it is an ester.

Its structural formula is $R-\overset{O}{\overset{\|}{C}}-O.R'$

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R and R' are alkyl groups which may be same or different. The structural formula of ethyl acetate is

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

Preparation.

1. By reaction of acetic acid and ethyl alcohol:- When acetic acid is treated with ethyl alcohol in presence of conc. sulphuric acid then ethyl acetate is formed by removal of water.

$$\underset{\text{Acetic acid}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O\boxed{H+HO}}\underset{\text{Ethyl alcohol}}{C_2H_5} \xrightleftharpoons{H_2SO_4\ (Conc)} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-C_2H_5 + H_2O$$

Physical Properties

(i) It is a liquid having pleasant fruity smell.
(ii) Its melting point is 77°C.
(iii) Its specific gravity is 0.9 at 20°C.
(iv) It is less soluble in water but more soluble in alcohol and ether.

Chemical reactions:

(i) Hydrolysis in acidic medium:- Ethyl acetate hydrolyses in acidic medium forming acetic acid and ethyl alcohol.

$$\underset{\text{Ethyl acetate}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O\,C_2H_5} + H.OH \xrightleftharpoons{H_2SO_4\ (dil)} \underset{\text{Acetic acid}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

(ii) Hydrolysis in basic medium:- Ethyl acetate on treating with 10% NaOH solution, forms sodium acetate and ethyl alcohol.

$$\underset{\text{Ethyl acetate}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O\,C_2H_5} + NaO\,H(10\%) \rightleftharpoons \underset{\text{Sodium acetate}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-ONa} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

Uses:

(i) It is a liquid with pleasant smell.
(ii) It occurs in pine apple.
(iii) It is used as good solvent for paints, varnishes, oils, fats, gums, resins, cellulose etc.

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(iv) It is used as plasticiser i.e. reduces brittleness and improves elasticity of plastics.
(v) It is used for preparation of artificial flavours and essences.

ASSIGNMENT

1. What do you mean by mono, di and trihydric alcohols? Give two examples of each class.

2. What do you mean by primary, secondary and tertiary alcohols? Give the structure and name of a 1°, a 2° and a 3° alcohol of the molecular formula $C_6H_{11}OH$.

3. Outline the structure of each of the following:

(i) sec-butyl alcohol (ii) neo-pentyl alcohol (iii) 3-methylbutanol
(iv) Isobutyl alcohol (v) ter-butyl alcohol
(vi) 3–ethyl –3–methyl –2–pentanol
(vii) 2,2–dimethyl –1- 4 hexandiol
(viii) Resorcinol (ix) 4–bromophenol (x) 2-4-6-tribromophenol
(xi) 4–methylphenol (xii) 2–naphthol
(xiii) 2-4-6-trinitrophenol
(xiv) Di–isopropyl ether (xv) Ethyl–ter–butyl ether
(xvi) Isobutyl methyl ether (xvii) 2–methoxy hexane
(xviii) 2–methyl–2–methoxy butane (xix) 3–ethoxy heptane
(xx) Pentan–2– one (xxi) 4–5–dimethyl–3–heptanone
(xxii) Isobutyraldehyde (xxiii) 2– chloropropanal
(xxiv) 1–bromo–3–methyl hexan–2–one (xxv) Methyl – ter – butyl ketone
(xxvi) 3– chloropentanoic acid (xxvii) α,β –dimethyl butyric acid
(xxviii) Valeric acid (xxix) 2–bromo–3–methyl hexanoic acid
(xxx) Isopropyl butanoate (xxxi) Butyl propionate
(xxxii) Methyl hexanoate (xxxiii) Isobutyl formate

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4. Give the I.U.P.A.C. names of each of the following, where possible, give also the common names.

(i) $(CH_3)_2CH-CH_2CH_2OH$ (ii) $(CH_3)_2CHOH$

(iii) $CH_3-\underset{OH}{CH}-\underset{OH}{CH}-CH_3$ (iv) $CH_3-\overset{OH}{CH}-CH_2-CH_2-\overset{OH}{CH}-CH_2-CH_3$

(v) $(CH_3)_3C-OCH_3$ (vi) $C_2H_5-OCH(CH_3)_2$

(vii) $CH_3-OCH_2-CH_2-CH_3$ (viii) $(CH_3)_3C-O-CH_2-CH_2-CH_2-CH_3$

(ix) $CH_3-\overset{CH_3}{CH}-\overset{C_2H_5}{CH}-CH_2-CHO$ (x) $CH_3CH_2CH_2CHO$

(xi) $CH_3-\overset{Br}{\underset{CH_3}{C}}-CHO$ (xii) $CH_3-\underset{CH_3}{CH}-CH_2-CHO$

(xiii) $CH_3-\overset{O}{\overset{\|}{C}}-CH(CH_3)_2$ (xiv) $(CH_3)_2CH-\overset{O}{\overset{\|}{C}}-C(CH_3)_3$

(xv) $CH_3-\overset{CH_3}{CH}-CO-\overset{C_2H_5}{CH}-CH_2-CH_3$ (xvi) $CH_3-\underset{CH_3}{CH}-\underset{CH_3}{CH}-COOH$

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(xvii) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-COOH$

(xviii) $Br-\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}-COOH$

(xix) $CH_3-\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_2COOH$

(XX) $CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-COOH$

(xxi) $CH_3-CH_2.COOCH_2CH_3$

(xxii) $C_2H_5-\overset{\overset{O}{\|}}{C}-OCH_3$

(xxiii) $CH_3-\overset{\overset{O}{\|}}{C}-OCH(CH_3)_2$

(xxiv) $CH_3CH_2CH_2-CH_2-COOC(CH_3)_3$

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CHAPTER 10

CHEMISTRY OF LIFE

10.1 DEFINITION AND INTRODUCTION

Chemistry of life, in short written as Biochemistry (Bio = Life + Chemistry), is a branch of Chemistry which deals with the study of chemical and physical processes, by means of which the chemical compounds such as vitamins, lipids, carbohydrates proteins and nucleic acids are transformed into one another by the cell itself in order to maintain its organized structure and activities.

The biochemistry is a new science in comparison to other physical sciences and the reason of its late development was sophisticated techniques and concepts needed to study the structure and function of a living system.

10.2 FOOD AND NUTRITION

Introduction:- Food and Nutrition is a field of biochemistry which deals with the nutrient and caloric requirement of the living body. It deals with the effect on growth and metabolism of the living system arising from the imbalanced diet. For instance the statistical survey data of food and nutrition showed that 30% of population was suffering from the diseases of malnutrition (Faulty nutrition). Diseases like decayed and crocked teeth, bone deformation,lack of mental alertness and under weight were real outcome of the unbalanced food and diet.

Classification:- The food is required by the body to achieve three purposes: (a) Energy (b) Growth and maintenance of tissues (c) Regulation of body processes and for the sake of simplicity,it is classified into six groups:

(i) Carbohydrates

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(ii) Lipids and fats

(iii) Proteins

(iv) Vitamins

(v)Minerals

(vi) Water

Elements Of Nutrition:– For healthy performance, each day the diet must supply the body with:

(a) Adequate calories

(b) Vitamins

(c) Mineral salts

(d) Water

It becomes therefore necessary to choose foodstuff in a diet which can cover all the above needs of the living system and such diet is known as a balanced diet. A malnutrition or bad nutrition is a state in which body is poorly nourished due to long use of a diet which lacks in essential elements and becomes subject to deficiency diseases and other disorders.

The energy and the fuel value of foods which supply this energy is measured in calories. In nutrition, the use of large Calorie (written with capital C) or kilo calorie is employed and is equal to amount of heat required to raise the temperature of 1 Kg of water by 1°C.

An energy requirement for a person of normal size and weight, working under moderate conditions of climate may vary around 2500–3000 calories depending upon the nature of job. Concentrated brain work, for example, study and office work require no additional calories. Comparatively young persons need more calories than the older ones.

The energy expenditures in some typical pursuits are given below (in Calories per hour):

Walking at 3.75 Km p.h	140
Walking at 6.Km p.h	240
Sawing wood	450
Masonry labour	270
Sweeping and Cleaning	100
Dish washing/Sewing	70
Concentrated brain work	Nil

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Almost all the physiological activities of the body are energy dependent and this comes from the break down of carbohydrates, fats and proteins, the three major nutrients. Carbohydrates and to lesser extent fats are the cheaper sources of the calories than the proteins. Nevertheless the proteins are primarily necessary for the tissue growth and repair but if intake of other two sources of calories are insufficient then the protein is also burned for energy.

The quantity of food needed to provide required calories for an individual could be calculated as follows:

Carbohydrates give	4 calories per gram
Fats give	9 calories per gram
Proteins give	4 calories per gram

(i) Carbohydrate Intake:- Carbohydrates are the cheap and an efficient source of energy for animals. They serve as staple food for most of the countries. Carbohydrates furnish 60–80% of the total calories intake. A minimum quantity of 5g of carbohydrate per 100 K cal of the total diet is necessary to prevent the development of ill–effects of fasting or of high fat and protein diet.

The main sources of carbohydrates are (i) cereals or grains–wheat, maize, rice, oats, barley, sorghum and millets. (ii) roots and tubers–Potatoes, sweet potatoes, (iii) sugar, honey, beat roots, fruits and sugar–cane.

(ii) Fat Intake:- Fats are important components of our diet, because these not only make our diet more palatable but also provide energy double than that of proteins or carbohydrates and therefore they serve as an effective source of energy store in both animals and plants (seeds). The available fat sources also provide the fat soluble vitamins because most of their sources are carrier of such vitamins.

The minimum daily requirement of appropriate fats varies from 15–25 g per day depending upon the intake of calories from other sources of diet. The level of recommended fat can go up to 100 g/day, in case when it is ingested for calorific purposes.

However, 35% of the total calories required per day, are acquired from fats containing 10% poly unsaturated fatty acids and 10% saturated fatty acids.

Main sources of Fats (i) Animal sources –Tallow, butter, (ii) vegetable source – Oils from seeds of all kinds of sunflower, cotton seed, coconuts, soybean and mustard.

(iii) Protein Intake: Normally, like carbohydrates or fats, proteins are not an energy supplying nutrients. However when the required calories per daily

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diet are not adequately met by the carbohydrates or fats,the proteins do furnish energy.

Protein as nutrient,is more important for the maintenance of body growth and repair of tissues than to supply calories. Because the protein of tissues is constantly being broken down and synthesized, it is imperative to supply some amount of protein in daily diet, so as to meet wear and tear quota of the body.

Nutritive value of proteins depends on their content of essential amino-acids; for instance gelatin is a protein which lacks an essential amino–acid, the tryptophan and similarly feints of corn are low in both tryptophan and lysine. Such incomplete proteins are unable to support growth if given as the only source of protein in diet. Therefore, a mixed diet is suggested and preferable. eg, bread or rice with milk, fish and cornmeal.

There are ten amino-acids which body cannot synthesize and therefore are called essential amino-acids, namely methionine, tryptophan, threonine, histidine, arginine, leucine, isoleucine, valine, phenylalanine and lysine.

The percent of energy requirement of the body per day opted from food groups is suggested as under:

(i)	Carbohydrates	58%
(ii)	Fats	35%
(iii)	Proteins	12%

The proteins in addition to other important functions also constitute important sources of nitrogen, sulphur and phosphorus. Proteins can also supply some amino-acids which like glucose function as an energy donor, that fat can not do so.

The energy deficiency is always accompanied by the symptoms of proteins deficiency and results in certain ailment.

The main sources of protein are : (i) Meat (ii) Milk and eggs (iii) Pulses, beans, peas, lentil (iv) Edible seeds, nuts and oil containing fruits.

(iv) <u>Vitamin Intake:-</u> Vitamins are necessary food factors which act as stimulant and unlike major nutrients such as carbohydrates,proteins, fats or water, they are required only in small amounts in the range of milligrams per day. Chemically vitamins are organic in nature and are classified according to their

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solubility as fat soluble vitamins such as A, D, E, K or water soluble vitamins such as B–Complex and C.

Water soluble vitamins are more readily absorbed than the fat soluble and are not stored in the body thus taken in excessive amounts than the body requirements are excreted and therefore their toxic effects are rarely known. On the other hand, fat soluble vitamins are stored in large amounts, mainly in the liver hence need not be taken daily. One large dose is sufficient to over come the deficiency state. Repeated intake in excess amounts of fat soluble vitamins causes severe toxic effects.

For instance vitamin A is required for normal growth, for vision in dim light and for keeping skin and the mucous linings of the body healthy. If it is taken as little as 7.5 mg per day over a period of 20–30 days, the excess of vitamin A will cause an increase in cerebral spinal fluid pressure, headaches and irritability.

Many vitamins are labile and could be destroyed by over cooking and too many washing or refinement of cereal grains so the rigorous treatment of washing or cooking should be avoided.

(v) **Mineral Intake:–** Inorganic elements present in diet do not supply any energy/calories like other nutrients such as carbohydrates fats or proteins but their role in the diet is equally important for maintenance, building and rebuilding of tissues.

Although living matter contains traces of all elements found in its surroundings, only 23 elements have been observed to be essential for life. Out of these eleven are non metals (C,H, O, N, S, P, Cl, F, I, B, Si) and the rest are metals (Ca, Na, K, Mg, Fe, Cu, Zn, Co, Al, Ni, Mo, Se). Not all of these elements have been shown to be required by all species. However, for instance H, C, N, O, Na, K, Mg, Ca, S, P are of universal importance.

Bones and teeth require calcium and phosphorus. Iron is picked up for the production of haemoglobin and cytochrome system of body. Iodine is needed in thyroxine, the hormone of thyroid gland. In other words mineral salts control acid–base balance of the body, and as cofactors of the many enzymes and thus activate the metabolic system.

Eggs, meat, and cereals are common acid forming foods. Fruits, vegetables and milk are common base forming food. Sugar and fats are among neutral foods.

Many of these elements are usually found as ions, such as

Fe^{2+}, Na^{+}, K^{+}, Mg^{2+}, PO_4^{3-}, SO_4^{2-}, Cl^{-}, Ca^{2+}, CO_3^{2-}, NO_3^{-}

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The concentration of these ions present in body are maintained within narrow limits and small variations result in many abnormal biological functions.

The minerals are useful to maintain pH, osmotic pressure and act as ion antagonists. Requirement of the minerals varies from 100 mg or more, to a few micro grams per day. The elements required in microgram, are Cu^{2+}, Co^{2+}, Ni^{2+}, Al^{3+} etc.

(vi) **Water Intake:–** The daily intake of water is the most important item of the diet. Because an individual without food may survive for a month, but without water one can not live more than 15 to 16 days.

About 70% of the body weight is water, and weight remains constant from day to day, it shows that the water content of the body also remains constant and this concludes that the total water lost per day from the body is being balanced by the water intake per day.

The water requirement of the body per day is about 2.5 to 3 litres which is gained from three different sources mainly fluids, food and the oxidation of food stuffs, and the same amount is being lost through urine, skin (perspiration), lungs (expiration) and faeces.

10.3 CARBOHYDRATES

General:- Carbohydrates are an important class of naturally occurring compounds which play an important role in our daily life. They were called carbohydrates because the early discovered ones contained oxygen and hydrogen in the same proportion as in water and could be represented by a general formula $C_x(H_2O)_y$. But this definition proved to be erroneous because:

(a) Some compounds, such as Rhamnose, are definitely carbohydrates but their formulae do not conform to the general formula $C_x(H_2O)_y$.

(b) All compounds conforming to the formula $C_x(H_2O)_y$ are not carbohydrates e.g. formaldehyde, HCHO, [=C.H_2O]; and acetic acid, CH_3COOH, [= $C_2(H_2O)_2$] etc.

Now a days precise definition of carbohydrates, based on their structure is given as follows:

Carbohydrates include all polydric aldehydes or ketones (i.e they are either aldehyde or ketone having many–OH groups) and other substances which on hydrolysis produce such compounds.

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CLASSIFICATION

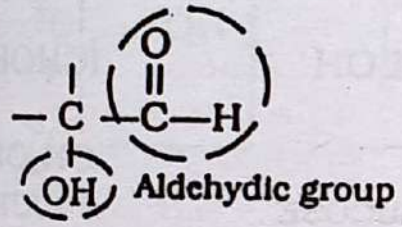
(A) Classification based on taste:- Based on taste carbohydrates are classified as:

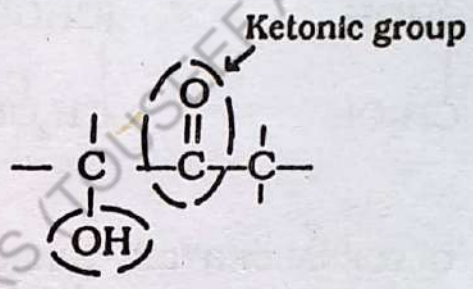
(i) Sugars:- These carbohydrates are sweet, crystalline and water soluble e.g. glucose, fructose, sucrose, etc.

(ii) Non-sugars:- These are tasteless, amorphous and insoluble in water, e.g. starch, cellulose etc.

Sugars can further be classified as.

(a) Reducing sugars:- These sugars reduce TOLLEN'S REAGENT and FEHLING'S SOLUTION. They contain free aldehydic or ketonic group alongwith hydroxyl (–OH) group on the carbon adjacent to these groups, as shown below:





Examples of reducing sugars are: all monosaccharides (e.g. glucose, fructose etc.) and all oligosaccharide except sucrose.

Non-reducing sugars:- These sugars do not reduce Tollen's reagent or Fehling's solution because they do not contain free aldehydic or ketonic group with adjacent hydroxyl (–OH) group.

Examples are: One oligosaccharide (i.e. sucrose).
All polysaccharides (i.e. starch, cellulose etc.).

(B) Classification based on molecular structure:- A more scientific classification is based upon the number of carbon atoms in a molecule or upon the number of simple sugar units present in their molecules. They are divided into three major classes:

(1) Monosaccharides
(2) Oligosaccharides
(3) Ploysaccharides

(1) Monosaccharides (Simple Sugars).
(Latin, Saccharum = Sugar)

These are the carbohydrates which cannot be further hydrolysed into simpler carbohydrate units. They contain 3 to 10 carbon atoms.

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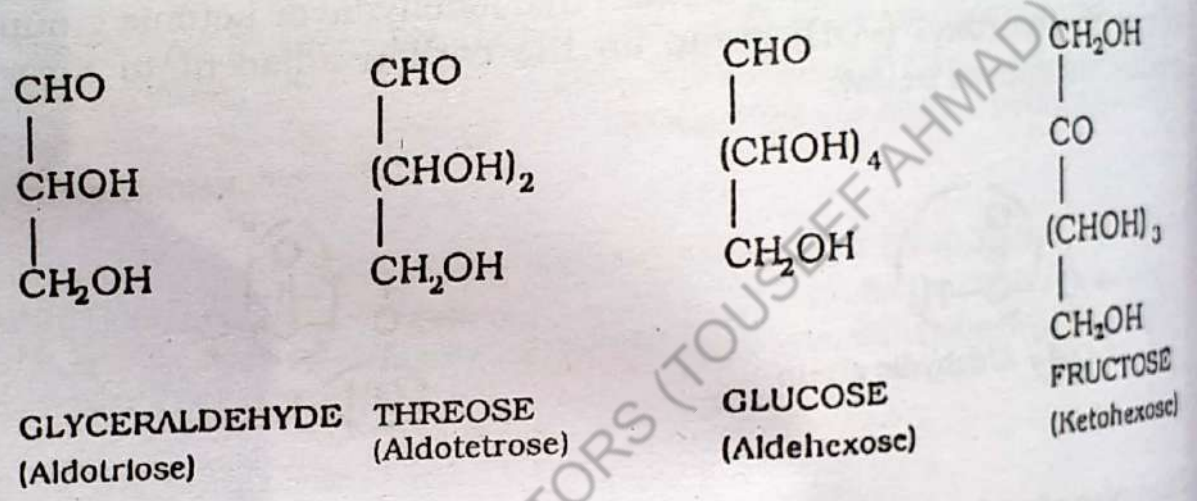
Those containing aldehydic group (–CHO) are called **ALDOSES** and those containing ketonic group ($-\overset{O}{\overset{\|}{C}}-$) are called **KETOSES**. The number of carbon atoms in their molecules is denoted by prefixes, tri, tetr, pent, hex etc.; thus glucose, ($C_6H_{12}O_6$) contains 6 C, and is an aldehyde so it is called Aldohexose whereas fructose, ($C_6H_{12}O_6$) contains 6 C but contains ketonic group hence it is called Ketohexose. Examples of Monosaccharides are:



Hexoses are very important monosaccharides; of these glucose, fructose, mannose, galactose are outstanding.

Glucose also called Dextrose, is found in fruits and honey. It has an open chain structure as well as closed chain structure.

All those sugars in which hydroxyl (–OH) group, on last but one carbon (i.e. C-atom farthest removed from carbonyl group) is on right hand side are called D–sugars, and when hydroxyl (–OH) group is on left hand side are called L–sugars.

Naturally occurring glucose is D–glucose. It has a property of rotating plane of polarized right to the right; hence it is called **Dextro-rotatory**. A symbol (+) is used for this purpose. The open structure of D(+) glucose is shown below. It also exists as two isomeric closed chain structures which inter–convert into one another via open chain form. This property is called **mutarotation**.

The closed chain structure, in which hydroxyl (–OH) group on C No. 1 is on right hand side, it is called α–isomer and when hydroxyl

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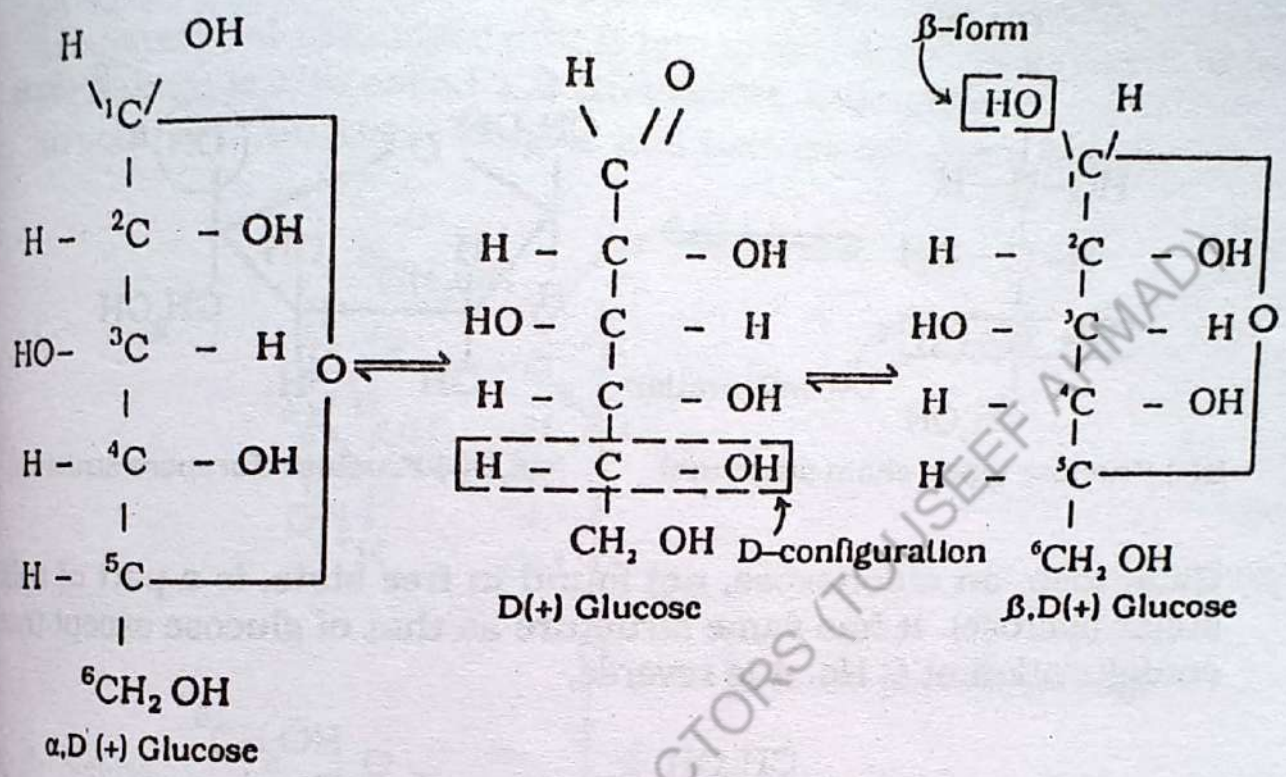
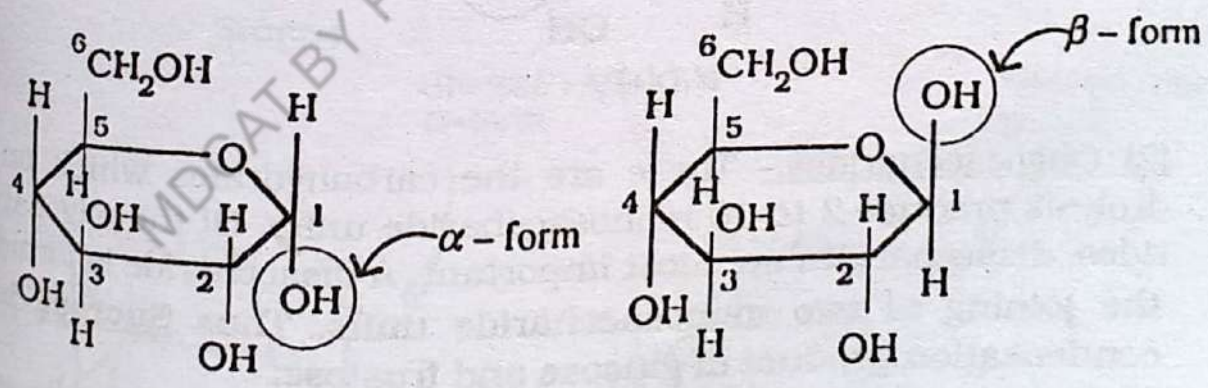
(-OH) group on C No.1 is on left hand side, it is called ß–isomer.



Closed chain forms of glucose are also represented in hexagonal forms called **PYRANOSE STRUCTURES** as shown below:



α,D(+)glucose β,D(+)glucose

Fructose, a ketohexose is also called **LEVULOSE** because it rotates the plane of polarized light to the left. A symbol (-) is used for this

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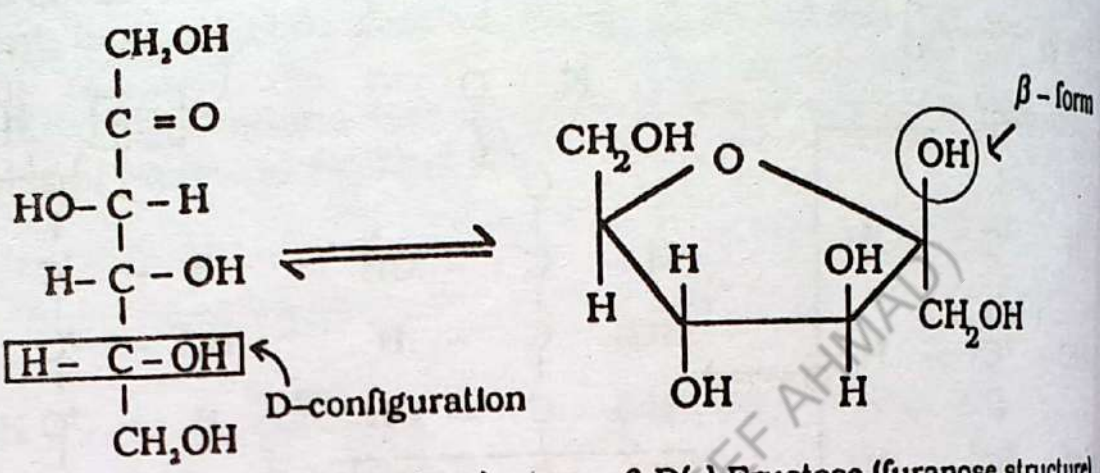
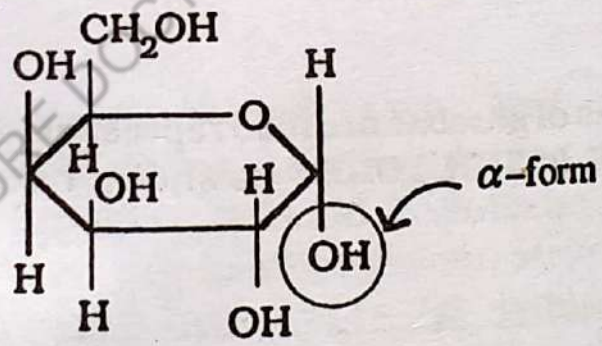
purpose; i.e. it is **LEVOROTATORY.** It is simplest of all sugars. Its structures are shown below. Its ring structure is called **FURANOSE** structure.



D(–) Fructose (open chain structure) ß,D(–) Fructose (furanose structure)

Galactose, an aldohexose, not found in free state, is a part of milk sugar (lactose). It has same structure as that of glucose except that configuration at C No. 4 is reverse.



α,D(+)

(2) Oligosaccharides:- These are the carbohydrates which on hydrolysis produce 2 to 10 monosaccharide units. Of the oligosaccharides, disaccharides are most important. A disaccharide is formed by the joining of two monosaccharide units. Thus **Sucrose** is the condensation product of glucose and frustose.
Maltose is obtained by the combination of two glucose units and **Lactose** (milk sugar) is composed of glucose and galactose units.

Sucrose is formed when α–glucose and β–fructose units join together through **GLYCOSIDIC LINKAGE.** A glycosidic linkage is the one in which a carbon atom is joined to two oxygen atoms through

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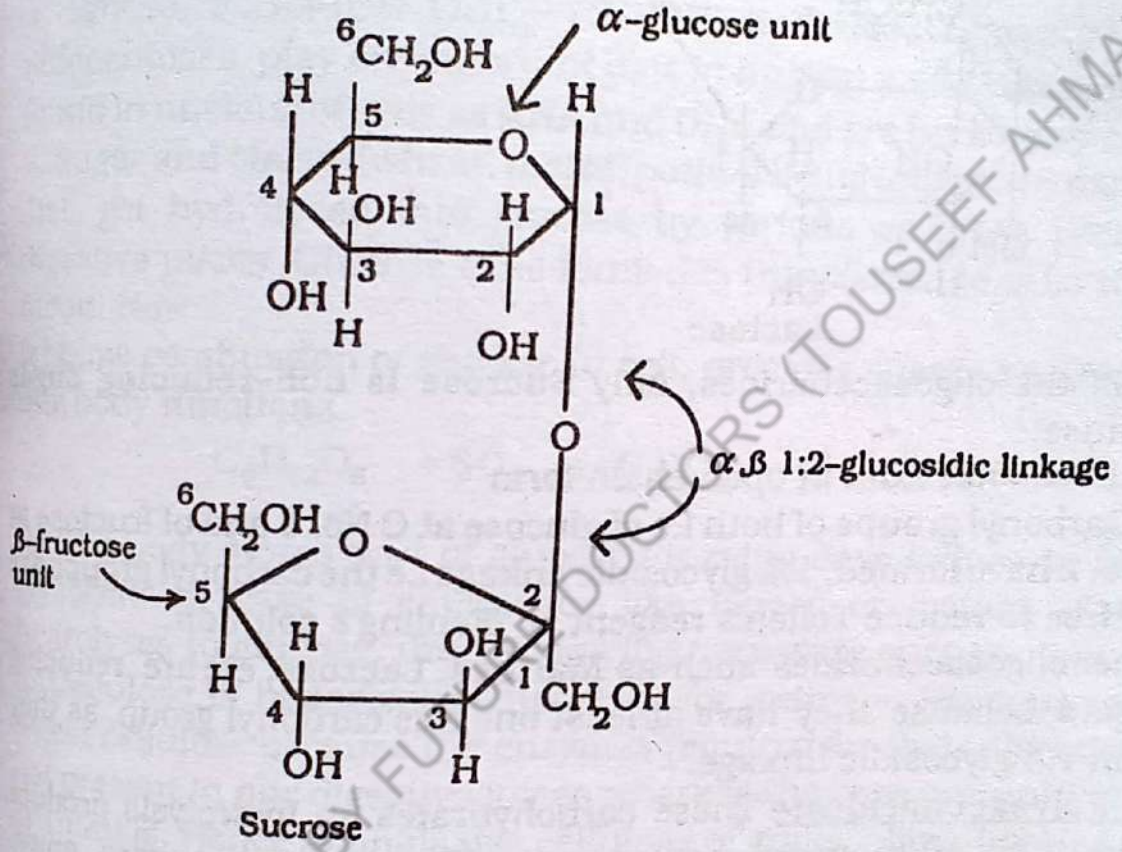
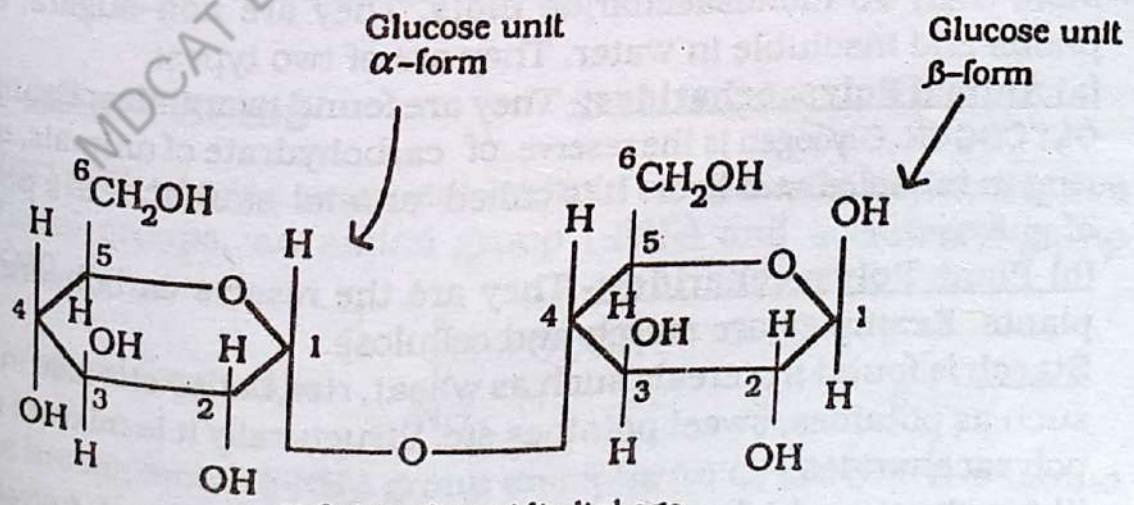
single bond i.e. (– O – C – O –). It differs from **ETHER LINKAGE** (–C–O–C–) in that, in the latter, oxygen is joined to two C–atoms). Glycosidic linkage is the characteristic of oligo– and poly–saccharides as it joins two or more **GLYCOSIDES** i.e. cyclic structures. In sucrose C–1 of glucose unit is joined to C–2 of fructose unit hence the linkage is also called **1,2 Glycosidic linkage.** Structures of Sucrose, Maltose and Lactose are given below:



Sucrose



Maltose

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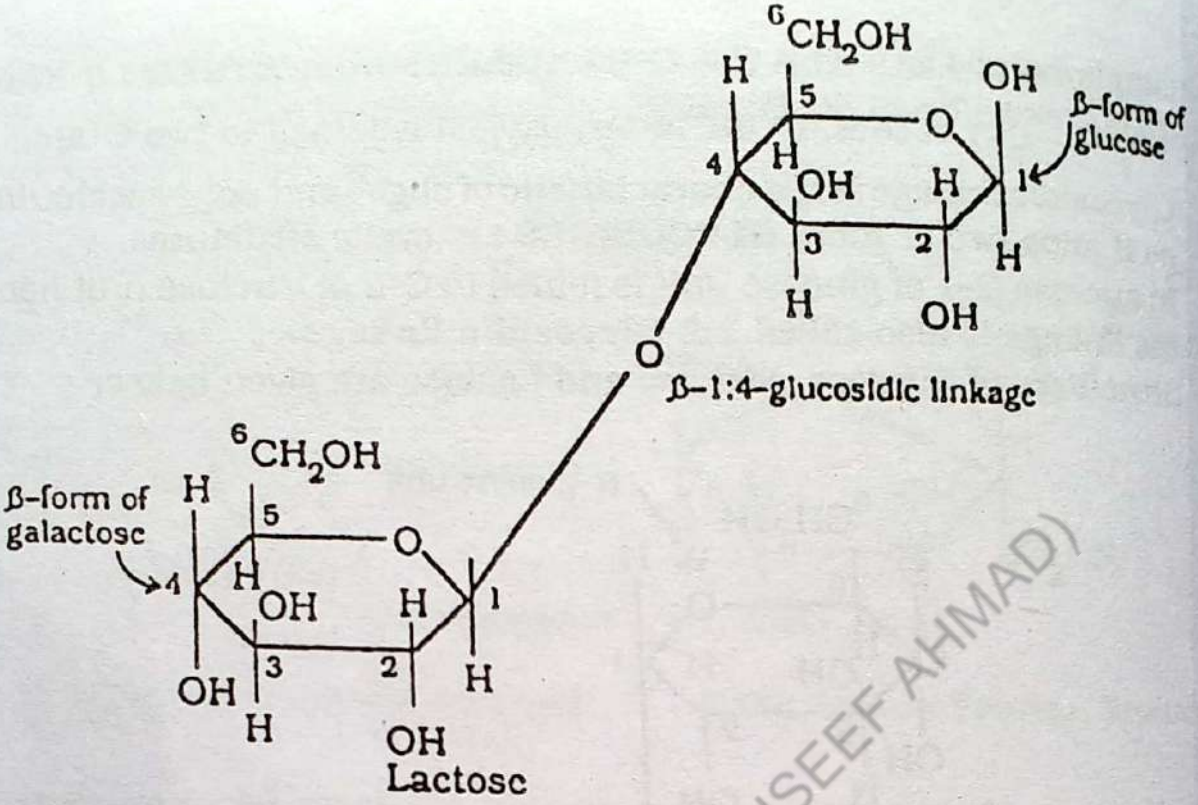

Of all the oligosaccharides, only **Sucrose is non-reducing sugar** because:

(a) It does not exist in open chain form

(b) Carbonyl groups of both i.e of glucose at C No. 1 and of fructose at C No. 2 have formed, 1:2 glycosidic linkage i.e the carbonyl groups are not free to reduce Tollen's reagent or "Fehling's solution.

Other oligosaccharides such as **Maltose, Lactose,** etc are reducing sugars because they have at least one free carbonyl group, as they form 1:4 glycosidic linkage.

(3) Polysaccharides:- These carbohydrates on hydrolysis produce more than 10 monosaccharide units. They are non-sugars, amorphous and insoluble in water. They are of two types:

(a) Animal Polysaccharides:- They are found in animlas. Example is GLYCOGEN. Glycogen is the reserve of carbohydrate of animals, occurring in muscles and liver. It is called "animal starch". It is a polymer of glucose.

(b) Plant Polysaccharides:- They are the reserve carbohydrates of plants. Examples are starch and cellulose.

Starch is found in cereals such as wheat, rice, barley etc: also in roots such as potatoes, sweet potatoes etc. Structurally it is mixture of two polysaccharides.

(I) **Amylose** in which α, D (+) glucose units are joined by 1:4 glycosidic linkage.

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(ii) **Amylopectin**, with highly branched structure in which α, D(+) glucose units are joined by 1:4 as well as 1:6 glycosidic linkage.

Cellulose is found in the cell walls of plants, hence it is main structural material of plants.

Its purest natural form is cotton which contains 95% cellulose. It is also abundant in wood, flase, linen, paper. Its molecule is made up of about 2000 β-glucose units jointed by 1:4 linkage.

BIOLOGICAL IMPORTANCE OF CARBOHYDRATES.

1. Ribose, $(CHO-(CH\ OH)_3-CH_2OH)$ and deoxyribose which are aldopentoses, play an important part in human metobolism. They are found in nucleus of cells as **RNA** and **DNA** and are hereditory carriers.
2. Sugar and starch (wheat, maize, potato) being important part of our diet, get hydrolysed into glucose by various enzymes present in digestive juices. Glucose thus formed is transferred to cells through blood. Now

(a) Slow combustion of glucose in cell, provides energy necessary for our body functions.

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6\ CO_2 + 6H_2O + 2832\ K.J.$$

(b) The body stores part of glucose for rainy days in liver in form of glycogen. In case of emergency like illness or fasting, glycogen hydrolyses to glucose, thus supplying necessary energy.

3. Cellulose is biologically important for animals. Humans cannot digest cellulose because the enzymes required for their digestion are not present in our digestive juices whereas they are present in those of animals. Hence animals use cellulose of grass, plant, bark as their food.

10.4 AMINO ACIDS

DEFINITION:- Amino acids are organic compounds containing two functional groups, an amino group $(-NH_2)$ and a carboxyl group (-COOH).

Their general formula is
$$\overset{\beta}{R}-\overset{\alpha}{\underset{\underset{NH_2}{|}}{C}}H-COOH$$

Those having amino $(-NH_2)$ group on alpha (α) C, are called α-amino acids.

Those having amino $(-NH_2)$ group on beta (β) C, are called β-amino acids.

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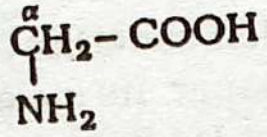
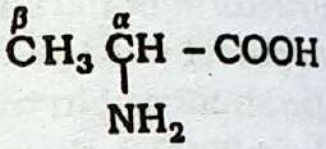
Those having amino ($-NH_2$) group on gamma (γ) C, are called γ-amino acids.

Examples are



Glycine



Alanine

A complete list of amino acids is given in table 10.1

Table 10.1 : The structural Differences in Amino acids.

Name of Amino acid	Abbreviation	Structure of R in $H_3\overset{+}{N}-\underset{R}{\underset{\mid}{C}}-\overset{H}{\overset{\mid}{C}}-\overset{O}{\overset{\|\|}{C}}-O^-$		
Glycine	Gly.	Non-polar	(A)	$-H$
Alanine	Ala.	R–		$-CH_3$
Valine	Val.	R–		$-CH(CH_3)-CH_3$
Leucine	Leu.	R–		$-CH_2-CH(CH_3)-CH_3$
Isoleucine	Ile.	R–		$-CH(CH_3)-CH_2-CH_3$
Methionine	Met.	R–		$-CH_2-CH_2-S-CH_3$
Phenylalanine	Phe.	R–		$-CH_2-C_6H_5$
Tyrosine	Tyr.	R–		$-CH_2-C_6H_4-OH$
Tryptophane	Trp.	R–		$-CH_2-C_8H_6N$

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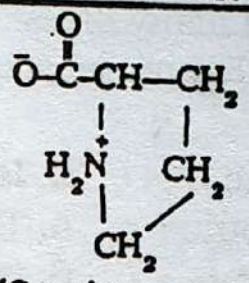
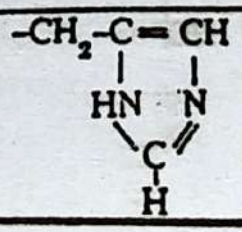
Name of Aminoacid	Abbreviation	Structure of R in $H_3\overset{+}{N}-\underset{R}{\underset{\mid}{C}}-\overset{H}{\overset{\mid}{C}}-\overset{O}{\overset{\|\|}{C}}-\bar{O}$		
Proline	Pro.	R–		 (Complete structure)
Serine	Ser.	Polar R–		$-CH_2-OH$
Threonine	Thr.	R–		$-\underset{CH_3}{\underset{\mid}{CH}}-OH$
Cysteine	Cys.	Group R–		$-CH_2-S-H$
Aspargine	Asn.	R–	(B)	$-CH_2-\overset{O}{\overset{\|\|}{C}}-NH_2$
Glutamine	Gln.	R–		$-CH_2-CH_2-\overset{O}{\overset{\|\|}{C}}-NH_2$
Aspartic Acid	Asp.	Acidic group R–	(C)	$-CH_2-\overset{O}{\overset{\|\|}{C}}-OH$
Glutamic Acid	Glu.	Acidic group R–		$-CH_2-CH_2-\overset{O}{\overset{\|\|}{C}}-OH$
Lysine	Lys.	Basic group R–		$-CH_2-CH_2-CH_2-CH_2-NH_2$
Arginine	Arg.	Basic group R–	(D)	$-CH_2-CH_2-CH_2-NH-\overset{NH}{\overset{\|\|}{C}}-NH_2$
Histidine	His.	Basic group R–		

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ESSENTIAL AMINO ACIDS:- These are the amino acids which cannot be synthesized by our body but they are essential for growth of infants and Transmission of impulses in the nervous system. Their deficiency results in many diseases. They must be supplied to our body through our diet. Examples are:

1. Leucine 2. Isoleucine
3. Methionine 4. Threonine
5. Arganine 6. valine etc.

About 10 amino acids are essential.

Classification:- Amino acids have been classified according to their neutral, acidic or basic nature.

Neutral amino acids:- These exhibit amphoteric nature. These contain one basic amino ($-NH_2$) group and one acidic ($-COOH$) group.

Examples are:

1. Glycine NH_2-CH_2-COOH.

2. Alanine $CH_3-\underset{}{\overset{NH_2}{\overset{|}{CH}}}-COOH$

3. Valine $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>CH-\overset{NH_2}{\overset{|}{CH}}-COOH$

4. Leucine $(CH_3)_2\ CH-CH_2-\overset{NH_2}{\overset{|}{CH}}-COOH$

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5. Isoleucine $(CH_3)_2CH-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{NH_2}{|}}{CH}-COOH$ etc.

ACIDIC AMINO ACIDS:– They exhibit acidic nature. They contain one basic amino ($-NH_2$) group and more than one acidic ($-COOH$) groups. Examples are:

1. Aspartic acid $COOH-\overset{\overset{NH_2}{|}}{CH}-CH_2-COOH$ etc.

2. Glutamic acid $COOH-\underset{\underset{NH_2}{|}}{CH}-CH_2-CH_2-COOH$

BASIC AMINO ACIDS:– They exhibit basic nature. They contain one acidic ($-COOH$) group and more than one basic amino ($-NH_2$) groups. Examples are:

1. Arginine $COOH-\overset{\overset{NH_2}{|}}{CH}-(CH_2)_3-NH-\overset{\overset{NH}{||}}{C}-NH_2$ etc.

2. Lysine $COOH-\overset{\overset{NH_2}{|}}{CH}-(CH_2)_3-NH_2$

DIPOLAR NATURE OF AMINO ACIDS (ZWITTERION):– A dipolar, charged but overall electrically neutral ion is called **ZWITTERION**. In amino acid, carboxyl ($-COOH$) group is acidic i.e. ionizes to donate proton (H^+), whereas amino ($-NH_2$) group with a lone pair of electrons behaves as proton acceptor i.e Lewis base. Hence amino acids exists more as dipolar ion i.e. Zwitterion than in an unionized form.

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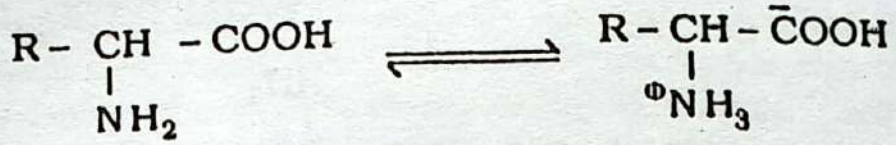
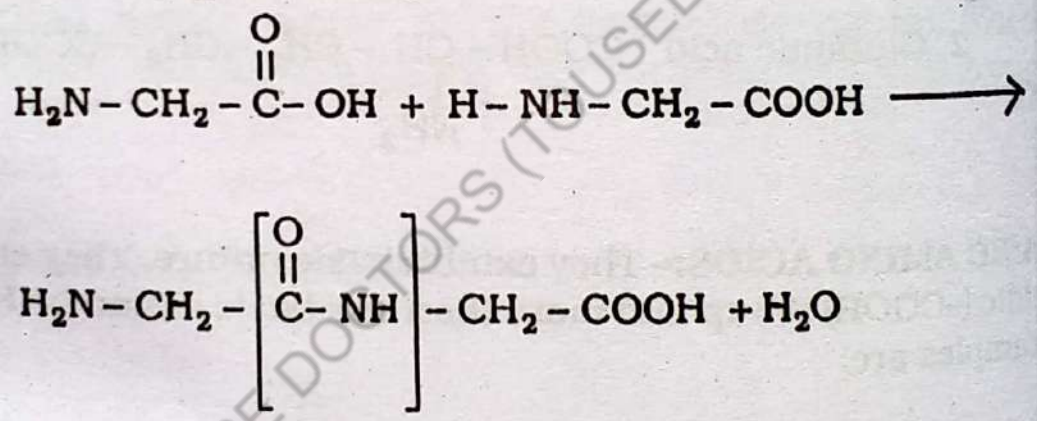


Neutral form Zwitterion

Due to the Zwitter ion form, amino acids are soluble in water but insoluble in organic solvents. They are solids. They have high melting points and donate or accept proton which they react with the medium in which they are dissolved.

PEPTIDE BOND FORMATION:– Thousands of amino acid molecules condense together through peptide linkage forming proteins. The carboxyl (–COOH) group of one molecule of amino acid and amino ($-NH_2$) group of other molecule of amino acid interact by elimination of H_2O molecule to form a product called **PEPTIDE** and the group (–CO–NH–) is called peptide linkage.



Peptide bond

Protein is polypeptide i.e contains a large number of such peptide linkages.

ROLE OF AMINO ACIDS IN HUMAN BODY:– When food containing protein is taken, many enzymes act on protein and hydrolyse it completely into amino acids. After hydrolysis the blood receives the amino acids by absorption through the walls of intestine; and carries them to cells where one of the following three things may take place:

(1) The amino acid may be synthesized back into body protein.

(2) Oxidation may take place to provide energy.

(3) If the diet is low in carbohydrates or fats, body protein may be transformed into either of these or used to make hormones and other body necessities.

10.5 PROTEINS

The most important of the known components of living matter is a protein and without that life would not be possible.

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Proteins are a vast class of substances of almost unbelievable diversity in both structure and function.

Only living beings can synthesize proteins, however some proteins such as ribonuclease and insulin have been synthesized in laboratory, after putting up lot of labour in terms of time and money. Proteins are made by plants from the inorganic substances like carbon dioxide, water, nitrates, sulphates and phosphates. Animals are unable to prepare proteins from inorganic material, therefore they are dependent on plants or other animals for their source of dietary proteins and do synthesize their own proteins from the simple organic molecules.

Other elements such as phosphorus, calcium, and iron may be the essential constituents of the some specialized proteins. e.g Casein, the main protein of milk contains calcium and phosphorus and haemoglobin is the iron containing protein necessary for the process of transportation of oxygen in the body. The relative high concentration of nitrogen in protein differentiate proteins from fats or carbohydrates.

The molecular weight of the protein molecule varies from protein to protein depending upon its source, and nature. For instance the molecular weight of albumin obtained from egg is about 43000 and the molecular weight of the serum albumin is 70,000 in general the molecular weight of protein ranges in between 34000–50,000,000 daltons, remember that 1 dalton = 1 a.m.u (atomic mass unit). Amino acids may be considered as building units of proteins. When proteins are hydrolysed with dilute acids, a mixture of alpha amino-acids is obtained.

Classification Of Proteins:– Proteins, according to the recommendation of joint committee of the American Society of Biological Chemists and American Physiological Society, are classified as:–

1. Simple proteins 2. Conjugated Proteins 3. Derived Proteins and each of these groups are subdivided into several classes on the basis of their physical and chemical properties, like solubility and heat coagulability.

1. **Simple Proteins:–** All those proteins which on hydrolysis yield only aminoacids or their derivatives are called simple proteins. These are further classified according to their differences in solubility and coagulability. e.g albumin.

(a) **Albumins:–** These are water soluble proteins and may be precipitated from solution by high concentration of Ammonium sulphate. Coagulated by heat, examples are egg albumin, serum albumin, lactalbumin (milk albumin), and leucosin (wheat albumin).

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(b) Globulin:– The globulins are insoluble in water but soluble in (5% NaCl) dilute salt solution and are coagulated by heat. Insoluble in higher concentrated solution at 30–50% saturation examples are egg, globulin, serum globulin, myosin (muscle globulin) and amandin (almonds).

(c) Glutelins:– These proteins are insoluble in neutral solution but soluble in dilute acids and alkalis. Coagulated by heat, examples are glutenin in wheat and oryzenin in rice.

(d) Gliadins (Prolamine):– These proteins are soluble in 70–80% ethyl alcohol and insoluble in water or absolute ethyl alcohol. Typical prolamines are gliadin (wheat), hordein (barley) and zein (Maze corn).

(e) Albuminoids:– The albuminoids are insoluble proteins in the solvents mentioned for the above proteins and are dissolved only by hydrolysis eg; keratin in hair, horn, feather, nails, casein and collagen (tendons and developing bones).

2. Conjugated proteins:– Conjugated proteins are composed of simple proteins combined with non–proteinous substance. The non–proteinous substance is usually called prosthetic group e.g Haemoglobin, cytochromes, lipoprotien.

(a) Nucleo–proteins:–These proteins consist of basic proteins (Composed of basic amino acids eg; lysine and arginine) associated with nucleic acids. They are present in the nuclei of living cells and soluble in isotonic salt solution. These in true sense are not conjugated proteins because nucleic acids are not the prosthetic groups of the protein.

(b) Glyco–proteins:– Such proteins are in combination with carbohydrate moieteis, including hexoses, hexosamine, hexuronic acids. For instance mucin in saliva and mucoids in tendon and cartilage.

(c) Phospho–proteins:– Proteins like casein from milk and vitellin in egg yolk, are examples of phospho–protein which contain phosphoric acid in their structure.

(d) Chromo–proteins:–These proteins are coloured due to their prosthetic group (non–protein group). For instance haemoglobin contains haeme an iron containing protoporphyrin and melanin contains carotenoid pigments in wool, feathers and skin proteins.

(e) Lipo–proteins:– Membrane proteins and adipose tissues are the lipoproteins chemically and are composed of lecithin, cephalin and cholesterol with simple proteins.

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3. **Derived proteins:–** As the name implies, the proteins like peptones, peptides and proteoses are not naturally occurring proteins and may be considered as protein derivatives obtained by action of enzymes, i.e chemical agents and various physical methods applied on simple and conjugated proteins which result in above substances of different sizes.

The proteins can also be classified on the lines of their functions:

Table 10.2 Classification of proteins based on their functions.

Name of Protein	Function	Examples
Enzymes	Biological catalyst They catalyze biological reactions	Amylase, protease: e.g. pepsin and trypsin, Catalyzes the breakdown of proteins in stomach. Lipase and oxido - reductose.
Structural proteins	Provide structural support in tendons, bones and muscles.	Collagen, Keratin e.g proteins of hair, feathers, collagen e.g connective tissues of muscles, silk, chitin.
Storage proteins	Store iron and other substances.	Ferritin stores iron in spleen.
Transport proteins	Bind and transport specific molecules in blood, like oxygen and lipids	Haemoglobin and albumins.
Respiratory proteins	Help in the respiratory system.	Haemoglobin, cytochrome, haemocyanin, myoglobin.
Hormones	Regulation of metabolism.	Insulin and glycogen, regulate glucose and fat metabolism.
Contractile proteins	Perform contraction and movement of the muscles.	Myosin
Antibodies	Proteins formed in response to antigens the foreign bodies.	Globulins and γ–globulins

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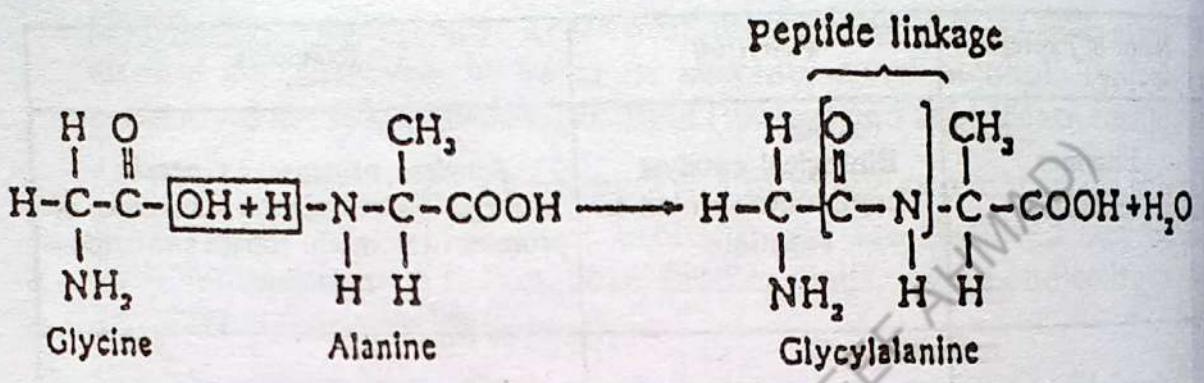
Peptide Linkage Or Peptide Bond:- The amino acids in protein molecules are united through an acid-amide type bond, called peptide bond or peptide linkage. The peptide bond is formed when the amino group attached to α-carbon of one amino acid gets linked covalently with the carboxyl group attached to α- carbon of another amino acid through the elimination of water molecule. This type of linkage is illustrated by the condensation of alanine and glycine molecules which give glycylalanine.



Since glycylalanine is formed by joining of 2 molecules of amino acids through a peptide bond so it is called DIPEPTIDE. The combination of three amino acids will yield tripeptide. In this way when several amino acids are combined through peptide linkages, a substance so formed would be called polypeptide.

Polypeptide chains are unbranched chains and there may be more than one, polypeptide chains in protein molecule e.g. insulin has two polypeptide chains. Each type of protein molecule has specific chemical composition, molecular weight and the sequential order of the amino-acids united together.

Molecular weight of water soluble Proteins is very high.

10.6 LIPIDS

General:- Lipids are fats and fat like substances. They are naturally occurring group of heterogeneous compounds with only one common property namely their solubility in Bloor's Reagent which is a mixture of solvent ether (i.e diethyl ether) and ethyl alcohol in a ratio of 2:1. They mostly contain carbon, hydrogen and oxygen as their elements but some contain nitrogen and phosphorus as well.

TYPES OF LIPIDS:- Bloor classified lipids on the basis of their structures as:

(a) Simple Lipids (b) Compound lipids and (c) Steroids

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(a) Simple Lipids:– They include naturally occurring (1) Oils and fats (2) Waxes.

(1) Oils and Fats:– Oils and fats are of either animal or vegetable origin. They provide energy for different metabollic activities. Chemically they are triester of glycerol with fatty acids hence they are also called **triglycerides or triacylglycerol.**

Fatty acids are naturally occurring long chained saturated or unsaturated carboxylic acids with 12 to 20 carbon atoms. They are obtained by the hydrolysis of oils or fats.

The main acids commonly forming oils and fats are:

ACIDS	FORMULA	NATURE
(i) Palmitic acid	$C_{15}H_{31}COOH$	Saturated
(ii) Stearic acid	$C_{17}H_{35}COOH$	Saturated
(iii) Oleic acid	$C_{17}H_{33}COOH$	Unsaturated (One double bond)
(iv) Linoleic acid	$C_{17}H_{31}COOH$	Unsaturated (Two double bonds)
(v) Linolenic acid	$C_{17}H_{29}COOH$	Unsaturated(Three double bonds)

Essential fatty acids are those fatty acids which our body can not synthesize so they must be taken as diet. All essential fatty acids are unsaturated i.e

(i) Linoleic acid ($C_{17}H_{31}COOH$)
(ii) Linolenic acid ($C_{17}H_{29}COOH$)
(iii) Arachidonic acid ($C_{19}H_{31}COOH$): etc.

The functions of essential fatty acids are:

(a) They prevent deposition of cholesterol in artries and veins.
(b) They help in reproductive functions and blood clotting.

Their deficiency results in (a) loss of weight in children (b) development of eczema.

Oils are esters of glycerol with unsaturated fatty acids such as oleic, linoleic and linolenic acids.

Fats are esters of glycerol with saturated fatty acids i.e palmitic and stearic acids etc.

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The general formula for oils or fats i.e **TRIGLYCERIDES** is

$$\begin{array}{l} CH_2-OCOR \\ | \\ CH-OCOR' \\ | \\ CH_2-OCOR'' \end{array}$$

(Where R' and R'' are higher alkyl radicals, having same or different number of C-atoms)

When all the three hydroxyl (-OH) groups of glycerol are esterified with same fatty acid, the triglyceride is known as **simple glyceride** or **simple triacyl glycerol**. i.e

$$\begin{array}{l} CH_2-O-\boxed{H+HO}OC-C_{15}H_{31} \\ | \\ CH-O-\boxed{H+HO}OC-C_{15}H_{31} \\ | \\ CH_2-O-\boxed{H+HO}OC-C_{15}H_{31} \end{array} \longrightarrow \begin{array}{l} CH_2-OOC-C_{15}H_{31} \\ | \\ CH-OOC-C_{15}H_{31}+3H_2O \\ | \\ CH_2-OOC-C_{15}H_{31} \end{array}$$

Glycerol Palmitic acid (3 molecules) Simple Glyceride (Tripalmitin) (A wax)

When all the three hydroxyl (-OH) groups of glycerol are esterified by different fatty acids, the triester is called **mixed glyceride** or **mixed triacyl glycerol**, examples are:

$$\begin{array}{l} CH_2-OOC-C_{17}H_{35} \\ | \\ CH-OOC-C_{15}H_{31} \\ | \\ CH_2-OOC-C_{17}H_{35} \end{array} \qquad \begin{array}{l} CH_2-OCO-C_{17}H_{35} \\ | \\ CH-OCO-C_{15}H_{31} \\ | \\ CH_2-OCO-C_{15}H_{31} \end{array}$$

Olco-palmito-stearin Stearo-dipalmitin

An ordinary oil or fat is a mixture of more than one simple and mixed glycerides.

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Difference between oils and fats:– Chemically there is no difference between oils and fats as they are naturally occurring esters of long-chain carboxylic acids and glycerols and are called **TRIACYGLYCERIDES.** The difference is only of physical state:

(i) Oils are liquids at ordinary temperature (m.p. below 20 °C), while fats are solid (m.p. about 20 °C). Actually a substance may be fat in one season and oil in other season e.g coconut oil.

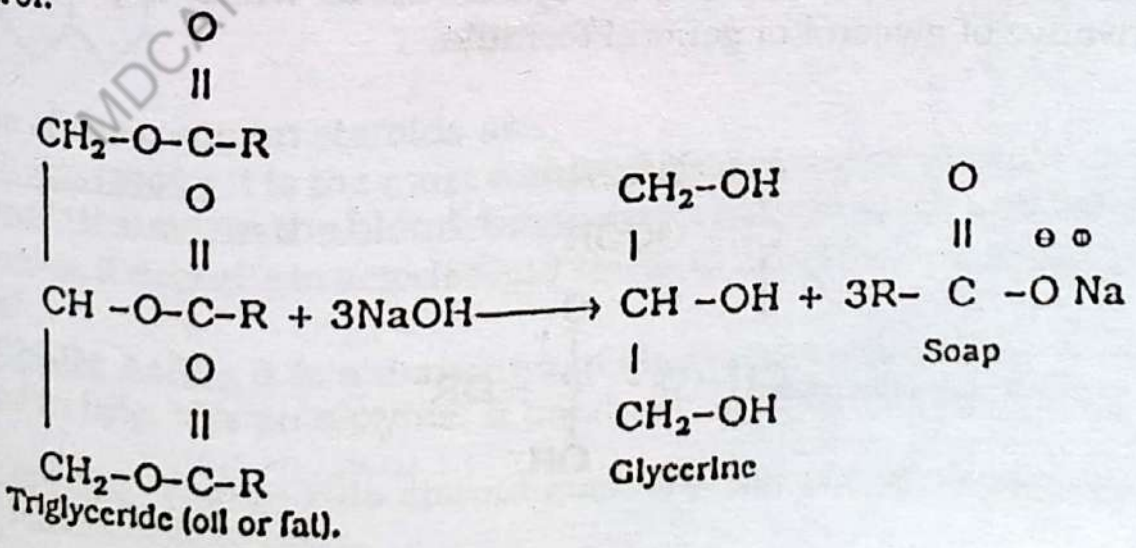
(ii) Oils contain higher proportion of glycerides of unsaturated fatty acids while fats contain high proportion of glycerides of saturated fatty acids.

Drying and non-drying oils:– Drying oils contain large number of glycerides of unsaturated fatty acids as linoleie and linolenic acids. When exposed to air they undergo oxidation whereas double bonds open up forming peroxides which then polymerise to form a dry, hard tough film.

Non-drying oils contain negligible amount of glycerides of unsaturated fatty acids.

Rancidification of oils and fats:– When oils and fats are left exposed to warm, moist air for a long time, they give off offensive odour and become off-taste. This process is called rancidification. Rancidification is due to (i) hydrolysis of ester linkage to give original fatty acid of sour taste, and (ii) Oxidation at double bond forming volatile aldehydes of bad odour.

Saponification of oils and fats:– Hydrolysis of oils or fats on boiling with a solution of strong alkali (NaOH, KOH) to form sodium or potassium-salt of long chain fatty acid (SOAP) alongwith glycerol, is called saponification. It is the reverse process of esterification of glycerol.



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Analysis of oils and fats:– Quality and purity of an oil or fat is judged by the following values:

(i) Acid value:– It is the number of milligram of KOH required to neutralize free acids in one gram of oil or fat.

(ii) Saponification value:– It is the number of milligram of KOH required to complete saponify 1 gram of oil or fat.

(iii) Iodine value:– It is the number of grams of iodine absorbed by 100 gm. of oil.

(2) WAXES: Waxes are naturally occurring esters of long-chain carboxylic acids (C_{16} or greater) with long chain alcohols (C_{16} or greater). They are low melting solids, having a waxy feeling.

They are of two types:

(i) True Waxes:– These are simple lipids. Commonly found true waxes are:

(i) Bees wax $C_{25}H_{31} - COO - C_{16}H_{33}$

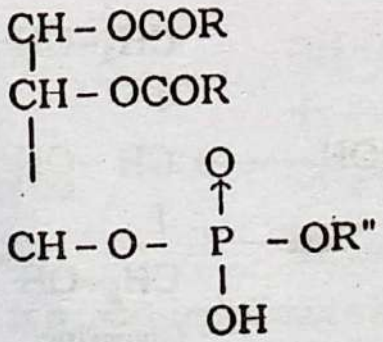
(ii) Spermacetic $C_{15}H_{31} - COO - C_{16}H_{33}$

(from oil of sperm whale)

(ii) Non-True Waxes:– They are esters of cholesterol, vitamin A and vitamin D. Waxes usually form protective covering in plant and animals. They protect living organism against bacteria and insects.

(B) Complex Lipids:- These lipids are also known as **CONJUGATED LIPIDS**. These are esters of glycerol with two fatty acids (which may be saturated or unsaturated) and some other compound such as carbohydrate, amino acid, amine derivative, phosphoric acid (H_3PO_4) residue, protein, etc.

Simplest, complex lipid is **PHOSPHOLIPID** which is phosphate derivative of glycerol of general formula.



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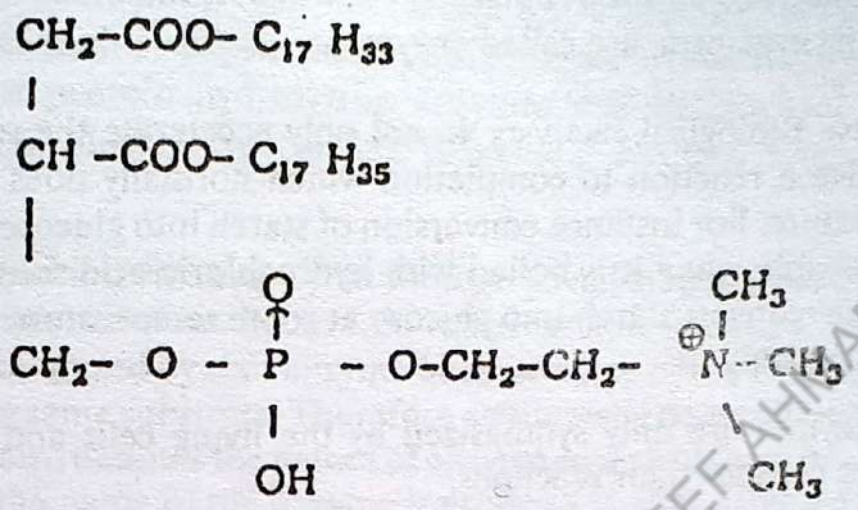
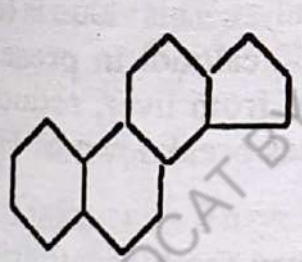
Three major types of phospholipids in human body are:
(i) LECITHINS (ii) CEPHALINS (iii) SPHINGOMELINS.
Structure of lecithin is shown below:

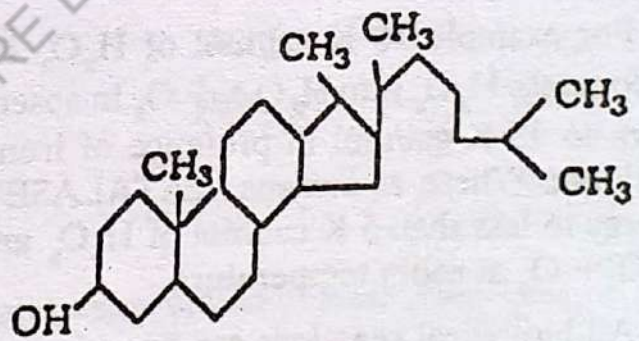


(Lecithin)

The carbohydrate derivatives of lipids are called GLYCOLIPIDS.
The protein derivatives of lipids are called LIPOPROTEINS.
Most important function of phospholipids is participation in the formation of cell membrane.

(c) Steroids:– Steroids are the non-saponifiable lipids which contain the following ring system.





Some of the common steroids are:

(i) Cholesterol:– It is the most common steroid found virtually in all animal tissues, in the blood, brain and also spinal column. Where in excess, it deposits in arteries and restricts blood flow causing heart attack.

(ii) Cholic Acid:– It is a derivative of cholesterol. Its sodium salt is found in bile. If is an enzyme. It breaks down fats into fatty acids.

(iii) Progesterone:– This steroid controlls the sexual development and functioning of body.

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10.7 ENZYMES

A class of proteins which catalyze all types of biochemical reactions, such as digestion, respiration, muscular contraction and metabolism taking place in the living organism, are called enzymes.

These Biological catalysts do not only accelerate the rate of reaction, but also drive a reaction to completion which normally does not occur at room temperature. For instance conversion of starch into glucose in the laboratory is only possible when it is boiled with hydrochloric acid solution while enzyme, 'amylase' convert starch into glucose at room temperature without the help of acid or heating.

Enzymes are only synthesized by the living cells and do not necessarily require cells for their reactions.

Enzymes are catalysts because these modify the speed of a reaction and do not appear as the part of a product. At the end of the reaction these are regenerated unchanged and take part again and again.

A reaction before it can proceed, requires some form of energy, it may be heat which is provided from the external sources, is called energy of activation. Enzymes lower the amount of activation energy far more efficiently than the inorganic catalysts and therefore, catalyze the reaction at lower temperature.

For example 18 K cal/mol of H_2O_2 is the activation energy needed to decompose H_2O_2 into $H_2O + \frac{1}{2} O_2$ in absence of catalyst. This value is lowered down to 13 K cal/mol in presence of iron; and 12K cal/mol in presence of platinum. Where as enzyme 'CATALASE' obtained from liver, reduces this energy to less than 5 K cal/mol of H_2O_2 and catalyses breakdown of H_2O_2 in $H_2O + O_2$ at room temperature.

All biological reactions are enzyme catalyzed even the biosynthesis of an enzyme by living cell is catalyzed by the enzyme.

Some enzyme require a non–protein component called a cofactor to the catalytic activity. Cofactors may be bound permanently to the enzyme (i.e prosthetic group) or may form transient associations e.g coenzyme and metal ions.

Several different enzyme molecules catalyze the same chemical reactions, such families of enzymes are called isoenzyme.

Certain enzymes are in the form of inactive protein molecules called zymogen or proenzyme e.g.(pepsinogen ⟶ pepsin. Trypsinogen ⟶ Trypsin)

Sugar less

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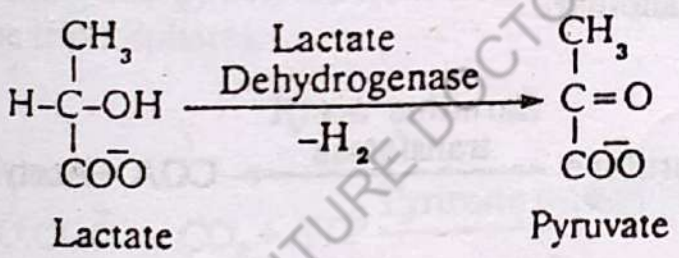
Nomenclature:– The substance on which the enzyme acts is called the substrate of that enzyme. And enzymes, according to trivial nomenclature systems are named after the substrate by adding 'ase' to the root of the name of the substrate e.g sucrase for sucrose, lactase for lactose and urease for urea. Certain enzymes such as pepsin and trypsin, present in stomach and intestine respectively are protein hydrolyzing enzymes and their trivial names are retained as such. However according to general analogy, these are called "Proteases".

The naming of individual enzyme through trivial system after putting 'ase' at the substrate as mentioned above do not accurately describe the nature of reaction to be catalyzed by that enzyme because some of the enzymes catalyze differently using same substrate. Therefore a systematic nomenclature has been adopted which also denotes the nature of enzyme catalyzed reaction. According to this system, the name of the enzyme is established after using suffix "ase" to the name of reaction catalyzed by the enzyme instead of its substrate e.g Dehydrogenases, that catalyze dehydrogenation of their substrates.



Oxidases:– Enzymes that catalyze oxidation of their substrates.

$$H_2O_2 \xrightarrow{\text{Oxidases}} H_2O + \tfrac{1}{2}O_2$$

Hydroxylases:– Enzymes that catalyze the introduction of hydroxyl group into their substrates.

$$\text{e.g} \quad CO_2 + HOH \xrightarrow[\text{hydroxylase}]{\text{Carbonic}} H_2CO_3$$

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Oxygenases:– Enzymes that catalyze the incorporation of oxygen molecule into their substrates.

Transferases:– Enzymes that catalyze the transfer of a particular group between two substrates.

Classification:– According to the recommendation by the commission on enzymes of the International union of Biochemistry, a classification of the enzymes is established on the basis of the type of the reaction catalyzed by the enzymes.

Enzymes are divided in six major groups or classes, as given below:

(1) **Oxido–Reductase:–** These enzymes catalyze the oxidation and reduction reaction.

$$\text{e.g } \underset{\text{Ethyl alcohol}}{CH_3.CH_2OH} \xrightarrow{\text{Alcohol dehydrogenase}} \underset{\text{Acetaldehyde}}{CH_3.CHO} + H_2$$

(2) **Transferase:–** These enzymes catalyze the reaction of group transfer from one substrate to another.

$$\text{e.g (i) Acetyl–COA + Carnitine} \xrightarrow{\text{Carnitine acetyl transferase}} \text{COA + Acetyl carnitine}$$

$$\text{(ii) L–Asparticacid + 2 oxoglutaric acid.} \xrightarrow{\text{Aspartate aminotransferase}} \text{Oxaloacetate + Glutamic acid}$$

(3) **Hydrolases:–** These enzymes catalyze the hydrolytic reaction.

$$\text{e.g (i) Amylose} \xrightarrow[+H_2O]{\text{Amylase}} \text{Glucose}$$

$$\text{(ii) Proteins} \xrightarrow[+H_2O]{\text{Protease}} \text{Amino acids}$$

$$\text{(iii) Lipids} \xrightarrow[+H_2O]{\text{Lipase}} \text{Fatty acids + Glycerol}$$

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(4) **Lyases:–** These enzymes catalyze the addition of groups to double bonds or vice versa.

e.g (i) Threonine $\xrightarrow{\text{Threonine aldolase}}$ Glycine + Acetaldehyde

(ii) Acetoacetate $\xrightarrow{\text{Acetoacetate decarboxylase}}$ Acetone + CO_2

(iii) L-aspartic acid $\xrightarrow{\text{Aspartate ammoniase}}$ Fumerate + NH_3

(5) **Isomerase:–** These enzymes catalyze the reaction of isomerization with the result that an intramolecular rearrangement occurs.

e.g (i) L-alanine $\xrightarrow{\text{Alanine racemerase}}$ D- alanine

(ii) ADP- glucose $\xrightarrow[\text{epimerase}]{\text{ADP Glucose}}$ ADP – Galactose.

(6) **Ligases:–** These enzymes catalyze the reaction of condensation of two molecules using energy derived from cleavage of other molecules such as ATP (Adenosine triphosphate).

e.g.

(i) $CH_3.CO.CO\bar{O} + CO_2 + ATP \xrightarrow{\text{Pyruvate carboxylase}}$ Oxaloacetate + ADP

(ii) Acetyl-COA + CO_2 + ATP $\xrightarrow{\text{Acetyl-COA carboxylase}}$ Malonyl-COA + ADP

Properties Of Enzymes:– 1. Enzymes in water solution kept for a long period of time lose their activity. 2-They become inactive by any treatment that coagulate the protein material.3.Excessive heat, alcohol, salts of heavy metals and concentrated solutions of inorganic acids will stop the activity of an enzyme i.e. all those treatments which affect the protein structure would also destroy the enzymatic activity.

The enzyme activity remains with the active centre in protein molecule of the enzyme. This active centre combines with the substrate and starts the

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reaction, that is catalyzed by the enzyme. Similarly this active centre if combined with some other substance which is not the real substrate could destroy the activity temporarily or permanently.

3. As it is observed and as mentioned above that every substance has its own enzyme to catalyze its change, therefore enzymes are supposed to be specific for a particular substrate. For example lipase will hydrolyse lipids and has no effect on carbohydrates or proteins.

Factors That Influence The Rate Of Enzyme action:– Temperature and pH of solution are important factors which control the speed of reaction.

1. Every enzyme has optimum temperature at which these show the maximum activity and most of the enzymes present in body show their optimum (maximum) activity between 37°–50°C, beyond this temperature enzymes lose their activity permanently. However at lower temperature enzyme does lose its activity and will resume its activity when its temperature is again raised.

2. pH: The hydrogen ion concentration also influences the rate of catalytic activity and therefore every enzyme has its own optimum pH at which these show maximum activity. For example the optimum pH for pepsin is 1.6, while trypsin shows optimum activity at pH 8.2; which are provided to the enzymes in stomach and in intestine respectively.

3. Other factors, for example, enzyme concentration, substrate concentration, nature of the products formed, presence of certain ions, effectively control the speed of reaction.

10.8 VITAMINS

Vitamins, also called accessory food factors, are organic substances, and quite different from carbohydrates, proteins and lipids. These are normally available to the body from the diet we take, for the purpose to regulate energy transformation and metabolism.

Vitamins are effective in very small amounts, and none of these are formed in the body and must be obtained from animals or plant sources. However, the exceptions are there; for instance vitamin 'A' is formed from its pre–cursor carotene, vitamin 'D' by the action of ultra–violet light on the skin. The bacteria in the intestine synthesized folic acid and vitamin 'K'; similarly rats can synthesize vitamin 'C' and therefore do not develop scurvy.

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Vitamins are different from each other in their chemical composition and function and have been synthesized or isolated from their plant or animal sources.

Vitamins are chemically unstable under adverse conditions of heat, light and oxidation (especially in alkaline medium),strong acids and aging hence they lose their activity.

Nomenclature:– Vitamine, a word derived from (Vital + Amine); and since all these substances were not amines, therefore Mecollum proposed terminology vitamin by dropping (e) from vitamine.

Originally these substances were commonly known by letters of the alphabet such as vitamin A,B,C,D,E,K.

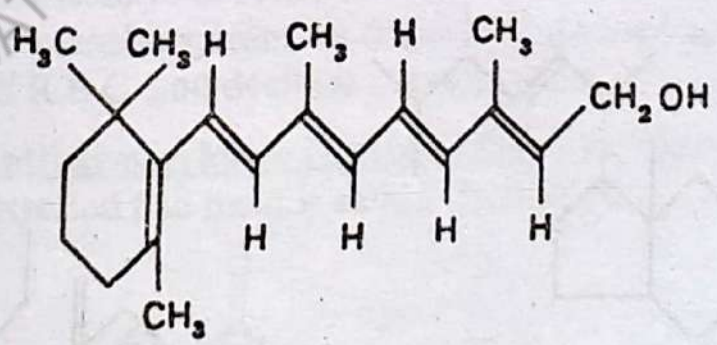
After understanding the composition and chemical structure of these vitamins, their alphabet nomenclature is being replaced by their chemical names.

Classification:– Vitamins are classified on the basis of their solubility.

1. The vitamins which are soluble in fats or in fat solvents are called fat soluble vitamins and are usually formed associated with lipids of natural foods. Vitamins A,D,E, and K are examples of fat soluble vitamins.

2. The vitamins which are soluble in water are known as water soluble vitamin and are observed in the juices of fruits, their examples are 'B' complex vitamins and vitamin 'C'.

Vitamin – A (Retinol)



Vitamin A :– It is found in fats of milk, eggs and liver fat. Fish liver oils specially cod liver oil is the chief source of vitamin 'A'.

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Vitamin A is absent from vegetable oils and fats e.g olive oil, linseed oil, sunflower oil, ground nut oil. Margarine made from these oils is supplemented vitamin A during its manufacture.

In plants vitamin A occurs in a precursor form as provitamin A. These precursors belong to a family of pigmented hydrocarbon called carotenes. B–Carotene,the hydrocarbon is most active physiologically and two molecules of vitamin A, in an alcohol form, are derived by cleavage of the hydrocarbon at the central bond.

$$C_{40}H_{56} + 2H_2O \longrightarrow 2C_{20}H_{29}OH$$

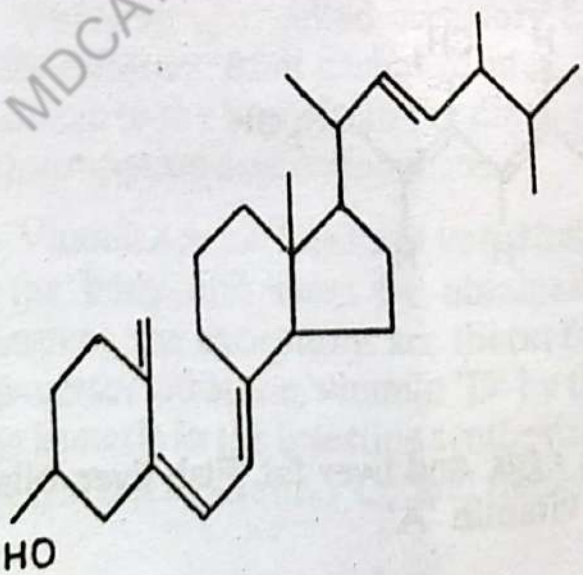
Carotenes are found in green vegetables and carrots. These are converted to vitamin 'A' in the intestinal tract of animal.

A deficiency of vitamin 'A' causes night blindness in early stages and ultimately leads to xerophthalmia.

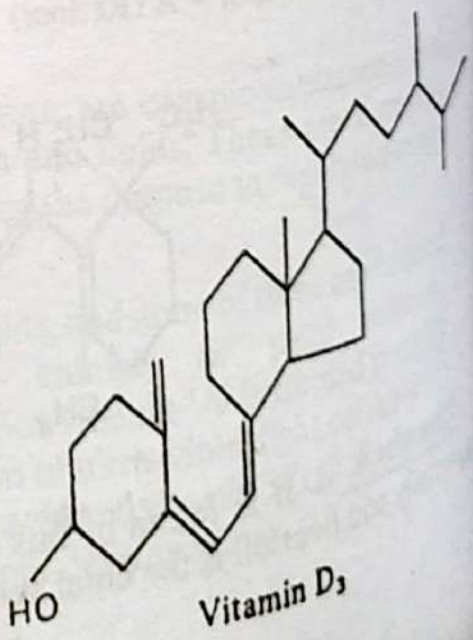
Daily requirement is around 1000 μg of retinal.

The main function of vitamin 'A' is to form visual pigment. It transports nutrients across the cell membrane.

Vitamin 'D' (Antirachitic):– Chemically, vitamin 'D' is related to sterols. The active vitamin was proved to be calciferol which could be formed from its provitamin ergosterol, a plant sterol, by the ultraviolet rays irradiation. The provitamin in animals was shown to be f–dehydrocholesterol, which upon irradiation gave rise to vitamin D_3.



Calciferol (Vitamin D_2)



Vitamin D_3

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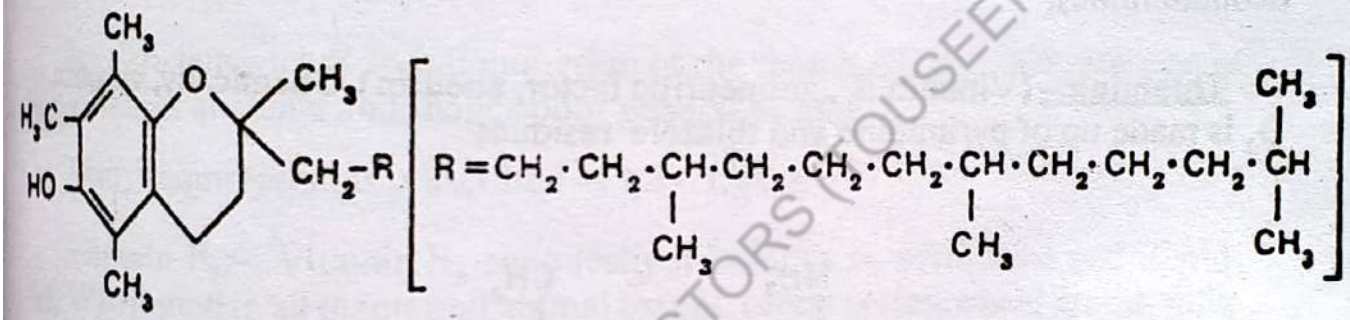
It is crystalline in nature and controls the metabolism of calcium and phosphorus in the body. If the diet does not supply this vitamin, then the depletion of calcium and phosphorus takes place. Deficiency of this vitamin causes teeth decay, softness of bones, continued deficiency leads to the disease known as "Rickets". Because of this reason, this vitamin is known as "Antirachitic" vitamin. Rickets generally occurs in the early stages of growth of a child. Excess amounts of vitamin D are also harmful and cause loss of appetite, thickening of bones and calcification of joints and soft tissues.

Daily requirement of vitamin 'D' is 7.5 μg of calciferol. The main sources of vitamin 'D' are fish oil, liver.

Vitamin 'E' (Tocopherol):– Like vitamin 'A' and 'D' vitamin E is soluble in fat solvents and insoluble in water. It is resistant to heat (upto 200°C) but fairly easily oxidized and destroyed by ultraviolet rays.



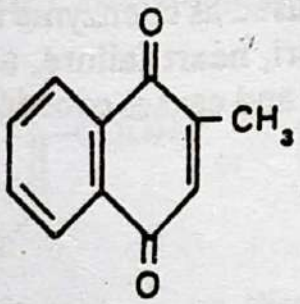
α – Tocopherol

The presence of all three methyl groups attached to the benzene ring is necessary for its full activity.

Dietary requirement per day is 10 mg.

Vitamin E is found in green leafy vegetables, oils and wheat grains. It is required for the maintenance of cell membrane. It maintains normal physiology of the muscular and vascular system. Its deficiency causes fragility of red blood cells/Haemolysis of R.B.C. and declines in respiration.

Vitamin 'K' (Antihaemorrhagic Compound):– The vitamin isolated from alfalfa and from putrefied fish meat is called vitamin 'K'.



Menadione

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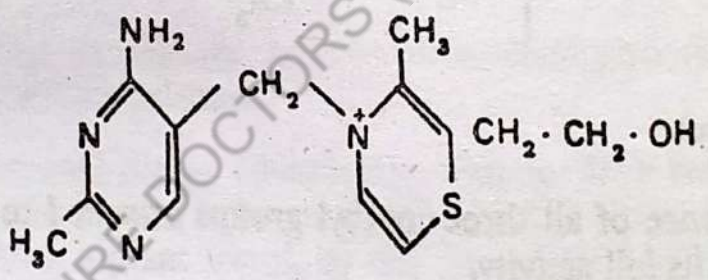
Dietary requirement per day recommended is 70–140 μg. This could be acquired from green vegetables.

It helps the synthesis of prothrombin and other blood clotting factors in liver. Its deficiency causes the failure of blood clotting mechanism.

Vitamin 'B' Complex:– A group of water soluble vitamins obtained from liver, yeast and other sources are found effective for growth, and appetite, reduce sugar content in diabetes, help in treatment of the various infections and are collectively known as vitamin 'B' complex.

The nutritionally important vitamins acquired by the body, through various sources of food are B_1, B_2, B_6 Niacin or Nicotinic acid, and vitamin B_{12} (Cyanocobaltamine).

Thiamine:– (Vitamin B_1, antineuritic factor, aneurin) Chemically, vitamin B_1 is made up of pyrimidine and thiazole residues.



Thiamine

Thiamine (B_1) is present is almost all types of food material but its content is very small. It is abundant in liver, kidney, whole cereal grains, nuts, egg yolk, fruits and legumes. By improper cooking and too many washings, thiamine present in these food material could be lost.

Vitamin B_1 is useful for growth, used as coenzyme in carbohydrate metabolism. Its deficiency leads to beri–beri, heart failure, and mental disturbances, digestive disturbance, loss of weight and causes constipation.Daily requirement recommended is 1.1 – 1.5 mg.

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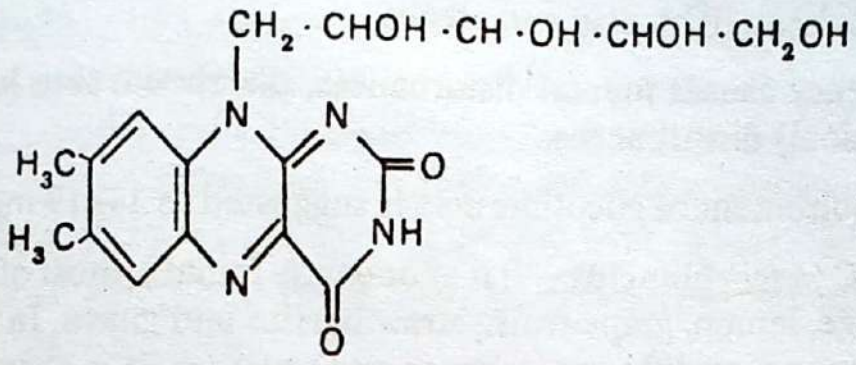
Riboflavin (Vitamin B_2) or Lactoflavin: Riboflavin is also called vitamin B_2, has the following formula



Riboflavin (6:7 dimethyl –9–D– Pribitylisoalloxazine)

It is found in milk, egg, liver, leafy vegetables, whole meal flour, fish poultry. Riboflavin is relatively heat stable but destroyed by light and disappears from milk when it is kept in sun light.

Its deficiency leads to inflammation of the mouth, tongue and also causes eye diseases anaemia and shapes poor general health.

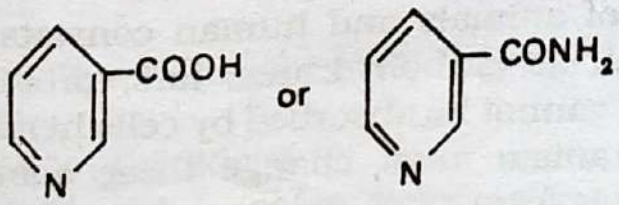
Daily requirement is prescribed as 1.3 – 1.7 mg.

Vitamin B_6:– Vitamin B_6 chemically it belongs to pyridoxine and is widely distributed in all plants and animal tissues, cereal grains, wheat grains, milk and eggs.

Pyridoxine

It is required by the body for its metabolic activities in form of coenzymes for aminoacids and fatty acid metabolism. Its deficiency causes skin disorders. Daily dose is 2.2 mg. It loses its activity in presence of sun light and air or heat.

Nicotinic acid (Niacin):– This compound is used as vitamin and is derived from the pyridine.



Nicotinic Acid Nicotinamide

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Liver, meat, yeast and peanuts are the good sources of nicotinic acid. It is stable towards heat, light, acid and alkalis.

Its deficiency causes mental disturbances, diarrhoea, skin lesions pellagra (gastro intestinal) disturbances.

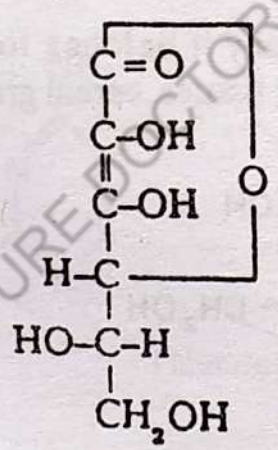
Daily requirement of Nicotinic acid is suggested as 14–19 mg.

Vitamin C (Ascorbic acid):– It is abundantly found in most of the fresh fruits such as orange, lemon, grape fruits, straw berries and guava. In vegetables it is present in tomato, cauliflower, cabbage and potatoes. It is absent in meat, egg and fish.

It is soluble in water. It is easily destroyed by heat and oxidation, washing of vegetables and improper cooking specially in materials of iron, copper. Quick frozen food does not destroy vitamin C.

Deficiency of vitamin C lowers the body resistance to infection and causes bleeding of teeth. Its deficiency in severe cases causes anaemia and scurvy.

Chemical formula is $C_6H_8O_6$
Structure is as follows,



$= C_6H_8O_6$

Ascorbic acid

Functions:– It is essential to the formation of intracellular cement substances in variety of tissues, including skin dentine and bone matrix. It helps in healing of wounds and fractures of bones prevents scurvy and facilitates absorption of iron.

10.9 DIGESTION OF FOOD

The food of animals and human consists of complex organic substances such as carbohydrates, fats, proteins etc. These substances as such cannot be absorbed by cells hence it is necessary that our body mechanism must change these complex molecules into simple absorbable form.

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Digestion:– It is the process of breaking down of food mechanically and chemically into simple water soluble units, suitable of being absorbed into the body fluids.

In human digestion and absorption of food occur in the alimentary canal which is about 9 meter long. The digestion is extracellular within the gut cavity and mainly is the enzymatic hydrolysis of food.

Different parts of alimentary canal perform their specific action in digestion as follows:

(a) Digestion in mouth (Buccal digestion):– The digestion of man starts in mouth. Mastication and chewing of food by teeth break the food into smaller particles and the tongue blends them. SALIVARY GLANDS in buccal cavity are stimulated by sight, smell and taste of food, which secrete saliva. It is slightly alkaline fluid containing 90% water, a lubricant MUCIN and enzymes AMYLASE also called PTYALIN.

The saliva performs the following functins:

(i) It lubricates the food.
(ii) Its enzyme PTYALIN hydrolyses starch to maltose.

$$\text{Starch} \xrightarrow[\text{pH} = 7]{\text{Amylase}} \text{Maltose}$$

No digestion of lipid and protein occurs in mouth. The action of tongue and cheeks mould the food into a ball (the bolus) and pushes it towards pharynx from where it is swallowed into the oesophagus. The food moves down the oesophagus by peristalsis towards the stomach.

(b) Digestion in Stomach (Gastric digestion):– The stomach is the first region of gut where any significant digestion of food takes place. It is a muscular bag with inner folded membrane called **GASTRIC MUCOSA** which secretes **GASTRIC JUICES** which contain:

(i) 0.5 % HCl
(ii) Enzymes: (a) Inactive PEPSINOGEN which is
(b) Gastric LYPASE
(c) **RENIN** only in young children
(iii) Lubricant **MUCIN**, it lubricates gastric mucosa and prevents it from corrosive action of HCl.

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Hydrochloric acid performs the following functions:

(a) It provides necessary pH (1 to 2) for enzyme action.

(b) It acts as antiseptic and kills bacteria present in food.

(c)It changes inactive enzyme, **PEPSINOGEN** to its active form, **PEPSIN.**

(d) It dissolves collagen, splits nucleoproteins and some other complex molecules and makes the food soft.

Digestive action of gastric juice:– Except for a limited hydrolysis of sucrose, no major digestion of carbohydrates takes place in stomach.

Enzyme lypase acts upon small amount of lipids to produce saturated fatty acids and glycerine. Duc to low pH, lypase can not play any important role in hydrolysis of fat.

Enzyme **PEPSIN** commences the breakdown of protein into simple proteins i.e Proteoses and Peptones called Polypeptides.

$$\text{Protein} + H_2O \xrightarrow{\text{PEPSIN}} \text{Proteoses} + \text{Peptones}$$

RENIN is active in stomach of babies. It changes soluble milk protein CASEINOGEN into insoluble curd protein, **CASEIN** which then combines with calcium ion (Ca^{2+}) in milk to form insoluble semisolid **CALCIUM CASEINATE**. It is then converted to **POLYPEPTIDE** by the action of pepsin.

$$\underset{\text{(Soluble)}}{\text{CASEINOGEN}} \xrightarrow{\text{Renin}} \underset{\text{(Insoluble)}}{\text{CASEIN}} \xrightarrow{Ca^{2+}} \text{CALCIUM CASEINATE} \xrightarrow{\text{Pepsin}} \text{POLYPEPTIDE}$$

The churning movements of the wall of stomach thoroughly mixes the food with gastric juice and changes it into a semi liquid form called **CHYME** which gradually enters the duodenum. The chyme is periodically allowed to leave the stomach by way of **PYLORIC SPHINCTER** muscles.

(c) Digestion in small Intestine: (Intestinal digestion):– Duodenum is the first part of small intestine. It is the main seat of digestion. It receives three digestive juices:

(i) **BILE** from liver.

(ii) **PANCREATIC JUICE** from pancreas

(iii) **SUCCUS ENTERICUS** from the duodenum walls

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(i) BILE:- Bile is an alkaline (pH 7 to 8) greenish fluid produced by liver. It contains no enzyme. The digestive components of bile are **BILE SALTS** which contain (a) Sodium glycocholate (b) Sodium taurocholate (c) $NaHCO_3$. Functions of bile are:

(a) It neutralizes the acidic chyme.

(b) It provides alkaline medium for action of enzymes of pancreatic juice and succus entericus.

(c) It emulsifies the fats, oils, lipids changing them to numerous small droplets thus providing large surface area for the action of enzyme-lypase.

(ii) PANCREATIC JUICE:- This juice contains four enzymes. Their functions are as follows:

(a) Pancreatic amylase:- It completes the conversion of starch to maltose.

(b) Pancreatic lipase:- It changes lipids to glycerol and fatty acids.

(c) Trypsin:- It is produced in an inactive form trypsinogen. It changes peptones and proteoses into smaller polypeptides.

(d) Peptidases:- It releases free amino acids from polypeptides.

(iii) Succus Entericus:- It contains following enzymes which complete the process of food digestion:

(a) Etereokinase:- It activates trypsinogen and changes it to active form trypsin.

(b) Erepsin:- It changes remaining proteins (polypeptides and dipeptides) to amino acids.

(c) Maltase:- It converts maltose to glucose.

(d) Sucrase:- It hydrolyses sucrose to glucose and fructose.

(e) Lactase:- It changes milk sugar lactose to glucose and galactose.

(f) Nuclease:- It converts DNA and RNA into phosphate, ribose sugar and different nitrogen bases etc.

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DIGESTIVE ACTION (Tabular form)

REGION OF ALEMENTARY CANAL	SOURCE OF JUICE	DIGESTIVE JUICE PRODUCED	ENZYMES IN JUICES	CLASS OF FOOD ACTED UPON	SUBSTANCE PRODUCED	NOTES
MOUTH	Salivary glands	Saliva	Salivary amylase	Starch	Maltose	Lubricant MUCIN help form bolus
STOMACH	Gastric mucosa	Gastric juice	(i) Gastric Lypase	Lipid	Saturated fatty aids and glycerine	HCl (5%) is also produced by gastric mucosa. It provides acidic medium for pepsin and kills bacteria.
			(ii) Pepsin	Protein	Polypeptides	
			(iii) Renin	Milk Protein	Casein, polypeptide	
SMALL INTESTINE	Liver	Bile	Nill	Emulsifies fats		
	Pancreas	Pancreatic juice	(i) Pancreatic amylase	Starch	Maltose	
			(ii) Pancreatic lipase	Glycerol	Fatty acids	
			(iii) Trypsin	Peptones; proteoses	Smaller polypeptides	
			(iv) Peptidases	Polypeptides	Amino acids	
	Duodenum walls	Succus entericus	(i) Eterokinase			Eterokinase activates the inactive trypsinogen into active trypsin.
			(ii) Erepsin	Poly–; dipeptides	Amino acid	
			(iii) Maltase	Maltose	Glucose	
			(iv) Sucrase	Sucrose	Glucose; fructose	
			(v) Lactase	Lactose	Glucose	
			(vi) Nuclease	DNA: RNA	Phosphate; sugars etc.	

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10.10. ABSORPTION OR ASSIMILATION

After digestion, the water soluble simple forms of food i.e glucose, fructose, fatty acids, amino acids glycerols etc pass through the walls of small and large intestines into blood. This process is called absorption or assimilation.

(a) Absorption in stomach:– Water, glucose, ethanol, certain minerals and certain drugs may be absorbed by osmosis, diffusion and active transport into cells lining the stomach.

(b) Absorption in small intestine:– Much of the absorption takes place in small intestine in which the internal surface area is greatly increased by infoldings and finger like projections called **VILLI**. Each villus is constantly contracting and relaxing and in doing so aids transport of nutrients which enter the capillary vessels and lacteals (lymph vessels of villi). The monosaccharides mainly **GLUCOSE** and **AMINO ACIDS** are directly absorbed into the blood capillaries. Fatty acids and **GLYCEROL** enter the lacteal vessel. Mineral salts, vitamins and water are also absorbed by small intestine.

The outer surface of the **EPITHELIUM**, lining the small intestine has numerous micro villi which are able to engulf small food particles and fluid by a process called pinocystosis.

(c) Absorption in large intestine:– Water absorption takes place in the **COLON** region together with active intake of certain mineral ions. Most of the water present in the original saliva, gastric, bile and pancreatic juices is recovered by absorption here in large intestine.

(d) Egestion or Defaecation:– The unabsorbed substances are left in the form of **FAECES**. Mucus containing the mucin is secreted by the walls of intestine to lubricate the faeces. Before the act of egestion, the faeces move into rectum from where they leave through the anus.

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ASSIGNMENT

1. What do you know about Food and Nutrition? Explain the balanced and unbalanced diet. Illustrate the effects of unbalanced diet.

2. Illustrate the elements of nutrition.

3. Give important uses of water and minerals.

4. Define monosaccharide, disaccharides and polysaccharides.

5. Give the structure of monosaccharide and identify the compound as aldose or ketose.

6. Draw the linear structure and ring structure of glucose.

7. Enlist three hexoses and one pentose that play important roles in human.

8. Write and differentiate the ether linkage and glycosidic linkage.

9. Define reducing and nonreducing sugars. Why lactose and maltose are reducing sugars and sucrose is not?

10. Define the following terms and give examples of each:

    (a) Simple proteins
    (b) Conjugated proteins
    (c) Amino acid
    (d) Amphoteric substances
    (e) Peptide bond
    (f) Essential amino acid.

11. How can an aminoacid act as buffer.

12. Write the general structure of an amino acid.

13. What are the functions of proteins? Why adequate amount of proteins is essential for development and growth

14. Use your own words to define each of the following and give example of each:

    (a) Simple lipids
    (b) Compound lipids
    (c) Saturated and unsaturated fatty acids
    (d) Wax
    (e) Triacylglyceride

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15. Write the equation for the saponification by NaOH of triacyl glycerol or triglyceride.
16. Define essential fatty acids.
17. Differentiate the following:
    (i) Simple and compound lipids
    (ii) Simple and mixed triacylglycerol
    (iii) Saturated and unsaturated fatty acids.
    (iv) Saponifiable and nonsaponifiable lipid.
18. What are enzymes? Illustrate its nature of catalytic activity.
19. Discuss the nomenclature and classification of enzymes.
20. Explain the effect of various factors which influence the rate of enzyme action.
21. Name and classify the vitamins. Why should dietary intake of fat soluble vitamins be carefully controlled?
22. Name the vitamin whose deficiency causes each of the following diseases and give their dietary source and daily requirement:
    (a) Pernicious anaemia
    (b) Hemolytic anaemia
    (c) Rickets
    (d) Scurvy
    (e) Pellagra
23. Describe fat process by which carbohydrates, proteins and fats taken at the breakfast of half fried egg and toast are digested and absorbed.
24. Why the excess food calories in the body are stored as body fat and not glycogen or proteins
25. Differentiate: (i) Gastric digestion and intestinal digestion. (ii) Pancreatic juice and bile.

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CHAPTER 11

CHEMICAL INDUSTRIES IN PAKISTAN

11.1 FERTILIZERS

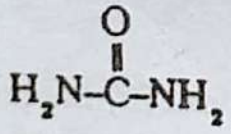
Fertilizers are mostly inorganic salts and contain elements such as nitrogen, phosphorus, potassium etc, which are very essential for the growth and development of plants.

The yield of agricultural crops can be increased by introducing fertilizers to the soil.

The fertilizers help the soil to make up the deficiency and become fertile again. Moreover, fertilizers maintain the pH of the soil near neutrality or slightly alkalinity i.e from pH 7 to 8. The soil having pH above 10 or below 3 is sterile.

There are two types of fertilizers, organic and mineral fertilizers. The organic fertilizers include manures and peat etc. Mineral fertilizers are obtained from mineral raw materials. Below are described the important mineral fertilizers:

(i) <u>Nitrogenous Fertilizers:–</u> They contain Nitrogen as essential element; e.g urea, ammonium nitrate, ammonium sulphate etc.



Urea ; NH_4NO_3 ; $(NH_4)_2SO_4$

Ammonium nitrate Ammonium sulphate

(ii) <u>Potassic Fertilizers:–</u> Such as chile saltpeter, KNO_3.

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(iii) **Phosphatic Fertilizers:–** Such as super phosphate and triple phosphate. The raw material for these fertilizers is phosphate rock or phosphorite, $[Ca_3(PO_4)_2]_3CaF_2$ which being water insoluble can not be assimilated directly by the plants. Therefore it should be converted into soluble form before it can be taken in through the roots.

Super Phosphate:– It is obtained by mixing phosphorite with sulphuric acid in special chambers. Following reaction takes place:

$$Ca_3(PO_4)_2 + 2H_2SO_4 \longrightarrow \underset{\text{Calcium di–hydrogen phosphate}}{Ca(H_2PO_4)_2} + \underset{\text{Gypsum}}{2CaSO_4}$$

The mixture of primary phosphate $Ca(H_2PO_4)_2$ and gypsum is known as the super phosphate. It contains about 18–20% of assimilable P_2O_5.

Triple phosphate:– It is obtained by decomposing phosphorite with phosphoric acid.

$$Ca_3(PO_4)_2 + 4H_3PO_4 \longrightarrow 3Ca(H_2PO_4)_2$$

Triple phosphate contains about 48% of the assimilable P_2O_5 (about three times that of ordinary super phosphate).

Pakistan is basically an agricultural country. The government has been ensuring timely availability of right type of chemical fertilizer, in all regions, for all crops. This has been a major factor in achieving self–sufficiency in food crops during the past five years. In fact, Pakistan is not only able to meet its requirements of nitrogenous fertilizer but is exporting it as well. In 1983–84, it exported 345,000 metric tons of surplus urea and another 457,000 metric tons during 1984–85.

Pakistan is now importing only phosphatic and potassic fertilizers. During 1984–85, approximately 564,000 metric tons of phosphatic and potassic fertilizers were imported to meet the requirements of farmers and to maintain the required reserve.

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A general review of fertilizer situation in the country between April 1984 and June 1985 is given as under:–

	N	P	K	Total
Local Production	1176	114	–	1290 Tons
Imports	87	234	26	347 Tons
Off-take	1030	333	28	1391 Tons
Off take April 1983 to June 1984	1099	319	31	1449 Tons
% (+), (–)	(–) 6%	(+) 4%	(–) 10%	(–) 4%

The important fertilizer factories of Pakistan are enlisted below:-

1. TSF Plant and urea fertilizer plant, Hazara.
2. Faisalabad Fertilizer Ltd.
3. Pak American Fertilizer Ltd. at Daud Khel.
4. Single Super Phosphate Plant at Jaran Wala.
5. Natural Gas Fertilizer Factory, Multan.
6. Dawood Urea Plant, Lahore.
7. Dhariala Potash Fertilizer Project, Dhariala.
8. Fauji Urea Complex, Sadiqabad.
9. Exxon Fertilizer Co. Dahrki.
10. Urea Plant, Mirpur Mathelo.

11.2 DETERGENTS

Detergents are soapless cleansing agents. They are complex organic salts with long chain molecules. They react with the ions of the salts that cause hard

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water, thereby producing soluble compounds in which dirt and grease are readily carried away.

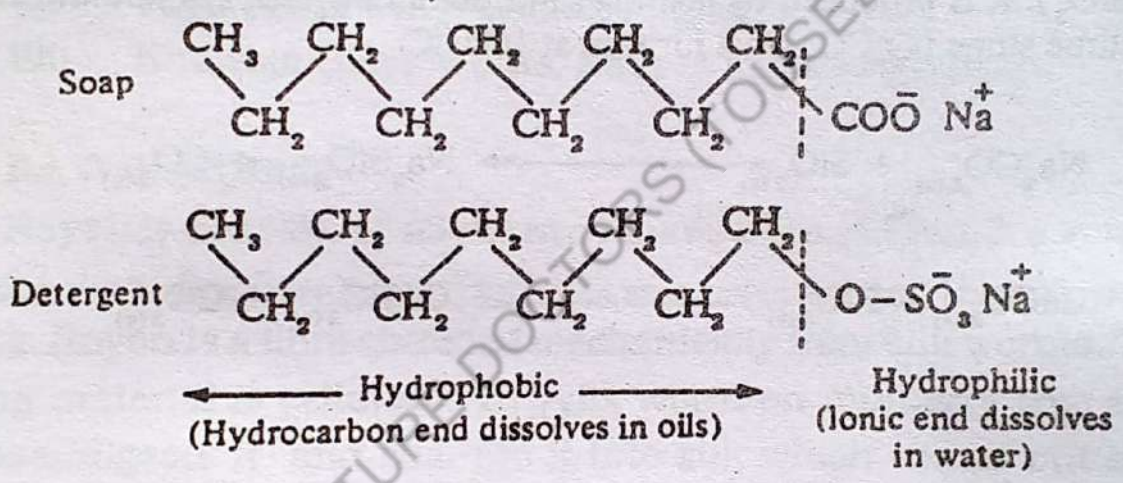
<u>Structure:-</u> All the detergents have the same basic structure. They are made up of two parts:

(i) Hydrophobic (Water repelling)

(ii) Hydrophilic (Water attracting).

Hydrophobic part is the long hydro carbon chain which is covalently bonded. Being nonpolar in nature, it attracts oil and grease which are also nonpolar.

Hydrophilic part is small ionic group like sulphonate (SO_3^{-1}), sulphate ($-O-SO_3^{-2}$), quaternary ammonium groups (NR_4^{+1}) or hydroxyl groups ($-OH^{-1}$). (In a soap this group is carboxyl, COO^-).



The essential characteristics of soaps and detergents are the same. The hydrocarbon chain ($-CH_2-$) is obtained from petroleum and the ionic group (SO_3^-, $-O-SO_3^-$) is introduced synthetically by means of sulphuric acid (Conc).

The presence of two groups (hydrophobic and hydrophilic) allows the mixing of water with nonpolar substances such as oil and grease.

A detergent removes dirt very easily. Grease is an organic covalent compound. The hydrophobic part of the detergents readily dissolves in grease (both being nonpolar). The hydrophilic part of the detergent dissolves in water (both being polar) so that slight agitation removes the grease and it is carried away with the water alongwith dirt.

The calcium and magnesium salts of detergent are soluble in water whereas corresponding salts of soaps are insoluble. This means that a detergent can be used in hard water and there is no wastage in the shape of scum (Precipitate).

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There are thousands of detergents which are used as washing powders and washing liquids. Specific detergents can be manufactured for a particular purpose by using a certain kind of hydrocarbon chain or by inserting more than one ionic groups.

Pakistan has developed a large detergent industry and detergents are sold under various brand names like Brite, Surf etc.

One disadvantage of detergent over soap is that hydrocarbon chain, unlike those of soaps which are derived from food substances (fats and oils) cannot be broken down by bacteria and dispersed.

11.3 GLASS

Glass is one of the most important artificial silicates. Ordinary soft glass or soda glass is a mixture of sodium silicate (Na_2SiO_3) and calcium silicate ($CaSiO_3$). It is produced by heating sand, soda (Na_2CO_3) or sodium sulphate and lime stone ($CaCO_3$) in a furnace at 1400°C.

$$Na_2CO_{3(s)} + SiO_{2(s)} \longrightarrow Na_2SiO_{3(s)} + CO_{2(g)}$$

$$CaCO_{3(s)} + SiO_{2(s)} \longrightarrow CaSiO_{3(s)} + CO_{2(g)}$$

Or

$$Na_2CO_3 + CaCO_3 + 6SiO_2 \longrightarrow 2CO_2 + \underset{\text{Glass}}{Na_2O.CaO.6SiO_2}$$

Glass is not a true solid because molecules are not arranged in a definite pattern. In fact a glass is a super cooled liquid i.e a solid solution without crystallization. The molecules are arranged in random positions as in case of liquids that's why a glass does not have sharp melting point. On heating it gradually becomes more and more plastic in nature.

Glass is attacked by hydrofluoric acid. This acid is used to make designs on glass. This process is called etching.

<u>Types of Glass:-</u> As mentioned earlier, ordinary window glass is a mixture of sodium and calcium silicates. It is manufactured from sand, soda and limestone. The refractory potassium glass is obtained by using potash K_2CO_3 instead of soda. This is used for making chemical glass ware.

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Pyrex glass is a borosilicate mixture which is produced by using boron oxide in place of some of silica; this glass can withstand sudden changes of temperature. You must have seen pyrex glass apparatus in your laboratory. In fact pyrex glass has a very low coefficient of expansion i.e it expands greatly when heated. Pyrex glass is not manufactured in Pakistan. Coloured glass is manufactured by adding certain transition metal oxides. For example CuO gives light blue, CoO dark blue and Cr_2O_3 green. Addition of selenium oxide and zinc oxide gives red coloured glass.

Position in Pakistan:- In Pakistan there are about 25 glass industries which are producing about 75,000 tons of glass per year. Now a days, there is definite improvement in the quality of glass.

The names of some of the glass producing factories are:-

(i) Indus Glass Work, Hyderabad.

(ii) Toyo Nasik Glass Factory, Lahore.

(iii) Khawaja Glass Works, Khyber Pakhtunkhuwah.

11.4 RAYON (FIBRE)

Rayon is considered as the man-made fibre. A French scientist "Chardonnet", discovered it in 1884. He was investigating the silk worm disease. Rayon is a fibre obtained mechanically from silk worms. The starting material is cellulose. The silk worm on mulberry tree eats cellulose, digests it and changes it into silk which comes out in a viscous form and solidifies on contact with air and becomes silk thread. Man does the same with cellulose, when preparing silk mechanically.

The term rayon is the name given to all the synthetic fibres which are manufactured from cellulose such as cellulose acetate, nitrocellulose, cupra silk, viscose rayon etc.

<u>Viscose Rayon</u> is manufactured from cellulose when it is digested with sodium hydroxide solution. When carbon disulphide is passed through the solution, a mixture of sodium cellulose xanthate is formed which is soluble in NaOH.

$$R\text{–}OH + CS_2 + NaOH \longrightarrow S{=}C\begin{matrix} OR \\ SNa \end{matrix} + H_2O$$

(R = Cellulose)

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Due to very high viscosity, the silk thus obtained is called viscose rayon. The solution is forced through a spinneret into H_2SO_4 bath where cellulose is precipitated as fine threads. This artificial silk is cheaper than cellulose acetate silk or nitrocellulose silk. It is produced in the largest quantity.

Synthetic fibres are the man made polymers which consist of macro-molecules (Poly = many; macros = parts). The polymers are built by linking together of many smaller units called monomers. This process is called polymerization.

Synthetic fibres are usually prepared by condensation polymerization in which linking of two different substances occurs with the elimination of water. The resulting polymers are known as copolymers. The examples of important synthetic fibres are Nylon, Rayon, Dacron, Terylene etc.

Nylon:- Chemical structure of nylon is not similar to that of material silk but resembles it to certain extent. It is made of diamines and dibasic acids which can be synthesized from the common raw materials i.e coal, water and air.

Nylon is the type of polymer in which amide linkages (–CONH–) hold the chain together. Nylon 6,6 is a condensation polymer of hexamethylene diamine with two amino groups and adipic acid (hexan dioic acid) with two carboxyl groups. The name Nylon 6.6 is also derived from the fact that both the components consist of six carbon atoms each. Elimination of water forms the amide linkage.

$$\underset{\text{Hexa methylene-diamine}}{NH_2.(CH_2)_6NH_2} + \underset{\text{Adipic acid}}{COOH.(CH_2)_4.COOH} \longrightarrow$$

$$[-NH(CH_2)_6.NH-CO(CH_2)_4.CO-NH(CH_2)_6-NH-CO(CH_2)_4CO-]_n$$

This is the same type of linkage found in proteins.

Terylene is a polyester fabric which is formed from many ester molecules. The monomers for the manufacture of terylene are ethylene glycol and terephthalic acid. During condensation polymerization, water molecule is eliminated giving rise to ester linkage.

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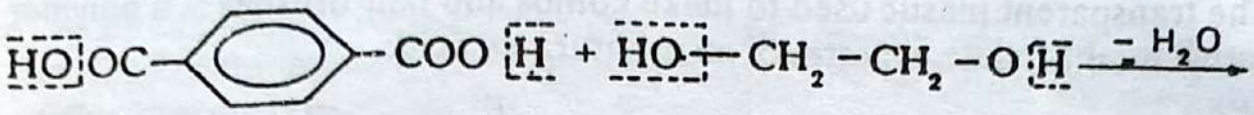
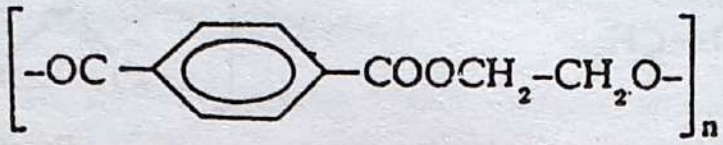


Terephthalic acid (1,4–benzene dicarboxylic acid). Ethylene glycol (Ethane–1,2,diol)



Terylene

Terylene is mainly used in clothing and fishing lines.

Among the advantages of synthetic fibers are:

(i) Lightness of weight (ii) Ease of ironing

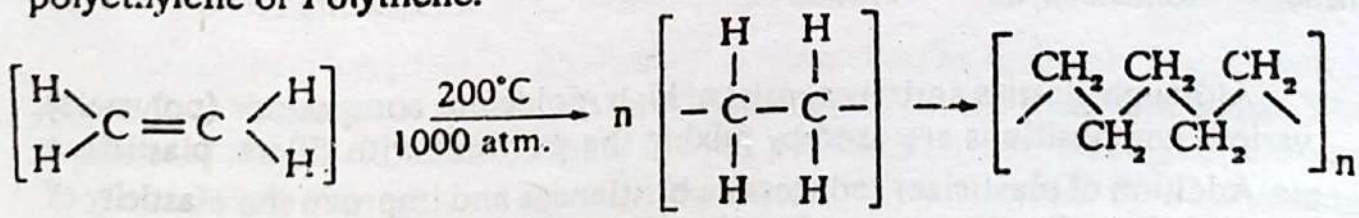
(iii) Softness and (iv) Heat retention or heat conductivity.

<u>Position in Pakistan:–</u> The manufacture of synthetic fibers is one of the branches of the chemical industry that has been developing at a very fast rate in our country. Govt. of Pakistan is taking all the measures to increase the production of all kinds of artificial and synthetic fibers in the coming years.

A number of industries have been established to manufacture synthetic fibers.

11.5 PLASTICS

Modern plastics are assuming an ever increasing importance in our economy. These are macromolecules, formed by the polymerization of simple molecules. In other words, plastics are also polymers formed from monomers. Ethylene, for example, is an unsaturated hydrocarbon polymerized in presence of suitable catalysts. The extra bond opens, forming an unstable molecule which joins with many others of its own kind to form macro molecules called polyethylene or Polythene.



Polyethylene is the most common plastic used to form polythene bags and to package foods. Poly propylene is superior to polyethylene in its resistance to breakage and to temperature.

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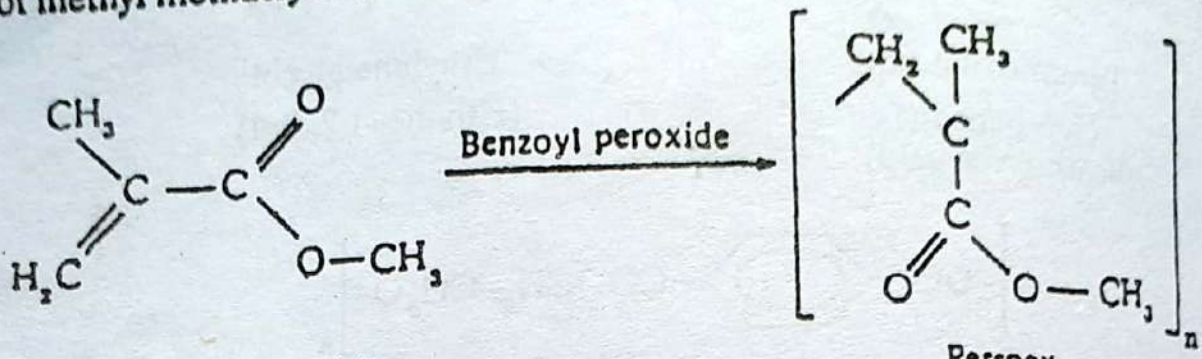
The transparent plastic used to make combs and hair brushes is a polymer of methyl methacrylate, an ester of an unsatura ed acid.



Methyl methacrylate

Perspex

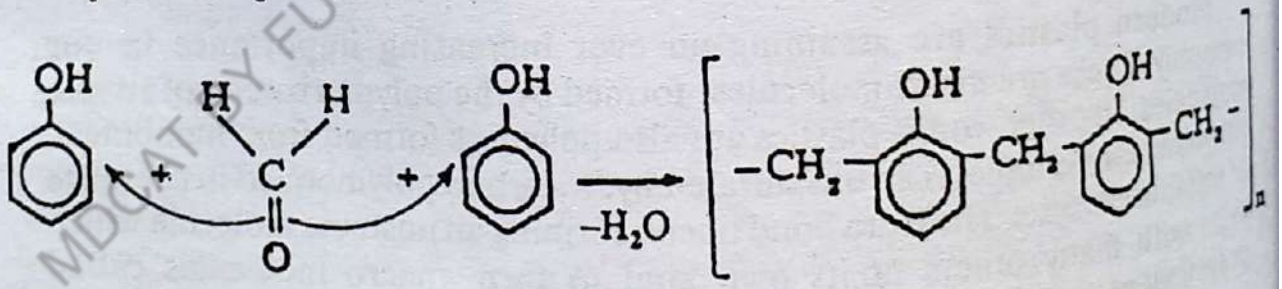
Glass like transparency and resistance to weathering make it useful as a glass substitute e.g. in aircraft windows, reflectors on auto vehicles, T.V guard screens and street light fittings.

PVC or Poly vinyl chloride is the polymer of vinyl chloride ($CH_2=CHCl$). In the presence of catalyst hydrogen peroxide at the temperature of 80°C, vinyl chloride polymerizes to poly vinyl chloride. PVC is used for the insulating covering for electrical cables, for the manufacture of gramophone records, suit-case coverings etc.

PVA (Poly vinyl acetate) is the polymer of vinyl acetate ($CH_2=CHO.CO.CH_3$) is used in the manufacture of chewing gum and in the water proofing of textiles.

Bakelite is a polymer of phenol and formaldehyde.

Bakelite is used to make buttons, switches, electrical boards, cameras, radio and telephone components.



Phenol formaldehyde Phenol Bakelite

Although plastics entirely consist of high molecular compounds (polymers), various compositions are used by mixing the polymer with fillers, plasticizers etc. Addition of plasticizer reduces the brittleness and improve the elasticity of plastics. One disadvantage of artificial plastic is an increase in the rigidity and loss of elasticity when solvent evaporates.

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Fillers usually increase the mechanical strength of plastics and make the savings of the more costly polymer. Various fillers which are used are wood flour, saw dust.

Plastics are generally tough, resistant to the action of acids and alkalis and not very much affected by the change of temperature. The plastics have a fair range of deformability and mouldability due to which articles of any desired shape and form can be manufactured.

Plastic Industry in Pakistan:– Plastic Industry in Pakistan essentially consists of moulding of plastic powders into various articles of daily use.

Types of Plastic:– Plastics are of two types:

(i) Thermoplastic (ii) Thermosetting

(i) A Thermo plastic or thermosoftening plastic is a material which softens on heating and hardens on cooling. This process of heating, softening, moulding and cooling can be repeated and it does not affect the properties of plastics. Such plastics are easily moulded into shapes but are not very heat resistant. The examples are: nitro cellulose, cellulose acetate and vinyl polymers.

(ii) Thermosetting plastics are those materials which can be heated only once before they set i.e they can not be reworked. In other words, thermosetting plastics do not soften on reheating. The examples are phenol formaldehyde, urea formaldehyde, silicones etc.

11.6 PAINTS

You must be familiar with the walls, doors, windows, etc. that are painted for the decorative and protective purposes. Iron articles are painted to prevent them from corrosion or rusting.

A paint is usually composed of three components:–

(i) **A binder** or vehicle which hardens to form a continuous film.

(ii) **A pigment** which supplies the desired colour and

(iii) **A volatile solvent** which evaporates.

In an Oil – based paint, linseed oil is often used as a binder. The solvent is usually turpentine, a mixture of hydrocarbons obtained from pine trees. The pigment may be titanium dioxide, TiO_2 (White), carbon black (C), chrome yellow ($PbCrO_4$), oxides of iron (brown or red) or organic dyes of various colours. White lead having approximate composition [$Pb(OH)_2.2PbCO_3$) was once extensively used, but it has now been banned for interior use due to high toxicity of lead. Infant illnesses have been attributed to the ingestion of chips of old lead paint.

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In Water based paint (Emulsions) a synthetic polymer with rubber like properties is used as the binder. These "Latex" paints are emulsified in water to give a variety of spreading characteristics. Dyes and pigments may be added to give desired colours. Among the plastics used in latex paints are polyvinyl acetate, polymethyl methacrylate, polystyrene, styrene–butadiene copolymers and polytetrafluoro ethylene (Teflon). Paints can be formulated with fantastic variety of colours, textures and resistances.

Varnishes:– Varnish is a mixture of resins, a volatile organic solvent such as ether, and a drying oil such as linseed oil. Resin is dissolved in a volatile organic solvent and then a drying oil is added when varnish is obtained.

The drying oils (linseed oil) consist of esters of highly unsaturated acids containing two or more double bonds. Such oils absorb oxygen when exposed to air and form tough solid water insoluble film.

A varnish which also contains a drying oil when it is applied on a surface, forms tough, solid, durable and glossy film. As a matter of fact, the volatile organic solvent evaporates quickly and the drying oil absorbs oxygen, dries up forming water insoluble tough film on the surface. The glossy appearance is due to the presence of resin.

Paint Industry in Pakistan:– A number of multinational companies are involved in the preparation of paints of various kinds.

Names of some of industries in Pakistan are given below:

1. Berger Robbialac, Karachi.
2. I.C.I. Dulux, Lahore.
3. Buxly's paints, Karachi.

ASSIGNMENT

1. What is a fertilizer? Give names and uses of some of the fertilizers.
2. What is a detergent? Describe the cleaning action of detergent.
3. What do you know about glass? Describe in detail.
4. Write short note on synthetic fibers. How nylon is prepared and state its characteristics?
5. What do you know about plastics?
6. Write short notes on:

   (i) Paints (ii) Varnishes
7. What is the difference between a manure and a fertilizer?

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