DEPARTMENT OF CHEMISTRY HONOURS

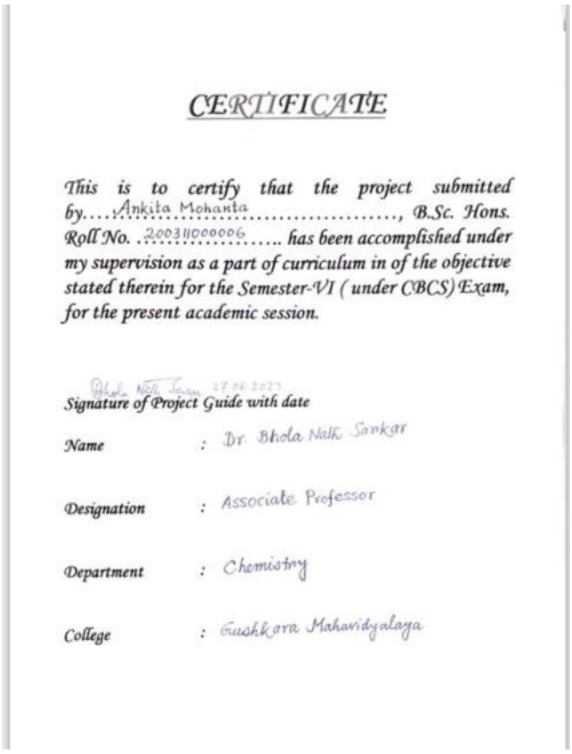
LIST OF STUDENTS: 04

1. ANKITA MOHANTA
2. SOUVICK MAL
3. SUMIT SIL
4. TITHI MONDAL

TITLE OF THE PROJECT : **1. Coordination compound (bonding and supramolecular chemistry)**
2. Adsorption
3. Nuclear magnetic resonance spectroscopy
4, Polymer chemistry

DURATION WITH DATE :01.04.2023 to 26.06.2023

PROJECT WORK COMPLETION CERTIFICATE



CERTIFICATE

This is to certify that the project submitted by....Ankita Mohanta......................................., B.Sc. Hons. Roll No. ..20031l000006..... has been accomplished under my supervision as a part of curriculum in of the objective stated therein for the Semester-VI (under CBCS) Exam, for the present academic session.

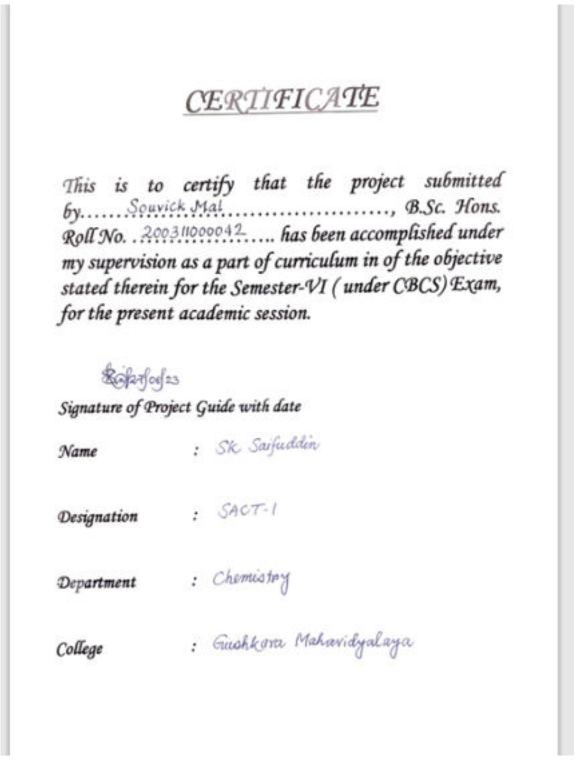
Bhola Nath Sarkar 27.06.2023
Signature of Project Guide with date

Name : Dr. Bhola Nath Sarkar

Designation : Associate Professor

Department : Chemistry

College : Gushkara Mahavidyalaya



CERTIFICATE

This is to certify that the project submitted by......Souvick Mal......................................., B.Sc. Hons. Roll No. ..20031l000042..... has been accomplished under my supervision as a part of curriculum in of the objective stated therein for the Semester-VI (under CBCS) Exam, for the present academic session.

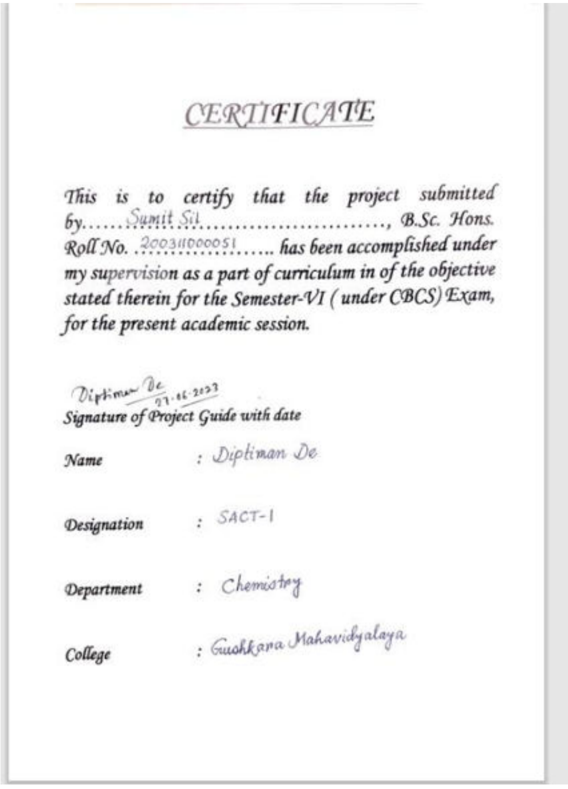
27/06/23
Signature of Project Guide with date

Name : Sk Saifuddin

Designation : SACT-I

Department : Chemistry

College : Gushkara Mahavidyalaya



CERTIFICATE

This is to certify that the project submitted by......Sumit Sil............................, B.Sc. Hons. Roll No. .20031100051........ has been accomplished under my supervision as a part of curriculum in of the objective stated therein for the Semester-VI (under CBCS) Exam, for the present academic session.

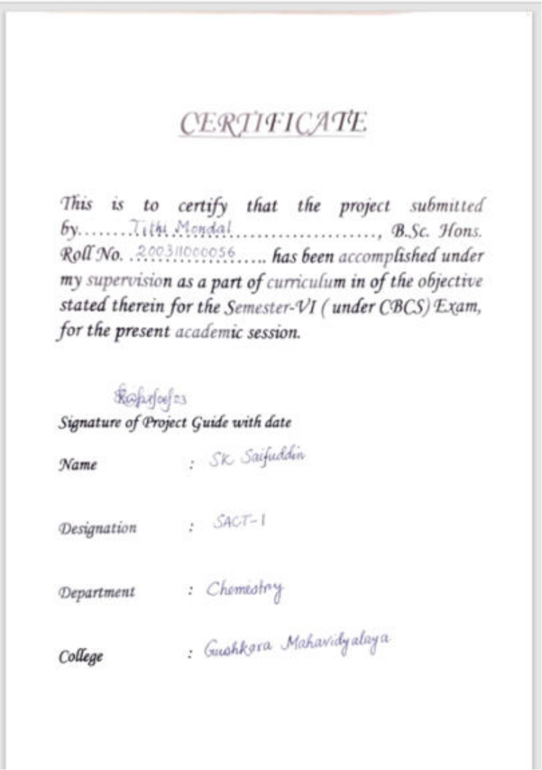
Diptiman De 27.06.2023
Signature of Project Guide with date

Name : Diptiman De

Designation : SACT-I

Department : Chemistry

College : Gushkara Mahavidyalaya



CERTIFICATE

This is to certify that the project submitted by.......Tithi Mondal......................, B.Sc. Hons. Roll No. .20031100056....... has been accomplished under my supervision as a part of curriculum in of the objective stated therein for the Semester-VI (under CBCS) Exam, for the present academic session.

Signature of Project Guide with date

Name : SK Saifuddin

Designation : SACT-I

Department : Chemistry

College : Gushkara Mahavidyalaya

REPORT OF THE FIELD WORK: (PDF OF THE REPORT OF THE STUDENT)

1. **PDF OF ANKITA MOHANTA**
2. **PDF OF SOUVICK MAL**
3. **PDF OF SUMIT SIL**
4. **PDF OF TITHI MONDAL**

SAMPLE PHOTOGRAPH OF THE FIELD WORK:

- **PERMISSION LETTER FOR FIELD WORK FROM COMPETENT AUTHORITY**
- **ACCORDING TO B.SC. HONS. SEM - 6 (DSE-4) SYLLABUS OF BURDWAN UNIVERSITY.**

THE UNIVERSIY OF BURDWAN

B. SC. 6TH SEMESTER (HONOURS) EXAMINATION 2023(CBCS)

Presentation

SOUVICK MAL

By

Sc. 6th Sem Chemistry Hons. Examination -202

- Name: **SOUVICK MAL**
- Registration No: 202001004821 of 2020-2021
- University Roll No: 200311000042
- Course Tittle: Dissertation Followed by Power Point Presentation
- Course Code: **DSE-4**
- Semester: VI

ADSORPTION

BY

SOUVICK MAL

der the supervision
:

Dr.Bholanath Sarkar
Dr. Pialee Roy
Sk. Saifuddin
Diptiman De

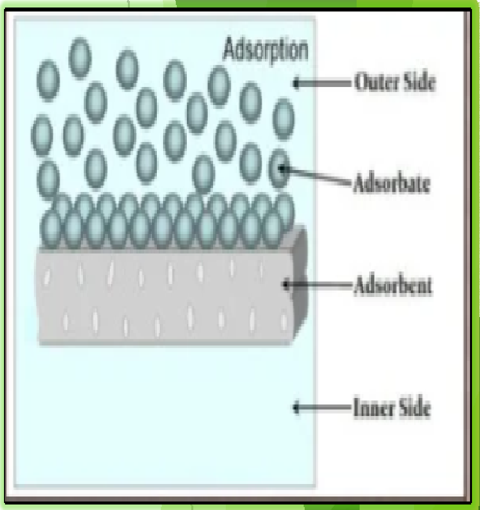
CONTENTS

Introduction:

ce chemistry research is an interdisciplinary area on
rontiers of physical chemistry, chemical physics,
ial science and nanoscience. Residual unbalanced
exist on the surface of a solid. As a result of these
ual forces, the surface of a solid has a tendency to
t and retain molecules of other species with which it
ught into contact. As these molecules remain only at
rface, their concentration is more at the surface than
bulk of the solid.

rm 'Adsorption' was introduced by Kayser in 1881.

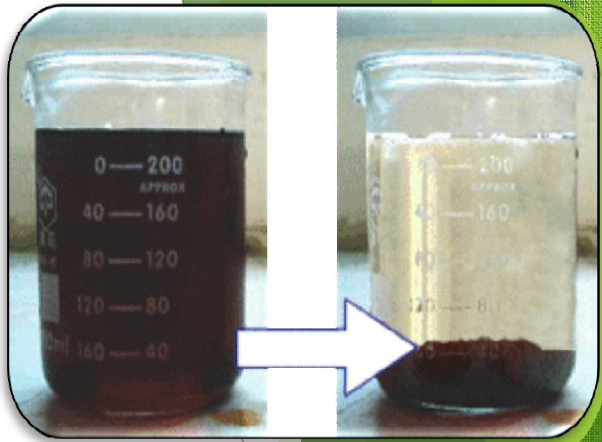
henomenon of higher concentration of any molecular species at the surfa
n the bulk of a solid is known as **Adsorption**.

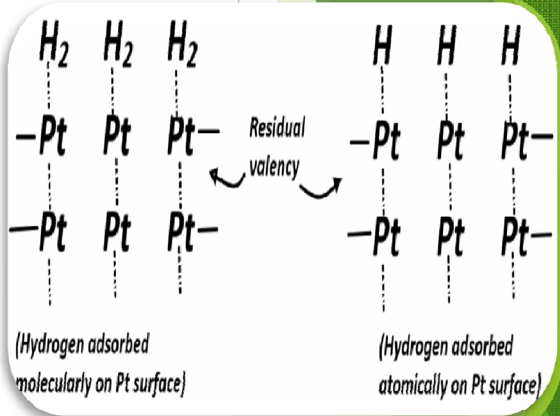


Adsorption:

orption is to be carefully distinguished from
rption. The latter term implies that a substance is
ormly distributed throughout the body of a solid or
uid. Thus, while water vapours are absorbed by
drous calcium chloride.

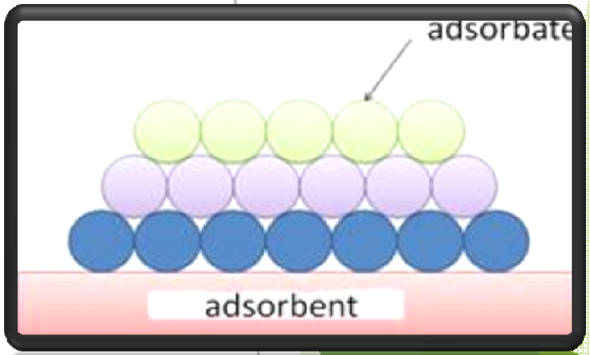
adsorbed atoms or molecules can be held to the
ce of a solid such as finely divided platinum
l (Pt) by physical (Van der Waal's forces) or
ical forces due to residual valance bonds.

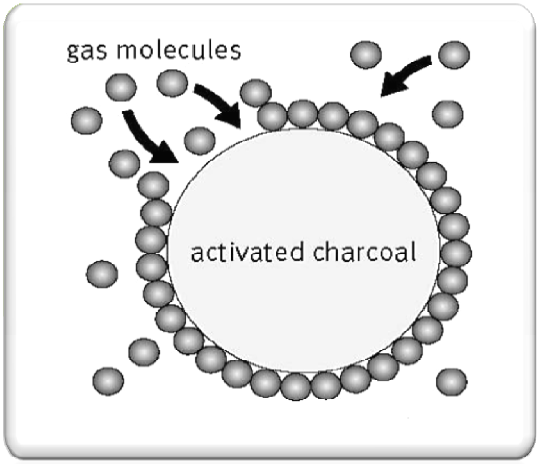




dsorbent & Adsorbate:

e solid that takes up a gas, vapour or a solute
om a solution, e.g., silica gel, charcoal, clay etc.

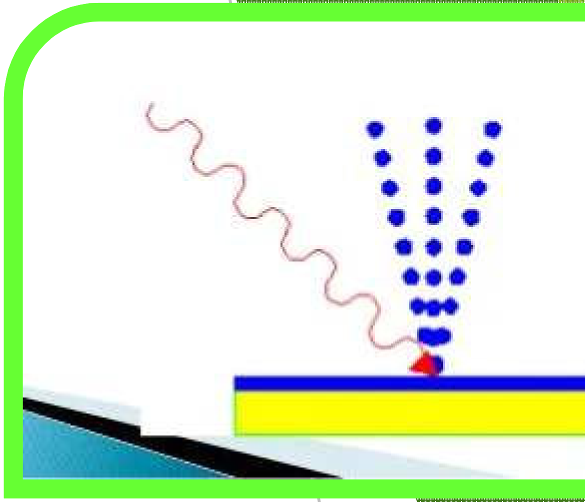




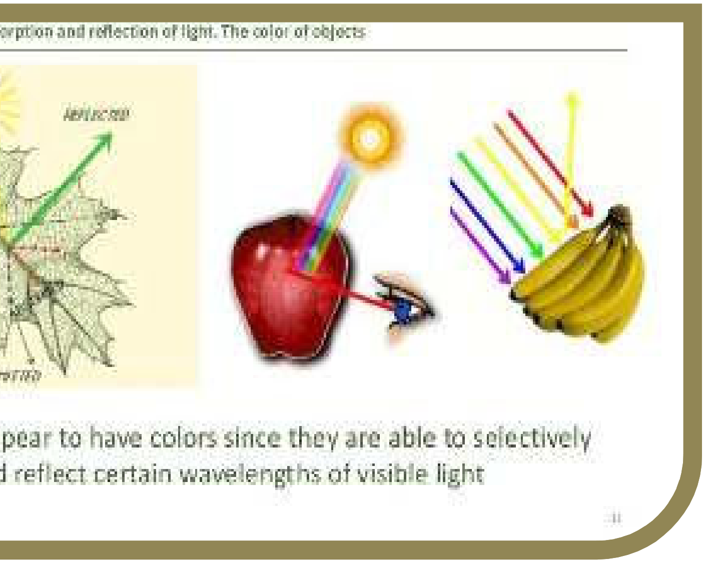
- ○ The gas vapour or the solute, which is held
surface of the solid, e.g., water vapou
poisonous gases (NH_3, phosgene) etc.

esorption & Absorption:

The process of removal of adsorbed substances rom the surface on which it is absorbed.



Desorption



rption and reflection of light. The color of objects

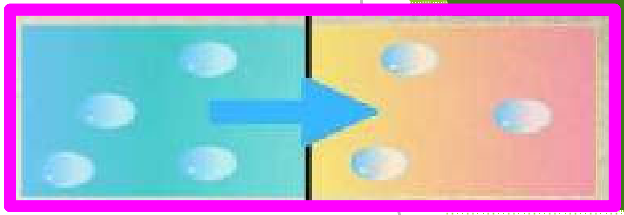
pear to have colors since they are able to selectively d reflect certain wavelengths of visible light

Absorption

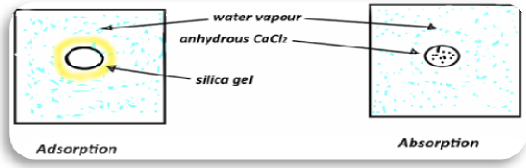
- When the molecules of a substance uniformly distributed through out the body another substance, the phenomenon is ca Absorption.

DIFFERENCE BETWEEN ADSORPTION AND ABSORPTION

mulation of the molecular species at urface rather than in the bulk of the or liquid is termed as Adsorption.	**Definition**	- Assimilation of molecular species th the bulk of the solid or liquid is t Absorption.
surface phenomenon.	**Phenomenon**	- It is a bulk phenomenon.



ermic Process	**Heat exchange**	- Endothermic Process.
avoured by low temperature.	**Temperature**	- It is not affected by temperature.
dily increases and reaches brium.	**Rate of reaction**	- It occurs at a uniform rate.
concentration of the bottom of bent is different from that in bulk.	**Concentration**	- It is constant throughout the medium
gel adsorbs water vapour.		✓ Anhydrous $CaCl_2$ absorbs water vapo



Heat of Adsorption:

✓Attractive interaction takes place.

✓Energy released.

✓Adsorption is an exothermic process.

✓ΔH = (-) ve

The amount of heat evolved when 1 mole of an adsorbate ge
adsorbed on the surface of an adsorbent is called Molar Heat
Molar Enthalpy of Adsorption.

Adsorption in terms of Gibbs-Helmholtz Equation:

dsorption → exothermic reaction.

$H = (-)$ ve

$S = (-)$ ve

ibbs- Helmholtz Equation

➢ $\Delta G = \Delta H - T.\ \Delta S$

$= (-)$ ve $- T\ (-)$ ve

$H > \Delta S$

$H = T.\ \Delta S$

$G = 0$

et adsorption is 0.

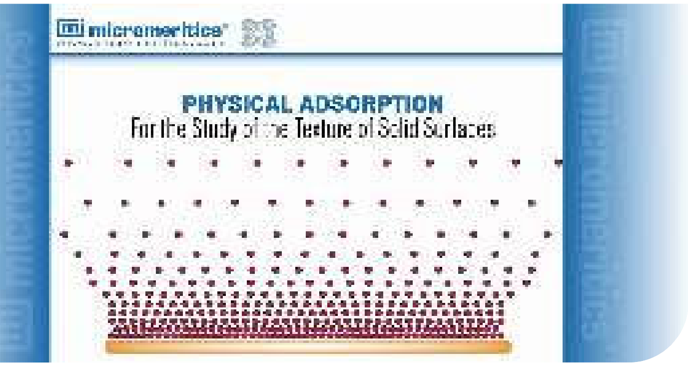
❑ Types of Adsorption:

Physical Adsorption or Physisorption

Chemical Adsorption or Chemisorption

Physical Adsorption occurs when he adsorbate gas molecules are eld by physical forces like Van er Waal's forces.

Example: H_2, O_2 on charcoal.

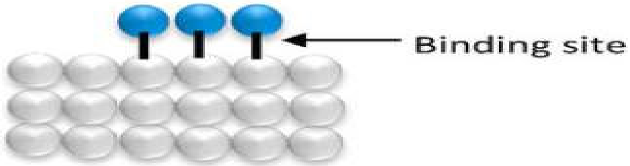

micromeritics

PHYSICAL ADSORPTION

For the Study of the Texture of Solid Surfaces

Chemical Adsorption occurs when
adsorbate molecule is held on the adsor
surface by chemical forces as short cova
chemical bonding occurs by the sharing
electrons.

Example: Hydrogen is chemisorbed on Ni

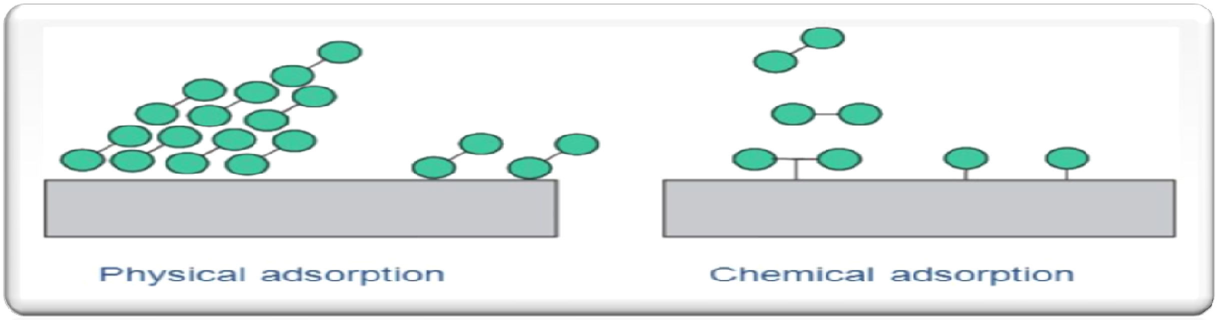


The chemical bond is formed between adsorbate and adsorbent surface.

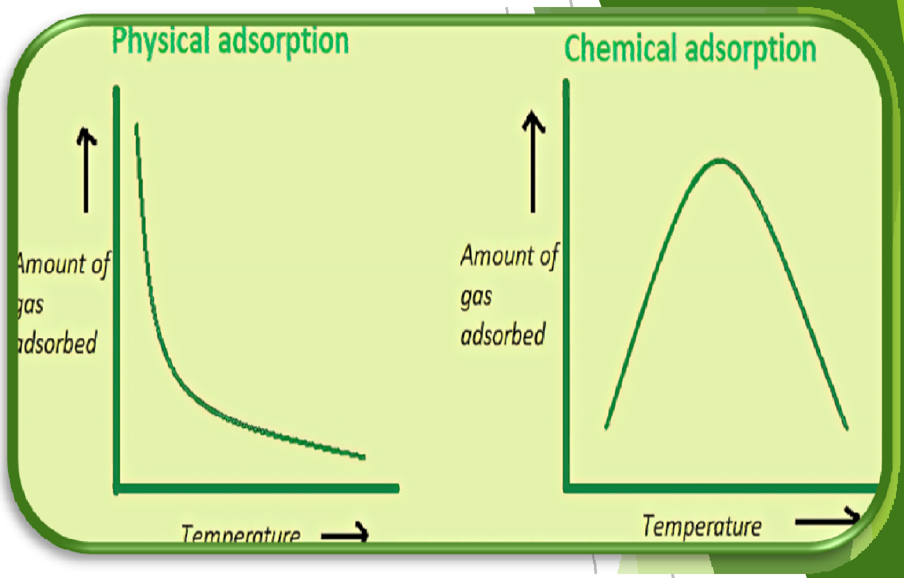
Chemical adsorption

Difference between Physisorption & Chemisorption:

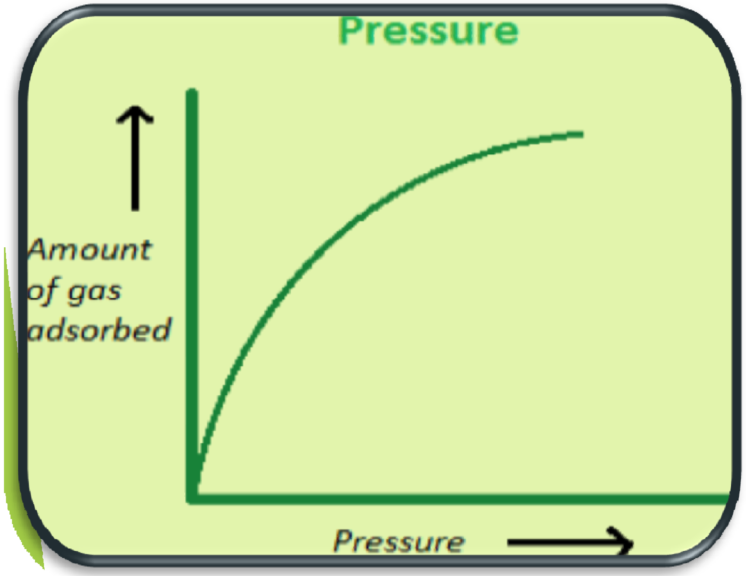
k, long range forces, Van der Waal's action.	**Bonding**	Strong, short range forces, chemical bondin involving orbital overlap and charge transfe
curs at low temp and decreases with rease in temperature.	**Effect of temp**	Occurs at high temp and increases with increase in temperature.
reases with increase in pressure of sorbate.	**Effect of pressure**	Decreases with increases of pressure.
Multi- layer	**Saturation**	Mono- layer
Reversible	**Nature**	Irreversible
Not needed	**Activation energy**	High activation energy needed.



ect of Temperature and Pressure on Adsorption:



- *Adsorption increases as temperature decreases.*



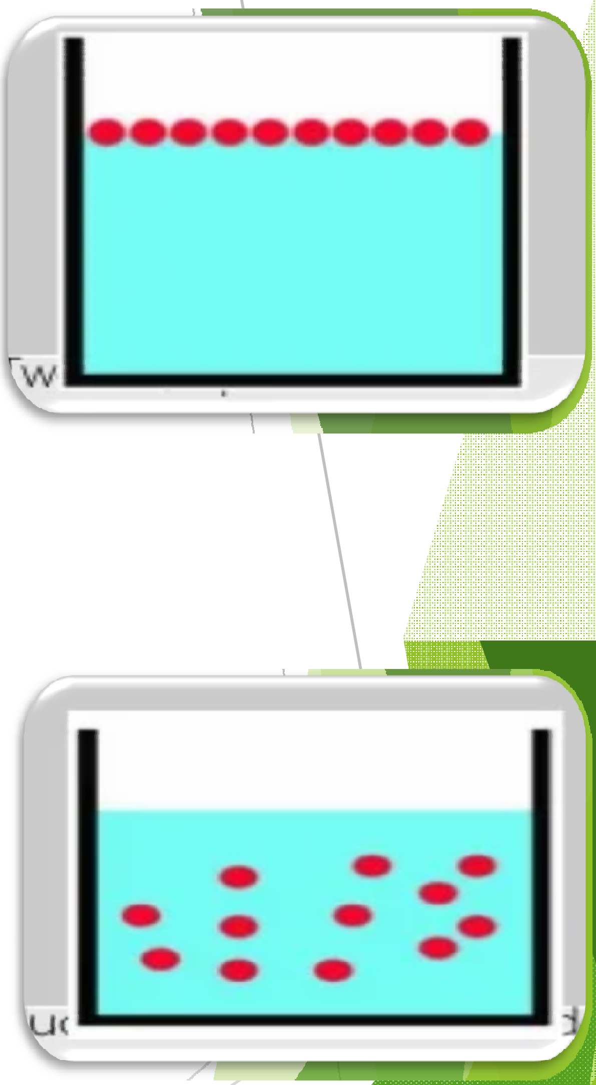
- *Magnitude of Adsorption increases with increase in pressure.*

Positive & Negative Adsorption:

olid to Adsorption is the Adhesion of atoms, ions or molecules from a gas, liquid or dissolved a surface.

In adsorption, if the concentration of a substance in the interface is high, then it is called positive adsorption.

If it is less, then it is called negative adsorption.



Factors affecting on Adsorption:

re of a gas

Easily liquefiable gases easily gets absorbed.

ure of
orbent

More the surface area per unit mass of the adsorbent, more will be the adsorption.

ropy

Adsorption decreases with decreasing entropy.

alpy

ΔS = (-) ve for adsorption, ΔH = (-) ve

rature

Adsorption increases as temperature decreases.

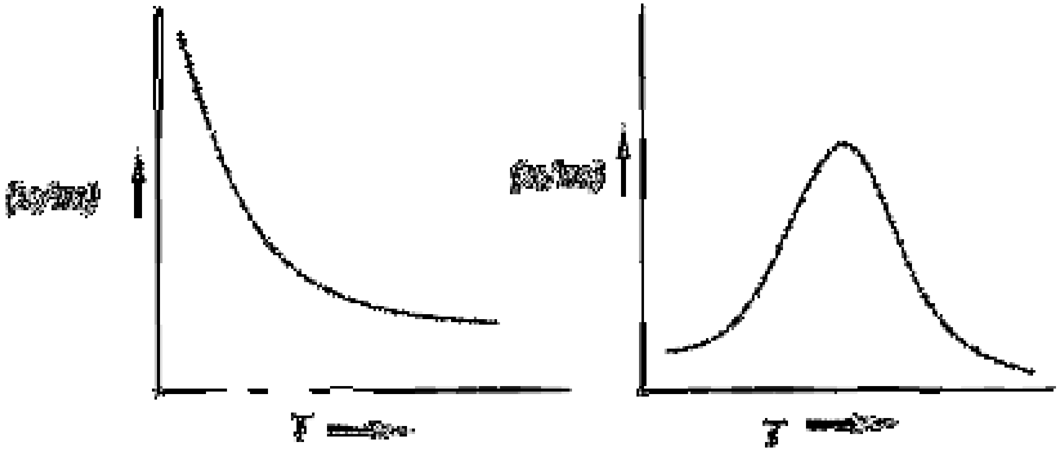
ure

Magnitude of adsorption increases with increase in pressure.

solid + gas $\underset{\text{desorption}}{\overset{\text{adsoption}}{\rightleftharpoons}}$ soli

Adsorption Isobar:

sorption Isobar is a graph between the amount adsorbed (x/m) and the temperatur
the adsorbate at constant pressure.



(Physical Adsorption) (Chemical Adsorption)

dsorption Isothertm

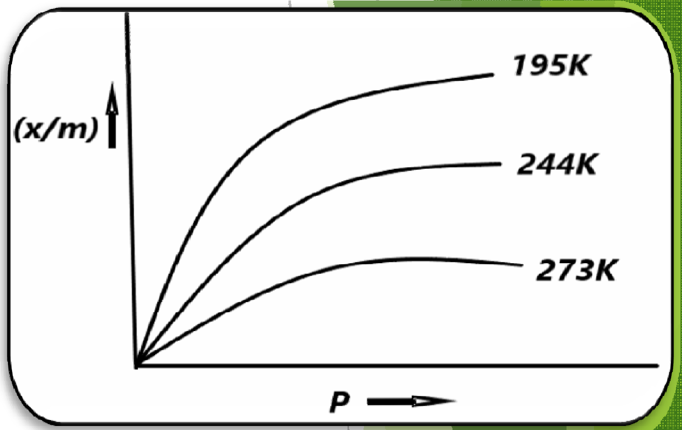
rocess of adsorption is studied through graph known as Adsorption Isotherm.

f vacancieLimited numbers s on the surface f the adsorbent.

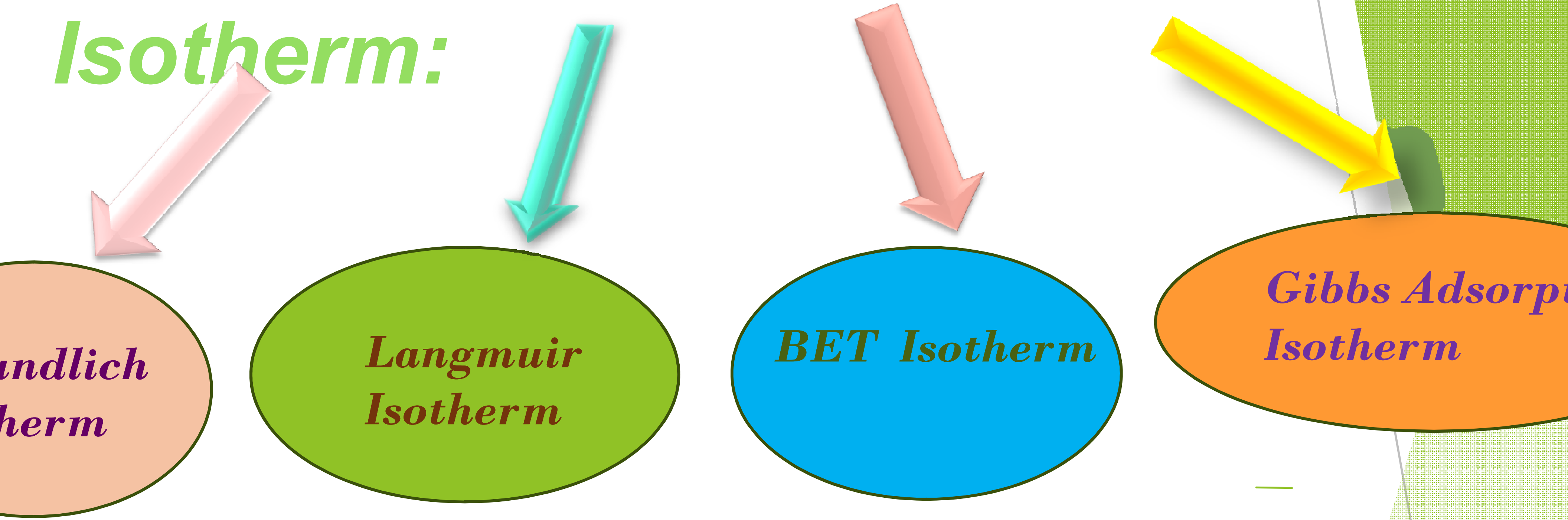
fter saturation pressure P_S adsorption oesn't occur anymore.

t high pressure a stage is reached when all he sites are occupied and further increase in ressure doesn't cause any difference in dsorption process.

t high pressure, adsorption is independent f pressure.



Different types of Adsorption Isotherm:



ndlich
herm

Langmuir
Isotherm

BET Isotherm

Gibbs Adsorp
Isotherm

Freundlich Adsorption Isotherm :

1909, Dr. Herbert Freundlich gave this isotherm, which was an empirica
ression that accounts for surface heterogeneity by multilayer adsorption,
onential distribution of active sites of adsorbent and their energies towa
orbate.

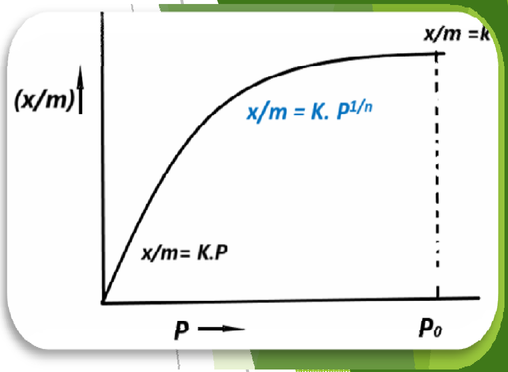
ic
umptions:

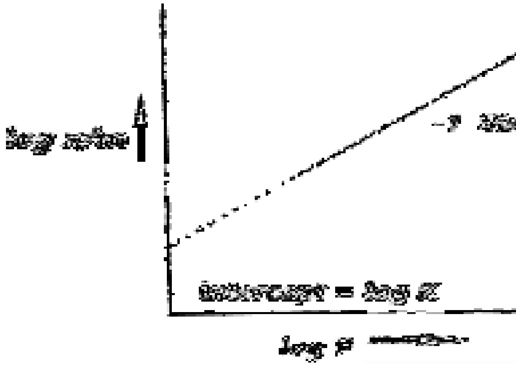
- *urface roughness*
- *Adsorbate – adsorbate interactions*
- *nhomogeneity*

Derivatiion

is the amount of substance(adsorbate) adsorbed by “m” gm of
ent at constant temperature, then according to Freundlich ---
$x/m = k.P^{1/n}$ ---- This equation is known as Freundlich
tion isotherm, where
essure under which the adsorption equilibrium is established.
nstant
l integer greater than one
ot of x/m vs P is of the following type---
he graph, we conclude that, at lower pressure, $x/m \alpha P$ or $x/m =$

ry high pressure, the adsorption becomes almost independent of
re, i.e. $x/m = k.P^0$
e intermediate range of pressure , x/m is proportional to
re raised to some fractional power between 1 to 0 .
$n = k.P^{1/n}$
$x/m) = \log(k) + 1/n \log(p)$





LIMITATIONS OF FREUNDLICH ADSORPTION ISOTHERM:

- ✓ Freundlich equation is purely empirical and has theoretical basis.
- ✓ The equation is valid only up to a certain pressure an invalid at higher pressure.
- ✓ The constants k & n vary with temperature.
- ✓ Freundlich ‘s adsorption isotherm fails at high concentration of the adsorbate.

Langmuir Adsorption Isotherm:

1916, Dr. Irving Langmuir derived an expression for the variation in the extent o
sorption with pressure on the basis of following assumptions

Bassic assumptions

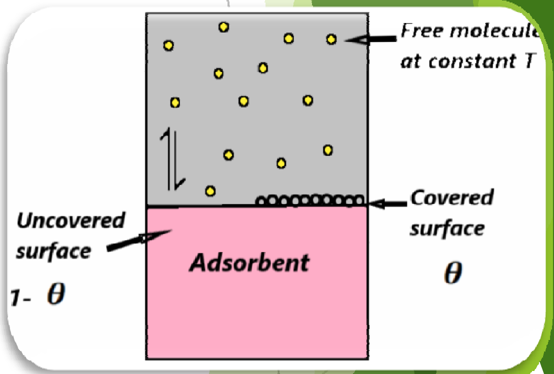
- *The surface is homogeneous*
- *All sites are equivalent*
- *Mono-layer adsorption only*
- *No interactions between adsorbate molecules on adjacent site*
- *Heat of adsorption is constant and equivalent for all sites*
- *Adsorbate molecules have tendency to get adsorb and desorb fr surface*

Derivation

s consider a dynamic equilibrium between free molecules and those
bed on the fraction of the solid surface . At the state of adsorption
brium, in a chemisorption process, the rate of adsorption becomes equal
rate of desorption . If at this equilibrium, (θ)is the fraction of the
e of the adsorbent covered by the adsorbate molecule, then Rate of
ption is equal to (1 - θ) as well as the number of molecule stricking per
rea (μ) and rate of desorption becomes proportional to (θ) .

of adsorption $\alpha\ (1-\theta\ ).\mu = \alpha\ (1-\theta).\ \mu \quad \alpha\ =$
ortionality constant
of desorption $\alpha\ \ \beta \quad = \beta.\theta \qquad \beta\ =$
ortionality constant
e equilibrium, rate of adsorption = rate of desorption
$-\ \theta\ ).\mu = \beta.\theta$ *or,* $\alpha\mu - \alpha\theta\mu = \beta\theta$ or, $\alpha\mu = \theta(\beta + \alpha\mu)$ or, $\theta\ =$
$(\beta + \alpha\mu)$
(μ) is the number of molecules striking per unit area, it is directly
rtional to pressure of the gaseous adsorbate .
$\mu\ =\ k\,.\,P$ *,then* $\alpha\mu\,/\,(\beta + \alpha\mu)\ =\ \alpha kp\,/\,(\beta + \alpha kp) = (\,\alpha k\,/\,\beta)\,.\,P\,/$
$\alpha kP/\beta\ =\ aP\,/\,1 + aP$

$=\ aP\,/\,1 + aP$ *Where* $a = \alpha k\,/\,\beta\ =$ *constant*



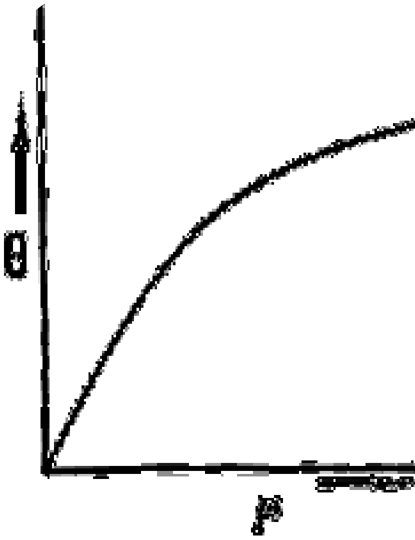
Langmuir Volume and Langmuir Pressure:

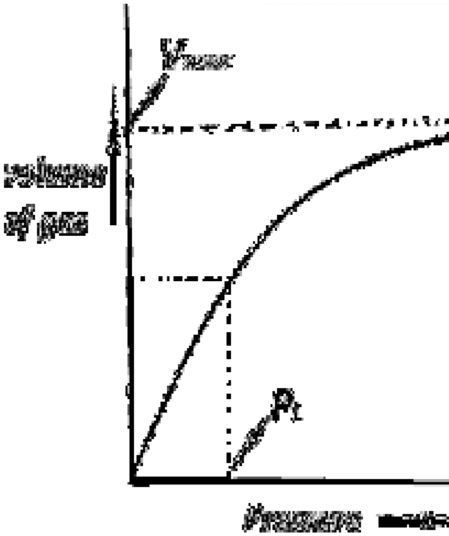
When maximum amount of gas adsorbed upon the solid surface to form a mono- layer is called Langmuir Volume.

Langmuir Volume = v_{max}

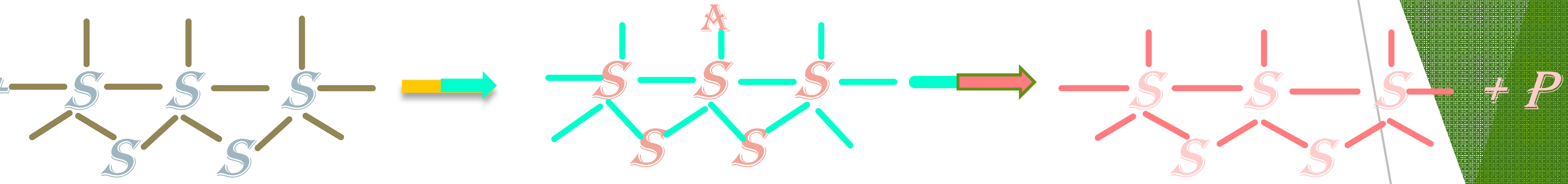
Similarly, Langmuir Pressure is the pressure at which one half of the Langmuir volume can be adsorbed

Langmuir Pressure $(P_L) = v_{max}/2$





DISSOCIATION OF A SINGLE SUBSTANCES (GAS) ON A SOLID SURFACE:



he rate of reaction:-

$$- dP/ dt = K.\ \theta = K.\ aP/ (1+aP)$$

adsorption is very low:

$aP) \sim 1$

$dP/ dt= K.\ aP$

$= K.\ P^1$

st order reaction

xample:

issociation of HI

n Pt

When adsorption is high:

$(1+aP)\sim aP$

$\therefore$ $- dP/ dt= K.\ aP/ aP$

$= K.\ P^0$

○ Zero order reaction

○ Example:

Dissociation of HI on gold.

When adsorption is mode

$-dP/ dt= K.\ P^n$

Where $1> n> 0$

○ The order of the reaction will be fractional one.

○ Example:

Decomposition of Stibine on Antimony.

BET Adsorption Isotherm :

Brunauer, , Emmet and Teller extended the LANGMUIR approach by postulating ultimolecular adsorption i.e., the adsorption involves the formation of many molecu layers on the surface rather than a single layer.

The relation derived on this basis is expressed as-

$$P/v\,(P^0 - P) = 1/\,(v_m.\,C) + (C\text{-}1)/\,(v_m.\,C) \times P/P^0$$

This is often called BET Equation.

Where,

v= volume of gas adsorbed under pressure P

P^0= Saturated vapour pressure at the same temperature.

$_m$= volume of gas adsorbed when the surface is covered with a Uni- molecular Layer.

C= Constant for a given adsorbate, such that

$$c = e^{(E1\text{-}EL)/RT}$$

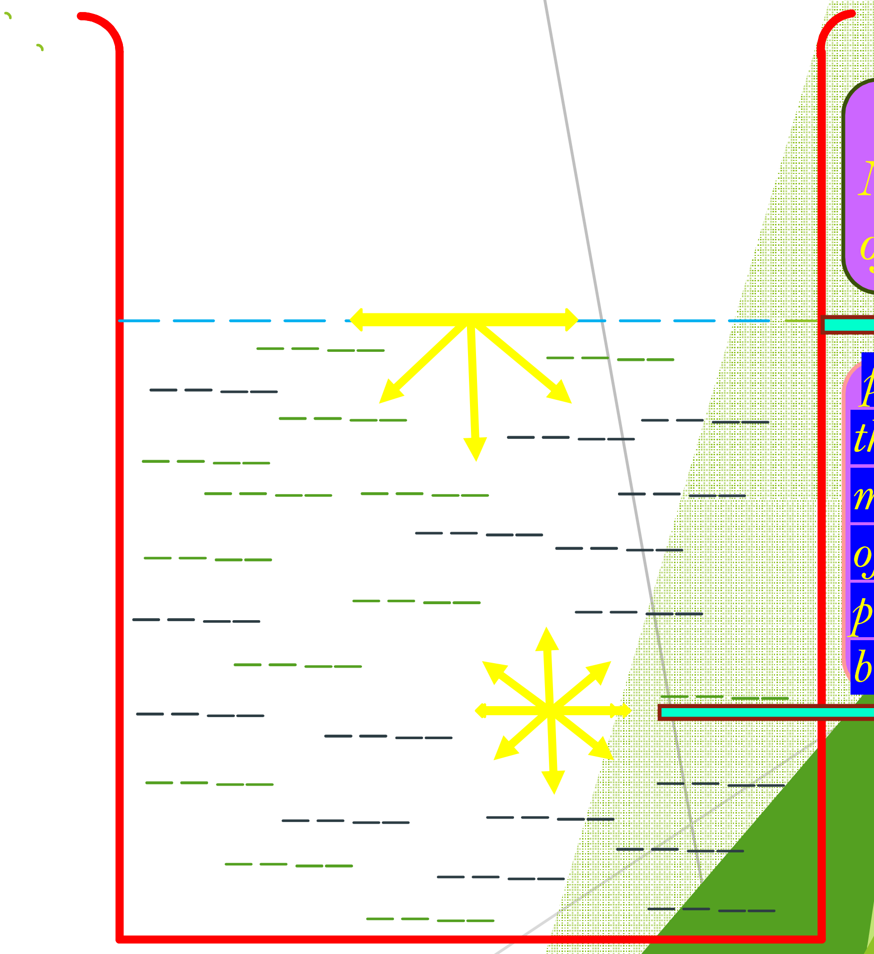
Where, E_1 = Heat of adsorption in the first layer (always negative) and

E_L= Heat of liquefication of the gas (always negative).

dsorption on Liquid urface:

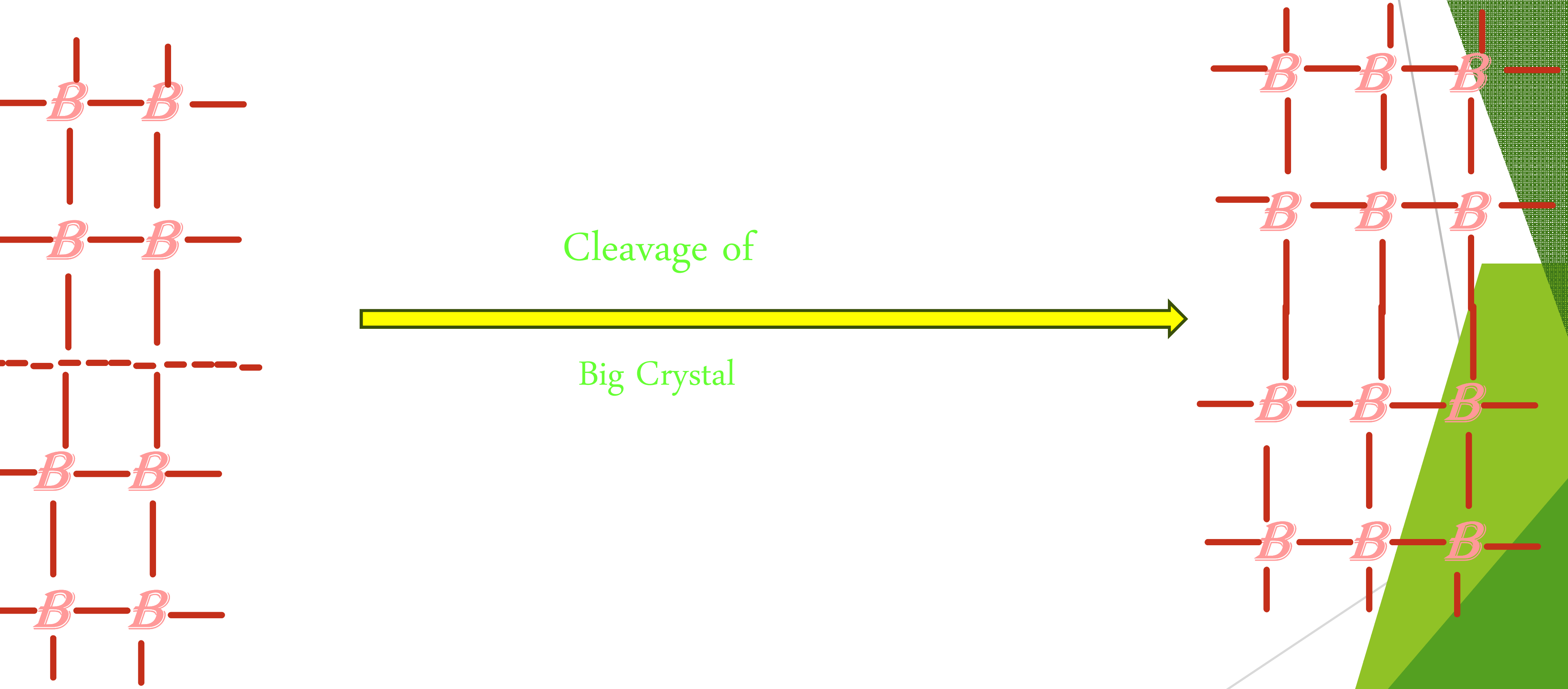
n substances which when added to lower its surface tension are called ace Active Agents. It also acts as rgents or soaps.

in when inorganic electrolytes such laCl, KCl, KBr etc. are added to H_2O ontact with air, then surface tension $_2O$ increases. This is due to increase oncentration of the solute in the bulk tion compare to that of H_2O/air face. Such substances are called ace Inactive Agents.



Adsorption on Solid Surface:

LEAVAGE OF A BIG CRYSTAL OF SOLID INTO SMALLER UNITS IS DONE TO
ASE SURFACE AREA.



Cleavage of

Big Crystal

ibbs Adsorption Isotherm:

This equation represents an exact relationship between the rption and change in surface tension of a solvent due to prese of a solute. This equation was derived by

- ✓ Willard Gibbs (1878)
- ✓ and afterwards independently by J. J. Thomson, 1888.

vation:

The total energy content within a two component system is- $G = n_1 \mu_1 + n_2 \mu_2 + \gamma S$

Where, n_1, n_2 *are the number of moles of solvent and solute,* μ_1 *and* μ_2 *is their respective potential and* γ *= surface tension, S= area of the surface.*

The associated change in free energy dG becomes $dG = dn_1 \mu_1 + dn_2 \mu_2 + \gamma dS$*-----------------(i)*

Since, G is an exact differential, then $dG = \mu_1 dn_1 + \mu_2 dn_2 + \gamma dS + n_1 d\mu_1 + n_2 d\mu_2 + S d\gamma$ *-----------(ii)*

Substracting (i) from (ii) we get- $n_1 d\mu_1 + n_2 d\mu_2 + S d\gamma = 0$*----------------(iii)*

vithin the bulk of the solution, suppose there are n_2^0 *moles of solute and* n_1^0 *moles of solvent present. Then wi bulk of the solution Gibbs- Duhem relation is valid. Then,* $n_1^0 d\mu_1 + n_2^0 d\mu_2 = 0$

$$\therefore d\mu_1 = -(n_2^0 / n_1^0)\, d\mu_2$$

Substituting this value in equation (iii) we get- $n_1(-n_2^0/n_1^0 \times d\mu_2) + n_2 d\mu_2 + S d\gamma = 0$

$$d\mu_2 (n_2 - n_1 \times n_2^0/n_1^0) + S d\gamma = 0$$

$$S d\gamma = (n_1 \times n_2^0/n_1^0 - n_2)\, d\mu_2$$

$$.\text{Now, } \mu_2 = \mu_2^0 + RT \ln a_2$$

$$d\mu_2 = RT\, d\ln a_2$$

$$S d\gamma = (n_1 \times n_2^0/n_1^0 - n_2)\, RT\, d\ln a_2$$

$$d\gamma / d\ln a_2 = -1/S\, RT\, (n_2 - n_1 \times n_2^0/n_1^0)$$

quantity $1/S\, RT\, (n_2 - n_1 \times n_2^0/n_1^0)$ *is called Surface excess* ($\Gamma 2$)

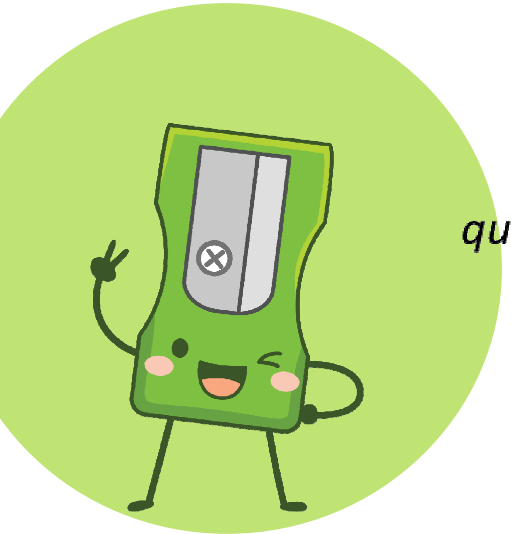
$$d\gamma / d\ln a_2 = -RT\, \Gamma 2$$

$$\gamma / (da_2/a_2) = -RT\, \Gamma 2$$

$$d\gamma / da_2 = -RT/a_2\, \Gamma 2$$

a dilute solution,

$$d\gamma / dc_2 = -RT/c_2\, \Gamma 2$$



Applications of Adsorption:

- Gas masks
- Chromatographic
- Controlling humidity
- Heterogeneous catalyst
- Forth flotation process
- Production of high vacuum
- Curing diseases
- Removal of coloring matter
- Purification

Conclusion:

n this chapter, we know about adsorption, factors upon which it depends, its
rence between physical and chemical adsorption the order of various chemi
esses. Surface chemistry research is an interdisciplinary area on the frontier
ical Chemistry, chemical physics, materials science, and nanoscience. Its imp
ndustrial processes and technology has grown over the years and will continu
in future. Residual unbalanced forces exist on the surface of a solid. As a re
hese residual forces, the surface of a solid has a tendency to attract and reta
ecules of other species with which it is brought into contact. As these molec
in only at the surface, their concentration is more at the surface than in the
olid. Solids, when finely divided, have a large surface area and, therefore, sho
property to a large extent. Colloids, on account of their extremely small
ensions, process enormous surface area per unit mass and are, therefore, goo
rbents. The examples are charcoal, silica gel, alumina gel, clay, etc.

References:

- PRINCIPLE OF PHYSICAL CHEMISTRY: PURI/ SHARMA/ PATHANIA.
- PHYSICAL CHEMISTRY: P. C. RAKSHIT
- Atkins, P. W. & Paula, J. de Atkin's, Physical Chemistry
- WIKIPEDIA

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but never the least, I also keep on record the moral & emotional support provided by my paren
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Souvick Mal

Thank you

GUSHKARA MAHAVIDYALAYA

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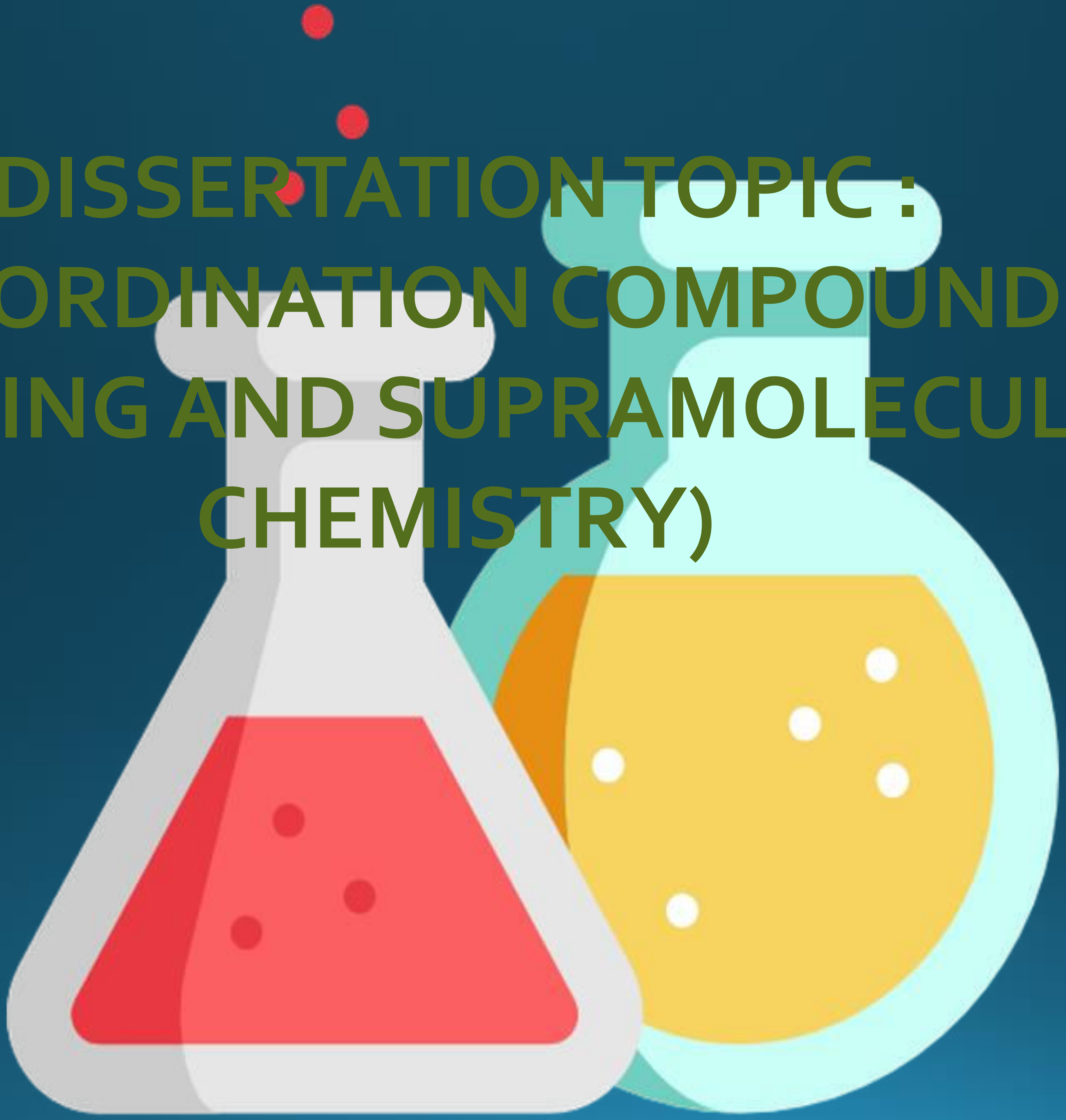


DISSERTATION TOPIC :
COORDINATION COMPOUND (BONDING AND SUPRAMOLECULAR CHEMISTRY)

CONTENT

Introduction to Coordination Compounds

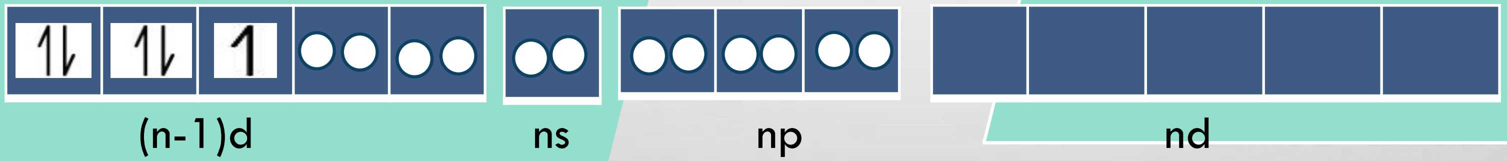
- Coordination Compounds also known as complex compounds consist of a central metal ion or atom surrounded by Ligands.
- Alfred Werner is considered the Father of Coordination Chemistry. His theory of Coordination Compounds earned Noble Prize in 1913.
- Examples : $[Cu(NH_3)_4]^{2+}$, $[Fe(CN)_6]^{4-}$

Bonding Theories of Coordination Compounds

❖ Valence Bond Theory (VBT) :-

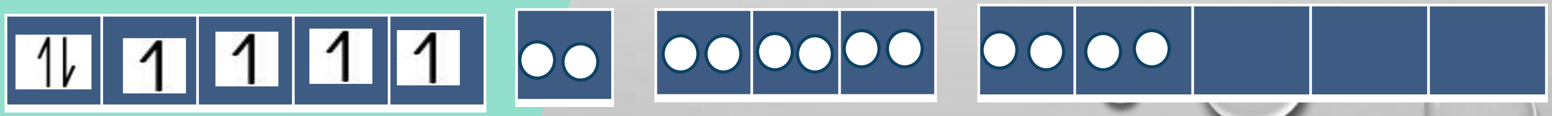
- VBT describes the formation of Coordination Compounds through the overlapping of Atomic Orbitals between metal ion and ligands .
- VBT considers the hybridization of metal and ligand orbital .
- VBT provides insights on the stability , reactivity and electronic structure of Coordination Compounds.
- It explains geometry of Coordination Compounds based on their hybridization of the orbitals .
- There are two types of compounds classified by VBT –
  - Inner orbital complex

    Example: $[Fe(CN)_6]^{4-}$



  - Outer orbital complex

    Example: $[Fe(OH2)_6]^{2+}$



Demerits of Valence Bond Theory

- Valence Bond Theory fails to explain the conditions to outer and inner orbital complex.
- No explanation for colours of coordination compounds and their magnetic properties.
- There is no prediction given regarding the preference of geometry of the complex.
- VBT can’t explain the reason behind the nonexistence of many complexes.

❖Crystal Field Theory

- Crystal Field Theory was first proposed by Bethe (in 1929).
- CFT considers the electrostatic interaction between the metal and the ligands to explain colour and magnetic properties of coordination compounds.

- There are some basic features of CFT –
  - Ligands are considered as point like charge.
  - Wave mechanical identity of metal’s atomic orbital has to be considered.
  - There will be no covalent interactions between metal and ligand.

- Crystal Field Splitting:
  - The electric field generated by the ligands cause the d-orbitals to split into two energy levels .
    - ➢ Lower energy orbitals
    - ➢ Higher energy orbitals

Crystal Field Splitting : The splitting of the d-orbitals mainly depend on the geometry of the coordination compounds.

❑ For Octahedral geometry →

Lower energy orbitals will be t2g :- d_{xy} , d_{yz} , d_{xz}

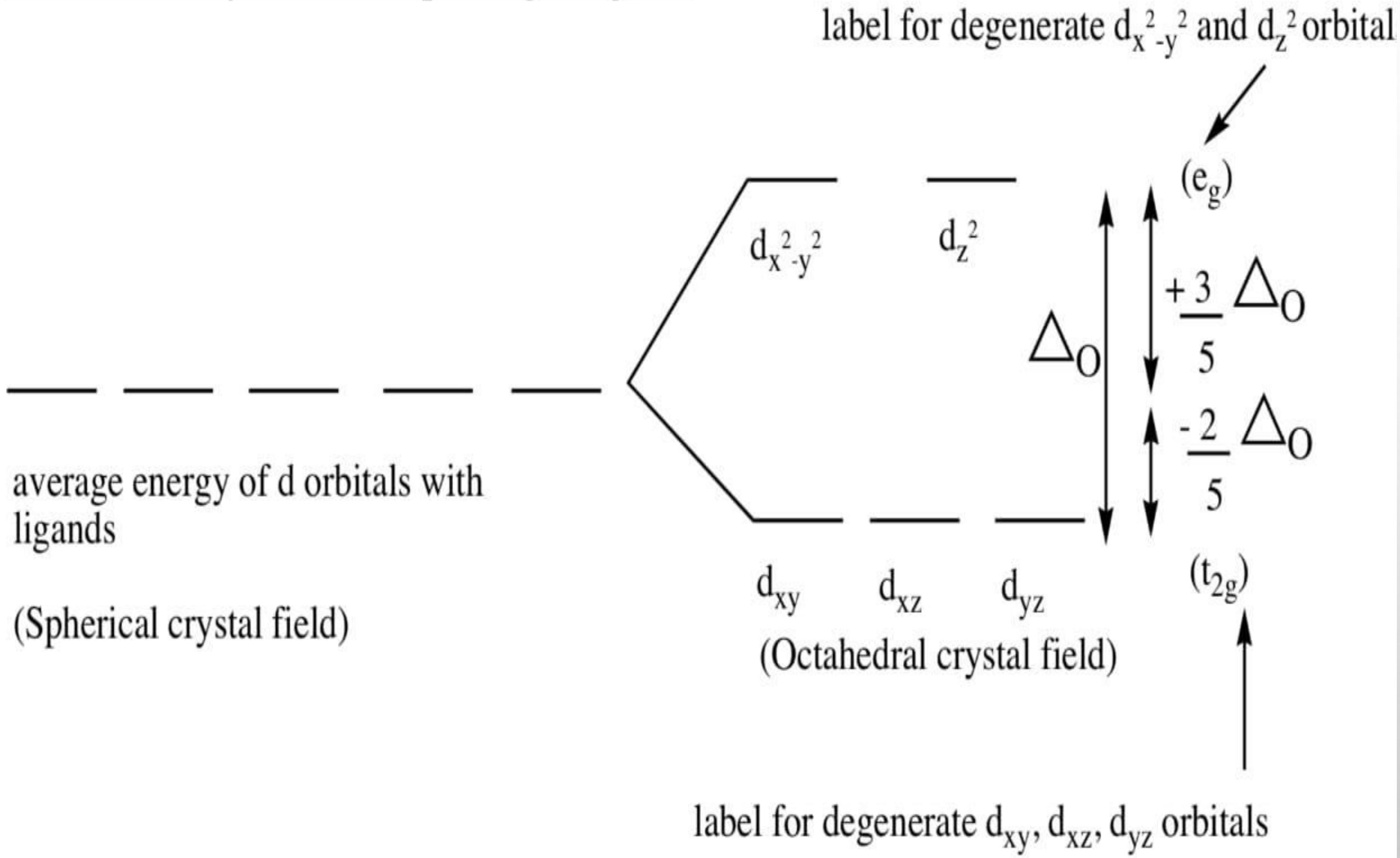
Higher energy orbitals will be eg :- $d_{x^2-y^2}$, d_{z^2}

❑ For Tetrahedral geometry →

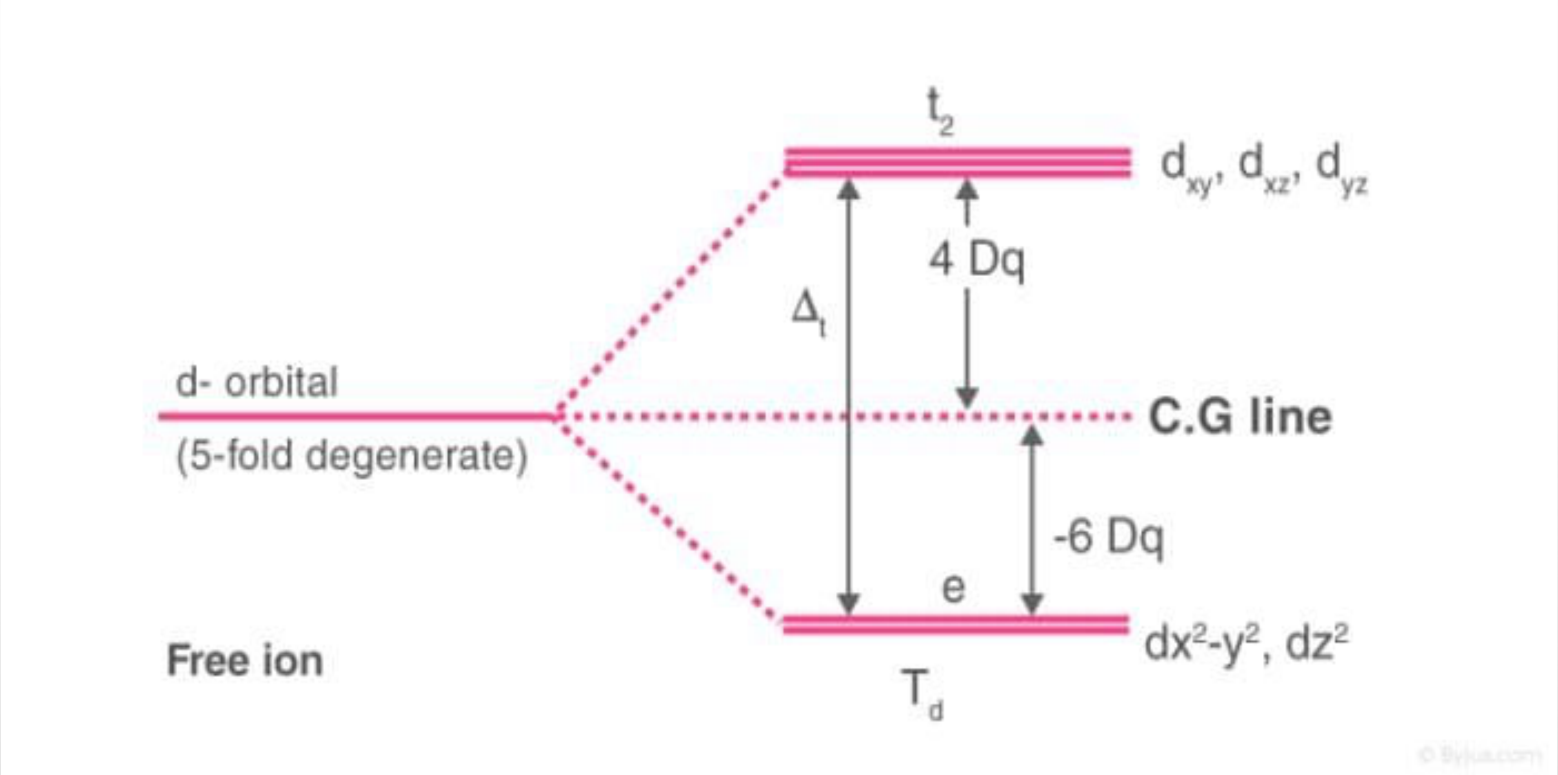
Higher energy orbitals will be t2 :- :- d_{xy} , d_{yz} , d_{xz}

Lower energy orbitals will be e - $d_{x^2-y^2}$, d_{z^2}

Octahedral Crystal Field Splitting Diagram

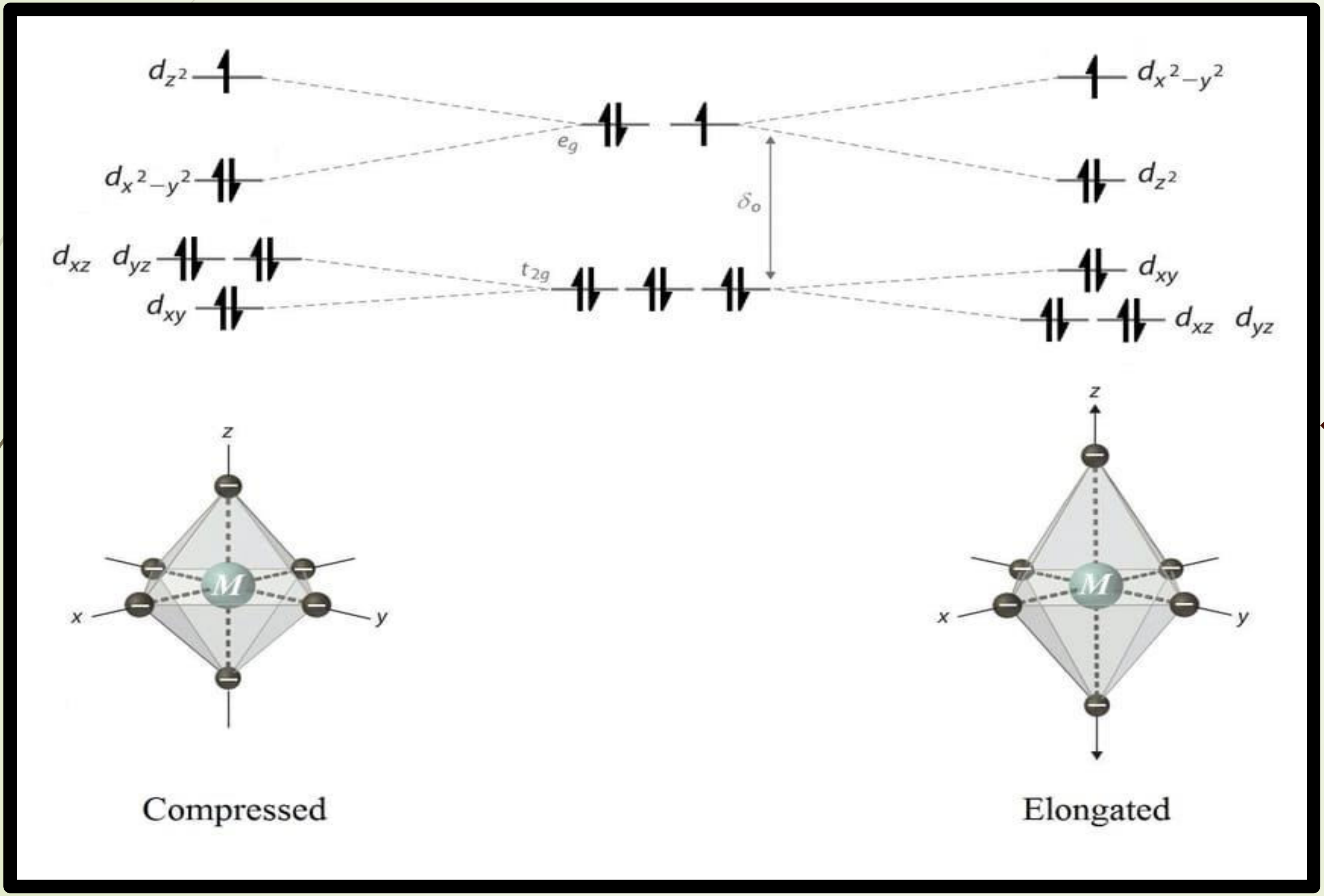


Tetrahedral Crystal Field Splitting Diagram

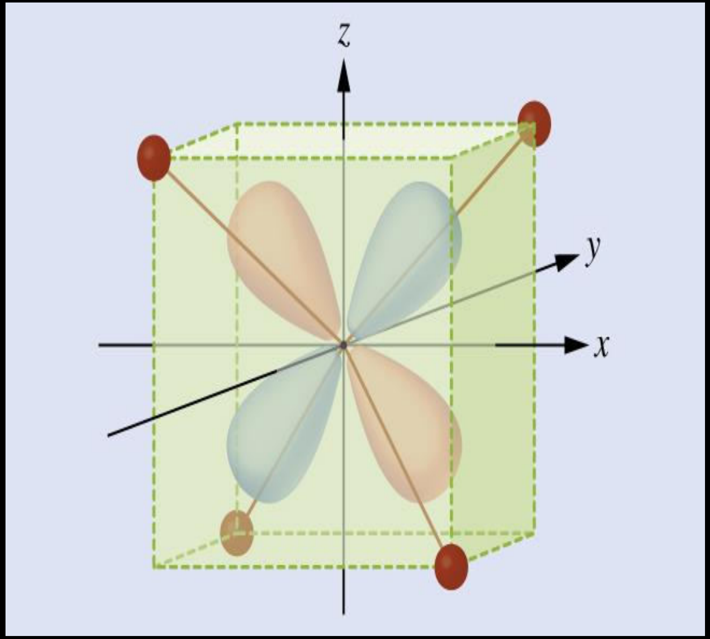


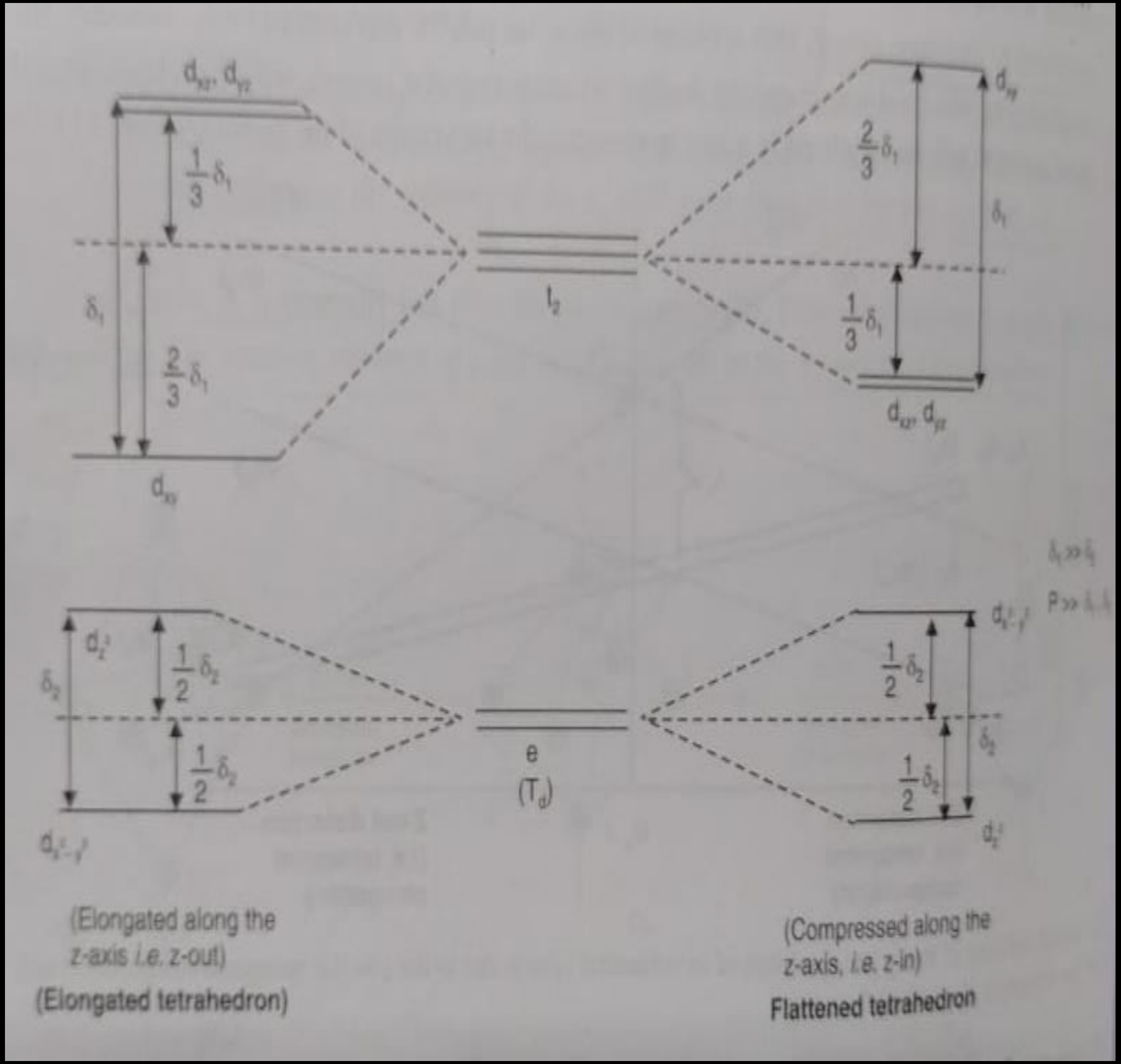
JAHN- TELLER DISTORTION

In the Octahedral system , if the two trans – ligands lying along the z-axis are compressed or elongated compared to the other four ligands lying in the xy plane, then we get the tetragonally distorted octahedrons.



Splitting of t_{2g} and e_g orbitals of an octahedral system due to Z-in (compressed) and Z-out (elongated).





Splitting of t_{2g} and e_g orbitals of an tetrahedral system due to Z-in (compressed) and Z-out (elongated).

❖Merits and Demerits of Crystal Field Theory

Merits

- ✓ Spectral properties of coordination compounds can be clearly explained by Crystal Field Theory.
- ✓ Crystal Field Theory can interpret the magnetic properties of Coordination Compounds .
- ✓ The distortions in the geometry of Coordination Compounds can be explained by CFT.
- ✓ CFT can explain the stereochemical preferences.

Demerits

- ✓ As ligands are considered as point like charge but metal's wave mechanical term is considered . Thus , self – contradictory.
- ✓ CFT assumes Coordination Compounds as purely electrostatic models which can never be strictly true as there are experimental supports for overlapping interaction like Nephelauxetic effect , reduction of interelectronic repulsion etc.
- ✓ This theory is unable to explain some significant order of spectrochemical series.
- ✓ This purely electrostatic model fails to explain the origin of the intense charge transfer band.

Supramolecular chemistry

Introduction

Supramolecular chemistry also known also as “chemistry beyond molecule” deals with the study of molecular assemblies and the interactions that govern their formation , stability and function

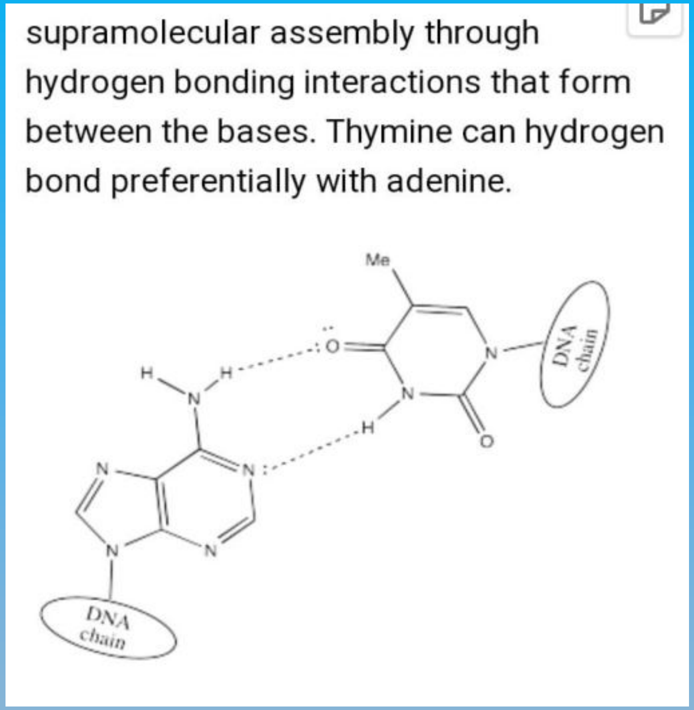
IN 1987 THE Noble Prize in chemistry was awarded jointly to Donald J Cram , Jean Marie Lehn and Charles J for Supramolecular chemistry

The assemblies are held together by weak noncovalent bond – Hydrogen bonding , Van Der Waals interaction and π-π stacking.

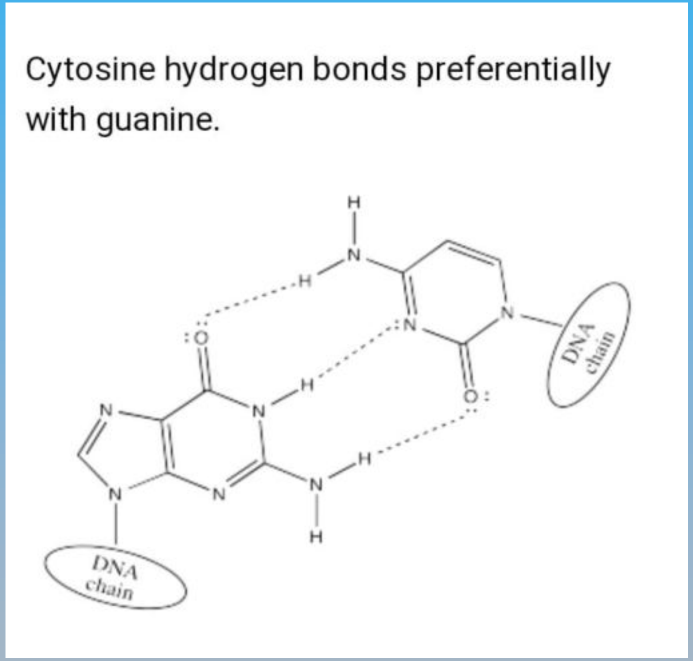
Supramolecular Chemistry techniques such as self-assembly and molecular recognition can be used to design and control the formation of supramolecular structures.

Example – The DNA structure

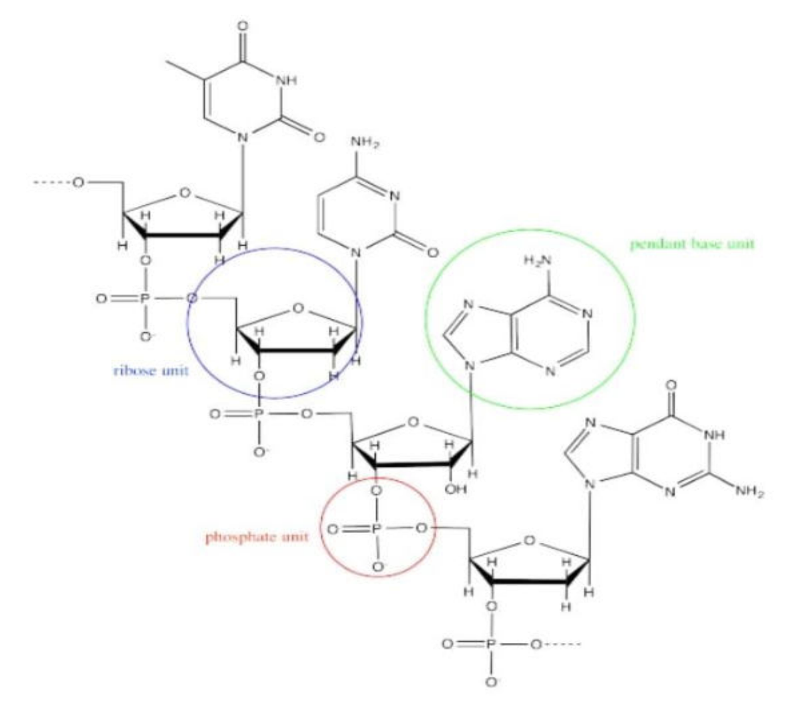
The structure of DNA



supramolecular assembly through hydrogen bonding interactions that form between the bases. Thymine can hydrogen bond preferentially with adenine.

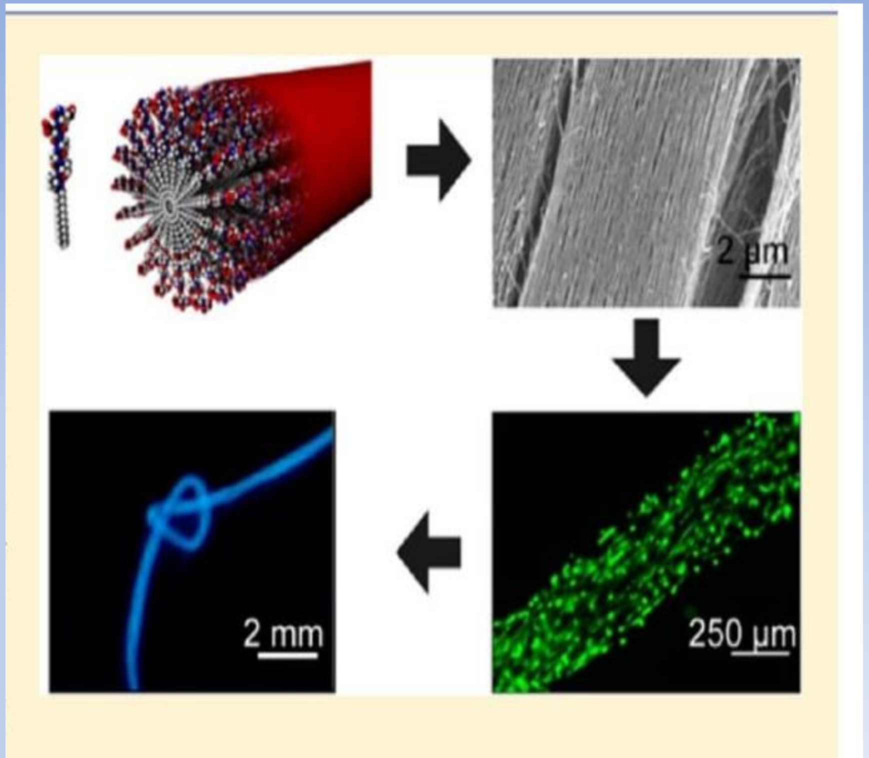


Cytosine hydrogen bonds preferentially with guanine.



Relation between Supramolecular Chemistry and Coordination Compounds

- Coordination Compounds are used as building blocks for Supramolecular architectures.
- Coordination bond provides strong and directional interactions which helps to form molecular assemblies.
- Coordination compounds serve as component to Supramolecular chemistry.



Self Assembly

The spontaneous organization of molecules under near thermodynamic equilibrium conditions into structurally well-defined and stable arrangements through non covalent bond

The molecular components need complementary properties such as specific surface , characteristics , surface charge , polarizability and surface functionalities to self assemble.

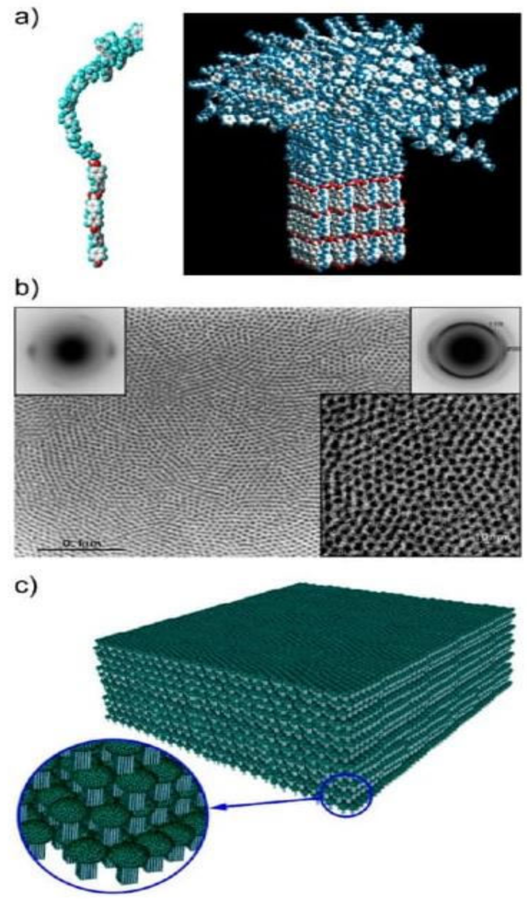


Figure 1. (a) Chemical structure of rodcoil molecules. (b) Electron micrographs and electron diffraction patterns (inset) show formation of ordered mushroom assemblies. (c) Schematic of the layering and polar ordering of the mushroom assemblies. Adapted with permission from ref 6. Copyright 1997 AAAS.

Types of Self-Assembly in Coordination Compounds

Polymeric self-assembly: Formation of extended polymeric structures through coordination bonds between metal centers and ligands

Supramolecular cages and capsules: Assembly of discrete three-dimensional structures that can encapsulate guest molecule

.Coordination-driven self-assembly: Formation of complex structures through coordination interactions between multiple metal centers and ligands.

Examples of Self-Assembly in Coordination Compounds

Metal-organic frameworks (MOFs): Crystalline materials with a porous structure formed through self-assembly of metal ions or clusters and organic linkers

Supramolecular helicates: Coordination complexes with helical structures formed through the self-assembly of metal ions and chiral ligands

Self-assembled monolayers (SAMs): Molecular assemblies formed on a surface through self-assembly of molecules with specific functional groups.

Metal-Organic Frameworks (MOFs): Definition:-

MOFs are a class of coordination compounds consisting of metal ions or clusters connected by organic ligands to form a porous three-dimensional framework . MOFs possess an exceptionally high surface area due to their porous nature, providing abundant space for guest molecule adsorption.

Structural Features of MOFs:-

Nodes: Metal ions or clusters that act as the connecting points in the MOF structure. Struts: Organic ligands that link the nodes together, forming the framework. Pores: The void spaces within the MOF structure that allow for guest molecule storage and transport.

Coordination Compounds as Building Blocks:-

Coordination bonds: MOFs are constructed using coordination compounds as building blocks, combining the metal nodes and organic ligands in a controlled manner. The formation of coordination bonds between metal nodes and ligands is the primary driving force for MOF assembly.

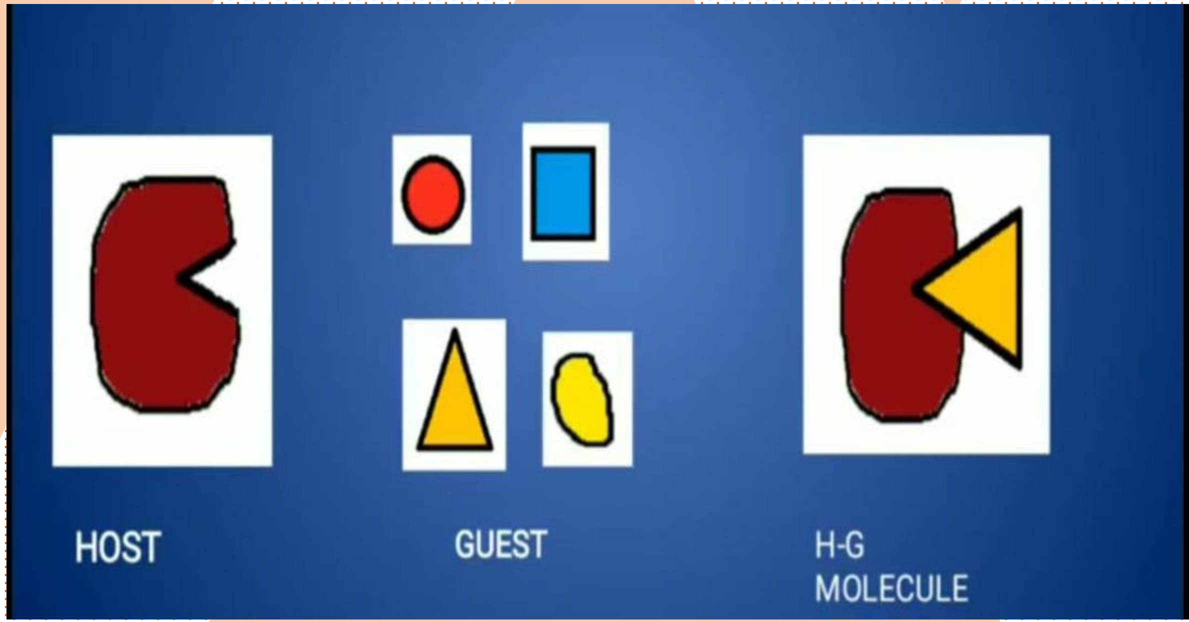
Versatile ligands: Various types of ligands can be employed, offering a wide range of structural possibilities and properties. The choice of ligands plays a crucial role in determining the structure and properties of the MOF.

Applications of MOFs

- Gas storage and separation
- Water Harvesting
- Catalysis
- Energy storage
- Drug Delivery
- Carbon capture and storage
- Sensing and Detection

❖Molecular Recognition

- Molecular recognition refers to the ability of molecules to selectively interact and bind with specific complementary molecules or ions.
- Host Guest Chemistry : Inclusion complexes , clathrates and cryptands are example of Host-Guest system.



Significance of Coordination Compounds on Molecular recognition

- Selective Binding in Host-Guest Chemistry
- Chiral Recognition
- Chelation Effect
- Recognition of biomolecules by Metalloprotiens
- Steric and Electronic effect

Significance of Coordination Chemistry in Supramolecular Chemistry

The bonding of coordination compo ds plays a crucial role in the formation and stability of supramolecular architectures. Supramolecular architectures refer to large-scale assemblies formed through non-covalent interactions between molecules or molecular components. These architectures can exhibit unique structural, electronic, and functional properties that are distinct from those of individual molecules. Here are the key significance of coordination bonding in supramolecular architectures

- Structural stability
- Control of Assembly
- Hierarchical Assembly
- Diversity of Architectures

Design of Coordination Compounds for Functional Materials

The design of coordination compounds plays a crucial role in the development of functional materials with tailored properties and applications. By carefully selecting ligands, metal centers, and coordination geometries, researchers can control the bonding interactions and molecular architecture of coordination compounds, leading to the desired functional properties. Here are some examples of how coordination compounds can be designed for specific functional materials:

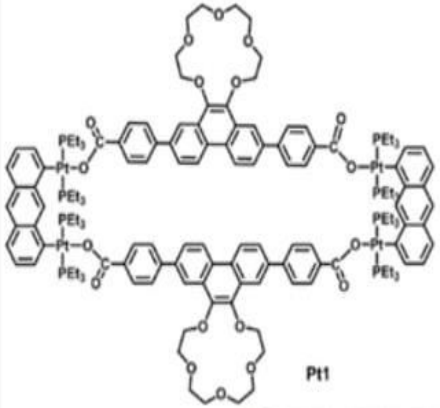
- Luminescent Materials
- Magnetic Materials
- Catalytic Materials
- Conducting Materials
- Porous Materials

Coordination Compounds as Building Blocks in Supramolecular architectures

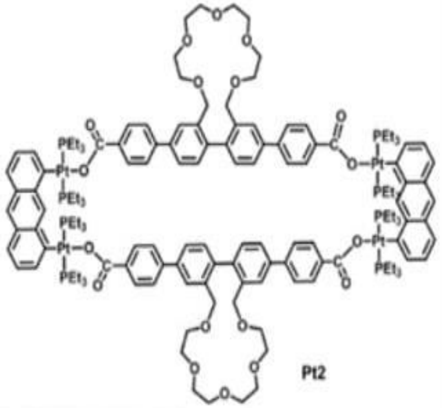
Synthesis and study of crown – ether appendel Tetraplatinum(II) Macrocyclic chemosensors for cation detection

Six Hg(II) coordination compounds containg 2-((pyridine-3-ylmethylene)amino)phenol and 4-((pyiridin-4-ylmethylene)amino)phenol

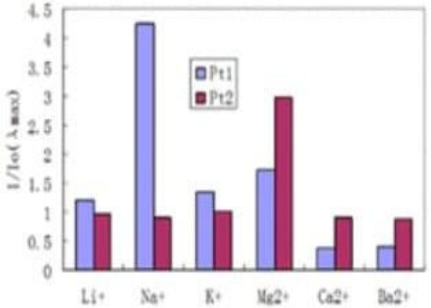
Organometallic polyphosrous complexes as diversified building blocks in Coordination compounds

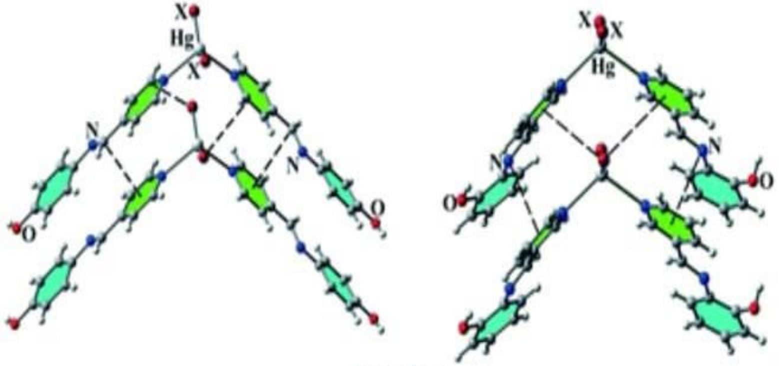


Pt1

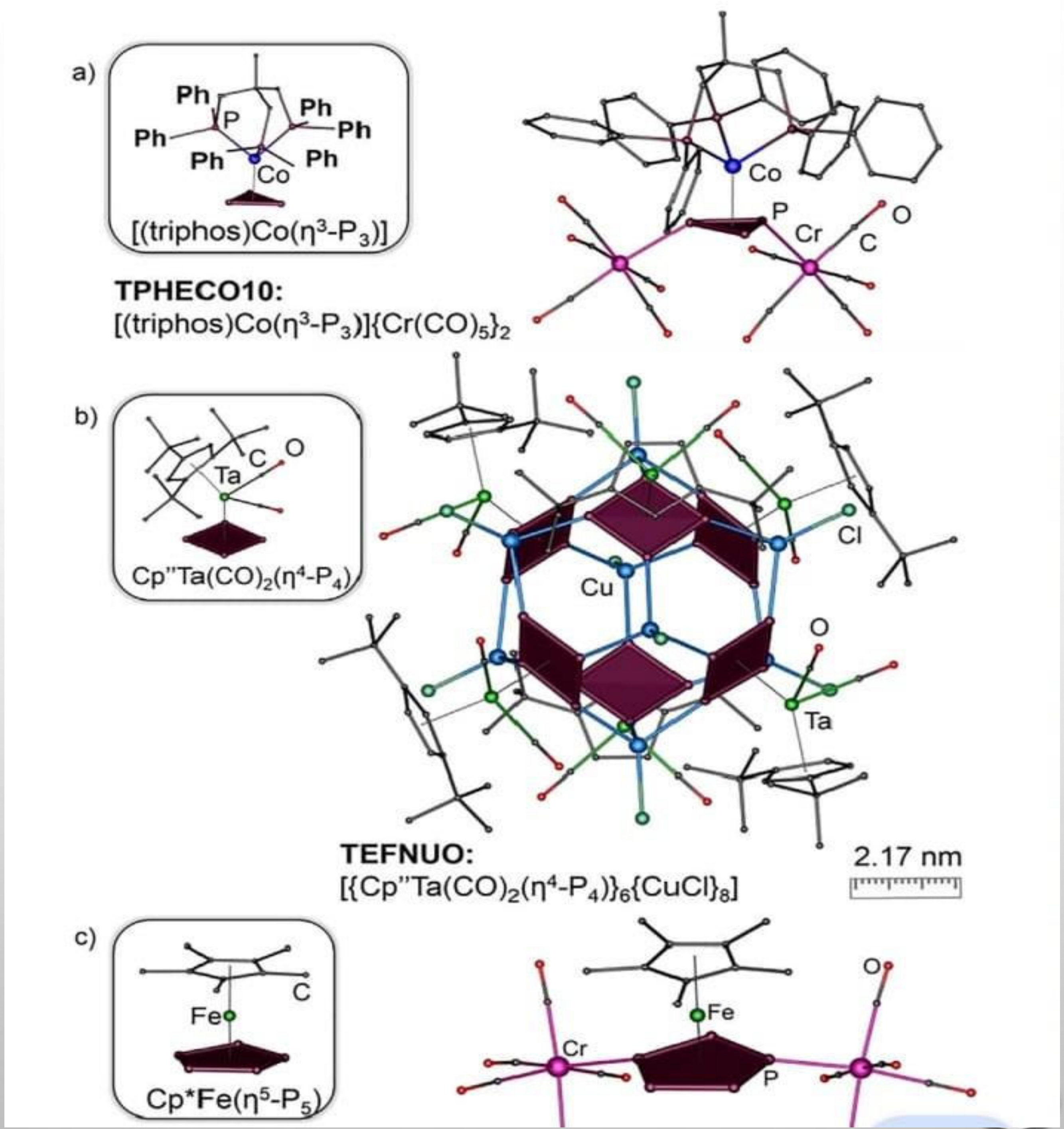


Pt2





X=Cl, Br, I


a)
Ph
P
Ph
Ph
Ph
Ph
Ph
Co
[(triphos)Co(η³-P₃)]
Co
P
Cr
O
C
TPHECO10:
[(triphos)Co(η³-P₃)]{Cr(CO)₅}₂
b)
C
O
Ta
Cp''Ta(CO)₂(η⁴-P₄)
Cl
Cu
O
Ta
TEFNUO:
[{Cp''Ta(CO)₂(η⁴-P₄)}₆{CuCl}₈]
2.17 nm
c)
C
Fe
Cp*Fe(η⁵-P₅)
Fe
O
Cr
P

Future Scope of Coordination Compounds and Supramolecular Chemistry

- Advance supramolecular architectures
- Supramolecular Catalysis
- Biomedical Applications
- Supramolecular Electronics
- Molecular Recognition and Host – Guest Chemistry
- Responsive and Stimuli-Responsive System
- Functional Materials

CONCLUSION

Coordination compounds play a pivotal role in supramolecular chemistry as they serve as versatile building blocks for the construction of complex supramolecular architectures. The unique properties of coordination compounds, arising from the coordination of metal ions with ligands, make them highly attractive for creating functional supramolecular systems.

Bibliography

- Gary L. Miessler & Donald A Tarr. Inorganic Chemistry , Third Edition.
- Asim K Das & Mahua Das Fundamental Concepts of Inorganic Chemistry , Volume 4
- Jonathan W. Steed and Jerry L. Atwood Supramolecular Chemistry , Second Edition
- https://en.m.wikipedia.org/wiki/Supramolecular_chemistry

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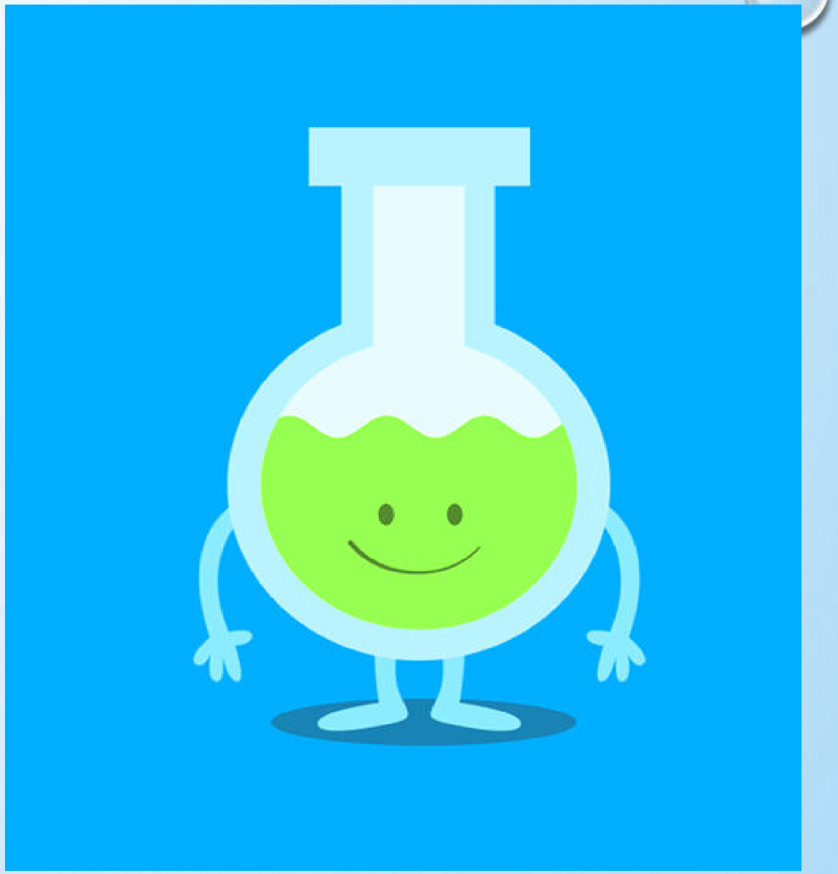
Thank You



THE UNIVERSITY OF BURDWAN

GUSHKARA MAHAVIDYALAYA

Dissertation on Nuclear Magnetic Resonance Spectroscopy

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- **REGISTRATION NO.** : 202001004831 OF 2020 TO 21
- **SEMESTER** : 6
- **COURSE CODE** : DSE-4

NMR SPECTROSCOPY

B.Sc 6th Semester Chemistry Hons Examination -2023

DISSERTATION ON “NMR SPECTROSCOPY”

By

Sumit Sil

Roll No:- 200311000051

Registration No:- 202001004831 of 2020-21

Course code - DSE 4

Under the guidance of

Dr. Bholanath Sarkar

Dr. Pialee Roy

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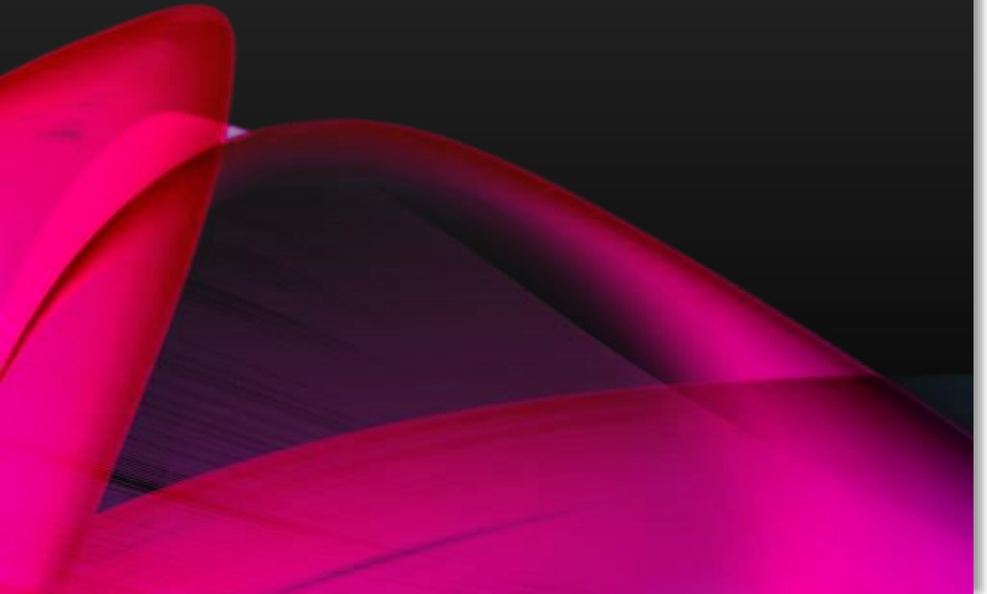
The Department of Chemistry, Guskara Mahavidyalaya,
Guskara

INDEX

INTRODUCTION

- Nuclear Magnetic Resonance (NMR) is a spectroscopy technique which is based on the absorption of electromagnetic radiation in the radio frequency region 4 to 900 MHz by nuclei of the atoms.
- Proton Nuclear magnetic resonance spectroscopy is one of the most powerful tools for elucidating the number of hydrogen or proton in the compound.
- It is used to study a wide variety of nuclei:
  - ^{1}H
  - ^{19}F
  - ^{13}C
  - ^{15}N
  - ^{31}P

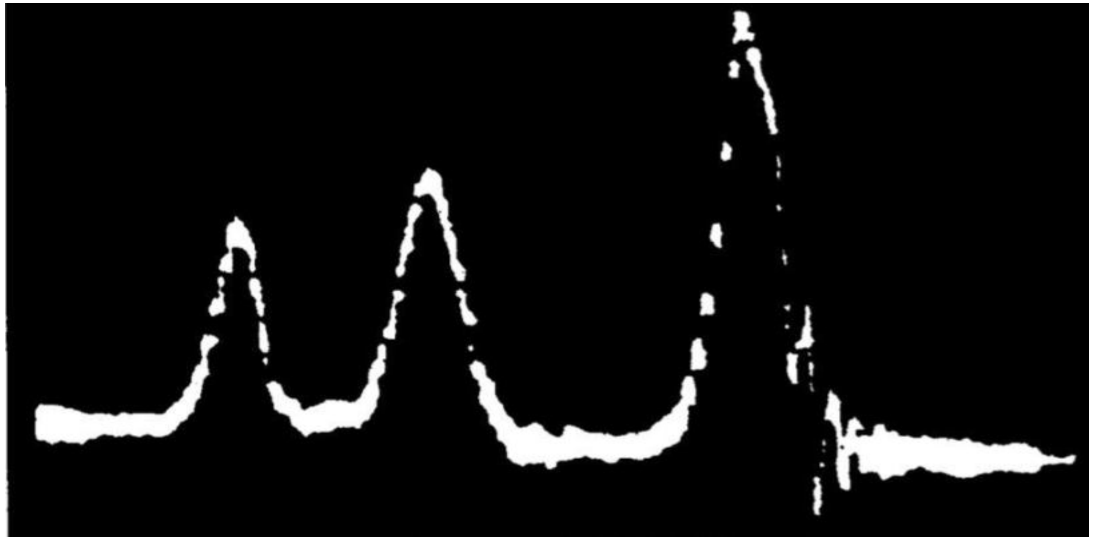
TYPES OF SPECTROSCOPY



- Absorption spectroscopy
- Electrochemical impedance spectroscopy:
- ESR Spectroscopy
- Emission spectroscopy
- Fluroscence spectroscopy
- Infrared spectroscopy
- Mossbauer spectroscopy
- Nuclear magnetic resonance spectroscopy
- Raman spectroscopy
- UV-visible spectroscopy

HISTORICAL PERSPECTIVE

Discovery of NMR Phenomenon in 1945.



The first published “high resolution”
NMR spectrum of ethanol at 30 MHz

Purcell and Bloch –
Nobel prize in Physics – 1952
for the discovery of NMR.

Richard Robert Ernst-Nobel prize in Chemistry-1991

BASIC THEORY

- **NMR-Nuclear Magnetic Resonance**
- **Dealing with magnetic properties of atomic nuclei**
- **Atomic nucleus has mass and it spins on its own axis**
- **Due to the spin, it possesses angular momentum(P)**
- **Due to the charge and the spin it possesses magnetic momentum(μ)**
- **Only certain nuclei have non-zero magnetic moment. In others the "Net magnetic momentum" can be zero**
- **Only nuclei with non-zero magnetic moment are "magnetically active"**
- **Both (P) and (μ) are vector quantities and also quantized**
- **The ratio of magnetic momentum to angular momentum is called "Gyromagnetic ratio".**
- **It is very characteristic of a given nuclei. It is a constant for a given nucleus.**
- **Gyromagnetic ratio = [γ] = (μ)/(P)**

A SIMPLE WAY TO FIND OUT NUCLEAR SPIN- EVEN/ODD RULE

ATOMIC MASS	ATOMIC NUMBER	NUCLEAR SPIN
EVEN	EVEN	ZERO
EVEN	ODD	MULTIPLE OF 1
ODD	EVEN OR ODD	MULTIPLE OF 1/2

Example:

I=0, $^{12}C_6$, $^{16}O_8$,

I=integer, $^{14}N_7(1)$, $^{10}B_5(3)$, $^{2}H_1(1)$

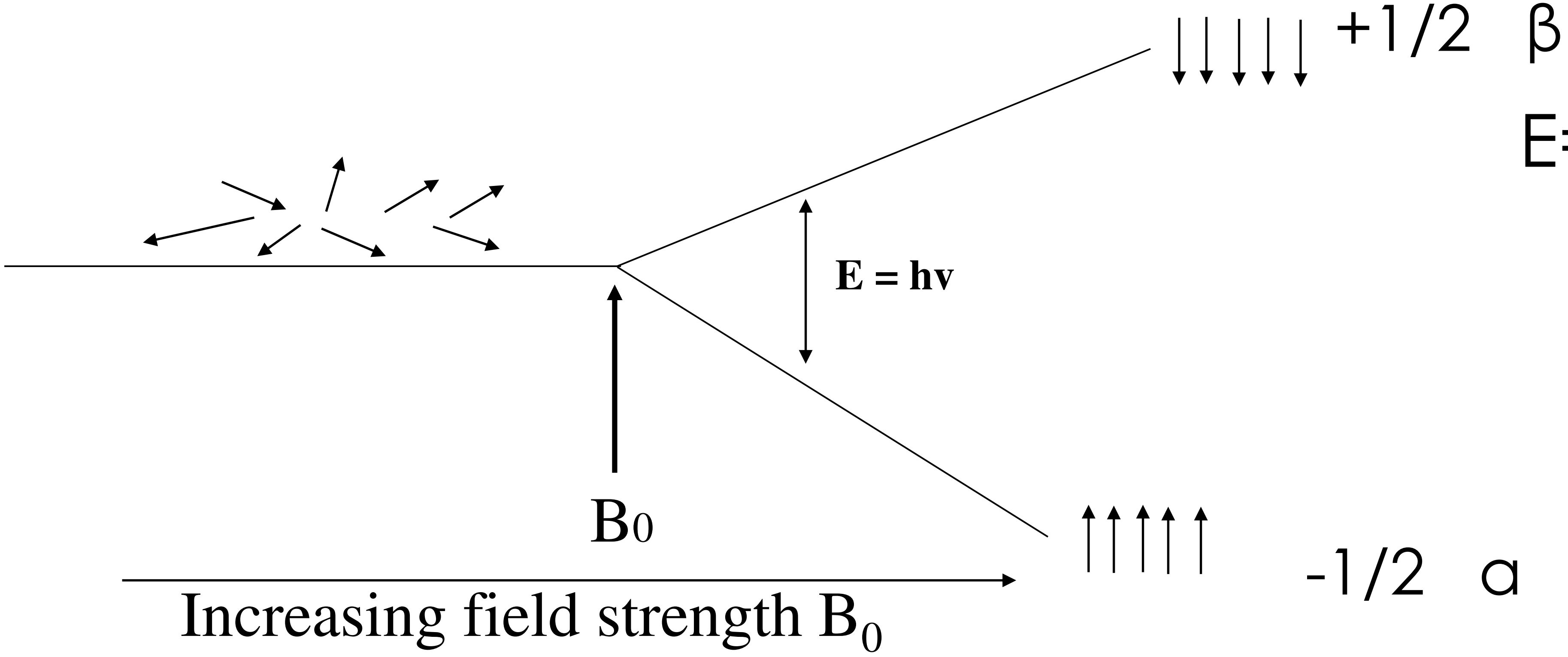
I=half integer,

$^{1}H_1(1/2)$, $^{13}C_6(1/2)$, $^{15}N_7(1/2)$

$^{17}O_8(5/2)$, $^{33}S_{16}(3/2)$, $^{11}B_5(3/2)$

NUCLEAR SPIN

CHANGE IN SPIN STATE IN PRESENCE OF MAGNETIC FIELD



$$E = h\nu = (h/2\pi) B_0 \gamma$$

$$\nu = (B_0 \gamma)/2\pi$$

Resonance condition

The energy gap between the spin states corresponds to radio frequency region

POPULATION DENSITY

- EACH LEVEL HAS A DIFFERENT POPULATION (N), AND THE DIFFERENCE BETWEEN THE TWO IS RELATED TO THE ENERGY DIFFERENCE BY THE BOLTZMMAN DISTRIBUTION

$$\frac{N_{upper}}{N_{lower}} = e^{-\Delta E/kT} = e^{-hv/kT}$$

$h = 6.624 \times 10^{-34}$ J.sec

$k = 1.380 \times 10$ J/K .molecule

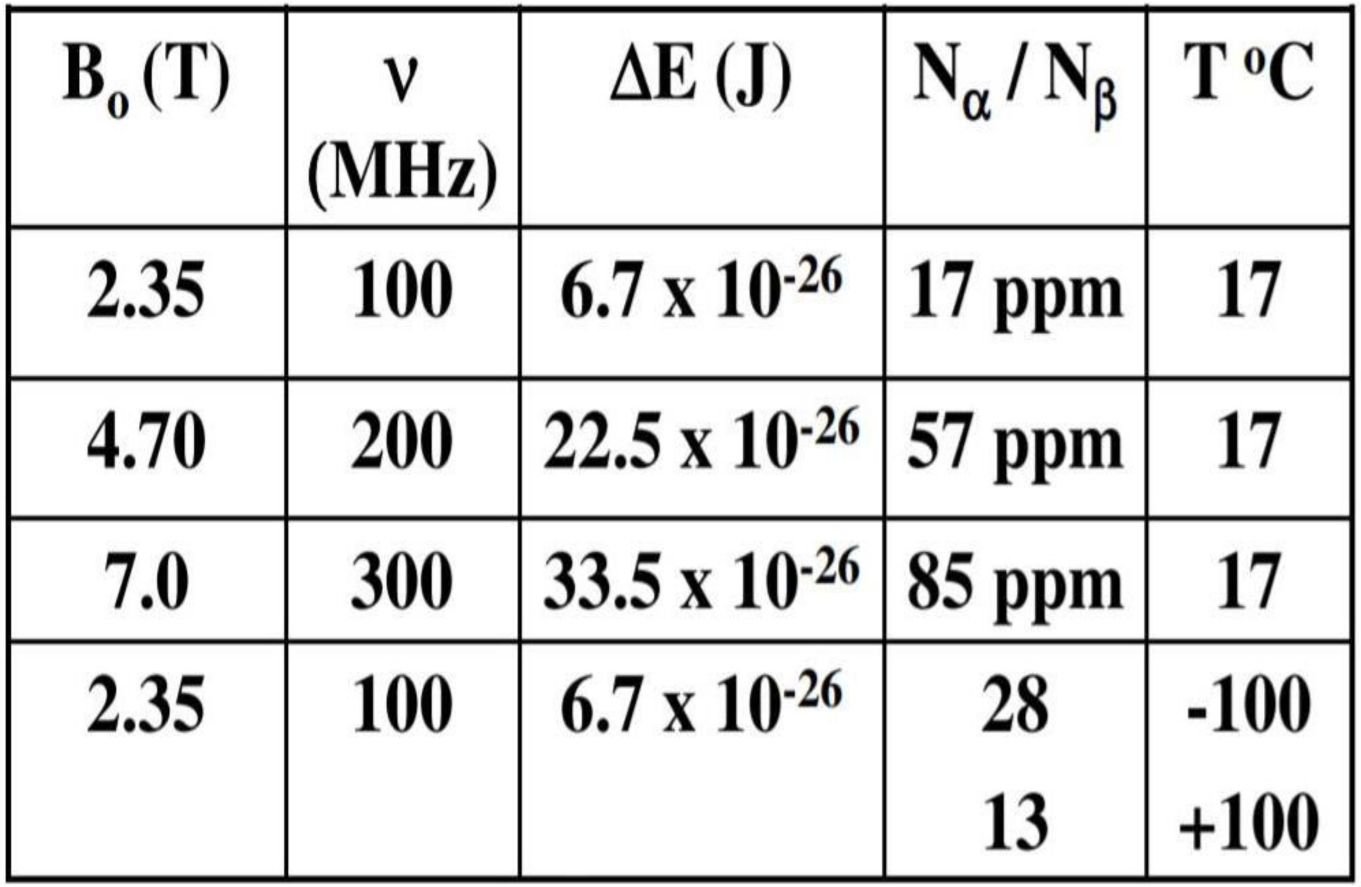
T= absolute temperature (K)

POPULATION EXCESS

Using equation, one can calculate that at 298 K(25°C), for an instrument operating at 60 MHz there are 1,000,009 nuclei in the lower (favored) spin state for every 1,000,000 that occupy the upper spin state.

This excess of 9 nuclei is called the population excess.

The spins in the excited state return back to ground state by
(a) spin lattice relaxation and
(b) spin-spin relaxation

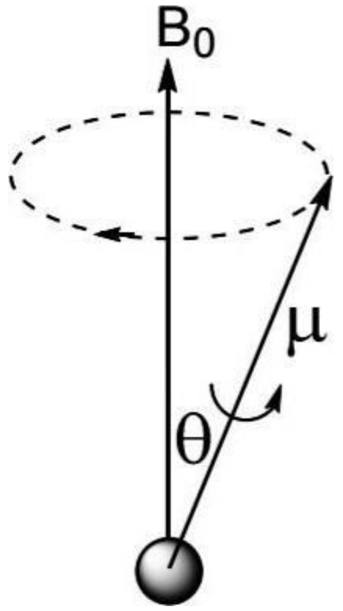


B_0 (T)	ν (MHz)	ΔE (J)	N_α / N_β	T °C
2.35	100	6.7×10^{-26}	17 ppm	17
4.70	200	22.5×10^{-26}	57 ppm	17
7.0	300	33.5×10^{-26}	85 ppm	17
2.35	100	6.7×10^{-26}	28 13	-100 +100

Higher the magnetic field strength – higher the sensitivity and resolution

Lower the temperature – higher the sensitivity

LARMOR FREQUENCY



Spinning nucleus

The interaction of magnetic field with nuclear magnetic moment induces the nuclear magnetic moment to preces about the applied magnetic field with certain frequency called Larmor frequency

Precessing spin about the applied magnetic field direction

ω_0 – Larmor frequency

CLASICAL DESCRIPTION OF NMR

$$\nu=(B_0\Upsilon)/2\pi$$

From the above equation one infers that all the hydrogen nuclei in a molecule, say ethanol should have the same resonance frequency, irrespective of its chemical nature, at a given magnetic field.

But this is not true. Hydrogens in different chemical environment give different resonance frequencies in the NMR.

DEFINATION OF CHEMICAL SHIFT

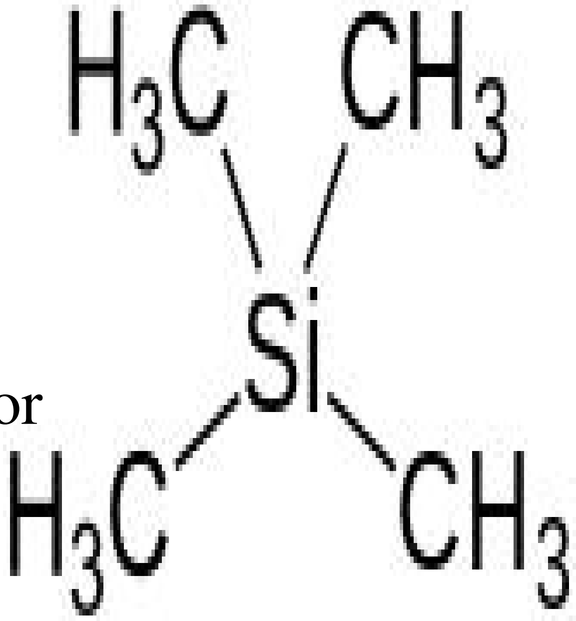
It is inconvenient to refer to proton frequency as 398.432 MHz

δ (in Hz) = $v_{sample} - v_{reference}$ (Spectrometer dependent)

$$\delta =. \frac{(vsample - vreference) * 10^6}{spectrometer\ frequency}$$ (in ppm)

Chemical shift expressed in δ is a dimensionless quantity and also does not depend on the spectrometer frequency

REFERENCE FOR ^{1}H-NMR SPECTROSCOPY



- Tetramethylsilane (TMS) is used as a reference
- The chemical shift of TMS is lower than most protons in organic molecules, so it is taken as zero
- All the protons in TMS are equivalent and hence only one signal for all the 12 protons – high signal intensity
- TMS is a liquid and miscible with most solvents
- It is also volatile and hence easy to remove
- It is inert and does not react with the sample

FACTORS AFFECTING CHEMICAL SHIFT

Electrone gativity , indactive and resonance effects

TMS=0.0 CH_4=0.23 (all in ppm)

MeI	2.2	MeOH	3.4	MeCl	3.1
MeBr	2.6	MeF	4.3	CH_2Cl_2	5.2
MeCl	3.1	$MeNO_2$	4.3	$CHCl_3$	7.2
MeF	4.3				

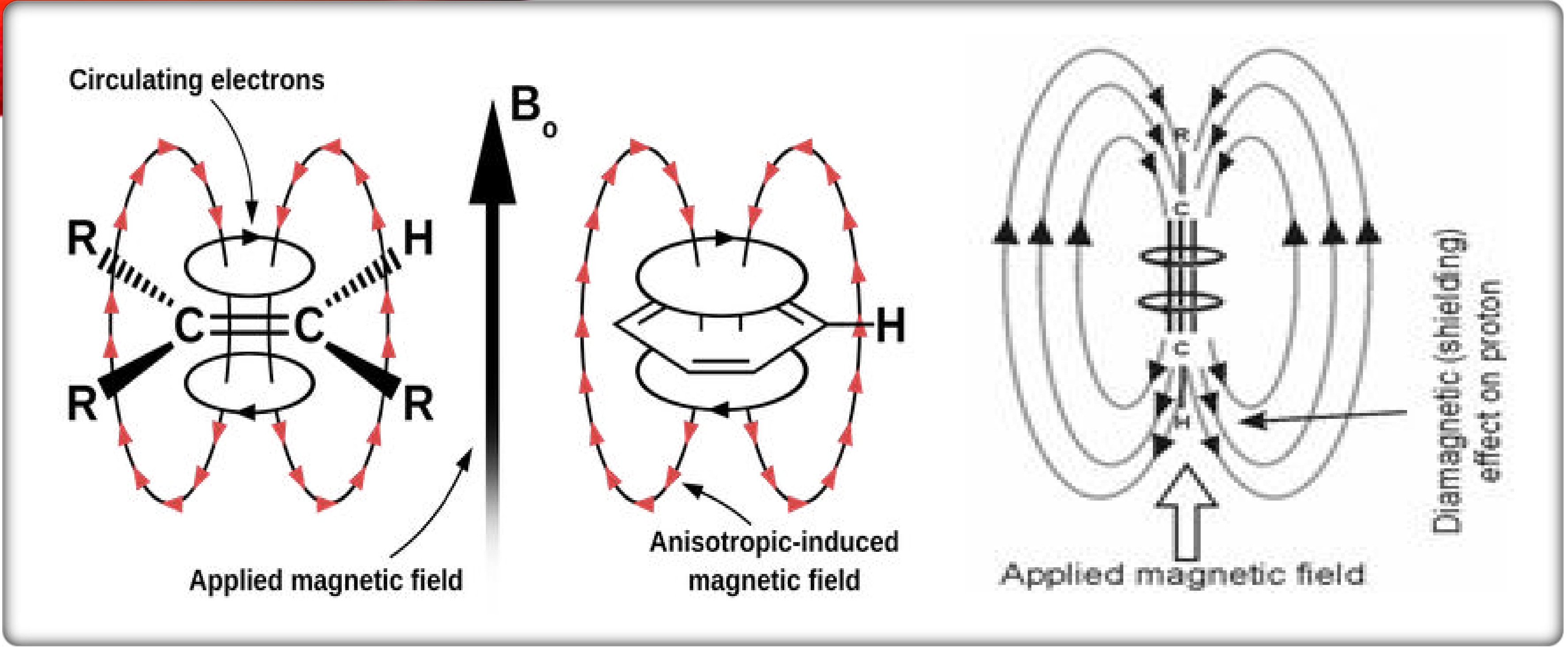
ANISOTROPIC EFFECT

Spherical electron density – induced magnetic field will be uniform in space – isotropic effect

For example –s electron

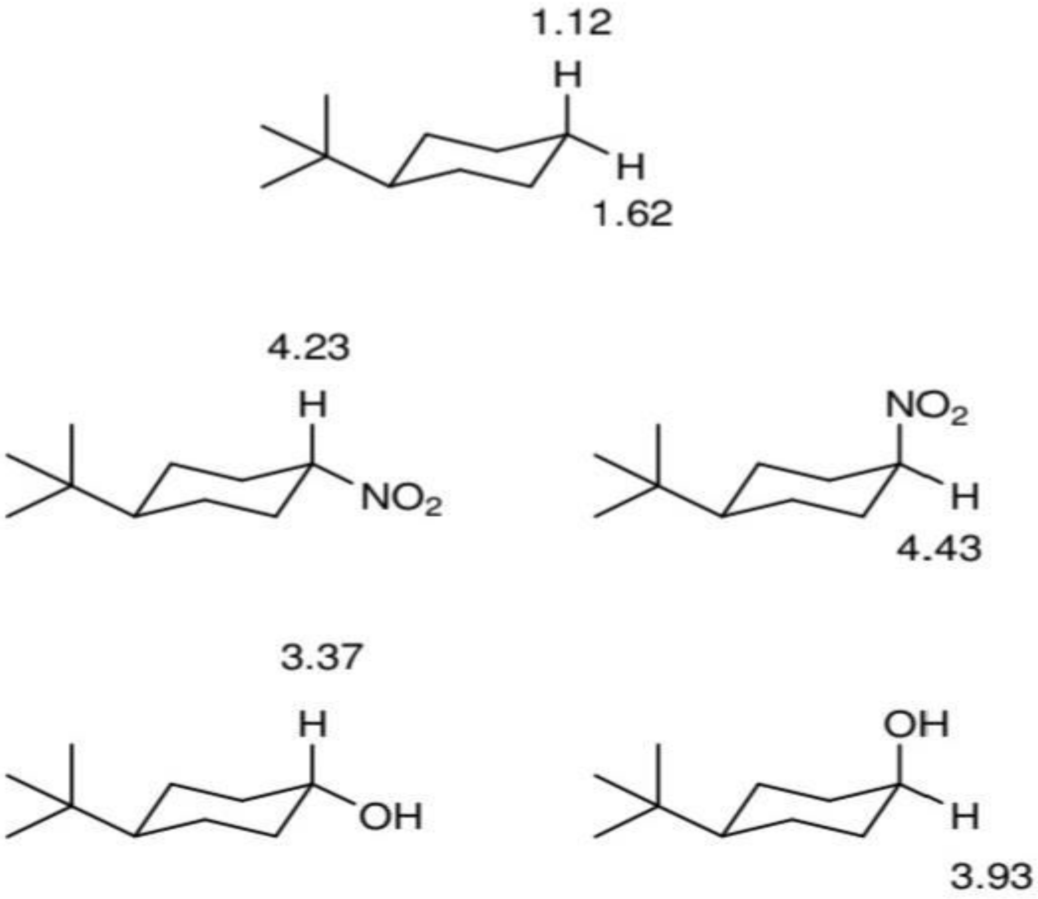
Non-spherical electron density – induced magnetic field will be non-uniform in space – anisotropic

Example: π electron cloud of aromatic ring, C=C and C=O type – most common feature of organic molecules

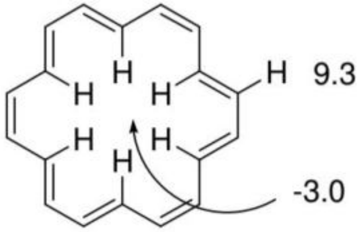


DIAMAGNETIC ANISOTROPY

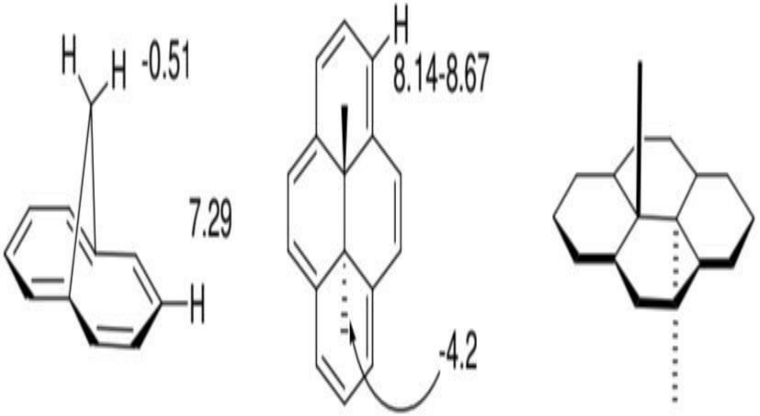
Anisotropic effect of sigma bond



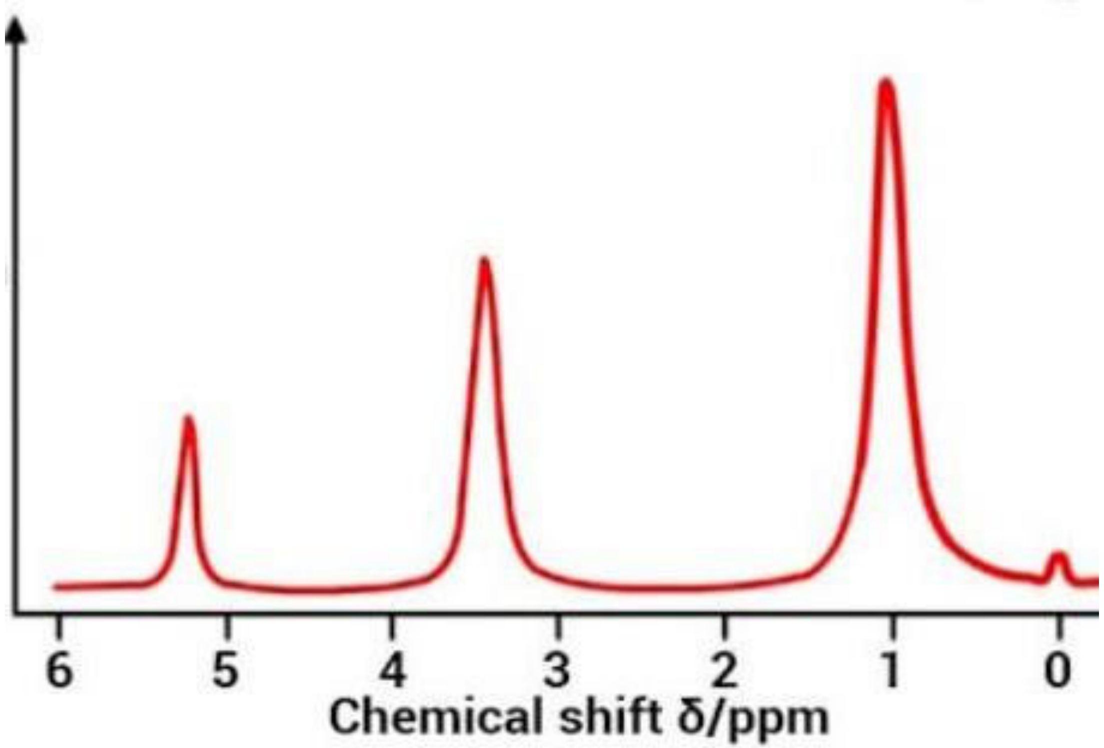
Interesting case of [18]annulene



Examples of effect of anisotropy on chemical shift

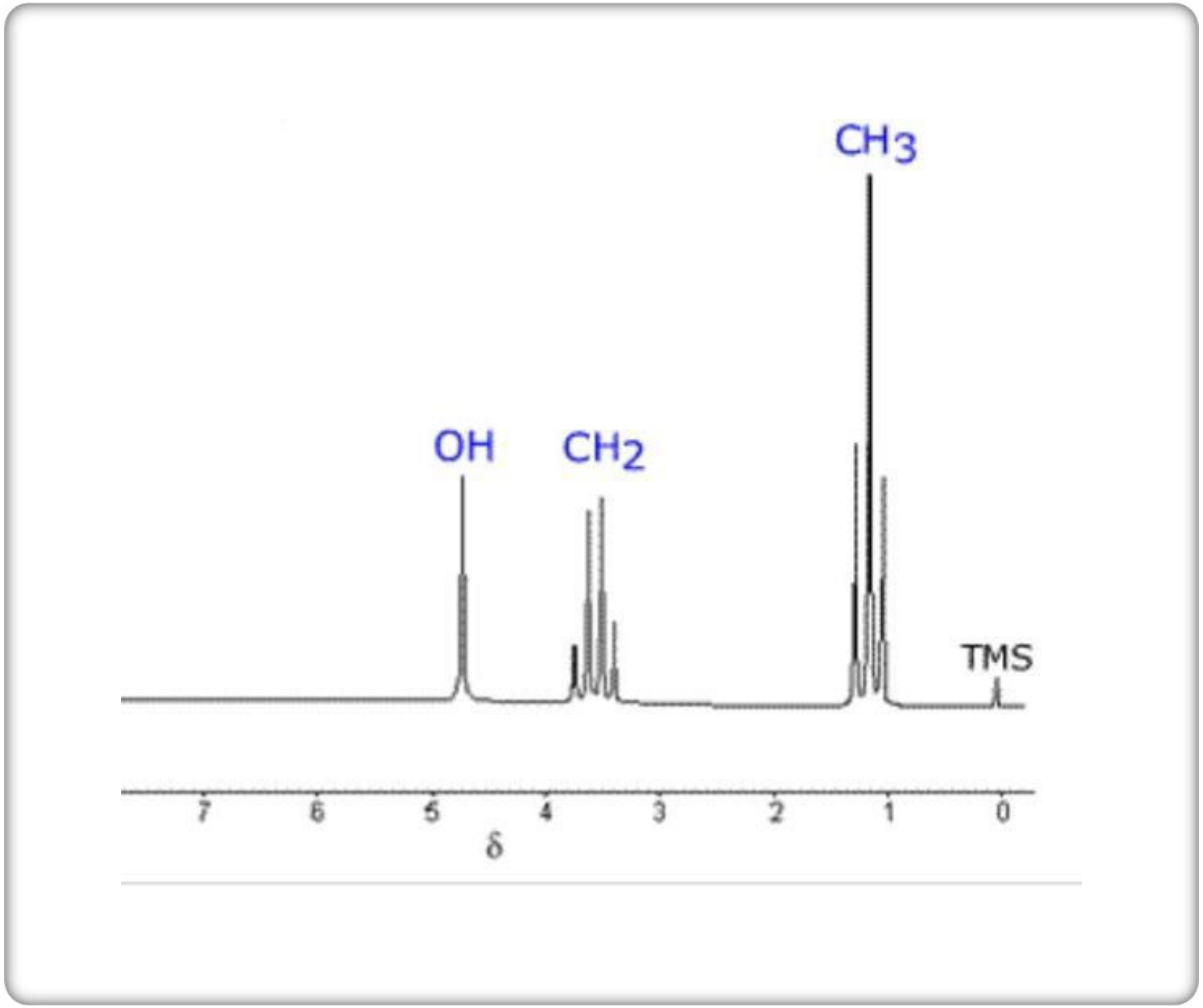


NMR SPECTROSCOPY FOR ETOH



IN LOW RESOLUTION:

IN HIGH RESOLUTION:



SPIN-SPIN COUPLING (SPLITTING)

Protons of the same group do not interact among themselves.

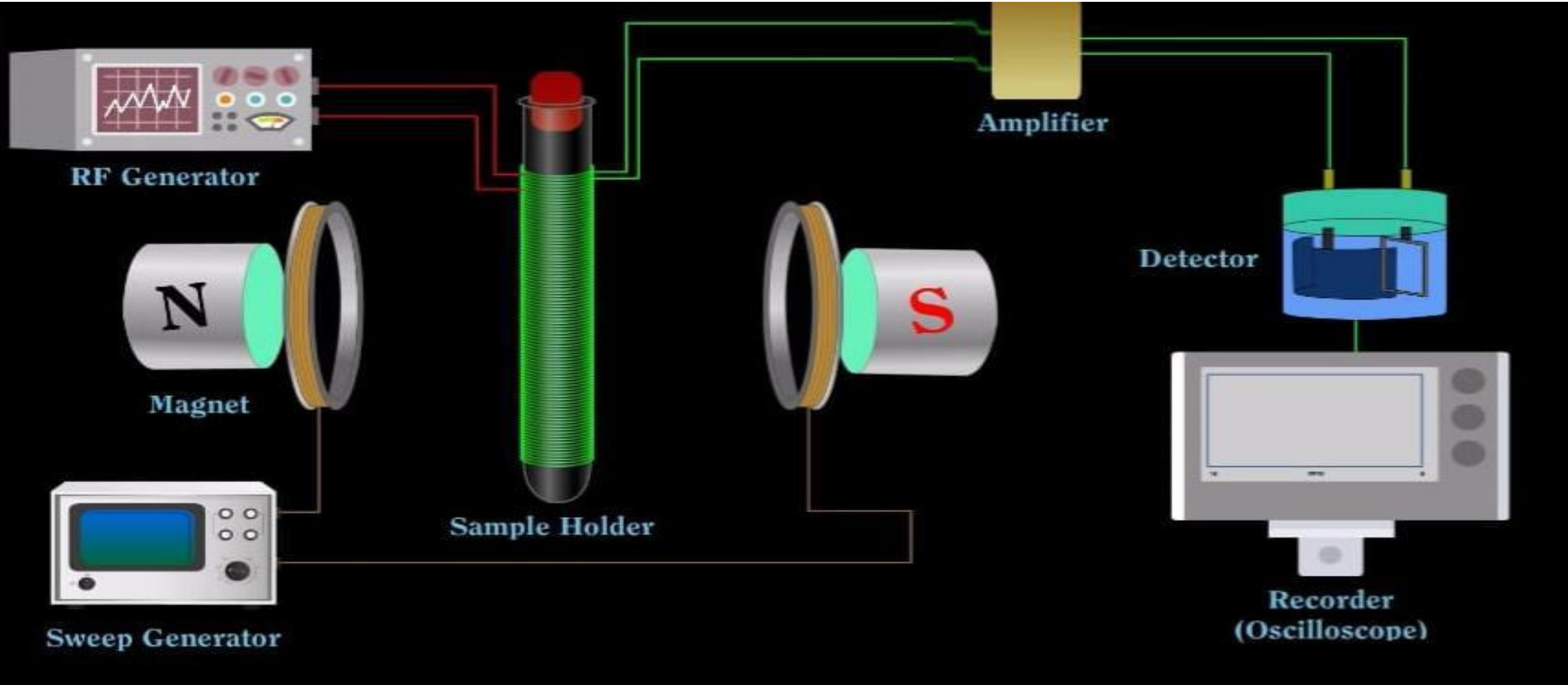
If n numbers of equivalent protons interact or couple with the protons on adjacent C atom, the resonance peak splits into (n+1) signals.

The intensities are symmetric about the mid point of the group and relative intensities of the (n+1) peaks and it is determined by the Pascal's triangle.

THE PASCAL'S TRIANGLE

Singlet	1
Doublet	1 1
Triplet	1 2 1
Quartet	1 3 3 1
Quintet	1 4 6 4 1
Sextet	1 5 10 10 5 1
Septet	1 6 15 20 15 6 1

NMR INSTRUMENTATION



APPLICATION OF NMR SPECTROSCOPY

- ^{I}H NMR used for structural elucidation of organic and inorganic solids
- determines the physical and chemical properties of atoms

Application in medicine….

- Anatomical imaging
- Measuring physiological function
- Flow measurement and angiography
- Tissue perfusion studies
- Tumours
- MRI

Application in medicine...

BRAIN

Distinguishing grey matter & white matter
Imaging posterior fossae, brain stem, spinal cord
Detect demyelinating lesions, tumour, haemorrhage, infarctions

ABDOMEN

Metabolic liver disease
Focal areas of inflammation in chronic active hepatisis

KIDNEY

Distinguishing renal corta & medulla
To evaluate transplanted kidney

PELVIS

Differentiate between benign prostatic hyperplasia & prostatic carcinoma

REFERENCES

- Organic spectroscopy by William Kemp
- Instrumental method of chemical analysis by Wchatwal
- Introduction to Spectroscopy by Donald L. Pavia
- Instrumental methods of analysis by Willard
- https://www.iitm.ac.in/
- https://www.slideshare.net/solairajananant/nmr-spectroscopy-13887430
- http://sydney.edu.au/science/chemistry/facilities/nmr/nmr-applications.shtml
- https://www.google.com/url?sa=t&source=web&rct=j&url=https://www.wikipedia.org/&ved=2ahUKEwiZ1PLXs9n_AhUoXWwGHWu_C04QFnoECBUQAQ&usg=AOvVaw3ay7vaEtH0yTTYdDmrvinX

CONCLUSION

The total project on NMR spectroscopy has influenced me a lot. In today's developing world gives us today a chance of stepping ourselves towards a better tomorrow. After the whole project, the utility and the fundamental function of NMR spectroscopy is quite vivid. So to have a better movement towards a better tomorrow, the progress of NMR spectroscopy is just needless to say.

Thank You

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GUSHKARA MAHAVIDYALAYA

Dissertation Followed by Power Point Presentation

Course Code - DSE-4

Topic: Polymer Chemistry

Presented by **Tithi Mondal**

Contents of this template

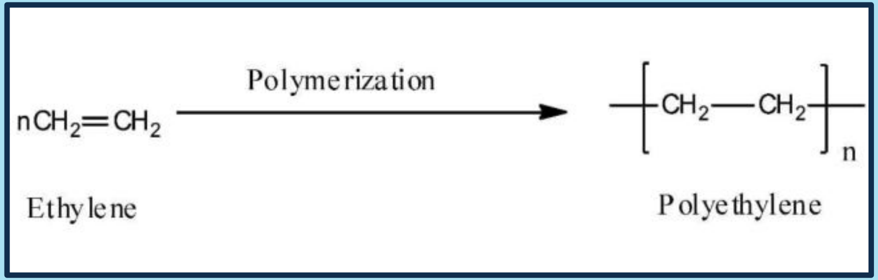
Introduction

The term 'Polymer' in Greek means 'many parts'.

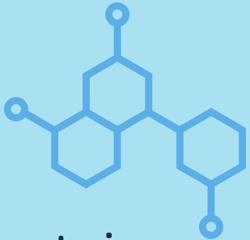
Polymers can be found all around us, from the strand of our DNA, which is a naturally occurring biopolymer, to polypropylene which is used throughout the world as plastic. Polymers can be naturally found in plants and animals or can be human- made. Different polymers have a number of unique physical and chemical properties, due to which they find usage in everyday life.

What is Polymer?

- Polymer is a high molecular weight compound containing many many repeating unit join in a regular fashion.



Monomers



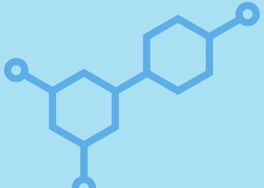
- ❖ Simple reactive species, contain some functional group, join together to form Polymer.

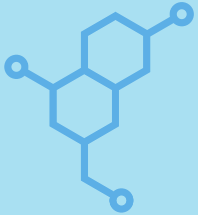
Example:

☐ $CH_2=CH_2$ (Mono functional Momoner)

☐ CH_2-OH
|
CH_2-OH

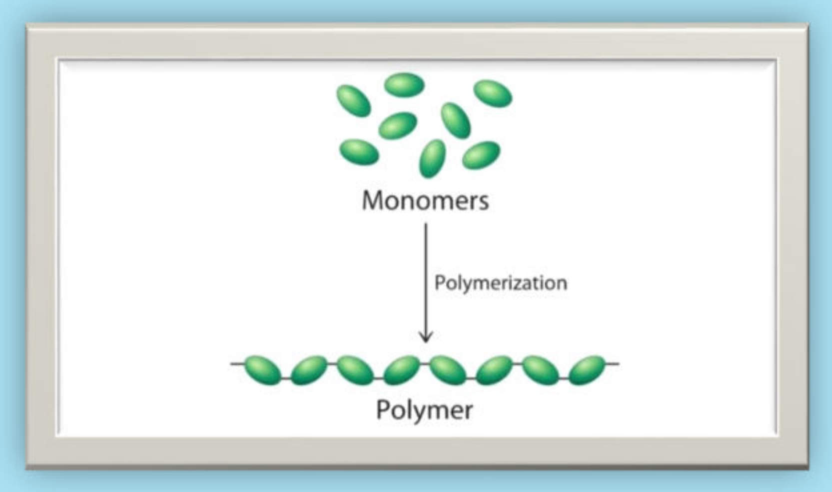
$$\left.\begin{array}{l}CH_2\text{-}OH\\ \quad |\\ CH_2\text{-}OH\end{array}\right. \left\{ \text{Bi functional Momomer} \right\}$$





Polymerization

- An overall process by which a Polymer is formed from its Monomer.



Classification of Polymer

❑ · Classification Based on Source

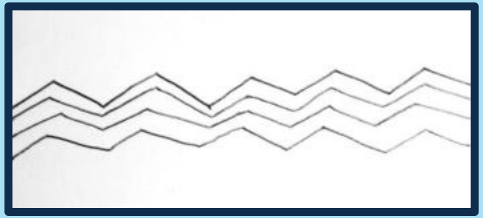
A) **Natural Polymer:** Obtained from nature.
Example – Rubber, Silk, Wool, Protein

B) **Semi Synthetic Polymer:** They are obtained from nature but undergo further chemical modification.
Example – Cellulose Nitrate

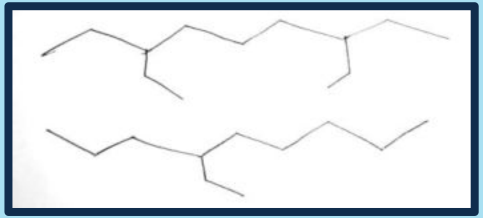
C) **Synthetic Polymer:** Obtained by synthesis in a laboratory.
Example – PVC, Nylon, Polyester.

Classification Based on Structure

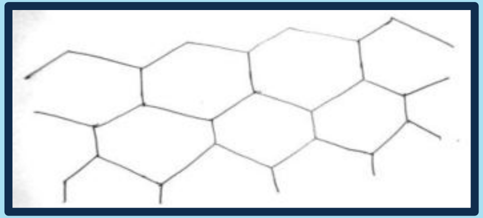
A) **Linear Chain Polymer:** Contain one main chain, have no side chain .
Example - PVC, Nylon



B) **Branched Chain Polymer:** Have some branches along with the main chain.
Example - LDPE



C) **Crossed Linked Polymer:** Have Crossed linked between the main chain, So we get a 3D network structure.
Example - Novalac, Backelite



Classification Based on Molecular Forces

A) **Elastomer:** Very weak intermolecular attractive force between the Polymer Chain

Example - Rubber

B) **Fibres:** Have Strong intermolecular attractive force.

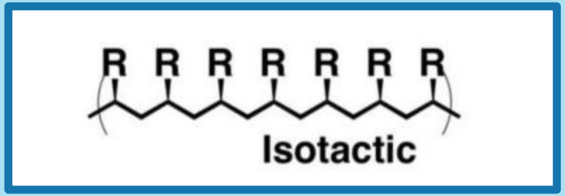
Example - Nylon 6,6 , Terilene

C) **Thermoplastic:** Intermolecular attractive force is in between Elastomer and Fibres.

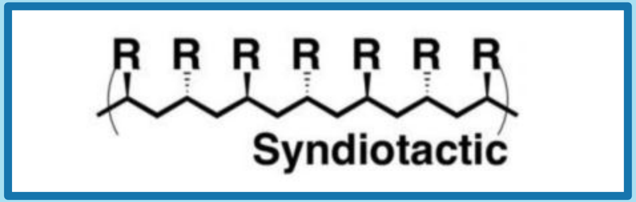
Example - PVC

Classification Based on Stereochemistry of Monomer

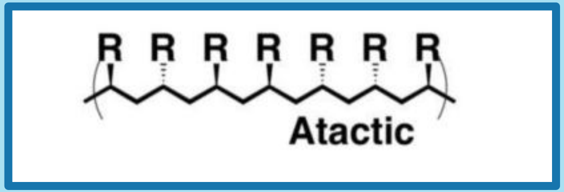
A) **Isotactic Polymers:** The side chain present in same order with the main chain.



B) **Syndiotactic Polymer:** Side chain follow alternative order.



C) **Atactic Polymer:** Follow no order.

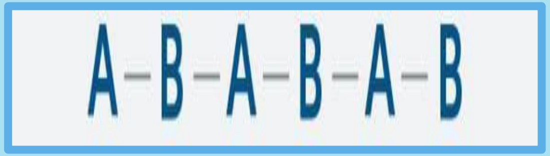


Classification Based on Monomer

A) **<u>Homo Polymer:</u>** Obtained from one type of Monomers.
Example - PVC

A-A-A-A-A-A

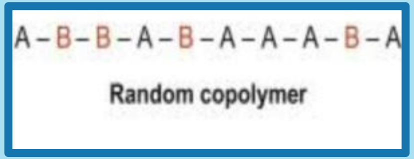
B) **<u>Co- Polymer:</u>** Obtained from two different monomer.
Example - Nylon 6,6



A-B-A-B-A-B

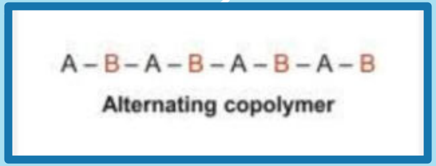
Co Polymer

Random Co Polymer



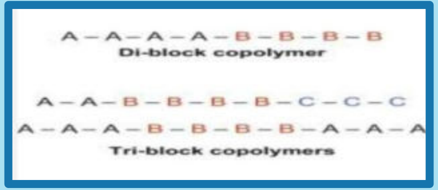
Random copolymer

Alternate Co Polymer



Alternating copolymer

Blocked Co Polymer

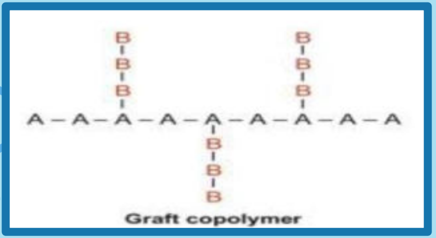


Di-block copolymer

Tri-block copolymers

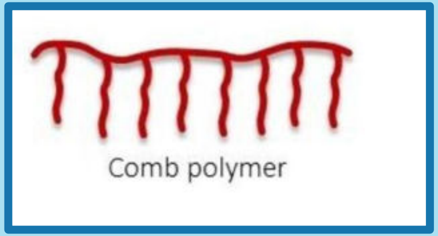
Branched Co Polymer

Graft Polymer



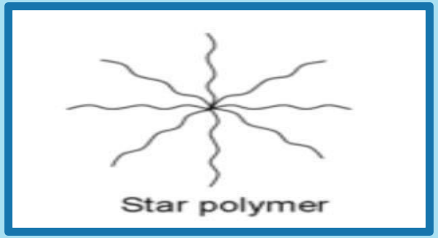
Graft copolymer

Comb Polymer



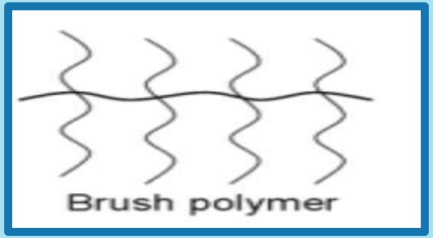
Comb polymer

Star Polymers



Star polymer

Brush Polymer



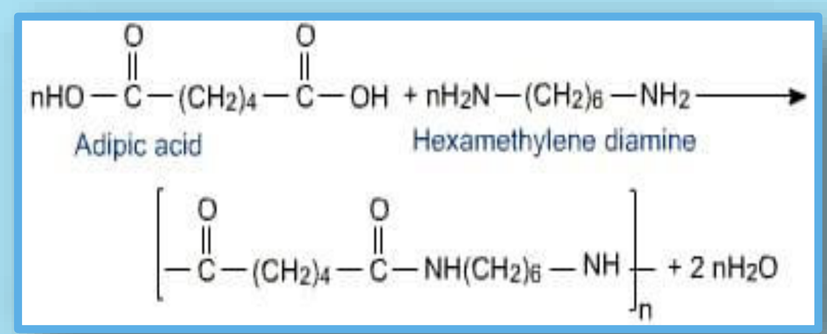
Brush polymer

Classification based on Synthesis

A) **Addition Polymer:** Obtained from one type of monomer by addition reaction.

Example: Ethylene --> Polyethylene

B) **Condensation Polymer:** Obtained from two different types of monomer by Condensation Reaction.



$$nHO-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-OH + nH_2N-(CH_2)_6-NH_2 \longrightarrow$$

$$\left[-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-NH(CH_2)_6-NH-\right]_n + 2\,nH_2O$$

Kinetics of Addition Polymerization

- It follows four step:

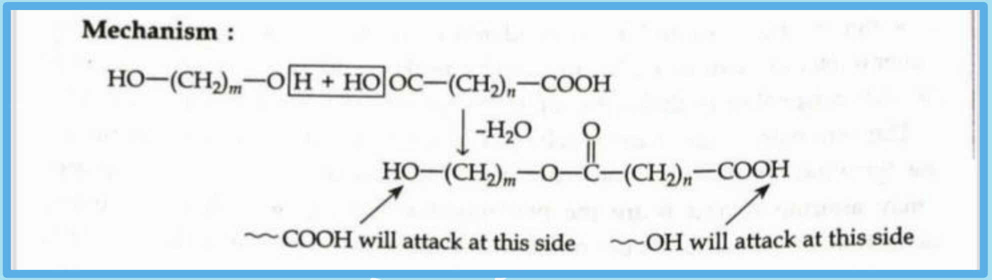
$$\left. I \xrightarrow{k_d} 2R\cdot \right\} \text{decomposition}$$

$$\left. R\cdot + M \xrightarrow{k_i} RM_1\cdot \right\} \text{initiation}$$

$$\left.\begin{array}{r} RM_1\cdot + M \xrightarrow{k_p} RM_2\cdot \\ RM_2\cdot + M \xrightarrow{k_p} RM_3\cdot \\ RM_3\cdot + M \xrightarrow{k_p} RM_4\cdot \\ \vdots \\ RM_{(x-1)}\cdot + M \xrightarrow{k_p} RM_x\cdot \end{array}\right\} \text{Propagation}$$

$$\left. RM_x\cdot + RM_y\cdot \xrightarrow{k_t} dead\ polymer \right\} \text{termination}$$

Kinetics of Condensation Polymerization



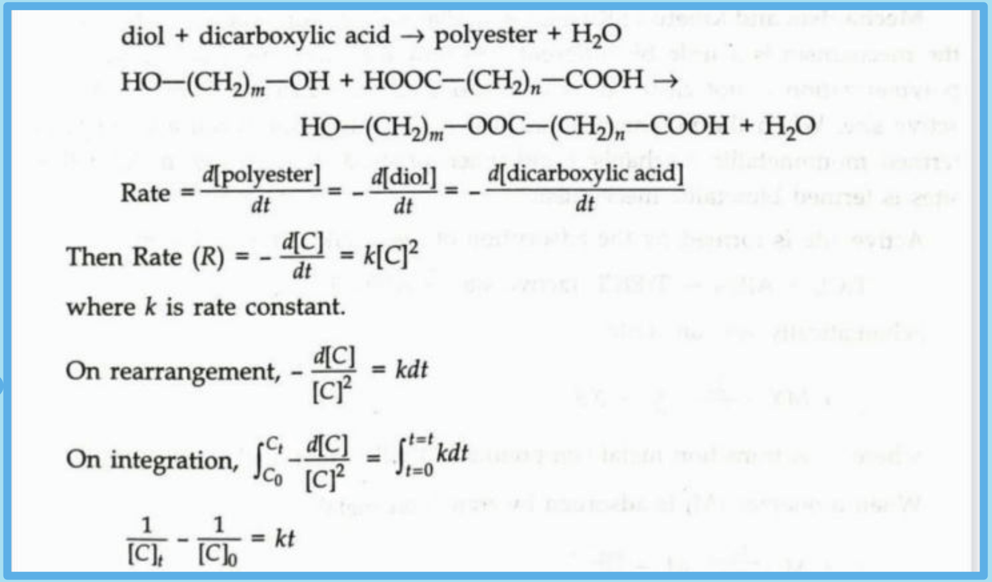
Mechanism :

$$HO—(CH_2)_m—O\boxed{H + HO}OC—(CH_2)_n—COOH$$

$$\downarrow -H_2O$$

$$HO—(CH_2)_m—O—\overset{\overset{O}{\|}}{C}—(CH_2)_n—COOH$$

~COOH will attack at this side ~OH will attack at this side



diol + dicarboxylic acid → polyester + H_2O

$$HO—(CH_2)_m—OH + HOOC—(CH_2)_n—COOH \rightarrow$$

$$HO—(CH_2)_m—OOC—(CH_2)_n—COOH + H_2O$$

$$\text{Rate} = \frac{d[\text{polyester}]}{dt} = -\frac{d[\text{diol}]}{dt} = -\frac{d[\text{dicarboxylic acid}]}{dt}$$

Then Rate $(R) = -\frac{d[C]}{dt} = k[C]^2$

where k is rate constant.

On rearrangement, $-\frac{d[C]}{[C]^2} = kdt$

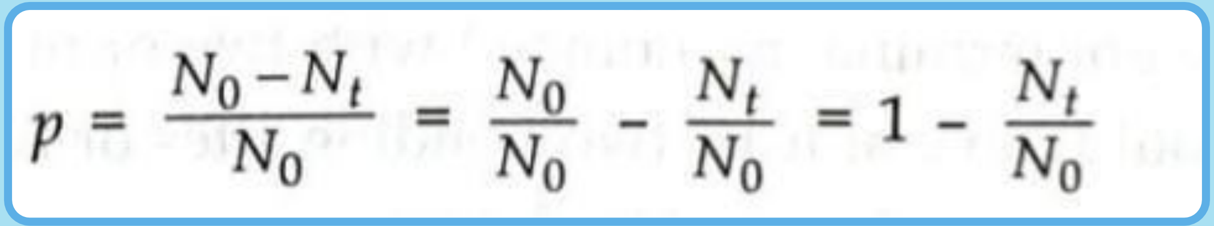
On integration, $\int_{C_0}^{C_t} -\frac{d[C]}{[C]^2} = \int_{t=0}^{t=t} kdt$

$$\frac{1}{[C]_t} - \frac{1}{[C]_0} = kt$$

Extent of reaction

- ☐ Extent of Reaction (P):

$$P = \frac{\text{Number of Monomer unit take part in polymer formation}}{\text{Total number of Monomer Unit taken intially}}$$



$$p = \frac{N_0 - N_t}{N_0} = \frac{N_0}{N_0} - \frac{N_t}{N_0} = 1 - \frac{N_t}{N_0}$$

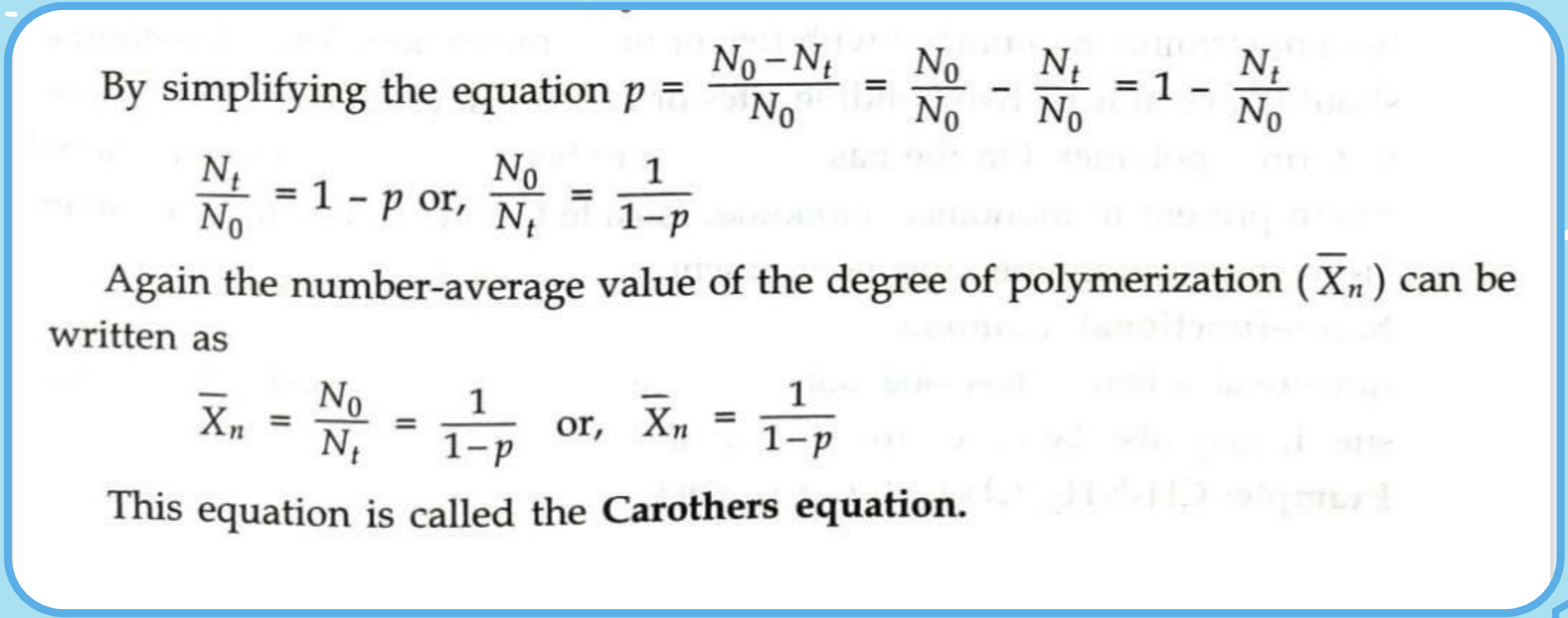
Number average degree of Polymerization

❑

$$\bar{X}_n = \frac{\text{Total number of monomer taken initially}}{\text{Number of monomer present after time t.}}$$

$$X_n = \frac{N_0}{N}$$

Carothers Equation



By simplifying the equation $p = \frac{N_0 - N_t}{N_0} = \frac{N_0}{N_0} - \frac{N_t}{N_0} = 1 - \frac{N_t}{N_0}$

$$\frac{N_t}{N_0} = 1 - p \text{ or, } \frac{N_0}{N_t} = \frac{1}{1-p}$$

Again the number-average value of the degree of polymerization ($\bar{X}_n$) can be written as

$$\bar{X}_n = \frac{N_0}{N_t} = \frac{1}{1-p} \quad \text{or,} \quad \bar{X}_n = \frac{1}{1-p}$$

This equation is called the **Carothers equation.**

Molecular Weight of Polymer

- A) Number average Molecular Weight:

$$\bar{M}_n = \frac{\text{Total weight of Polymer}}{\text{Total number of different monomer present with in the Polymer}}$$

$$= \frac{n_1M_1 + n2M2 + n3M3 + ...}{n_1 + n2 + n3 + ...}$$

$$M_n = \frac{\sum M_i N_i}{\sum N_i},$$

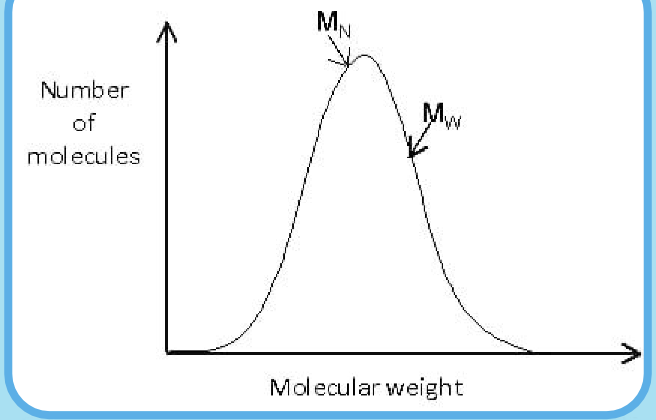
❑ B) Weight average molecular weight:

$$\bar{M}_w = \frac{W_1M_1 + W_2M_2 + \ldots\ldots}{W_1 + W_2 + \ldots\ldots}$$

As, $n = \frac{W}{N}$

So, $\bar{M}_w = \frac{n_1M_1^{2} + n_2M_2^{2} + \ldots..}{n_1M_1 + n_2M_2 + \ldots..}$

$$M_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i},$$



Poly Dispersity Index

❑ $PDI = \frac{\bar{M}_w}{\bar{M}_n}$

Generally, $M_w > M_n$

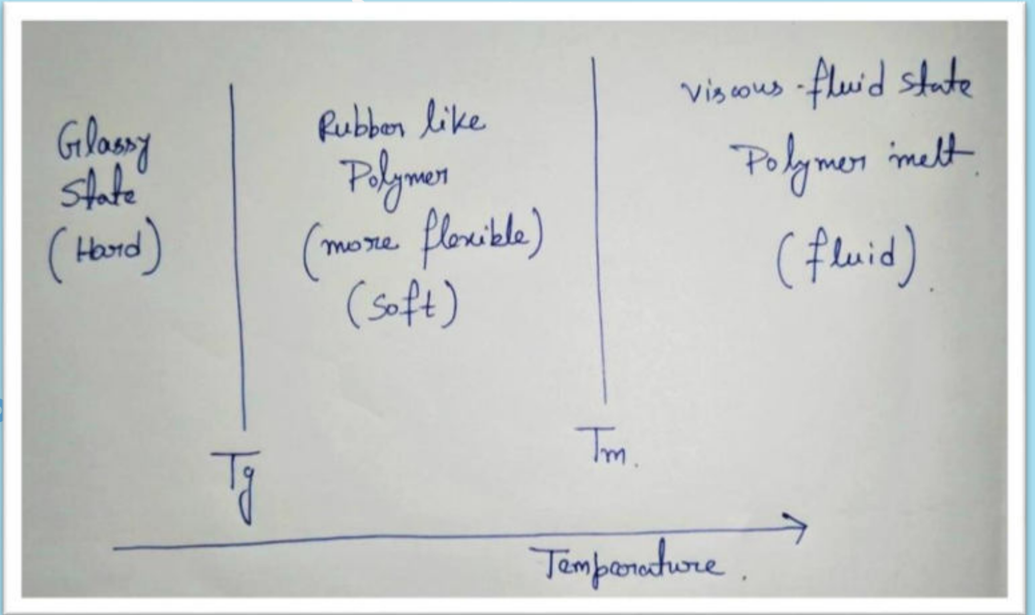
So, PDI > 1

If $M_n = M_w$, then PDI = 1 (Homogeneous Polymer)

If $M_w > M_n$, PDI>1 (Heterogeneous Polymer)

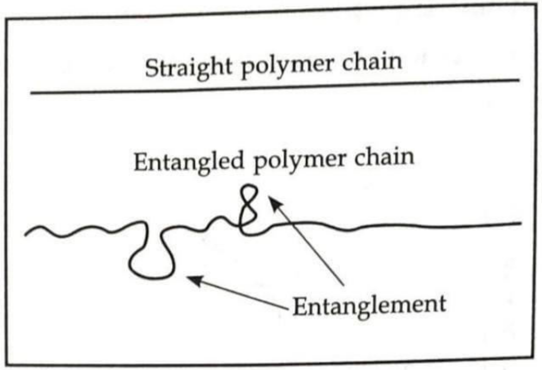
Glass Transition Temperature or Tg

- The temperature below which a polymer is hard and above which it is soft.



Free Volume Theory

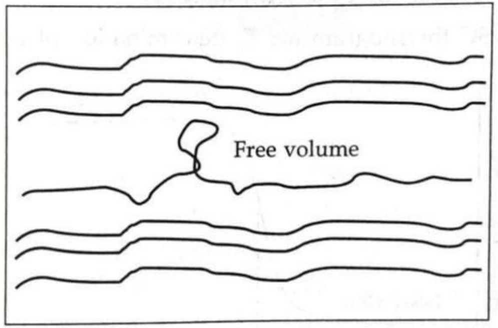
❑ Sometimes during polymerization, some chain are entangled, due to this entanglement, the volume of polymer increase.



Polymer chain entanglement

❑ $V=V_0+V_f$ [V= Volume Occupied by the polymer
V_f= Free volume due presence of entanglement
V_0= Volume occupied by the Polymer, due to their existence]

So the excess volume occupies by the Polymer called Free Volume.



Free volume of polymer originates from chain entanglement

Tg in terms of Free Volume

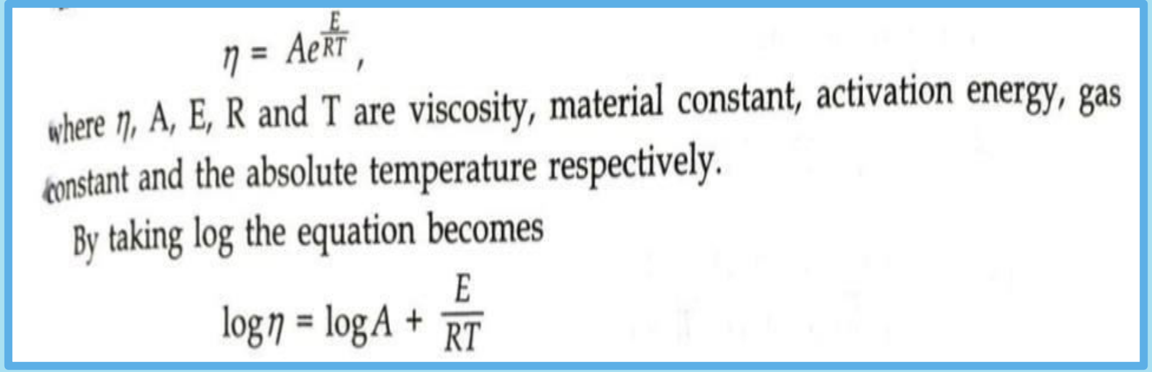
- The presence of entanglement, result to more free volume. The Polymer chain can easily move. So the flexibility or mobility depends upon free volume.

  As T increases flexibility increases, Free Volume also increases

  By Decreasing T, at a certain temperature , free volume suddenly decreases. So, flexible Polymer converted to hard, Rigid Polymer. This temperature is called Tg.

WLF Equation

- Scientist Williams, Landle and Ferry proposed an equation how viscoelastic property depend upon Temp.



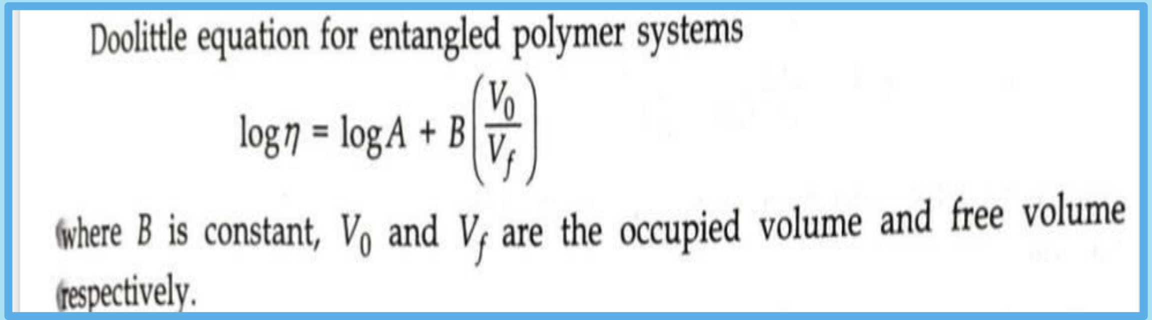
$$\eta = Ae^{\frac{E}{RT}},$$

where η, A, E, R and T are viscosity, material constant, activation energy, gas constant and the absolute temperature respectively.

By taking log the equation becomes

$$\log \eta = \log A + \frac{E}{RT}$$

- It is Valid for Newtonian fluid whose molecular weight is very low, but for polymer, due to High molecular weight This equation is not applicable.



Doolittle equation for entangled polymer systems

$$\log \eta = \log A + B\left(\frac{V_0}{V_f}\right)$$

where B is constant, V_0 and V_f are the occupied volume and free volume respectively.

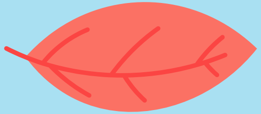
Polymer Solvent

- A) **Good Solvent:** Polymer Solvent interaction is much stronger compare to Solvent-solvent interaction.

  $\Delta H=(-)ve$,. $\Delta S= (+)ve$

  B) **Bad Solvent:** Polymer-Solvent interaction is much weaker.

  $\Delta H=(+)ve.$ $\Delta S=(-)ve$



Application

- **Polythene:** A widely used and common item, plastic bags and containers are in fact a polymer made of polythene.

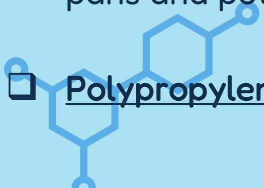
- **LDPE:** Low-density polythene is used for making various parts of machines, pipes, tubes, plastic bottles.
- **HDPE:** Due to its high density and crystalline structure, it is used for food packaging, fuel tanks wiring and cable

- **PVC:** The most common use of polyvinyl chloride is in the electric wires and other insulated equipment that is coated in PVC. They are also used in water pipes that provide corrosion-free applications.

- **Nylon:** Nylon fibers are used for making water- resistant clothing like raincoats and umbrellas. They are also used in carpets, parachutes, ropes, and textiles.

- **Rubber:** Rubber is commonly used for making tires,though is also important for making machine parts, lubricants, gloves, and so on.

- **Teflon:** Teflon is most commonly seen in kitchen appliances wherein a Teflon coat is provided on the surface of pans and pots to make them "non-stick."



- **Polypropylene:** It is used for automotive industry, furniture, laboratory apparatus, textiles.

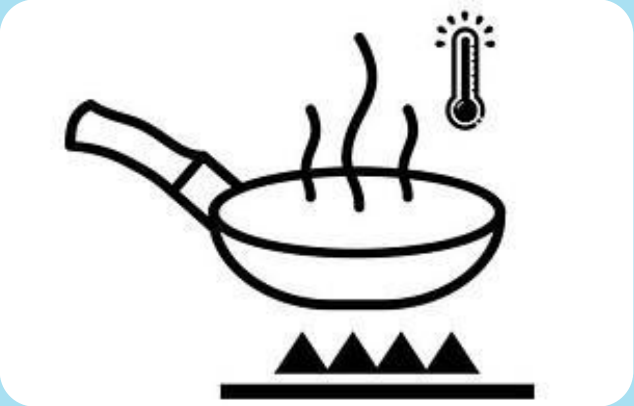
Synthetic Polymer-
A long term threat to Environment

- ❑ Synthetic Polymers are often dispose of in landfill where they will remain for centuries into the future, slowly leaching harmful toxins into soil as time passes.

According to the Clean Air Council Organisation, Americans alone use 102.1 billion plastic bags - a synthetic polymer - each year. Less than 1% of these bags are recycled.

❑ Oceans provide a home for hundreds of thousands of species on Earth, and it is essential for human life. Unfortunately, while many species depend on the ocean for its ability to create food and oxygen, human activities negatively impact the ocean and its wildlife.

Synthetic polymers also cause huge health risks, such as birth deformities, reproductive disorder, liver problems, skin disorders, damage to immune system, cancer, respiratory diseases.

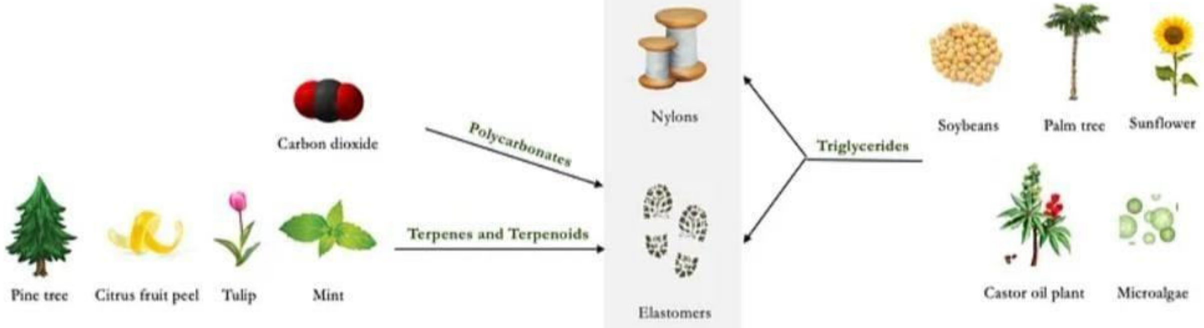


❑ With the overuse and overheating of non-stick pans, the organic chemicals can be mixed with food and air.

Green Polymer Chemistry and Biobased Palstic- Dreams Vs Reality

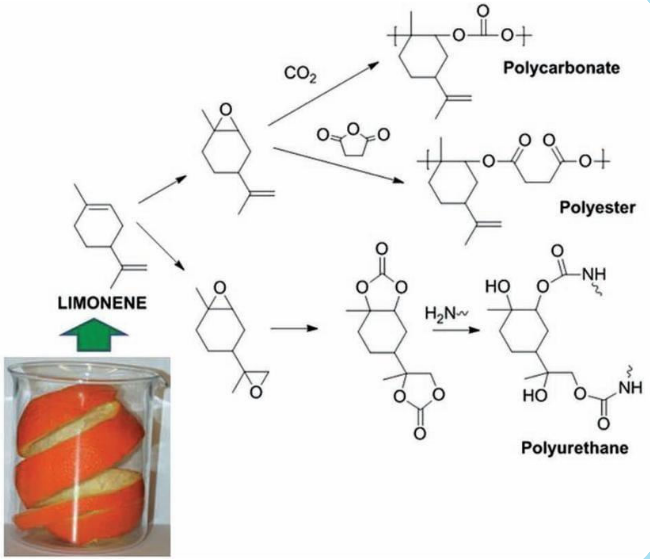
- Biodegradable or Biobased plastics are derived from natural resources like Corn, Starch, Biomass and Food Waste. Therefore, bioplastics are relatively less harmful to the environment.

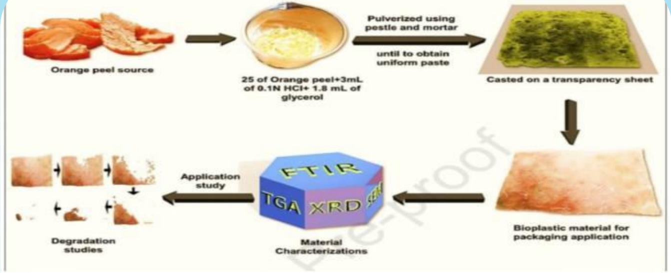
  The first bioplastic were made by using traditional agricultural and renewable resources such as cellulose, Casein and Soybeans



Bio Based Polymer from Orange Peel

- ❑ It is proven that the orange peel derived biocomposite film is more biodegradable.

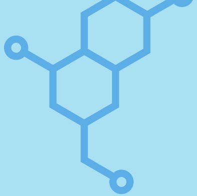




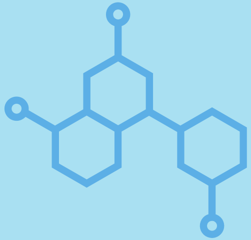
Use of Eggshell as biofiller

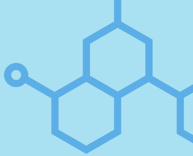
- ❑ The biofiller obtained from egg shell as a source of calcium carbonate could be successfully used to modify Polymer Materials.

The Egg Shell in Epoxy Resin has functioned as a flame retardant and smoke suppression modifier.

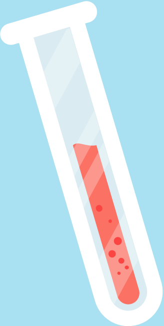


Expectation	Vs	Reality
☐ Reducing demand for non-renewable fossil raw materials.		☐ Increasing demand for renewable raw materials. Competition with food production.
☐ Low greenhouse gas emission.		☐ Potential growth of greenhouse gas emission.
☐ Usage of agricultural and forestry wastes to a full degree.		☐ Partial use of agricultural and forestry wastes **
☐ Biodegradation.		☐ Biodegradation is time-consuming and leaves traces *
☐ No toxicity and no health hazards.		☐ Potential health hazards and toxicity of micro- and nanoparticles releasing during the biodegradation.
☐ Low price.		☐ Still remain too expensive.



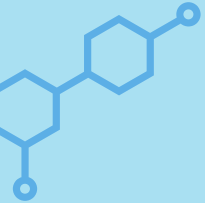


Conclusion



- It is no exaggeration to say that the concept of materials coming from nature is very attractive to the consumers and to the industry.

  The future looks bright if we all move someday to a world where plastics will be biodegradable and made without fossil resources. Potentially bioplastics could become an eco-friendly and economically successful new group of materials with manifold applications and beneficial properties.



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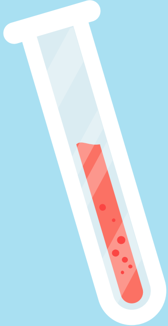

- F. W. Billmeyer, Textbook of Polymer Science, 3rd Edition
- https://medium.com/@stonev/bioplastics-dreams-and-reality-87cd86e85825
- https://sciencing.com/environmental-problems-caused-by-synthetic-polymers-12732046.html
- https://doi.org/10.1016/j.jmrt.2021.09.016
- https://www.researchgate.net/figure/Dream-left-and-reality-right-of-a-closed-carbon-loop-in-bioplastic-economy_fig1_360952953

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Tithi Mondal

Thank you