GOVERNMENT ARTS AND SCIENCE COLLEGE NAGERCOIL – 629 004

[Affiliated to Manonmaniam Sundaranar University, Tirunelveli – 12]

DEPARTMENT OF PHYSICS

COURSE MATERIAL

NAME OF THE SUBJECT: ALLIED CHEMISTRY

SUBJECT CODE : SACH11

YEAR : II B.Sc. PHYSICS

SEMESTER : III

STAFF IN-CHARGE : Ms. R.S PRIYA DHARSHINI, Dr. G.M. CARMEL VIGILA BAI

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Ms. R.S PRIYA DHARSHINI

ALLIED CHEMISTRY - I

Objective

To learn about atomic structure and bonding. To learn the principles of reactions of organic compounds. To study about photochemical reactions. To learn about the importance of polymers and polymer science. To study about lubricants and some cosmetics in the modern world.

Unit I –

Inorganic chemistry Atomic structure : electronic configuration - Aufbau principle - Pauli's exclusion principle- Hund's rule. Bonding : electrovalent, covalent, hydrogen bonds-orbital overlap - s-s, s-p. Hybridization and VESPR theory - CH4, C2H4, C2H2- BeCl2, BF3, NH3, H2O, PCl5, IF5, IF7.

Unit II –

Organic chemistry – Principles of reactions Heterolytic and homolytic cleavage - nucleophiles and electrophiles-reaction intermediates – preparation and properties of carbonium ions, carbanions and free radicals - type of reactions - substitution, addition, elimination and polymerisation reactions.

Unit III-

Physical chemistry - Photochemistry Definition-comparision between thermal and photochemical reactions-Laws of photochemistry-Beer Lambert‘s law-Grothus Draper law-Einstein‘s law-Quantum yield-low and high quantum yield-determination of quantum yield-fluorescence, phosphorescence, thermoluminescence, chemiluminescence and bioluminescence-definition with examplesphotosensitisation.

Unit IV-

Polymer Chemistry Definition- Monomers, Oligomers and Polymers - Classification of polymers- natural, synthetic- linear, cross linked and network- plastics, elastomers, fibres- homopolymers and co-polymers Thermoplastics: polyethylene, polypropylene, polystyrene, polyacrylonitrile, poly vinyl chloride, nylon and polyester - Thermosetting Plastics : phenol formaldehyde and epoxide resin- Elastomers: natural rubber and synthetic rubber - Buna - N, Buna-S and neoprene.

Unit V-

Applied Chemistry Lubricants-classification-criteria of good lubricating oils-synthetic lubricating oilspoly glycols and poly alkene oxides-greases or semi solid lubricants-examples-solid lubricants- graphite Prepration and uses of shampoo, nail polish, sun screens, tooth powder, tooth paste, boot polish, moth ball and chalk piece.

Reference Books

1. B. R. Puri, L. R. Sharma and K. C. Kalia, Principles of Inorganic Chemistry

2. P. L. Soni, Text Book of Inorganic Chemistry

3. K. S. Tewari and N. K. Vishnoi, A Text Book of Organic Chemistry.

4. Arun Bahl and B.S. Bahl, Advanced Organic Chemistry, S. Chand and Sons.

5. M.K. Jain and S. C. Sharma, Modern Organic Chemistry

6. K.K.Rohatgi Mukherjee, Fundamentals of photochemistry , Wiley Eastern Ltd.

7. B.R. Puri and L.R. Sharma, Principles of Physical Chemistry, Chand & Co.

8. Malcom P. Stevens, Polymer Chemistry – An Introduction

9. V.R. Gowariker, Polymer Science, Wiley Eastern, 1995.

10. Sawyer.W, Experimental cosmetics, Dover publishers, New york, 2000

MSU / 2017-18 / UG-Colleges / Part-III (B.Sc. Chemistry) /Semester – III /

Allied Practical -I Inorganic Quantitative Analysis

Objective:

To enable the students to acquire the quantitative skills in volumetric analysis. Acidimetry and alkalimetry

1. Estimation of oxalic acid – Std. oxalic acid

2. Estimation of Na2CO3 – Std. Na2CO3

3. Estimation of hydrochloric acid – Std. oxalic acid Permanganometry

4. Estimation of ferrous ammonium sulphate – Std. ferrous ammonium sulphate

5. Estimation of oxalic acid – Std. oxalic acid

6. Estimation of ferrous sulphate – Std. oxalic acid

Internal –50 marks

25 marks - Regularity

25 marks – Average of best four estimations in regular class work

External -50 marks

10 marks – Record (atleast 4 volumetric estimations)* 10 marks –

Procedure 30 marks

– Result *Experiments done in the class alone should be recorded (Students having a bonafide record only should be permitted to appear for the practical examination)

UNIT - I

INORGANIC CHEMISTRY

ATOMIC STRUCTURE

ELECTRONIC CONFIGURATION

An atom consists of a charged body at its centre. It is called the "nucleus". It is surrounded by electrons in various orbitals. The distribution of electrons in various orbitals is known as "electronic configuration". The order of filling of orbitals with electrons is governed by the following rules:

1. Pauli's exclusion principle

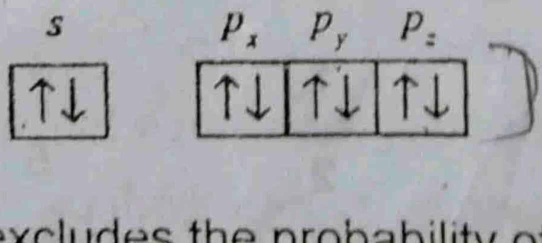
According to this principle, no two electrons in an atom can have all the four quantum numbers identical. If two electrons have the same value for n, *l* and m, they must have different values of s.

n = 1	l = 0	m = 0	s = +1/2 (for one electron)
n = 1	l = 0	m = 0	s = -1/2 (for second electron)

Significance of the principle

It predicts that

i) A sub-orbital can accommodate a maximum of two electrons with opposite spin



Since it excludes the probability of accomodating more than 2 electrons in a sub-orbital, the principle is called *exclusion principle*.

ii) The maximum number of electrons that can be accomodated in an orbital = $4l + 2$.

Value of l	Obital	No. of electrons
0	s	2
1	p	6
2	d	10
3	f	14

2. Aufbau principle (German : *Aufbau* = building up)

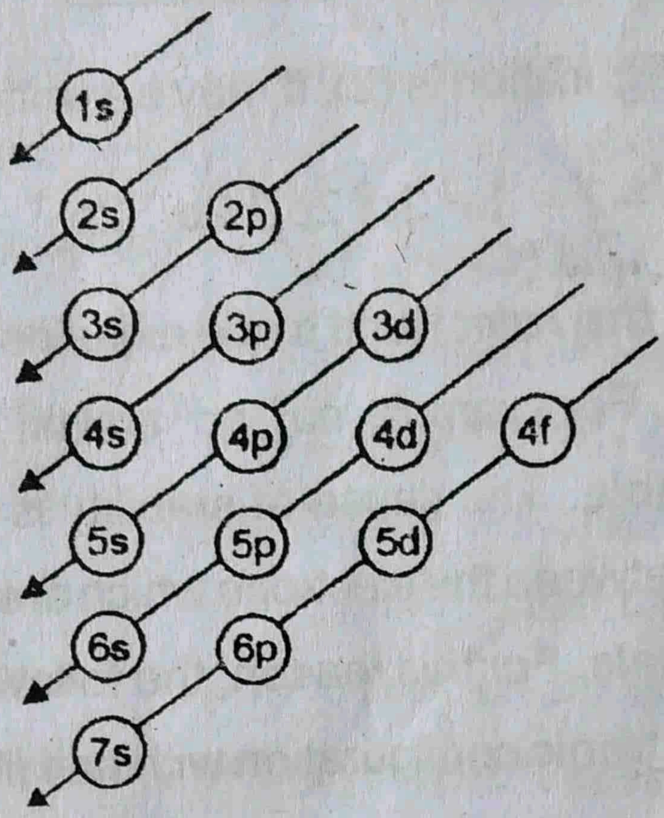
According to this principle, the electrons are filled in various orbitals in the order of their increasing energies. This means that an orbital with lowest energy will be filled first. The energy of an orbital depends upon its n + l value. The orbitals with the lowest n + l value is filled first. When two orbitals have the same n + l value, the one with the lower n value will be filled first. This is known as $(n + l)$ rule.

Orbital	*n*	*l*	*n + l*
1s	1	0	1
2s	2	0	2
2p	2	1	3
3s	3	0	3
3p	3	1	4
3d	3	2	5
4s	4	0	4

It is evident from the above table that order of increasing energies and hence the order of filling up of orbitals is

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d$$

The order is diagramatically illustrated below:



3. Hund's rule of maximum multiplicity

According to this rule, electrons never pair in a p, d or f orbital until all the available sub-orbitals have one electron each.

2P - 6 electrons
3S _ 2electron etc.

Explanation of Hund's rule: The repulsive force between electrons will be minimum when they have parallel spins and occupy different sub-orbitals. Consider the three p sub-orbitals (p_x, p_y and p_z) of equal energy. If three electrons are to be accommodated they prefer to enter different p sub-orbitals singly rather pair up in the same sub-orbital.

Example

			p_x	p_y	p_z	
N = 7	↑↓	↑↓	↑↓	↑		---- (1)

			p_x	p_y	p_z	
N = 7	↑↓	↑↓	↑	↑	↑	---- (2)

The correct configuration is (2). It may be written as

$$N = 7 = 1s^2\,2s^2\,2p_x^{\;1}\,2p_y^{\;1}\,2p_z^{\;1}$$

Significance of the rule: Hund's rule explains the stability of half-filled orbitals. For example, np^3, nd^5 and nf^7 configurations are the most stable. The cause of stability is the minimum repulsive force between the electrons which are singly filled in p, d or f sub-orbitals. For this reason, the following elements tend to have electronic configuration with half filled orbitals.

$Cr = 24 = [Ar]^{18}\,3d^5\,4s^1$

$Mo = 42 = [Kr]^{36}\,4d^5\,5s^1$

$Gd = 64 = [Xe]^{54}\,4f^7\,5d^1\,6s^2$

At. No.	*Element*	*Symbol*	*Electronic configuration*
1	Hydrogen	H	$1s^1$
2	Helium	He	$1s^2$
3	Lithium	Li	$1s^2\,2s^1$
4	Beryllium	Be	$1s^2\,2s^2$
5	Boron	B	$1s^2\,2s^2\,2p^1$
6	Carbon	C	$1s^2\,2s^2\,2p^2$
7	Nitrogen	N	$1s^2\,2s^2\,2p^3$

8	Oxygen	O	$1s^2 2s^2 2p^4$
9	Fluorine	F	$1s^2 2s^2 2p^5$
10	Neon	Ne	$1s^2 2s^2 2p^6$
11	Sodium	Na	$1s^2 2s^2 2p^6 3s^1$
12	Magnesium	Mg	$1s^2 2s^2 2p^6 3s^2$
13	Aluminium	Al	$1s^2 2s^2 2p^6 3s^2 3p^1$
14	Silicon	Si	$1s^2 2s^2 2p^6 3s^2 3p^2$
15	Phosphorus	P	$1s^2 2s^2 2p^6 3s^2 3p^3$
16	Sulphur	S	$1s^2 2s^2 2p^6 3s^2 3p^4$
17	Chlorine	Cl	$1s^2 2s^2 2p^6 3s^2 3p^5$
18	Argon	Ar	$1s^2 2s^2 2p^6 3s^2 3p^5$
19	Potassium	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
20	Calcium	Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

CHEMICAL BONDING

1. IONIC BOND

(Transfer)

Ionic bond is formed by the transfer of electrons from one atom to the other. The atom which loses the electron produces cation while the atom which gains the electron forms anion. The electrostatic force of attraction between the ions is called ionic or electrovalent bond.

$$Na \rightarrow Na^+ + e^-$$
$$Cl + e^- \rightarrow Cl^-$$
$$Na^+ + Cl^- \rightarrow Na^+ Cl^-$$

Cation ⇒ + charge
anion ⇒ - charge

Favourable conditions for the formation of anionic compound M^+X^-

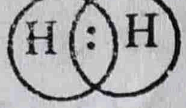
1. The ionisation energy of atom M should be low. $Na^+ Cl^-$
2. The electron diffinity of atom X should be high.

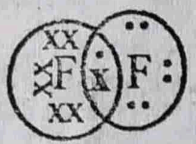
affinity

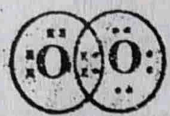
3. The atoms M and X should have high electronegativity difference.

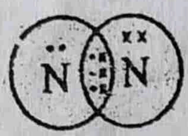
2. COVALENT BOND (Sharing)

A covalent bond is formed between two atoms when they equally share one, two or three pairs of electrons with each other.

 → H - H

 → $\overset{xx}{\underset{xx}{\overset{x}{\underset{x}{}}F}} - \ddot{\underset{\cdot\cdot}{F}}:$ (or) F – F

 → $:\ddot{O}=\ddot{O}:$ (or) O = O

 → $\ddot{N}\equiv\ddot{N}$ (or) $N\equiv N$

Favourable conditions for the formation of covalent compound

1. The two atoms A and B should higher values of ionisation potential.
2. Electornegativity of A and B should be equal or almost equal

Overlapping of Atomic orbitals

According to valence Bond theory (VBT)

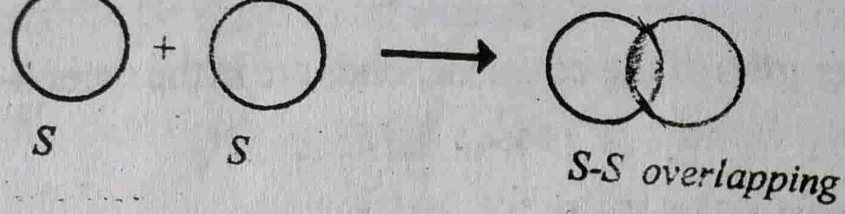
i) A covalent bond is formed by the overlapping of two atomic orbitals with unpaired electrons.

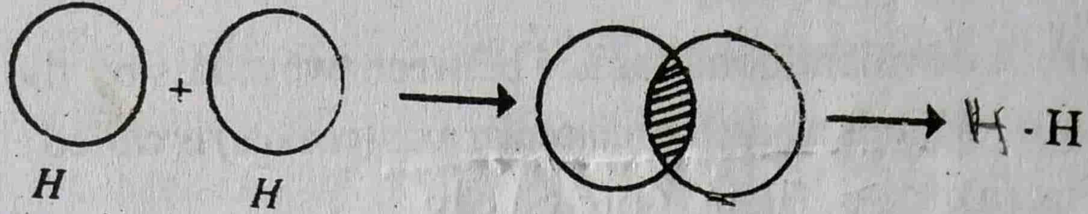
ii) The strength of the covalent bond is proportional to the eetant (amount) of overlapping of orbitals.

Types of overlapping

i) s-s Overlapping : e.g. Hydrogen

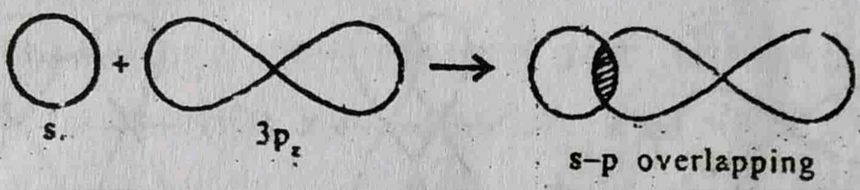
The 1s orbitals of two hydrogen atoms overlap to form an s-s covalent bond.

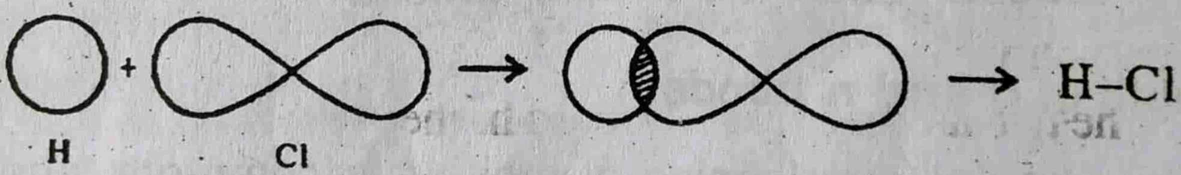




ii) s-p Overlapping: e.g. HCl

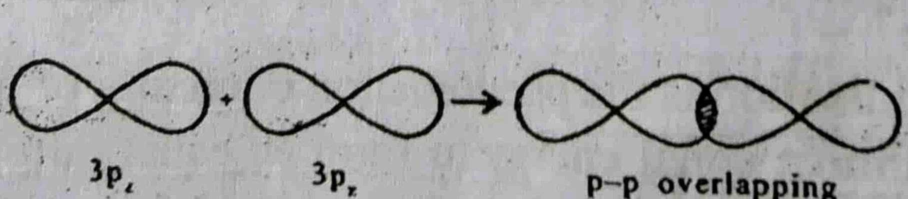
The 1s orbital of hydrogen and the half filled $3p_z$ orbtial of chlorine overlap and form a **s-p** covalent bond.

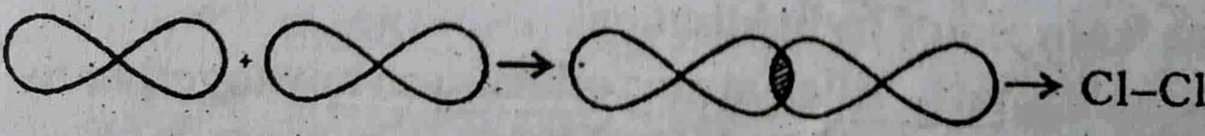




iii) p-p Overlapping: e.g. Chlorine.

The $3p_z$ orbitals of two chlorine atoms with one electron each overlap to form a **p-p** covalent bond.



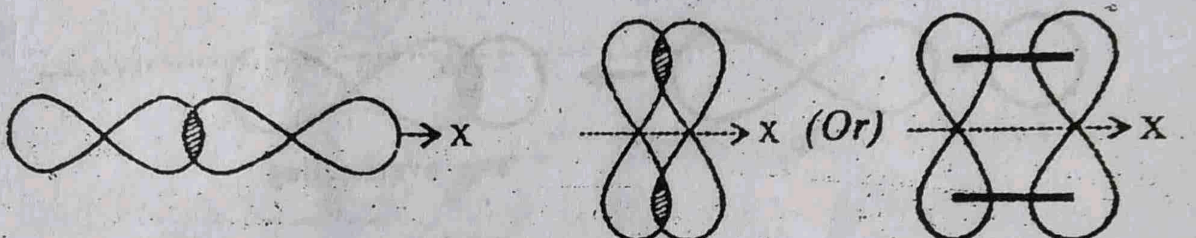


The strengths of the covalent bonds are in the order s-s bond < s-p bond < p-p bond

Sigma (σ) and Pi (π) bonds

i) σ bond : A covalent bond formed between two atoms by the overlapping of orbitals along the molecular axis (coaxial) is called a σ - bond Fig. (a). ⇒ it is complete ⇒

i) π bond : A covalent bond formed between two atoms by the overlapping of orbitals along a line perpendicular to the molecular axis (lateral) is called a π bond Fig. (b).



σ-bond   π-bond

Strength of σ and π bonds

The coaxial overlapping of orbitals is complete and effective and hence the σ bonds are strong. On the other hand, the lateral overlapping is only partial and hence π bonds are weak.

Hybridisation

Definition :

Hybridisation is the phenomenon of mixing of atomic orbitals of almost equal energy to form an equal number of mixed (hybrid) orbitals of identical energy and shape.

Salient features of hybridisation

1. Generally, half - filled atomic orbitals can mix together to form an equal number of hybrid orbitals.

2. In some cases, completely filled orbitals are also involved in hybridisation.

3. The hybrid orbitals are arranged in space as for away from one another as possible so that the force of repulsion between them is minimum.

4. The geometry of a molecule depends upon the type of hybridisation and the orientation of hybrid orbitals in space.

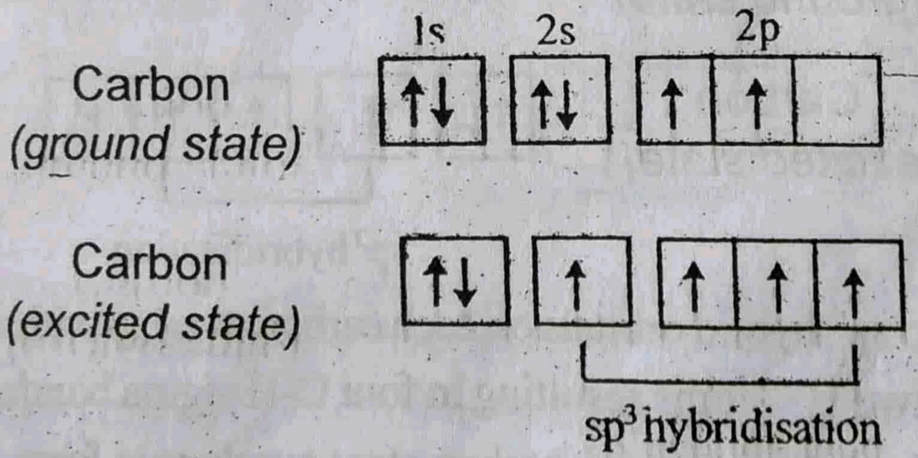
Types of hybridisation and shapes of molecules

1. sp^3 hybridisation

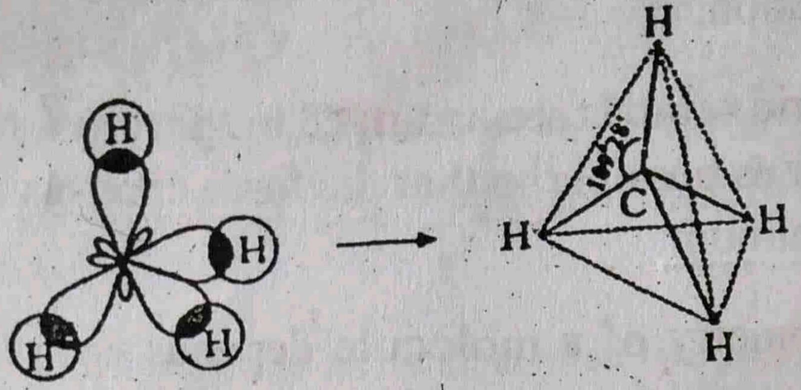
The mixing of one s and three p orbitals to form four hybrid orbitals is known as sp^3 *hybridisation.*

According to Sidwick-Powell theory, the four orbitals should be directed towards the four corners of a regular tetrahedron sc that the force of repulsion between them is minimum. The angle between the hybrid orbitals is 109°28′.

Example : Geometry of CH_4 molecule



The four hybrid orbitals of carbon overlap with the 1s orbitals of four H-atoms to form sigma bonds. The bonds are directed towards the four corners of a regular terahedron. Thus, methane molecule has tetrahderal shape with a bond angle of 109°28′.

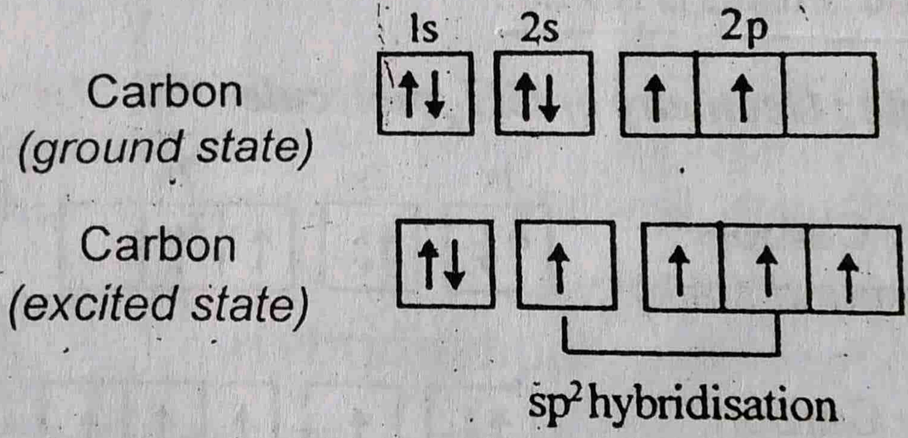


2. sp² hybridisation

This type of hybridisation involves the mixing of one s and two p orbitals to form three hybrid orbitals.

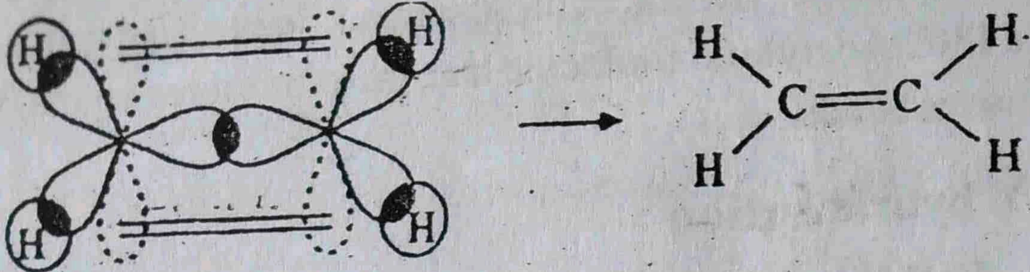
The repulsion between the hybrid orbitals will be minimum if they are distributed at an angle of 120⁰. Thus, a molecule formed by sp² hybridisation will assume *trigonal planar* shape.

Example: Geometry of C_2H_4 molecule



Two sp² hybrid orbitals on each carbon overlap with the 1 s orbitals of two H - atoms resulting in four C-H sigma bonds. The third hybrid orbital from each carbon atom overlaps to form a C-C sigma bond.

The unhybridised p-orbital on each carbon atom overlaps sidewise with each other forming a C-C- pi bond.

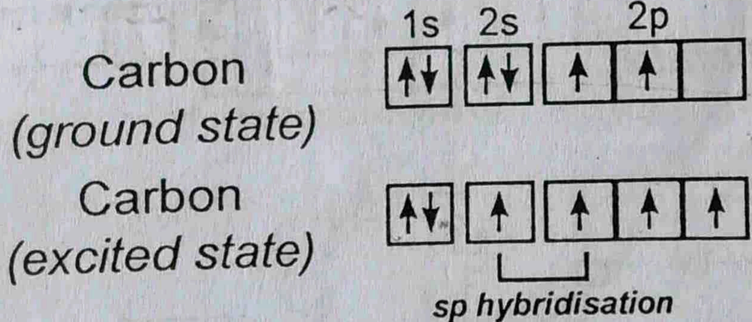


The so called double bond in ethylene is, therefore, a combination of one σ bond and one π bond. Shape of the molecule is trigonal planar and bond angle is 120°. Ethylene molecule has therefore, five σ bonds and one π bond.

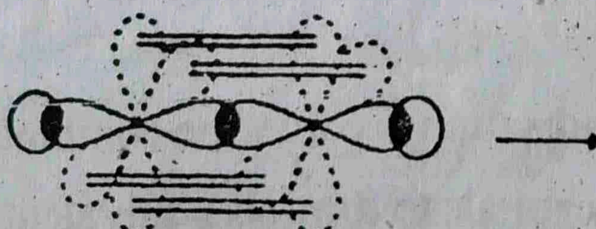
3. sp hybridisation

Combination of one s and one p orbitals to form two hybrid orbitals is termed *sp hybridisation.* These orbitals are linear and make an angle of 180° so as to have minimum repulsion.

Example: Geometry of C_2H_2 molecule



Overlapping of one sp hybrid orbital of each carbon atom forms a C-C sigma bond. The second hybrid orbital on each carbon atom overlaps with the 1s orbitals of two H-atoms to give two C-H sigma bonds.



H−C≡C−H

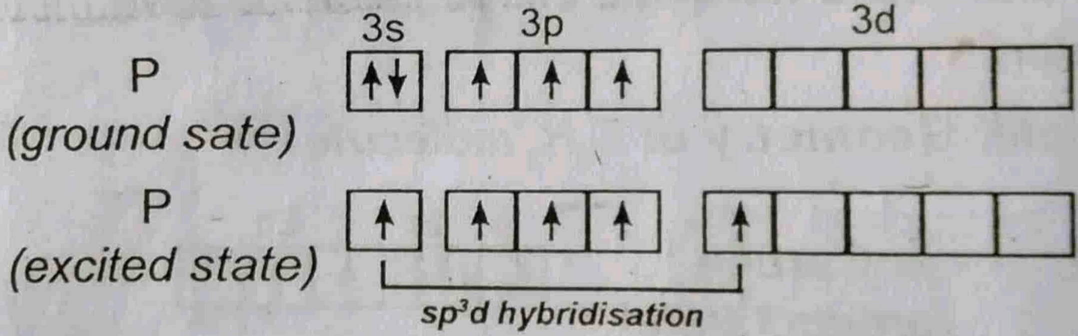
Thus, the triple bond in acetylene is a combination of one σ bond and two π bonds. The molecule assumes a linear shape with a bond angle 180^0. Acetylene molecule has, therefore, three sigma bonds and two pi bonds.

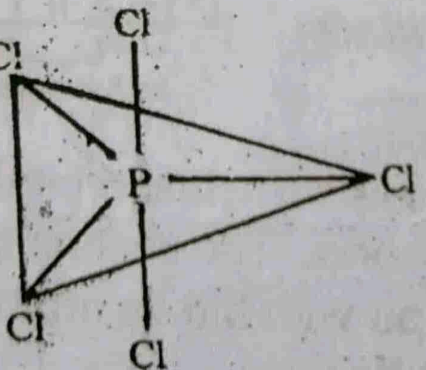
4. sp^3d hybridisation

In this hybridisation, one s, three p and one d orbitals combine together to form five sp^3d hybird orbitals. This type of hybridisation leads to trigonal bipyramid geometry.

Example : Geometry of PCl_5 molecule

In PCl_5 the p atom undergoes sp^3d hybridisation.



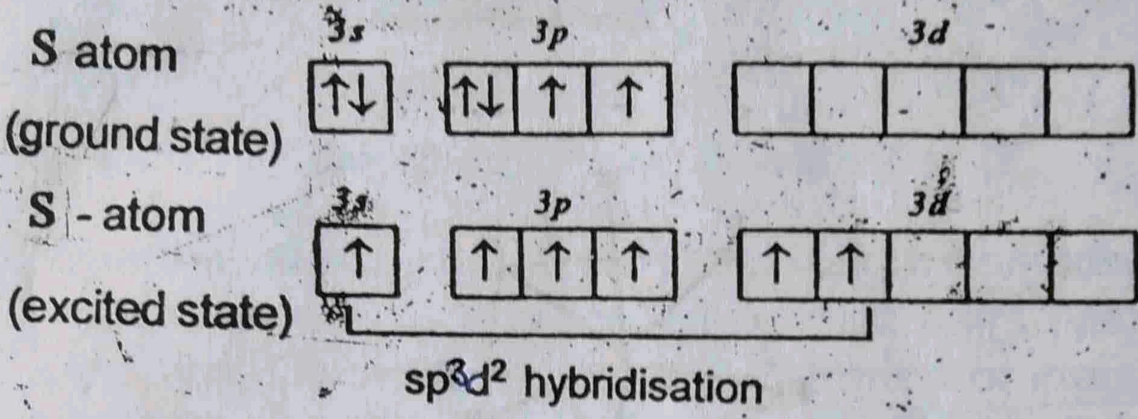


5. sp^3d^2 hybridisation

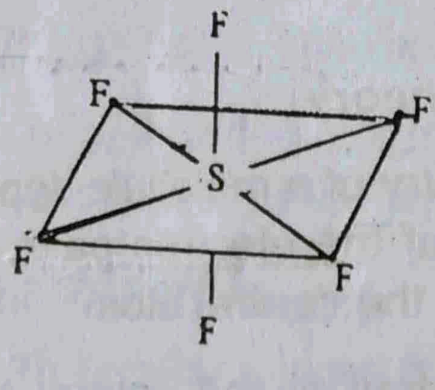
This type of hybridisation involves the combination of one s, three p and two d orbitals to form six equivalent hybird orbitals. The hybrid orbitals are directed towards the six corners of a regular octahedron with bond angle 90^0.

Example : Geometry of SF_6 molecule

In SF_6 molecule, S atom undergoes sp^3d^2 hybridisation.



The six hybrid orbitals overlap with the p - orbitals of six F - atoms to form SF_6. The geometry of SF_6 molecule is *octahedron.*

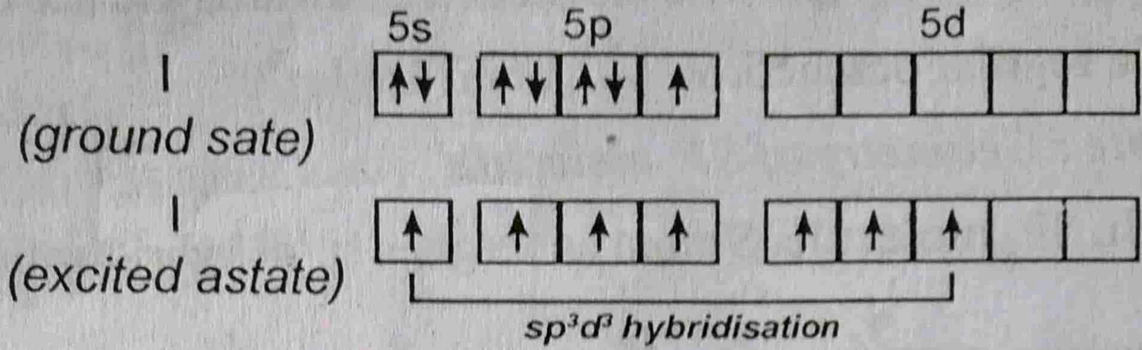


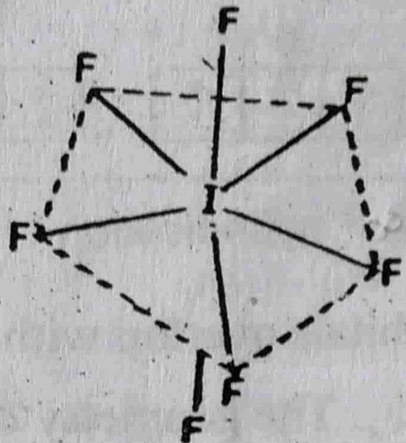
6. sp^3d^3 hybridisation

In this hybridisation, one s, three p and three d orbitals combine to form seven sp^3d^3 hybrid orbitals. This type of hybridisation leads to *pentagonal bipyramid* geometry.

Example : Geometry of IF_7 molecule

The I - atom in IF_7 molecule is sp^3d^3 hybridised. The shape of IF_7 molecule is *pentagonal bipyramid.*





VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

Postulates of VSEPR theory

1. The shape or geometry of a molecule depends upon the number and nature of the electron pairs present in the valence shell around the central atom.

2 When the valence shell of the central atom has only σ-bonding electron pairs (σ-bps), the molecule will have a regular geomerty. The geometry depends upon the number of σ-bps which tend to keep away from one another to have minimum electrostatic repulsion. Thus, the geometry with large bond angle is more stable

No of σ-bps	*Geometry*	*Bond angle*	*Example*
2	Linear	180^0	$BeCl_2$
3	Trigonal planar	120^0	BF_3
4	Tetrahedral	$109^0 28'$	CH_4
5	Trigonal bipyramid	120^0	PCl_5
6	Octahedral	90^0	SF_6
7	Pentagonal	72^0 and 90^0	IF_7

3. Whe the valence shell of the central atom has bonded (σ-bps) as well as non-bonded or lone pairs (lps) of electrons, the molecule will have distrorted or irregular geometry. Consequently, the bond angle decreases from the regular value. The magnitude of distortion and the decrease in bond angle depends upon the number of lone pairs of electrons. This is due to greater repulsive force of the lps. The repulsion is in the order

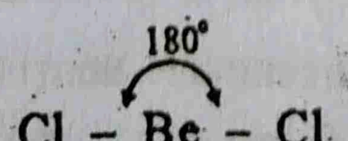
lps - lps > lps - bps > bps - bps

4. The presence of π-bps does not influence the spatial arrangement of σ-bps and hence the geometry of the molecule.

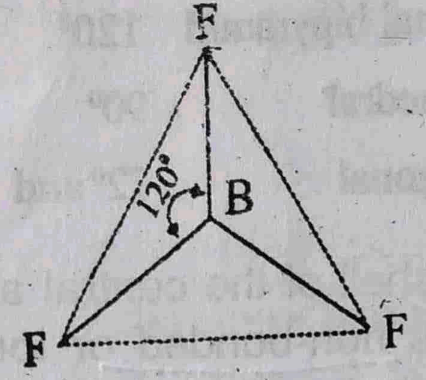
Applications of VSEPR theory

1. Molecules with regular geometry

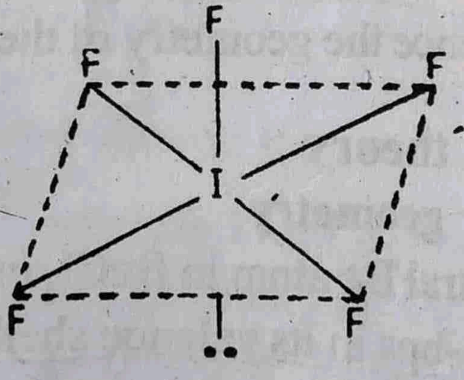
i) $BeCl_2$ molecule: The central Be atom in $BeCl_2$ molecule in the vapour phase has two σ-bps in its valence shell. They arrange themselves at an angle of 180^0 to have minimum repulsion. Thus, the molecule assumes a *linear shape*.



ii) BF_3 molecule: The B - atom in BF_3 is surrounded by three σ-bps. There will be minimum repulsion when they are arranged at an angle of 120^0. Thus, the molecule has *trigonal planar geometry.*



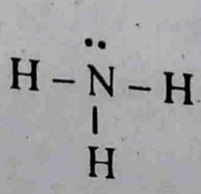
iii) IF_5 molecule: The central I - atom in IF_5 molecule contains five bond pairs and one lone pair of electrons. They are directed towards the six corners of an octahedron. Due to greater lone pair - bond pair repulsion, the geometry is distorted and IF_5 molecule assums *square pymidal geometry.*



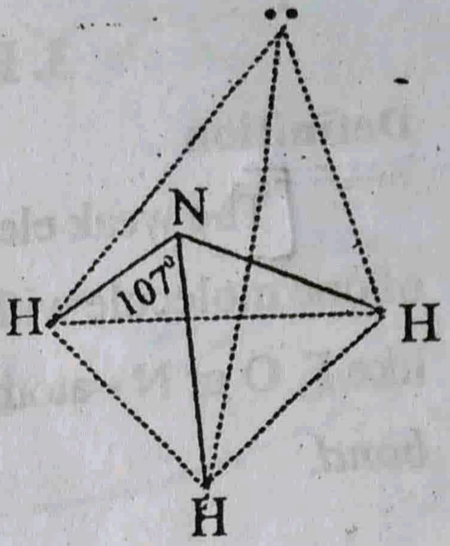
2. Molecules with Irregular geometry

i) NH_3 molecule

The valence shell of the central N-atom in NH_3 contains three bond pairs and one lone pair of electrons.



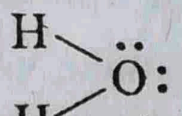
In order to have minimum repulsion, the electron pairs are directed towards the four corners of a tertrahedron. The repulsion among the electron pairs is not equal. The lone pair - bond pair repulsion is greater than the bond pair - bond pair repulsion.



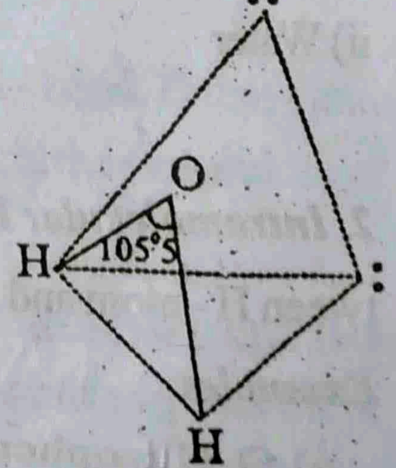
As a result, the bond pairs move away from the lone pair and come closer to each other. Thus, NH_3 molecule has an irregular or distorted tetrahedral geometry and the bond angle is decreased form $109^0 28'$ to 107^0. This distorted tetrahedral geometry is also known as *pyramidal geometry.*

ii) H_2O molecule

The central O - atom in water has four electron paris viz two bond pairs and two lone paris in its valence shell.



They are directed towards the four corners of a tetrahedron so that there will be minimum repulsion between them. Since the lone pair electrons exert more repulsion on the adjacent lone pair and bond pair electrons, H_2O molecule has an irregular tetrahedral geometry. It is also known as *bent or angular or V - shaped geometry*. Due to the presence of two lone pairs of electrons the bond angle is decreased from $109^0 28'$ to $104^0 27'$



3. HYDROGEN BOND

Definition

The weak electrostatic force which binds the H - atom of one molecule with a small but highly electronegative atom like F, O or N - atom of another molecule is called *hydrogen bond.*

H - F ----- H - F ----- H - F
↑
H - bond

Thus, the electronegative atoms of two neighbouring molecules are bridged through a H - atom. For this reason, H - bonding is also called H - bridging.

Types of H - bonding

i) Inter molecular H - bonding **:** This type of H bond is formed between H atom of one molecule and F, O or N atom of another molecule.

Examples

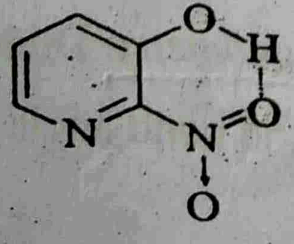
i) Hodrogen flouride H - F ---- H - F ---- H - F

ii) Water H - O ---- H - O ---- H - O (each O bonded to H below)

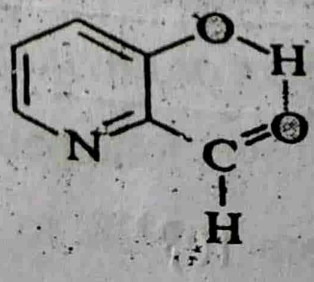
2. Intramolecular H - bonding: This type of H bond is formed between H - atom and O - or N - atom of the same molecule.

Examples

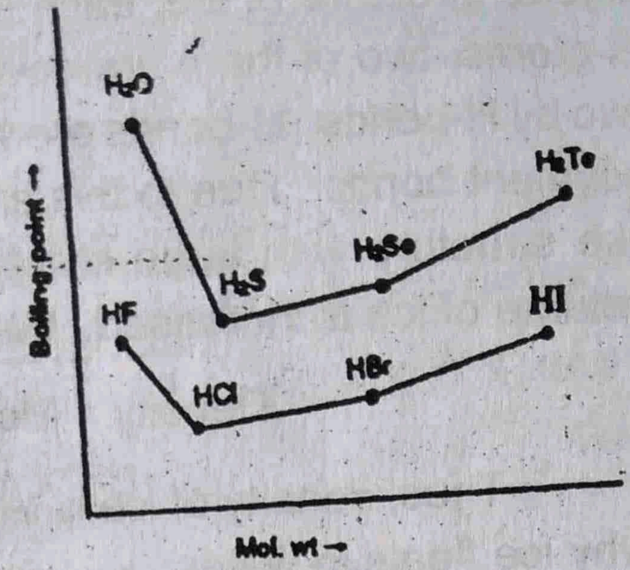
i) O-Nitrophenol



ii) Salicylaldehyde



Effects of H - bonding



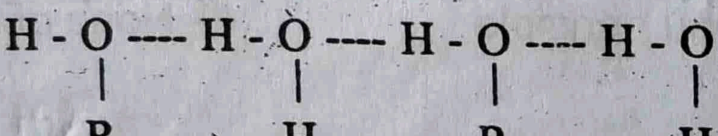
1. Abnormal boiling points: Molecules get associated by H- bonding. A large amount of energy is needed to separate such molecules. Therefore, the boiling points of hydogen bonded compounds are much more than similar compounds without hydrogen bond. For example, HF, H_2O and NH_3 have higher boiling points than the hydrides of other elements of the same group.

2. H_2O is a liquid while H_2S is a gas: Boiling point usually varies with the molecular weight. However, H_2O (mol.wt = 18) is a liquid (b.pt = 100°C) while H_2S (mol.wt = 34) is a gas (b.pt = -59.6°C) at ordinary temperature. The abnormally high boiling point of water is due to molecular association through H - bonding.

***3. Difference in melting points of nitrophenols*:** The m - and p - nitrophenols have higher melting points than o - nitrophenol. This is because of molecular association by H - bonding.

o - Nitrophenol forms intramolecular H - bond. But m - and p - nitrophenols form intermolecular H - bond and the molecules get associated.

4. Solubility of alcohol in water : Covalent compounds which can show the property of H - bonding are highly soluble in water. For example, ammonia, alcohol and sugar are readily soluble in water due to intermclecular H - bonding with water.



5. *Density of ice is lower than that of water:* In the crystal structure of ice, each O-atom is surrounded by four H-atoms, two of them are covalently bonded and the other two by H-bonds. H-bonds are weaker and hence longer than covalent bonds. Due to this arrangment, ice attains a cage like structure with large empty space. Consequently, the volume of ice is increased. We know that,

Density = Mass/Volume

Thus, density of ice is less than that of water. That is why ice floats in water.

QUESTIONS

PART-A

1. The shape of NH_3 is

   a) Pyramidal b) Tetrahedral

   c) Bent shaped d) V-shaped

2. Maximum electrons present in "s" orbital is

   a) 4 b) 2

   c) 6 d) 1

3. Which orbital is having the lowest energy?

   a) 2s b) 2p

   c) 4s d) 3d

4. Electrons never pair up in p, d or f orbital until all the available sub-orbitals have one electron each. This is called

   a) Pauli's exclusion principle b) Hund's rule

   c) Aufbau principle d) None of these

5. Two atoms with almost equal electronegativities form

a) Electrovalent bond b) Covalent bond

c) Hydrogen bond d) None

6. IF_7 molecule is formed by

a) sp^3d hybridisation b) Sp^3d^2 hybridisation

c) sp^3d^3 hybridisation d) None of these

PART-B

7. Explain sp^3d hybridisation with an example.

8. Write notes on hydrogen bonding.

9. State and explain Hund's rule.

10. Explain s-s and s-p overlap of orbitals.

PART-C

11. Explain VSEPR theory.

12. Explain sp^3d and sp^3d^2 hybridisation with an example.

13. Explain the geometry of C_2H_4 by hybridisation principle.

14. Explain the geometry of BF_3 molecule by VSEPR theory.

15. Explain the consequences of hydrogen bonding.

UNIT - II

ORGANIC CHEMISTRY

PRINCIPLES OF REACTIONS

CLEAVAGE OF BONDS

A covalent bond is nothing but a pair of electrons shared by two atoms. There are two modes of cleavage of a covalent bond.

1. Homolytic bond fission

In homolytic fission, the covalent bond breaks in such a way that each fragment retains a single unpaired electron. Such fragments having one unpaired electron are called *free radicals* or simply *radicals*.

$$A + B \longrightarrow A^{\bullet} + B^{\bullet}$$

This type of cleavage is commonly observed in organic molecules where the covalent bond links two atoms or groups of equal electronegativity.

$$\underset{\text{Ethane}}{CH_3 \vdots CH_3} \longrightarrow \underset{\text{Methyl radicals}}{CH_3^{\bullet} + CH_3^{\bullet}}$$

$$\underset{\text{Propane}}{CH_3 \vdots CH_2 - CH_3} \longrightarrow \underset{\text{Methyl radical}}{CH_3^{\bullet}} + \underset{\text{Ethyl radical}}{CH_3CH_2^{\bullet}}$$

2. Heterolytic bond fission

This type of cleavage usuallyl occurs at a covalent bond between two atoms of different electronegativities. The bond breaks up in such a manner that the pair of electrons remains with one of the fragments producing charged species called *ions.*

$$A - B \longrightarrow A^{+} + :B^{-}$$

$$A - B \longrightarrow :A^{-} + B^{+}.$$

The more electronegative atom or group acquires the electron pair and becomes negatively charged ion (anion). The other atom or group forms the positively charged ion (cation) due to the loss of electrons. A cationic species carrying a positive charge on carbon is called a *carbonium ion* (or *carbo cation*) while the anion carrying a negatively charged carbon centre is termed *carbanion* (or *carbo anion*)

$$CH_3 - X \longrightarrow CH_3^{+} + :X^{-}$$

Carbonium ion

$$CH_3 - H^{+} \longrightarrow :CH_3^{-} + H^{+}$$

Carbanion

ATTACKING REAGENTS

An organic reaction proceeds by the attack of a reagent on a substrate molelcule. Depending on the nature of the attacking reagent, the reaction follows a definite mechanism. Attacking reagents may be broadly divided into two classes :

i) Nucleophiles

ii) Electrophiles

1. Nucleophiles

Nucleophiles are electron rich species which have strong affinity for electron deficient substrates. They have affinity for H^+ which is the smallest nucleus and hence named nucleophiles (*nucleo* = nucleus ; *philic* = loving). They possess an unshared pair of electrons and have the tendency to supply them to the substrate. Nucleophiles can be classified as

i) Negative nucleophiles

ii) Neutral nucleophiles

Negative nucleophiles : are those which carry a negative charge owing to the possession of an electron pair.

Examples

Halide ion	X^-
Hydroxyl ion	OH^-
Ethoxide ion	$C_2H_5O^-$
Amino ion	NH_2^-
Cynide ion	CN^-
Carbanion	R^- (e.g. $CH_3CH_2^-$)

Neutral nucleophiles : possess unshared electron pair (s) but are electrically neutral.

Examples

Ammonia	$:NH_3$
Water	$H - \ddot{\underset{..}{O}} - H$
Alcohol	$R - \ddot{\underset{..}{O}} - H$

2. Electrophiles

Electrophiles are electron deficient species which have strong affinity for electron rich substrates (*electro* = electron; *philic* = loving). Electrophiles usually have six electrons in the outermost orbit and are thus short of a pair of electrons to attain stable electronic configuration. Therefore, they have a tendency to take a pair of electrons from electron rich substrates. Electrophiles are of two types :

i) Positive electrophiles

ii) Neutral electrophiles

Positive electrophiles : are those which carry a positive charge. They are short of a pair of electrons from an octet and hence behave as electron seeking reagents.

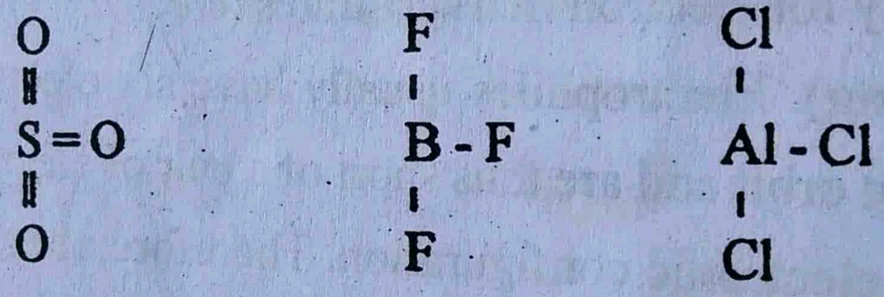
Examples

Proton	H^+

Hydronium ion	H_3O^+
Ammonium ion	NH_4^+
Carbonium ion	R^+ (e.g. CH_3^+)
Chloronium ion	Cl^+
Bromonium ion	Br^+
Nitronium ion	NO_2^+

Neutral electrophiles : are those which have six electrons in the outer most orbit but are electrically neutral..

Examples



REACTION INTERMEDIATES

1. Carbonium ions

Definition

These are organic ions containing positively charged carbon center (carbo cation). The carbon centre has only six electrons in three bonds and has a marked tendency to complete the octet (eight electrons in four bonds). Hence, the carbonium ions are highly reactive. They are formed by the heterolytic fission of a covalent bond.

$$\begin{array}{c} CH_3 \\ | \\ CH_3-C-Cl \\ | \\ CH_3 \end{array} \longrightarrow \begin{array}{c} CH_3 \\ | \\ CH_3-C^+ \\ | \\ CH_3 \end{array} + Cl^-$$

Methods of formation

1. ***Direct ionisation :*** Many organic halides undergo ionisation in a highly polar medium such as SO_2 to form stable carbonium ions.

$$(CH_3)_3C-Cl \longrightarrow (CH_3)_3C^+ + Cl^-$$

t. Butyl chloride

$$(C_6H_5)_3C-Cl \longrightarrow (C_6H_5)_3C^+ + Cl^-$$

Triphenyl chloride

$$CH_2=CH-CH_2Cl \longrightarrow CH_2=CH-CH_2^+ + Cl^-$$

Allyl chloride

2. ***Protonation of unsaturated compounds :*** Carbonium ions may be produced by dissolving olefins, carbonyl compounds and nitriles in proton donating solvents or treating them with Lewis acids.

$$-CH=CH- + H^+ \longrightarrow -\overset{+}{C}H-CH_2$$

$$>C=O + H^+ \longrightarrow >\overset{+}{C}-OH$$

$$-C \equiv N + H^+ \longrightarrow -C^+ = N - H$$

Properties

1. ***Elimination of proton :*** A carbonium ion may eliminate proton to form an olefin

$$\underset{\text{Propyl carbonium ion}}{CH_3 - \overset{\overset{\large H}{|}}{C}H - CH_2} \xrightarrow[-H^+]{} \underset{\text{Propylene}}{CH_3 - CH = CH_2}$$

2. ***Rearrangement to form a more stable carbonium ion***

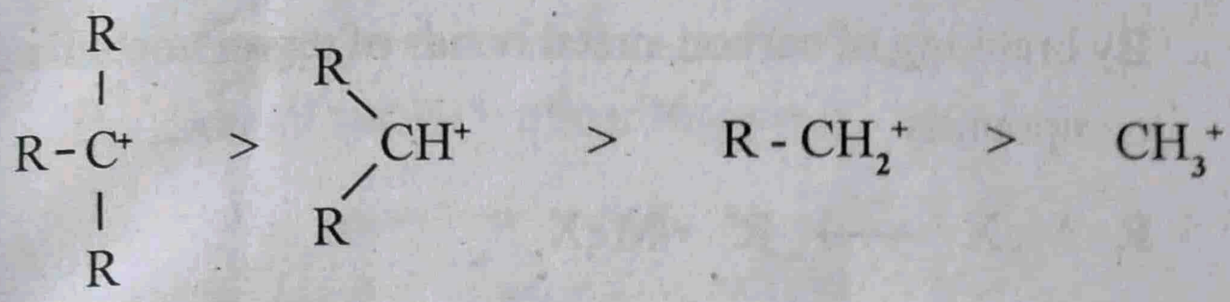
$$\underset{(1^0\text{, less stable})}{CH_3 - CH_2 - CH_2 - \overset{+}{C}H_2} \longrightarrow \underset{(2^0\text{, more stable})}{CH_3 - CH_2 - \overset{+}{C}H - CH_3}$$

3. ***Combination with nucleophile***

$$\underset{\text{Ethyl carbonium ion}}{CH_3\overset{+}{C}H_2 + Br^-} \longrightarrow \underset{\text{Ethyl bromide}}{CH_3CH_2Br}$$

Stability

Tertiary carbonium ion is more stable than secondary carbonium ion which in turn is more stable than primary carbonium ion.

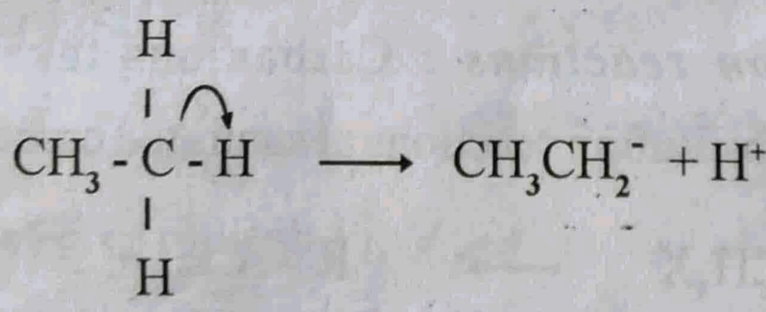


Tertiary Secondary Primary

2. Carbanions

Definition

These are organic ions possessing a negative charge and a pair of electrons on the central carbon atom (carbo anion). They have three bonds and an unshared pair of electrons. The presence of an unshared pair of electrons makes them very reactive. Carbanions are formed by the heterolytic fission of a covalent bond.



Methods of formation

1. By removal of proton from an aromatic hydrocarbon in the presence of a base

$$(C_6H_5)_3CH + OH^- \longrightarrow (C_6H_5)_3C^- + H_2O$$

Triphenyl methane Triphenyl methyl carbanion

.. By breaking of carbon-metal bonds of organometallic compounds

$$R - MgX \longrightarrow R^- + MgX$$

3. By decarboxylation of carboxylate anion

$$RCOO^- \longrightarrow R^- + CO_2$$

Properties

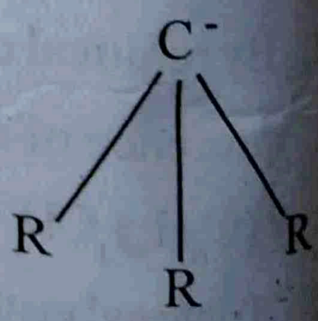
1. Addition reactions : Carbanions add on to the carbonyl group of aldehydes and ketones in condensation reactions.

2. Substitution reactions : Carbanions take part in nucleophilic substitution reactions at saturated carbon atoms.

$$R^- + CH_3X \longrightarrow R - CH_3 + X^-$$

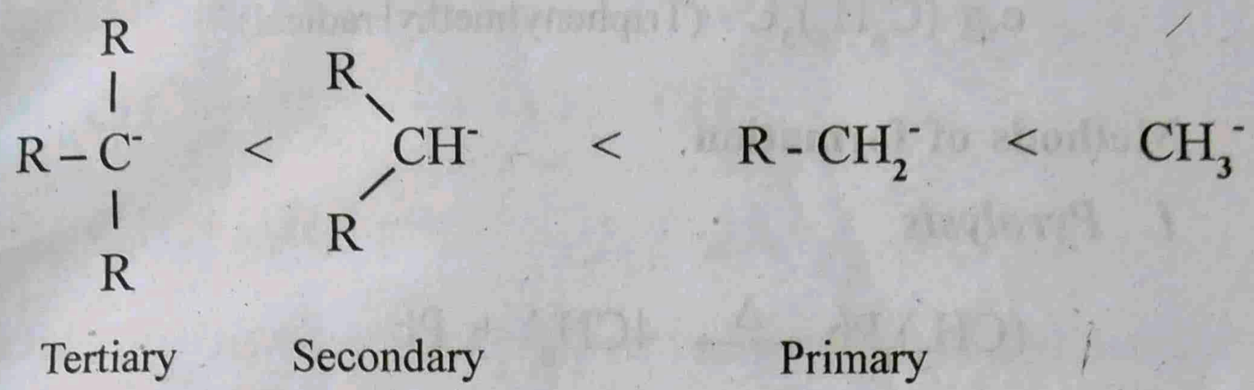
Structure

The carbon centre of a carbanion is in sp^3 hybridized state and the unshared electron pair occupies one of the corners of a regular tetrahedron. This gives rise to a pyramidal shape to the carbanion with a bond angle less than 109°28'.



Stability

The order of stability of carbanions is



3. Free radicals

Definition

Free radicals or radicals are electrically neutral species carrying an unpaired electron. These are formed by the homolytic fission of a covalent bond by heat or light.

$$CH_3 \vdots CH_3 \longrightarrow 2\, CH_3^{\cdot}$$

(Methyl radicals)

Types of Free radicals

Free radicals have been divided into two classes on the basis of their stabilities:

1. ***Short-lived (or transient) free radicals***

$Cl^{\cdot}$	(Chlorine radical)	$OH^{\cdot}$	(Hydroxyl radical)
$CH_3^{\cdot}$	(Methyl radical)	$C_6H_5^{\cdot}$	(Phenyl radical)

$C_6H_5CH_2^{\cdot}$ (Benzyl radical) $(CH_3)_3C^{\cdot}$ (Trimethylmethyl radical)

2. *Long-lived (or stable) free radicals*

e.g $(C_6H_5)_3C^{\cdot}$ (Triphenylmethyl radical)

Methods of formation

1. *Pyrolysis*

$$\underset{\text{TML}}{(CH_3)_4Pb} \xrightarrow{\Delta} \underset{\text{Methyl radical}}{4CH_3^{\cdot}} + Pb$$

$$\underset{\text{Benzoyl peroxide}}{C_6H_5CO\text{-}O\text{-}O\text{-}COC_6H_5} \xrightarrow{\Delta} 2C_6H_5COO^{\cdot} \xrightarrow{-2CO_2} \underset{\text{Phenyl radical}}{2C_6H_5^{\cdot}}$$

$$\underset{\text{Azomethane}}{CH_3\text{-}N{=}N\text{-}CH_3} \xrightarrow{\Delta} \underset{\text{Methyl radical}}{2CH_3^{\cdot}} + N_2$$

2. *Photolysis*

$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{h\nu} \underset{\text{Methyl radical}}{CH_3^{\cdot}} + \underset{\text{Formyl radical}}{CHO^{\cdot}}$$

$$\underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow{h\nu} \underset{\text{Methyl radical}}{CH_3^{\cdot}} + \underset{\text{Acetyl radical}}{CH_3CO^{\cdot}}$$

$$\underset{\text{Chlorine}}{Cl_2} \xrightarrow{h\nu} \underset{\text{Chlorine radical}}{2Cl^{\cdot}}$$

$$\underset{\text{Azobenzene}}{CH_3\text{-}N{=}N\text{-}CH_3} \xrightarrow{h\nu} 2CH_3^{\cdot} + N_2$$

Methane

Properties of Free radicals

1. Dimerisation : Free radicals readily undergo dimerisation to form stable molecules.

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3 - CH_3$$

$$\dot{C}_6H_5 + \dot{C}_6H_5 \longrightarrow C_6H_5 - C_6H_5$$

2. Disproportionation : At higher temperature, ethyl radical undergoes disproportionation to form ethylene and ethane

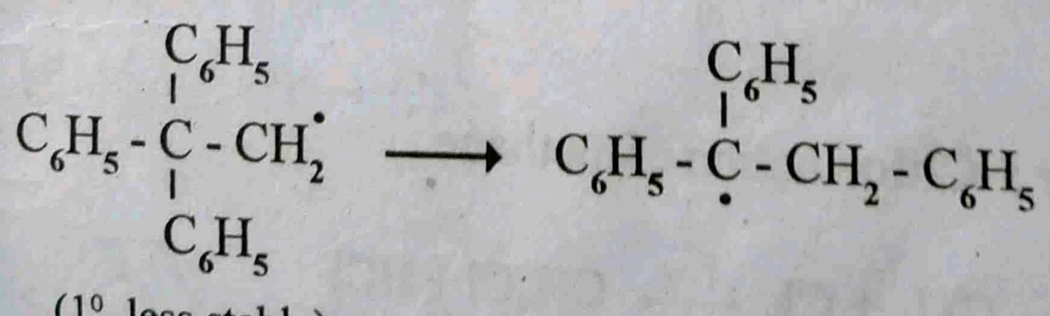
$$CH_3\dot{C}H_2 + CH_3\dot{C}H_2 \longrightarrow CH_2 = CH_2 + CH_3 - CH_3$$

3. Addition reactions : Free radicals react readily with iodine, zinc etc to form addition compounds

$$2\,\dot{C}H_3 + I_2 \longrightarrow 2\,CH_3I$$

$$2\,\dot{C}H_3 + Zn \longrightarrow (CH_3)_2Zn$$

4. Rearrangement : Free radicals undergo rearrangement to form more stable free radical.



(1°, less stable) (2°, more stable)

5. Reaction with olefins : Free radicals add on the double bond of olefins during polymerization reaction.

$$R^{\cdot} + CH_2{=}CH_2 \longrightarrow R{-}CH_2{-}CH_2^{\cdot} \xrightarrow{nCH_2{-}CH_2} {-}(CH_2{-}CH_2{-})_n + R^{\cdot}$$

TYPES OF REACTIONS

Organic compounds undergo different types of reactions such as substitution, addition, elimination, polymerization etc.

1. Substitution reactions

Reactions in which an atom or group linked to carbon is replaced by another atom or group are called *substitution reactions*. There are three types of substitution reactions.

i) Free radical substitution

ii) Electrophilic substitution

iii) Nucleophilic substitution

1. Free radical substitution reactions

These are substitution reactions initiated by free radicals

Example : Chlorination of methane

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$

Mechanism

$$Cl_2 \longrightarrow Cl^{\cdot} + Cl^{\cdot} \text{ (Initiation)}$$

$$CH_4 + Cl^{\cdot} \longrightarrow CH_3^{\cdot} + HCl$$
$$CH_3^{\cdot} + Cl_2 \longrightarrow CH_3Cl + Cl^{\cdot}$$
(Propagation)

$$Cl^{\cdot} + Cl^{\cdot} \longrightarrow Cl_2$$
(Termination)

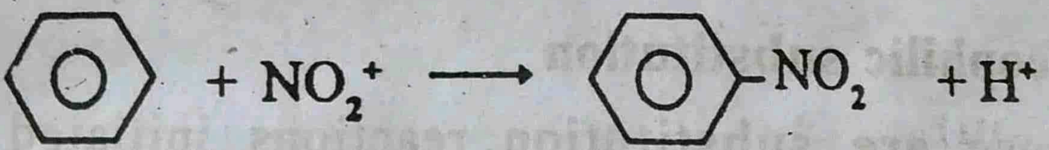
2. Electrophilic substitution

These are substitution reactions initiated by electrophiles. In the case of aromatic compounds, the H - atom of the benzene ring is displaced.

Examples

i) Nitration of benzene

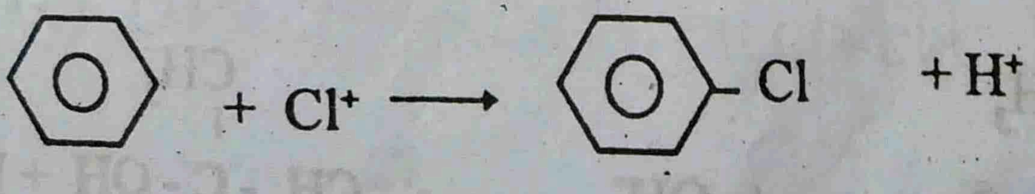
$$HNO_3 + H_2SO_4 \longrightarrow NO_2^+ + HSO_4^- + H_2O$$



(Benzene) (Electrophile) (Nitrobenzene)

ii) Chlorination of benzene

$$Cl_2 \xrightarrow{\Delta} Cl^+ + Cl^-$$



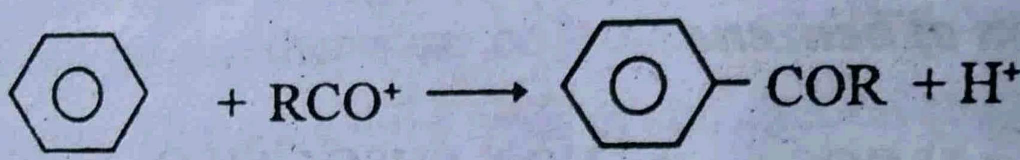
(Benzene) (Electrophile) (Chlorobenzene) *iii) Alkylation of benzene :*

$$RCl + AlCl_3 \longrightarrow R^+ + AlCl_4^-$$

(Benzene) (Electrophile) (Alkylbenzene)

iv) Acylation of benzene

$$RCOCl + AlCl_3 \longrightarrow RCO^+ + AlCl_4^-$$



(Benzene) (Electrophile) (Acylbenzene)

3. Nucleophilic substitution

These are substitution reactions initiated by nucleophiles.

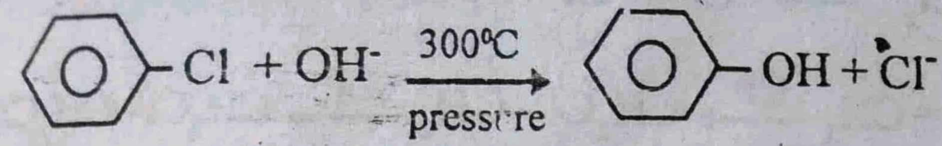
$$RX + OH^- \longrightarrow ROH + X^-$$

(Nucleophile)

Examples

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br + OH^- \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH + Br^-$$

t - Butyl bromide (Nucleophile) (t - Butyl alcohol)



Chlorobenzene Phenol

2. Additoin reactions

Compounds containing a double bond (C=C) or a triple bond (C ≡ C) have a tendency to add a molecule of the attacking reagent (addendum) without eliminating any atom or group. Such reactions are called *addition reactions.*

There are three types of addition reactions.

i) Free radical addition

ii) Electrophilic addition

iii) Nucleophilic addition

1. Free radical addition

Addition of halogens to alkenes in the presence of light takes place by a free radical mechanism

$$Cl_2 \longrightarrow Cl^{\cdot} + Cl^{\cdot} \qquad \text{(Initiation)}$$

$$\left.\begin{array}{l} CH_2{=}CH_2 + Cl^{\cdot} \longrightarrow CH_2Cl - CH_2^{\cdot} \\ CH_2Cl - CH_2^{\cdot} + Cl^2 \longrightarrow CH_2Cl - CH_2Cl + Cl^{\cdot} \end{array}\right\} \text{(Propagation)}$$

$$Cl^{\cdot} + Cl^{\cdot} \longrightarrow Cl_2 \qquad \text{(Termination)}$$

2. Electrophilic addition

Addition of halogens to alkenes in the absence of sunlight is initiated by electrophiles.

$$Cl_2 \longrightarrow Cl^+ + Cl^-$$

$$\underset{\text{Ethylene}}{CH_2=CH_2} \xrightarrow{Cl^+} CH_2Cl-\overset{+}{C}H_2 \xrightarrow{Cl^-} \underset{\text{Ethylene dichloride}}{CH_2Cl-CH_2Cl}$$

3. Nucleophilic addition

Addition of HCN to carbonyl compounds is initiated by the nucleophile, CN^-

$$HCN \longrightarrow H^+ + CN^-$$

$$>C=O \xrightarrow{CN^-} >C(CN)-O^- \xrightarrow{H^+} >C(CN)-OH$$

3. Elimination reactions

Elimination reactions are those in which two atoms or groups are lost from the adjacent carbon atoms to produce a C=C double bond. This is called *1,2 or β - elimination.*

$$\underset{\text{Ethyl bromide}}{\underset{|\quad\;\;|}{\boxed{H\quad Br}}\!\overset{}{CH_2-CH_2}} \xrightarrow{\text{a/c. KOH}} \underset{\text{Ethylene}}{CH_2=CH_2} + HBr$$

$$\underset{\text{Ethyl alcohol}}{CH_2(H)-CH_2(OH)} \xrightarrow{H_2SO_4} \underset{\text{Ethylene}}{CH_2=CH_2} + H_2O$$

4. Polymerisation reactions

The combination of several simple molecules to form a long-chain high molecular weight compound is known as a *polymerisation reaction.* The high molecular weight compound thus formed is called a *polymer* (GK : *poly* = many: *meros* = parts). The simple molecules from which a polymer is formed is called *monomers*. Polymerisation is of two types :

1. Addition polymerization
2. Condensation polymerization

Addition polymerization

These are reactions in which a polymer is formed by the addition of the monomer molecules without eliminating any simple molecule.

Examples

i) $nCH_2 = CH_2 \longrightarrow \left(CH_2\text{-}CH_2 \right)_n$

Ethylene — Polyethylene

ii) $nCH_2 = CHCl \longrightarrow \left(CH_2\text{-}CHCl \right)_n$

Vinyl chloride — Polyvinylchloride

Mechanism

i) Initiation

$R\cdot + CH_2 = CH_2 \longrightarrow R - CH_2 - \dot{C}H_2$

Initiator Manomer

ii) Propagation

$R - CH_2 - \dot{C}H_2 + n\,CH_2 = CH_2 \longrightarrow R \left(CH_2 - \dot{C}H_2 \right)_n$

iii) Termination

$$R-(CH_2-\dot{C}H_2)_n \longrightarrow R\cdot + (CH_2-CH_2)_n$$

Polymer

2. Condensation polymerization

These are reactions in which a polymer is formed by the addition of the monomer molecules followed by elimination of simple molecules like water, methanol etc. Addition followed by elimination of simple molecules is referred to as condensation.

Example 1 **: The condensation of adipic acid and hexamethylenediamine yields nylon 6,6**

$$HOOC(CH_2)_4CO\,\boxed{OH + H}\,HN(CH_2)_6NH_2$$

Adipic acid Hexamethylenediamine

$$\downarrow -H_2O$$

$$HOOC(CH_2)_4CONH(CH_2)_6NH_2$$

$$\downarrow$$

$$-[OC(CH_2)_4CONH(CH_2)_6NH]-_n + nH_2O$$

Nylon 6, 6

Example 2 **: The condensation of ethylene glycol and dimethyl terephthalate yields polyester.**

$$nH]OCH_2CH_2O\,\boxed{H + nCH_3O}\,OC\text{-}C_6H_5CO[OCH_3 \longrightarrow$$

Ethylene glycol Dimethyl terephthate

$$\downarrow -nCH_3OH$$

$$\left[O\text{-}CH_2CH_2OOC\text{-}C_6H_5CO \right]_n$$

Polyester (Dacron)

QUESTIONS

PART-A

1. Homolytic bond fission leads to the formation of

a) Carbonium ion b) Carbanion

c) Free radical d) None of these

2. $CH_3CH_2^-$ is a

a) carbonium ion b) carbanion

c) catalyst d) catalytic poison

3. NH_3 is a

a) electrophile b) free radical

c) nucleophile d) carbonium ion

4. Which is a nucleophile ?

a) H^+ b) OH^-

c) BF_3 d) SO_3

5. BCl_3 is a

a) nucleophile b) electrophile

c) carbonium ion d) carbanion

6. Which one of the following pairs represents a set of electrophiles ?

a) $AlCl_3$ and Cl^+

b) CN^- and NH_3

c) BR^+ and CCl_2

d) H^+ and H_2O

7. Which alkyl radical is the most stable ?

a) methyl

b) primary

c) secondary

d) tertiary

8. .... is a nucleophile

a) H_3O^+

b) $AlCl_3$

c) BF_3

d) NH_3

PART - B

9. Explain the electrophilic substitution reaction in benzene.

10. How are carbonium ions formed ? Mention any two of its properties.

11. Describe the classification of organic reactions with examples.

12. Give any two methods of preparation of carbonium ion ? Write its structure.

13. What are nucleophiles and electrophiles ? Give examples

PART - C

14. Explain the four types of organic reactions with examples

15. Discuss the aromatic electrophilic substitution reaction of benzene with atleast four examples.

16. What are free radicals ? How are they formed ? Mention any two properties of short lived free radicals.

UNIT - III

PHYSICAL CHEMISTRY

PHOTO CHEMISTRY

Introduction

It has been found that some substances are sensitive to light. They undergo chemical reaction when exposed to light. Such reactions are called *photochemical reactions* or *photolysis*. *Photochemistry* mainly concerns with the physical changes and chemical reactions brought about by the low frequency electromagnetic radiations such as visible and UV rays. The chemical reactions brought about by the high frequency radiations like X-rays are studied under *Radiation chemistry* such reactions are called *radiolysis*.

Distinction between Thermal and Photochemical reactions

Thermal or dark reaction	*Photochemical reaction*
i) are initiated by activation due to molecular collisions	are initiated by activation due to absorption of light.
ii) are temperature dependent	are temperature independent.
iii) can occur in darkness	proceed only in light.
iv) reaction rate changes with temperature	reaction rate changes with light intensity

v) have high temperature coefficient	have negligible temperature coefficient.
vi) are always accompanied by decrease of free energy	some of them involve increase of free energy
vii) some of them cannot take place at oridinary temperature	occur invarialy at ordinary temperature

LAWS OF PHOTOCHEMISTRY

1. Grothus-Draper law

When light falls on a substance, a fraction of light is absorbed and the remaining transmitted. It is only the absorbed light that can bring about a chemical change. This is known as *Grothus-Draper law.*

The law is purely qualitative and gives no quantitative relationship between the amount of light absorbed and the number of molecules reacted.

2. Beer-Lambert's law

Beer-Lambert's law states that *when a beam of monochromatic light is passed through a solution containing a light sensitive substance, the intensity of radiation decreases exponentially with increase in the thickness and concentration of the solution.*

Mathematically,

$$I = I_0 e^{-kcx}$$

$$\text{(or) } \ln \frac{I}{I_0} = -kcx$$

$$\text{(or) } 2.303 \log \frac{I}{I_0} = -kcx$$

$$\text{(or) } \log \frac{I}{I_0} = -\frac{kcx}{2.303}$$

$$= -\varepsilon cx$$

where, I_0 = intensity of the incident light

I = Intensity of the transmitted light

x = Thickness of the medium

c = Concentration of the solution

k = Proportionality constant

$\varepsilon = \frac{k}{2.303}$ is called *extinction coefficient*

Significance of the law

Beer-Lambert's law is the basis of colourimetric analysis.

3. Stark-Einstein's law of photochemical equivalence

The law states that each molecule taking part in a photochemical reaction absorbs only one quantum of light

The law implies a quantitative relationship between the number of reacting molecules and the number of quanta of light absorbed.

i) Energy of one quantum of ligh is ε

$$\varepsilon = hv = hc/\lambda$$

where, h = Planck's constant (6.626×10^{-34} J sec)

v = Frequency of light

ii) Energy of one Einstein of light is E

$$E = N\varepsilon = Nhv = Nhc/\lambda$$

where, N = Avogardo number (6.023×10^{23})

Solved Problems

1. Calculate the energy in calories associated with one Einstein of light with wavelength i) 800nm ii) 2000A⁰

i) $E = Nhv = \frac{Nhc}{\lambda}$ $(\because v = c/\lambda)$

$$= \frac{6.023 \times 10^{23} \times 6.626 \times 10^{-34} \times 3 \times 10^{8}}{800 \times 10^{-9}}$$ (1 nm = 10^{-9} m)

$= 1.4958 \times 10^{5}$ J mol^{-1}

$$= \frac{1.4958 \times 10^{5}}{4.184}$$

$= 3.575 \times 10^{4}$ cal mol^{-1}

ii) $E = \frac{Nhc}{\lambda}$

$$= \frac{6.023 \times 10^{23} \times 6.626 \times 10^{-34} \times 3 \times 10^{8}}{2000 \times 10^{-10}} \quad (1A^0 = 10^{-10}m)$$

$= 5.983 \times 10^5$ J mol^{-1}

$$= \frac{5.983 \times 10^5}{4.184}$$

$= 1.43 \times 10^5$ cal mol^{-1}

---

2. Calculate the energy in joules a) per quantum b) per Einstein for radiation of wavelength 1000 A^0

---

i) $\epsilon = \frac{hc}{\lambda}$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{1000 \times 10^{-10}} \quad (1A^0 = 10^{-10}m)$$

$= 1.988 \times 10^{-18}$ J molecule^{-1}

ii) $E = N\varepsilon$

$= 6.023 \times 10^{23} \times 1.988 \times 10^{-18}$

$= 1.196 \times 10^6$ J mol^{-1}

Quantum yield

The efficiency of a photochemical reaction is often expressed in terms of quantum yield which is defined as the number of molecules reacting per quantum of light absorbed.

$$\phi = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of quanta of light absorbed in the same time}}$$

$$\phi = \frac{\text{Number of moles reacting in a given time}}{\text{Number of Einsteins of light absorbed in the same time}}$$

Deviations in Quantum yield

The Einstein's law of photochemical equivalence implies that the quantum yield of photochemical reactions should be unity ($\phi = 1$). But in most cases, ϕ is greater or less than unity. This is due to secondary thermal reactions.

According to Bodenstein, molecules are activated, each molecule absorbing one quantum of light. This is called *primary process.* The molecules thus activated undergo a series of thermal reactions without further absorption of light. These are called *secondary processes.* The quantum yield of a reaction is determined by the nature of the secondary process.

1) Reactions with $\phi = 1$

When the activated molecules instantaneously decompose into the product without entering into secondary processes, the quantum yield becomes unity.

Examples

i) $Cl_2 + O_2 \longrightarrow Cl_2O_2 \qquad \phi = 1$

ii) $H_2 + O_2 \longrightarrow H_2O_2 \qquad \phi = 1$

iii) $H_2S \longrightarrow H_2 + S \qquad \phi = 1$

iv) $C_6H_{14} + Br_2 \longrightarrow C_6H_{13}Br + HBr \qquad \phi = 1$

2. *Reactions with $\phi < 1$*

In this type of reactions, the activated molecules get deactivated to certain extent by collision in the secondary process. That is, the active species of the primary process reunite to give back the reactant molecules in the secondary process. Thus, the quantum yield of the reaction is less that unity.

Examples

i) $2NH_3 \longrightarrow N_2 + 3H_2 \qquad \phi = 0.2$

ii) $H_2 + Br_2 \longrightarrow 2HBr \qquad \phi = 0.01$

iii) $CH_3COOH \longrightarrow CH_4 + CO_2 \qquad \phi = 0.5$

iv) $CH_3COCH_3 \longrightarrow C_2H_6 + CO \qquad \phi = 0.3$

3. *Reactions with $\phi > 1$*

There are phtochemical reactions in which the activated molecules produce free radicals in the primary process. The free radicals may then start subsequent secondary reactions with other molecules without the use of light. As a result, for every quantum of radiation absorbed more than one molecules can enter into reaction. Thus, the quantum yield of such reactions is greater than unity.

Examples

i) $3O_2 \longrightarrow 2O_3 \qquad \phi = 2$

ii) $2HI \longrightarrow H_2 + I_2 \qquad \phi = 2$

iii) $2NO_2 \longrightarrow 2NO + O_2 \qquad \phi = 2$

iv) $2HClO \longrightarrow 2HCl + O_2 \qquad \phi = 4$

In some cases, a series of secondary processes involving several thousands of molecules may take place. This leads to a *chain reaction* with very high quantum yield.

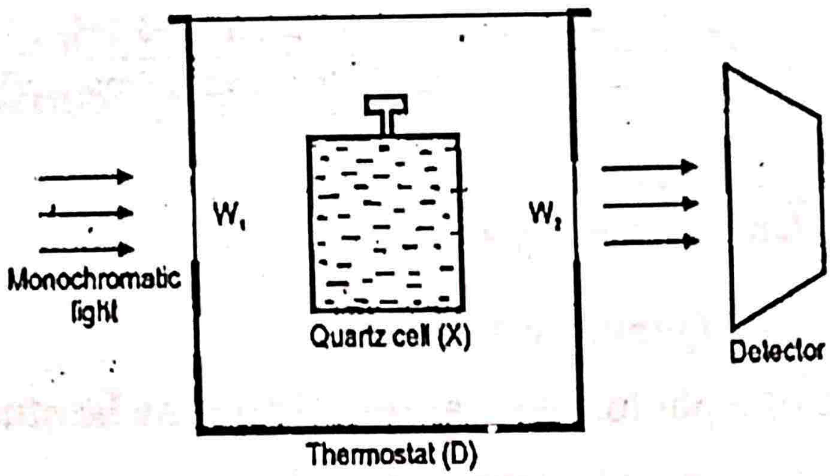
Examples

i) $CO + Cl_2 \longrightarrow COCl_2 \qquad \phi = 10^3$

ii) $H_2 + Cl_2 \longrightarrow 2HCl \qquad \phi = 10^4 - 10^6$

Determination of Quantum yield

The experimental arrangement for the measurement of quantum yield is schematically given below :



i) The reaction mixture is taken in a glass or quartz cell X with optical plane windows W_1 and W_2. The cell is kept in a thermostat, D. A narrow beam of monochromatic light is allowed to pass through the reaction mixture for a known time. The reaction mixture absorbs a portion of light. The residual portion of light is then allowed to enter a detector which measures the light intensity. Thermopiles or Chemical actinometers are generally used as detectors.

Then, the intensity of light is determined keeping the reaction vessel empty. In case of solutions, it is filled with the solvent. The difference between the two readings will give the amount of light energy (Einstein) absorbed by the reaction mixture.

ii) The rate of reaction of the mixture under investigation is determined by the usual methods used in chemical kinetics. This gives the number of moles reacting in a given time.

$$\phi = \frac{\text{No. of moies reacting in a given time}}{\text{No. of Einsteins absorbed in the same time}}$$

$$= \frac{\text{Rate of the reaction}}{\text{Amount of energy absorbed}}$$

Significance of Quantum yield

1. The rate of a photochemical reaction may be studied by the measurement of quantum yield.

2. The nature of a reaction can be determined from its quantum yield. A chain reaction has very high quantum yield whereas a thermal reaction will have zero quantum yield.

Photophysical processes

Absorption of light lifts the atoms or molecules of a material to an excited state. Since the excited state is unstable, the atoms or molecules return to the ground state with emission of light. This is a photophysical process and the light thus emitted has the same or higher wavelength than that of the incident light.

Types of Photophysical process

1. Fluorescence

Definition : When a beam of light (visible or UV) is allowed to fall on certain substances, they emit visible light which stops as soon as the incident light is cut off. This phenomenon of instantaneous emission of light is called *fluorescence*. The light thus emitted has the same wavelength as that of the incident light.

Examples

i) Minerals - Fluorite (natural CaF_2), Petroleum, uranyl sulphate

ii) Dyes - Fluorescein, eosin

iii) Metals - Vapours of mercury and sodium.

2. Phosophorescence

Definition : What a beam of light (visible or UV) is allowed to fall on certain substances, they emit visible light which persists for some more time even after the incident light is cut off. This phenomenon of delayed emission of light is called *phosphorescence*. The light thus emitted will have wavelength greater than that of the incident light.

Examples

i) Phosphors (CaS, SrS, BaS)

ii) Zinc sulphide

iii) Dyes in fused boric acid

iv) Aspirin, cocaine, procain, nicotine

Distinction between Fluorescence and Phosphorescence

Fluorescence	*Phosphorescence*
i) instantaneous process	delayed process
ii) life-time is short	life-time is long
iii) stops as soon as the incident light is cut off.	persists for some time even after the incident light is cut off.
iv) given by gases, liquids and solids.	given mostly by solids.
v) less selective and sensitive	more selective and sensitive
vi) carried out with visible or UV light at room temperature	carried out mostly with UV light at low temperature

3. Chemiluminescence

Definition

The phenomenon of emission of visible light as a result of chemical reaction at a temperature at which a black body normally does not emit visible light is known as *chemiluminescence*. It is the reverse of photochemical reaction which occurs by absorption of light.

Examples

i) Yellow phosphorus glows with a greenish yellow light. It is due to the oxidation of phosphorus vapour by atmospheric oxygen.

$$4P + 5O_2 \longrightarrow 2P_2O_5 + h\nu$$

ii) When a solution of strontium chloride is added to dil.H_2SO_4 in the dark, a feeble glow is observed.

$$SrCl_2 + H_2SO_4 \longrightarrow SrSO_4 + 2HCl + h\nu$$

iii) A red light is emitted when Cl_2 or hypochlorite ion is oxidised by alkaline H_2O_2 solution.

iv) A solution of p - bromophenyl magnesium bromide in ether undergoes oxidation by air emitting a brilliant green light even in day time.

v) A red light is emitted when a mixture of pyrogallol and formaldehyde is oxidised by hydrogen peroxide.

vi) When a stream of atomic hydrogen is allowed to fall on the surface of mercury, a blue light appears.

vii) When a mixture of siloxene and rhodamine - B (dye) is oxidised by acidified $KMnO_4$ solution, a red light characteristic of the dye is observed. This is an example of sensitised chemiluminscene.

4. Bioluminescence

Definition

Certain living organisms emit visible light as a result of chemical reaction. This phenomenon of chemiluminescence in living organisms is called *bioluminiscence.*

Examples

i) Fire-flies produce an yellowish green light. It is believed to be due to the oxidation of luciferin, a protein by atmospheric oxygen in the presence of an enzyme luciferase. The intensity of light thus emitted is very low and hence observed only in the dark.

ii) Certain marine animals like jelly-fish emit visible light.

iii) Fox-fire which occurs in marshy places is probably due to some luminous bacteria present in the decaying wood.

5. Thermoluminescence

Definiton

Certain substances can absorb light at room temperature and emit it as visible light at higher temperatures. This phenomenon is known as *thermoluminescence.*

Example

Phosphor (SrS) is illuminated with light at room temperature. Then, the light is turned off and the phosphor is heated steadily at the rate of 2.5° per second. Visible light is emitted and its intensity increases upto a certain temperature and then decreases.

Photochemical processes

1. Photosensitisation

Definition : There are some photochemical reactions in which the reacting substances are not light sensitive. They are unable to absorb light directly. However, when a light sensitive material is added, it absorbs light and passes on the absorbed light to the reactants without itself taking part in the reaction. Such an added material is known as a *photosensitiser* and the phenomenon is called *photosensitisation*.

Examples : i) Plants synthesise carbohydrate by reaction between atmospheric CO_2 and H_2O. Being colourless, CO_2 and H_2O can not absorb light but chlorophyll which is a green pigment can do so. Thus, chlorophyll present in plant leaves absorbs light and passes on the absorbed light to CO_2 and H_2O molecules. Thus, the reaction starts in the process of photosynthesis (*photo* = ligh; *synthesis* = to build up)

$$\text{Chlorophyll} + h\nu \longrightarrow [\text{Chlorophyll}]^*$$

$$CO_2 + H_2O + [\text{Chlorophyll}]^* \longrightarrow 1/6\,(C_6H_{12}O_6) + O_2 + \text{Chlorophyll}$$

ii) The dissociation of molecular hydrogen into atomic hydrogen is photosensitised by mercury vapour.

$$Hg + h\nu \longrightarrow Hg^*$$

$$Hg^* + H_2 \longrightarrow Hg + 2H$$

iii) Chlorine acts as a photosensitiser in the decomposition of ozone by UV light.

$$Cl_2 + h\nu \longrightarrow 2Cl$$

$$Cl + O_3 \longrightarrow ClO_3$$

$$2\,ClO_3 \longrightarrow Cl + 3O_2$$

iv) The decomposition of oxalic acid is photosensitized by uranyl sulphate.

$$UO_2SO_4 \longrightarrow UO_2^{2+} + SO_4^{2-}$$

$$UO_2^{2+} + h\nu \longrightarrow [UO_2^{2+}]^*$$

$$[UO_2^{2+}]^* + \begin{matrix} COOH \\ | \\ COOH \end{matrix} \longrightarrow UO_2^{2+} + CO_2 + CO + H_2O$$

QUESTIONS

PART - A

1. The quantum yield of N_2 and H_2 photochemical reaction is

a) 1 b) < 1

c) > 1 d) None of these

2. Plants synthesise their food by the process

a) Photosynthesis b) Fluorescence

c) Phosphorescence d) Luminescence

3. Absorption of light by chlorophyll of plant leaves is an example of

a) fluorescence b) phosphorescence

c) photosensitization d) chemiluminscence

4. The quantum yield of H_2 - Br photochemical reaction is

a) < 1 b) 1

c) > 1 d) None of these

5. $2HI \xrightarrow{h\nu} H_2 + I_2$

The quantum yield of this photochemical reaction is

a) 10^2 b) 10^3

c) 2.0 d) 0.01

6. The element which exhibits photosensitization is

a) cadmium b) calcium

c) chlorine d) sodium

7. Fire-flies emit light in the night due to

a) Chemiluminescence b) Thermoluminescence

c) Bioluminescene d) Fluorescence

PART - B

8. Explain the laws of photochemistry.

9. What do you understand by photochemical reaction ? How can the rate of such a reaction studied ?

10. Define and explain the quantum yield of photochemical reaction.

11. Explain Stark-Einstein's law and quantum yield.

12. What is meant by quantum yield ? How can we determine the nature of a photochemical reaction with quantum yield ?

13. What is quantum yield ? How is it measured ?

14. Bring out the differences between thermal and photochemical reactions.

15. Write a note on photosensitization.

PART - C

16. State and explain the various laws of photochemistry.

17. Write notes on :

i) Fluorescence

ii) Phosphorescence

iii) Chemiluminescence

18.i) Explain th
law.
ii) Write sho

19. Distinguish
i) Thermal a
ii) Phosphor

20. What is mear
stand by phot

21. What is quant
of certain reac

18.i) Explain the Grothus - Draper law and Beer - Lambert's law.

ii) Write short notes on photosynthesis.

19.Distinguish the following:

i) Thermal and photochemical reactions.

ii) Phosphorescence and fluorescence

20.What is meant by photochemistry ? What do you understand by photosynthesis ?

21.What is quantum yield ? Explain why the quantum yield of certain reactions very high.

UNIT - IV

POLYMER CHEMISTRY

Monomers

A polymer is made up of many small molecules. The individual small molecules from which the polymer is made are called *monomers* (meaning, single part). The monomers are usually the repeating chemical units which are held together by covalent bonds in a polymer. For example, ethylene is the monomer or repeating unit of polythylene (polymer).

Polymers

A polymer (GK : *poly* = many ; *meros* = parts or units) is a macromolecule of very high molecular weight. The molecular weight of a polymer is in the range of 10,000 to several millions. For example, polybutadiene (synthetic rubber) has a molecular weight of about 2,00,000.

A polymer may be defined as *a macromolecule containing a number of repeating chemical units held together by covalent bonds.*

Oligomers

A low molecular weight macromolecule composed of a few repeating units is termed a *oligomer* (*oligo* meaning a few). Oligomers are usually liquid polymers of molecular weight of the order of 2,000 or so.

CLASSIFICATION OF POLYMERS

Polymers may be classified in different ways :

1. Natural and Synthetic polymers

i) **Natural polymers :** These are the polymers which are isolated from natural materials. Typical examples are : Cellulose, starch, silk, wool, shellac and rubber.

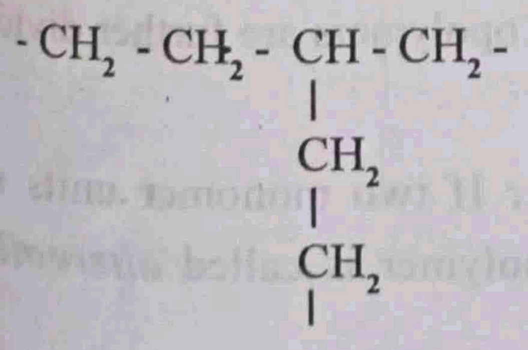
ii) **Synthetic polymers :** These are the polymers which are synthesised from low molecular weight compounds. Typical examples are : Polyethylene, PVC, nylon and terylene.

2. Linear, Branched and Net work polymers

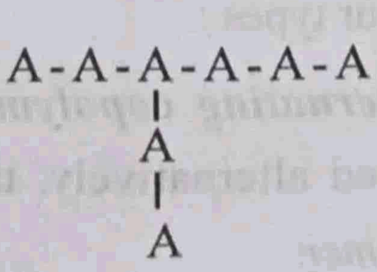
i) Linear polymers : These are polymers in which the monomeric units are linked in a linear fashion to form a straight chain

$-CH_2-CH_2-$ $\qquad$ $-A-A-A-A-A-A-$

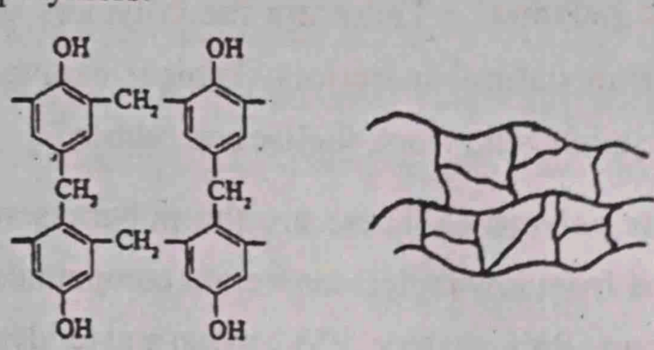
ii) Branched polymers : These are polymers in which some of the monomeric units are attached as side chains to the main linear chain.



(LDPE)



iii) Net work polymers : These are polymers in which many chains are cross-linked through side chains at random positions. These are having a network of chain segments in all the three dimensions. Thus, cross-linked polymers are also known as network polymers.



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3. Homopolymers and Copolymers

i) Homopolymers : Polymers containing identical monomeric units are called *homopolymers.*

$$-A-A-A-A-A-A-A-$$

Examples : $\left(CH_2 - CH_2 - CH_2 - CH_2 \right)_n$

(Polyethylene)

ii) Copolymers : Polymers having different types of momeric units are called *copolymers.* Copolymers are further divided into four types :

a) Alternating copolymers : If two monomer units are arranged alternatively, the polymer is called *alternating copolymer.*

-A-B-A-B-A-B-

Example : Vinyl chloride (A) - Vinylidene chloride (B) copolymer

*b) **Random copolymer :*** A random copolymer has the different monomer units arranged in a chain at random.

-A-B-A-A-B-B-B-

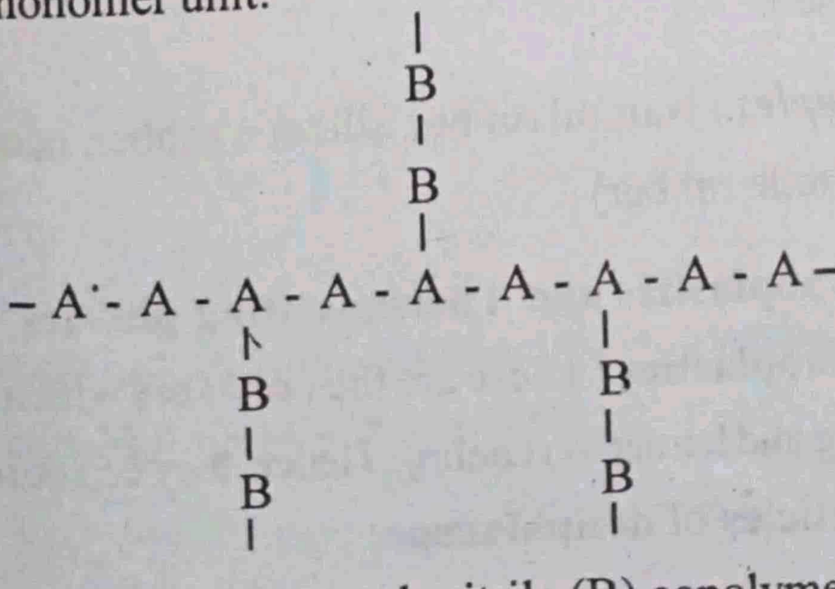
Example : Sty rene (A) - Butadiene (B) copolymer

*c) **Block copolymer :*** In block copolymer, the different monomers are arranged in blocks.

-A-A-A-A-B-B-B-A-A-A-

Example : Styrene (A) - Isoprene (B) copolymer

*d) **Graft copolymer :*** In graft copolymer, the main chain is made of one monomer unit while the branch chains are made of another monomer unit.



Example : Styrene (A) - Acrylonitrile (B) copolymer

4. Plastics, Fibres and Elastomers

i) Plastics

* Plastics are materials which can be moulded into any desired shape by the application of heat and pressure.

* *Examples :* Polyethylene (PE), polypropylene (PP), polystyrene (PS), PVC.

ii) Fibres

* Fibres are polymeric materials which can be drawn into long filaments or threads.

* A fibre is atleast 100 times its diameter.

* *Examples :* Nylon, terylene, orlon

iii) Elastomers

* Elastomers are rubber like materials that can be stretched to atleast twice its original length by applying force.

* They come back to their original length when the force is released.

* *Examples :* Natural rubber, silicone rubber, neoprene (synthetic rubber)

5. Thermoplastics and Thermosetting plastics

i) Thermoplastics : These are the polymers which soften on heating and harden on cooling. Hence, they can be remoulded into articles of desired shape.

Examples : Polyethylene, polypropylene, polystyrene. polyvinyl chloride (PVC), nylon

ii) **Thermosetting plastics :** There are rigid polymers which soften on heating and set to a hard infusible mass on cooling. Once set, they can not be remoulded.

THERMOPLASTICS

1. Polyethylene (or polythene)

There are two varieties of polyethylene.

a) High density polyethylene (HDPE)

b) Low density polyethylene (LDPE)

a) High density polyethylene

Preparation

High density polyethylene (HDPE) is prepared under low pressure (2 - 4 atm) and at temperature in the range of 50 - 75°C using triethyl aluminium - titanium tetrachloride catalyst (Ziegler - Nutta catalyst)

$$\underset{\text{Ethylene}}{n\,CH_2=CH_2} \longrightarrow \underset{\text{HDPE}}{\left(CH_2 - CH_2 \right)_n}$$

Uses

HDPE is used for making toys, detergent bottles and household articles like buckets, dust bins etc.

b) Low density polyethylene (LDPE)

Preparation

Low density polyethylene is prepared under high pressure and at temperature in the range of 180 - 250°C using oxygenas the initiator.

$$n\ CH_2=CH_2 \qquad\qquad -\!\!\left(CH_2-\underset{\underset{\underset{|}{CH_2}}{|}}{\underset{CH_2}{\underset{|}{CH}}}-CH_2\right)\!\!-_n$$

Ethylene — LDPE

Uses

i) LDPE films are used for packing frozen foods, bakery items and textile products.

ii) LDPE sheets are used as table cloths.

iii) LDPE pipes are used for irrigation purposes.

iv) LDPE is used in cable insulation in rador, TV and telephone.

2. Polypropylene (PP)

Preparation

Polypropylene is produced by the polymerisation of propylene using Ziegler - Natta catalyst (e.g. $Et_3Al - TiCl_4$)

$$n\ CH_2=\underset{\underset{CH_3}{|}}{CH} \longrightarrow -\!\!\left(CH_2-\underset{\underset{CH_3}{|}}{CH}\right)\!\!-_n$$

Propylene — PP

Uses

i) PP is used for making components of refrigerator, radio, T.V and washing machine.

ii) It is also used for making automobile seat covers, carpets, ropes, pipes, package films and storage tanks.

3. Polystyrene (PS)

Preparation

Polystyrene is prepared by the polymerisation of styrene at 90⁰C using benzoyl peroxide initiator.

$$n\,CH_2=\underset{\substack{|\\ C_6H_5}}{CH} \longrightarrow -\!\!\left(CH_2-\underset{\substack{|\\ C_6H_5}}{CH}\right)\!\!-$$

Styrene → PS

Uses

Polystyrene is widely used for making TV cabinets, toys, jars, bottles, combs, buttons, buckles and refrigerator parts.

4. Polyacrylonitrile (PAN)

Preparation

PAN is prepared by the polymerisation of acrylonitrile using peroxide initiators.

$$n\,CH_2=\underset{\substack{|\\ CN}}{CH} \longrightarrow -\!\!\left(CH_2-\underset{\substack{|\\ CN}}{CH}\right)\!\!-_n$$

Acrylonitrile → PAN

Uses

i) PAN is used to produce synthetic fibres such as acrylon, orlon etc.

ii) It is copolymerised with butadiene to produce nitrile rubber.

5. Polyvinyl chloride (PVC)

Preparation

PVC is prepared by the emulsion polymerisation of vinyl chloride at 20^0C under pressure in the presence of benzoyl chloride in an outoclave.

$$n\,CH_2=\underset{\underset{Cl}{|}}{CH} \longrightarrow \left(CH_2-\underset{\underset{Cl}{|}}{CH}\right)_n$$

Vinyl chloride → PVC

There are three varieties of PVC

i) Rigid PVC

ii) Plasticized PVC

iii) Chlorinated PVC

Uses

i) Rigid PVC is used for making irrigation and drainage pipes.

ii) Rigid PVC sheets are employed for making trays, helmets and mud guards.

iii) Rigid PVC dissolved in plasticizers give flexible or plasticized PVC. It is used for making sofa cover, automobile seat cover and canvas shoes.

iv) Chlorinated PVC is produced by dissolving rigid PVC in chlorobenzene. The main use of chlorinated PVC is to produce adhesives, coatings and fibres (e.g. Saran and Vinyon)

6. Nylon

Aliphatic polyamides are generally called *nylons*. There are a number of varieties of nylons :

i) Nylon - 6,6

ii) Nylon - 6

iii) Nylon - 10, 6

iv) Nylon - 11

The number indicates the number of carbon atoms present in the monomer molecules from which the polymer is made.

a) Nylon 6,6

Preparation

Nylon 6, 6 is produced by the polycondensation between adipic acid and hexamethylene diamine.

$$n\,HOOC\,(CH_2)_4\,COOH + n\,H_2N\,(CH_2)_6\,NH_2$$

(Adipic acid) (Hexamethylene diamine)

$$\downarrow$$

$$-\!\!\left[OC(CH_2)_4CONH\,(CH_2)_6\,NH \right]\!\!-_n + n\,H_2O$$

Nylon 6, 6

Uses

i) About 60% of nylon 6, 6 production goes to make carpets, parachute cloth, glider rope, conveyor belt, fishing net, socks and under garments.

ii) About 10% of nylon 6, 6 is used to produce tyre cords.

iii) It is also used as a substitute for metals in gears and bearings. Nylon moving parts do not require lubrication.

b) Nylon 6

Preparation

Nylon 6 is prepared by the ring opening polymerisation of a polyamide e.g. caprolactam.

$$\underbrace{\overline{\lfloor HN\,(CH_2)_5\,CO \rfloor}}_{\text{Caprolactam}} \longrightarrow \underbrace{-\!\!\left(HN\,(CH_2)_5\,CO \right)\!\!-_n}_{\text{Nylon 6}}$$

A mixture of caprolactam, water and acetic acid is introduced into a reactor in the presence of nitrogen. The mixture is heated to 25°C for 12 hours at 15 atm pressure. After polymerisation, the unreacted monomer and the low molecular weight polymer are removed by washing with water before nylon 6 is melt spun.

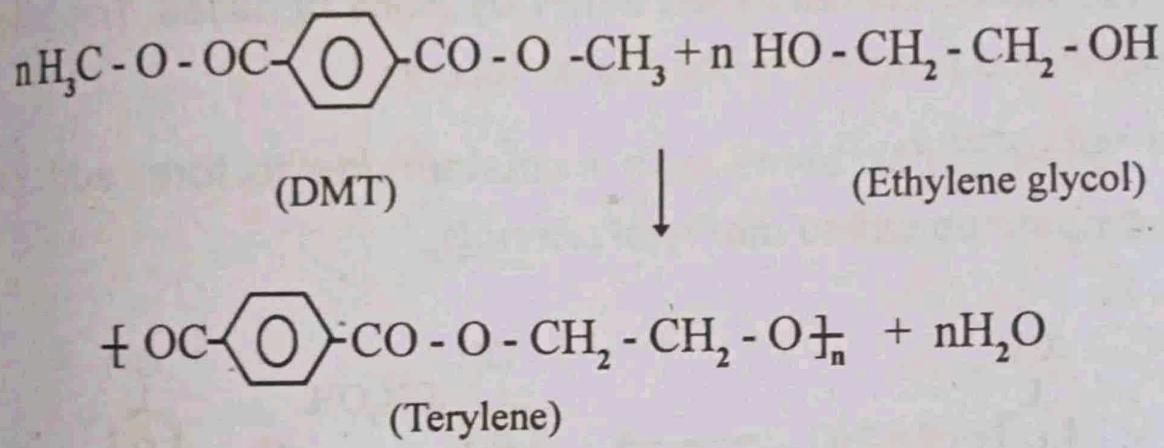
Uses

Nylon 6 is used for the manufacture of tyre cord and non-woven fabrics.

7. Polyester (Terylene)

Preparation

Polyethyleneterephthalate (PET) is a polyester which is sold in the market under the name *terylene* (in England) and *dacron* (in USA), It is prepared by the condensation of dimethyl terephthalate (DMT) with ethylene glycol.



Uses

i) Polyester is extensively used to make textile fibres. Garments made from polyester fibres resist the formation of wrinkles. They retain crease and can be washed repeatedly without subsequent ironing (wash and wear cloths)

ii) PET is made unto film called *mylor* which is used for making cassette tapes and photographic films.

iii) Polyester fibres are used in the manufacture of conveyor belts, fishing nets, parachute cloth, glider ropes and felts (thermal insulator in refrigerators).

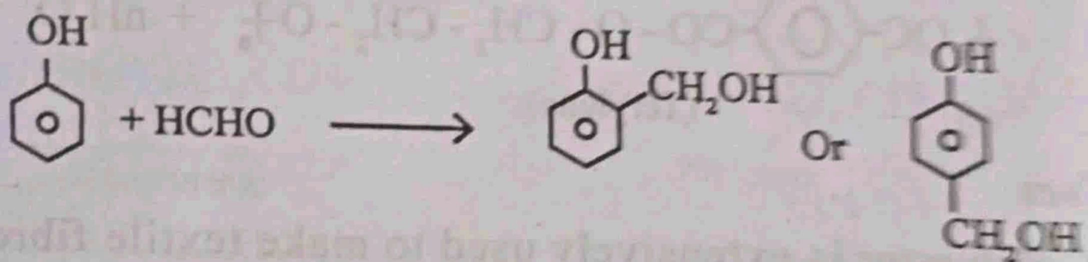
1. THERMOSETTING PLASTICS

1. Phenol-formaldehyde resins

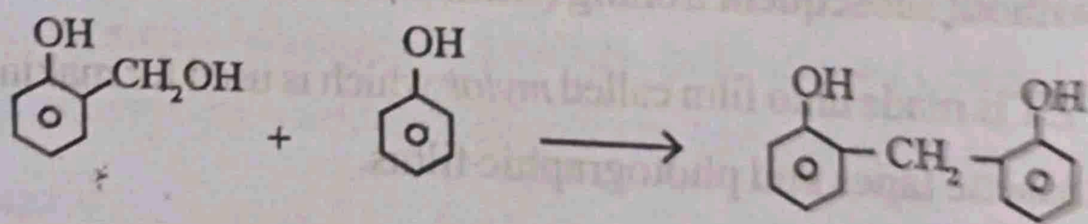
Preparation

Phenol fromaldehyde (PF) resins are obtained by the polycondensation reaction between phenol and formaldehyde. The reaction is catalysed either by acids or bases. The base catalysed reaction proceeds as follows:

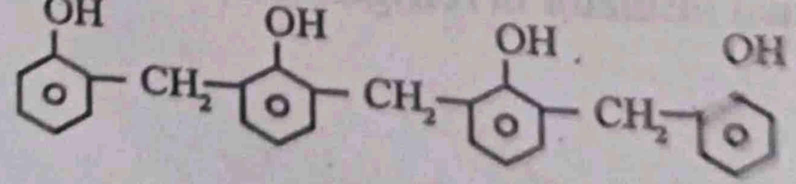
1. Phenol combines with formaldehyde to form addition compounds called *methylol phenols.*



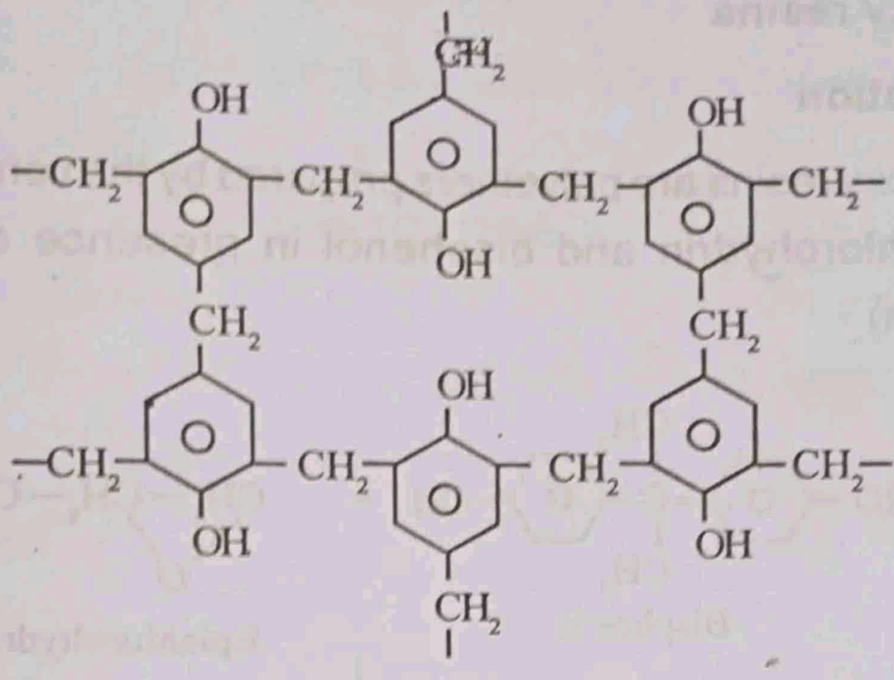
2. Further condensation between the methylol phenols and phenols occurs to form compounds with *methylene bridges.*



3. The reaction continues and a linear polymer called *resol* is formed.



4. Resol on heating gets converted into a cross-linked three-dimensional polymer called *bakelite*.



Uses

i) Phenolic resins are widely used as adhesives for plywood, in cementing electric bulbs, for making adhesive wheels, sand paper and brake linings.

ii) Phenolic resins compounded with wood, paper or convas cloth are used in making decorative laminates. (eg. sun mica sheets). Laminates are used for counter tops, wall coverings, wall clock cases and TV cabinets.

iii) Phenolic resin compounded with absestos powder or sawdust is called *bakelite*. It is used for making electric switches and plugs, telephone parts etc.

iv) The resol type resin is used for making plastic articles.

v) The alkaline solution of PF resin is used as protective coatings (paints, varnishes and lacquers).

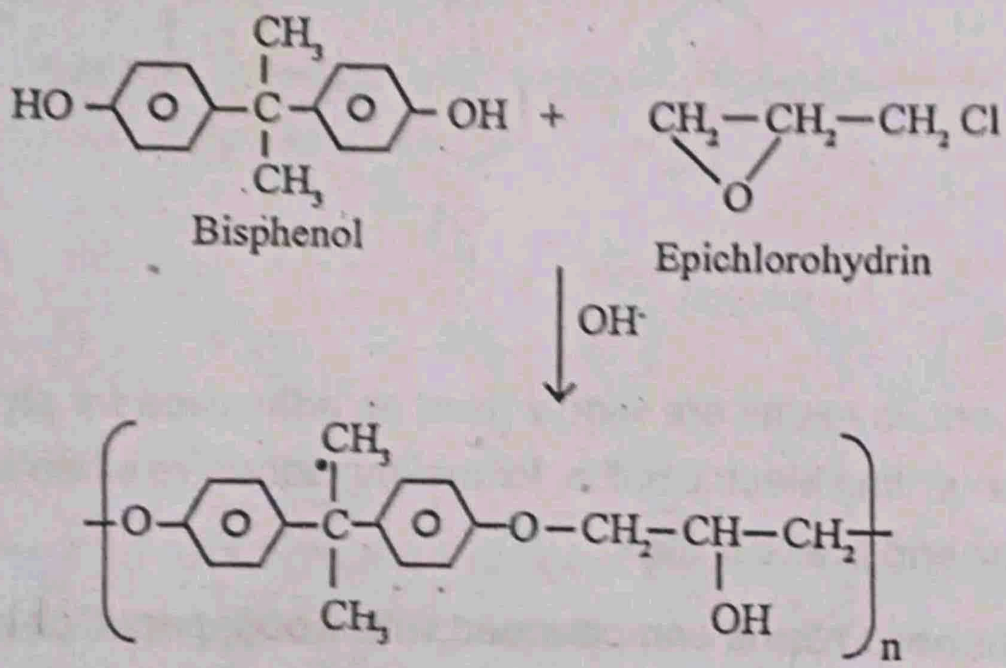
vi) PF resin is used as cation exchange resin in water softening.

vii) Resols mixed with sand find use as binders in foundaries.

2. Epoxy resins

Preparation

Epoxy resins are polyethers prepared by the condensation of epichlorohydrin and bisphenol in presence of a base (catalyst)



Epoxy resin

Uses

i) The liquid epoxy resins (e.g. Araldite, M-seal) are used as adhesives for glass, metals, etc.

ii) Expoxy resins compounded with polysulphides or polyamides give very tough materials. These are used as surface coatings for skid resistant roads in highways and in industrial flooring.

iii) They are applied on cotton, rayon and bleached fibres to impart crease resistance and shrinkage control.

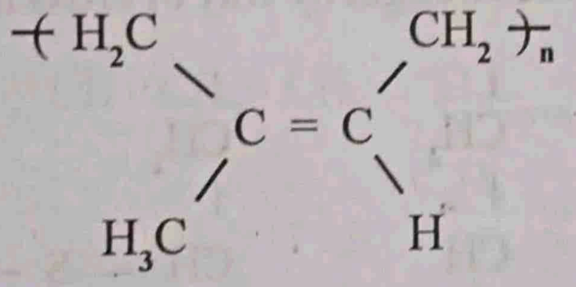
iv) They are used as dental cement.

v) The cured epoxy resins are used to mould aircraft and automobile parts.

ELASTOMERS

1. Natural rubber

Natural rubber is a high molecular weight polymer of isoprene, in which the isoprene units have the cis - 1,4 configuration.



(Cis 1, 4 - Polyisoprene)
Natural rubber

Preparation

Natural rubber is obtained from the saps (latex) of rubber trees especially *Hevea brasiliensis*. The latex is diluted and treated with 1% acetic acid (coagulant). The coagulated mass of solid rubber is washed and sent through rollers when rubber sheets are obtained.

Uses

Natural rubber is used for making automobile tyres and tubes.

Drawbacks of Natural rubber

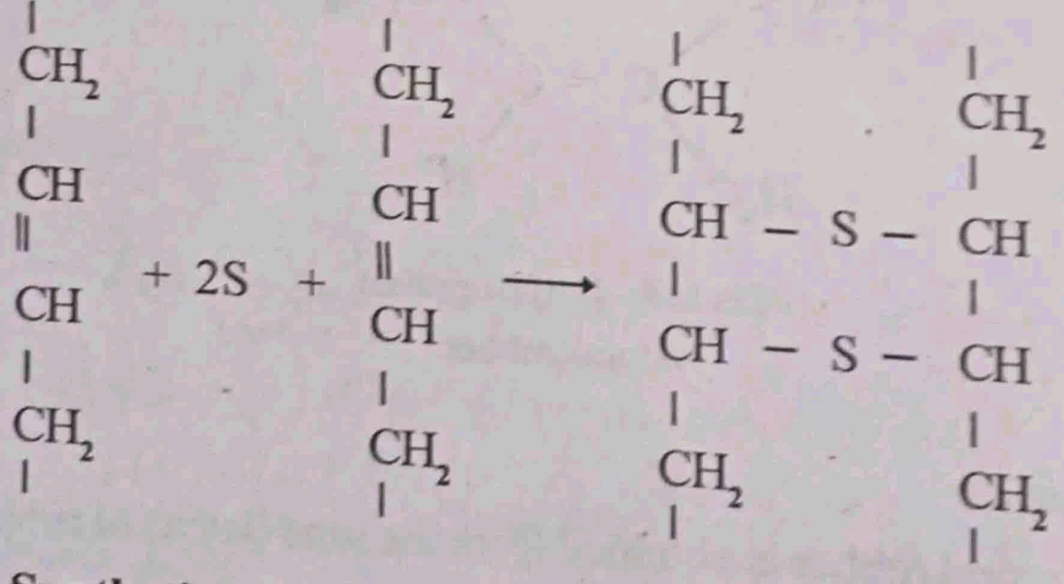
i) It becomes soft and sticky at high temperature and is too brittle at low temperature.

ii) It perishes due to oxidation in air

iii) It swells in organic solvents and gradually disintegrates.

iv) It has low tensile strength.

The above properties of natural rubber make it unsuitable for use as automobile tyres and tubes. To improve the properties, rubber is cured by what is known as *vulcanization*. It is carried out by heating rubber with sulphur or S_2Cl_2. Vulcanination improves the tenside strength by way of cross linking.



2. Synthetic rubber

Man - made rubber - like polymers are termed *synthetic rubbers*. Copolymers of butadiene and styrene (SBR) and those of butadiene and acrylonitrile are two commercially important synthetic rubbers. In early days, sodium metal suspended in mineral oil was used as the initiator and hence the butadiene rubbers were named *Buna rubbers.*

a) Styrene rubber (SBR or Buna - S)

Preparation

It is a copolymer of styrene with butadiene (SBR). It is made by emulsion polymerisation of styrene and butadiene using cumene hydroperoxide as initiator.

$$m\ CH_2=CH-CH=CH_2 \ (\text{Butadiene}) + nCH_2=CH(C_6H_5) \ (\text{Styrene})$$

$$\downarrow$$

$$-\!\!\left(CH_2-CH=CH-CH_2-CH_2-\underset{\displaystyle C_6H_5}{CH}\right)\!\!-_{m+n}$$

(Buna - S)

Uses

i) SBR is a good substitute for natural rubber in making automobile tyres.

ii) It is superior to natural rubber for the manufacture of conveyor belts, shoe soles, gloves, tank lining, floor tiles, gaskets and electrical insulation.

b) Nitrile rubber (Buna - N)

It is a copolymer of acrylonitrile with butadiene (ANBR). It is prepared by emulsion polymerisation of acrylonitrile and butadiene using azo initiators.

$$m\ CH_2=CH-CH-CH_2 + n\ CH_2=\underset{\displaystyle CN}{\underset{|}{CH}}$$

(Butadiene) Acrylonitrile

$$\downarrow$$

$$\left(CH_2-CH=CH-CH_2-CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}\right)_{m+n}$$

(Buna - N)

Uses

i) Nitrile rubber has better oil resistance than natural rubber and hence used for making hoses for oil transport.

ii) It is also used as oil seals (oil resistant cable insulation)

c) Neoprene rubber

Preparation

Polychloroprene is called neoprene. It is made by the emulsion polymerisation of chloroprene.

$$n\ CH_2=\underset{\displaystyle Cl}{\underset{|}{C}}-CH=CH_2 \longrightarrow \left(CH_2-\underset{\displaystyle Cl}{\underset{|}{C}}=CH-CH_2\right)_n$$

(Chloroprene) Polychloroprene (Neoprene)

Uses

Neoprene rubber has better oil resistance than natural rubber and hence used for making industrial hoses to carry oil and for oil resistant cable insulation.

QUESTIONS

PART - A

1. The polymer formed between styrene and isoprene is classified under
   a) Random copolymer b) Alternating copolymer
   c) Block copolymer d) Graft copolymer

2. The monomer of neoprene rubber is
   a) acrylic acid b) methyl acrylate
   c) chloroprene d) acrylonitrile

3. Phenol - formaldehyde resin is called
   a) PVC b) Nylon
   c) Bakelite d) Shellac

4. Buna - S rubber is prepared from
   a) Vinyl chloride + Vinyl acetate
   b) Butadiene + Acrylonitrile
   c) Butadiene + Styrene
   d) Styrene + Divinyl benzene

5. The monomer required to synthesise nylon 6 is
   a) Adipic acid b) Caprolactam
   c) Hexamethylene diamine d) None of these

6. Which among the following is a natural polymer ?
   a) Cellulose b) Nylon
   c) Terrylene d) None of these

7. Which is acrylonitrile ?

a) CH_3CN b) $CH_2=CH-CN$

c) C_6H_5CN d) CH_3CONH_2

8. Trade name of polyester is

a) Dacron b) Terylene

c) Orlen d) Both (a) and (b)

9. The polymer used in the manufacture of toys is

a) HDPE b) LDPE

c) PVC d) None of these

10. The compound used in vulcanisation is

a) S_2Cl_2 b) $TiCl_4$

c) $MnCl_2$ d) CCl_4

11. Which of the following is a thermosetting plastic ?

a) Bakelite b) PVC

c) Nylon d) Terylene

12. Block copolymer type is

a) $m_1\ m_2\ m_2\ m_1\ m_1\ m_1\ m_2$

b) $m_1\ m_2\ m_1\ m_2\ m_1\ m_2$

c) $m_1\ m_1\ m_1\ m_2\ m_2\ m_2$

d) $m_1\ m_2\ m_2\ m_1\ m_2$

PART - B

13. Discuss the preparation and uses of PVC.

14. Write the applications of LDPE and HDPE.

15. Explain homopolymer and copolymer with suitable examples.

16. Explain the term HDPE. How is it prepared ?

17. Hos is polypropylene prepared ? Write its uses.

PART - C

18. What are nylons ? Discuss the preparation of various types of nylons and their applications.

19. Write an account of synthetic rubber.

20. What are polyesters ? Discuss their preparation and applications.

21. How is PVC prepared ? Wirte the applications of rigid, plasticised and chlorinated PVC.

22. List out the uses of phenol formaldehyde resin and buna - S rubber.

23. What are epoxy resins ? How are they prepared ? Write their applications.

APPLIED CHEMISTRY

LUBRICANTS

Definition

Any substance introduced between two moving or sliding surfaces with respect to one another, with a view to reduce the frictional resistance between them is called a *lubricant.*

Classification

Lubricants are classified into three groups :

i) Liquid lubricants or Lubricating oils

ii) Semi-slid lubricants or Greases

iii) Solid lubricants

1. Lubricating oils

Lubrication in watches, clocks, guns, sewing machines, cycles, scientific instruments etc are done with lubricating oils.

Properties of Lubricating oils

1. Viscosity index

The rate of change of viscosity of an oil with temperature is measured in terms of *viscosity* index. It is defined as the average decrease in viscosity per degree rise of temperature.

2. Flash and Fire point

Flash point is *the lowest temperature at which the lubricating oil gives off enough vapours that ignite for a moment when a small flame is brought near it.*

Fire point is *the lowest temperature at which the vapours of the lubricating oil burn continuously for at least fire seconds when a small flame is brought near it.*

3. Cloud and pour point

The temperature at which a cloudy appearance is noticed when the lubricating oil is cooled is called its cloud point.

The temperature at which the lubricating oil just solidifies and will not flow or pour is called its pour point.

4. Oiliness

Oiliness is a measure of the sticking capacity of the lubricating oil on the surface of the machine parts under heavy load or pressure.

Criteria of good lubricating oils

1. Viscosity of lubricating oils decrease with increase of temperature. This makes the lubricants unsuitable under working conditions. Therefore, a good lubricating oil should have minimum change in viscosity for a wide range of temperature.

2. They should have good oiliness to use under high load and speed conditions. Vegetable and animal oils have good oiliness.
3. They should have high boiling points i.e. low volatility.
4. A good lubricating oil should have flash and fire points well above the operating temperature to avoid fire accidents.
5. A good lubricating oil should have cloud and pour points well below the operating temperature to avoid jamming of the machines due to solidification.
6. A good lubricating oil should have high thermal stability i.e. it should not undergo decomposition at the operating temperature.
7. They should have high oxidation resistance.
8. They should be non-corrosive.

Types of Lubricating oils

1. Vegetable and Animal oils

i) These oils have good oiliness but low thermal stability.
ii) They undergo oxidation easily and hence used as additives rather than lubricants.

Examples

Vegetable oils : Olive oil, Palm oil, Castor oil

Animal oil	:	Whale oil, lard oil, tallow oil

2. Mineral oils

i) These are obtained by distillation of petroleum.

ii) Mineral oils are cheap and stable under working conditions but possess poor oilness.

iii) To improve oiliness, small quantities of vegetable or animal oil are added.

3. Blended oils

i) No single oil serves as the most satisfactory lubricant for all machineries.

ii) Mineral oils are unsuitable for use in high speed engines and machineries. Therefore, additives are added to improve the performance of the lubricants. These are called *Blended oils.*

Additive	*Function*
i) Vegetable and animal oils	Increase oiliness
ii) Organic phosphorus, sulphur and chloro compounds	Withstand high pressure
iii) High molecular weight compounds like polystyrene	Reduce the change of viscosity with temperature

iv) Polyalkylated naphthalene	Lowers pour point
v) Organic phosphorus and antimony compounds	Prevent metal surfaces from corrosion.
vi) Glycol, glycerol	Prevent foam formation
vii) Soaps	Improve sticking power.

4. Synthetic Lubricating oils

i) Mineral oils tend to oxidise at high temperature and wax separation occurs at low temperature. Hence, they are unsuitable for use in high speed engines (e.g. air craft engines) which operate below -26^{0}C and above 121^{0}C. In such cases, synthetic lubricating oils can be used.

ii) Synthetic lubricating oils possess the following distinguishing features :

a) non - inflammable

b) high flash point

c) high viscosity index

d) good thermal stability

iii) Important synthetic lubricants are

a) Polyglycols

(e.g. Polyethylene glycol, polypropylene glycol)

Polyethylene glycol can be prepared by heating ethylene glycol with a dehydrating agent such as phosphoric acid.

$$HOCH_2CH_2O\boxed{H + HO}CH_2CH_2OH \xrightarrow[-H_2O]{\Delta}$$

Ethylene glycol Ethylene glycol

$$HOCH_2CH_2OCH_2CH_2OH \longrightarrow H\left(OCH_2CH_2OCH_2CH_2O\right)_n H$$

Diethylene glycol Polyethylene glycol

b) **Polyalkene oxides** (e.g. Polyethylene oxide, Polypropylene oxide).

Polyethylene oxide can be prepared by the polymerisation of ethylene using aluminium oxide (catalyst)

$$n\ CH_2 = CH_2 \xrightarrow{Al_2O_3} -O-(CH_2-CH_2)_n$$

2. **Greases**

i) Grease is a semi-solid lubricant made by dispersing soap in a lbricating oil.

ii) The lubricating oil may be a petroleum oil or synthetic oil.

iii) The function of soap is to thicken the lubricating oil.

Types of Greases

1. ***Lime-based grease***

i) It is prepared by mixing calcium hydroxide and hot petroleum oil.

ii) It is insoluble in water and hence water resistant.

iii) It is used in pumps and tractors

2. ***Soda - based grease***

   i) It is prepared by mixing sodium soap and petroleum oil.

   ii) It is suitable for use in ball bearings where much heat is produced due to friction.

3. ***Lithium - based grease***

   i) It is prepared by mixing lithium soap and petroleum oil.

   ii) It is insoluble in water and hence water resistant.

   iii) It is used in aircrafts.

4. ***Axle grease***

   i) It is prepared by mixing lime, fatty acids and resins.

   ii) It is insoluble in water and hence water - resistant

   iii) It is used in axles where load is high and speed is low

3. **Solid lubricants**

Solid lubricants are used where

i) the operating temperature or load is very high

ii) lubricating oils and greases can not maintain lubricating film

iii) combustible lubricants are not desirable.

Examples

Graphite, molybdenum sulphide, talc, mica, teflon. Among these, graphite and MoS_2 are widely used

Advantages of Solid lubricants

i) They have low shear strength.

ii) They have good adhesion power.

iii) They have good thermal conductivity.

iv) They can withstand high temperature.

v) They are non inflammable.

vi) They are chemically inert.

Graphite

Manufacture

Graphite is obtained by heating a mixture of sand and coke in presence of iron oxide as catalyst at 3000°C in an electric arc furnace.

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

$$SiC \longrightarrow Si + C \text{ (graphite)}$$

Properties and uses

i) Graphite is non-inflammable and not oxidisable upto 370°C.

ii) It can withstand high temperature.

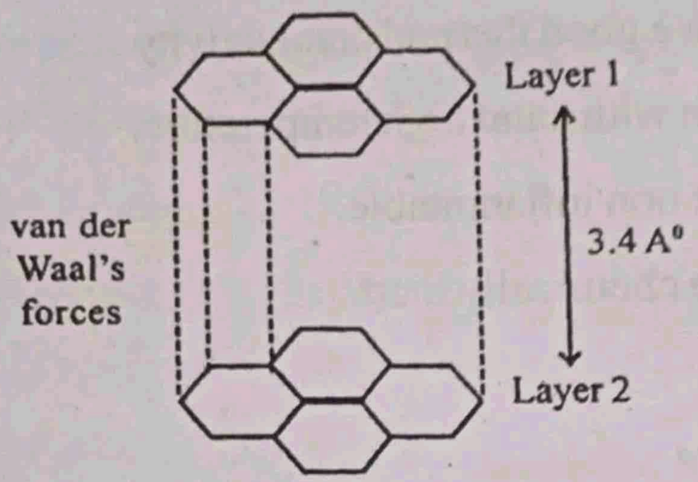
iii) It can be used as a dry power or as a colloidal suspension.

iv) Graphite dispersed in water is called *aquadag* and that in oil is called *oildag*.

v) Graphite is widely used as a solid lubricant in air-compressors, lathes, railway track joints, open gears, internal combustion engines etc.

Structure

Graphite has a laminar structure with several layers.



Carbon atoms are arranged hexgonally in each layer. They are held by strong covalent bonds. The layers are held by weak van der Waal's forces and can slide one over the other. This property is responsible for the lubricating action of graphite.

DOMESTICALLY USEFUL CHEMICAL PRODUCTS

1. Shampoo

Shampoo is used to remove grease, dirt and skin debris from the hair and scalp. It makes hair soft, lustrous and easy to comb.

Method of preparation

Raw materials used

i) Sodium lauryl sulphate - Cleansing agent

ii) Cetyl alcohol - Opacifier

iii) Ethyl alcohol	-	Solubilizer (to dissolve additives)
iv) Sodium stearate	-	Thickener (to increase viscosity)
v) Sodium tripolyphosphate	-	Foam booster in hard water
vi) Lanolin	-	Hair softener (to make hair lustrous)
vii) *p*-Chloro-*m*-cresol	-	Preservative
viii) Dye	-	Colouring agent
ix) Perfume oil	-	Fragrant

Method

i) Sodium lauryl sulphate, cetyl alcohol, sodium stearate, sodium tripolyphosphate and lanolin are heated with water at 80°C and stirred well to get a homogeneous viscous solution.

ii) Small amounts of *p*-chloro-*m*-cresol and perfume oil are added. To improve their solubility, a small amount of ethyl alcohol is added.

iii) The mass is cooled to 40°C and the colourant is added.

iv) The shampoo paste is finally packed in plastic containers.

2. Nail polish

Nail polish is used to decorate and enhance the appearance of the nail.

Method of preparation

Raw materials used

i) Nitrocellulose	-	Film former
ii) Synthetic resin	-	Thickener
iii) Ethyl acetate iv) Butyl acetate	-	Solvents
v) Tricresyl phosphate	-	Plasticizer
vi) Toluene	-	Diluent
vii) Eosin	-	Colourant

Method

i) Toluene is taken in a stainless steel tank provided with turbine or propeller type agitators.

ii) With the agitator running, nitrocellulose is added and thoroughly wetted with the diluent.

iii) Solvents, plasticizer and resin are then added in this order and agitation is continued for several hours until a clear solution is obtained.

iv) The clear liquor is stored in air-tight containers and used.

v) Nail polishes of different colours are prepared with suitable pigments.

Ultramarine blue	-	Blue
Chrome oxide	-	Green
Lamp black	-	Black

3. **Sunscreens**

i) Sunscreens are creams or lotions which can radiate or absorb UV radiations and protect the skin from sunburn and skin cancer.

ii) Sunscreens contain one or more of the following ingredients :

a) Inorganic compounds such as zinc oxide, titanium dioxide etc.

b) Organic compounds such as p - amine benzoic acid (PABA), ethyl p - amino benzoate, octyl salicylate etc.

iii) Sunscreen can be prepared by incorporating PABA and TiO_2 in a suitable vehicle like paraffin wax. A small amount of glycerol is added as humectant to prevent drying of the cream. This on treatment with a mixture of water and mineral oil gives sunscreen lotion.

4. **Tooth powder**

Tooth powder is used to polish the surfaces of the teeth. It acts as an abrasive when rubbed with hand.

Method of preparation

Raw materials used

i) Precipitated calcium carbonate ii) Magnesium carbonate	-	Polishing agents
iii) Soap powder	-	Foaming agent
iv) Thymol v) Menthol vi) Peppermint oil	-	Flavouring agents
vii) Saccharin	-	Sweetening agent

Method

i) All the ingredients except the flavouring agents are mixed thoroughly in proper proportions in an enamelled vessel.

ii) Thymol and menthol are separately powdered and mixed to form a liquid. It is triturated well with the polishing powder.

iii) Finally, the peperment oil is added and the powder is stirred well with a spatula and packed in wax paper.

5. Tooth paste

Tooth pastes are suspensions of polishing agents and detergent in a suitable binder. It polishes the surfaces of teeth by rubbing with a tooth brush.

Method of preparation

Raw materials used

i) Dicalcium phosphate	- Polishing agent
ii) Sodium lauryl sulphate	- Foaming agent
iii) Gum	- Binding agent
iv) Saccharin	- Sweetening agent
v) Glycerol	- Humectant to prevent drying of paste
vi) Menthol vii) Thymol viii) Pepermint oil	- Flavouring agents
ix) Methyl - *p* - hydroxy benzoate	- Preservative

Method

i) All the ingredients except the flavouring agents are mixed thoroughly in proper proportions in an enamelled vessel.

ii) Menthol and thymol are separately powdered and mixed to form a liquid.

iii) Finally, the peppermint oil is added and the powder is treated with the required amount of water and stirred well.

iv) The resulting paste is packed in flexible aluminium or plastic tubes.

6. Boot polish

Boot polish is used to enhance the appearance of shoes and boots.

Method of preparation

Raw materials used

i) Carnauba wax ii) Montan wax iii) Paraffin wax	- Base materials
iv) Turpentine	- Solvent
v) Benzene	- Thinner
vi) Black nigrosine dye vii) Brown coal tar dye	- Colourants

Method

i) For making black boot polish, the carnauba wax (m.Pt = 85 - 87^{0}C) is broken into small pieces and melted at 90 - 92^{0}C in a jacketted stainless steel vessel with constant stirring.

ii) To the molten mass, black nigrosine dye neutralised with stearic or oleic acid is added.

iii) The montan wax (m.pt = 80 - 90^{0}C) is broken into small pieces and melted in another jacketted vessel. To this, paraffin wax (m.pt = 50 - 52^{0}C) is added.

iv) The above mixture is added to the carnauba wax dyed with nigrosine.

v) The black molten wax mixture is treated with turpentine oil and benzene.

vi) Finally, the resulting mixture is filled in small round tin boxes at about 50^0C and cooled slowly. The solvent gets evaporated and a semi-solid mass is left behind.

vii) Brown boot polish is made in a similar manner using a brown coal tar dye which does not require neutralisation.

7. Moth balls

Moth balls are used to kill moths and protect textile garments, paper and food grains.

Method of preparation

Raw materials used

i) Crude naphthalene	-	Insecticide
ii) Caustic soda iii) Sulphuric acid	-	Reagents
iv) Camphor		Insecticide
v) Phenol vi) Ceresin	-	Moisture absorbents

Method

i) Crude naphthalene is purified by melting and treating successively with conc. H_2SO_4 and caustic soda solution.

ii) It is then washed with water and crystallised.

iii) The crystals are finally distilled under vacuum when a refined product melting at 79.5 - 80°C is obtained.

iv) The purified naphthalene is mixed with the other ingredients in a tank maintained at 85°C.

v) The resulting solution is poured into the round cavities of aluminium moulds and dried to get balls of desired size.

8. Chalk pieces

Chalk pieces are used to write on black boards in schools and colleges.

Method of preparation

Raw materials used

i) Plaster of Paris	-	Base materials
ii) China clay		
iii) Precipitated $CaCO_3$		
iv) Ultramanine blue	-	Whitener
v) Dyes	-	Colourants

Method

i) Plaster of paris is powdered and mixed with china clay and precipitated $CaCO_3$ in suitable proportions in an enamelled bowl.

ii) A pinch of ultramarine blue is then added.

iii) Finally, water is added in required quantity slowly and the mixture is kept under constant and vigorous stirring till a homogeneous slurry is obtained.

iv) The slurry is poured into cylindrical cavities of aluminium moulds. For easy removal of the chalk pieces, the cavities are lubricated with a mixture of kerosine oil and groundnut oil in the ratio 4 : 1.

v) After a few minutes, the wet chalk pieces are removed from the cavities, dried first in diffused sun light and then in direct sun light.

vi) The dried chalk pieces are packed in wooden boxes.

vii) For making coloured chalk pieces, suitable pigments are added to the slurry and fed into moulds.

QUESTIONS

PART - A

1. Viscosity of lubricating oil .... with increase of temperature

   a) increases b) decreases

   c) does not change d) None of these

2. Silicon fluid is a

   a) mineral oil b) synthetic oil

c) vegetable oil   d) None of these

3. An example of solid lubricant
   a) graphite   b) soap
   c) grease   d) None of these

4. The role of glycerol in tooth paste is to prevent
   a) fungus growth   b) sedimentation
   c) drying   d) decomposition

5. The raw material used to make chalk pieces is
   a) Starch   b) Calcium carbonate
   c) Gypsum   d) None of these

6. Glycerol is added to tooth paste
   a) to prevent drying of the paste
   b) as a lubricant
   c) as a binder
   d) none of these

7. The function of lanolin in shampoo is
   a) as a foam booster   b) as a hair softener
   c) as an opacifier   d) none of these

8. The colou:ant used in nail polish
   a) Nigrosine   b) Eosin
   c) Ultramarine   d) None of these

9. The dye used in black shoe polish

a) Nigrosine b) Eosin

c) Coal tar dye d) None of these

10. The detergent used in making shampoo

a) olive oil b) sodium lauryl sulphate

c) sodium stearate d) none of these

PART - B

11. Write the criteria of good lubricating oils.

12. Write notes on greases.

13. Write a note on classification of lubricants.

14. What are the various ingredients of tooth powder ?

15. Describe the method of preparation of nail polish.

16. Write notes on sunscreens.

PART - C

17. What are lubricants ? How are they classified ? Give one example for each class.

18. What are the raw materials rquired for making shampoo? Describe the method of preparation of shampoo on a small scale.

19. Describe the small scale preparation of

i) moth balls ii) boot polish

DEPARTMENT OF PHYSICS

GOVERNMENT ARTS AND SCIENCE COLLEGE, NAGERCOIL

Internal Exam I (12/10/2020)

Time: 1 hour Total: 20 marks

Allied Chemistry

PART A (2x1=2)

1. The electrostatic forces of attraction between the ions is called------------- bond

2. Positive electrophile behave as ---------------

PART B (2x5=10)

3. Explain Pauli's exclusion principle

4. Define

    i) Nucleophiles with two examples

    ii) Electrophiles with two examples

PART C (1x8=8)

5. i) Write the Postulates of VSEPR theory (4 marks)

   ii) Write any two applications of VSEPR theory (4marks)

or

6. i) Write the Cleavage of Bonds (1 mark)

   ii) Write the Hemolytic bond fission (3 marks)

   iii) Write the Heterolytic bond fission (4 marks)

DEPARTMENT OF PHYSICS

GOVERNMENT ARTS AND SCIENCE COLLEGE

INTERNAL TEST-II

SACH11 – Allied chemistry

Time: 1 hour Total: 20 marks

PART A (1×2=2)

1. The carbon centre of a carbanion is in _______ state
2. Free radicals are formed by the ___________

PART B (2×5= 10)

3. Write the notes on carbanions
4. Write addition reaction

PART C (1×8= 8)

5. i) what is polymerization Reaction
   ii) write the type of polymerization
   (or)
6. Write on free radical reaction (Definition, Types, method, properties)

GOVERNMENT ARTS AND SCIENCE COLLEGE, NAGERCOIL.

THIRD SEMESTER

ALLIED CHEMISTRY-SCSB5A

Time: 3 hours   Maximum:75 marks

PART A-(10x1=10 marks)

Answer all questions.

Choose the correct answer:

1. Which of the following molecule has only bonded pair of electrons?
   a. NH_3
   b. H_2O
   c. HF
   d. CH_4

2. The electronic configuration of copper atom is____________
   a. $3d^9\ 4s^2$
   b. $3d^{10}\ 4s^2$
   c. $3d^{10}\ 4s^1$
   d. $3d^9\ 4s^1$
3. Which of the following is an electrophile?
   a. H^+
   b. H_3O^+
   c. NO_2^+
   d. All the above
4. A species with an unshared pair of electrons and a negative charge on the central carbon atom is called______________
   a. Carbonium ion
   b. Carbanion
   c. Free radical
   d. Carbene
5. Emission of light as a result of chemical reaction is called
   a. Fluorescence
   b. Phosphorescence
   c. Chemiluminescence
   d. Bioluminescence
6. For a reaction that obeys Einstein law
   a. $\emptyset = 1$

b. $\emptyset > 1$
c. $\emptyset < 1$
d. $\emptyset = 0$

7. An example of fibre is
   a. Natural rubber
   b. Nylon
   c. Freon
   d. PVC
8. Which of the following is a thermosetting plastic?
   a. PVC
   b. Nylon
   c. Shellae
   d. Bakelite
9. Which of the following is a lubricating oil?
   a. Graphite
   b. Benzene
   c. Poly glycols
   d. CCl_4
10. The main raw material present in moth ball is
   a. Benzene
   b. Toluene
   c. Phenol
   d. Naphthalene

PART B- (5x5=25 marks)

Answer all questions, choosing either (a) or (b)

Answer should not exceed 250 words.

11. (a) What is hybridisation? Explain.

Or

(b) Define:

(i) Electro valent bond.

(ii) Covalent bond.

12. (a) What are electrophiles? Give examples.

Or

(b) Write the preparation of carbonium ion and carbanions.

13. (a) Explain chemiluminescence with example.

Or

(b) What is quantum field of a photochemical reaction? Give it's significance.

14. (a) What are elastomers? Explain.

Or

(b) How will you prepare phenol formaldehyde resin?

15. (a) Write the uses of shampoo and tooth paste.

Or

(b) What are synthetic lubricating oils? Explain.

PART C-(5x8=40 marks)

Answer all questions, choosing either (a) or (b).

Answer should not exceed 600 words.

16. (a) Write note on the following

(i) Aufban principle

(ii) Pauli's exchision principle.

(iii) Hunt's rule.

Or

(b) Draw the structure of CH_4, BF_3, NH_3 and H_2O Molecule.

17. (a) Give the preparation and properties of free radicals.

Or

(b) Explain different types of reaction with example.

18. (a) Write the laws of photochemistry.

Or

(b) Give the differences between thermal and photochemical reaction.

19. (a) Define the following with example.

(i) Monomers

(ii) Polymers

(iii) Oligomers

Or

(b) Write note on:

(i) Thermoplastics (4)

(ii) Thermo setting plastics (4)

20. (a) Write the preparation and uses of chalk piece.

Or

(b) Write note on:

(i) Lubricating oil (4)

(ii) Solid lubricants. (4)