CHEMISTRY FOR TECHNOLOGISTS L T P C
3 0 2 4

Common to I sem. B.Tech. – BIO. TECH, CHEMICAL and FOOD TECHNOLOGY

OBJECTIVES

- To acquire molecular level understanding of matter
- To understand the basics of surface chemistry and nanomaterials
- To attain knowledge on natural products and polymers

UNIT I - CHEMICAL BONDING 9

Types of chemical bonds - electronegativity - bond polarity and dipole moments, partial ionic character of covalent bonds - VB theory - concept of hybridization. Molecular orbital theory - LCAO - bonding in homonuclear and heteronuclear diatomic molecules. Intermolecular forces - types - hydrogen bonding - importance of hydrogen bonding in biomolecules - van der Waals forces – consequences.

UNIT II - SURFACE CHEMISTRYAND CATALYSIS 9

Adsorption-difference between adsorption and absorption-types-factors influencing adsorption-adsorption from solutions- types of isotherms-Freundlich adsorption isotherm -Langmuir adsorption isotherm -industrial applications of adsorption - applications of surface active agents - detergency-wetting - water repellency- emulsifiers - CMC and defoamers.
Catalysis - general characteristics -types of catalysis -acid -base catalysis - enzyme catalysis - characteristics-Michaelis - Menton equation -effect of temperature on enzyme catalysis - Langmuir- Hinshelwood mechanism for heterogeneous catalysis.

UNIT III - NANO MATERIALS 9

Basics-distinction between nanoparticles and bulk materials - size-dependent properties - nanoparticles - nanocluster – nanorod - nanotube and nanowire - synthesis of nanoparticles - chemical methods -metal nanocrystals by reduction ,solvothermal synthesis, photochemical synthesis, sonochemical synthesisandchemical vapor deposition -physical methods - ball milling ,electrodeposition - biogenic synthesis - properties and applications.

UNIT IV - HETEROCYCLIC COMPOUNDS AND NATURAL PRODUCTS 9

Heterocyclic compounds-synthesis and reactions of pyrrole -furan - thiophene- pyridine-quinoline-isoquinoline.
Terpenoids- Isolation - Isoprene rule-structural elucidation of citral and menthol.

UNIT V - POLYMERS 9

Polymers-definition - polymerization - types - addition and condensation polymerization - free radical polymerization mechanism - effect of structure on the properties of polymers - strength, plastic deformation, elasticity and crystallinity - plastics - preparation - properties and uses of

PVC, teflon, polycarbonate, polyurethane, nylon-6,6, PET,KEVLAR-Green polymers-Introduction –poly lactic acid (PLA)

TEXT BOOKS

1. P. C. Jain and Monika Jain, “Engineering Chemistry”, DhanpatRai Publishing Company (P) LTD, New Delhi, 2015
2. Bahl B. S., and Arun Bahl, “A Text Book of Organic Chemistry”, S. Chand, New Delhi, 2016.

REFERENCES

1. R.D. Madan, “Modern Inorganic Chemistry”, S. Chand, New Delhi, 2012
2. I L Finar “Organic Chemistry” ELBS (1994)
3. Gowarikar V. R., Viswanathan N.V. and Jayadev Sreedhar, ―Polymer Science‖, New Age International (P) Ltd., New Delhi, 2011

4. B.S. Murthy, P.Shankarand others,“Text book of Nano-science and nanotechnology”, University Press, IIM.

Syllabus for Chemistry Laboratory 30

(Any 10 experiments tobe conducted)

1. Estimation of mixture of acids by conductometry
2. Estimation of copper / ferrous ions by spectrophotometry
3. Estimation of acid by pH metry.
4. Estimation of alkalinity by indicator method.
5. Estimation of chloride by argentometric method
6. Determination of total, temporary and permanent hardness by EDTA method.
7. Estimation of DO by winkler’s method
8. Estimation of sodium and potassium in water by flame photometry
9. Determination of corrosion rate on mild steel by weight loss method
10. Determination of molecular weight of a polymer by viscometry method.
11. Verification of adsorption isotherms (acetic acid on charcoal)
12. Phase change in a solid.
13. Preparation of simple drug
14. Determination of rate constant of a reaction
15. Determination of distribution coefficient
16. Preparation of Thiokol rubber.

TOTAL PERIODS 75

OUTCOMES

On completion of the course students will be able to

- Be conversant with basics of molecule formation and interactions
- measure molecular/bulk properties like absorbance, molecular weight, DO and chloride
- Apply the knowledge of surface chemistry in practical and industrial applications
- Be familiar with structure and properties of natural products
- Be assertive on various types of polymers and their properties including green polymers

UNIT I
CHEMICAL BONDING

1.1 TYPES OF CHEMICAL BONDS

The chemical bonds can be classified based on the nature of the interaction between the bonded atoms. Two major types of chemical bonds are covalent bonds and ionic bonds. Generally metals reacts with non-metals to form ionic compounds, and the covalent bonds are present in the compounds formed by nonmetals.

Octet rule-Duet role:

When the electronegativity difference between the two combining atoms is large, the least electronegative atom completely transfers one or more of its valence electrons to the other combining atom so that both atoms can attain the nearest inert gas electronic configuration. The complete transfer of electron leads to the formation of a cation and an anion. Both these ions are held together by the electrostatic attractive force which is known as ionic bond. While undergoing a chemical reaction, atoms of group 1A-7A elements tend to gain, lose, or share sufficient electrons to achieve an electron configuration having eight valance electrons. After gaining, losing, or sharing, ions/atoms will have the electron configuration like that of the noble gases nearest to them in atomic number.

Cation : loses one, two or three electrons and in losing electrons, the atom becomes a positively charged ion called a **cation** (Na^+, Ca^{2+}, Mg^{2+}) (usually metals). Cation has an electron configuration like that of the noble gas nearest to it in atomic number.
Anion :gains one, two or three electrons and in gaining electrons, the atom becomes a negatively charged ion called an a**nion** (Cl^-, O^{2-}, S^{2-}) (usually nonmetals). Anion has an electron configuration like that of the noble gas nearest to it in atomic number.

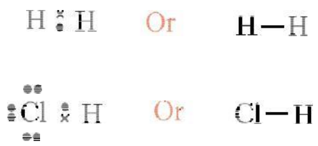
1.1.1 Ionic bonds: ionic bonds usually form between a metal and a nonmetal. In ionic bonding, electrons are completely transferred from one atom to another. In the process of either losing or gaining negatively charged electrons, the reacting atoms form ions. The oppositely charged ions are attracted to each other by electrostatic forces, which are the basis of the ionic bond. There are enormous differences between the chemical and physical properties of an atom and those of its ion(s).

For example sodium is a soft metal and it reacts violently with water. Chlorine is a gas and it is very unstable and reactive. Both sodium and chlorine are poisonous. However, NaCl (common table salt made up of Na^+ and Cl^-) is quite stable and unreactive.

$$Na\ (1s^2\ 2s^2\ 2p^6\ 3s^1) + Cl\ (1s^2\ 2s^2\ 2p^6\ 3s^1\ 3p^5) \rightarrow Na^+\ (1s^2\ 2s^2\ 2p^6) + Cl^-\ (1s^2\ 2s^2\ 2p^6\ 3s^1\ 3p^6)$$

1.1.2 Covalent bonds: Covalent bonds usually form between two nonmetals or a metalloid and a nonmetal. In covalent bonds, the atoms share one or more pairs of electrons (by using their valence electrons) between each other to obtain a filled valence level. This type of mutual sharing of one or more pairs of electrons between two combining atoms results in the formation of a chemical bond called a covalent bond.

The valence electrons which are shared between two atoms are called “shared pair of electrons” or “bonding pair of electrons”. The valance electrons which are not shared are called “unshared pair of electrons” or “lone pairs”. These electrons are not involved in bonding.

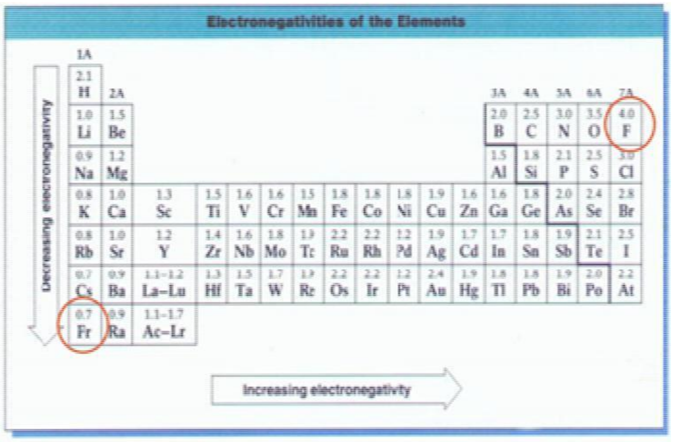


If two atoms share just one pair of electron a single covalent bond is formed as in the case of hydrogen molecule. If two or three electron pairs are shared between the two combining atoms, then the covalent bond is called a double bond or a triple bond, respectively.

1.2 ELECTRONEGATIVITY: Electronegativity is measure of an atom’s attraction for the electrons it shares in a chemical bond with another atom. The electronegativity shows, how tightly an atom holds the electrons that it shares with another atom. When the electronegativity increases, the ionisation energy also increases.

Note:

1.Electronegativity generally increases from left to right across a row of the Periodic Table.
2.Electronegativity generally increases from bottom to top within a column of the Periodic Table.



Electronegativities of the Elements

1A	2A											3A	4A	5A	6A	7A
2.1 H																
1.0 Li	1.5 Be											2.0 B	2.5 C	3.0 N	3.5 O	4.0 F
0.9 Na	1.2 Mg											1.5 Al	1.8 Si	2.1 P	2.5 S	3.0 Cl
0.8 K	1.0 Ca	1.3 Sc	1.5 Ti	1.6 V	1.6 Cr	1.5 Mn	1.8 Fe	1.8 Co	1.8 Ni	1.9 Cu	1.6 Zn	1.6 Ga	1.8 Ge	2.0 As	2.4 Se	2.8 Br
0.8 Rb	1.0 Sr	1.2 Y	1.4 Zr	1.6 Nb	1.8 Mo	1.9 Tc	2.2 Ru	2.2 Rh	2.2 Pd	1.9 Ag	1.7 Cd	1.7 In	1.8 Sn	1.9 Sb	2.1 Te	2.5 I
0.7 Cs	0.9 Ba	1.1–1.2 La–Lu	1.3 Hf	1.5 Ta	1.7 W	1.9 Re	2.2 Os	2.2 Ir	2.2 Pt	2.4 Au	1.9 Hg	1.8 Tl	1.8 Pb	1.9 Bi	2.0 Po	2.2 At
0.7 Fr	0.9 Ra	1.1–1.7 Ac–Lr														

1.3 POLARITY OF BONDS

Polarity: A molecule will be polar if it has two properties at the same time:

1. It has polar bonds.

2. Its centers of partial positive charge and partial negative charge lie at different places within the molecule.

In order to find the polarity of a molecule, we should:

1. Draw the Lewis Structure.
2. Determine the bond angle and the shape of the molecule.
3. Predict the electronegativity of which atom is higher than others.
4. Indicate partial positive charge and partial negative charge for each atom and draw the dipole signs.
5. If the centers of partial positive charge and partial negative charge lie at the different places within the molecule, molecule would be polar. Otherwise, molecule is nonpolar.

1.4 DIPOLE MOMENT:

The molecule possesses the dipole moment can be defined as the product of the magnitude of the charge and the distance between the centres of positive and negative charge as a result of polarisation.The polarity of a covalent bond can be measured in terms of dipole moment which is defined as

$$\text{Dipole moment } (\mu) = \text{charge } (Q) \times \text{distance of separation } (r)\ [\mu = Q \times 2d]$$

Where μ is the dipole moment, Q is the charge and 2d is the distance between the two charges. The dipole moment is a vector and the direction of the dipole moment vector points from the negative charge to positive charge.

The unit for dipole moment is columb meter (C m). It is usually expressed in Debye unit (D). The conversion factor is 1 Debye = 3.336×10^{-30} C m

Diatomic molecules such as H_2, O_2, F_2 etc... have zero dipole moment and are called non polar molecules and molecules such as HF, HCl, CO, NO etc... have non zero dipole moments and are called polar molecules.

Molecules having polar bonds will not necessarily have a dipole moment. For example, the linear form of carbon dioxide has zero dipole moment, even though it has two polar bonds. In CO_2, the dipole moments of two polar bonds (CO) are equal in magnitude but have opposite direction. Hence, the net dipole moment of the CO_2 is, $\mu = \mu_1 + \mu_2 = \mu_1 + (-\mu_1) = 0$

1.5 PARTIAL IONIC CHARACTER IN COVALENT BOND:

When a covalent bond is formed between two identical atoms (as in the case of H_2, O_2, Cl_2 etc...) both atoms have equal tendency to attract the shared pair of electrons and hence the shared pair of electrons lies exactly in the middle of the nuclei of two atoms. However, in the case of covalent bond formed between atoms having different electronegativities, the atom with higher electronegativity will have greater tendency to attract the shared pair of electrons more towards itself than the other atom. As a result the cloud of shared electron pair gets distorted.

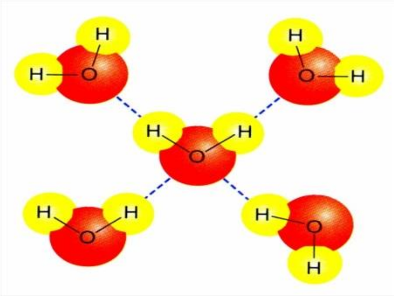
Let us consider the covalent bond between hydrogen and fluorine in hydrogen fluoride. The electronegativities of hydrogen and fluorine on Pauling's scale are 2.1 and 4 respectively. It means that fluorine attracts the shared pair of electrons approximately twice as much as the hydrogen which leads to partial negative charge on fluorine and partial positive charge on hydrogen. Hence, the H-F bond is said to be polar covalent bond. Here, a very small, equal and opposite charges are separated by a small distance (91 pm) and is referred to as a dipole.

In a covalent bond:

1. The electronegativity differences in the 2 atoms involved is not extreme, so the electrons that are interacting are shared (less than 2.1 difference)
2. It may not be an equal sharing, but at least the electrons are being shared.
3. When a covalent bond forms with unequally shared electrons, the bond is said to be a polar covalent bond. (between 2.1 & 0.4 electronegativity difference)
   a. The uneven sharing causes the more electronegative atom to have a partial negative charge.
   b. The other atom will have a partial positive charge.

Polar Covalent!

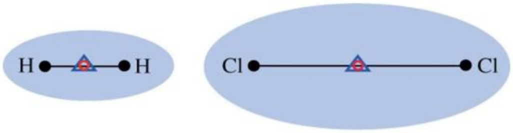
1. If the whole molecule has a tendency to develop a positive end and a negative end to it, because of differences in electronegativity it is called a polar molecule
2. These oppositely charged "poles" set up by the electronegativity differences in atoms causes interaction between molecules.
3. The partial negative charges of one molecule attracts the positive end of another molecule and so on setting up a network of loose connections
4. These connections lead to different chemical properties; such as higher boiling points because it takes more energy to pull the molecules apart



We classify covalent bonds into two categories:

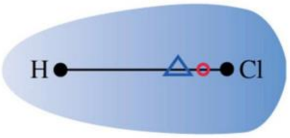
1. **<u>Nonpolar covalent bonds</u>:** bonding with an equal sharing of electrons.

H-H Cl-Cl



<u>2.Polar covalent bonds</u>: bonding with an unequal sharing of electrons. The number of shared electrons depends on the number of electrons needed to complete the octet.

Examples : O-H O-F N-H



The less electronegative atom has a lesser fraction of the shared electrons and obtains a partial positive charge (δ+). The more electronegative atom gains a greater fraction of the shared electrons and obtains a partial negative charge (δ-). This separation of charge produces a **dipole** (two poles). We show a bond dipole by an arrow, with the head of the arrow near the negative end of the dipole and a cross on the tail of the arrow.

δ+ δ-
H - Cl

Note: we use the following table to find the type of a chemical bond:

Electronegativity difference between bonded atoms	**Type of bond**
less than 0.5	nonpolar covalent
0.5 to 1.9	polar covalent
greater than 1.9	Ionic

Examples:

H-Cl	3.0 - 2.1 = 0.9 Polar covalent bond
C-H	2.5 - 2.1 = 0.4 Nonpolar covalent bond
Zn-O	3.5 - 1.6 = 1.9 Ionic bond

1.6 VALENCE BOND THEORY

QUANTUM OR WAVE MECHANICS

Electrons have certain properties of particles and certain properties of waves. Electrons have mass and charge like particles, because they are so small and are moving so fast, electrons have no defined position. Their location is best described by wave mechanics (i.e. a three- dimensional wave) and a wave equation called the Schrödinger equation.Solutions of the Schrödinger equation are called wave functions and are represented by the Greek letter psi (Ψ).Each wave function describes a different orbital.There are many solutions to the Schrödinger equation for a given atom.The sign of the wave function can change from positive (+) to negative (-) in different parts of the same orbital. This is analogous to the way that waves can have positive or negative amplitudes. The sign of the wave function does not indicate anything about charge.The value of the square of the wave function is proportional to the probability of finding electron density at a given point in an orbital. Note that the sign of square of the wave function is always positive, because the square of even a negative value is still positive.

In a 2p orbital, it is just as probable to find electron density in the negative lobe as it is to find electron density in the positive lobe. A node is any place in an orbital at which the value of the wave function is zero. A nodal surface or nodal plane are surfaces or planes where the value of the wave function is zero. There is absolutely no electron density at a node, a nodal surface, or a nodal plane.

The Schrödinger equation can in principle describe covalent bonding, but, even with powerful computers the equation is too complicated to be solved exactly for large molecules.

VALENCE BOND THEORY

- For elements more complicated than hydrogen, it is helpful to combine (hybridize) the valence atomic orbitals on a given atom before looking for overlap with orbitals from other atoms.
- For C, N, and O hybridization means the 2s atomic orbital is combined with one, two, or all three 2p atomic orbitals.
- The results of the orbital combinations are called hybrid orbitals, the number of hybrid orbitals are equal to the number of atomic orbitals combined.
- An sp^3 hybrid orbital is the combination of one 2s orbital with three 2p orbitals. (Fig. 1.12 in text)
- Four sp^3 orbitals of equivalent energy are created.
- Each sp^3 orbital has one large lobe and a smaller one of opposite sign pointing in the opposite direction (with a node at the nucleus). The large lobes point to different corners of a tetrahedron (109.5° bond angle). This explains the tetrahedral structure of molecules like methane, CH_4.
- An sp^2 hybrid orbital is the result of combining the 2s orbital with two 2p orbitals.
- Three sp^2 orbitals of equivalent energy are created.

- Each sp^2 orbital has one large lobe and a smaller one of opposite sign pointing in the opposite direction (with a node at the nucleus). The large lobes point to a different corner of a triangle (120° bond angle). This explains the trigonal planar structure of molecules like formaldehyde, CH_2=O.
- The left over 2p orbital lies perpendicular of the plane formed by the three sp^2 orbitals.
- An sp hybrid orbital is the combination of one 2s orbital with one 2p orbital.
- Two sp orbitals of equivalent energy are created.
- Each sp orbital has two lobes of opposite sign pointing in opposite directions (with a node at the nucleus). The lobes with like sign point in exactly opposite directions (180° bond angle). This explains the linear structure of molecules like acetylene.
- The two left over 2p orbitals are orthogonal to each other, and orthogonal to the two sp hybrid orbitals as well.
- Carbon atoms in molecules are either sp^3, sp^2, or sp hybridized. 1s orbitals are not considered for hybridization with C, N, or O because the 1s orbitals do not participate in covalent bonding.

Salient features of VB Theory:

1. When half filled orbitals of two atoms overlap, a covalent bond will be formed between them.
2. The resultant overlapping orbital is occupied by the two electrons with opposite spins. For example, when H_2 is formed, the two 1s electrons of two hydrogen atoms get paired up and occupy the overlapped orbital.
3. The strength of a covalent bond depends upon the extent of overlap of atomic orbitals. Greater the overlap, larger is the energy released and stronger will be the bond formed.
4. Each atomic orbital has a specific direction (except s-orbital which is spherical) and hence orbital overlap takes place in the direction that maximizes overlap

1.7 MOLECULAR ORBITAL THEORY

Molecular orbital theory assumes that individual electron pairs are found in molecular orbitals that are distributed over the entire molecule. Molecular orbitals are analogous to atomic orbitals and are described by the following four rules:

1.Combination of n atomic orbitals in a molecule or ion forms n molecular orbitals, each of which extends over the entire molecule or ion. The number of molecular orbitals is equal to the number of atomic orbitals combined, because atomic orbitals can be combined by both in phase and out of phase addition.

2. Molecular orbitals, just like atomic orbitals, are arranged in order of increasing energy.

3. Filling of molecular orbitals is governed by the same principles as the filling of atomic orbitals.

4. Electrons are placed in molecular orbitals starting with the lowest energy orbitals first.

Salient features of MO Theory:

- A molecular orbital cannot hold more than two electrons.
- Two electrons in the same molecular orbital have opposite spins.
- When two or more degenerate (same energy) molecular orbitals are available, one electron is placed in each before any one of them gets two electrons.
- When two atomic orbitals combine to form a molecular orbital, the wave functions are combined both in phase and out of phase to create one bonding molecular orbital and one antibonding molecular orbital, respectively.
- A bonding molecular orbital occurs when the electron density of the orbital is concentrated between the atomic nuclei.
- Electrons in bonding molecular orbitals stabilize covalent bonds because they serve to offset the repulsive forces of the positively-charged atomic nuclei. Both nuclei are attracted to the electrons between them.
- The energy of a bonding molecular orbital is lower than the energy of the uncombined atomic orbitals.
- An antibonding molecular orbital (designated with an *) occurs when the electron density of the orbital is concentrated in regions of space outside the area between the atomic nuclei.
- Electrons in antibonding molecular orbitals do not stabilize covalent bonds because the electrons are not positioned to offset the repulsive forces of the positively charged atomic nuclei.
- The energy of an antibonding molecular orbital is higher than the energy of the uncombined atomic orbitals.
- A sigma bond occurs when the majority of the electron density is found on the bond axis.
- For example, a sigma bond results from the overlap between two 1s orbitals.Because rotating sigma bond does not decrease the overlap of the orbitals involved (sigma bonds have cylindrical symmetry), a sigma bond can rotate freely about the bond axis.
- For example, a pi bond results from the overlap of two 2p orbitals that are parallel to each other, and orthogonal to the sigma bond that exists between the two atoms. A pi bond occurs when the majority of the electron density is found above and below the bond axis. Because rotating a pi bond by 90° destroys the orbital overlap, pi bonds cannot rotate around the bond axis.
- An electronic ground state occurs when all of the electrons are in the molecular orbitals of lowest possible energy. An electronic excited state occurs when an electron n a lower lying orbital is promoted to an orbital that is higher in energy.

1.8 LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO)

The wave functions for the molecular orbitals can be obtained by solving Schrödinger wave equation for the molecule. Since solving the Schrödinger equation is too complex, approximation methods are used to obtain the wave function for molecular orbitals. The most common method is the linear combination of atomic orbitals (LCAO).

We know that the atomic orbitals are represented by the wave function Ψ. Let us consider two atomic orbitals represented by the wave function ψ_A and ψ_B with comparable energy, combines to form two molecular orbitals. One is bonding molecular orbital($\psi_{bonding}$) and the other is antibonding molecular orbital($\psi_{antibonding}$). The wave functions for these two molecular orbitals can be obtained by the linear combination of the atomic orbitals ψ_A and ψ_B as below.

$$\psi_{bonding} = \psi_A - \psi_B$$

$$\psi_{antibonding} = \psi_A - \psi_B$$

The formation of bonding molecular orbital can be considered as the result of constructive interference of the atomic orbitals and the formation of anti-bonding molecular orbital can be the result of the destructive interference of the atomic orbitals. The formation of the two molecular orbitals from two 1s orbitals is shown below.

1.9 HYBRIDISATION

Bonding in simple molecules such as hydrogen and fluorine can easily be explained on the basis of overlap of the respective atomic orbitals of the combining atoms. But the observed properties of polyatomic molecules such as methane, ammonia, beryllium chloride etc... cannot be explained on the basis of simple overlap of atomic orbitals. For example, it was experimentally proved that methane has a tetrahedral structure and the four C-H bonds are equivalent. This fact cannot be explained on the basis of overlap of atomic orbitals of hydrogen (1s) and the atomic orbitals of carbon with different energies ($2s^2$ $2p^2$ 2p 2p).

In order to explain these observed facts, Linus Pauling proposed that the valence atomic orbitals in the molecules are different from those in isolated atom and he introduced the concept of hybridisation. Hybridisation is the process of mixing of atomic orbitals of the same atom with comparable energy to form equal number of new equivalent orbitals with same energy. The resultant orbitals are called hybridised orbitals and they posses maximum symmetry and definite orientation in space so as to minimize the force of repulsion between their electrons.

1.9.1 Theory of Hybridisation

The failures of VB theory based on pure orbital overlaps are explained agreeably based on the concept of hybridisation of orbitals or mixing up of orbitals. There are three major processes that are considered to occur in hybridisation of orbitals. These are:

i) Promotion of electrons to higher or similar energy levels
ii) Mixing up of various s,p,d,f orbitals to form the same number of new orbitals and
iii) Stabilisation of the molecule through bond formations involving hybrid orbitals by release of certain amount of energy which compensates the energy requirement in the electron promotion process.

i) Promotion (Excitation) of Electrons

Atoms of elements like Beryllium, Boron and Carbon have electronic configuration as,

Be (At. no : 4) : $1s^2 2s^2$
B (At. no : 5) : $1s^2 2s^2 2px^1$
C (At. no : 6) : $1s^2 2s^2 2px^1 2py^1$

According to VB theory, Beryllium is expected to behave like a noble gas due to its filled shells, which in practice forms a number of compounds like BeF_2 and BeH_2 proving its bivalency. In case of Boron VB theory predicts univalency due to the presence of one unpaired electron but in practice Boron is trivalent since compounds as BCl_3, BH_3 etc. are found.

The stable state (Ground State) electronic configuration of C is $(2s^2 2p^1 2p^1)$. Electronic configuration of C suggests only bivalency. But carbon forms over a million compounds in all of which carbon is tetravalent. This suggests only tetravalency. This deficiency is overcome by allowing for **promotion** (or) **the excitation** of an electron to an orbital of higher energy. Although for electron promotion energy is needed, if that energy is recovered back during a covalent bond formation, or by a bond with a greater strength or by many number of bonds formation, then the electron promotion becomes energetically allowed and assumed to take place initially. In carbon, promotion of an electron to an orbital which is close to itself with an empty orbital of only slightly higher energy which is the $2p_z$ orbital can take place. Then the electron pair is unpaired itself by absorbing the required energy available by the atom from its surrounding and one of the electrons in the original orbital 2s or 2p shifts to the empty higher energy orbital.

Ground state electronic configuration of C

↑↓	↑	↑	
2s	$2p_x$	$2p_y$	$2p_z$

Excited state configuration of C.

↑	↑	↑	↑
2s	$2p_x$	$2p_y$	$2p_z$

Thus promotion of an electron leads to four unpaired electron in the excited state electronic configuration of carbon atom. Each electron can now be utilised to form a covalent bond by sharing an electron coming from the combining atom. Thus four o covalent bonds are possible, each with equivalent strength and overlapping tendency. Further, chemical and physical evidences reveal the four bonds of carbon to be equivalent and that they are tetrahedrally oriented. The promotion of an electron from 2s to 2p orbital leads to four half filled orbitals which can form four bonds leading to greater energy lowering. This energy is more than the initial energy required for the promotion of
2s electron to 2p orbital.

(ii) Hybridization of atomic orbitals (mixing of orbitals)

Orbital hybridization was proposed in the 1930's to explain the geometry of polyatomic molecules. Covalent bonding was presumed to arise due to the overlap of atomic orbitals and the sharing of electron pairs. However, the known geometries of even simple covalent molecules like methane could not be correctly predicted by the Wave Mechanical Model, and the theory needed modification. Linus Pauling in 1931 showed mathematically that an s orbital and three p orbitals can combine (or *hybridize*) to form four equivalent atomic orbitals called sp^3 hybrids.

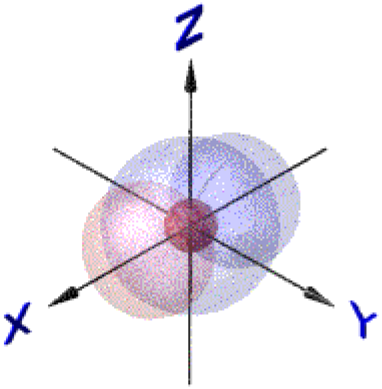
The rationale was that by expending energy to "reshuffle" electrons away from their normal atomic orbitals into *hybridized* orbitals prior to bonding, bonding could occur at less hindered angles. This allowed more effective orbital overlaps, better separation of bonding electron pairs, and produced more stable molecules.

The method of handling this in valence bond theory is via the mixing of the basic atomic orbitals mathematically to form *hybrid* orbitals pointing in the required directions.

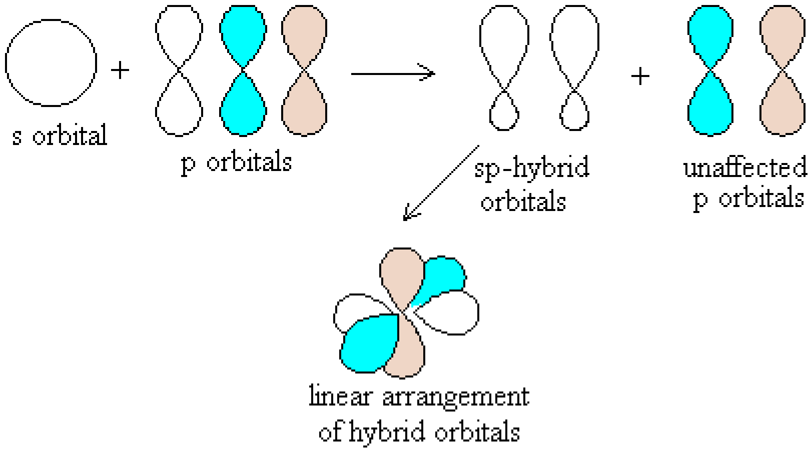
Linear *sp* hybrids. These are composed of the valence shell s-orbital and one of the three p-orbitals. The other two p-orbitals remain unhybridized and may hold lone pairs or participate in π-bonding. The two equivalent sp hybrid orbitals pointat 180° to each other and their formation is depicted graphically and mathematically below:

The diagram below shows the 2s and $2p_x$ orbitals superimposed in the same space before hybridization. The colours represent the relative signs of □. The signs/colors for the 2p orbital would be reversed by the negative sign in first equation which follows the diagram:

$$\psi_1 = 1/\sqrt{2}\psi_s - 1/\sqrt{2}\psi_p$$
$$\psi_2 = 1/\sqrt{2}\psi_s + 1/\sqrt{2}\psi_p$$

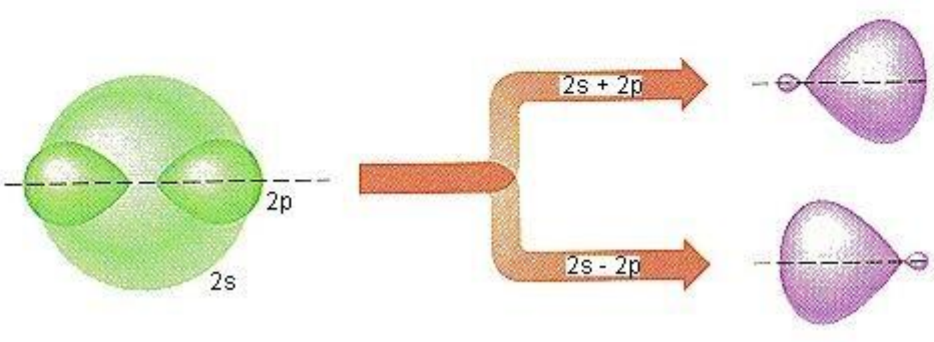


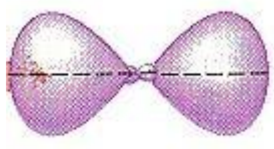
The hybrids corresponding to two the equations above are shown separately for clarity below. Where the blue outer part of the 2s orbital combines with the red part of the 2p orbital there is destructive interference and only the little red knob is left. Where both orbitals are blue the main part of the hybrid is formed. Remember, the negative sign in the first equation causes the signs/colours of the p-orbital to be reversed and the hybrid on the left results. The other results from the second equation:



Two bonds could then be formed by overlap with each of the two sp-hybrid orbitals. The two unaffected p orbitals are still present, located perpendicular to each other and perpendicular to the line of the sp-hybrid orbitals. These p orbitals were available for sideways overlap to form two pi bonds, as in acetylene (or ethyne) shown below. In the case of acetylene, both carbons in the carbon-carbon triple bond are sp- hybridized.

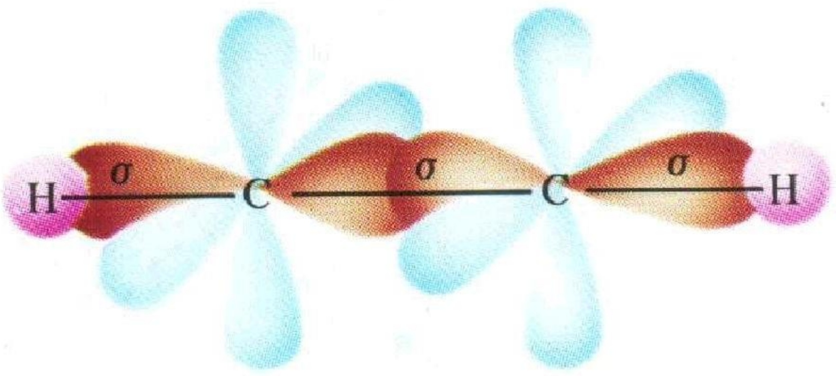
Linear sp Hybridization



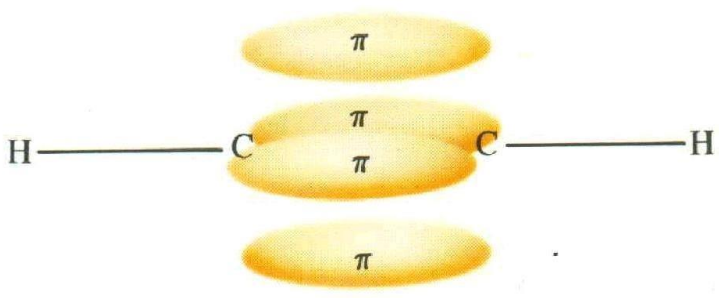


Acetylene or ethyne C_2H_2

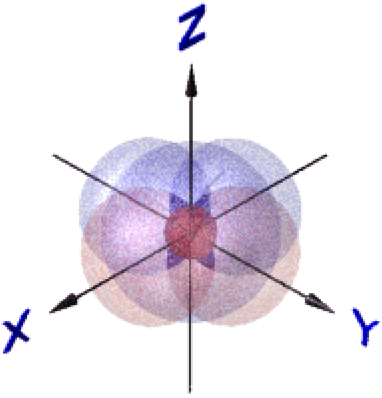
σ bonds



π bonds

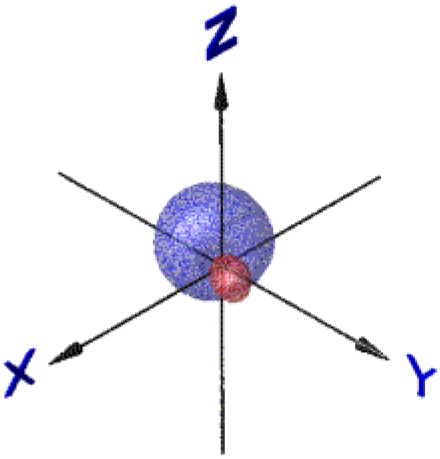


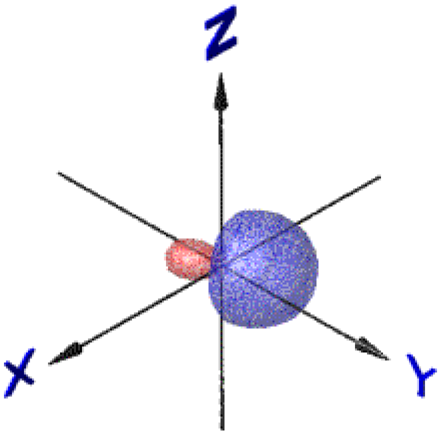
Trigonal sp^2 hybrids. These are composed of the valence shell s-orbital and two of the p-orbitals, say the p_x and p_y to produce a set of hybrids directed in the xy plane at 120° to eachother. The p_z orbital will be left to hold a lone pair or participate in π-bonding. The diagram below shows the 2s, $2p_x$ and $2p_y$ orbitals superimposed in the same space before hybridization. They are combined to form the hybrids according to the equations which follow the diagram:

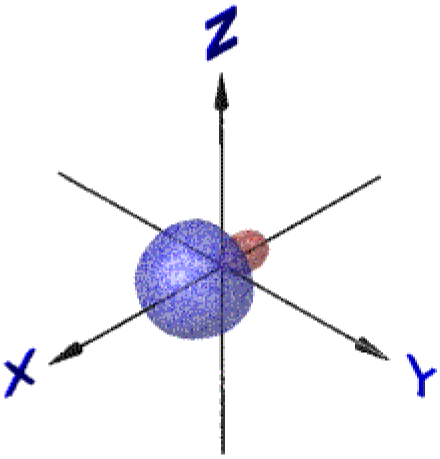


$$\psi_1 = 1/\sqrt{3}\psi_s + 1/\sqrt{6}\psi_{px} + 1/\sqrt{2}\psi_{py}$$
$$\psi_2 = 1/\sqrt{3}\psi_s + 1/\sqrt{6}\psi_{px} - 1/\sqrt{2}\psi_{py}$$
$$\psi_3 = 1/\sqrt{3}\psi_s - 2/\sqrt{6}\psi_{px}$$

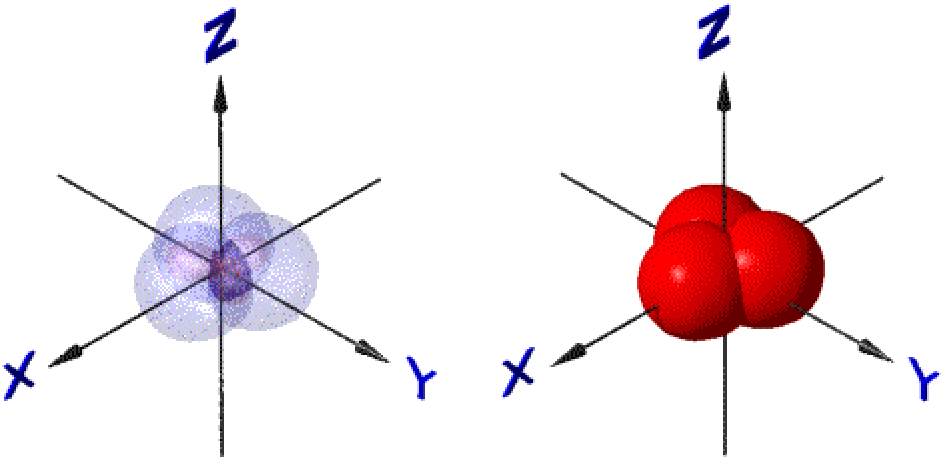
Below, the hybrids corresponding to the three equations above are shown separately (in order from top to bottom):



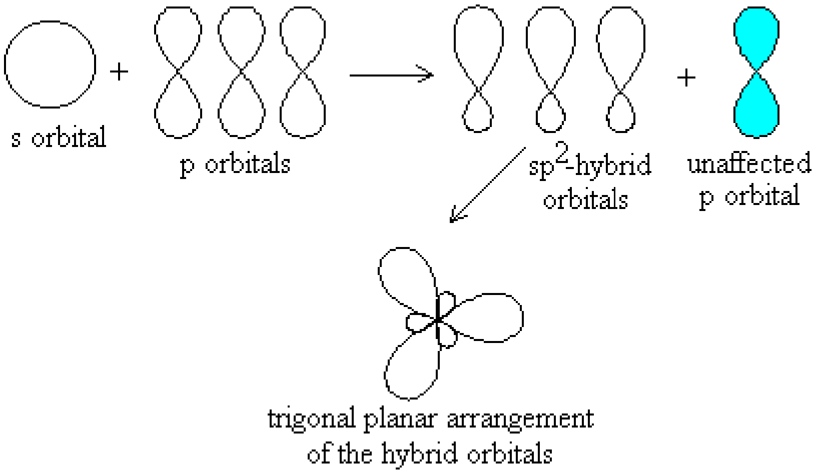




In the diagrams below, the trio of hybrids are superimposed in the same space as they should be. Two diagrams are shown: On the left the antinodes are shown transparent. The small knob of each hybrid is buried deeply. The right hand diagram shows the equivalent hybrid enclosure surfaces and hides the internal structure. Note the "three-fold" symmetry:



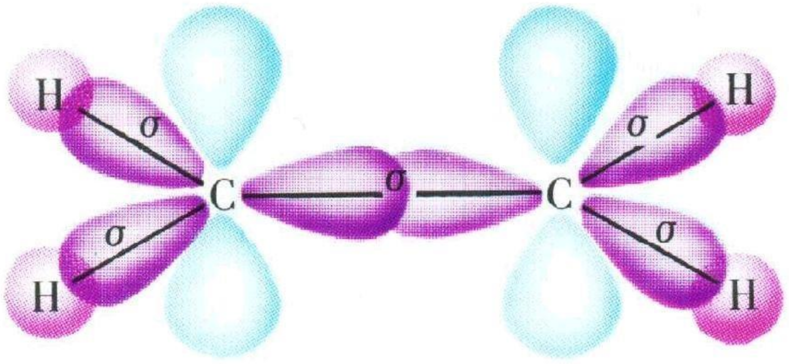
sp^2 hybridization was postulated for the possibility of an s orbital hybridizing with two p orbitals:



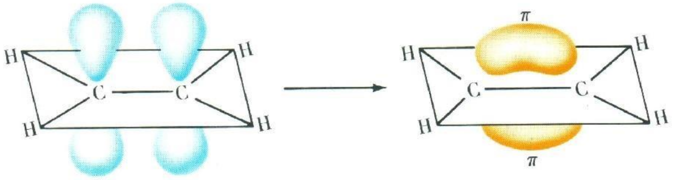
Three bonds could then be formed by overlap with each of the three sp^2-hybrid orbitals. The unaffected p orbital is perpendicular to the plane of the three sp^2-hybrid orbitals, available for sideways overlap to form a pi bond, or, in molecules like boron trifluoride (shown below), the p orbital is left empty.

Ethylene or ethyene C_2H_4

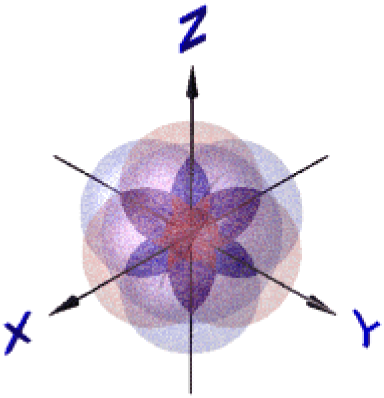
σ bonds



π bonds

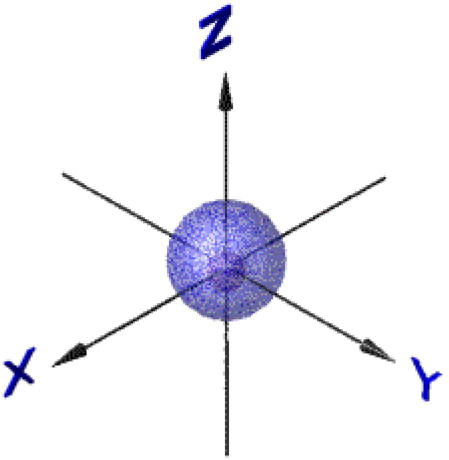


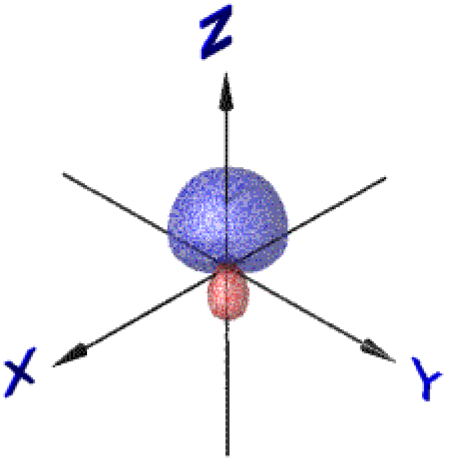
Tetrahedral sp^3 hybrids. These are composed of the valence shell s-orbital and all three p-orbitals. The diagram below shows these superimposed in the same space before hybridization. They are combined according to the equations which appear below the diagram:

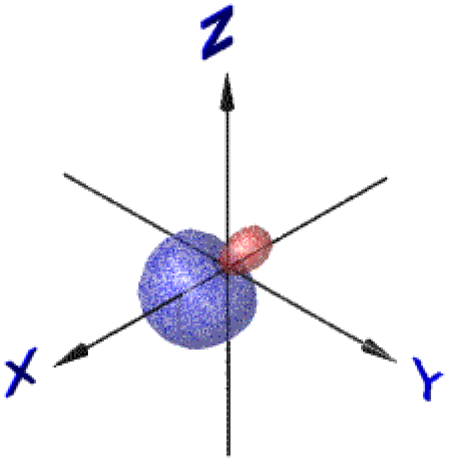


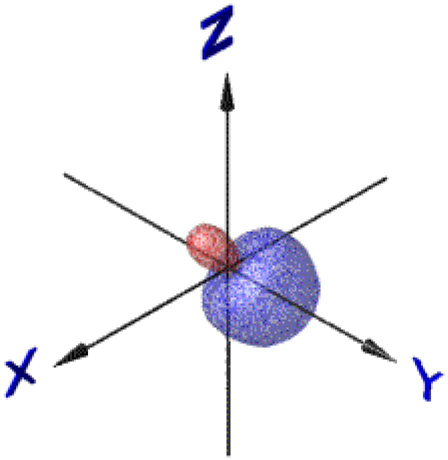
$$\psi_1 = 1/\sqrt{4}\psi_s + 1/\sqrt{4}\psi_{px} + 1/\sqrt{4}\psi_{py} + 1/\sqrt{4}\psi_{pz}$$
$$\psi_2 = 1/\sqrt{4}\psi_s - 1/\sqrt{4}\psi_{px} - 1/\sqrt{4}\psi_{py} + 1/\sqrt{4}\psi_{pz}$$
$$\psi_3 = 1/\sqrt{4}\psi_s + 1/\sqrt{4}\psi_{px} - 1/\sqrt{4}\psi_{py} - 1/\sqrt{4}\psi_{pz}$$
$$\psi_4 = 1/\sqrt{4}\psi_s - 1/\sqrt{4}\psi_{px} + 1/\sqrt{4}\psi_{py} -1/\sqrt{4}\psi_{pz}$$

Below, the hybrids corresponding to the four equations above are shown separately (in order, left to right and top to bottom):

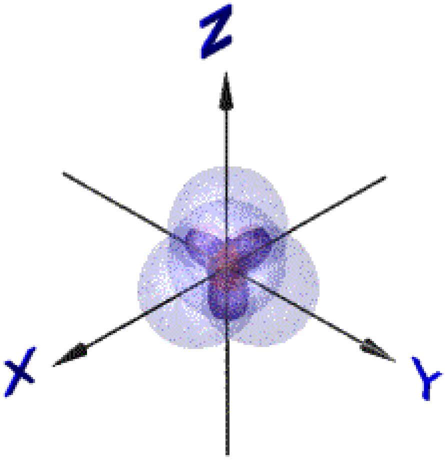


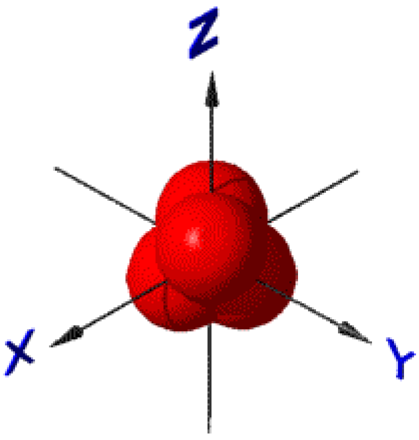






In the diagrams below, the quartet of hybrids are superimposed in the same space as they should be. Two diagrams are shown: On the left the antinodes are shown transparent. Again, the small knob of each hybrid is buried deeply. The right hand diagram shows the equivalent hybrid enclosure surfaces and hides the internal structure. Note the tetrahedral symmetry of the group:

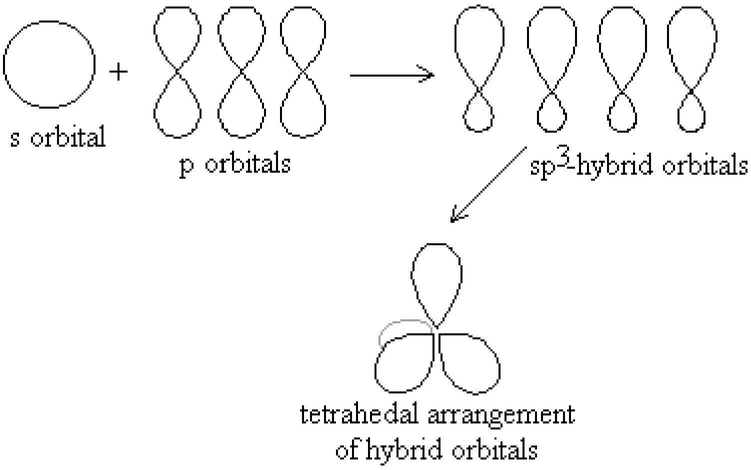




Notes on the equations: Each component atomic orbital must be "shared out" completely between the hybrids which leads to the condition that the sum of the squares of the coefficients for a particular atomic orbital add to one. In additon, individual hybrid orbitals must be "normalized", that is, the probability of an electron occupying one of them *somewhere* must be 1. This leads to the condition that the sum of the squares of the coefficients in one of the formulae must also add to 1.

In order to produce angles which differ from the ideal values, the equations are modified. Increasing the ratio of p to s character in any subset will decrease the appropriate inter-hybrid angles.

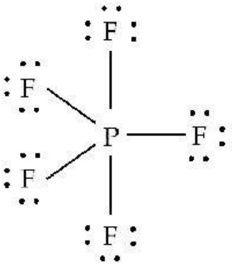
These sp^3-hybridized orbitals were centered about the nucleus, pointing toward the corners of a regular tetrahedron.



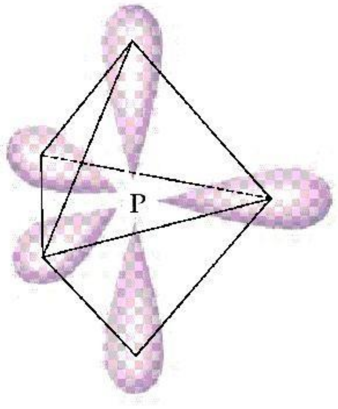
Four bonds could then be formed by overlap with each of the four sp^3-hybrid orbitals. The resulting molecule would have a tetrahedal shape around this sp^3-hybridized atom. This fit the known geometry and bond characteristics of methane (shown below).

Trigonal bipyramidal sp^3d hybrids. These are composed of the valence s-orbital, all the p-orbitals and one of the d-orbitals (normally, the $d_z{}^2$ or one of the two in the xy plane i.e. d_{xy} or d ^{2} ^{2}). The choice depends on the atoms involved so it is not possible to write down a unique set x –y of equations like those above.) The remaining d-orbitals could be involved in π-bonding.

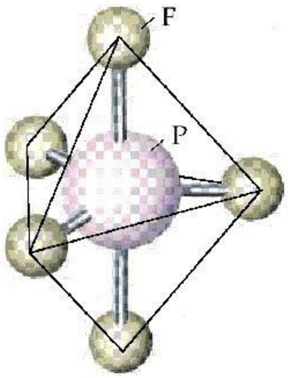
Sp^3d hydrids in PF_5



Lewis dot structure



Electron-pair geometry

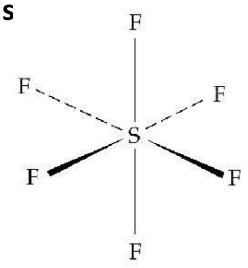


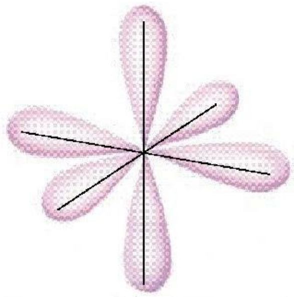
Molecular geometry

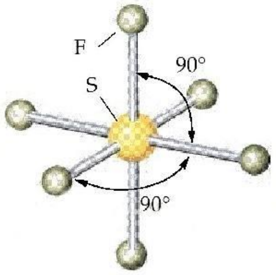
Octahedral sp^3d^2 hybrids. These are composed of the valence s-orbital, the three p-orbitals and two d-orbitals (normally the d_{z^2} and one of the two in the xy plane.) The remaining d-orbitals can

participate in π-bonding.

sp^3d^2 hybrids



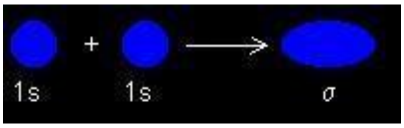




1.10 HOMONUCLEAR DIATOMIC MOLECULES

The hydrogen molecule

A bond between two atoms is formed when a pair of electrons is shared by two overlapping orbitals, according to the VB theory. For example, in a hydrogen molecule, the two 1s orbitals from each H atoms overlap and share electrons.



1.11 HYDROGEN BONDING

Nitrogen, oxygen and fluorine are the highly electronegative elements. When they are attached to a hydrogen atom to form covalent bond, the electrons of the covalent bond are shifted towards the more electronegative atom. This partially positively charged hydrogen atom forms a bond with the other more electronegative atom. This bond is known as hydrogen bond and is weaker than the covalent bond. For example, in HF molecule, the hydrogen bond exists between hydrogen atom of one molecule and fluorine atom of another molecule.

Here, hydrogen bond acts as a bridge between two atoms which holds one atom by covalent bond and the other by hydrogen bond. Hydrogen bond is represented by a dotted line (– – –) while a solid line represents the covalent bond. Thus, hydrogen bond can be defined as the attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule.

Cause of Formation of Hydrogen Bond

When hydrogen is bonded to strongly electronegative element 'X', the electron pair shared between the two atoms moves far away from hydrogen atom. As a result the hydrogen atom becomes highly electropositive with respect to the other atom 'X'. Since there is displacement of electrons towards X, the hydrogen acquires fractional positive charge (δ^+) while 'X' attain fractional negative charge (δ^-). This results in the formation of a polar molecule having electrostatic force of attraction which can be represented as :

H - - - - - X ------- H ------ X ------ H ------ X ---

The magnitude of H-bonding depends on the physical state of the compound. It is maximum in the solid state and minimum in the gaseous state. Thus, the hydrogen bonds have strong influence on the structure and properties of the compounds.

Types of H-Bonds

There are two types of H-bonds

(i) Intermolecular hydrogen bond
(ii) Intramolecular hydrogen bond

(i) **Intermolecular *hydrogen bond* :** It is formed between two different molecules of the same or different compounds. For example, H- bond in case of HF molecule, alcohol or water molecules, etc.

(iii) **Intramolecular *hydrogen bond* :** It is formed when hydrogen atom is in between the two highly electronegative (F, O, N) atoms present within the same molecule. For example, in *o*-nitrophenol the hydrogen is in between the two oxygen atoms.

1.12 VAN DER WAALS FORCES

Van der Waals Forces are the weak forces which contribute to intermolecular bonding between molecules. Molecules inherently possess energy and their electrons are always in motion, so transient concentrations of electrons in one region or another lead electrically positive regions of a molecule to be attracted to the electrons of another molecule. Similarly, negatively-charged regions of one molecule are repulsed by negatively-charged regions of another molecule.

Van der Waals forces are the sum of the attractive and repulsive electrical forces between atoms and molecules. These forces differ from covalent and ionic chemical bonding because they result from fluctuations in charge density of particles. Examples of van der Waals forces include hydrogen bonding, dispersion forces, and dipole-dipole interactions.

There are four major contributions to van der Waals forces:

1. There is a negative component that prevents molecules from collapsing. This is due to the Pauli exclusion principle.
2. Either an attractive or repulsive electrostatic interaction occurs between permanent charges, dipoles, quadrupoles, and multipoles. This interaction is called Keesom interaction or Keesom force, named for Willem Hendrik Keesom.
3. Induction or polarization occurs. This is an attractive force between a permanent polarity on one molecule and an induced polarity on another. This interaction is called the Debye force for Peter J.W. Debye.
4. London dispersion force is the attraction between any pair of molecules due to instantaneous polarization. The force is named after Fritz London. Note even nonpolar molecules experience London dispersion.

UNIT – II
SURFACE CHEMISTRY

2.1 INTRODUCTION

Surface chemistry is the branch of chemistry which deals with study of the phenomena occurring at the surface or interface, i.e., at the boundary separating two bulk phases.

The two bulk phases can be pure compounds or solutions. The interface is represented by putting a hyphen or a slash between the two bulk phases involved, e.g., solid- liquid, solid-gas. Many important phenomena, noticeable amongst these being corrosion, electrode processes, heterogeneous catalysis, dissolution and crystallisation occur at interfaces. The subject of surface chemistry finds many applications in industry, analytical work and daily life situations.

2.1.1 DEFINITIONS

1. Adsorption

When a solid surface is exposed to a gas or a liquid, molecules from the gas or the solution phase accumulate (or) concentrate at the surface.

The phenomena of concentration or assimilation of a gas or liquid at a solid surface is called **adsorption**. This is accompanied by decrease in residual forces.

E.g:

- When a dilute solution of litmus is shaken with animal charcoal the surface of latter carries away some of the litmus.
- Atmospheric moisture gets adsorbed over the surface of silica.

2. Adsorbent

The material surface on which adsorption occurs is known as **adsorbent.**

Example: Charcoal, Silica gel, clay, Fuller's earth, alumina gel, Ni. Pt, Pd etc…

3. Adsorbate

The substances that get adsorbed or attached on the surface of the solid is known as **adsorbate.**

E.g : Gas (H_2, N_2), Liquid (NH_3) etc...

4. Interface

The interface is the boundary between two spatial regions occupied by different matter, or by matter in different physical states.

5. Absorption

- Absorption is a bulk phenomenon in which the substance assimilated is uniformly distributed throughout the body of the solid or liquid.
  E.g: When a blotting paper comes in contact with ink, the latter is absorbed and penetrates uniformly into the adsorbent
  Atmospheric moisture is absorbed by $CaCl_2$**.**
  Lump of sugar dipped in water.
- Adsorption is a fast process when compared to absorption, which is slow due to diffusion of adsorbate into the interior of the adsorbent.

6. Sorption

It is the phenomenon in which both adsorption and absorption takes place simultaneously.

E.g

- Uptake of gases by zeolites.
- When ammonia is passed through water in contact with charcoal sorption takes place.
- Water dissolves ammonia (absorption) and then it is absorbed by charcoal crystals.

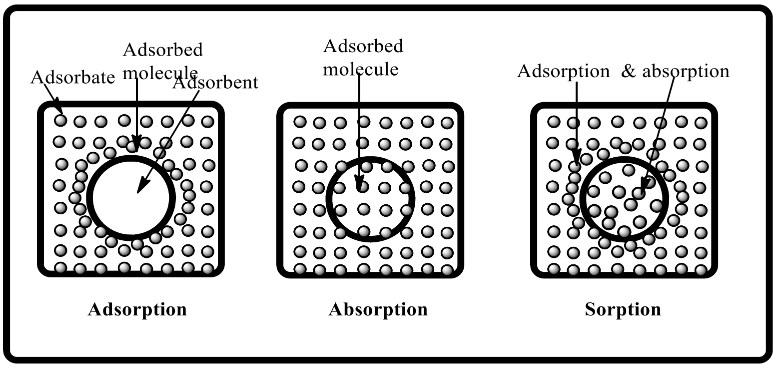


Fig: 2.1 **Illustration of adsorption, absorption and sorption**

7. Desorption

The removal of the adsorbed substance from the surface is called desorption.

Table 2.1 Difference between Adsorption and Absorption

Adsorption	Absorption
It is the phenomena of assimilation of a gas or liquid at the solid surface.	It is phenomena in which the substance assimilated is uniformly throughout the body of the solid or liquid.
It is a surface phenomena	It is a bulk phenomena
It is not a diffusion process	Diffusion processes
Equilibrium is attained easily	Equilibrium is attained slowly
It is a fast process	It is a slow process
It depends on the surface area of the adsorbent	It requires porous structure in a substance that absorbs simple molecules.
Example: Adsorption of atmospheric moisture on silica gel.	**Example:** Absorption of atmospheric moisture by $CaCl_2$

2.1.2 CHARACTERISTICS OF ADSORPTION

Important characteristics of adsorption phenomenon are

1. ***Adsorption on surface of a solid is always spontaneous*** because more number of new surfaces are created by ordinary breaking of the lump. Thereby an unbalanced or residual force generated holds any molecules with its immediate proximity.
2. ***Adsorption is always accompanied by evolution of heat*** because adsorption of gases decreases the residual forces, thereby it results decrease in surface energy which in turn appears in the form of heat.

3. ***Adsorption is always accompanied by decrease in enthalpy and entropy of the system*** because gas adsorbed on solid adsorption surface has restricted movement, which decreases entropy of the system. Since adsorption is always a spontaneous process, the free energy change must be negative.
4. ***Adsorption is a selective process***. i.e., A given adsorbent always show preference for one adsorbate over another.

   E.g: Gases like NH_3, Cl_2, HCl, SO_2, etc., which are liquefiable, get readily adsorbed, whereas N_2, H_2, O_2, etc. are less readily adsorbed. It is observed that gases with low volatility are adsorbed readily than others.
5. ***Adsorption is specific*** and its extent under a given set of conditions depends both on the nature of adsorbent and adsorbate.
6. ***Increase of partial pressure of gas being adsorbed increases adsorption*** permit mass of the adsorbent till a saturation point is reached.
7. ***The rate of adsorption depends on temperature*** because adsorption is an exothermic process.

2.2 TYPES OF ADSORPTION

The adsorption of a gas on a solid surface is of two types, which is based on the nature and affinity between the adsorbate and adsorbent.

1. Physical adsorption (or) physisorption (or) Vander Waals adsorption
2. Chemical adsorption (or) Chemisorption (or) Activated adsorption

2.2.1 Physical adsorption (or) Physisorption (or) Vander Waal's adsorption

When a gas is adsorbed on the surface of a solid by vander waal's forces without resulting in the formation of any chemical bond between the adsorbate and adsorbent, it is known as physical adsorption or vander waal's adsorption.

E.g: Adsorption of H_2 (or) O_2 on charcoal.

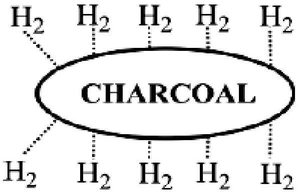


Fig 2.2 **Adsorption of H_2 (or) O_2 on charcoal**

Characteristics of physical adsorption

- The adsorbate is held on adsorbent by vander vaals forces (inter molecular).
- The heat evolved during physisorption is low i.e. 20-40 kcal/mole.
- This is reversible.
- Increase of pressure causes more gas to be adsorbed and the release of pressure frees the adsorbed gas.
- Decrease of temperature increases adsorption but the gas adsorbed at low temperature can be freed again by heating.
- Physical adsorption is usually multilayer.
- In physical adsorption, the adsorbate molecules are held by comparatively weak vander Waal's forces. Hence, the activation energy of desorption is very low.

- Physical adsorption occurs appreciably at very low temperatures i.e. below the boiling point of the adsorbate.
- Physical adsorption takes place between every gas and a solid i.e. It is not specific in nature because it involves Vander Waal's forces.

2.2.2 Chemical adsorption (or) Chemisorption

When a gas is held on the surface of a solid by forces similar to that of a chemical bond, the type of adsorption is known as chemical adsorption or chemisorption.

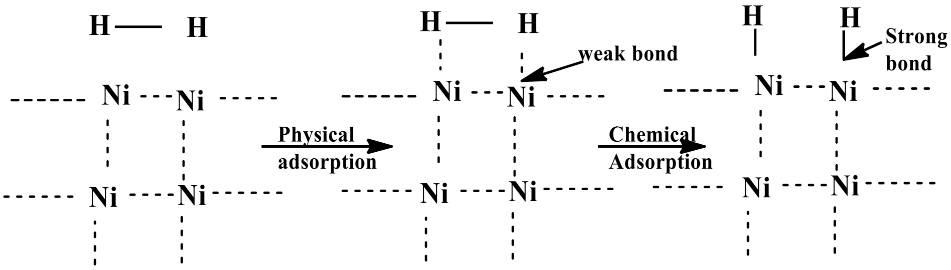


Fig 2.3 **Adsorption of H_2 on Ni**

E.g: Adsorption of H_2 on Ni

H_2 molecule is first adsorbed by Vander Walls' forces and then undergoes dissociation to hydrogen atoms. Then the hydrogen atoms are chemisorbed on Ni.

Characteristics of chemical adsorption

- The adsorbate is held on adsorbent by chemical forces (chemical bond).
- The heat evolved during chemisorption is high i.e. 40-400 kcal/mole.
- The magnitude of chemisorption increases with the rise in temperature.
- The chemisorption is irreversible.
- Chemisorption is specific in nature.
- Chemisorption is monolayer since the chemical forces operate within short distance only.
- In chemisorption the adsorbate molecules are held by comparatively strong valence forces. Hence, the activation energy of desorption is very high.

Table 2.2 Difference between Physisorption and Chemisorption

S.No	Physisorption	Chemisorption
1	Caused by intermolecular Vander Waal's forces (weak)	Caused by chemical bond formation (strong)
2	Heat of adsorption is low (20 – 40 kcal/mol)	Heat of adsorption is high (40 – 400 kcal/mol)
3	Occurs in gases, which are easily liquefiable.	Occurs in gases, which have potentiality to form compound.
4	No appreciable energy of activation.	Energy of activation may be involved.
5	Does not show any specificity.	Highly specific.
6	Rate of adsorption increases with increase of pressure.	Change of pressure has no such effect.
7	Adsorption is completely reversible	Adsorption is irreversible
8	Adsorption decreases with increase in Temperature	Adsorption increases with Temperature

9	Multilayer adsorption is possible	Only monolayer adsorption
10	Equilibrium is established rapidly.	Requires time
11	No surface compound formation	Surface compound is formed
12	The amount of adsorption depends only on adsorbate alone	Depends on adsorbate and adsorbent.

2.3 ADSORPTION OF SOLUTES FROM SOLUTIONS

Porous or finely divided solid substances can also adsorb dissolved substances from solution. Thus, activated charcoal is used to remove coloured impurities from solutions.

E.g :

- Activated charcoal removes coloured impurities from sugar solution.
- Activated charcoal adsorbs certain acids like acetic acid & oxalic acid present in water.
- The precipitate of $Mg(OH)_2$ changes blue due to adsorption of MAGNESON by it.
- Adsorption from solution follows the same principles as laid down for adsorption of gases by solids and is subjected to the same factors. Thus,
- Some adsorbents specifically adsorb certain solute more effectively than others.
  (i.e) i. Charcoal adsorbs non-electrolytes more readily than electrolytes from a solution.
  ii. Alumina adsorbs electrolytes more readily than non-electrolytes.
- An increase of temperature decreases the extent of adsorption.
- An increase in surface area increases the extent of adsorption.
- Adsorption of solute also establishes an equilibrium between the amount adsorbed and the concentration of the solute in solution.

  For adsorption from solutions, the amount of the solute adsorbed on the adsorbent depends on the concentration of solute in the solution. The Freundlich isotherm, using concentration ‘C’, instead of pressure.

$$\frac{x}{m} \propto C^{1/n}$$

$$\frac{x}{m} = KC^{1/n} \qquad ......(1)$$

where,

x = mass of solute adsorbed on a mass ‘m’ of adsorbent
C = equilibrium concentration
K & n = are constants

Taking logarithms on (1) and we get

$$\log\frac{x}{m} = \log k + \frac{1}{n}\log C \qquad .....(2)$$

A plot of log x/m Vs log C gives a straight line with a slope l/n and

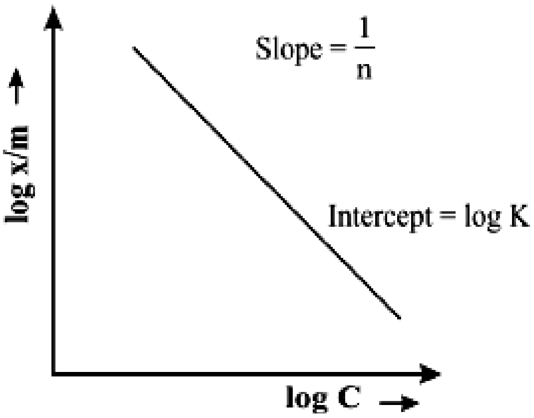


Fig 2.10 **Verification of Freundlich Isotherm**

The validity of the Frendlich isotherm for adsorption from solution can be tested by shaking equal weights of activated charcoal with 100 ml each of different solution of oxalic acid of known concentrations.

When adsorbent is added into a solution, either the solute or solvent may be adsorbed.

(i) If solute is adsorbed by adsorbent, it is known as ***positive adsorption.***

E.g : From concentrated solution of KCl, charcoal adsorbs KCl than water thereby salt (KCl) concentration decreases.

(ii) If solvent is adsorbed by the adsorbent, it is known as ***negative adsorption***.

E.g : From the dilute solution of KCl, Charcoal adsorbs water thereby the salt concentration is increased.

2.4 ADSORPTION ISOTHERM

The adsorption of a gas on a solid adsorbent in a closed vessel is a reversible process.

$$\text{Free gas} \rightleftharpoons \text{gas adsorbed on solid.}$$

The amount of gas adsorbed depends on the equilibrium pressure at a given temperature. (i.e.) adsorption increases with increase in pressure of the gas at a given temperature. However, this increase is not always directly proportional to the applied pressure. It is found to be somewhat less at high pressures.

So, Adsorption (a) = f (p) at constant T

"The graphical relation between the amounts of gas adsorbed with pressure at constant temperature" is known as **adsorption isotherm.**

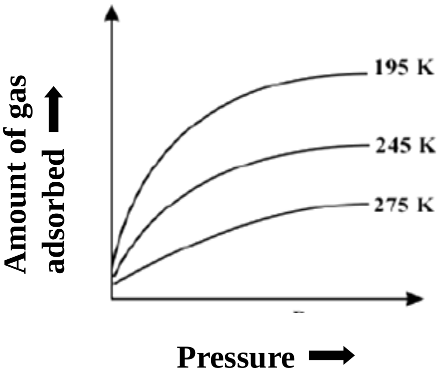


Fig 2.5 **Isotherm for adsorption of N_2 on charcoal**

E.g: Adsorption of nitrogen on charcoal

2.4.1 Freundlich adsorption isotherm

Freundlich proposed an empirical relation in the form of a mathematical equation

$$\frac{x}{m} = kP^{1/n} \qquad .....(1)$$

Where, x – amount of the gas adsorbed on a mass 'm' of adsorbent at a pressure 'P'.
k and n are constants at a particular temperature for a particular adsorbent and a gas.

This relation is generally represented in the form of a curve obtained by plotting the mass of the gas adsorbed per unit mass of adsorbent (x/m) against equilibrium pressure 'P'.

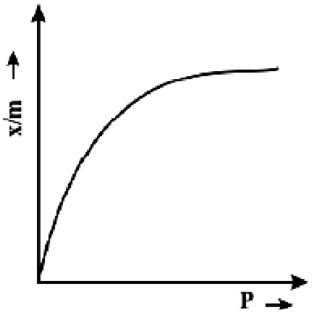


Fig 2.6 **Freundlich adsorption isotherm**

Taking logarithm on both sides of the equation (1).
We get,

$$\log\frac{x}{m} = \log k + \frac{1}{n}\log P \qquad .....(2)$$

This is equation for a straight line. Thus a plot of log x/m Vs. log P, should be a straight line with slope 1/n and intercept log k.

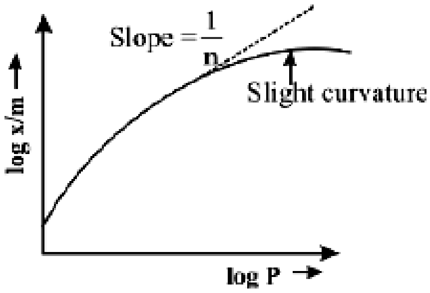


Fig 2.7 **Freundlich isotherm**

From the graph it is found that, the behavior of a adsorption.
i. At low pressure the plot is almost a straight line,

$$\frac{x}{m} \propto P \text{ (or) } \frac{x}{m} = kP$$

ii. At intermediate pressure x/m lies between 0 – 1 pressure (fractional pressure), sharing that

$$x/m = k.\ p^{1/n}$$

iii. At high pressure x/m becomes almost independent of pressure.

$$x/m = \text{constant (or) } x/m = k$$

Limitations

- It is an empirical formula, there is no theoretical foundation.
- It is valid only for certain range of pressure (not applicable to high pressures).
- The constant k and n are temperature dependent, they vary with increase or decrease in temp.

- It fails, when the concentration of adsorbate is very high.

2.4.2 LANGMUIR'S ADSORPTION ISOTHERM

In 1916, Irving Langmuir proposed a new model isotherm for gases adsorbed to solid, which retained his name.

Assumptions (Postulates)

- The adsorbed gas behaves ideally.
- The thickness of the adsorbed layer is same as the thickness of a molecule of the adsorbate (the adsorbed layer is uniform all over the adsorbent).
- The adsorption takes place only on the surface (monolayer) alone.
- There is no lateral interaction between the molecules adsorbed.
- There is a dynamic equilibrium between the rate of adsorption and rate of evaporation (desorption).

Derivation of Langmuir Isotherm

Langmuir considered that the gas molecules strike the solid surface and get adsorbed. Some of the adsorbed molecules then desorbed (evaporate) from the surface and go back to the body of the gas. Therefore, a dynamic equilibrium is established between adsorption and desorption. If A is a gas molecule and M is the surface.

$$A_{(g)} + M_{(surface)} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AM$$

Let the fraction of the total surface covered by the adsorbed molecule = θ

The fraction of uncovered (vacant) area = (1 – θ)

The rate of desorption R_d ∞ covered surface area (θ).

$$R_d = k_d \theta \qquad \text{-------- (1)}$$

Where k_d is rate constant for the desorption.

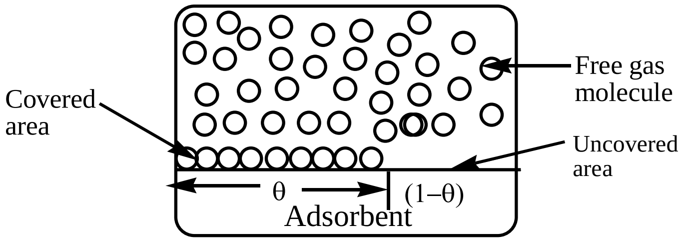


Fig 2.8 **Equilibrium between free molecule and adsorbed molecules.**

The rate of adsorption R_a ∞ uncovered surface area (1- θ).

$$R_a = k_a (1-\theta) P \qquad \text{--------- (2)}$$

Where k_a is rate constant for the adsorption

At equilibrium; Rate of desorption = Rate of adsorption

$$R_d = R_a$$

$$\therefore k_d \theta = k_a (1-\theta) P = k_a - k_a \theta P$$

$$k_d \theta + k_a \theta P = k_a P$$

$$\theta (k_d + k_a P) = k_a P$$

$$\theta = \frac{k_a P}{(k_d + k_a P)} \qquad \text{———————— (3)}$$

Dividing (3) by k_d:

$$\theta = \frac{(k_a/k_d)P}{1+(k_a/k_d)P} \quad \text{or} \quad \theta = \frac{\mathrm{KP}}{1+\mathrm{KP}} \qquad \text{———} \quad (4)$$

Where,

$k_a / k_d = K$ = Equilibrium constant. (**Absorption coefficient)**

But, the amount of gas adsorbed per gram of the adsorbent is proportional to θ.

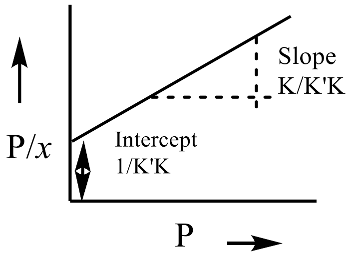
$$\therefore x \propto \theta \qquad \text{--------------}(5)$$

$$\text{Comparing (4) \& (5):} \quad x \propto \frac{\mathrm{KP}}{1+\mathrm{KP}} \qquad x = K'\frac{\mathrm{KP}}{1+\mathrm{KP}} \quad \text{-------------} (6)$$

Where, K' is a new constant

Eqn (6) gives the relation between the amounts of gas adsorbed to the pressure of the gas at constant temperature and is known as **Langmuir Adsorption Isotherm.**

Eqn. (6) can be rewritten as $1+\mathrm{KP} = \frac{\mathrm{K'KP}}{x}$; $\frac{1}{\mathrm{K'K}} + \frac{KP}{\mathrm{K'K}} = \frac{P}{x}$; $\frac{1}{\mathrm{K'K}} + \frac{K}{\mathrm{K'K}}P = \frac{P}{x}$ ------- (7)



The graph between P/x Vs P should be a straight line with slope K/K'K and intercept 1/K'K

Fig 2.9 **plot of P/*x* Vs P**

This equation if found valid in all cases

Case (i): At low pressure

$$\text{At low P,} \quad \frac{K}{\mathrm{K'K}}P \quad \text{is negligeble;} \quad i.e., \quad \frac{1}{\mathrm{K'K}} >> \frac{K}{\mathrm{K'K}}P$$

$$\text{Hence eqn (7) becomes:} \quad i.e., \quad \frac{1}{\mathrm{K'K}} = \frac{P}{x} \quad ; \quad x = \mathrm{PK'K}$$

i.e., The amount of adsorption per unit weight of adsorbent is directly proportional to P.

Case (ii): At high pressure

$$\text{At high P,} \quad \frac{1}{\mathrm{K'K}} \quad \text{is negligible;} \quad i.e., \quad \frac{\mathrm{K}}{\mathrm{K'K}}P >> \frac{1}{\mathrm{K'K}} \quad \text{the eqn (7) becomes}$$

$$\frac{\mathrm{K}}{\mathrm{K'K}}P = \frac{\mathrm{P}}{x} \qquad \text{(or) } x = \mathrm{K'} \text{ (constant)}$$

i.e., extend of adsorption is independent of pressure of the gas, because the surface becomes completely covered at high pressure.

Case (iii) At normal pressure

If the pressure is normal (intermediate) the eq. (7) becomes

$$x = \mathrm{K'P}^{n} \text{ ----------} (8)$$

Where n lies between 0 to 1 Equations (8) is called Frendlich's adsorption isotherm.

Merits – Langmuir's adsorption isotherm holds good at low pressure.

Demerits - It fails at high pressure.

2.5 INDUSTRIAL APPLICATIONS OF ADSORPTION

1. Activated Charcoal

- It is used in gas masks, which will adsorb undesirable (toxic) gases, thereby air gets purified.
- It is also used for removing colouring materials or odorous substances.

2. Silica and alumina gels

These are used as adsorbents for removing moisture to control the humidity.

3. In water softening

In permutit process, water containing Ca^{2+} and Mg^{2+} ions are removed by adsorption, while passing through sodium alumino silicate (Zeolite) bed.

$$Na_2Ze + Ca^{2+} \text{ (or) } Mg^{2+} \longrightarrow CaZe \text{ (or) } MgZe + 2Na^{+} \text{ (in solution)}$$

4. Refining of petroleum and vegetable oils

Fuller's earth is used in large quantities for refining petroleum and other vegetable oils, which adsorbs unwanted materials.

5. Surface active agents

The substances which lowers the surface tension of water are called as surface-active agents.

Example: soaps, detergents and emulsifiers.

These are used as wetting agents. For example liquid drops on the surface of a metal tend to remain as isolated drop. However, the drop spread into a thin film when comes in contact with wetting agents.

6. In curing diseases

A number of drugs are adsorbed on the germs and kills them or these are adsorbed on the tissues and heal them.

7. As Mordant

In dying industry, Mordants adsorb coloring matter without attaching to the fabrics.

8. In water conservation

- Due to scarcity of water during summer a layer of stearic acid is spread over water lakes and reservoirs.
- The adsorbed stearic acid on the surface of water minimizes evaporation of water.

9. Chromatography

This method is used for the isolation or purification of naturally occurring organic compounds or separation of the constituents from a mixture by differential adsorption.

10. In Heterogeneous catalysis

In heterogeneous catalysis, the molecules are adsorbed on the surface of catalyst which form adsorption complex. Then it decomposes to form product.

Example:

i. Manufacture of SO_3 by contact process.

ii. Hydrogenation of oils.

2.6 APPLICATIONS OF SURFACE ACTIVE AGENTS

Surface active agents play an important role as cleaning, wetting, dispersing, emulsifying, foaming and anti-foaming agents in many practical applications and products, including: paints, emulsionsadhesives, inks, biocides (sanitizers), shampoos, toothpastes, firefighting (foams), detergents, insecticides, deinking of recycled papers, ski waxes, spermicides.

There are 4 types of surfactants with a brief review of each as follows. These classifications are based upon the composition of the polarity of the head group: nonionic, anionic, cationic, amphoteric.

Trade name	Structure/name	Applications
Triton™ X-100	Polyoxyethylene glycol octylphenol ethers: C8H17–(C6H4)–(O-C2H4)1–25–OH	Wetting agent – coatings
Nonoxynol-9	Polyoxyethylene glycol alkylphenol ethers: C9H19–(C6H4)–(O-C2H4)1–25–OH	Spermacide
Polysorbate	Polyoxyethylene glycol sorbitan alkyl esters	Food ingredient
Span	Sorbitan alkyl esters	Polishes, cleaners, fragrance carriers
Poloxamers, Tergitol™, Antarox	Block copolymers of polyethylene glycol and polypropylene glycol	Various

2.7 DETERGENCY

Definitions

Process by which soil is removed from a surface and undergoes solubilization or dispersion. Result of several physicochemical phenomenons taking place at the interface of three phases : surface/soil/detergent.

The phenomenons are :

1. Wetting of surface.
2. Removal of soil from surface.
3. Avoiding re-deposition of soil on surface.

Step 1 wetting

The detergent must come into contact with the surface so that (Fa = adherence force)

$$F_{detergent/surface} > F_{soil\ /surface}$$

Step 2 Removal of soil

The detergent solution wets the surface, is absorbed by it and lowers the surface’s attraction to allow the soil to separate itself from the surface.

surface / soil + detergent → surface / detergent + soil / detergent

Step 3 Avoiding re-deposition

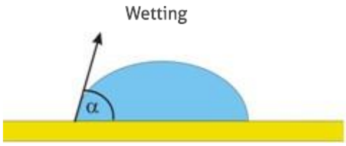
The following chemical reactions undergoing to avoid the re-deosition

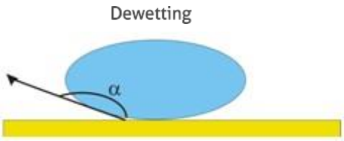
- lipids undergo saponification
- mineral soil undergoes solubilization
- soil undergoes emulsification

2.8 WETTING

Wetting is the ability of liquids to form interfaces with solid surfaces. To determine the

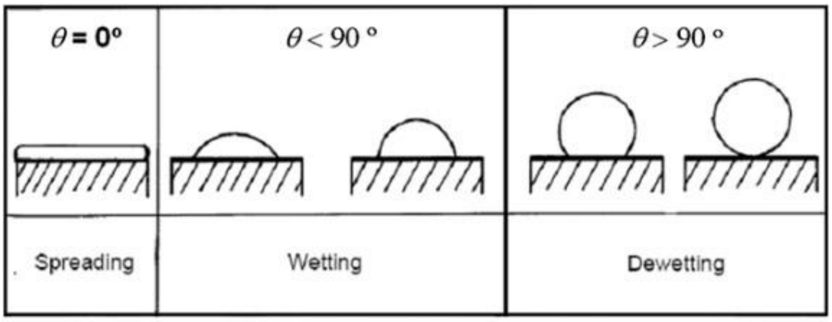
degree of wetting, the contact angle (q) that is formed between the liquid and the solid surface is measured. The smaller the contact angle and the smaller the surface tension, the greater the degree of wetting.





Wetting	Dewetting
Adhesion Forces> Cohesive Forces	**Adhesion Forces< Cohesive Forces**
Spreading of the liquid on the surface of the solid.	**The liquid pulls itself together into the shape of a droplet**
Contact Angle*q* :0 <*q*< p/2	**Contact Angle *q* :p/2 <*q* < p**

For maximum adhesion the adhesive must completely cover the substrate, i.e. spreading is necessary. The contact angle is a good indicator of adhesive behavior.



Wettability is a tendency of a liquid to spread on a solid surface. Measurement of the contact angle is the way to estimate wettability when the tested fluids are pure and the contact surface (solid or liquid) is perfectly flat, mainly because the surface tension of the interfaces is constant when no surfactants or other compounds are present to alter the wetting. When using Young's equation it was assumed that the surface is rigid, homogeneous and perfectly flat – in such a case a single, specified contact angle for each three-phase system could be obtained.

2.9 EMULSIFIER

When water and oil are mixed together and vigorously shaken, a dispersion of oil droplets in water - and vice versa - is formed. When shaking stops, the phases start to separate. However, when an emulsifier is added to the system, the droplets remain dispersed, and a stable emulsion is obtained.

An emulsifier consists of a water-loving hydrophilic head and an oil-loving hydrophobic tail. The hydrophilic head is directed to the aqueous phase and the hydrophobic tail to the oil phase (see figure 1). The emulsifier positions itself at the oil/water or air/water interface and, by reducing the surface tension, has a stabilising effect on the emulsion.

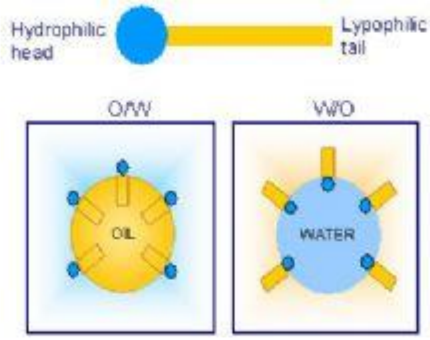


Figure 1: An oil-in water (left) and water-in-oil (right) emulsion
The tube on the left contains an emulsion. The two separated layers are shown on the right.

In addition to their ability to form an emulsion, emulsifiers have the ability to interact with other food ingredients. In this way, various functionalities can be obtained, for example interaction with proteins or carbohydrates. The emulsifier may be an aerating agent, starch complexing agent and/or crystallisation inhibitor (read more in applications).

2.10 DEFOAMERS

Foam, in general, is a colloidal system of dispersed or trapped gases as fine bubbles. i.e. it is essentially an aggregate of bubbles. More precisely, it is a dispersion of gas in liquid, where liquid forms the continuous phase. The phenomenon of foaming is primarily governed by the properties of the interfaces involved and foaming is always accompanied by an increase in the interfacial area of the system, and hence its total free energy. Foams are basically unstable and therefore self-destroying and their stability is, among other factors, determined by the gas/liquid interfacial free energy. Before understanding the ways of eliminating foam, one must know the problems associated with foaming in textile processing industries. Foam generated due to vigorous circulation of liquor in presence of various surfactant based additives and air during wet processing of textiles, can cause detrimental effects.

Problems due to foam in textile wet-processing :

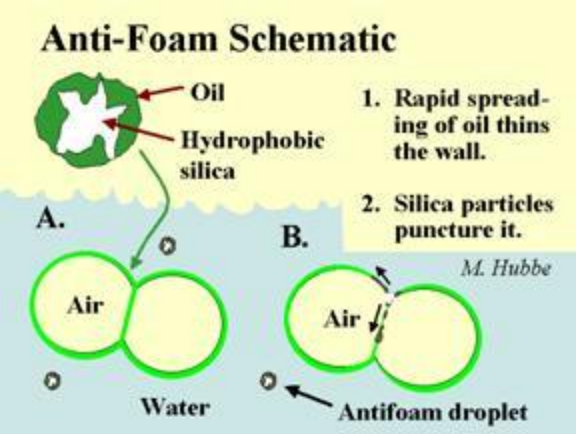
1. Dense foam leads to serious entanglements of fabric with consequences of stoppages of machines, uneven absorbency, and patchy dyeing.
2. In the dyeing of hanks and knitted fabrics, foaming of the dye liquor can cause the material to float resulting in uneven application of dye.
3. The foam in printing paste, especially in rotary screen and roller printing machine can cause ‘fish eye’ spots on printed fabrics.

To eliminate above problems, it is required to control foaming by careful optimization of process parameters, and by using a defoamer/anti-foaming agent etc.

The term de-foaming agent and anti-foaming are two different terms. The term de-foamer describes a product that is added to destroy existing foam; whereas anti-foaming agent is a product that is added to a system in order to prevent the foam from occurring.

Mechanism of defoamers:

The surface-active nature of the defoamer causes it to spread very rapidly onto any air-water interface that it encounters. This is especially the case if that interface already is covered by the types of surface-active materials that tend to stabilize foams. The function of hydrophobic silica particles is to pierce the surfaces of foam bubbles, causing them to coalesce when the defoamer spreads at the interface. Depending on the particular antifoam and the foaming system, one can expect differences in the relative importance of these factors:



1. Dispersion of antifoam in the foaming solution
2. Transport of antifoam droplets from bulk to the bubble interface
3. Entry of the droplet into the gas/liquid interface
4. Spreading
5. Bubble rupture

Most foam is stabilized by surface active stabilizers in the films. A powerful surfactant spreads rapidly over the large surface area of the film and displaces the surfactants that are tending to stabilize the foam, useful in light foams. Whereas in dense foams, additional penetration of defoaming agent into the thicker aqueous is required.During textile wet-processing, we encounter foam during all stages, such as desizing, bleaching, scouring, dyeing & finishing, etc. Due to the diverse conditions during processing of textiles, careful selection of de-foamers is needed, based on factors like pH, temperature, type of machine, shear forces, and the foaming media.

CATALYSIS

2.12 CATALYST

“A Catalyst is a substance which alters the rate of a chemical reaction without undergoing any chemical change and can be recovered after the completion of the reaction”. The process is called catalysis.

2.12.1 EFFECT OF A CATALYST

A catalyst can either increases or decreases the rate of a chemical reaction by altering the activation energy of a reaction.

The nature of catalyzed and non-catalyzed reaction path way could be understood from the above graph. The energy barrier for a catalyzed reaction is lower than non catalyzed reaction. Hence lowering of activation energy with the help of a catalyst has impact upon the rate of the reaction.

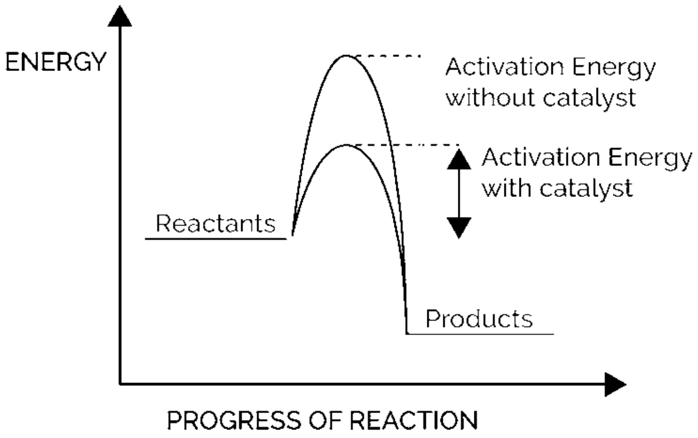


Fig 2.16 **Effect of catalytic reaction**

Catalysts either can increase the speed of the reaction or can decrease. Based on that it can be divided in to two types,

1. Positive catalyst and 2.Negative catalyst

1. Positive catalyst

A catalyst which enhances the rate of a reaction is called positive catalyst.

E.g:

- Decomposition of $KClO_3$ in presence of manganese dioxide.

$$2KClO_3 \xrightarrow[\Delta]{MnO_2} 2KCl + 3O_2$$

- Decomposition of hydrogen peroxide in presence of colloidal platinum.

$$2H_2O_2 \xrightarrow{Pt} 2H_2O + O_2$$

2. Negative catalyst

A catalyst which retards the rate of a reaction is called negative catalyst.

E.g:

- Oxidation of sodium sulphite by air is retarded by alcohol.

$$2Na_2SO_3 + O_2 \xrightarrow{C_2H_5OH} 2Na_2SO_4$$

- **Brucine** retards the atmospheric oxidation of alkaline sodium bisulphate.

2.9.2 Types of Catalysis

Catalysis is classified into two broad types.

1. Homogeneous catalysis
2. Heterogeneous catalysis

1. Homogeneous catalysis

The reaction in which the catalyst as well as the reactants are in the same phase (i.e.) the reactants are solid or liquid or gas, the catalyst are also solid or liquid or gas respectively.

E.g:

a. Homogeneous catalysis in gas phase.

- Oxidation of SO_2 to SO_3 in the presence of NO (nitric oxide) as a catalyst.

$$2SO_{2\ (g)} + O_{2\ (g)} \xrightarrow{NO_{\ (g)}} 2SO_{3\ (g)}$$

- Decomposition of acetaldehyde is catalyzed by Iodine vapours.

$$CH_3CHO_{\ (vapour)} \xrightarrow{I_{2\ (vapour)}} CH_{4\ (g)} + CO_{\ (g)}$$

b. Homogeneous catalysis in liquid phase.

- Hydrolysis of an ester in the presence of acid or alkali catalyst.

$$CH_3COOC_2H_5\,_{(l)} + H_2O_{(l)} \xrightarrow{H_3O^+} CH_3COOH_{(l)} + C_2H_5OH_{(l)}$$

- Inversion of cane sugar

$$C_{12}H_{22}O_{11\,(l)} + H_2O_{(l)} \xrightarrow{H_2SO_{4\,(l)}} C_6H_{12}O_{6\,(l)} + C_6H_{12}O_{6\,(l)}\,)$$

2. Heterogeneous catalysis

The reaction in which the catalyst is in a different physical phase from the reactants is termed as Heterogeneous catalysis.

In this kind of catalysis, the reactants are in gas phase while the catalyst in a solid phase, that's why this process is also called as contact catalysis which has great industrial importance.

E.g:

- In contact process of manufacture of H_2SO_4, sulphur dioxide is directly oxidized to sulphur trioxide by atmospheric oxygen in the presence of platinum or vanadium pentoxide as catalyst.

$$2SO_{2\,(g)} + O_{2\,(g)} \xrightarrow[\text{or } V_2O_5]{Pt_{(s)}} 2SO_{3\,(g)}$$

- In Haber's process for the manufacture of NH_3, nitrogen and hydrogen are combine with each other in the presence of iron as a catalyst.

$$N_{2\,(g)} + 3\,H_{2\,(g)} \xrightarrow{Fe_{(s)}} 2NH_{3\,(g)}$$

- Decomposition of aqueous hydrogen peroxide in the presence of platinum as a catalyst.

$$2H_2O_{2\,(l)} \xrightarrow{Pt\ (\text{colloidal})} 2H_2O_{(l)} + O_{2\,(l)}$$

Table 2.3 The differences between homogeneous catalysis and heterogeneous catalysis

S. No	Homogeneous catalysis	Heterogeneous catalysis
1	Reactants, products and catalyst are in same phase. Either in solid, liquid and gaseous phases.	Reactants, products and catalyst are in different phases.
2	Catalyst cannot be regenerated.	Catalyst can be regenerated and reused.
3	Thermal stability of catalyst is low.	Thermal stability of catalyst is high.
4	Catalyst performs under low temperature and low pressure.	Catalyst performs under high temperature and high pressure.
5	Temperature can increase the rate of the reaction.	Temperature can increase the rate of the reaction.
6	Selectivity of the catalyst does not depend on the physical nature.	Selectivity of the catalyst depends on the physical nature.

2.13 CRITERIA OR CHARACTERISTICS OF CATALYTS

The following are the characteristics which are common to most of catalytic reactions.

1. A catalyst remains unchanged in mass and chemical composition at the end of the reaction. But it can change its physical state and colour.

E.g:
The granular MnO_2 is converted into fine powder of MnO_2, when it is used as a catalyst in the thermal decomposition of $KClO_4$.

2. **A small quantity of the catalyst is generally sufficient to catalyze the reactions.**
   E.g:
   In the decomposition of hydrogen peroxide, one gram of colloidal platinum can catalyze 10^6 liters of hydrogen peroxide.
   For example in Friedel craft's reaction, anhydrous aluminum chloride is required in relatively large amount to the extent of 30% of the mass of benzene.

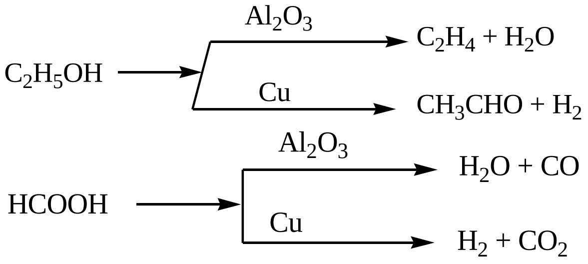
$$C_6H_6 + C_2H_5Cl \xrightarrow{AlCl_3} C_6H_5C_2H_5 + HCl$$

3. **The catalyst cannot initiate the reaction:** The function of the catalyst is to alter the speed of the reaction rather than to start it.
   E.g: A mixture of hydrogen and oxygen remains unchanged at room temperature but react in presence of catalyst Pt.

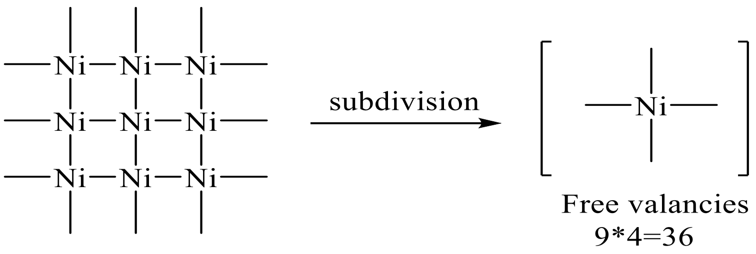
$$2H_2 + O_2 \xrightarrow{\text{room temp}} \text{No reaction}$$

$$2H_2 + O_2 \xrightarrow{\text{Pt black}} 2H_2O$$

4. **The catalyst is generally specific in nature:** A substance, which acts as a catalyst for a particular reaction, fails to catalyze the other reaction. Different catalysts for the same reactant may form different products.
   E.g: The same ethanol molecule gives different products when it is stimulated by different catalysts. The formic acid also performs similarly.



5. **The catalyst cannot change the position of equilibrium:** The catalyst catalyze both forward and backward reactions to the same extent in a reversible reaction and thus have no effect on the equilibrium constant.
6. **The catalyst is more effective, when it is finely divided:** When the fineness of the catalyst increase, the free surface area gets increased. Thereby free valencies increase (or) active centers, which are responsible for the adsorption increases, consequently the activity of the catalyst is also enhanced.



7. A catalyst is more active at a particular temperature called Optimum temperature.

8. **Catalytic poison**: A substance, which destroys the activity of the catalyst thereby reducing the rate of reaction, is called as catalytic poison.
9. **Catalytic promoters**: The activity of a catalyst can be increased by the addition of a small quantity of a foreign substance called promoter.

2.14 ACID–BASE CATALYSIS

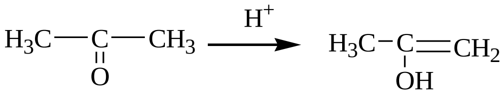
A number of homogeneous catalytic reactions which are catalyzed by acids or bases, or both acids and bases. These are often referred as Acid-Base catalysis.

E.g:

- Decomposition of the sucrose into glucose and fructose in sulfuric acid (or) Inversion of cane sugar.

$$C_{12}H_{22}O_{11\ (l)} + H_2O_{\ (l)} \xrightarrow{H^+} C_6H_{12}O_{6\ (l)} + C_6H_{12}O_{6\ (l)}$$

- Keto-enol tautomerism of acetone.



$$H_3C{-}\underset{\underset{O}{\|}}{C}{-}CH_3 \xrightarrow{H^+} H_3C{-}\underset{\underset{OH}{|}}{C}{=}CH_2$$

Keto form Enol form

- Hydrolysis of an ester in the presence of acid catalyst.

$$CH_3COOC_2H_{5(l)} + H_2O_{\ (l)} \xrightarrow[\text{or } OH^-]{H_3O^+} CH_3COOH_{\ (l)} + C_2H_5OH_{\ (l)}$$

E.g Base-specific (base catalysis)

In the addition of hydrogen cyanide to aldehydes and ketones in the presence of sodium hydroxide. Many reactions are catalyzed by both acids and bases.

2.15 ENZYME CATALYSIS

Enzymes are a type of catalysts which are responsible for increasing the rate of reaction in plants and animals. The catalysis in which enzymes act as a catalyst is called enzyme catalysis.

Enzymes are complex nitrogenous compounds, these are actually protein molecules of higher molecular mass. Numerous reactions occur in the body of animals and plants to maintain the life process are catalysed by enzymes. The enzymes are thus, termed as bio-chemical catalysts and the phenomenon is known as bio-chemical catalysis or enzyme catalysis.

E.g:

- Diastase acts as catalysts in the conversion of starch into maltose.

$$2(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{Diastase}} nC_{12}H_{22}O_{11}$$

Starch Maltose sugar

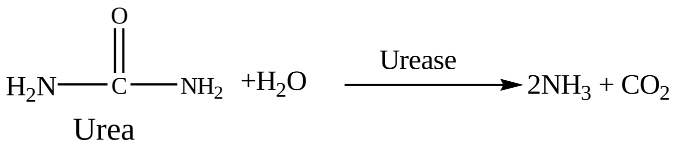
- Invertase converts cane sugar into a mixture of glucose and fructose.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{invertase}} C_6H_{12}O_6 + C_6H_{12}O_6$$

- Conversion of glucose into ethanol in the presence of Zymase as a catalyst.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{zymase}} \underset{\text{Ethanol}}{2C_2H_5OH} + 2CO_2$$

- Hydrolysis of urea with help of urease as catalyst.



$$\underset{\text{Urea}}{H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2} + H_2O \xrightarrow{\text{Urease}} 2NH_3 + CO_2$$

2.16 CHARACTERISTICS OF ENZYME CATALYSIS

1. A single molecule of this catalysis can transform a million molecules of the reactant per second by lowering the activation energy. Hence it is highly efficient.

Example: Decomposition of hydrogen peroxide.

$$2H_2O_{2\ (l)} \longrightarrow 2H_2O_{\ (l)} + O_{2\ (l)}$$

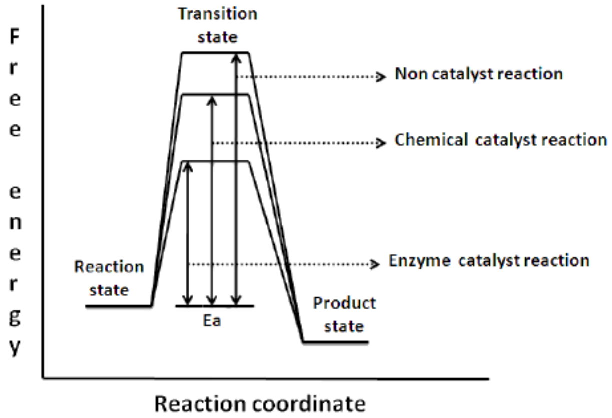


Fig 2.18 **Energy diagram of Enzyme Catalytic reaction**

Ea is without catalyst = 18 k.cal/mole.

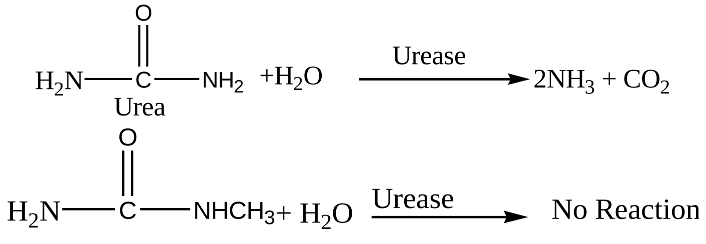
Ea is with colloidal platinum = 11.7 k.cal/mole.

Ea is with enzyme catalyst = >2 k.cal/mole.

Since the enzyme catalyst greatly lower the activation energy in the above example, it's more efficient than other catalysts.

2. Enzymes are highly specific, i.e. the same catalyst cannot be used in more than one reaction.

E.g: Urease enzyme catalyses the hydrolysis of urea only and not the hydrolysis of any other amide



$$\underset{\text{Urea}}{H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2} + H_2O \xrightarrow{\text{Urease}} 2NH_3 + CO_2$$

$$\underset{\text{methyl urea}}{H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NHCH_3} + H_2O \xrightarrow{\text{Urease}} \text{No Reaction}$$

3. The effectiveness of a catalyst is maximum at optimum temperature (37°C). The activity of the biochemical catalysts declines at either side of the optimum temperature.

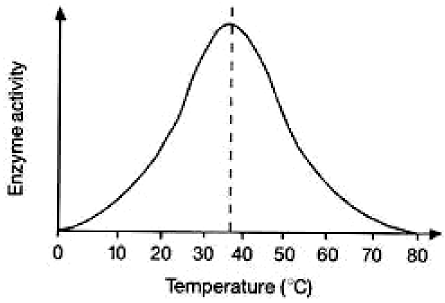


Fig 2.19 **Effect of temperature on enzyme activity**

4. Biochemical catalysis is dependent upon the pH of the solution. A catalyst works best at an optimum pH which ranges between 4-7 pH values.

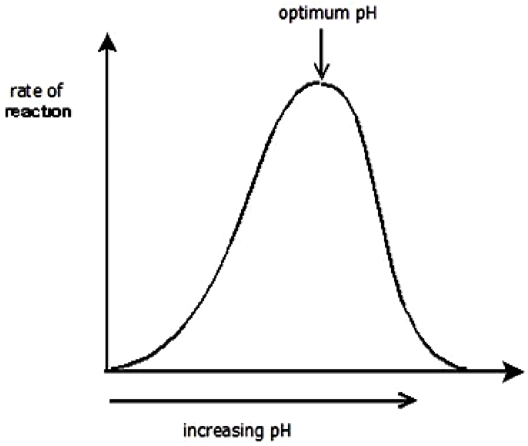


Fig 2.20 **Effect of pH on enzyme activity**

5. The activity of the enzymes usually increases in the presence of a co – enzyme or an activator such as Na$^+$, Co^{2+} Mn$^{2+,}$ Cu^{2+},etc..The rate of the reaction increases due to the presence of a weak bond which exists between the enzyme and a metal ion.

6. Catalytic poison: Enzymes are poisoned by other substances.

2.17 MICHAELIS - MENTEN EQUATION OR MECHANISM OF ENZYME CATALYST OR ENZYME KINETIC

In biochemistry, **Michaelis–Menten** kinetics is one of the best-known models of enzyme kinetics. It is named after German biochemist Leonor Michaelis and Canadian physician Maud Menten. The model takes the form of an equation describing the rate of enzymatic reactions.

In 1913, they proposed a mathematical model of the reaction. It involves an enzyme (E), binding to a substrate(S) to form a complex(ES), which in turn releases a product(P) regenerating the original enzyme. This may be represented schematically by the following equations,

$$\underset{\text{Enzyme}}{E} + \underset{\text{Substrate}}{S} \xrightarrow{k_1} \underset{\text{intermediate complex}}{X} \qquad \text{..........(1)}$$

$$X \xrightarrow{k_2} E + S \qquad \text{...........(2)}$$

$$X \xrightarrow{k_3} P \qquad \text{................(3)}$$

Where, k_1, k_2 and k_3 are rate constant for the respective reactions.

The rate of the formation of the complex X is given by the following equation

$$\frac{d[X]}{dt} = K_1[E][S] - K_2[X] - K_3[X]$$
$$= K_1[E]\,[S] - (K_2 + K_3)[X] \quad \ldots\ldots\ldots\ldots.. (4)$$

Where,

[E], [S] and [X] are molar concentrations of enzyme, substrate and intermediate complex.

The rate of the formation of the product P is given by the following equation,

$$\frac{d[P]}{dt} = K_3[X] \quad \ldots\ldots\ldots (5)$$

Since $[E_0] = [E] + [X]$, the equation (4) can be rewritten as,

$$\frac{d[X]}{dt} = k_1\{[E_0] - [X]\}[S] - (k_2 + k_3)[X] \quad \ldots\ldots\ldots.. (6)$$

∴ $[\,[E] = [E_0]-[X]\,]$

Where,

[E] is molar concentration of unreacted enzyme.

[X] is molar concentration of enzyme present in the complex.

$[E_0]$ is total molar concentration of the enzyme.

Since the intermediate complex is unstable it decomposes instantaneously, so

$$\frac{d[X]}{dt} = 0 \quad \ldots\ldots\ldots\ldots..(7)$$

This state is termed called as the stationary state.

At the stationary state, the equation (6) can be rewritten as,

$$k_1\{[E_0] - [X]\}[S] = (k_2 + k_3)[X] \quad \ldots\ldots\ldots\ldots (8)$$
$$k_1[E_0][S] - k_1[X][S] = (k_2 + k_3)[X]$$
$$k_1[E_0][S] = k_1[X][S] + (k_2 + k_3)[X]$$
$$k_1[E_0][S] = \{k_1[S] + (k_2 + k_3)\}[X]$$

$$\text{(or)}\quad [X] = \frac{k_1[E0][S]}{k_1[S] + k_2 + k_3} \quad \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

Dividing the equation (9) by $k_1[S]$ it is becomes,

$$[X] = \frac{[E_0]}{1 + \dfrac{k_2 + k_3}{k_1[S]}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(10)$$

Substituting this value of [X] in equation (5), we get

$$\frac{d[P]}{dt} = \frac{k_3[E_0]}{1 + \frac{k_2+k_3}{k_1[S]}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(11)$$

$$\frac{k_2+k_3}{k_1} = K_m \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textit{michaelis constant}$$

$$\frac{d[P]}{dt} = \frac{k_3[E_0]}{1 + \dfrac{K_m}{[S]}} \quad \ldots\ldots\ldots\ldots\ldots\ldots.(12)$$

$$\text{(Or)}\ r = \frac{k_3[E_0][S]}{[S] + K_m} \quad \ldots\ldots\ldots\ldots\ldots (13)$$

Equations 12 and 13 are known as Michaelis Menten equation.

It follows two important cases,

Case (i) at lower concentration:

When the concentration of substrate is less than k_m it may be neglected in the denominator.

Thus, [S] << km then,

$$\frac{d[P]}{dt} = \frac{k_3[E_0][S]}{k_m} \ldots \quad \ldots\ldots\ldots\ldots\ldots.(14)$$

So the rate of the reaction is first order with respect to the substrate and enzyme.

Case (ii) at higher concentration:

When the concentration of substrate is higher than k_m it may be [S] >>> k_m then,

$$\frac{d[P]}{dt} = \frac{k_3[E_0][S]}{[S]}$$

(or)

$$\frac{d[P]}{dt} = k_3[E_0] \qquad \ldots\ldots\ldots\ldots\ldots(15)$$

- So the rate of the reaction is zero order with respect to the substrate.
- In the above cases it is clear that the reaction rate of enzyme catalyzed reaction gets changed from first order to zero order with increase in the substrate concentration. This is because of more active sites of enzyme catalyst.

2.17.1 Significance of Michaelis Menten Equation

The Michaelis Menten equation can be simplified by assuming that all the enzymes have reacted with the high substrate concentration in such a case, the rate will be maximium and no free enzyme will remain, so that $[E_0] = [X]$

∴ From equation (5) we have

$$\frac{d[P]}{dt} = k_3[E_0] = v_{max} \qquad \ldots\ldots\ldots\ldots\ldots(15)$$

Where,

v_{max} = maximum rate

Now the equation (12) will be,

$$r = \frac{v_{max}[S]}{k_m + [S]}$$

$$[\text{where } v_{max} = k_3[E_0]\,]$$

If $k_{m=[S]}$ then,

$$r = \frac{v_{max}[S]}{[S]+[S]} = \frac{v_{max}[S]}{2\,[S]} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(16)$$

$$\text{(Or)} \qquad r = \frac{1}{2}v_{max}$$

Thus, of Michaelis constant is defined as “equal to the concentration of substrate [S] at which the rate of formation of product is half the maximum rate obtained at high concentration of the substrate [S].

2.17.2 Applications of Michaelis Menten Equation

Determination of Michaelis Menten constant (k_m)

Lineweaver-Burk equation (reverse of Michaelis Menten equation) is used to calculate Michaelis Menten constant (k_m). Thus,

$$\frac{1}{r} = \frac{1}{v_{max}} + \frac{k_m}{v_{max}\,[S]}$$

Form this above equation if plot a graph as $\frac{1}{r}$ vs $\frac{1}{[S]}$ gives a straight line with intercept $\frac{1}{v_{max}}$ and slope $\frac{k_m}{v_{max}}$ Michaelis Menten constant can be calculated.

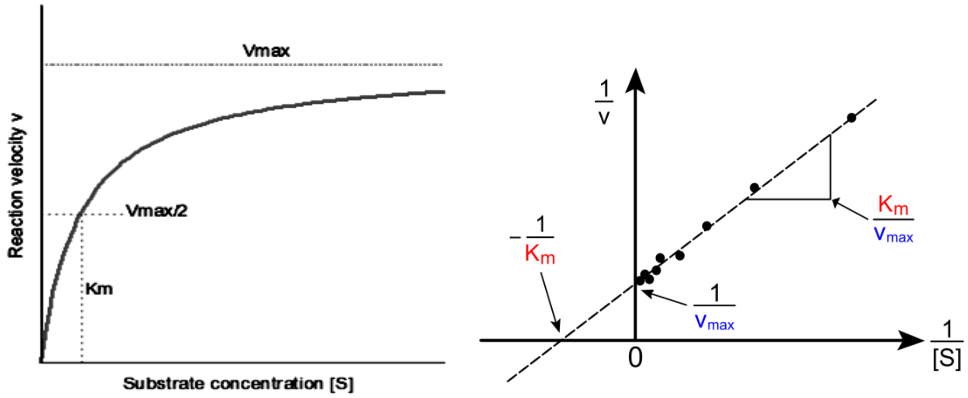


Fig 2.21 **Kinetics of enzyme catalyzed reaction**

Determination of Turn over number (k_3)

It is defined as the number of molecules converted into products in unit time by one molecules of enzyme. Mathematically,

$$\frac{d[P]}{dt} = \frac{k_3[E_0][S]}{k_m}$$

Where, the constant $\mathbf{k_3}$ in the above equation is known as Turn over number.

2.18 LANGMUIR-HINSHELWOOD

The rate equation derived from mechanistic model that simulates the actual surface phenomenon during the process is preferred for reactions involving solid catalysts. The Langmuir-Hinshelwood–Hougen-Watson(LHHW) approach is one of the most commonly used way of deriving rate expressions for fluid solid catalytic reactions. The advantages of this method are that:

(1) Rate derived by this method takes into account the adsorption/desorption process occurring over the surface along with the surface reaction.

(2) Rate equation derived can be extrapolated more accurately to concentrations lying beyond the experimentally measured values.

During this method of derivation of rate expression, all the physical transport steps like mass transfer from bulk phase to catalyst surface or diffusion of reactants from pore mouth to interior pore (intraparticle diffusion) are excluded. Thus, it is assumed that the external and internal mass transport processes are very rapid relative to the chemical rate process occurring on or within the catalyst particle. The chemical rate depends on:

(1) chemisorption steps
(2) surface reaction steps
(3) desorption steps

This simple kinetic model assumes isothermal condition about and within catalyst that is temperature gradient is zero.

In LHHW model development, the rate equation is first derived in terms of surface concentration of adsorbed species and vacant sites. Then, these surface concentrations are related to the fluid or bulk concentration that is directly measurable.

For the reaction

$$A + B \rightleftharpoons C + D$$

Let r_a= rates of adsorption ....(g moles/s.gm of catalyst)

r_s = rates of surface reaction.................................. ...(g moles/s.gm of catalyst)
r_d =rates of desorption ....(g moles/s.gm of catalyst)
C_{AS}= concentration of adsorbed A on surface ....(g moles/gm of catalyst)
C_{BS}= concentration of adsorbed B on surface ....(g moles/gm of catalyst)
C_{CS}= concentration of adsorbed C on surface ....(g moles/gm of catalyst)
C_{DS}= concentration of adsorbed D on surface.............. (g moles/gm of catalyst)
C_o= total concentration of active sites on surface........ (g moles/gm of catalyst)
C_v= concentration of vacant sites on surface.............. (g moles/gm of catalyst)
C_A= concentration of A in bulk gas phase ....(g moles/cm^3)
Similarly C_B,C_C ,C_D are concentration of B,C,D in bulk gas phase respectively.
Let the reaction follows the mechanism given below ;
(1) $A + S \rightleftharpoons A.S$ --- Adsorption of reactant A on surface vacant site S
(2) $B+S \rightleftharpoons B.S$ --- Adsorption reactant B on surface vacant site S
(3) $A.S+B.S \rightleftharpoons C.S+D.S$ --- Surface reaction between adsorbed A and B
(4) $C.S \rightleftharpoons C+S$ --- Desorption of product C from surface creating a vacant site
(5) $D.S \rightleftharpoons D+S$ --- Desorption of product D from surface creating a vacant site

Among the various steps described, the slowest step controls the overall rate of reaction and the other remaining steps are assumed to be at near equilibrium conditions. This approach greatly simplifies the overall rate expression, reducing the number of rate constants and equilibrium constants to be determined from experimental data. Further each step in this method is assumed to be elementary and the number of sites is conserved in each step.

Therefore, the controlling step can be either of the following:

(1) Surface reaction

(2) Adsorption

(3) Desorption

Now total concentration of active sites on surface, C_0, will be the summation concentrations of all sites on which either reactants or products are adsorbed and the concentration of vacant sites.

$$\therefore C_O = C_V + C_{AS} + C_{BS} + C_{CS} + C_{DS}$$

Where C_V is the concentration of vacant sites.

Case 1 : Rate is surface reaction controlling

The surface reaction is the slowest step and is the rate controlling. According to the mechanism, surface reaction occurs between adsorbed A and adsorbed B producing adsorbed C & adsorbed D.

$$AS + BS \rightleftharpoons CS + DS$$

The rate of surface reaction is given as

$r_S = k_S C_{AS} C_{BS} - k_S' C_{CS} C_{DS}$ k_S= rate constant for forward surface reaction

k_S' = rate constant for reverse surface reaction

$$= k_S \left[C_{AS} C_{BS} - \frac{k_S'}{k_S} C_{CS} C_{DS} \right]$$

$$= k_S \left[C_{AS} C_{BS} - \frac{1}{K_S} C_{CS} C_{DS} \right] \text{----(1)} \qquad K_S = \frac{k_S}{k_S'}$$

Now, since all the other steps are considered to be in equilibrium, therefore concentration of adsorbed species can be obtained as follows.

For adsorption steps and desorption steps :

From step (1) $K_A = \dfrac{C_{AS}}{C_{A.} C_V}$ from step (4)------ $K_C = \dfrac{C_{CS}}{C_{C.} C_V}$

From step (2) $K_B = \dfrac{C_{BS}}{C_{B.} C_V}$ From step (5)------- $K_D = \dfrac{C_{DS}}{C_{D.} C_V}$

K_A, K_B, K_C, K_D are adsorption equilibrium constant.

Then the adsorbed phase concentration can be written as

$$C_{AS} = K_A C_A C_V \quad C_{CS} = K_C C_C C_V$$

$$C_{BS} = K_B C_B C_V \quad C_{DS} = K_D C_D C_V$$

Substituting all these value in equation (1)

$$r_S = k_S\left[C_{AS}C_{BS} - \frac{1}{K_S}C_{CS}C_{DS}\right] = k_S\left[K_AC_AC_V.K_BC_BC_V - \frac{K_C}{K_S}C_CC_V.K_DC_DC_V\right]$$

or, $$r_s = k_S\left[K_AK_BC_AC_BC_V^2 - \frac{K_CK_D}{K_S}C_CC_DC_V^2\right]$$

(2)

or $$r_S = k_SK_AK_B\left[C_AC_B - \frac{K_CK_D}{K_SK_AK_B}C_CC_D\right]C_V^2$$

Now, $$C_O = C_{AS} + C_{BS} + C_{CS} + C_{DS} + C_V$$

$$C_O = K_AC_AC_V + K_BC_BC_V + K_CC_CC_V + K_DC_DC_V + C_V$$

$$= C_V\left[1 + K_AC_A + K_BC_B + K_cC_c + K_DC_D\right]$$

$$C_V = \frac{C_O}{1 + K_AC_A + K_BC_B + K_CC_C + K_DC_D} \qquad (3)$$

For the reaction A+B $\rightleftharpoons$ C+D, at equilibrium, the overall equilibrium constant is $K = \frac{C_CC_D}{C_AC_B}$.

All concentrations corresponds to the equilibrium conditions in gas phase

$$K = \frac{(C_{CS}/K_CC_V)(C_{DS}/K_DC_V)}{(C_{AS}/K_AC_V)(C_{BS}/K_BC_V)} = \frac{C_{CS}C_{DS}}{C_{AS}C_{BS}}.\frac{K_AK_BC_V^2}{K_CK_DC_V^2}$$

Or, $$K = \frac{K_AK_B}{K_CK_D}.K_S \qquad \because K_S = \frac{C_{CS}C_{DS}}{C_{AS}C_{BS}} \qquad (4)$$

Substituting (3) &(4) in equation (2),

$$r_S = k_S K_A K_B \left[C_A C_B - \frac{1}{K} C_C C_D \right] \frac{C_O^2}{\left(1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D\right)^2}$$

(5)

$$r_S = k_S K_A K_B C_O^2 \frac{C_A C_B - \frac{1}{K} C_C C_D}{\left(1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D\right)^2}$$

The above rate expression can also be derived in terms of bulk partial pressure.

Case 2: Rate is adsorption control

(a) Adsorption of A controlling

Let adsorption of A be the slowest step so that adsorption of B, surface reaction and desorption of C are at equilibrium.

Adsorption of A is given as

.... $A + S \rightleftharpoons AS$

Rate of adsorption $r_a = k_a C_A C_V - k_d C_{AS}$

(6)

$$r_a = k_a \left[C_A C_V - \frac{k_d}{k_a} C_{AS} \right]$$

Or, $r_a = k_a \left[C_A C_V - \frac{1}{K_A} C_{AS} \right]$ $\quad K_A = \frac{k_a}{k_d}$ (adsorption equilibrium constant for A)

$$r_a = k_a C_V \left[C_A - \frac{1}{K_A} \frac{C_{AS}}{C_V} \right]$$

Now as other steps are in equilibrium:

$$K_S = \frac{C_{CS} C_{DS}}{C_{AS} C_{BS}}$$

$$K_B = \frac{C_{BS}}{C_B C_V} \qquad K_C = \frac{C_{CS}}{C_C C_V} \qquad K_D = \frac{C_{DS}}{C_D C_V}$$

$$C_{BS} = K_B C_B C_V \qquad C_{CS} = K_C C_C C_V \qquad C_{DS} = K_D C_D C_V$$

Then ,

$$C_{AS} = \frac{C_{CS} C_{DS}}{K_S C_{BS}} = \frac{K_C C_C C_V . K_D C_D C_V}{K_S K_B C_B C_V} = \frac{K_C K_D}{K_S K_B} \frac{C_C C_D C_V}{C_B}$$

Substituting value in equation (6)

$$r_a = k_a C_V \left[C_A - \frac{1}{K_A C_V} \frac{K_C K_D}{K_S K_B} \frac{C_C C_D C_V}{C_B} \right] \tag{7}$$

$$r_a = k_a C_V \left[C_A - \frac{K_C K_D}{K_S K_A K_B} \frac{C_C C_D}{C_B} \right]$$

$$r_a = k_a C_V \left[C_A - \frac{1}{K} \frac{C_C C_D}{C_B} \right]$$

$K = \dfrac{K_S K_A K_B}{K_C K_D}$ = Overall equilibrium constant.

Now $C_0 = C_V + C_{AS} + C_{BS} + C_{CS} + C_{DS}$

$$= C_V + \frac{K_C K_D}{K_S K_B} . \frac{C_C C_D C_V}{C_B} + K_B C_B C_V + K_C C_C C_V + K_D C_D C_V$$

$$= C_V \left[1 + \frac{K_C K_D}{K_S K_A} \frac{K_A}{K_B} \left(\frac{C_C C_D}{C_B} \right) + K_B C_B + K_C C_C + K_D C_D \right]$$

$$= C_V \left[1 + \frac{K_A}{K} \frac{C_C C_D}{C_B} + K_B C_B + K_C C_C + K_D C_D \right]$$

$$C_V = \frac{C_O}{1 + \frac{K_A}{K} \frac{C_C C_D}{C_B} + K_B C_B + K_C C_C + K_D C_D} \quad \because K = \frac{K_S K_A K_B}{K_C K_D}$$

Substituting value of C_V in equation (7)

$$r_a = k_a C_0 \frac{C_A - \left[\frac{C_C C_D}{K C_B} \right]}{1 + \frac{K_A C_C C_D}{K C_B} + K_B C_B + K_C C_C + K_D C_D} \tag{8}$$

For a given catalyst C_0 is constant.

Similarly expression when desorption of product is the rate controlling step can be derived.

For desorption of C controlling the whole reaction, the rate expression can be derived as

$$r_d = k_d C_0 K \frac{C_A C_B - \left[\frac{C_C C_D}{K} \right]}{1 + K_A C_A + K_B C_B + K_C K C_A C_B + K_D C_D}$$

UNIT –III

NANO MATERIALS

3.1.**INTRODUCTION**

The world of materials is rapidly progressing with new and trendiest technologies, and obviously novel applications. Nano technology is among these modern and sophisticated technologies, which is creating waves in the modern times. Actually, nano technology includes the concept of physics and chemistry of materials. It beckons a new field coming to the limelight. So, nano technology is an interesting but emerging field of study, which is under constant evolution offering a very wide scope of research activity.

Nanoscience

Nanoscience is the study of the phenomena and manipulations of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at larger scales.

Nano chemistry

Nano chemistry is a relatively new branch of chemistry concerned with the unique properties associated with assemblies of atoms or molecules in nano dimension (approximately 1 to 100 nm). It also deals with the synthesis, characterization, properties and applications of these nanomaterials.

Nano-technology

Nano-technology is the design, fabrication, characterization and applications of materials at nano-level (1-100 nm) and converting them into useful devices.

Why Nano Technology ?

In the materials world, particularly in ceramics, the trend is always to prepare finer powder for the ultimate processing and better sintering to achieve dense materials with dense fine-grained microstructure of the particulates with better and useful properties for various applications. The fineness can reach up to a molecular level **(1 nm – 100 nm),** by special processing techniques. More is the fineness, more is the surface area, which increases the ‘reactivity’ of the material. So, the densification or consolidation occurs very well at lower temperature than that of conventional ceramic systems, which is finally ‘cost-effective’ and also improves the properties of materials like abrasion resistance, corrosion resistance, mechanical properties, electrical properties, optical properties, magnetic properties, and a host of other properties for various useful applications in diverse fields.

Nanoparticles

Nanoparticles are the simplest form of structures with the sizes in nm range. In principle, any collection of atoms bonded together with a structural radius of <100nm can be considered as a nanoparticle..

Nanomaterials

Nanometre is one billionth of a metre.

$1\text{nm} = 1\text{x}10^{-9}\text{m}$

The properties of a bulk material will be different from its nanosized particle.

The unique properties of nanosized particles is mainly due to

i) The smaller particles having a relatively larger surface area compared with their volume, making them chemically more reactive.

ii) When this size is below 100nm, quantum effects can change the optical, electronic or magnetic qualities of materials.

Nanocrystal

Nanocrystal is a material particle having one dimension lesser than 100nm and composed of atoms in either a single or polycrystalline arrangement.

Quantum dot

Quantum dot is a nanocrystal made of semiconductor materials.

Polymeric Nanoparticles

Polymeric nanoparticles are prepared from polymers. They are considered as potential drug delivery devices due to applications in drug targeting to particular organs and tissues.

Dendrimers

Dendrimers is one kind of polymeric nanoparticles constructed by the successive addition of layers of branching groups. The properties of dendrimers are dominated by the functional groups on the molecular surface. It finds its applications as solubilizing agents imaging agents, sensors, drug delivery, Gene therapy, detecting agents such as a dye molecule.

3.1.1.CLASSIFICATION OF NANOMATERIALS

The main classification of nanomaterials is based on the dimensions of their structural elements.

(i) **Zero-dimensional (0D) nanomaterials:** Nanomaterials having diameter less than 100nm.

Example: Nanoparticles, nanoclusters and nanocrystals.

(ii) **One-dimensional (1D) nanomaterials:** Nanomaterials having one dimension in the nanometer scale. It includes nanofibers, nanorods and nanotubes.

(iii) **Two-dimensional (2D) nanomaterials:** Nanomaterials having two dimensions in the nanometer scale. It includes nanofilms, nanowires, nanolayers and nano coatings.

(iv) **Three-dimensional (3D) nanomaterials:** Nanomaterials having three dimensions in the nanometer scale. It includes powders, fibrous, multilayer and polycrystalline materials.

Table:-1 Distinction between molecules,nano particles and bulk material

Property	**Atoms /Molecules**	**Nanomaterials**	**Bulk Materials**
Size	Few amstrongs(10^{-10}m)	Nanometres(10^{-9}m)	Microns to higher(10^{-6}m)
No.of constituent particles	One atom to few/many atoms	Few atoms to several thousand of atoms	Infinite/ of the order of Avogadro number
Electronic structure	Confined	Confined	Notconfined (continous)
Mechanical properties	NA	Properties depend on particle size	Properties independent of particle size
Wave nature	Applicable	Applicable	Applicable to limited extend
Random motion	Present	Present (Brownian)	Not Present
Stability	Stable	Canbe stable or unstable depending on surface energy	Stable
Examples	NaCl , CO_2	Carbon nanotube	Gold bar, silver bar

Table:2 Bulk gold materials Vs nanosized gold

Gold bulk	**Nanosized gold**
Shiny (metallic)	Insulator
Yellow	red (~10 nm particles absorb green light)
noble metal	excellent catalysts (2–3 nm nanoparticles)

fcc structure	icosahedral symmetry
non-magnetic	Magnetic
melts at 1064°C	Much lower melting temperature (sizes depending)
constant physical Properties. regardless of its size	size-dependent properties

3.1.2.SIZE DEPENDENT PROPERTIES OF NANO MATERIALS

The nano materials have different properties when compared to bulk due to the following reasons

- Large surface area can make nano materials more chemically reactive and affect their strength or electrical properties.
- Quantum effects can begin to dominate the behavior of matter at nanoscale, which affects several properties such as melting point, boiling point, band gap,optical properties, mechanical properties and magnetic properties.

Nanomaterials are composed of grains resulting a significant increase in the volume fraction of grain boundaries or interfaces, resulting defect configurations. Hence the mechanical and chemical properties of nanomaterials are significantly altered due to defect dynamics.

The elastic property of nanomaterials are different from that of bulk alloys due to the presence of increased fraction of defects

Example

1. Nanocrystalline ceramics are tougher and stronger than those with coarse grains
2. Nano-sized metals exhibit significant decreases in toughness and yield strength increases

1. Thermal properties (Melting points)

Nano-materials have a significantly lower melting point or phase transition temperature than bulk materials. This is due to

i. reduced lattice spacing between atoms.

ii. due to huge fraction of surface atoms in the total amount of atoms.

- Nano crystal size decreases → surface energy increases → Melting point decreases
- Example:- Melting point of 3nm CdSe – 700K,

  Bulk CdSe --1678 K.

2. Optical properties (absorption and scattering of light)

- Nano materials exhibit different optical properties due to quantum confinement of electrons within the nano particles increases the energy level spacing.
- Optical properties depend on size, shape, surface characteristics, interaction with surrounding environment etc.

Example:

Bulk gold –yellow in colour.

Nano gold can be orange (80 nm) red (20 nm) or purple depending on particle size.

The optical absorption peak of a semiconductor nano particles shifts to a short, wavelength, due to an increased band gap

The colour of metallic nano particles may change with their sizes due to surface plasma resonance

3. Magnetic properties

Magnetic properties of nano particles are different from that of the bulk materials. Ferro-magnetic behavior of bulk materials disappear, when the particle size is reduced and transfer to super- para magnetic. This is due to the huge surface area.

Example:

Material	Bulk	Nano scale
Fe,Co and Ni	Ferromagnetic	Super paramagnetism
Na,K	Paramagnetic	Ferromagnetic

4. Mechanical properties

The nano materials have less defects compared to bulk materials, which increases the mechanical strength. As nano-materials are stronger, harder and more wear resistant and corrosion resistant, they are used in spark plugs

Example:

Nano-crystalline carbides are much stronger, harder and wear resistant, which are used in micro drills.

5**. Electrical properties**

(i)Electrical conductivity decreases with a reduced dimension due to increased surface scattering. However, it can be increased, due to better ordering in micro-structure Nano-crystalline materials are used as very good separator plates in batteries, because they can hold more energy than the bulk materials.

Example:

Nickel-metal hydride batteries made of nanocrystalline nickel and metal hydride, require far less frequent recharging and last much longer.

3.2.1.NANO PARTICLES:

- Nanoparticles are the simplest form of structures with sizes in the nm range. In principle any collection of atoms bonded together with a structural radius of <100nm can be considered as a nanoparticle.
- Nanoparticles are very similar to nanoclusters but it contains larger aggregates containing 10^3 or more atoms.
- Nanoparticles may exhibit size-related properties that differ significantly from those observed in fine particles or bulk materials. These are made of metals, semiconductors, or oxides and they show good mechanical, electrical, magnetic, optical , chemical, thermal, diffusion properties.

- The properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant.

3.2.2.NANOCLUSTERS:

- Nano clusters constitute an intermediate state of matter between molecules and bulk materials.
- These are fine aggregates of atoms or molecules.
- A nanocluster is a nanometer sized particle made up of equal subunits. These subunits can be atoms of a single element, molecules or even combinations of atoms of several elements in subunits with equal stoichiometries

Example: Na_n, $(SF_6)_n$,$(H_2O)_n$, $(Cu_3Au)_n$, $(TiO_2)_n$ etc.

- The size of nanocluster ranges from sub-nanometer to 10 nm in diameter.
- It has been found that clusters of certain critical size (clusters with a certain number of atoms in the group) are more stable than others. Nanoclusters consisting of upto a couple of hundred atoms, but larger aggregates containing 103 or more atoms are called nanoparticles.
- Nanoclusters can be classified based on the nature of bonding present between the atoms of the aggregate.

They are

(a) vanderwaals cluster (b) ionic cluster

(c) metallic cluster and (d) network cluster.

(a) **Vander Waals cluster**: Here the interaction between the constituents of the cluster is weak vanderwaals forces (strength of bond is 0.3eV per atom or less). Weak binding leads to weak melting and boiling points.

Example: Molecular clusters like $(SF_6)_n$,$(I_2)_n$

(b)Ionic cluster: Here the force of attraction between the species is electrostatic force (strength of the bond is 2-4 eV per atom).

Example: $(NaCl)_n$

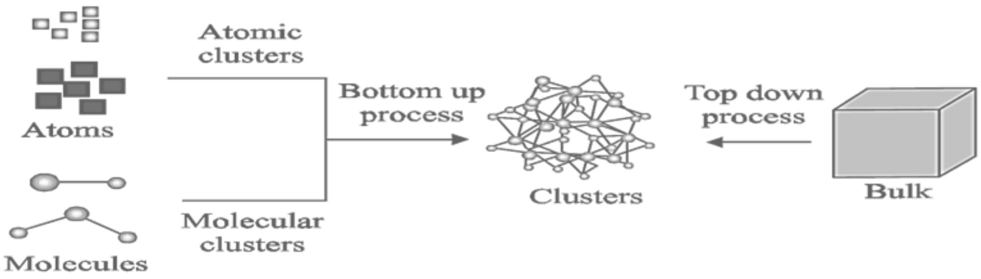
(c) Metallic cluster: Atoms are held together by metallic bonds. The force of attraction in metal clusters can range from moderate to strong (0.3 – 3 eV per atom).

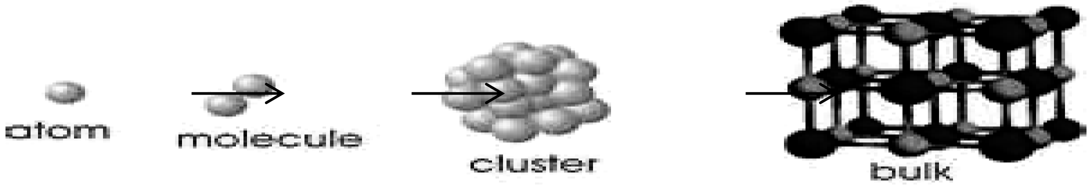
Example: $(Na)_n$,$(Cu_2 Au)_n$

(d) Network cluster: Covlent bonding can result in the formation of atomic network. Bonds in clusters are usually strong(1-4eV per atom).

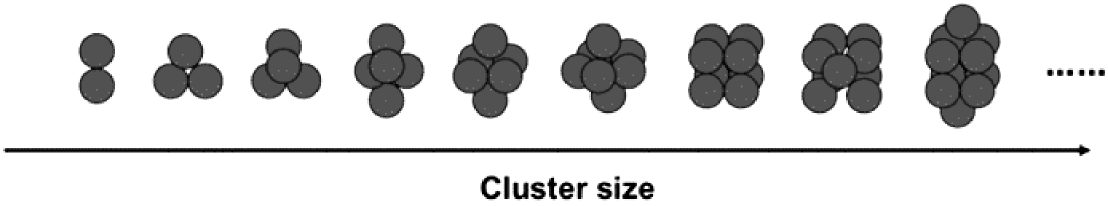
Example: C_{60}-fullerene

Production:





Aggregates of atoms



- Atomic clusters are formed by the nucleation of atoms.
- Molecular clusters are formed by the nucleation of molecules.

Properties of nano clusters:

- **Magic number:** Number of atoms present in the clusters of critical sizes with higher stability.
- Clusters containing transition metal atoms have unique electronic, chemical and magnetic properties.
- These properties vary with
  (a) The number of constituent atoms.
  (b) The type of element
  (c) The net charge on the cluster.
- The reactivity of nanoclusters are decreased due to their decrease in size.
- The melting point of nanoclusters are lower than the bulk materials due to high surface to volume ratio.
- The electronic structure of the nanocluster is more confined than the bulk materials.

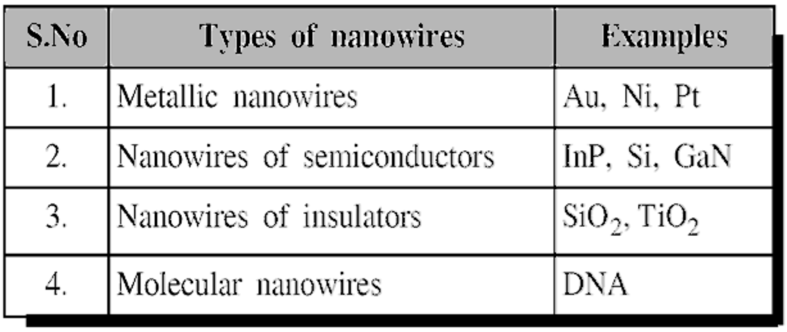
Applications of nanocluster

1. It is used as catalysts in many reactions.
2. It is used in nano based chemical sensors.
3. It is also used as a light emitting diode in quantum computers.

3.2.3.NANO WIRES:

- Nanowire is a two dimensional cylindrical solid material having an aspect ratio i.e, length to width ratio greater than 20. Diameter of the nanowire ranges from 10-100 nm.

Different types of nanowires are

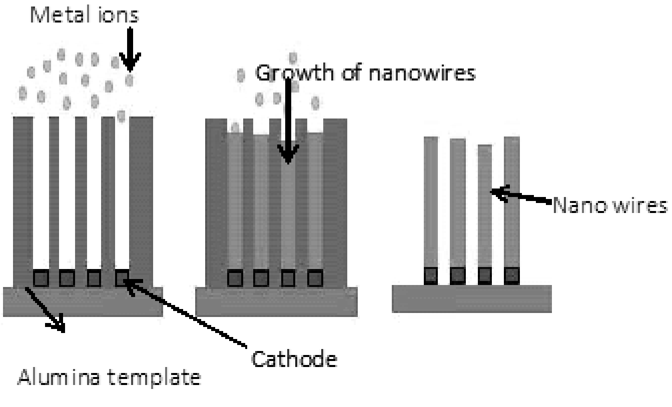


S.No	Types of nanowires	Examples
1.	Metallic nanowires	Au, Ni, Pt
2.	Nanowires of semiconductors	InP, Si, GaN
3.	Nanowires of insulators	SiO_2, TiO_2
4.	Molecular nanowires	DNA

Synthesis of nanowires

1. **Template-assisted synthesis**

Template assisted synthesis of nanowires is a simple way to fabricate nanostructures. These templates contain very small cylindrical pores or voids within the host material and the empty spaces are filled with the chosen material to form nanowires.

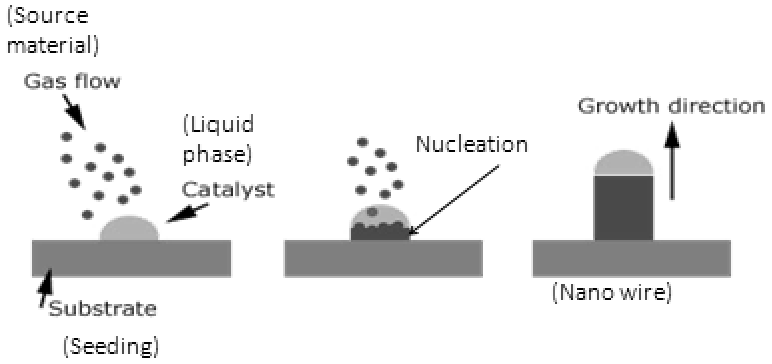


2. **VLS (Vapour-Liquid-Solid)method**

- Source material (Gas phase) is absorbed by the catalyst (liquid phase).
- Upon super saturation of the liquid alloy, a nucleation event generates a solid precipitate (Solid phase).
- This seed serves as a preferred site for further deposition of material at the interface of the liquid droplet.

- And promotes the elongation of the seed into a nanowire.

Reactant + Catalyst ⟶ Nanoparticles
(Gas phase) (Liquid phase) (Solid phase)



Properties of nanowires

- Nanowires are two-dimensional material.
- Conductivity is less than that of bulk materials.
- Due to its large surface area it exhibits different optical, chemical, thermal and Dlectric properties.

(Nano wire)

- Silicon nanowires show strong photoluminescence characteristics.

(Seeding)

Applications of nanowires

- Used to enhance mechanical properties of composites.
- Used to prepare active electronic components like *p-n* junction and logic gates.
- Semiconductor nanowire crossings are used in digital computing.
- It is used in high-density data storage either as magnetic heads or as patterned storage media.
- It replaces conventional coppers in computers, televisions etc.,
- Used to link tiny components into very small circuits.

3.2.4.NANO RODS:

Nanorods are one dimensional nanostructures, shaped like long sticks rods. One dimension is in nanometre, which produces quantum confinement and alters the properties of the material. Usually, diameter is in the nanoscale. If the ratio of length to width is 1-20, it called a nanorod.

Eg: Zinc oxide, admium sulphide, Gallium nitride nano rods.

- It is a two-dimensional cylindrical solid material.
- Length to width ratio < 20.
- **Examples:** ZnO, CdS nanorods etc.,

Synthesis of nanorods:

- It is produced by direct chemical synthesis.
- Combination of ligands is required to control the shape of the nanorods.
- Ligands bond to different facets of the nanorod with varying strengths.
- Thereby, elongated Nano rods grow with desired shape.

Properties:

- Two dimensional materials.
- It exhibits optical and electrical properties.

Applications of nanorods

- Nanorods find application in display technologies.
- It is also used in the manufacturing of micro mechanical switches.
- Nanorods are used in an applied electric field, micro electro mechanical systems etc.,
- Nanorods along with noble metal nanoparticle function as theragnostic agents.
- They are used in energy harvesting and light emitting devices.
- Used as cancer therapeutics.

3.2.5.NANO TUBES:

- Nano-tubes are one of the most widespread studied and used materials, consists of tiny cylinders of carbon and other materials like boron nitride.
- Nano-tubes of carbon and inorganic compounds with structures comparable to the layered structure of graphite have been prepared. Studies on carbon nano-tubes are quite extensive.

Carbon Nanotubes (CNT)

- Carbon nanotubes are allotropes of carbon with a nanostructure having a length-to-diameter ratio greater than 1,000,000.
- When graphite sheets are rolled into a cylinder, their edges joined and form carbon nanotubes
- Nanotubes naturally align themselves into “ropes” and held together by vanderwaals forces. But each carbon atoms in the carbon nanotubes are linked by the covalent bond.

- Their unique molecular structure results in extraordinary macroscopic properties, including high tensile strength, high electrical conductivity, high ductility, high heat conductivity and relative chemical inactivity.
- It has potential applications in electronic industry.

Types of carbon nanotubes

Carbon nanotubes are lattice of carbon atoms, in which each carbon is covalently bonded to three other carbon atoms. Depending upon the way in which graphite sheets are rolled, two types of CNTs are formed.

1. Single - walled nanotubes (SWNTs).

2.Multi – Walled nanotubes (MWNTs)

1. Single - walled nanotubes (SWNTs)

- SWNTs consist of one tube of graphite. It is one-atom thick having a diameter of 2 nm and a length of 100
- SWNTs are very important, because they exhibit important electrical properties.
- It is an excellent conductor.

Three kinds of nanotubes are resulted, based on the orientation of the hexagon lattice.

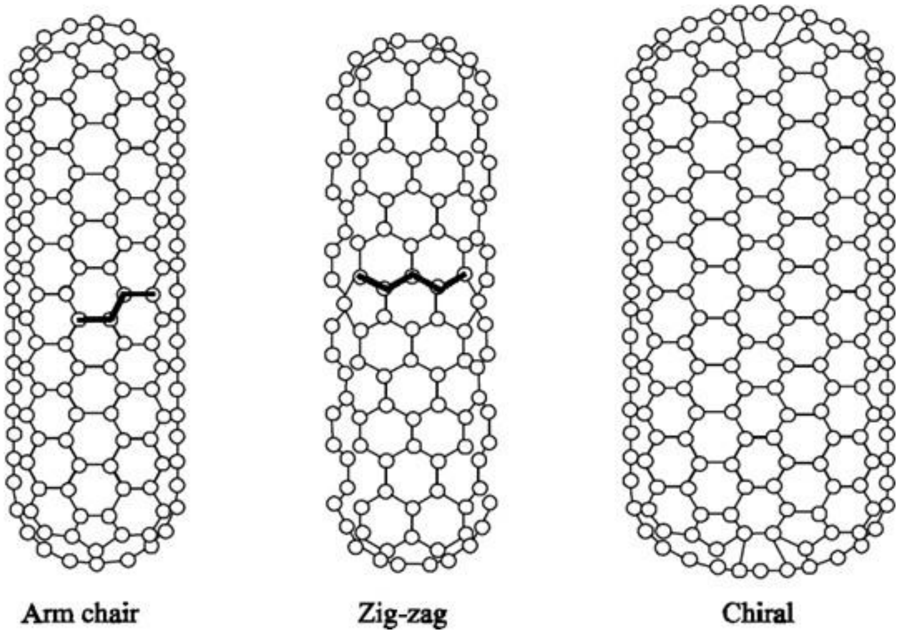


Fig :- Structure of Single walled carbon nanotubes

(a) Arm-chair structures: The lines of hexagons are parallel to the axis of the nanotube.

(b) Zig-zag structures: The lines of carbon bonds are down the centre.

(c) Chiral nanotubes: It exhibits twist or spiral around the nanotubes.

It has been confirmed that arm-chair carbon nanotubes are metallic while zig-zag and chiral nanotubes are semiconducting.

2. Multi - walled nanotubes (MWNTs)

MWNTs (nested nanotubes) consist of multiple layers of graphite rolled in on themselves to form a tube shape. It exhibits both metallic and semiconducting properties. It is used for storing fuels such as hydrogen and methane.

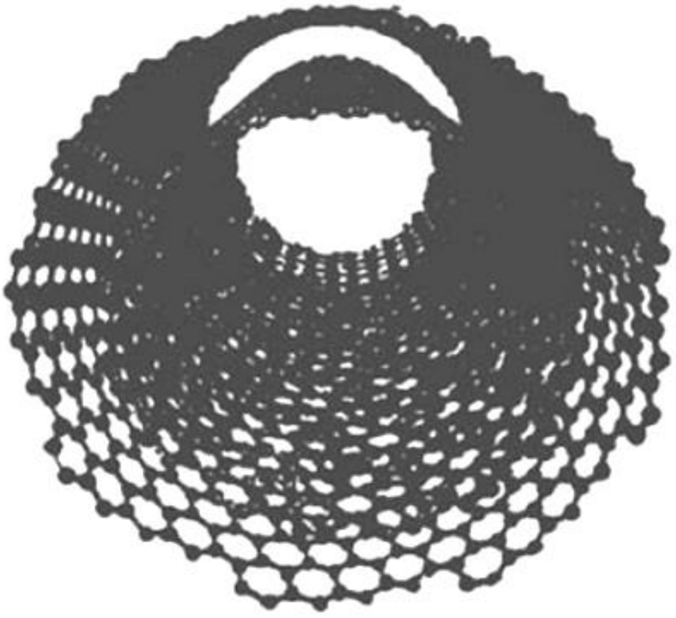


Fig :- Structure of Multi walled carbon nanotubes

Properties of CNTs

- CNTs are very strong, withstand extreme strain in tension and posses elastic flexibility.
- The atoms in a nano-tube are continuously vibrating back and forth.
- It is highly conducting and behaves like metallic or semiconducting materials.
- It has very high thermal conductivity and kinetic properties.

Applications of CNTs

- It is used in battery technology and in industries as catalyst.
- It is also used as light weight shielding materials for protecting electronic equipments.
- CNTs are used effectively inside the body for drug delivery.
- It is used in composites, ICs.

3.3.SYNTHESIS OF NANOPARTICLES

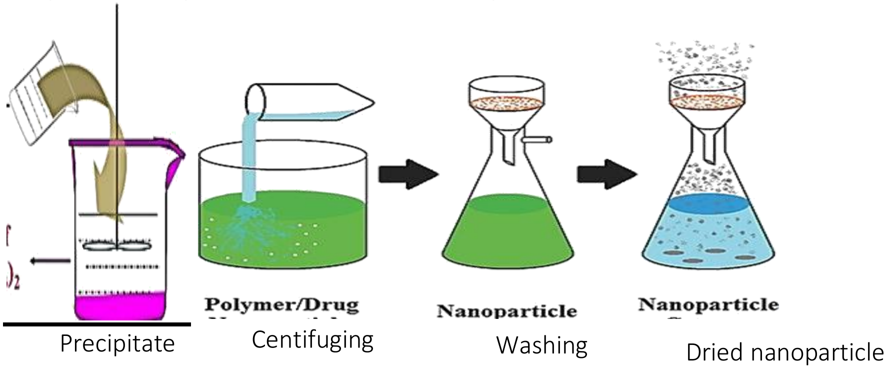
3.3.1.CHEMICAL METHODS

i).Metal Nanocrystals by Reduction

(a)Precipitation:

$$\textbf{Reactant} \xrightarrow[\text{stabilizing agent}]{\text{Water soluble inorganic}} \underset{\text{(Precipitate)}}{\textbf{Nanoparticles}}$$

Examples: Precipitation of $BaSO_4$ Nanoparticles:



Procedure:

10 gm of Sodium hexameta-phosphate (stabilizing agent)
+ 80 mL distilled water/250ml beaker
↓ i.Dissolve it
ii.Add 10 mL of 1M Sodium sulphate solution
+ 10 mL of 1M Barium nitrate solution
Stir it for 1 hour
↓
Precipitate is obtained
↓
Centrifuge, wash with distilled water and dry it in vacuum drier

Reaction:

$$Ba(NO_3)_2 + Na_2SO_4 \xrightarrow{\text{Stabilizing agent}} BaSO_4\downarrow + NaNO_3$$

In the absence of stabilizing agent, Bulk $BaSO_4$ is obtained.

(b).Precipitation by reduction: This method involves reduction of metal salts in appropriate solvents with variety of ***reducing agents***.

$$\text{Metal salt} \xrightarrow[\text{Reduction}]{} \underset{\text{(Nucleation centre)}}{\text{Metal atom}} \xrightarrow{\text{Stabilizing agent}} \underset{\text{(Atomic clusters)}}{\text{Nanoparticles}}$$

Clusters are surrounded by stabilizing molecule to prevent agglomeration.

Example-1:

Reduction of chloroaurate ions in aqueous solution by citric acid or sodium borohyd ride gives gold hydro sol (particle size in the range of 10-640 °A).

$$\textbf{Chloro aurite ions + Sodium boro hydride} \xrightarrow{\text{Reduction}} \textbf{Gold hydrosol}$$

Alcohol, glycol, metal borohydride, Phosphonium chloride are some of the reducing agents involved in this method.

Sols of metals and semiconductor nano particles are stabilized by the presence of ligand or stabilizing agent(Long chain amines, thiol or polymers)

Ex: PVA-PVP which prevent the aggregation of the particle

Nano crystal of CdS, CdSe, Zno, Zns, HgTe, Pbs, Cus, Cu_2 S, AgI and TiO2 were prepared by this method.

Example-2:

$$\underset{\text{(Dissolved in Toluene)}}{3MoCl_2} + \underset{\text{(Reducing agent)}}{6\ NaBH(C_2H_5)_3} \xrightarrow[\text{Room temperature}]{\text{Stabilizing agent}} 3\ Mo + 6NaCl + 3H_2 + 6B(C_2H_5)_3$$

ii. Thermolysis

It is the process of making nano particles by the decomposition of solids at high temperature having metal cations and molecular anions (or) metal organic compounds.

(eg)- Lithium nano particles are produced by the decomposition of Lithium azide(LiN_3) at 400 °C.

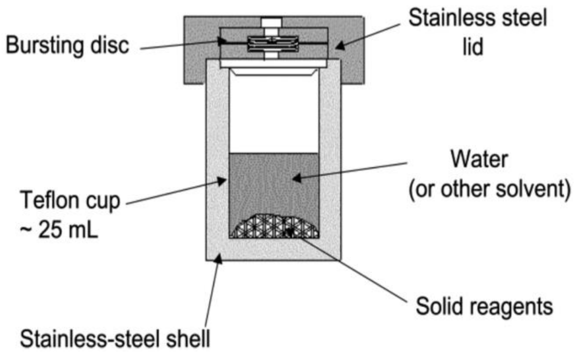
$$\mathbf{LiN_3} \xrightarrow[\mathbf{400\ ^\circ C}]{\text{Decomposition}} \textbf{Li-nano particle}$$

This method is of two types

a.Hydrothermal process

b.solvo thermal process

(a)Hydrothermal synthesis



- Hydrothermal synthesis is carried out in an autoclave under autogenous (high) pressure and below the supercritical temperature of water (374 °C).
- These conditions are favorable for the crystallization of products.
- pH of the medium tobe maintained, pH is generally made alkaline to increase the solubility of the reactants.

Example-Synthesis of ZnO nanoparticles

- This process is carried out in teflon lined sealed stainless steel autoclave at the temperature range of 100 – 200 °C for 6 – 12 hrs under autogenous pressure.
- The stock solution of $Zn(CH_3COO)_2.H_2O$ (0.1M) was prepared in 50ml methanol under stirring.
- 25 ml of NaOH(0.2 – 0.5M) solution prepared in methanol was added to maintain PH (8-11),Finally at the end of the reaction white ZnO nano particles are formed.

$$Zn(OH)_2 \xrightarrow{\quad\quad} Zn^{2+} + 2OH^-$$

$$Zn^{2+} + 2OH^- \xrightarrow{\quad\quad} ZnO + H_2O$$

- Metal oxides, Carbon nanotubes etc. can be prepared this way.

Advantages

- Solvent used is water.
- Rate of the reaction is much faster at high temperature and pressure.
- Ability to synthesize large crystals of high quality.
- Reagents and solvents can be regenerated.
- Used to prepare nanomaterials of different morphology (powder, rod, wire, tube, single crystals and nanocrystals).

Disadvantages:

- High cost of equipment.
- Sometimes, it is difficult to predict the morphology of the product.

(b)Solvothermal synthesis

A "solvothermal reaction can be defined as a chemical reaction (or a transformation) between precursor(s) in a solvent (in a close system) at a temperature higher than the boiling temperature of this solvent and under high pressure".

The Solvothermal method is identical to the hydrothermal method except that a variety of solvents other than water can be used for this process. This method has been found to be a versatile route for the synthesis of a wide variety of nanoparticles with narrow size distributions, particularly when organic solvents with high boiling points are chosen

It is a method for preparing a variety of materials such as metals, semiconductors, ceramics, and polymers.

- Solovothermal are usually thick walled steel cylinders with hermetic seal which must withstand high temperature and pressure for prolonged periods of times.
- The autoclave material must be inert with respect to the solovent. The closure is the most important element of the autoclave.
- To prevent corroding of the internal cavity of the autoclave, prodective inserts are genrally used. These may have the same shape of the autoclave and fit in the internal cavity.

- Inserts may be made up of carbon free iron, glass or quarts, copper or Teflon depending on the temperature and material used.
- The process involves the use of a non-aqueous solvent under moderate to high pressure (typically between 1 atm and 10,000 atm) and temperature (typically between 100 °C and 1000 °C) that facilitates the interaction between reactants during synthesis
- High temperature and pressure facilitates the dissolution of the reactants and products are generally obtained in the nanocrystalline form. It is then washed and then dried.

Example-1:- Nano crystal of CdSe have been prepared by reacting cadmium stereate with selenium powder using toluene as solvent,tetrahydro phenolphthalein as reducing agent.

$$\textbf{Cadmium stereate + Selenium} \xrightarrow{\text{Toluene}} \textbf{CdSe}$$

Example-2(eg-2):- Cadmium oxalate and chalcogens undergo reaction in presence of pyridine as solvent to produce cadmium nanoparticle**.**

$$CdC_2O_4 + E \xrightarrow{\text{Pyridine}} CdE$$

E = Chalcogenide(S,Se,Te)

Advantages:

- Relatively easy and cheap method.
- Products obtained are in crystalline form. So no purification required.
- Can be used for preparing nanomaterials of different morphology (powder, rod, wire, tube, single crystals and nanocrystals).
- Precise control over the size, shape distribution and crystallinity of nanoparticles by varying experimental conditions.
- Variety of organic solvents can be used as it helps the dispersion nanocrystallites and may stabilize some metastable phases.

Disadvantages:

- Inability to monitor crystals in the process of their growth.
- The need to expensive autoclave.
- Safety issues during the reaction process.

Applications

- Various kind of Nano structures canbe center sized of through solvothermal approaches including medal oxides carbonaceous Nano structures and etc.,

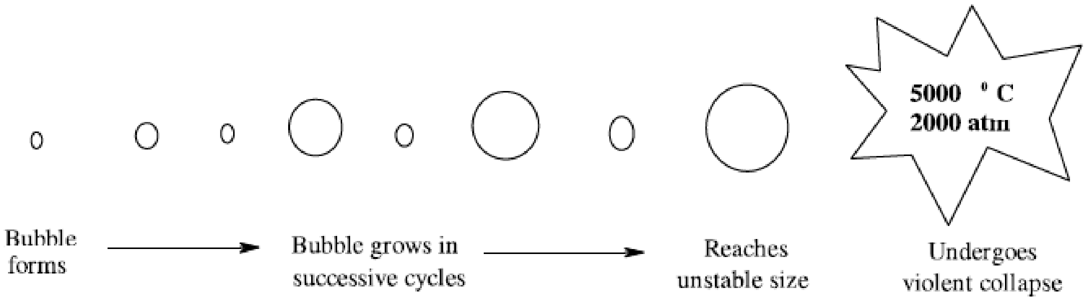
- This method can also be used produce zeolite ,nano wires, carbon nanotubes

iii. Sonochemical synthesis

- Sonochemistry is the research area in which molecules undergo chemical reaction due to the application of powerful ultrasound radiation (20 KHz–10 MHz).
- Application of ultrasound to chemical reactions and processes
- Ultrasound is the part of sonic spectrum (20KHz- 10Mhz),can be divided into 3 regions

1. Low frequency ,high power ultra sond (20-100KHz)
2. High frequency ,medium power ultra sound (100KHz- 1MHz)
3. High frequency ,low power ultra sound (1-10MHz)

- In this method, ultrasound wave is the driving force for the formation of various nanostructured materials.
- During sonication, microscopic bubbles are formed in the solution by a process known as cavitation and these bubbles grow and may implode.
- This cavity is called cavitation bubble and this process is called cavitation
- The implosion leads to the formation of large heat and pressure that speed up the reaction.
- During implosion, it forms extremely high temperatures as high as 5000^0K, and pressures upto 1800 atm and cooling rates can often exceed ~ 10^{10}K/s.
- This large amount of energy released can enhance the chemical reactivities and cause physical effects.
- In case of tellurium bundles of nanowhiskers, sonication leads to hot spots, which could cause local fluctuation in the solubility of tellurium an induce the seeding and growing t-Te.

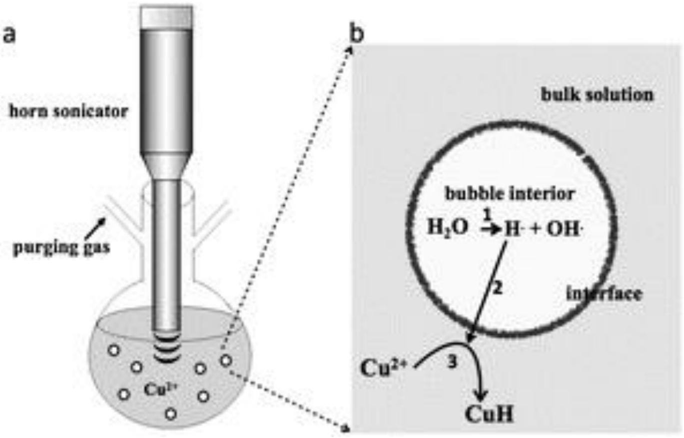


Cavitation bubble formation and collapse

Example-1

- Large-scale synthesis of bundles of t-Te nanowhiskers was carried out from metallic Te powder by sonication.
- In this synthesis, high-quality, uniform and crystalline nanowhisker bundles of t-Te were formed within 1 hour.
- Te powder along with KOH and water was stirred for form a dark purple solution.
- The unreacted Te powder was centrifuged and redispersed in water.
- The mixture was sonicated for 1 hour at 65-75^{0}C at different intervals of time

Example-2



- The reduction reaction from Cu^{2+} to CuH is a chemical effect of the ultrasound irradiation.
- As mentioned earlier, the collapsing cavitation bubbles are known to break down the water matrix into hydrogen atoms (H) and hydroxyl radicals (OH) (eqn (1)).
- Furthermore, the hydrogen atoms can reduce Cu^{2+} to Cu^{+} (eqn (2))
- In this synthesis, the solutions did not contain any stabilizing ligands for Cu^{+}. Therefore, Cu^{+} ions are not stable and disproportionate into Cu^{0} and Cu^{2+} (eqn (3)).
- Finally the Cu^{0} atoms can combine with the hydrogen atoms to form the CuH products

$$H_2O \xrightarrow{\text{ultrasound}} H^{\bullet} + OH^{\bullet} \qquad (1)$$

$$Cu^{2+} + H^{\bullet} \rightarrow Cu^{+} + H^{+} \qquad (2)$$

$$2Cu^{+} \rightarrow Cu^{0} + Cu^{2+} \qquad (3)$$

$$Cu^{0} + H^{\bullet} \rightarrow CuH \qquad (4)$$

Advantages

- Decrease of reaction time and increase of yield

- More uniform, smaller and pure crystals with minimal agglomerations are formed
- No chemical reducing agent is necessary for reaction
- Possible switching of reaction pathway
- Use of less or avoidance of phase transfer catalyst

Limitations

It produces only spherical metal nanoparticles

iv. PHOTOCHEMCAL SYNTHESIS

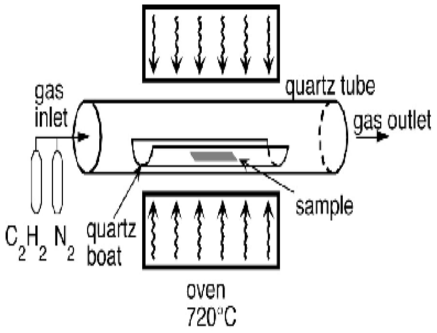
- In this method, metal nanoparticles are formed either by the direct photoreduction of a metal source or by the reduction of metal ions using photochemically generated intermediates such as excited molecules.radicals.
- It has been found that the reduction of metal salt precursors can also be done by radiolytic and photochemical methods.
- The main advantages of such a technique include the reduction of metal ions without using excess reducing agents.
- In this case, radiation is absorbed regardless of light-absorbing solutes and products. Also the rate of reduction reaction is known, since the number of reducing equivalents generated by radiation is well defined.
- Apart from this, photochemical synthesis does not require a specific and costly instrument
- Photochemical synthesis of nanoparticles is carried out by the light-induced decomposition of a metal complex or the reduction of a metal salt by photogenerated reducing agents such as solvated electrons.
- The former is called photolysis and the latter radiolysis.

Advantages:

- The convenience of use and the clean nature of the process,
- Controllable in situ generation of reducing agents,
- great versatility, and
- the possibility of nanoparticle synthesis in various medium including emulsions, surfactant micelles, polymer films, glasses, cells etc.

v. Chemical vapor deposition (CVD)

- Chemical Vapor Deposition is the formation of a non-volatile solid film on a substrate by the reaction of vapor phase chemicals (reactants) that contain the required constituents.
- The reactant gases are introduced into a reaction chamber and are decomposed and reacted at a heated surface to form the thin film.



- CVD involves the formation of nanomaterials from the gas phase at elevated temperatures usually onto a solid substrate or catalyst.
- The process involves passing a hydro carbon vapor through a tubular reactor containing catalyst
- At temperature (600–1200 °C) hydro- carbon decompose to carbon vapours, which condense on the cooler surface.
- The formed nanotubes diffuse to the growth sites.
- Desorption of products from the reacting surface.

The CVD method produces both single-wall and multi-wall nanotubes

Advantages:-

- Extremely high purity nanomaterials are produced.
- Can deposit which are hard to evoprate
- It can produce 1D nanomaterials

Dis advantages:-

- Expensive.
- Use of toxic gases causes a number of environmental problems

.

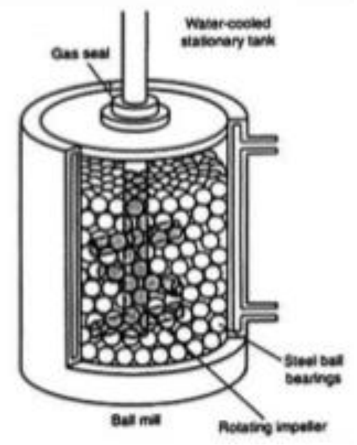
3.3.2.Physical Methods

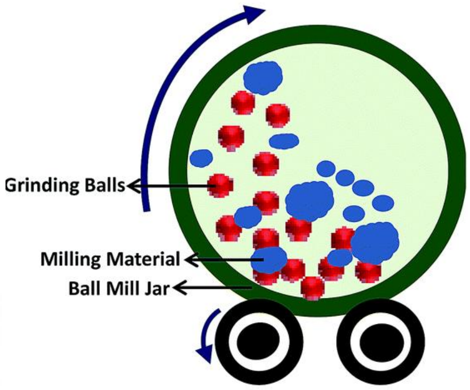
i.Ball Milling

Physical methods apply mechanical pressure, high energy radiations, thermal energy or electrical energy to cause material abrasion, melting, evaporation or condensation to generate NPs. These methods mainly operate on top-down strategy and are advantageous as they are free of solvent contamination and produce uniform monodisperse NPs. At the same time, the abundant waste produced during the synthesis makes physical processes less economical. High energy ball milling, laser ablation, electrospraying, inert gas condensation, physical vapour deposition, laser pyrolysis, flash spray pyrolysis, melt mixing are some of the most commonly used physical methods to generate NPs.

Principle: Small hard balls are allowed to rotate inside a container and then it is made to fall on a solid with high force to crush the solid into nano crystal.

Construction and Working: Hardened steel or tungsten carbide balls are put in a container along with powder of particles (50μm) of a desired material. The container is closed with tight lids.When the container is rotating around the central axis, the material is forced to press against the walls. The milling balls impart energy on collision and produce smaller grain size of nano particle. Ball milling is also known as Mechanical alloying or crushing.





- Consists of a container filled with hardened steel or tungsten carbide balls.
- Material of interest is fed as flakes
- 2:1 mass ratio of balls to materials
- Container may be filled with air or inert gas
- Containers are rotated at high speed around a central axis

- Material is forced to the walls and pressed against the walls.

- Control the speed of rotation and duration of milling- grind material to fine powder(few nm to few tens of nm)

- Some materials like Co, Cr, W, Al-Fe, Ag-Fe etc are made nanocrystalline using ball mill.

Advantages:

- Few mg to several kgs of nanoparticle can be synthesized in a short time.

- This technique can be operated at large scale.

- It is useful in preparation of elemental and metal oxide nano crystals like Co, Cr, Al-Fe, Ag-Fe and Fe.

- Variety of intermetallic compounds of Ni and Al can be formed.

- Ball milling method is useful in producing new type building materials, fire – proof materials, glass ceramics, etc.

Disadvantages:

- Contamination of the milling media

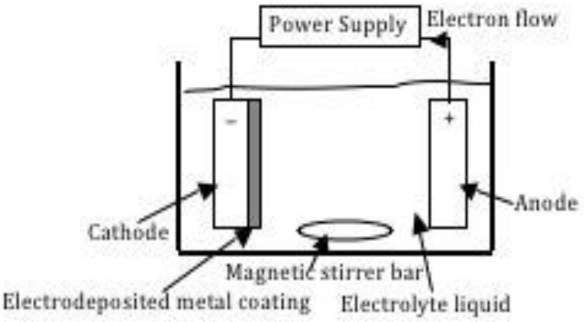
- Non-metal oxides require an inert medium, and vacuum or glove box to use powder particles.

ii.ELECTRODEPOSITION

The principle of electrodeposition is inducing chemical reactions in an aqueous electrolyte solution with the help of applied voltage, e.g.

Electrodeposition is a process in which metal ions in a solution are reduced electrochemically to coat on the surface of a conductive substrate.

- The cell usually contains a reference electrode, a specially designed cathode, and an anode or counter electrode.
- The cathode substrate on which electro deposition of the nanostructure takes place can be made of either nonmetallic or metallic materials



- Ions in solution are deposited onto the negatively charged cathode, carrying charge at a rate that is measured as a current in the external circuit.
- Using the surface of the cathode as a template, various desired nanostructures or morphologies can be synthesized for specific applications.
- Such a template-assisted electro deposition process can be broadly divided into two groups: active template-assisted and restrictive template-based electro deposition.
- The final size distribution of the electrodeposits, however, strongly depends on the kinetics of the nucleation and growth. The electro deposition process involves the formation of either an instantaneous or a progressive nucleation.

Advantages.

- It is relatively cheap and fast and allows complex shapes.
- It can be performed at low temperatures which will minimize inter diffusion of materials in the case of a multilayered thin film preparation.
- The film thickness can be controlled by monitoring the amount of charge delivered
- The composition and defect chemistry can be controlled by the magnitude of the applied potential, which can be used to deposit non-equilibrium phases.

3.3.3.Biogenic synthesis

- Biogenic synthesis employ biological systems like bacteria, fungi, viruses, yeast, actinomycetes, plant extracts, *etc.* for the synthesis of metal and metal oxide NPs.
- Bio-assisted methods, provides an environmentally benign, low-toxic, cost-effective and efficient protocol to synthesize and fabricate NPs.
- Bio-assisted methods can be broadly divided into three categories:

  (i) Biogenic synthesis using microorganisms

  (ii) Biogenic synthesis using biomolecules as the templates

  (iii) Biogenic synthesis using plant extracts

Synthesis using microorganisms

- Microorganisms are capable of interacting with metals coming in contact with them through their cells and form nanoparticles.
- The cell- metal interactions are quite complex
- Certain microorganisms are capable of separating metal ions.
- Pseudomonas stuzeri Ag259 bacteria are commonly found in silver mines.
- Capable of accumulating silver inside or outside their cell walls
- Numerous types of silver nanoparticles of different shapes can be produced having size <200nm intracellularly
- Low concentrations of metal ions (Au^+,Ag^+ etc) can be converted to metal nanoparticles by Lactobacillus strain present in butter milk.

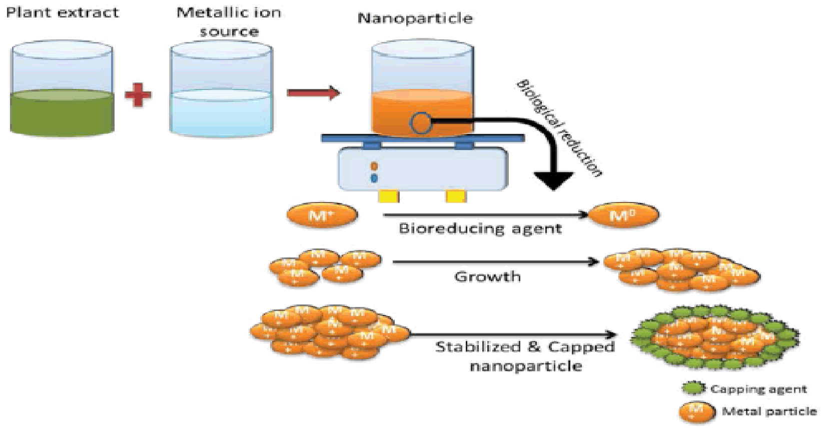
Fungi

- Fusarium oxysporum challenged with gold or silver salt for app. 3 days produces gold or silver nanoparticles extracellularly.
- Extremophilic actinomycete Thermomonospora sp. Produces gold nanoparticles extracellularly.
- Semiconductor nanoparticles like CdS, ZnS, PbS etc., can be produced using different microbial routes.
- Sulphate reducing bateria of the family Desulfobacteriaceae can form 2-5nm ZnS nanoparticle.
- Klebsiella pneumoniae can be used to synthesize CdS nanoparticles.
- when [$Cd(NO_3)_2$] salt is mixed in a solution containing bacteria and solution is shaken for about1 day at ~38°C ,CdS nanoparticle in the size range ~5 to 200 nm can be formed.

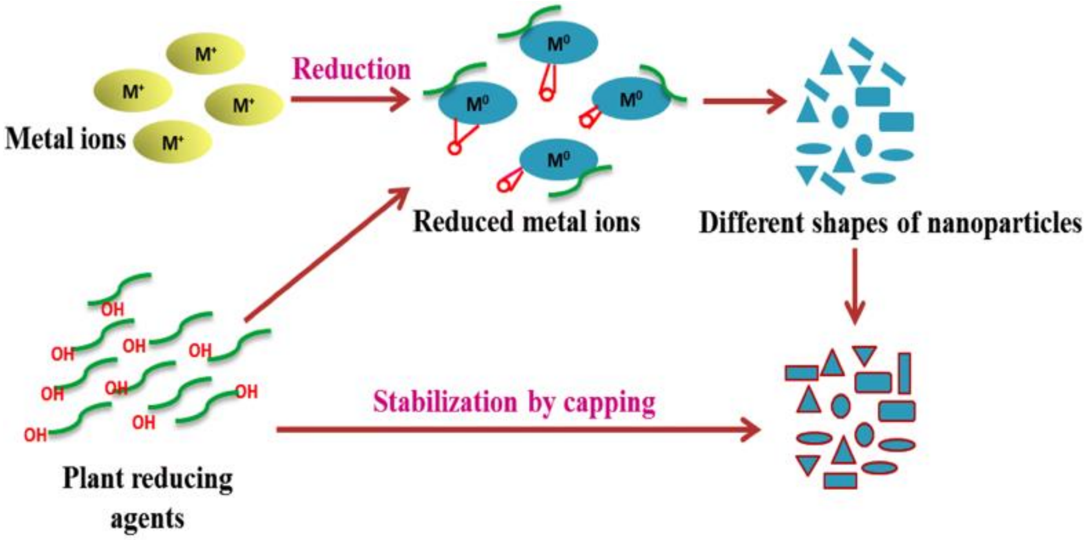
Synthesis using plant extracts

- Leaves of geranium plant (Pelargonium graveolens) have been used to synthesize gold nanoparticles
- Plant associated fungus- produce compounds such as taxol and gibberellins

- Exchange of intergenic genetics between fungus and plant.
- Nanoparticles produced by fungus and leaves have different shapes and sizes.
- Nanoparticles obtained using Colletotrichum sp., fungus is mostly spherical while those obtained from geranium leaves are rod and disk shaped.



Biological synthesis of nanoparticles using plant extracts



Finely crushed leaves (Erlenmeyer flask)

↓

boiled in water (1 min)

↓

cooled and decanted

↓

added to $HAuCl_4$ aq. Solution

↓

gold nanoparticles within a minute

Synthesis using DNA

- CdS or other sulfide nanoparticles can be synthesized using DNA.
- DNA can bind to the surface of growing nanoparticles.
- ds Salmon sperm DNA can be sheared to an average size of 500bp.
- Cadmium acetate is added to a desired medium like water, ethanol, propanol etc.
- Reaction is carried out in a glass flask- facility to purge the solution and flow with an inert gas like N_2.
- Addition of DNA should be made and then Na_2S can be added dropwise.
- Depending on the concentrations of cadmium acetate, sodium chloride and DNA ,nanoparticles of CdS with sizes less than ~10 nm can be obtained.
- DNA bonds through its negatively charged PO_4 group to positively charged (Cd^+) nanoparticle surface.
- Various inorganic materials such as carbonates, phosphates, silicates etc are found in parts of bones, teeth, shells etc.
- Biological systems are capable of integrating with inorganic materials
- Widely used to synthesize nanoparticles

Table 3: Comparative differences between biogenic and chemically synthesized nanoparticles

Properties	Chemical	Biological
Nature	Expensive, toxic	Cost effective, nontoxic
Reducing agent	Dimethylformamide, ethylene glycol, hydrazine hydrate, sodium borohydride, polyol, sodium citrate and N,N-dimethyformamide	Biomolecules include phenolics, polysaccharides, flavones, terpenoids, alkaloids, proteins, amino acids, enzymes, predominantly, nitrate reductase
Method	Stabiliser (surfactant) is added to the first solution to prevent the agglomeration of nanoparticles	There is no need to add a stabilising agent
Environmental impact	Environmental pollution is a disadvantage of the chemical method and the chemical reduction methods are energy-intensive	Synthesis carried out in environmental conditions and they are safe enough, and consume no energy
Antibacterial activity	The chemically synthesized nanoparticles showing	The nanoparticles synthesized from biological means are showing better

Properties	Chemical	Biological
	comparatively lower antimicrobial activity against pathogenic bacteria	antimicrobial activity against the pathogenic bacteria

Applications of different nanoparticles

NPs have wide range of applications from electronic, optoelectronic, magnetic, data storage, energy and energy storage, nanomedicines, bioimaging, *etc.*

Table - Key nanoparticles and their important applications in various scientific fields

Nanoparticles	Applications
Ag	• Nanomedicines: antibacterial agent (healthcare, food technology, textile coating, environmental cleaning, water disinfection), wound healing, cancer therapeutics, Supercapacitors • Diagnosis: designing highly sensitive biosensor electrodes/chips, biological tagging for quantitative detection • Solar cells, electroluminescent displays, optical sensors, surface enhanced Raman spectroscopy • To generate eco-friendly electrical contacts for electrical devices
Au	• Nanomedicines: drug and gene delivery, hyperthermia-assisted cancer phototherapy, photodynamic therapy • Biosensors: highly sensitive optical, electrochemical and plasmon resonance biosensors • *Ex vivo* and *in vivo* bio-imaging, two photon luminescence imaging, magnetic resonance imaging, photoacoustic tomography, Raman imaging, *etc.* • Antibacterial agent
Pt	• Biomedical applications: affinity probe for the detection of small biomolecules, catalytic nanomedicines, biosensors,Catalysis,solar cells.
Pd	• Surface enhanced Raman scattering and electrocatalysis, • Catalysis, Antibacterial activity ,fuel cell,biosensor
Ge	• Electronic/optoelectronic
CeO_2	• Potential regenerative antioxidant, • Therapeutic applications for reactive oxygen species (ROS)-related diseases *e.g.* cancer, diabetes, arthritis, infertility, macular degeneration • Catalytic convertor for removing toxic gases, Solid oxide fuel cells • Biosensors, Photocatalysis, Antibacterial activity
TiO_2	• Drug delivery, Antimicrobial coatings

Nanoparticles	**Applications**
ZnO	• As UV filters in sunscreens, toothpaste, cosmetics, *etc.* • Biosensors • Solar cells, Photocatalytic and hygienic coatings,b**iosensors** • Important additive for different cosmetics, ointments and food products • Cure activator for rubbers of different kinds, Antibacterial
Fe_2O_3	• Due to its excellent magnetic properties, they are being used in magnetic seals and inks, magnetic recording media, catalysts, and ferrofluids • Development of immunoassays, magnetic resonance imaging contrast agents, and targeted drug delivery vehicles, as well as in magnetic hyperthermia
CdS	• As fluorescent probes • Optical, electrochemical and photoelectrochemical biosensors • Photoluminescence devices
Carbon nanoparticles	• Cancer diagnostic and therapy, Designing of fluorescent imaging probe • Antibacterial, Solar cells, protective coatings and emission devices
Polymeric NPs	• Nanomedicines and drug delivery, Photoacoustic imaging • Fluorescent polymeric NPs for cell imaging

Drawbacks of bio synthesis :

- Time consuming – Rate of production is slow
- Difficulty in control over size distribution, shape and crystallinity.
- The nanoparticles are also not mono dispersed.

CONTENT BEYOND

NANOTECHNOLOGY , ENERGY AND ENVIRONMENT

- The most advanced nanotechnology projects related to energy are as follows: storage, conversion, manufacturing improvements by reducing materials and process rates, energy saving by better thermal insulation and enhanced renewable energy sources.

- Using nanotechnology more clean and less expensive ways for energy production is desired. Nanotechnology has great contribution on renewal energies from solar technology, to nanocatalysis, fuel cells and hydrogen technology.

- Carbon nanotube fuel cells are being used to store hydrogen. These are the environmentally friendly form of energy. Researchers are trying to increase effectiveness of carbon nanotube at storing hydrogen. This has the potential to power cars.
- Nanotechnology can contribute to the further reduction of combustion engine pollutants by nanoporous filters, which can clean the exhaust mechanically, by catalytic converters based on nanoscale noble metal particles or by catalytic coating on cylinder walls and catalytic nanoparticles as additive for fuels.
- Nanotechnology can help in developingnew environmental safe and green technologies that can minimize the formation of undesirable by-products or effluents.
- Currently used light bulbs only convert approximately 5 percent of the electrical energy into light. Nanotechnological approaches like LEDs(light-emitting diodes) or QCAs (quantum-caged atoms) could lead to a strong reduction of energy consumption for illumination.

NANOTECHNOLOGY IN SPACE EXPLORATION

- Rocket scientist are actively researching new forms of space propulsion systems because today's rocket engines rely on chemical propulsion.
- Nanotechnology can make the structure of space planes much light thus can greatly improve their viability.
- Nanotechnology can improve the performance of laser sails. Using nanotechnology sails with 20nm thickness can be constructed making them light and more durable.

NANOELECTRONICS

- Using electrodes made from nanowires that would enable flat panel displays to be flexible as well as thinner than current flat panel displays.
- Using semiconductor nanowires to build transistors and integrated circuits.
- Transistors built in single atom thick graphene film to enable very high speed transistors.
- Researchers have developed an interesting method of forming PN junctions, a key component of transistors, in graphene. They patterned the p and n regions in the substrate. When the graphene film was applied to the substrate electrons were either added or taken from the graphene, depending upon the doping of the substrate. The researchers believe that this method reduces the disruption of the graphene lattice that can occur with other methods.
- Combining gold nanoparticles with organic molecules to create a transistor known as a NOMFET (Nanoparticle Organic Memory Field-Effect Transistor).
- Using carbon nanotubes to direct electrons to illuminate pixels, resulting in a lightweight, millimeter thick "nanoemmissive" display panel.
- Using quantum dots to replace the fluorescent dots used in current displays. Displays using quantum dots should be simpler to make than current displays as well as use less power.
- Making integrated circuits with features that can be measured in nanometers (nm), such as the process that allows the production of integrated circuits with 22 nm wide transistor gates.

- Using nanosized magnetic rings to make Magnetoresistive Random Access Memory (MRAM) which research has indicated may allow memory density of 400 GB per square inch.

- Researchers have developed lower power, higher density method using nanoscale magnets called magnetoelectric random access memory (MeRAM).
- Developing molecular-sized transistors which may allow us to shrink the width of transistor gates to approximately one nm which will significantly increase transistor density in integrated circuits.
- Using self-aligning nanostructures to manufacture nanoscale integrated circuits.
- Using nanowires to build transistors without p-n junctions.
- Using buckyballs to build dense, low power memory devices.
- Using magnetic quantum dots in spintronic semiconductor devices. Spintronic devices are expected to be significantly higher density and lower power consumption because they measure the spin of electronics to determine a 1 or 0, rather than measuring groups of electronics as done in current semiconductor devices.
- Using nanowires made of an alloy of iron and nickel to create dense memory devices. By applying a current magnetized sections along the length of the wire. As the magnetized sections move along the wire, the data is read by a stationary sensor. This method is called race track memory.
- Using silver nanowires embedded in a polymer to make conductive layers that can flex, without damaging the conductor.
- IMEC and Nantero are developing a memory chip that uses carbon nanotubes. This memory is labeled NRAM for Nanotube-Based Nonvolatile Random Access Memory and is intended to be used in place of high density Flash memory chips.
- Researcher have developed an organic nanoglue that forms a nanometer thick film between a computer chip and a heat sink. They report that using this nanoglue significantly increases the thermal conductance between the computer chip and the heat sink, which could help keep computer chips and other components cool.

UNIT - IV
Heterocyclic compounds and natural products

Introduction:

Heterocyclic compounds are organic compounds that contain rings composed of carbon and other atoms-heteroatoms-in natural heterocycles mostly nitrogen, sulphur, and oxygen. Heterocycles exist as three-, four-, five-,six- and multi-membered rings.

The stability of heterocycles increases with less distorted bond angles (less strain) that are in five- and sic- membered rings, and with maximum number of conjugated double bonds, because the delocalized Π-bonding electron pairs form a molecular Π orbital filled with six electrons and the compound have the aromatic character.

Some rings, in spite of being five- or six-membered, are **not stable heterocycles**, e.g. **cyclic hemiacetals** (cyclic forms of monosaccharides) are in equilibria with their open (acyclic) forms, **cyclic esters** (lactones), **amides** (lactams), and cyclic dicarboxylic **acid anhydrides** can undergo hydrolytical splitting.

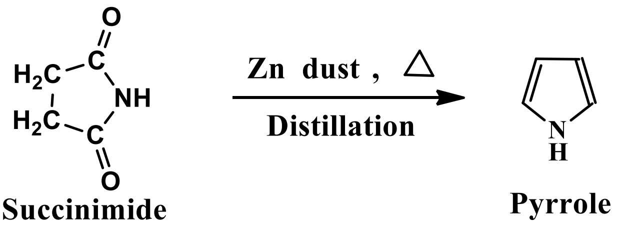
Nonaromatic heterocycles – **cyclic ethers**, **amines**, and **sulfides** behave like their acyclic analogs with the same functional group and do not require special discussion.

Aromatic heterocycles (with the maximum number of conjugated double bonds) are much more important.

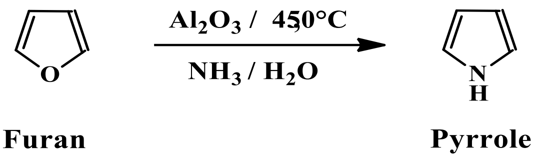
PYRROLE

Preparation

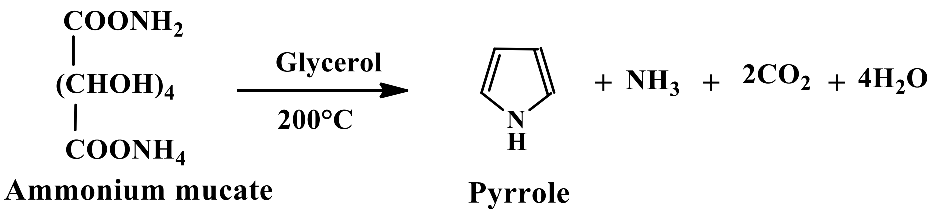
1. Distillation of succinimide with Zinc dust yields Pyrrole.



2. It is manufactured by passing a mixture of furan, ammonia and steam over heated alumina (450°C)

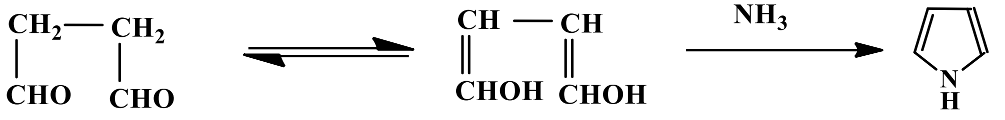


3. It is obtained by distilling ammonium mucate with glycerol



4. **Paul knorr synthesis**

Pyrrole and its derivative is obtained by heating 1,4-dicarbonyl compound (Succinaldehyde) with ammonia or primary ammine or hydrazine.



Succinaldehyde **Enol form** **Pyrrole**

Chemical reactions

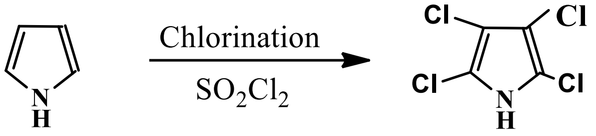
1. **Electrophilic substitution Reactions**

Halogenation:

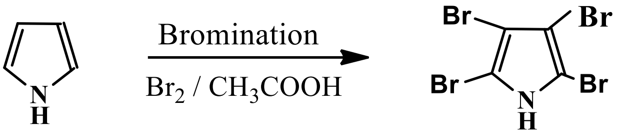
Halogenation reaction of Pyrrole occurs vigorously and requires careful control of reaction conditions.

1. Chlorination is carried out with sulfuryl chloride in ether at 0 °C.
2. Bromination with bromine in acetic acid at 0 °C.
3. Iodination with iodine in aqueous solution of potassium iodide.

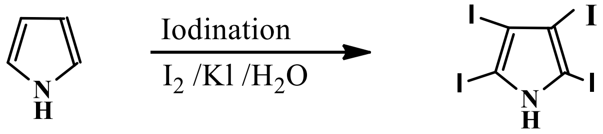
In each case tetra halogen derivative is obtained.



Pyrrole **2,3,4,5 tetrachloro pyrrole**



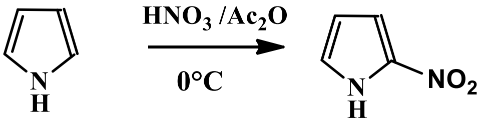
Pyrrole **2,3,4,5 tetrabromo pyrrole**



Pyrrole **2,3,4,5 tetra iodo pyrrole**

Nitration:

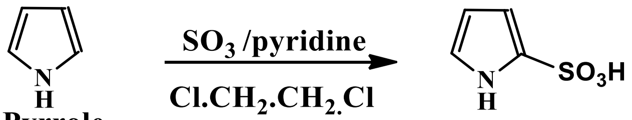
Pyrrole can be nitrated by cold nitric acid in acetic anhydride **[$Ac_2O = (CH_3CO)_2O$]** to give 2-nitropyrrole



Pyrrole **2- Nitro pyrrole**

Sulphonation

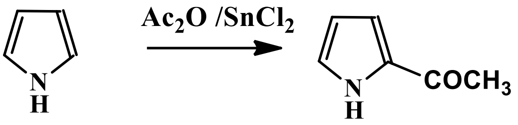
Pyrrole reacts with sulphur trioxide in pyridine in presence of ethylene chloride to give Pyrrole 2-sulphonic acid.



Pyrrole **Pyrrole 2- sulphonic acid**

Friedel Crafts Acylation

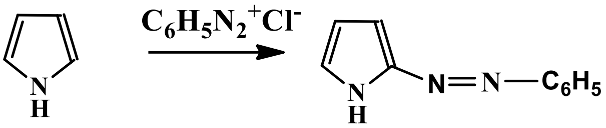
Pyrrole is acetylated with acetic anhydride **[$Ac_2O = (CH_3CO)_2O$]** in presence of stannous chloride [$SnCl_2$]to give 2-acetyl pyrrole



Pyrrole **2- acetylpyrrole**

Coupling Reaction

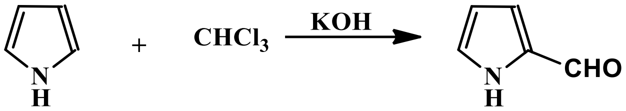
Pyrrole couples with benzene diazonium chloride in weakly acidic solution to give AZO DYE [2-phenyl azo pyrrole)



Pyrrole **Azo dye**

Reimer Tiemann Reaction

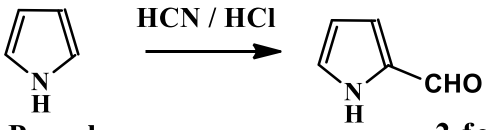
Pyrrole reacts with chloroform in presence of alkali to yield Pyrrole 2-carbaldehyde [2-formyl Pyrrole].



Pyrrole **2-formyl pyrrole**

Gattermann formylation

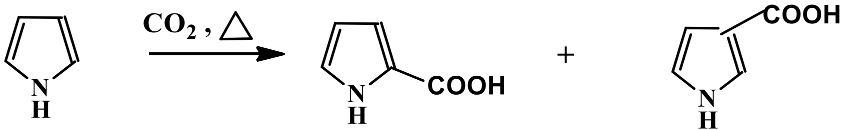
Pyrrole reacts with hydrogen cyanide in presence of hydrochloric acid to 2-formyl Pyrrole.



Pyrrole **2-formyl pyrrole**

Kolbe's reaction

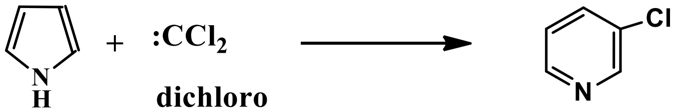
Pyrrole reacts with carbondioxide at 100 °C, in presence of base to give mixture of pyrrole-2-carboxylic acid and Pyrrole-3-carboxylic acid.



Pyrrole **Pyrrole 2- Carboxylic acid** **Pyrrole 3 -Carboxylic acid**

2.Ring expansion

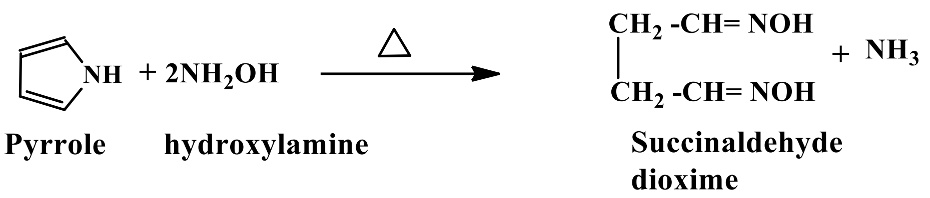
Pyrrole reacts with dicholorocarbene formed by interaction of chloroform and sodium ethoxide resulting in the formation of 3-chloro pyridine.



Pyrrole **dichloro carbene** **3-Chloro pyridine**

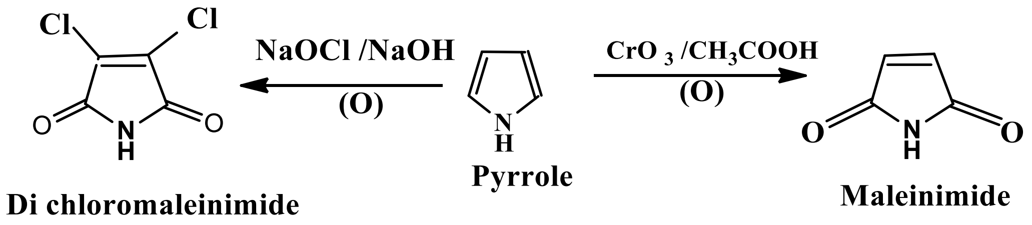
3.Ring opening

Pyrrole when refluxed with ethanolic solution of hydroxylamine yields succinaldehyde dioxime.



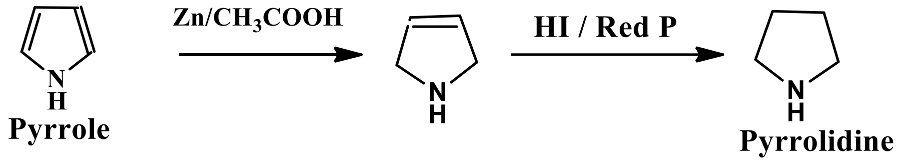
4.Oxidation

Pyrrole on oxidation by chromium trioxide in acetic acid to maleinimide and with sodium hypochlorite, it yields dichloromaleinimide.

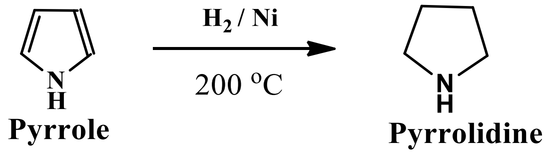


5.Addition reaction (Reduction or hydrogenation)

Pyrrole on reduction with zinc and acetic acid forms pyrrolone, which on heating with hydro iodic acid in presence of red phosphorous yield pyrrolidine.

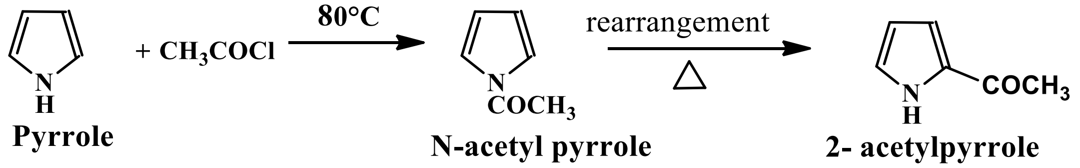


Catalytic reduction of Pyrrole at 200 °C yields pyrrolidine.

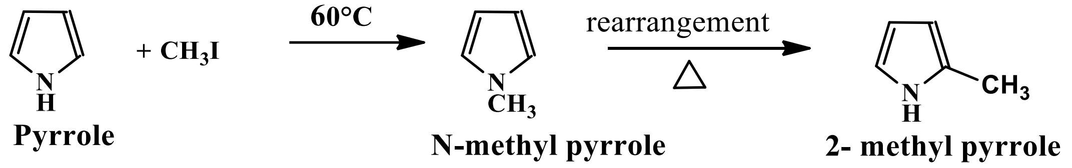


6.Resemblance with aromatic amines:

Pyrrole reacts with acid halides (acetyl chloride) at 80 °C to form N-acetylpyrrole, which on heating undergo rearrangement to yield 2-acetylpyrrole.



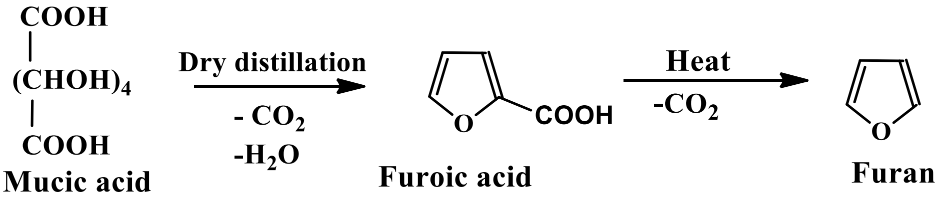
With methyl iodide it gives, N-methyl Pyrrole at 60 °C, which on heating rearranges to form 2-methylpyrrole.



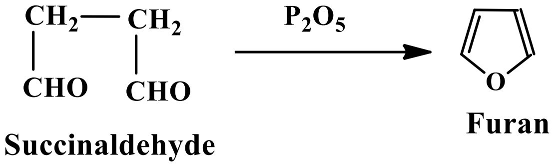
FURAN

Preparation

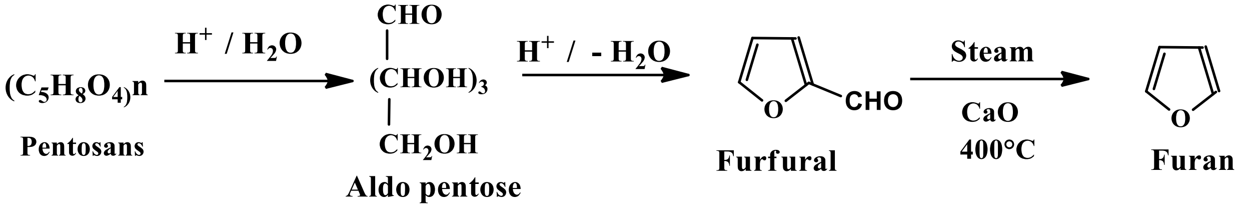
1.Dry distillation of mucic acid gives furoic acid ,which when heated at its boiling point decarboxylates to furan



2.It is obtained by heating succinaldehyde with phosphorous pentoxide



3. It is prepared by distilling agricultural waste products which is rich in pentoses with dil.sulphuric acid followed by steam distillation gives furfural,which on catalytic decomposition yields furan.

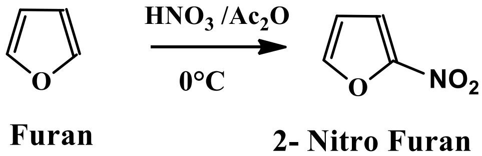


Chemical properties

1.Electrophilic substitution reaction

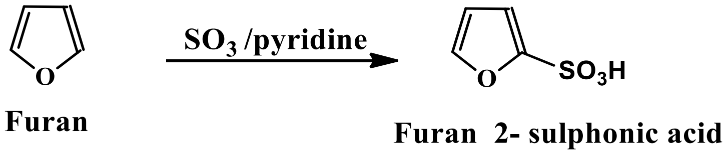
Nitration

Furan can be nitrated by cold nitric acid in acetic anhydride **[Ac_2O =$(CH_3CO)_2O$]** to give 2-nitro furan.



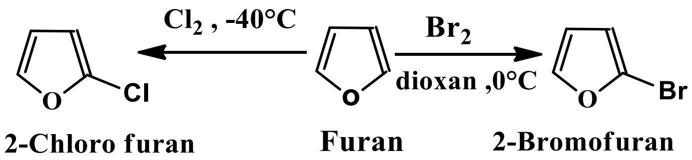
Sulphonation

Furan reacts with sulphur trioxide in pyridine at 70 °C to yield furan 2-sulphonic acid.

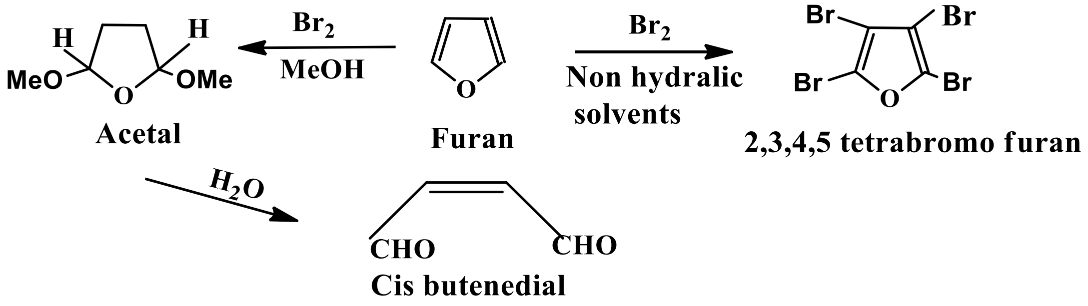


Halogenation

It reacts violently with halogens at room temperature leading to polyhalogenated compounds or destruction of ring.But under controlled conditions halogenation takes place to yield 2-halo derivatives.

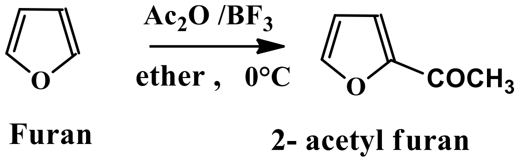


The reaction of furan with bromine in nonhydroxylic solvents, polybromination occurs , but in MeOH no bromine is added.



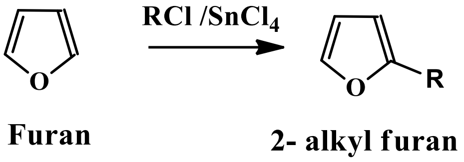
Friedel Crafts Acylation

Furan is acetylated with acetic anhydride **[Ac_2O =$(CH_3CO)_2O$]** in presence of boran trifluride [BF_3] and ether at 0°Cto give 2-acetyl furan



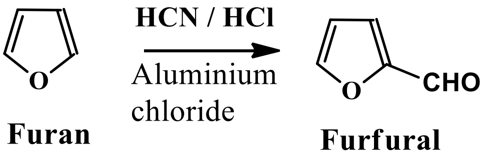
Friedel Crafts Alkylation

Furan is treated with alkyl halides in presence of stannic chloride [$SnCl_4$] to give 2-alkyl furan



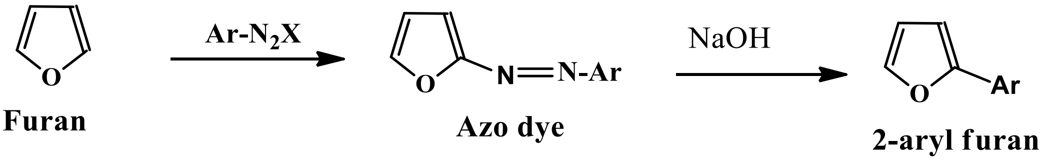
Gattermann formylation

Furan when treated with hydrogen cyanide and hydrogen chloride in presence of aluminium chloride to yield furfural



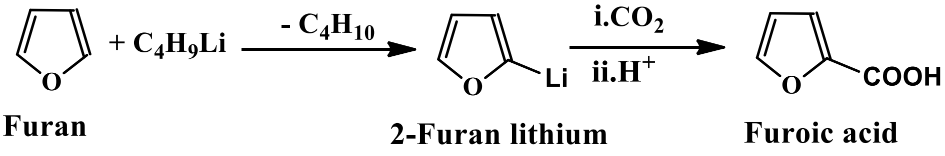
Coupling (Gamberg)Reaction

Furan couples with benzene di azonium chloride in weakly acidic solution to give AZO DYE [2-phenyl azo furan) which in presence of NaOH yields 2-aryl furan



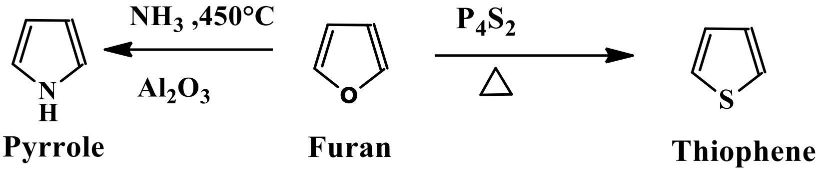
2.Formation of organo metallic compound

It reacts with butyl lithium to give 2-furan lithium which undergoes the usual reactions of organolithium compounds. (eg) It combines with carbon dioxide to form furoic acid.



3.Formation of Pyrrole and thiophene

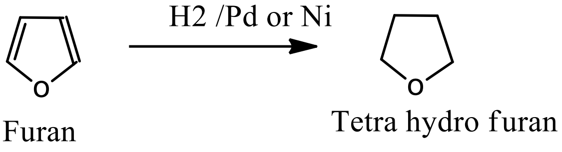
Furan reacts with ammonia at 450 °C in presence of alumina to form Pyrrole and with P_4S_2 it gives thiophene.



4.Addition reactions

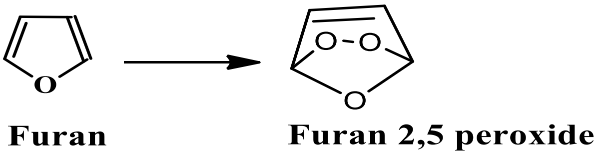
a.Hydrogenation

Catalytic reduction of furan in presence of Pd or Ni to form stable saturated cyclic ether known as tetra hydro furan.



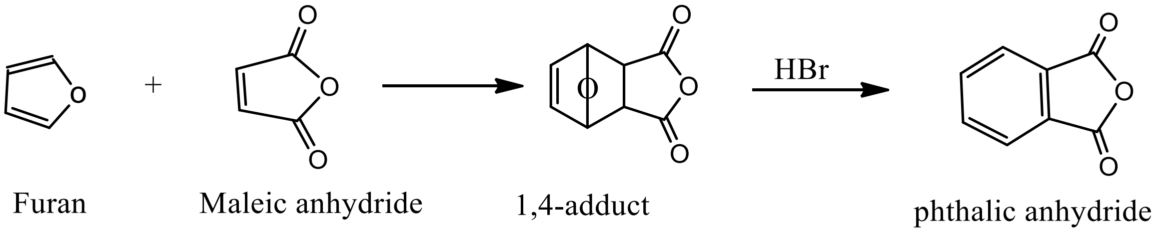
b.Reaction with air

It is unstable in air and reacts with oxygen to form 2,5 peroxide which readily undergoes polymerization



c.Diels alder reaction

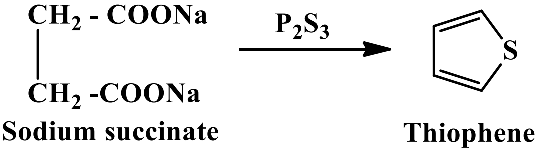
Furan behaves as diene ,thus with maleic anhydride it forms 1,4-adduct(Maleic anhydride adduct) which on treatment with mineral acid yields phthalic anhydride



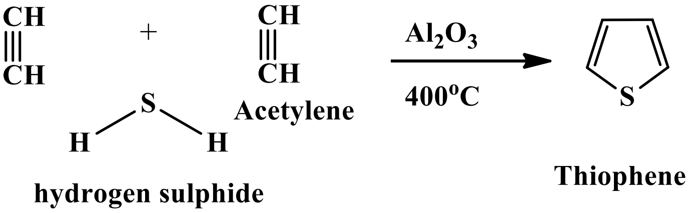
THIOPHENE

Preparation

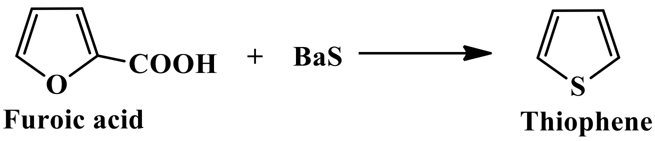
1.It is obtained by heating sodium succinate with phosphorous trisulphide



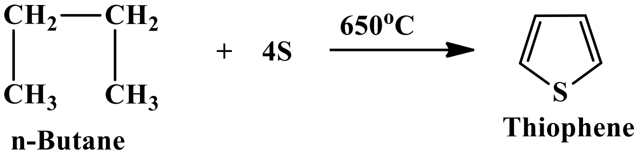
2. By passing the mixture of acetylene and hydrogen sulphide through a tube containing Al2O3 at 400 °C



3.By the distillation of furoic acid with barium sulphide yields thiophene.



4. By reaction of sulphur with n-butane in the gas phase at 650° C

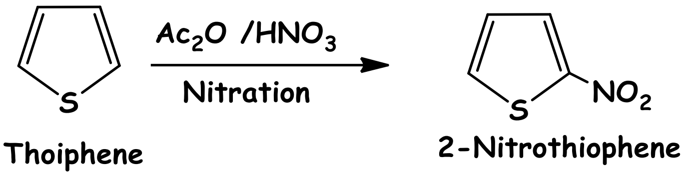


Chemical properties

1.Electrophilic substitution reaction

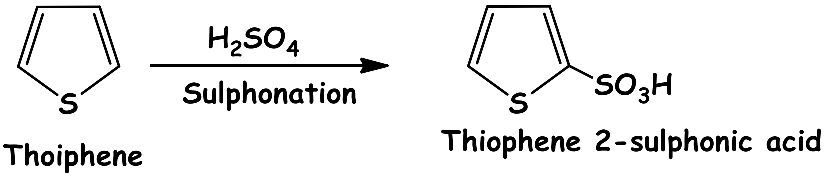
Nitration

Thiophene can be nitrated by nitric acid in acetic anhydride **[$Ac_2O = (CH_3CO)_2O$]** to yield 2-nitro thiophene.



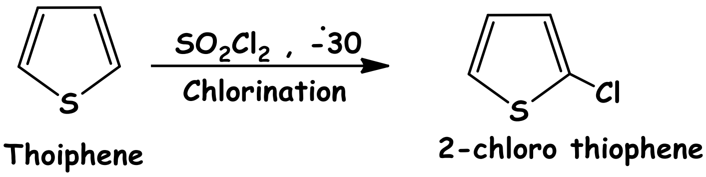
Sulphonation

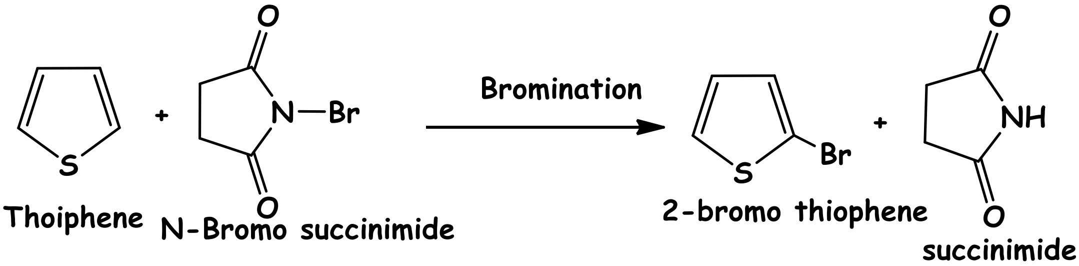
Thiophene reacts with con sulphuric acid to give thiophene 2-sulphonic acid.

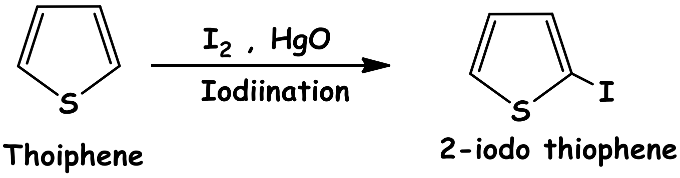


Halogenation

It reacts violently with chlorine and bromine at room temperature leading to polyhalogenated compounds or destruction of ring.But under controlled conditions halogenation takes place to yield 2-halo derivatives.

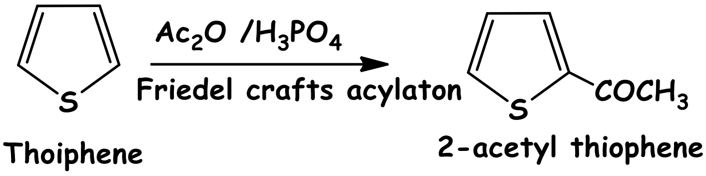






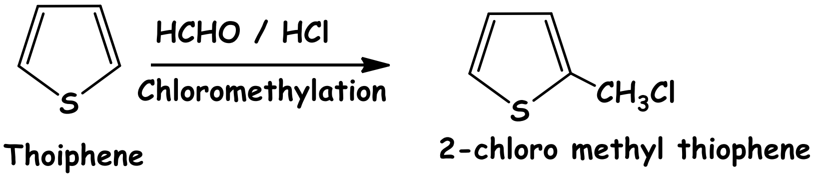
Friedel Crafts Acylation

Thiophene is acetylated with acetic anhydride **[$Ac_2O = (CH_3CO)_2O$]** in presence of phosphoric acid [H_3PO_4] to give 2-acetyl thiophene



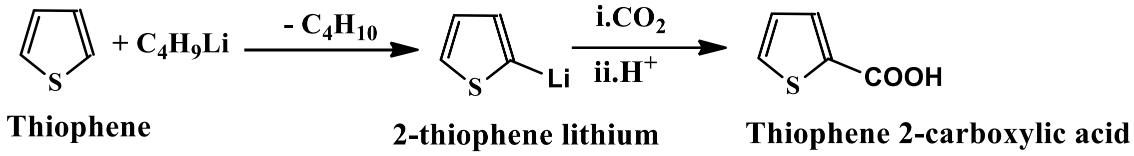
Chloromethylation

Thiophene reacts with formaldehyde and hydrochloric acid to give 2-chloro methyl thiophene.



2.Formation of organo metallic compound

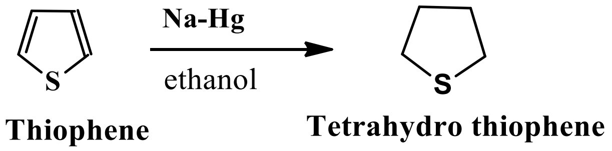
It reacts with butyl lithium to give 2-thiophene lithium which undergoes the usual reactions of organolithium compounds. (eg) It combines with carbon dioxide to form thiophene 2-carboxylic acid.



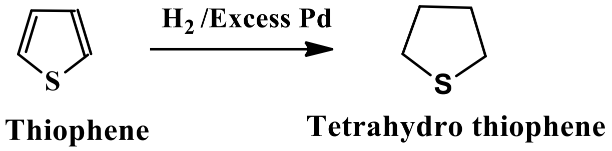
3.Addition reactions

a.Hydrogenation

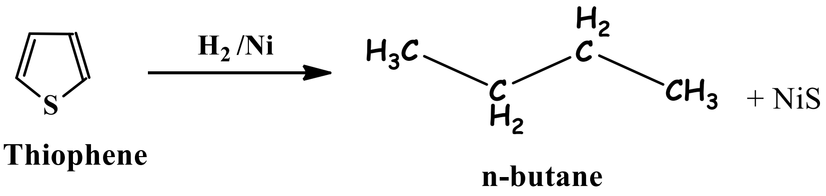
Thiophene may be hydrogenated by sodium amalgam and ethanol to form tetra hydro thiophene



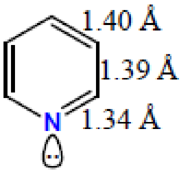
Catalytic reduction of thiophene in presence of excess Pd yields tetra hydro thiophene.

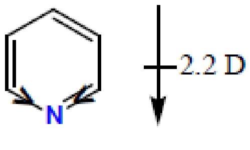


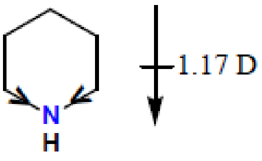
Catalytic reduction of thiophene in presence of Nickel forms n-butane .



Pyridines – Structure

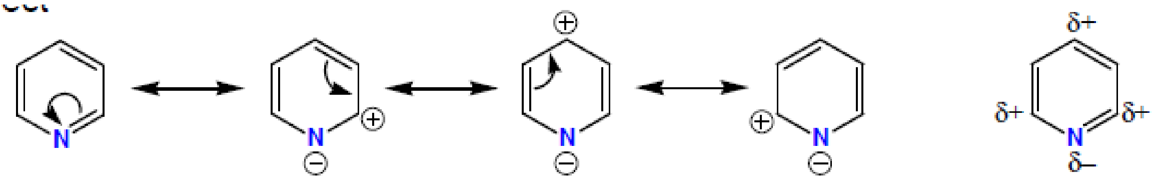




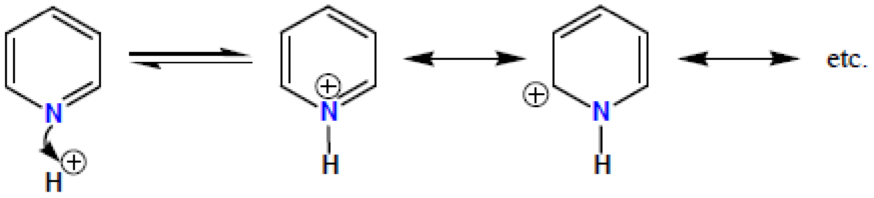


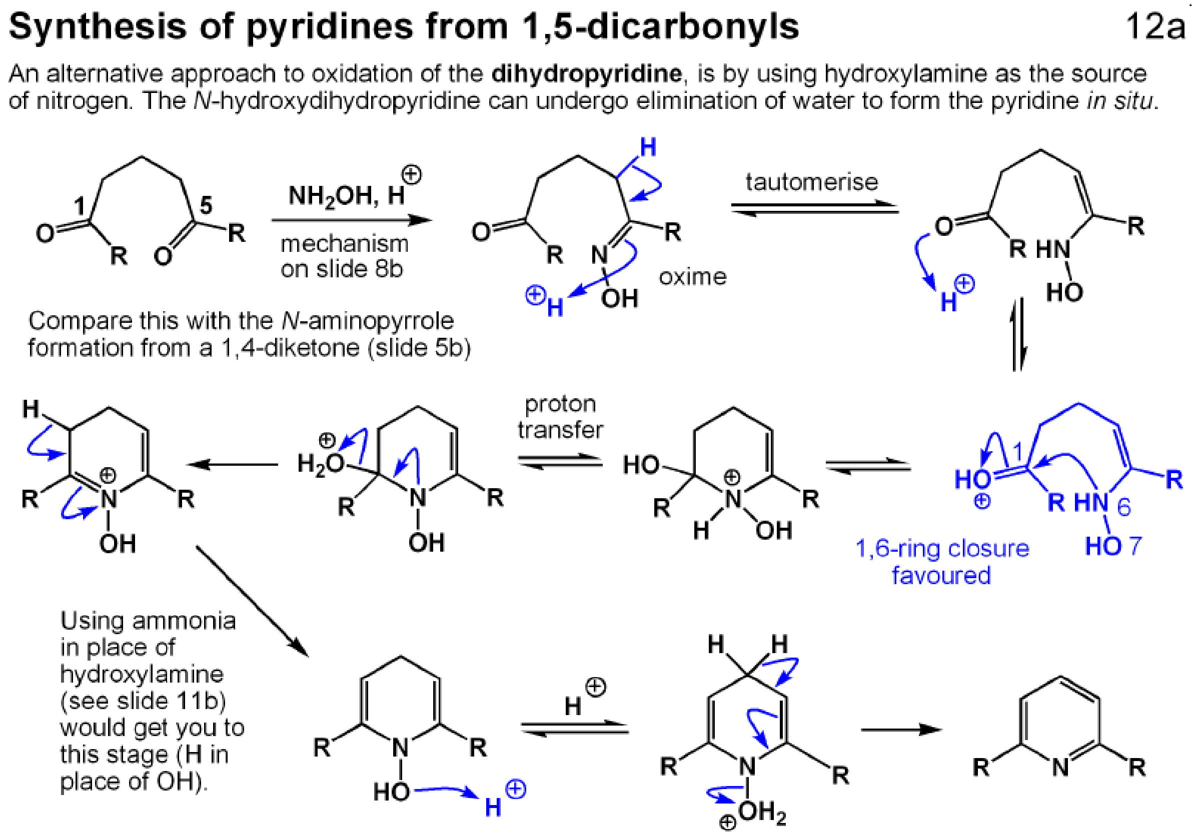
Isoelectronic with and analogous to benzene

- Stable, not easily oxidised at *C*, undergoes substitution rather than addition
- -I Effect (inductive electron withdrawal)
- -M Effect



- Weakly basic – pK*a* ~5.2 in H_2O (lone pair is **not** in aromatic sextet)
- Pyridinium salts are also aromatic – ring carbons are more d+ than in parent pyridine





Synthesis of pyridines from 1,5-dicarbonyls

An alternative approach to oxidation of the **dihydropyridine**, is by using hydroxylamine as the source of nitrogen. The *N*-hydroxydihydropyridine can undergo elimination of water to form the pyridine *in situ*.

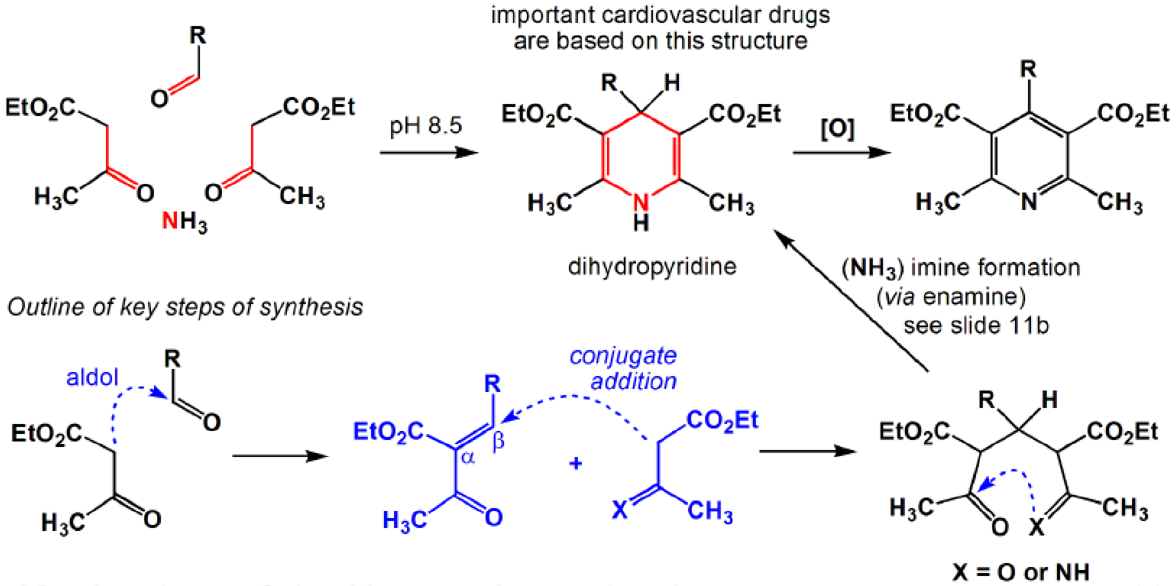
Compare this with the *N*-aminopyrrole formation from a 1,4-diketone (slide 5b)

Using ammonia in place of hydroxylamine (see slide 11b) would get you to this stage (H in place of OH).

The Hantzsch pyridine synthesis

As with the Paal-Knorr pyrrole synthesis, making pyridines from 1,5 diketones depends on the availabilty (accessibility) of the starting material. An alternative muliti-component approach, the Hantzsch synthesis, enables pyridines to be made from two β-keto esters (cf. the Knorr pyrrole route). The extra carbon atom comes in the form of the carbonyl carbon of an aldehyde.

The Hantzsch synthesis

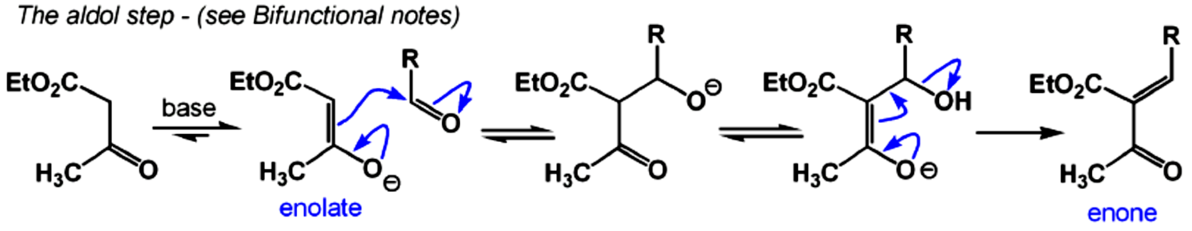


Outline of key steps of synthesis

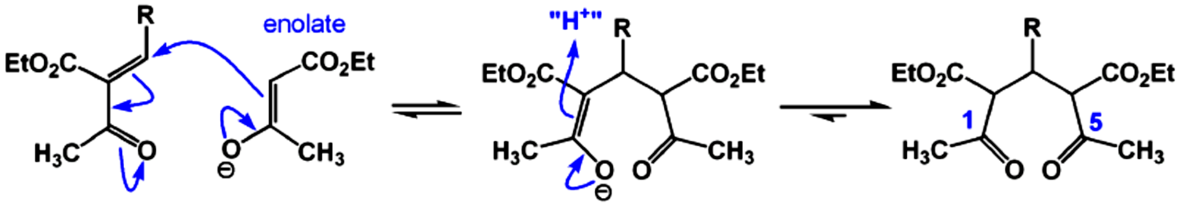
Mechanism of the Hantzsch synthesis

The exact sequence of events in a heterocyclic synthesis may vary depending on the conditions. In most cases a sensible guess can be made using knowledge of the chemistry of individual steps.

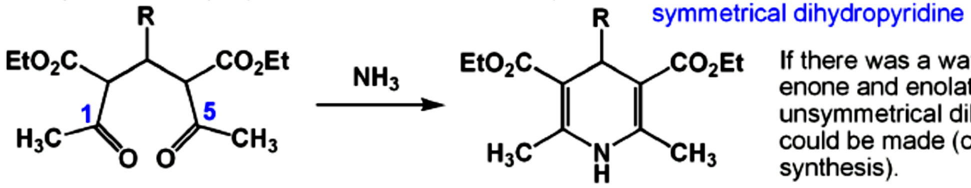
The aldol step - (see Bifunctional notes)



The conjugate addition step - (see Bifunctional notes)



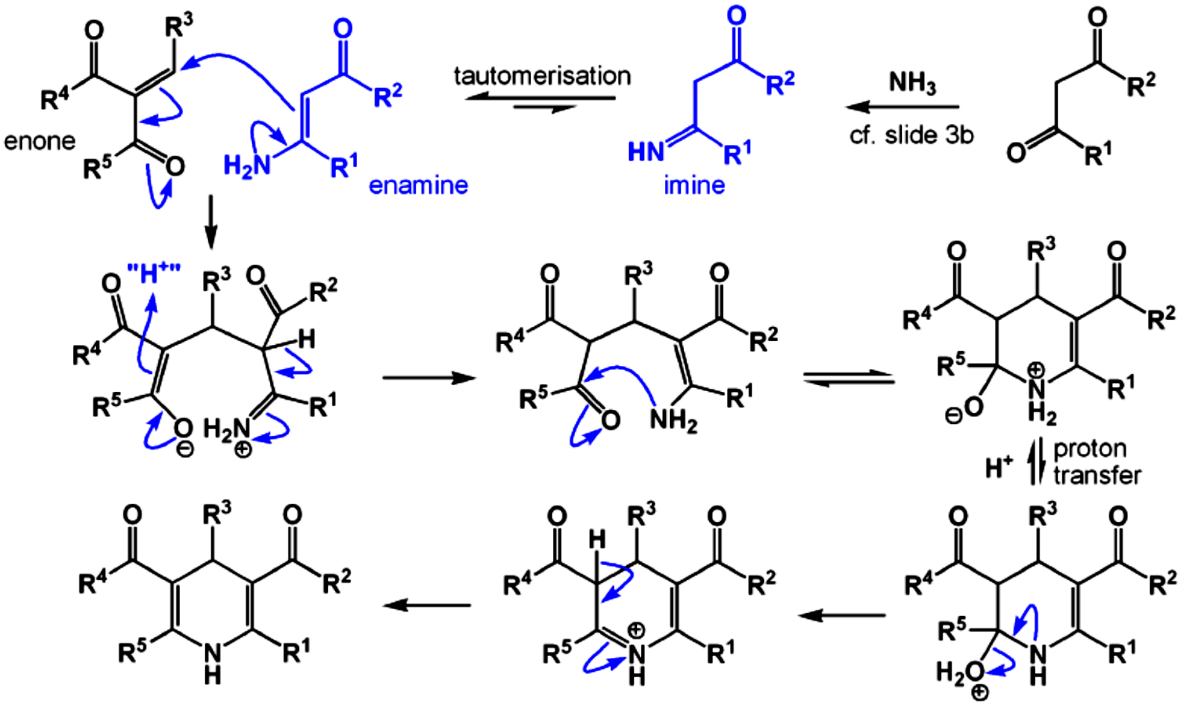
The cyclisation step - (see these notes - slide 12a)



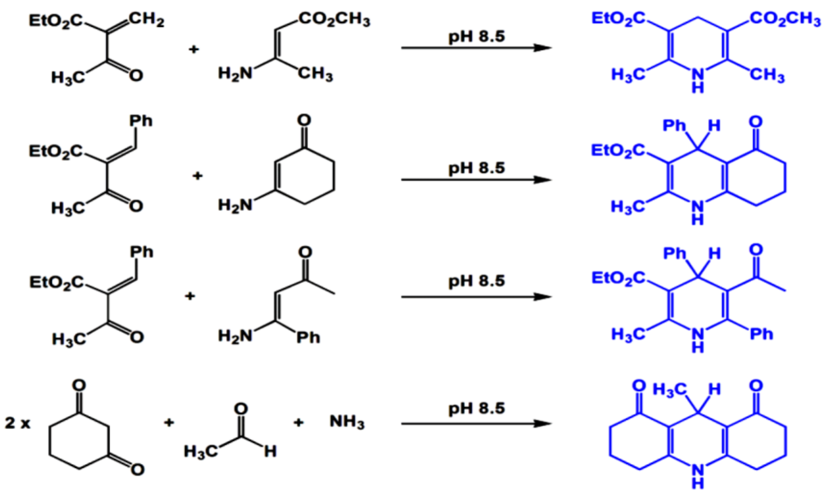
If there was a way to make the enone and enolate separately then unsymmetrical dihydropyridines could be made (cf. Knorr pyrrole synthesis).

Unsymmetrical pyridines from the Hantzsch synthesis

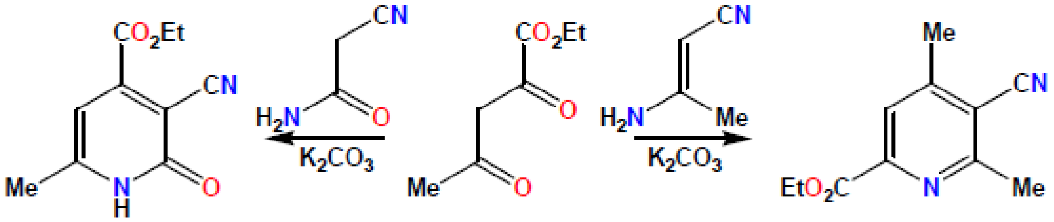
Making the enone component is relatively straightforward (see slide 13a), but in place of the enolate a (semi)stable enamine is used. The enamine is simply the tautomer of the imine derived from ammonia and in this way unsymmetrical dihydropyridines can be made.



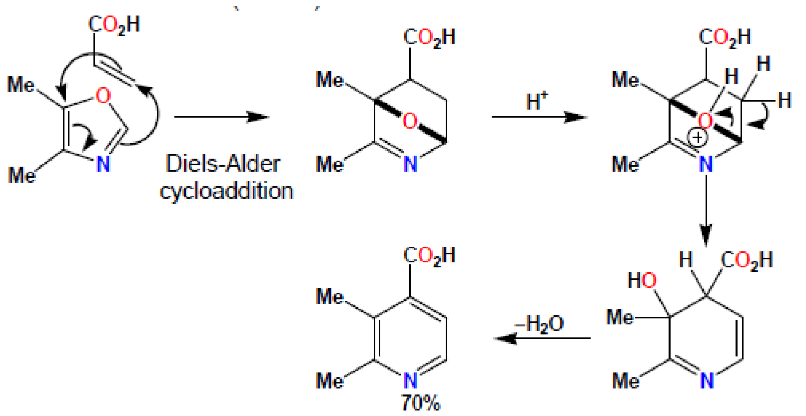
Hantzsch pyridine synthesis: examples



From Enamines or Enamine Equivalents – the Guareschi synthesis (“3+3”)



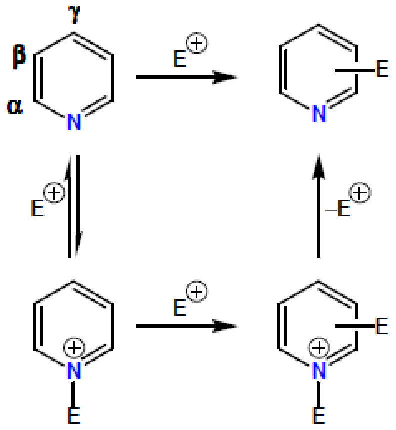
- The b-cyano amide can exist in the ‘enol’ form Using Cycloaddition Reactions (“4+2”)



Oxazoles are sufficiently low in aromatic character to react in the Diels-Alder reaction

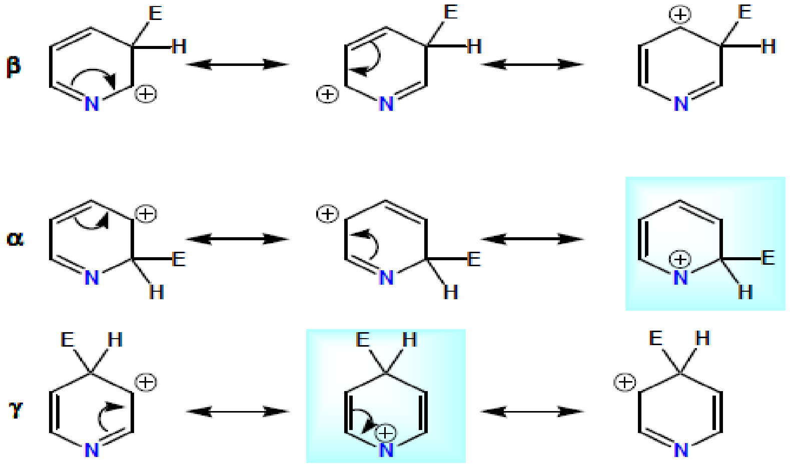
Pyridines – Electrophilic Reactions

Pathways for the Electrophilic Aromatic Substitution of Pyridines



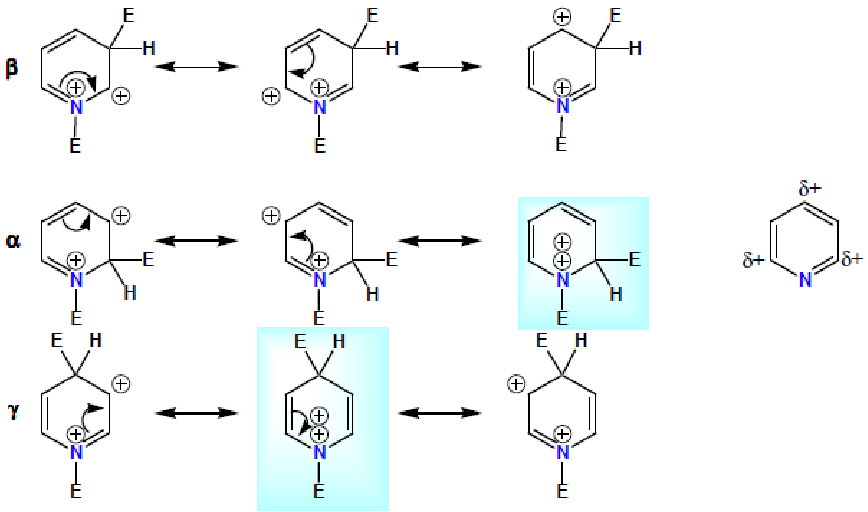
The position of the equilibrium between the pyridine and pyridinium salt depends on the substitution pattern and nature of the substituents, but usually favours the salt

Regiochemical Outcome of Electrophilic Substitution of Pyridines



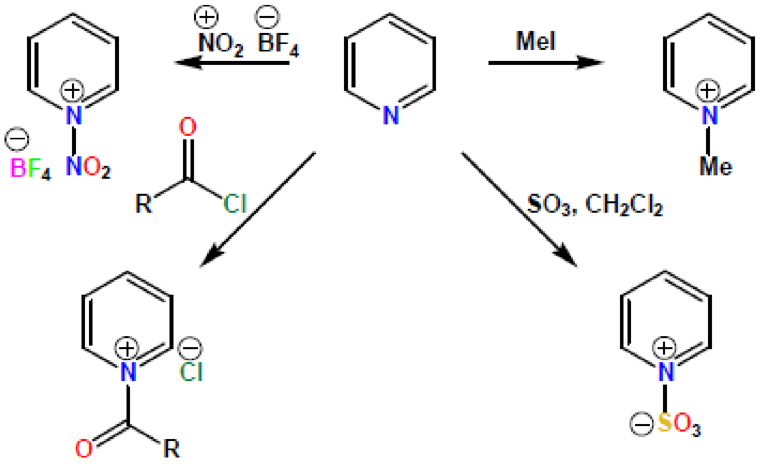
Resonance forms with a positive charge on *N* (i.e. 6 electrons) are very unfavourable
The β-substituted intermediate, and the transition state leading to this product, have more stable resonance forms than the intermediates/transition states leading to the α /γ products

Regiochemical Outcome of Electrophilic Substitution of Pyridinium Ions



- Regiochemical control is even more pronounced in the case of pyridinium ions
- In both pyridine and pyridinium systems, b substitution is favoured but the reaction is slower than that of benzene
- Reaction will usually proceed through the small amount of the free pyridine available

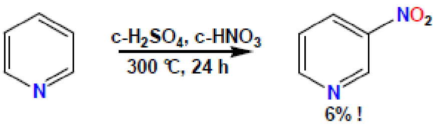
N Substitution



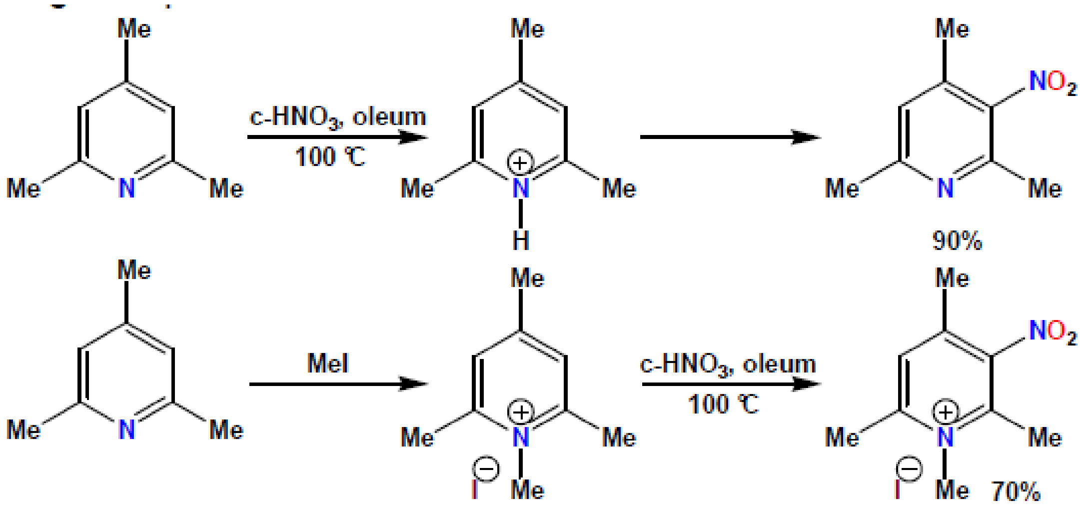
C Substitution

- Reaction at *C* is usually difficult and slow, requiring forcing conditions
- Friedel-Crafts reactions are not usually possible on free pyridines

Nitration of Pyridine

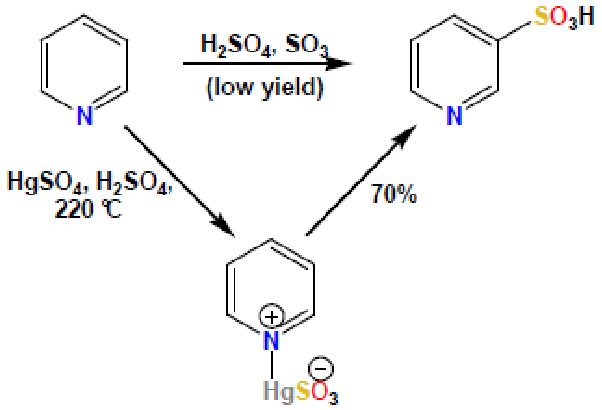


Use of Activating Groups



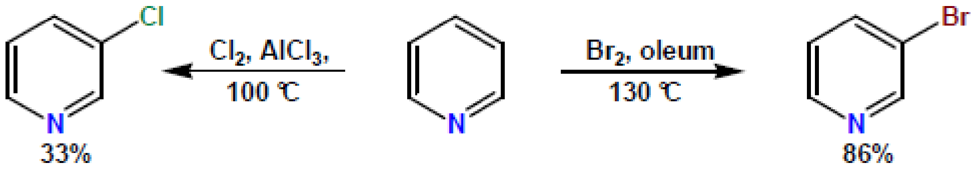
- Multiple electron-donating groups accelerate the reaction
- Both reactions proceed at similar rates which indicates that the protonation at *N* occurs prior to nitration in the first case

Sulfonation of Pyridine



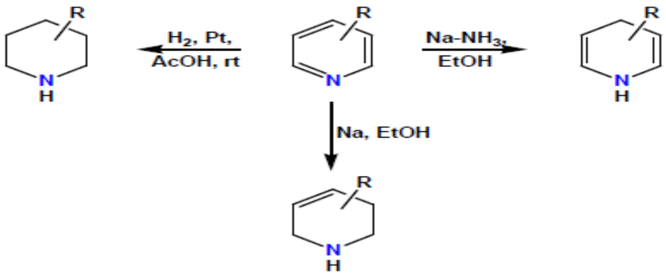
Low yield from direct nitration but good yield via a mercury intermediate

Halogenation of Pyridine



Forcing reaction conditions are required for direct halogenations

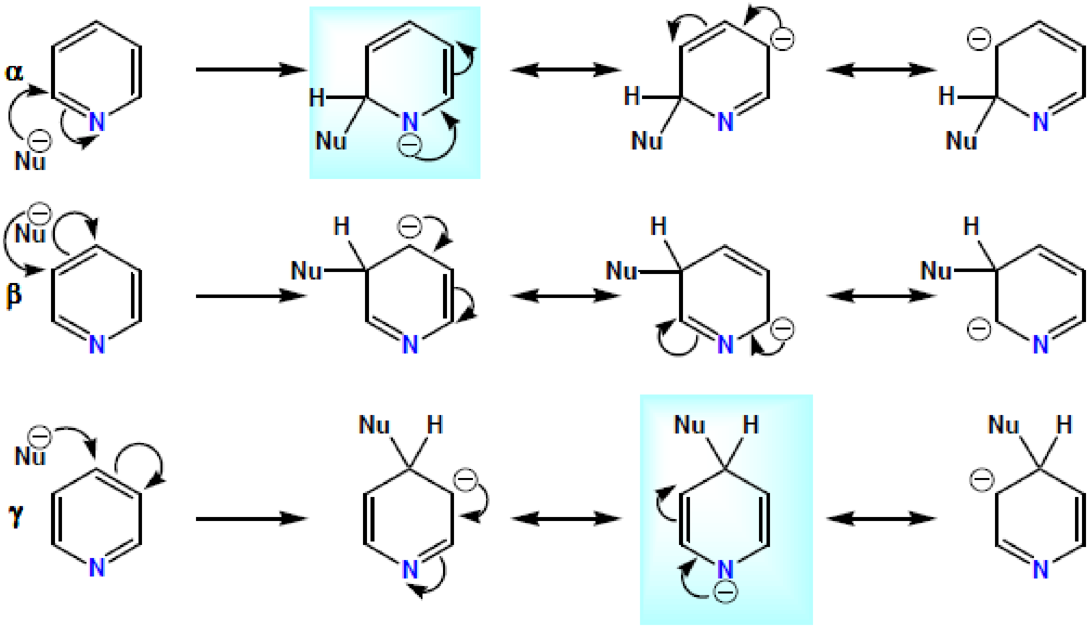
Full or Partial Reduction of Pyridines



- Pyridines generally resist oxidation at ring carbon atoms and will often undergo side-chain oxidation in preference to oxidation of the ring
- Full or partial reduction of the ring is usually easier than in the case of benzene

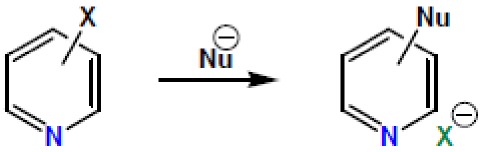
Pyridines – Nucleophilic Reactions

Regiochemical Outcome of Nucleophilic Addition to Pyridines



- Nitrogen acts as an electron sink
- β Substitution is less favoured because there are no stable resonance forms with the negative charge on *N*
- Aromaticity will is regained by loss of hydride or a leaving group, or by oxidation

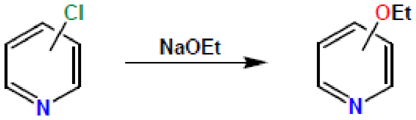
Nucleophilic Substitution

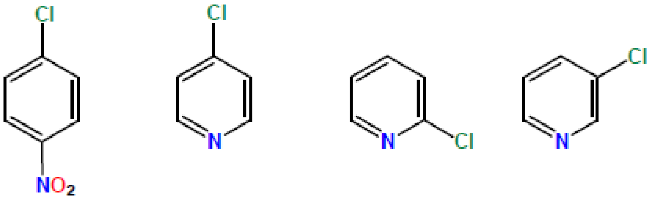


X = Cl, Br, I, (NO_2)

Nu = $MeO^{\ominus}$, NH_3, PhSH etc.

- Favoured by electron-withdrawing substituents that are also good leaving groups.
- The position of the leaving group influences reaction rate (γ > α >> β) but now α > γ

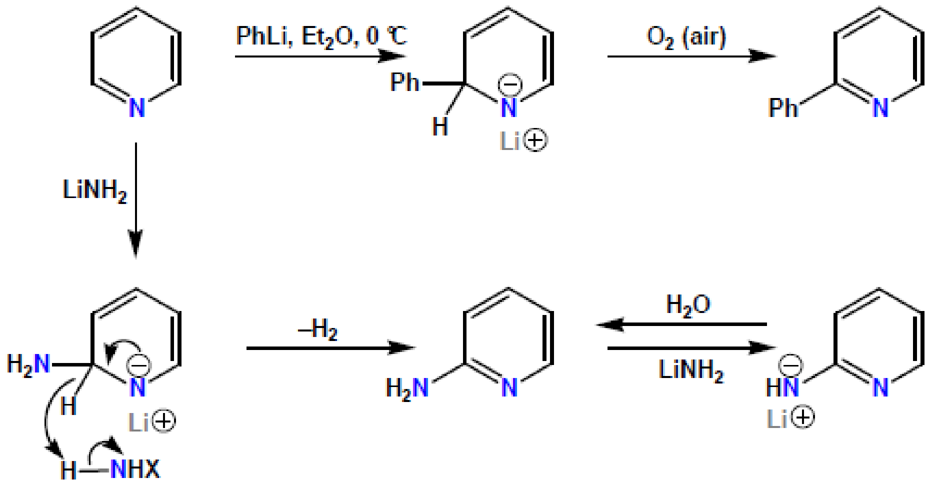




Relative rate	80	40	1	3 × 10^{-4}

Pyridines – Nucleophilic Reactions

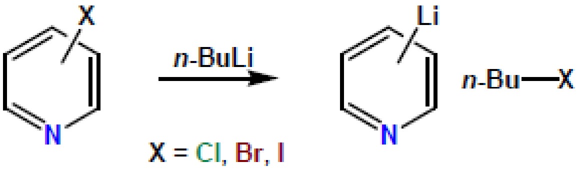
Nucleophilic Attack with Transfer of Hydride



X = H (NH$_3$) / 2-aminopyridine

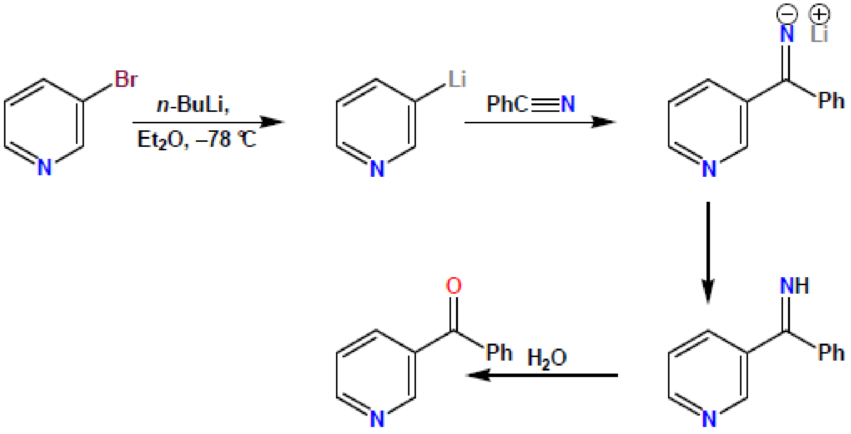
- A hydride acceptor or oxidising agent is required to regenerate aromaticity
- The reaction with LiNH$_2$ is referred to as the Chichibabin reaction

Metal-Halogen Exchange



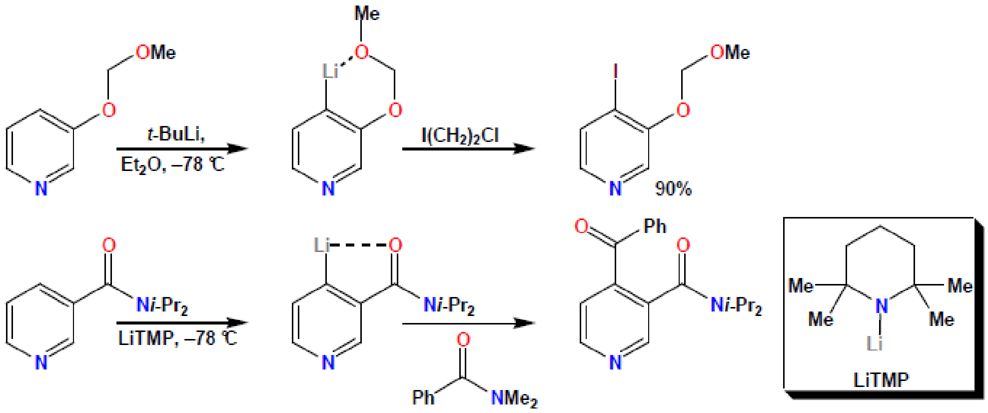
X = Cl, Br, I

- Halogenated pyridines do not tend to undergo nucleophilic displacement with alkyl lithium or alkyl magnesium reagents
- Metallated pyridines behave like conventional Grignard reagents



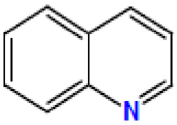
Directed Metallation

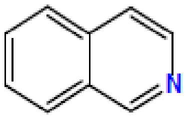
- Use of Directing Groups



- Directing groups allow direct lithiation at an adjacent position
- A Lewis basic group is required to complex the Lewis acidic metal of the base

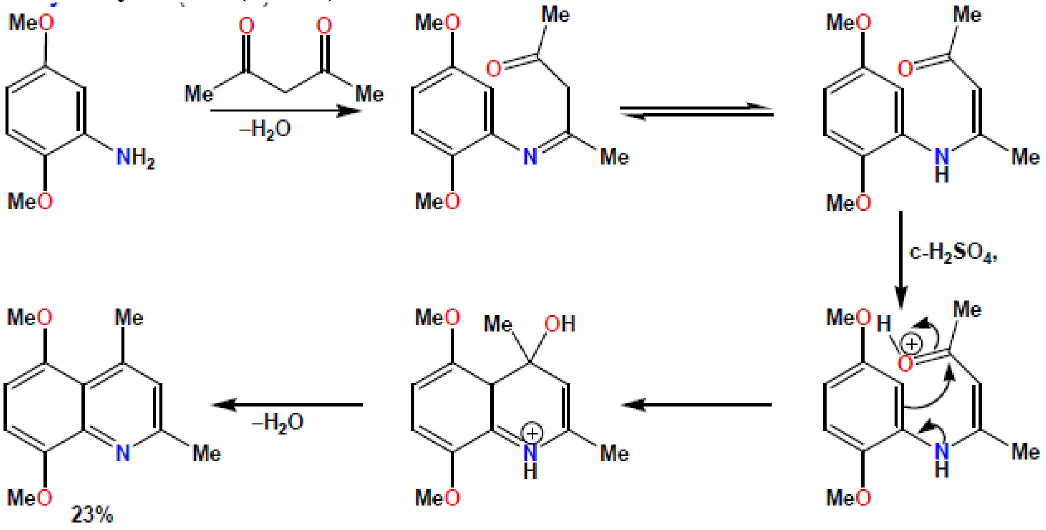
Quinolines – Synthesis



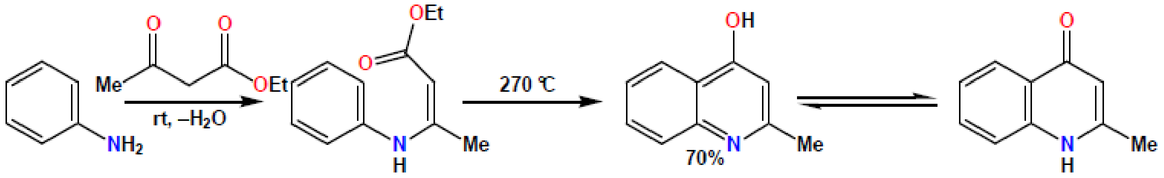


- pK*a* values (4.9 and 5.4) are similar to that of pyridine
- Possess aspects of pyridine and naphthalene reactivity e.g. form *N*-oxides and ammonium salts

Combes Synthesis ("3+3")

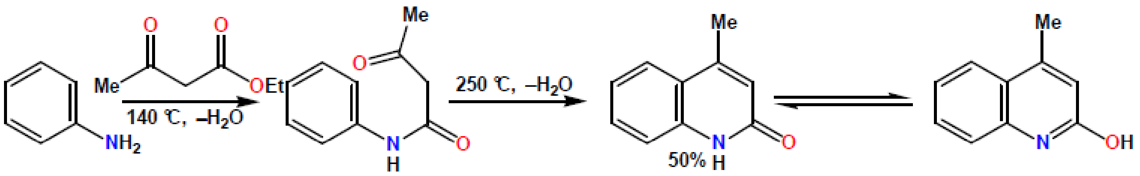


Conrad-Limpach-Knorr Synthesis ("3+3")

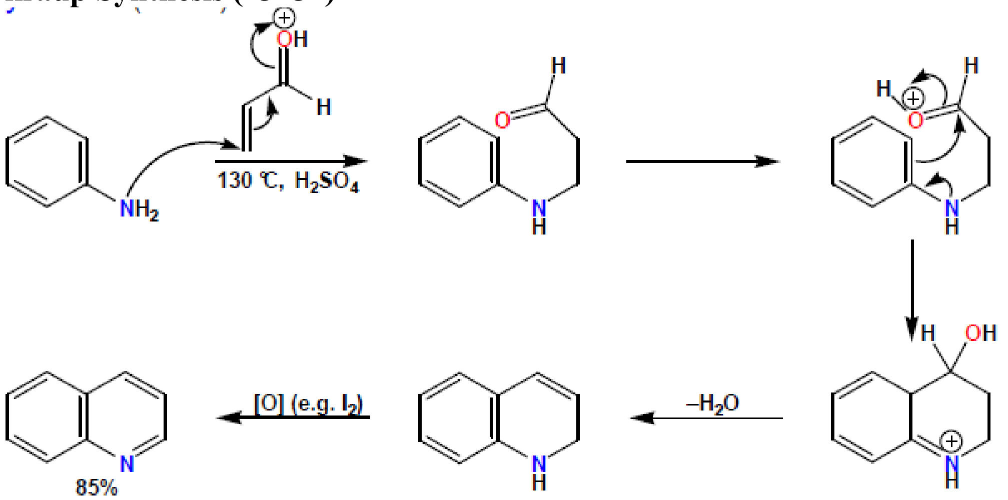


- Very similar to the Combes synthesis by a β-keto ester is used instead of a β-diketone

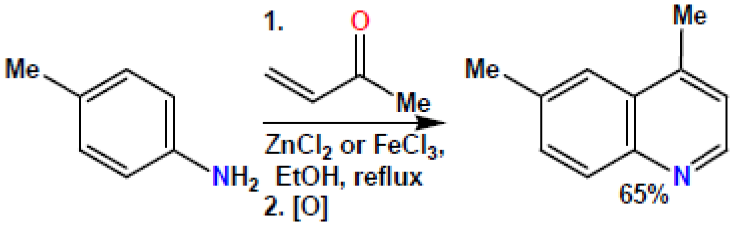
- Altering the reaction conditions can completely alter the regiochemical outcome



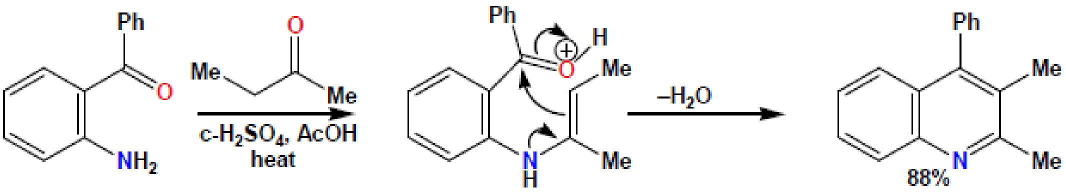
Skraup Synthesis (“3+3”)

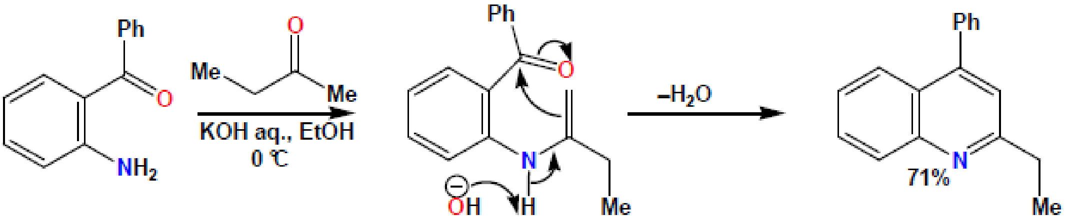


- Acrolein can be generated *in situ* by treatment of glycerol with conc. sulfuric acid
- A mild oxidant is required to form the fully aromatic system from the dihydroquinoline



Friedlander Synthesis (“4+2”)

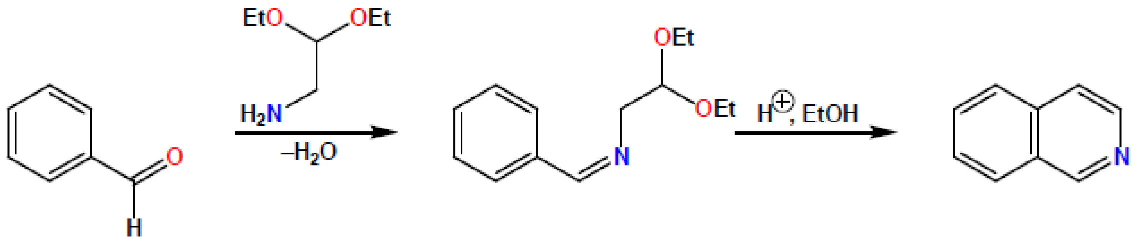




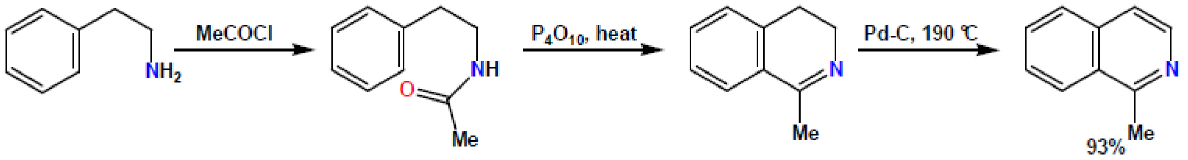
- The starting acyl aniline can be difficult to prepare
- Acidic and basic conditions deliver regioisomeric products in good yields

Isoquinolines – Synthesis

Pomeranz-Fritsch Synthesis (“3+3”)

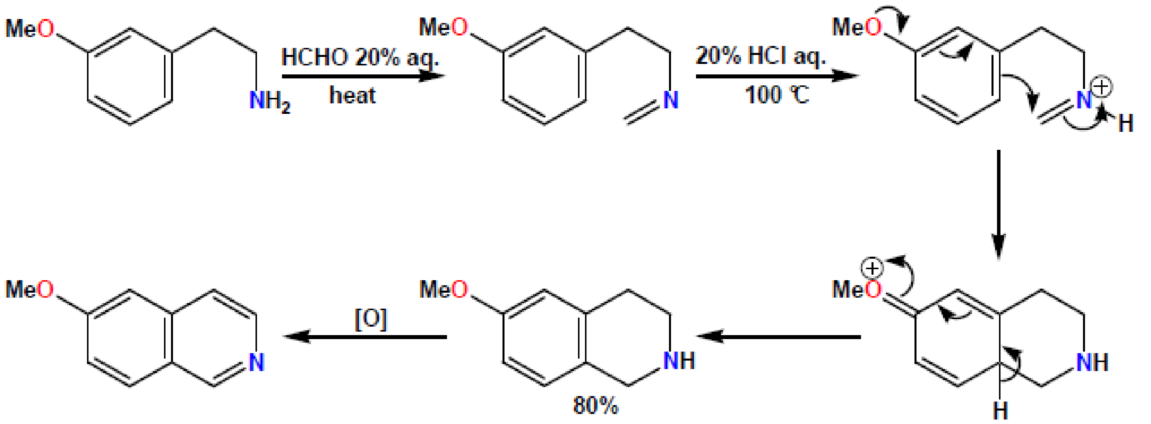


Bischler-Napieralski Synthesis (“5+1”)



- Cyclisation can be accomplished using $POCl_3$ or PCl_5
- Oxidation of the dihydroisoquinoline can be performed using a mild oxidant

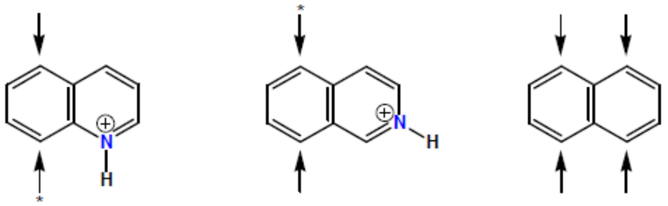
Pictet Spengler Synthesis (“5+1”)



- An electron-donating substituent on the carboaromatic ring is required
- A tetrahydroisoquinoline is produced and subsequent oxidation is required to give the fully aromatic isoquinoline

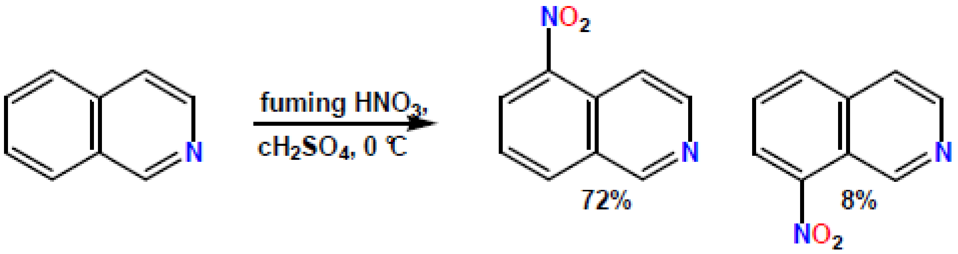
Quinolines/Isoquinolines –Electrophilic Reactions

Regiochemistry



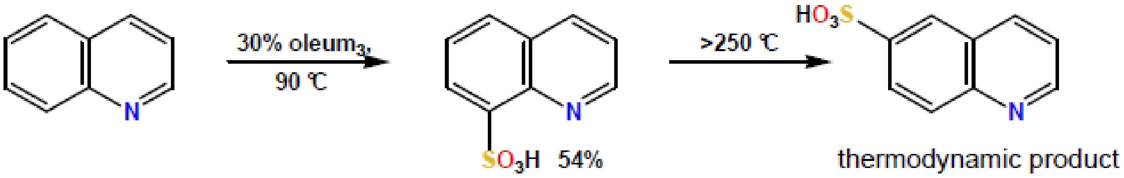
- Under strongly acidic conditions, reaction occurs *via* the ammonium salt
- Attack occurs at the benzo- rather than hetero-ring
- Reactions are faster than those of pyridine but slower than those of naphthalene

Nitration



In the case of quinoline, equal amounts of the 5- and 8-isomer are produced

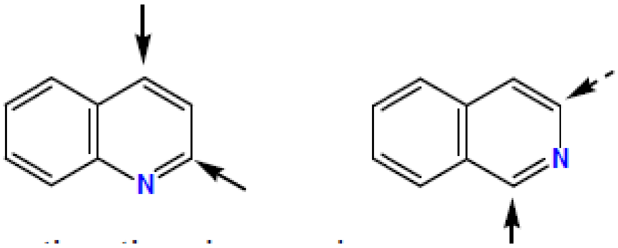
Sulfonation



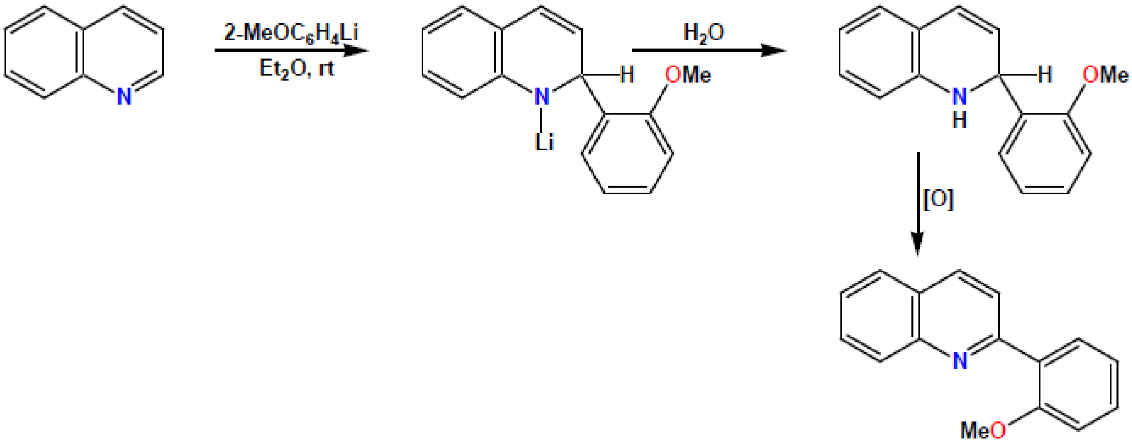
- Halogenation is also possible but product distribution is highly dependent on conditions
- It is possible to introduce halogens into the hetero-ring under the correct conditions.
- Friedel-Crafts alkylation/acylation is not usually possible

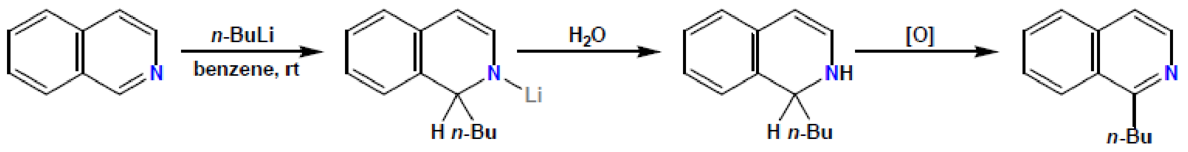
Quinolines/Isoquinolines –Nucleophilic Reactions

Regiochemistry



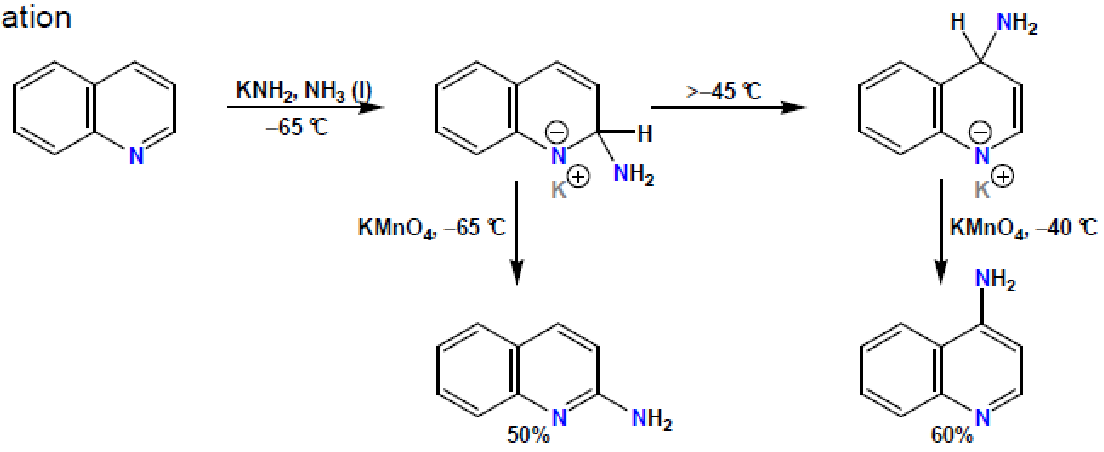
- Attack occurs at hetero- rather than benzo-ring
- They are enerally more reactive than pyridines to nucleophilic attack





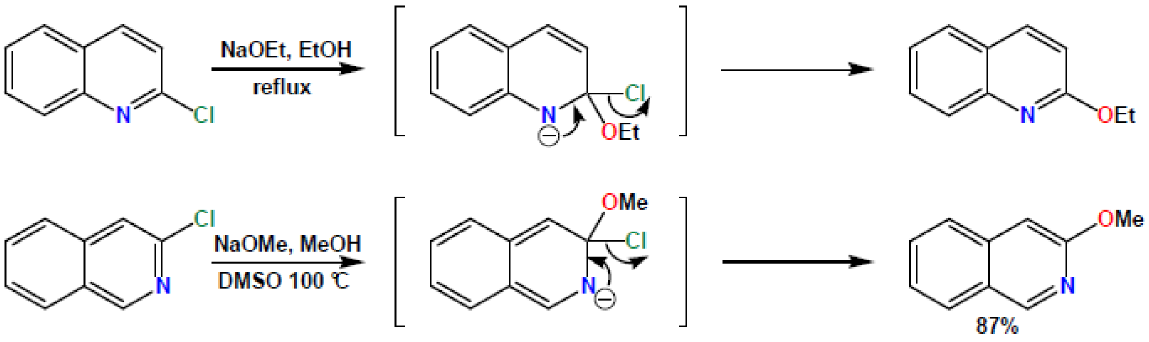
Oxidation is required to regenerate aromaticity.

Amination

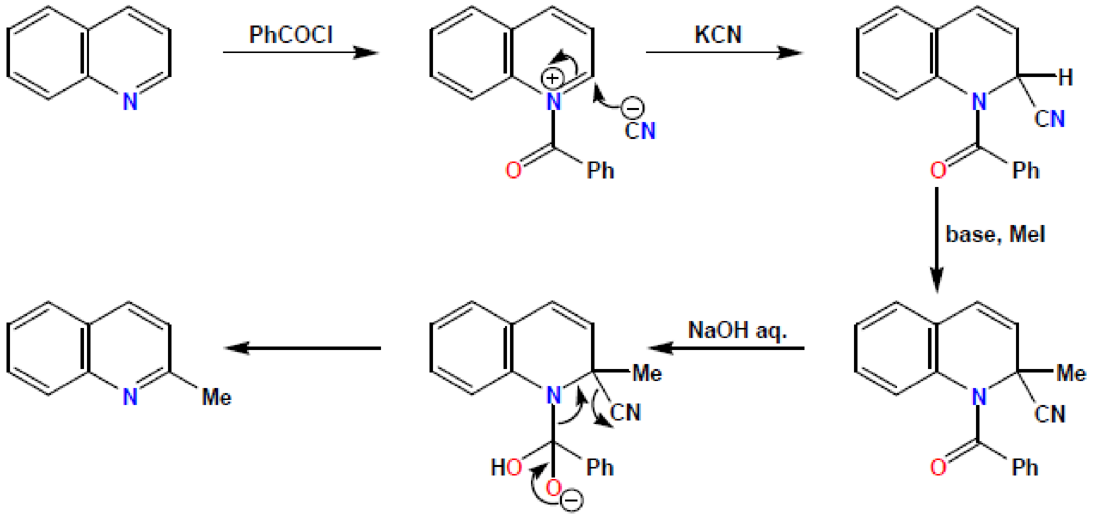


thermodynamic product

Displacement of Halogen



The Reissert Reaction



- The proton adjacent to the cyano group is extremely acidic
- The reaction works best with highly reactive alkyl halides

Terpenoids

Introduction:

- Terpenoids also form a group of naturally occurring compounds majority of which occur in plants, a few of them have also been obtained from other sources.
- Terpenoids are volatile substances which give plants and flowers their fragrance.
- They occur widely in the leaves and fruits of higher plants, conifers, citrus and eucalyptus. The term 'terpene' was given to the compounds isolated from terpentine, a volatile liquid isolated from pine trees.
- The simpler mono and sesqui terpenes are chief constituent of the essential oils obtained from sap and tissues of certain plant and trees.
- The di and tri terpenoids are not steam volatile. They are obtained from plant and tree gums and resins.
- Tertraterpenoids form a separate group of compounds called 'Carotenoids' The term 'terpene' was originally employed to describe a mixture of isomeric hydrocarbons of the molecular formula $C_{10}H_{16}$ occurring in the essential oils obtained from sap and tissue of plants, and trees. But there is a tendency to use more general term 'terpenoids' which include hydrocarbons and their oxygenated derivatives. However the term terpene is being used these days by some authors to represent terpenoids.
- By the modern definition: **"Terpenoids are the hydrocarbons of plant origin of the general formula (C_5H_8)n as well as their oxygenated, hydrogenated and dehydrogenated derivatives."**

Physical Properties:

- Terpeniods are colourless liquid.
- Soluble in organic solvents and insoluble in water.
- Most of the terpenoids are optically active.
- Volatile in nature.
- Boiling point 150-180^{o}C.

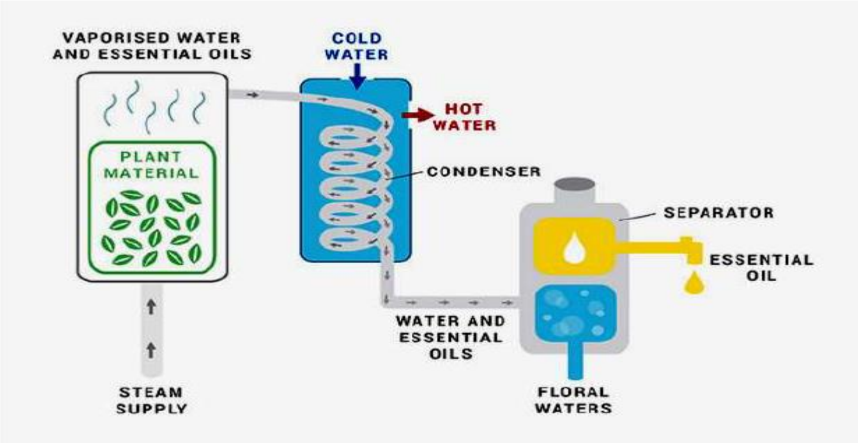
Chemical Properties:

- They are unsaturated compounds.
- They undergo addition reaction with hydrogen, halogen, halogen acids to form addition products like NOCl, NOBr and hydrates.
- They undergo polymerisation and dehydrogenation in the ring.
- On thermal decomposition, terpenoid gives isoprene as one of the product.

ISOLATION OF TERPENOIDS:

(i) Isolation of essential oils from plant parts

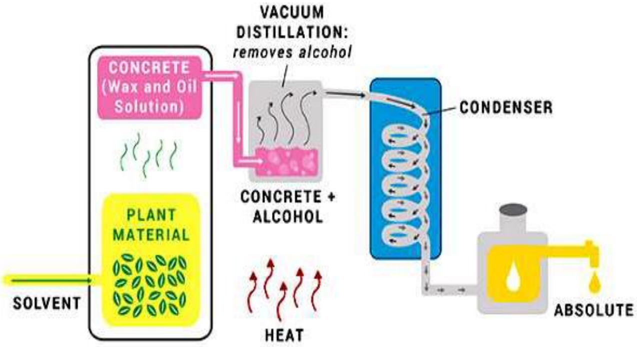
a) Steam distillation method



- Steam distillation is most widely used method.
- In this method macerated plant material is steam distilled to get essential oils into the distillate form these are extracted by using pure organic volatile solvents.
- If compound decomposes during steam distillation, it may be extracted with petrol at 50°C. After extraction solvent is removed under reduced pressure.

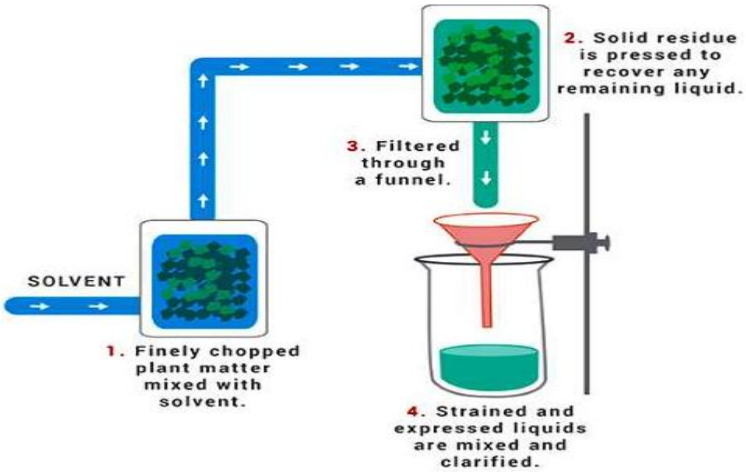
b) Solvent extraction

- Solvents like hexane and ethanol is used to isolate essential oils.
- It is used for the plant parts have low amount of essential oil.
- Plant material are treated with the solvent, it produces a waxy aromatic compound called a "concrete."
- Then it mixed with alcohol, the oil particles are released.
- Then it passess through a condenser then it separated out.
- This oil is used in perfume industry or for aromatherapy purposes



c) Maceration

- **Advantage:** More plant's essence is captured.
- In this method the plant material is converted into moderately coarse powder.
- Plant material is placed in a closed vessel.
- To this solvent is added.
- The mixture is allowed to stand for 1 week, then the liquid is strained.
- Solid residue is pressed to recover any remaining liquid.
- Strained and expressed liquids are mixed



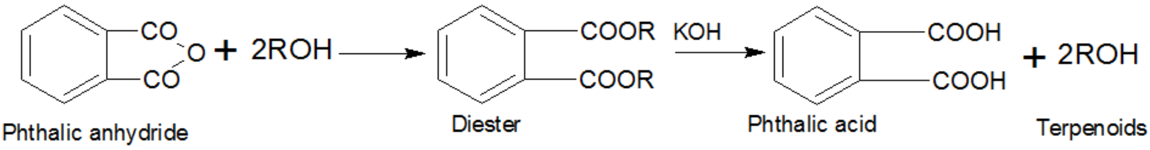
d) Adsorption in purified fats/ Enfluerage:

- The fat is warmed to 500C on glass plates.
- Then the fat is covered with flower petals and it kept for several days until it saturated with essential oils.
- Then the old petals are replaced by fresh petals, it is repeated.
- After removing the petals, the fat is treated with ethanol when all the oils present in fat are dissolved in ethanol.
- The alcoholic distillate is then fractionally distilled under reduced pressure to remove the solvent.
- Recently the fat is replaced by coconut charcoal, due to greatestability and higher adsorptive capacity.

(ii) Separation of terpenoid from essential oils

a) Chemical methods

- Essential oils containing terpenoid hydrocarbon + nitrosyl chloride in chloroform form crystalline adduct of hydrocarbons.
- Essential oil containing alcohols.



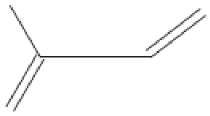
- Terpenoid containing aldehyde and ketone treated with $NaHSO_3$, phenyl hydrazine or semicarbazone.
- After separation it is decomposed to get terpenois.

b) Physical methods

- Chromatography
- Fractional distillation

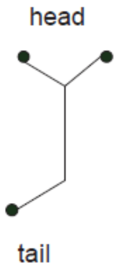
Isoprene rule:

- Thermal decomposition of terpenoids give isoprene as one of the product.
- Otto Wallach pointed out that terpenoids can be built up of isoprene unit.
- Isoprene rule stats that the terpenoid molecules are constructed from two or more isoprene unit.

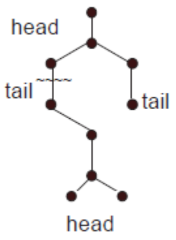


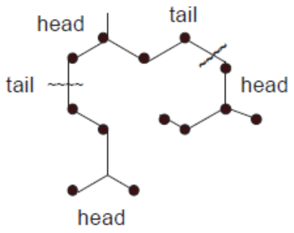
isoprene unit

- Further Ingold suggested that isoprene units are joined in the terpenoid via ‘head to tail’ fashion.
- **Special isoprene rule** states that the terpenoid molecule are constructed of two or more isoprene units joined in a ‘head to tail’ fashion.

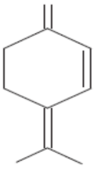


- But this rule can only be used as guiding principle and not as a fixed rule.
- For example carotenoids are joined tail to tail at their central and there are also some terpenoids whose carbon content is not a multiple of five.
- In applying isoprene rule we look only for the skeletal unit of carbon.
- The carbon skeletons of open chain monotrpenoids and sesqui terpenoids are,

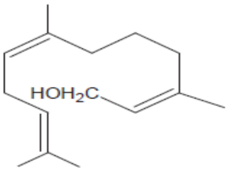




Examples.

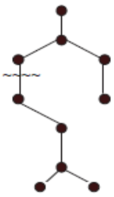


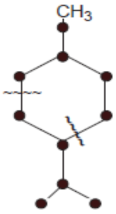
Myrcene
(monoterpene)



Farnesol (Sesquiterpene)

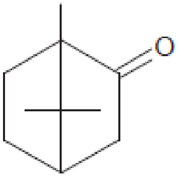
- Ingold (1921) pointed that a gem alkyl group affects the stability of terpenoids.
- He summarized these results in the form of a rule called ‘gem dialkyl rule’ which may be stated as "Gem dialkyl group tends to render the cyclohexane ring unstable where as it stabilizes the three, four and five member rings.”
- This rule limits the number of possible structure in closing the open chain to ring structure.
- Thus the monoterpenoid open chain give rise to only one possibility for a monocyclic monoterpenoid i.e the p-cymene structure.



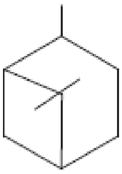


P-cymene structure

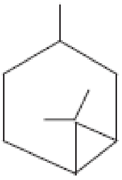
- Bicyclic monoterpenodis contain a six member and a three member ring.
- Thus closure of the ten carbon open chain monoterpenoid gives three possible bicyclic structures.



Camphor
(6+5) system



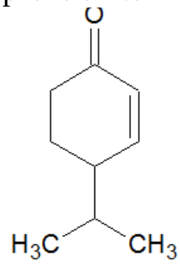
Pinane
(6+4) system



Carane
(6+3) System

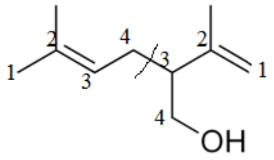
Violations of isoprene rule

- Carbon content of certain terpenoids are not a multiple of five.
- Eg: Cryptone, a naturally occurring ketonic terpenoid contains nine carbon atoms , it cannot be divided into two isoprene units



Cryptone

- In certain terpenoids isoprene rule is violated.
- Eg: Lavandulol is composed of two isoprene units are linked through C_3 and C_4.



Lavandulol (3,4-linkage)

STRUCTURAL ELUCIDATION OF CITRAL

Constitution of citral

- Molecular formula: $C_{10}H_{16}O$

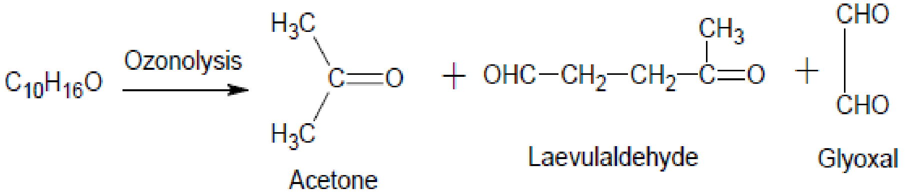
(a) Presence of two double bonds:

Citral is treated with bromine or hydrogen, it forms citratetrabromide.

- It indicates the presence of two double bonds.

$$C_{10}H_{16}O \xrightarrow{Br_2} C_{10}H_{16}O.Br_4$$

- Citral on ozonolysis yield acetone, laevulaldehyde and gyoxal.
- It indicate that citral is an acyclic compound containing two double bond.



(b) Presence of an aldehyde group:

- Formation of an oxime with hydroxylamine indicates the presence of an oxo group in citral.
- Citral on reduction with Na/Hg it gives an alcohol called geraniol and on oxidation with silver oxide to yield a Geranic acid with same number of carbon atom as citral.
- Indicate that oxo group in citral is an aldehyde group.

$$\underset{\text{Geranic acid}}{C_{10}H_{16}O_2} \xleftarrow[Ag_2O]{[O]} \underset{\text{Citral}}{C_{10}H_{16}O} \xrightarrow[Na/Hg]{2[H]} \underset{\text{Geraniol}}{C_{10}H_{18}O}$$

d) Citral as an acyclic compound:

- Formation of above products shows that citral is an acyclic compound containing two double bonds.
- Corresponding saturated hydrocarbon of citral (molecular Formula $C_{10}H_{22}$) corresponds to the general formula C_nH_{2n+2} for acyclic compounds, indicating that citral must be an acyclic compound.

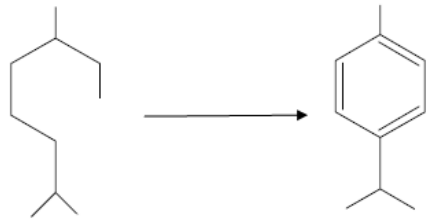
e) Carbon skeleton of citral:

- Citral is heated with potassium hydrogen sulphate, it gives pcymene (known compound).

$$C_{10}H_{16}O \xrightarrow[-H_2O]{KHSO_4} C_{10}H_{14}$$

P-cymene

- Formation of p-cymene and product obtained from the ozonolysis reveals that C-skeleton (I) of citral is formed by the joining of two isoprene units in the head to tail fashion.
- Formation of p-cymene also reveals the position of methyl and isopropyl group in citral.

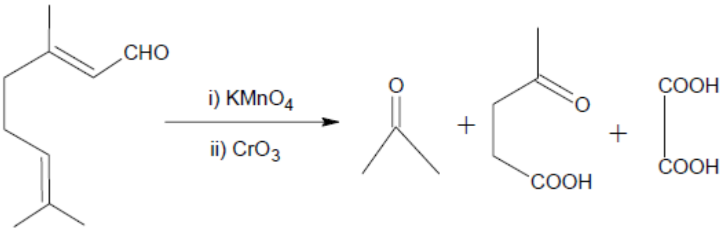


Carbon skeleton of citral P-cymene

(I)

f) Oxidation

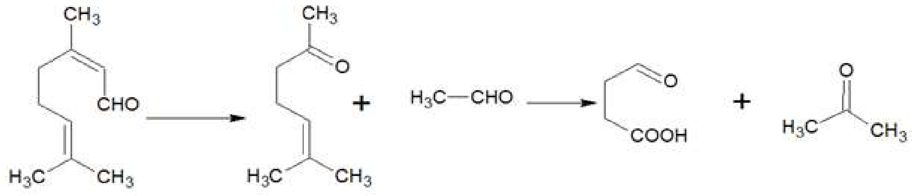
- Citral undergo oxidation with $KMnO_4$ followed by chromic acid yield acetone, oxalic acid and laevulic acid.
- These reactions are only explained if the citral has structure (II).



Citral (II) Acetone Laevulic acid Oxalic acid

Support for the structure (II)

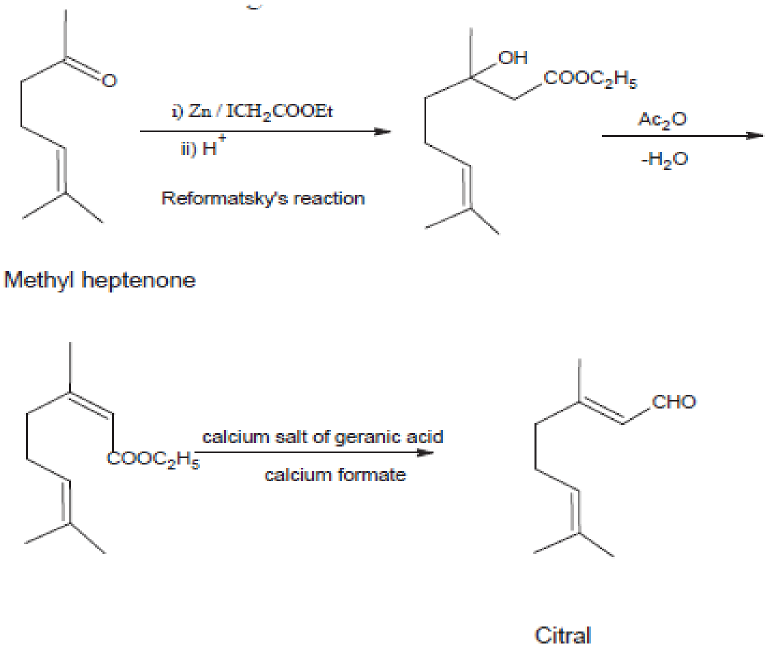
- Verley found that citral on boiling with aqueous potassium carbonate yielded 6-methyl hept-5-ene-2-one and acetaldehyde.
- The formation of these can only be explained on the basis of proposed structure of citral (II) if it undergoes cleavage at α,β- double bond.
- Further methylheptenone undergo oxidation yields acetone and laevulic acid.
- These can be only explained on the basis of structure (II).



Citral (II) 6-Methyl-5-en-2-one Laevulic acid Acetone

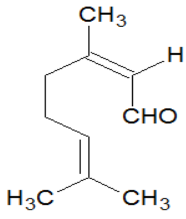
Confirmation synthesis of citral by Barbier-Bouveault-Tiemann's synthesis

- In this synthesis methyl heptenone is converted to geranic ester by using Reformatsky's reaction.
- Geranic ester is then converted to citral by distilling a mixture of calcium salts of geranic and formic acids.

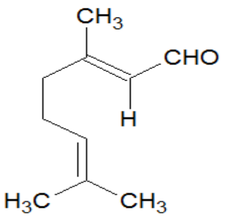


Isomerism of citral

- Two geometrical isomers occur in nature
- Two isomers are differ in the arrangement of aldehyde group about double bond in 2,3 position.
- One is cis-citral or Neral and other is trans- citral or geranial.



cis- citral (neral)



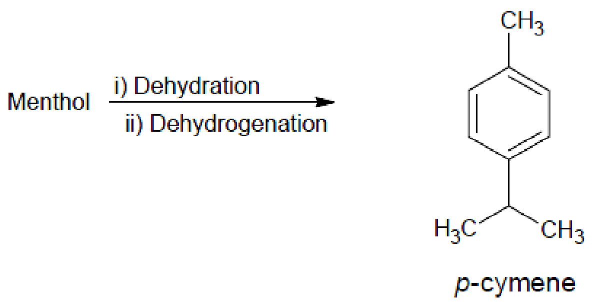
trans- citral (geranial)

STRUCTURAL ELUCIDATION OF MENTHOL

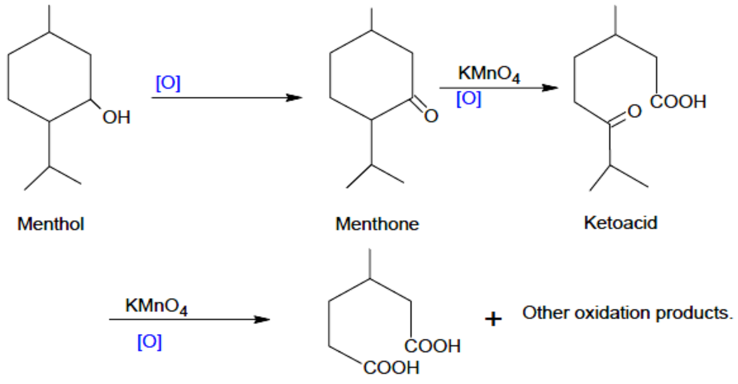
- Molecular formula: $C_{10}H_{20}O$
- Menthol forms esters readily with acids it means that it possess an alcoholic group.
- Menthol then oxidized to yield ketone, menthone ($C_{10}H_{18}O$) it indicate that the alcoholic group is secondary in nature.

$$\underset{\text{Menthol}}{C_{10}H_{20}O} \xrightarrow{[O]} \underset{\text{Menthone}}{C_{10}H_{18}O}$$

- On dehydration followed by dehydrogenation it yields *p*-cymene.
- It indicate the presence of *p*-cymene skeleton (p-menthane skeleton) in two compounds.

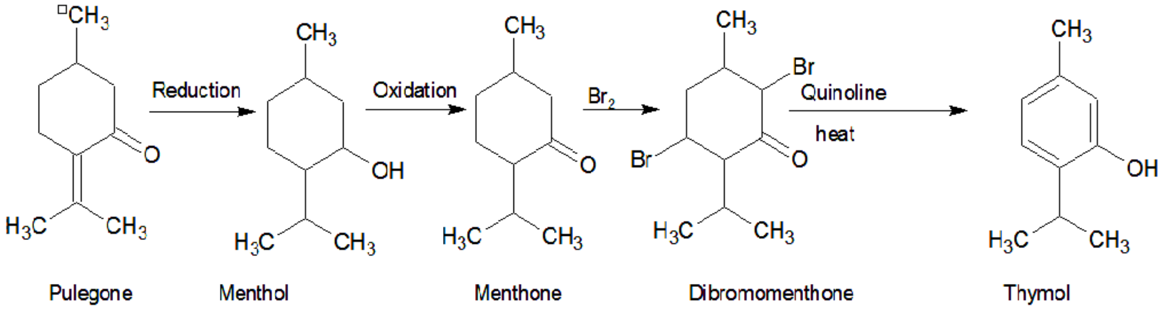


- Menthone on oxidation with $KMnO_4$ yields ketoacid $C_{10}H_{18}O_3$.
- It possess one keto group and one carboxyl group and is called ketomenthylic acid.
- It readily oxidized to 3-methyladipic acid.
- These reactions can be explained by considering the following structure of menthol.



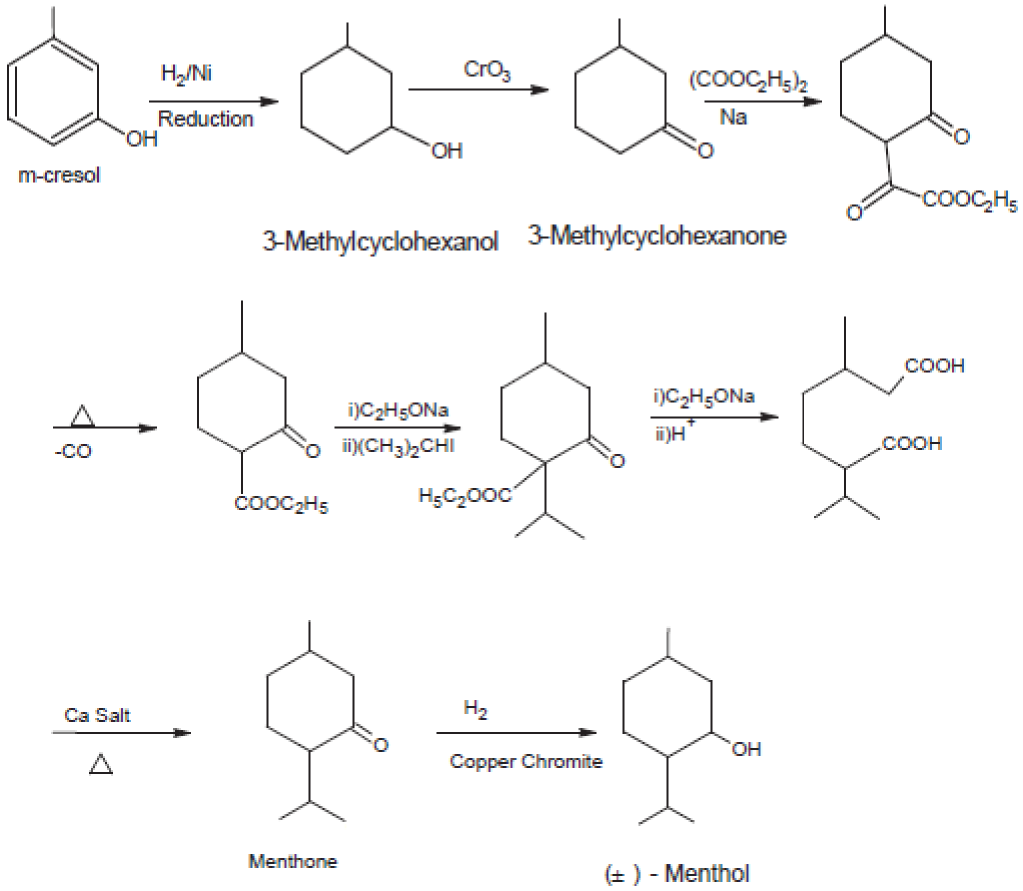
β-methyl adipicacid.

- Menthol was converted to *p*-Cymene [1-methyl-4-isopropylbenzene], which was also obtained by dehydrogenation of pulegone.
- Pulegone on reduction yields menthone which on further reduction gives menthol.



SYNTHESIS

Finally the structure of menthone and menthol have been confirmed by the synthesis given by Kotz and Hese from m-cresol.


m-cresol
OH
H_2/Ni
Reduction
OH
3-Methylcyclohexanol
CrO_3
O
3-Methylcyclohexanone
$(COOC_2H_5)_2$
Na
O
O
$COOC_2H_5$
Δ
-CO
O
$COOC_2H_5$
i)C_2H_5ONa
ii)$(CH_3)_2CHI$
O
H_5C_2OOC
i)C_2H_5ONa
ii)H^+
COOH
COOH
Ca Salt
Δ
O
Menthone
H_2
Copper Chromite
OH
(±) - Menthol

UNIT - V
POLYMERS

Polymers-definition - polymerization - types - addition and condensation polymerization - free radical polymerization mechanism - effect of structure on the properties of polymers - strength, plastic deformation, elasticity and crystallinity - plastics - preparation - properties and uses of PVC, teflon, polycarbonate, polyurethane, nylon-6,6, PET,KEVLAR-Green polymers- Introduction – poly lactic acid (PLA)

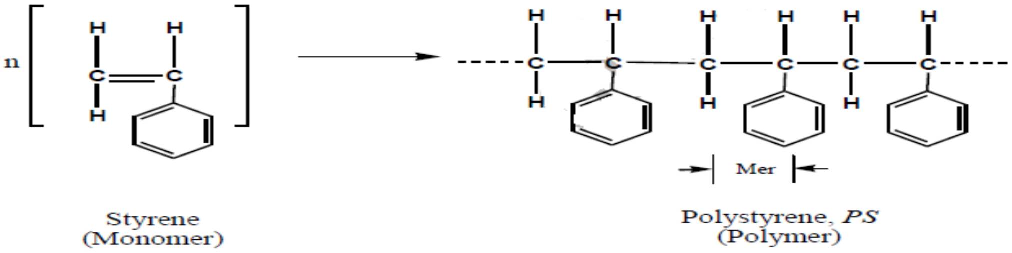
Introduction

Polymers' are 'macromolecules' built up by the linking together of a large number of small molecules or units. Thus, small molecules which combine with each other to form polymer molecules are termed *monomers*; and the "repeat unit" in a polymer is called as - mer.

For example, polythene is a polymer formed by linking together of a large number of ethene (C_2H_4) molecules. Similarly polystyrene is formed by the linking of styrene monomer molecules.

$$n(CH_2 = CH_2) \longrightarrow [-CH_2 - CH_2 -]_n$$

Ethylene (monomer) Polyethylene (Polymer)



Degree of polymerisation

The number of repeating units (n) present in the polymer chain is known as the degree of polymerisation.

$$\text{Degree of polymerisation} = \frac{\textbf{Molecular weight of the polymeric network}}{\textbf{Molecular weight of the repeating unit}}$$

$$5\, CH_2 = CH_2 \longrightarrow -(CH_2-CH_2)-_5$$

Degree of polymerisation = 5

Based on degree of polymerization they are into

i).Oligo polymers - having low degree of polymerization(500-5000)

ii). High polymers - are having higher degree of polymerization(10,000-2.00,000).

The process of formation of a polymer from its monomer units is termed as *polymerization.* Many polymers are naturally occurring like starch, cellulose etc., and as many are synthetically made such as polystyrene, PVC, etc. The organic polymers like starch, polyethene have carbon backbone, while the inorganic polymers have atoms other than carbon, which have catenation property like silicon, sulphur, phosphorous. E.g: silicates.

Tacticity

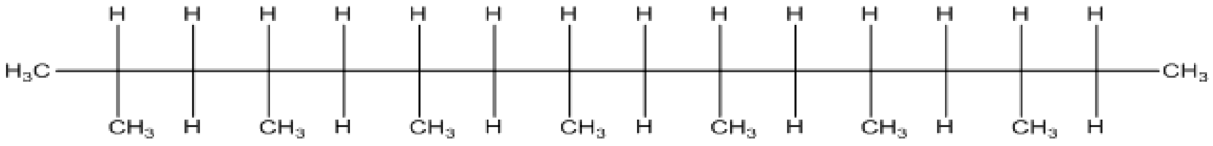
It is the orientation of functional groups in a polymer chain is known as Tacticity. The different orientation of groups (tacticity) can affect the physical properties of polymer.

There are three kinds of arrangements

1. ***Isotactic***
2. ***Atactic***
3. ***Syndiotactic***

1. Isotactic

It is the configuration or arrangement in which the functional groups are arranged in the same side of the

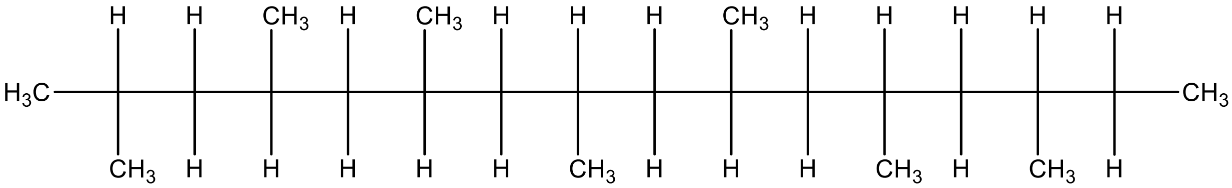


Isotactic polypropylene

For example, in isotactic polypropylene all the methyl groups are on the same side of the ring.

2. Atactic

It is the configuration or arrangement in which functional groups are arranged randomly.

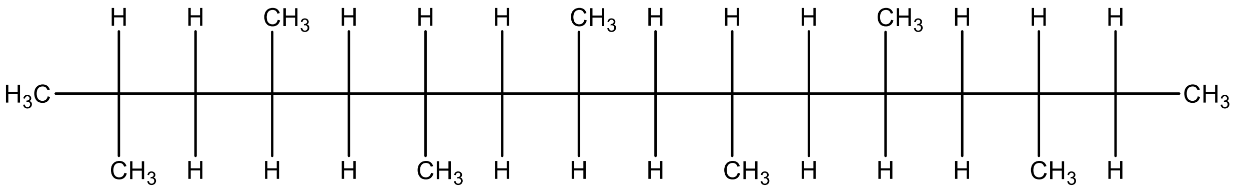


Atactic polypropylene

In Atactic polypropylene the methyl groups are arranged in random manner with respect to carbon backbone.

3. Syndiotactic

It is the configuration or arrangement in which functional groups are arranged in alternating fashion.



Syndiotactic polypropylene

In syndiotactic polypropylene the methyl groups are arranged in an alternating manner.

- Generally polypropylene exists as syndiotactic and isotactic forms.
- Polymethylmethacrylate (PMMA) exists as syndiotactic and isotactic forms

- Polybutadiene (PBD) exist as syndiotactic and isotactic forms
- Polystyrene (PS) exist as atactic and isotactic forms

Nomenclature of polymers

Polymers consisting of identical monomer units are called homo-polymers and monomers of different chemical unit structures are called hetero-polymers or co-polymers.

-M-M-M-M-M-M-M-M- -M1-M2-M1-M2-M1-M2-M1-M2-
Homopolymer **Hetero or copolymer**

Based on the arrangement of monomeric units (structural units), copolymers can be classified as:

Alternating copolymers: These polymers are formed by regularly altering the two different monomeric units.

-M1 – M2 – M1 – M2 – M1 – M2 –

Statistical copolymer (Random copolymer): These are copolymers in which the sequence of monomer units follows a statistical rule. The probability of finding a given type of monomer unit, at a particular point in the chain is equal to the mole fraction of that monomer unit in a chain.

-M1 – M2 – M2 – M2 – M1 – M2 – M1 – M1

Block copolymer: The copolymer consisting of two or more homopolymer subunits linked through covalent bonds is called a block copolymer.

-M1 – M1 – M1 – M1 – M2 – M2 – M2 – M2 – M3 – M3 – M3 – M3-

Functionality:

In the process of polymerization, for any molecule or unit to act as a monomer, it must have at least two reactive sites or bonding sites for the extension of a monomer to a dimer, trimer and ultimately a polymer.

The number of such reactive sites in the monomer is termed as its functionality.

Ex: In ethylene the double bond can be considered as site for two free valancies. Thus, ethylene is considered to be bifunctional.

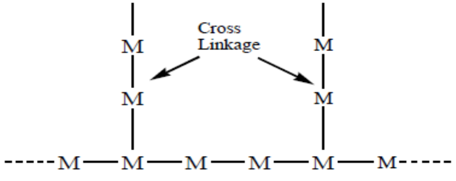
$CH_2 = CH_2$, $HOH_2C–CH_2OH$

Its functionality is 2.

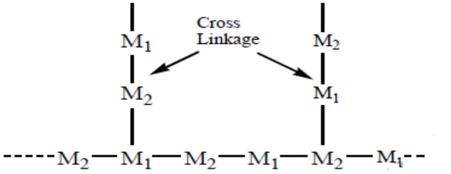
If the monomer has bifunctionality, it can only form a linear polymer. If the functionality is more than two, the monomer has a chance to form cross linked polymers having 2D or 3D structures.

Based on functionality and the process of polymerization, the polymer may be present in **linear, branched or cross-linked (three-dimensional) structure** as illustrated below:

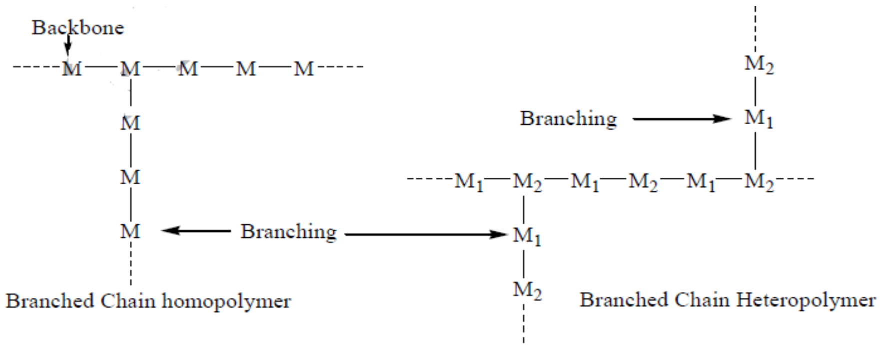
-M1 – M1 – M1 – M1 – M1 – M1 – M1 – M1 – M1– M1 – M1 – M1-
Linear homopolymer



Crosslinked Homopolymer



Crosslinked Heteropolymer



Methods of polymerization

The process of formation of a polymer from its monomer units is termed as *polymerization.*It involves union of two or more small, same or different monomer molecules to form a single large macro-molecule, called polymer. The conversion of a monomer into a polymer is an exothermic process and if heat is not dissipated or properly controlled, explosion may result. This is basically due to the difference in the mechanisms of the two different types of polymerization processes

i) Addition or chain polymerization and
ii) Condensation or step polymerization.

Addition or chain polymerization:

When monomer units are repeatedly added to form a long chain polymer without the elimination of any by-product molecule. The product formed is called addition polymer and the process involved is called addition polymerization.

$$\underset{\text{Ethene}}{nCH_2 = CH_2} \xrightarrow{\text{Polymerization}} \underset{\text{Polyethene}}{(CH_2 - CH_2)_n}$$

- Monomers must have atleast one double or triple bond.
- The polymerization is by self addition and follows free radical mechanism
- Monomers add on to give polymers and no by products are formed.
- The polymer product is formed at once.
- Molecular weight of the polymer is an integral multiple of the molecular weight of the monomer.**i.e., M = n. m**

where M and m are the molecular weights of the polymer and the monomer respectively and n is the degree of polymerization.

- The process is highly exothermic
- Mostly thermoplastic resins are obtained.

Example: PE, PP, PS, PVC, PVA, PAN, PTFE, etc.

Copolymerization.

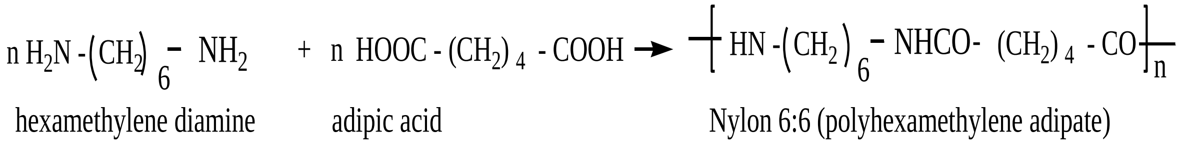
When two (or) more different monomers are used to form a polymer, the resulting product is called a copolymer and the process is known as ***copolymerization.***

Example : A mixture of 1,3 butadiene and styrene can form a copolymer.

Condensation polymerization

Condensation or step-polymerization may be defined as “a reaction occurring between monomers having simple polar functional groups (like -OH, COOH etc.,) forming a polymer by the elimination of small molecules like water, HCl, ammonia etc.

*Example :***Nylon 6,6 :** A polymer of hexamethylene diamine and adipic acid.



$$n\,H_2N-(CH_2)_6-NH_2 + n\,HOOC-(CH_2)_4-COOH \rightarrow \left[HN-(CH_2)_6-NHCO-(CH_2)_4-CO\right]_n$$

- Monomers must have atleast two identical or different polar functional groups.
- Monomers condense to give polymers and H_2O or HCl or CH_3OH etc., as by products.
- It follows condensation mechanism
- The polymer product is formed step-wise steadily
- Molecular weight of the polymer need not be an integral multiple.
- The process not exothermic.
- Mostly thermoset resins are obtained.

Example: Bakelite, polyesters, nylons, silicones, etc

Free Radical Polymerization (Mechanism of addition polymerization)

Free radical polymerization is catalyzed by the thermal initiator (organic peroxides). (eg) for initiators - acetyl peroxide or benzoyl peroxide.

They undergo hemolytic thermal decomposition to give free radicals at 60 to 70 °C

The above reaction steps can be represented as

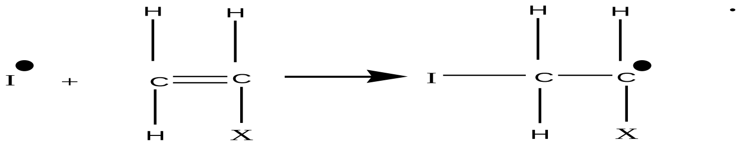
$$I-I \xrightarrow{\text{Thermal decomposition}} I^{\bullet} + I^{\bullet}$$

This mechanisms involves the following three steps

1. Chain Initiation
2. Chain Propagation and
3. Chain Termination

1. Chain Initiation:

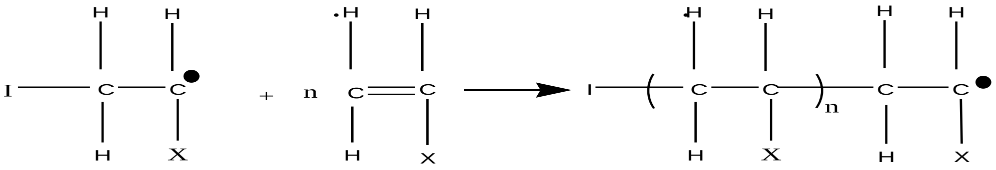
The free radical produced attacks the double bonded monomer to form chain initing species.



Chain initiating species

2. Chain Propagation

The chain initiating species (free radical) combined with more number of monomeric units to give a longer chain free radical. This propagated free radical is known as living polymer.



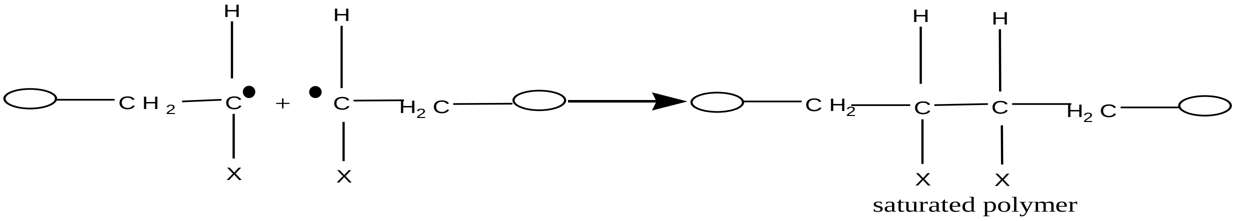
Living polymer

3. Chain Termination

(a) Termination of propagated polymer chain may occur either by coupling or disproportionation reaction

(a) Coupling reaction

It is done by coupling one propagated free radical end with another propagated free radical to form a long chain polymer.

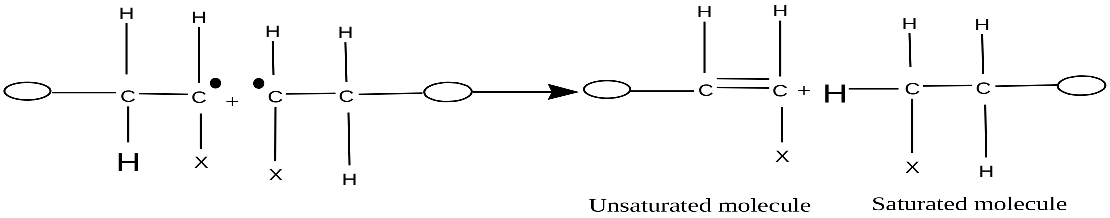


(Dead polymer)

⬭ - represents polymer back bone

(b) Disproportionation

It involves the shifting of hydrogen atom from one propagated chain end to another propagated chain end. This results in the formation of one saturated polymer and one unsaturated polymers.



Properties of polymers

Structure and chemical properties

a) **Chemical Reactivity:**

The polymer is prepared by linking small monomeric units. So their properties depend upon number and chemical nature of chemical groups present in the monomers. The thermal stability and mechanical strength of different polymers are related to difference in bonding and structure of the monomer. Polymers containing high electronegative atoms in their backbone chain undergo hydrolysis. E.g. Nylon and polyester. Polymers containing double bonds undergo ozonalysis.

E.g., Rubbers like isoprene, neoprene.

b) **Solubility and swelling nature**:

Polar polymers such as PVA, PVC, and polyamide are soluble in polar solvent like water, alcohol, phenol etc,, while non-polar polymers like PE, PP, PS can be dissolved in non-polar solvents like benzene, toluene, xylene, n - hexane etc. Polymers of aliphatic character are more soluble in aliphatic solvents, whereas aromatic polymers are soluble in aromatic solvents. Polymers dissolve in solvents and swell in size.

c) **Ageing and weathering**:
The reason for the stability of the polymer is bond strength between the atoms in the polymer chain. The stability of polymer can be enhanced by increasing bond strengths. Heat, ultraviolet light, high energy radiation, atmospheric effect and chemical environments are the main agencies to affect the properties of polymers. PTFE, PE and PVC have good stability towards light and heat due to the fact that the bond energies of these are greater than light energy. The heat stability of these polymers is in the order PTFE > PVC > PE

d) P**ermeability and diffusion**:
Diffusion occurs in polymers through vacant gaps between adjacent polymer molecules. Crystalline polymers resist in diffusion because of greater degree of molecular packing. Amorphous polymers above Tg have appreciable permeability The crystalline polymers have high resistance to permeability than amorphous polymers.

Physical Properties

a) **Crystallinity**:

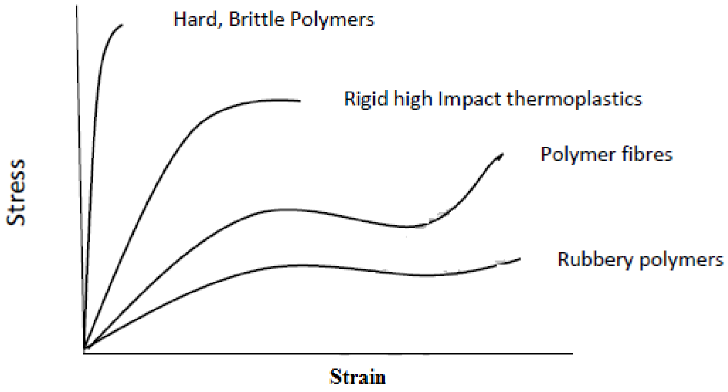
The degree of structural order arrangement of polymeric molecules is known as crystallinity. Crystallinity favours denser packing of molecules, thereby increasing the intermolecular forces of attractions. This accounts for a sharp and higher softening point, greater rigidity and strength. The polymers with low degree of symmetry and with long repeating units are partially crystalline and are amorphous in structure. The crystalline polymer units have packing close to each other through intermolecular forces. Completely crystalline polymers are brittle. The crystallinity influences properties like solubility, diffusion, hardness, toughness, density and transparency of polymers.

b) **Amorphous state**:
Random arrangement of molecules, less intermolecular forces lead to amorphous nature of a polymer. So they can be moulded into a desired shape. Both thermosetting and thermoplastic polymers can exist in amorphous state.

Mechanical properties:

a) **Strength**:
The polymer chains adjacent to each are held together by weak intermolecular forces. The strength of intermolecular forces can be increased by either increasing chain length or molecular weight or the presence of polar groups (-OH, -COOH, -OMe, -

COOR, -X). The lower molecular weight polymers are quite soft and gummy. High molecular weight polymers are tough and heat resistant.



The cross linked polymer chains are strongly linked to each other by strong covalent bonds, which cause greater strength, toughness, brittleness and low extensibilities. The strength of the polymer is characterized by the stress and strain curve. Strength of the polymers also depends on the shape of the polymer.

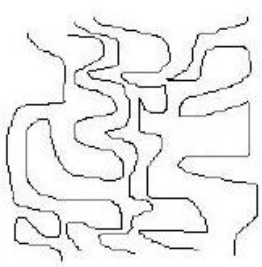
Eg: In PVC, large size chlorine atoms are present. The strong attractive forces restrict the movement of molecules and so PVC is tough and strong.

b) **Elastic character**:

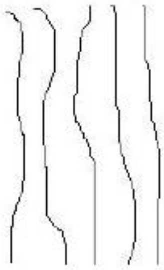
Elasticity is the relaxation to original shape after removal of applied stress. Polymers like nylon, having this stretching nature are called elastomers. Elastomers are slightly cross linked, amorphous and rubber like polymers. In the absence of deforming forces these polymers have peculiar chain configuration of irregularly coiled 'snarls'. So the polymer is amorphous due to random arrangement. When they are stretched cross-links begin to disentangle and straighten out.

c) **Plastic deformation**:

This is found in thermoplastics; These polymers have structure which is deformed under heat or pressure. This property is used to process them into desired shape. Due to weak inter molecular forces, these polymers show permanent deformation at high temperature and pressure. The Vander wall forces are weak in a linear polymer at high temperature and result in 'slippage'. The plasticity of a polymer decreases with temperature.



Snarls in unstretched condition



Snarls in stretched condition

d) **Structure and electric properties**:

Most of the polymers are electrical insulators and the insulating property can be removed by application of a strong field. The electronic polarization is responsible for dielectric constant in non-polar polymers. Water has high dielectric constant and conducting property so the absorbed water molecules enhance the conductivity of a polar polymer.

PLASTICS

Plastics are polymers which can be moulded into any desired shape or form, when subjected to heat and pressure in the presence of a catalyst. They undergo permanent deformation under stress termed as plasticity.

Plastics are obtained by mixing a resin with other ingredients to impart special engineering properties.

Properties of Engineering plastics

They possess

- High abrasion resistance
- High load bearing properties
- Fairly good thermal stability
- Light weight
- Readilymoldable into complicated shapes
- Rigidity
- Dimensional stability
- High performance properties which permit them to be used in the same
- manner as metals, alloys and ceramics

Disadvantages of plastics

- Softness
- Embrittlement at low temperature
- Deformation under load
- Low heat resistant
- Combustibility
- Tend to degrade upon exposure to heat and radiation
- Non bio – degradable

A plastic material should have sufficient rigidity, dimensional stability and mechanical system at room temperature to serve as a useful article. It may be moulded to shape by application of reasonable temperature and pressure.

Types of plastics

Thermoplastics

These are linear, long chain polymers, which can be softened on heating and hardened on cooling reversibly. Their hardness is a temporary property and it changes with the raise or fall of temperature. They can be reprocessed.

Examples: Polyethylene (PE), Polypropylene (PP), Polyvinyl chloride (PVC), polystyrene (PS), Nylons, Poly tetra fluoro ethylene (PTFE) etc.

Thermosets

These polymers, during moulding get hardened and once they are solidified, cannot be softened i.e, they are permanently set polymers. During moulding, these polymers acquire three dimensional cross- linked structure, with strong covalent bonds. Thermosets once moulded cannot be reprocessed.

Examples: Polyester (terylene), Bakelite, epoxy- resin (araldite), Melamine, urea-formaldehyde resin etc.

Thermoplastics *Vs* Thermosets

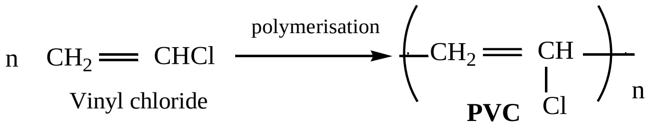
S.No	Thermoplastics	Thermosets
1	They soften on heating readily	They do not soften on heating. On prolonged heating, they get charred.
2	They consist of long – chain linear molecules.	Their set molecules have three- dimensional network structure, joined by strong covalent bonds
3	They are mostly formed by addition polymerization	They are formed by condensation polymerization
4	They can be softened, reshaped and reused by heating. (recycled)	They cannot be softened, reshaped and reused.
5	They are usually soft, weak and less brittle	They are usually hard, strong and brittle.
6	They can be reclaimed from wastes.	They cannot be reclaimed from wastes.
7	They are usually soluble in some organic solvents	They are insoluble in almost all organic solvents, because of their structures.

Poly vinyl chloride or PVC

Preparation:

It is a thermoplastic polymer and is obtained by the free radical addition polymerization of vinyl chloride in the presence of benzyl peroxide or hydrogen peroxide. In PVC the mass of chlorine is 57% of the total mass of the polymer. Vinyl chloride is obtained by treating acetylene with HCl at 60-800C in the presence of metal oxide catalyst.

$$\underset{\text{Acetylene}}{CH \equiv CH} + HCl \rightarrow \underset{\text{Vinyl chloride}}{CH_2 = CHCl}$$



$$n\ \underset{\text{Vinyl chloride}}{CH_2 = CHCl} \xrightarrow{\text{polymerisation}} \underset{\textbf{PVC}}{\left(-CH_2 = \underset{\displaystyle Cl}{\underset{|}{CH}} - \right)_n}$$

Properties:

- PVC is colorless, non – inflammable and chemically inert powder. It is strong but brittle.
- It is resistant to ordinary light, atmospheric gases, moisture, inorganic acids and alkalis, but undergoes degradation in heat or UV light.
- It is soluble in hot chlorinated hydrocarbons like ethyl chloride
- Pure resin possesses a high softening point.
- It has greater stiffness and rigidity compared to polyethylene

Applications:

- It is widely used as a synthetic plastic.

- Rigid PVC is used for making sheets, light fittings, safety helmets, refrigerator components, tyres, and cycle and motor cycle mudguards.
- Plasticized PVC is used in making continuous sheets (table cloths, raincoats, curtains etc)
- Used in injection moulding of articles like toys, tool – handles, radio – components, chemical containers, conveyor belts etc.

Teflon

Preparation:
Teflon is obtained by polymerisation of water emulsion of tetrafluoroethylene in presence of benzoyl peroxide under pressure

$$n\ CF_2 = CF_2 \xrightarrow{B_2O_3} \left(CF_2 - . CF_2 \right)_n$$

Properties:

- Extremely tough, flexible material. High softening point (350^0C)
- Good electrical mechanical properties
- Chemically resistant to all chemicals (except hot alkali metals and hot fluorine)
- Excellent thermal stability.
-

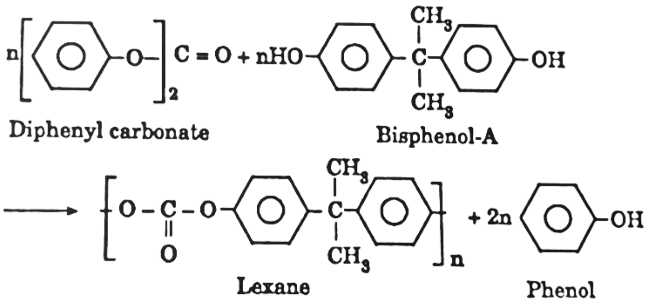
Applications:

- Electrical insulating material in motors, transformers
- Making gaskets, pump parts and tank linings
- Making non lubricating bearings
- Making non stick kitchen ware and stop cocks for burettes

Polycarbonate

Preparation:

Polycarbonates are prepared by the interaction of diphenyl carbonate with bisphenol –A



Properties:

- Characterised by high impact and tensile strength over wide range of temperature
- Soluble in organic solvents and alkalies
- Posses good dimensional stability, stiffness and transparency

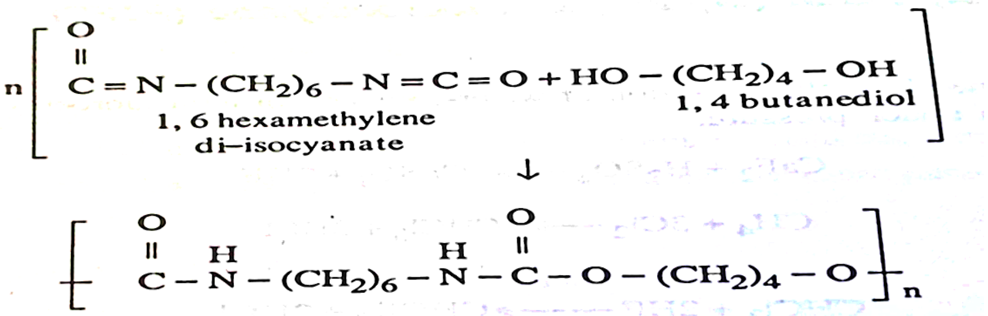
Applications:

Electrical insulators, sterilisable transparent containers, photographic material, feeding bottles,

Polyurethane

Preparation:

Polyurethanes is produced by the reaction of polyalcohols (**1,4- butanediol)** with di-isocyanates **(1,6-hexamethylene diisocyanate)**



Properties:

- It has high strength, good resistance to ozone and aromatic hydrocarbons and weather proof.
- It is highly resistant to oxidation, because of the saturated character. It have good resistance to many organic solvents.

Applications :

- It used for surface coatings, manufacture of foams & spandex fibres.
- PU flexible foams are employed as furniture material, insulation & crash pads.
- It is used for insulating wires, the PU coated wires can be soldered directly.

Nylon 6,6.

Preparation:

It is obtained by the polymerisation of hexamethylene diamine with adipic acid

$$n\,H_2N-(CH_2)_6-NH_2 \quad + \quad n\,HOOC-(CH_2)_4-COOH \rightarrow \left[HN-(CH_2)_6-NHCO-(CH_2)_4-CO \right]_n$$

hexamethylene diamine adipic acid Nylon 6:6 (polyhexamethylene adipate)

Properties:

- Nylons are Translucent ,whitest, horny and high melting polymers
- Possess high strength, elasticity and toughness.
- They provide excellent resistance to wear and abrasion.
- Insoluble in common organic solvents

Applications:

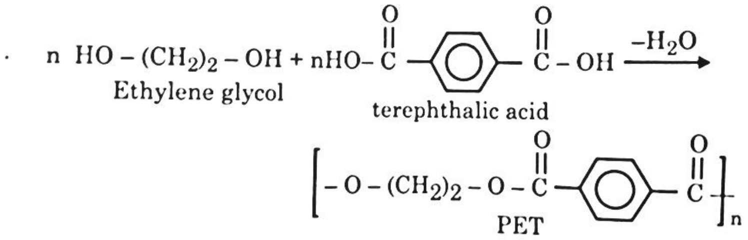
- Filaments for ropes, bristles for tooth brushes, films
- Gears and bearings

- Fibres for making socks, dresses and carpets.

PET

Preparation:

PET is nothing but Polyethyleneteterephthlate; it is prepared by the condensation of ethylene glycol and terephthalic acid(benzene-1,4-dicarboxylic acid).



Properties:

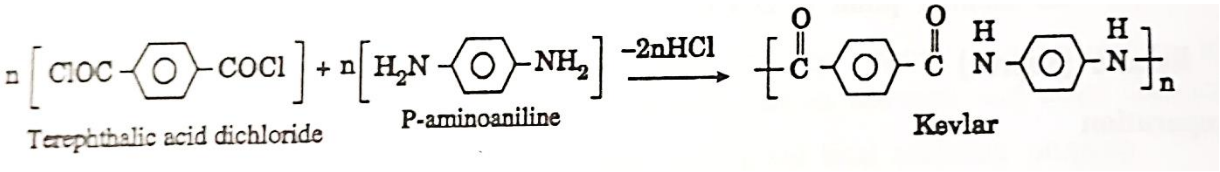
- Goodfibre – forming material
- Fibre possess high stretch resistance and wrinkle – resistance .
- Highly resistant to mineral & organic acids but less resistant to alkali.

Applications :

- for making synthetic fibres like terylene , Dacron , etc.,
- blended with wool to provide better wrinkle – resistance.
- In safety helmets , aircrafts , battery boxes , etc.,

KEVLAR

Kevlar is aromatic polyamide similar in structure to nylon-6,6.It is prepared by polycondesation between aromatic dichloride(terephthalic acid dichloride) with aromatic diamines(P-amino aniline).



Properties

- Kevlar is exceptionally strong
- It is 5 times stronger than steel of same weight
- It has high heat stability and flexibility
- It is very light when compared to its strength
- It has good impact and abrasion resistance
- It has very high tensile strength Thus it can be said as a Super strong plastic

Applications

- It is usually used as fibre reinforcement for polymer matrix composites
- Ballistic protective applications such as bullet proof vests

- Protective apparel such as gloves, motorcycle protective clothing and hunting gaitors, chaps and pants.
- Sails for sailboats, yachts etc
- Belts and hosing for industrial and automotive applications
- Aircraft body parts
- Boat hulls
- Fibre optic and electromechanical cables
- Friction linings such as clutch plates and brake pads
- Gaskets for high temperature and pressure applications
- Adhesives and sealants

Green polymers

Green polymers are derived from renewable biomass sources, such as vegetable oil, corn starch, pea starch or microbiota, rather than fossil-fuel plastics which are derived from petroleum.

Most of plastics are derived from petroleum products,when burned, they release the carbon dioxide into the atmosphere, leading to global warming.Bioplastics are environmentally friendly because, compared with traditional plastics, their production results in the emission of less carbon dioxide.

They are also biodegradable and the use of bioplastics offers significant advantages not only in an ecological sense but also in an economical sense.Today bioplastics are gaining popularity once again as newer techniques developed through biotechnology.

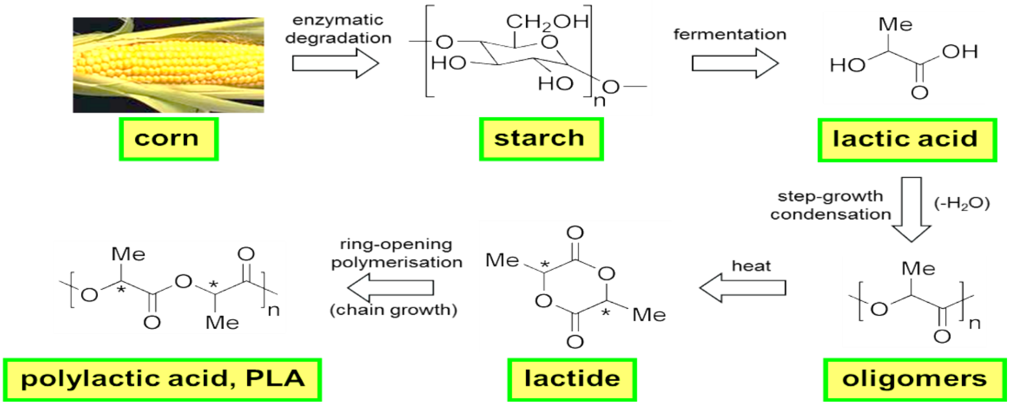
Example:- Soy protein, Starch, Polylactic acid, Triglycerides&Polyhydroxyalkanoates

Polylactic Acid (PLA)

- Highly versatile thermoplastic polymer
- Made 100% from renewable resources
- Lactic Acid is derived from various sources(Corn- Sugar Beets- Wheat)
- It is a biodegradable and bioactive polyester made up of lactic acid building blocks.

Preparation:

- It is can be produced by fermentative or chemical synthesis. The most popular route is fermentation, in which sugars and starches are converted into lactic acid by bacterial fermentation using an optimized strain of Lactobacillus.
- From lactic acid it is produced by direct polycondensation or ring opening polymerization of lactic acid cyclic dimmer, known as lactide.



Properties:

- The PLA is a semi-crystalline polymer
- Its glass transition temperature around 55 to 59°C and melting point is 174-184 ° C.
- It shows a good mechanical strength, high Young's modulus, thermal plasticity and has good processability
- It is biodegradable and biocompatible
- It is insoluble in water and soluble in chlorinated solvents, hot benzene, tetrahydrofuran, and dioxane.

Advantages :

- It is derived from renewable resources.
- It is biodegradable nature and used to make ecofriendly plastics.
- Degradation time is weeks or monthsdepending on the conditions
- Emission of greenhouse gases during its production is lower.
- The solid waste generated during its production is very low to a decrease in overall solid waste.
- Recyclable (can be converted back to monomer)

Disadvantages:

- It is unsuitable for high temperature applications
- It may show signs of getting soft or deforming on a hot summer day.

Applications:

- Single-use items like plates, cups, film wrap
- Plastic bottling and fast-food companies
- Textile industry
- Paper coatings, Clothing fibers, Compost bags
- Medical implants such as sutures, screws, rods, pins and mesh have been made due to its ability to degrade into non-toxic lactic acid and eliminating the need for further surgery.
- Polylactic acid injections for skin rejuvenation

- PLA fibers have been used to manufacture casual sports apparel, upholstery material, hygiene products, and diapers.
- PLA as material for food packaging due to increased aesthetics, better printability, good resistance to grease and oils, and reduced issues in taste and odor transfer.

QUESTIONS BANK
UNIT I - CHEMICAL BONDING

1. What are the types of chemical bond?

The chemical bonds can be classified based on the nature of the interaction between the bonded atoms. Two major types of chemical bonds are covalent bonds and ionic bonds.

2. What is octet rule? Explain with an example.

While undergoing a chemical reaction, atoms of group 1A-7A elements tend to gain, lose, or share sufficient electrons to achieve an electron configuration having eight valance electrons. After gaining, losing, or sharing, ions/atoms will have the electron configuration like that of the noble gases nearest to them in atomic number.

3. Define cation and Anion with example

Cation : loses one, two or three electrons and in losing electrons, the atom becomes a positively charged ion called a cation (Na^+, Ca^{2+}, Mg^{2+}) (usually metals).
Anion :gains one, two or three electrons and in gaining electrons, the atom becomes a negatively charged ion called an anion (Cl^-, O^{2-}, S^{2-}) (usually nonmetals).

4. State ionic bond

Ionic bonds usually form between a metal and a nonmetal. In ionic bonding, electrons are completely transferred from one atom to another. In the process of either losing or gaining negatively charged electrons, the reacting atoms form ions. The oppositely charged ions are attracted to each other by electrostatic forces, which are the basis of the ionic bond.

5. State covalent bond

Covalent bonds usually form between two nonmetals or a metalloid and a nonmetal. In covalent bonds, the atoms share one or more pairs of electrons (by using their valence electrons) between each other to obtain a filled valence level. This type of mutual sharing of one or more pairs of electrons between two combining atoms results in the formation of a chemical bond called a covalent bond.

6. What is electronegativity ?

Electronegativity is measure of an atom's attraction for the electrons it shares in a chemical bond with another atom. The electronegativity shows, how tightly an atom holds the electrons that it shares with another atom.

7. Why does the same covalent bond have different bond energies in different molecules?

The strength of the covelent bond depends on the amount of electron-density shared by the two atoms involved. This will be influenced by other atoms in the molecule.
For example, highly electronegative atoms will tend to attract electron-density away from the bond and so weaken it.

8. What are the shape of NF3, BF3 and ClF3 molecules? Explain

NF3 – trigonal pyramidal : BF3 – Trigonal planar ; ClF3 – T shaped

The shape differs because there is a different number of non-bonding pairs of electron around the central atom.

9. Compare the status of electronegativity in the periodic table

i. Electronegativity generally increases from left to right across a row of the Periodic Table.

ii. Electronegativity generally increases from bottom to top within a column of the Periodic Table.

10. Why does CCl4 not posses dipole moment?

CCl4 has tetrahedral structure and all the Cl-C-Cl bonds are identical.

11. What do understand by bonding molecular orbital?

The molecular orbital formed by the additive effect of the wave functions of atomic orbitals.

12. List the salient features of VB Theory:

i. When half filled orbitals of two atoms overlap, a covalent bond will be formed between them.
ii. The resultant overlapping orbital is occupied by the two electrons with opposite spins. For example, when H_2 is formed, the two 1s electrons of two hydrogen atoms get paired up and occupy the overlapped orbital.
iii. The strength of a covalent bond depends upon the extent of overlap of atomic orbitals. Greater the overlap, larger is the energy released and stronger will be the bond formed.
iv. Each atomic orbital has a specific direction (except s-orbital which is spherical) and hence orbital overlap takes place in the direction that maximizes overlap

13. Explain the formation of a chemical bond.

Existence of a strong force of binding between two or many atoms is referred to as a chemical bond and it results in the formation of a stable compound with properties of its own.

14. Write the favourable factors for the formation of ionic bond.

Favourable factors for the formation of ionic bond

i. Ease of formation of cation and anion form neutral atoms.
ii. Elements /Atoms with lower ionisation energies.
iii. Atoms with greater negative values of electron gain enthalpy.
iv. Cations and anions together form a stable crystal lattice by releasing large amount of energy.
v. Lattice enthalpy of ionic solids are extremely high.

15. Although both CO_2 and H_2O are triatomic molecules, the shape of H_2O molecule is bent while that of CO_2 is linear. Explain this on the basis of dipole moment.

The two bond dipoles must be oriented in opposite directions. This is possible iin CO_2 because the molecule is linear. Similarly H_2O has a dipole moment of 1.83D.Thus its molecule cannot be linear because the bond dipoles do not cancel each other. Thus, the H_2O molecule must have an angular shape.

16. Write the significance/applications of dipole moment.

Distinction between polar and non-polar molecules. Ionic character in a molecule. Shapes of molecules.

17. Electronegativity

Electronegativity of an element may be defined as the tendency of its atom to attract the shared pair of electrons towards it self in a covalent bond.

18. What is meant by hybridisation of atomic orbitals?

Hybridisation may be defined as the phenomenon of intermixing of atomic orbitals of slightly different energies to form new orbitals of equivalent energies and identical shapes.

19. Define Hydrogen bond

When hydrogen is bonded to strongly electronegative element 'X', the electron pair shared between the two atoms moves far away from hydrogen atom. As a result the hydrogen atom becomes highly electropositive with respect to the other atom 'X'. Since there is displacement of electrons towards X.

20. Why does chlorine atom not form hydrogen bond in liquid HCl ?

Due to large size, chlorine atom does not form H-bonds in liquid HCl.

21. Why does ammonia possess a higher boiling point?

N-H bond in ammonia is highly polar, so NH3 form intermolecular H-bonds

22. Boiling point of water is higher than that of HF. Explain why?

In HF molecule each HF molecule can form only two hydrogen bonds with two other HF molecules, due to the presence of one hydrogen atom per fluorine atom. On the other hand in water each water molecule can form four hydrogen bonds with four other water molecules. Consequently the extent of hydrogen bonding in water is much more than in HF.

23. What do understand by bonding molecular orbital?

The molecular orbital formed by the additive effect of the wave functions of atomic orbitals.

24. What is an antibonding molecular orbitals?

A molecular orbital obtained by subtraction of wave function of the atomic orbitals.

PART-B

1. What do you mean by chemical bond? How do atoms combine?How many types of bond are there?
2. Explain the salient features of covalent bond
3. Discuss the partial ionic character of covalent bonds
4. What do you understand by Linear combination of atomic orbitals in MO theory.
5. Explain the term hybridization. Give an account of the different types of hybridization with suitable examples
6. Discuss briefly the molecular orbital (MO) theory
7. What do you understand by the term hydrogen bonding? Discuss its importance
8. Explain the following terms (a) electronegativity (b) dipole moments
9. Write short note on van der Waals forces
10. Mention in brief about Valence bond (VB) theory

CONTENT BEYOND THE SYLLABUS

Metallic bonding

Metals have some special properties of lustre, high density, high electrical and thermal conductivity, malleability and ductility, and high melting and boiling points. The forces that keep the atoms of the metal so closely in a metallic crystal constitute what is generally known as the metallic bond. The metallic bond is not just an electrovalent bond(ionic bond), as the latter is formed between atoms of different electro negativities. Similarly, the metallic bond is not a covalent bond,as the metal atoms do not have sufficient number of valence electrons for mutual sharing with 8 or 12 neighboring metal atoms in a crystal.

Coordinate covalent bond

In the formation of a covalent bond, both the combining atoms contribute one electron each and the these electrons are mutually shared among them. However, in certain bond formation, one of the combining atoms donates a pair of electrons i.e. two electrons which are necessary for the covalentbondformation, andtheseelectrons are shared by both the combining atoms.

These type of bonds are called coordinate covalent bond or coordinate bond. The combining atom which donates the pair of electron is called a donor atom and the other atom an acceptor atom. This bond is denoted by an arrow starting from the donor atom pointing towards the acceptor atom. (Later in coordination compound, we will refer the donor atom as ligand and the acceptor atom as central-metal atom/ion.

UNIT II - SURFACE CHEMISTRYAND CATALYSIS

PART-A

1. Define adsorption.

When a solid surface is exposed to a gas or a liquid, molecules from the gas or the solution phase accumulate (or) concentrate at the surface.The phenomena of concentration or assimilation of a gas or liquid at a solid surface is called adsorption.

2. Define terms adsorbent and adsorbate giving suitable examples.

Adsorbent:The material surface on which adsorption occurs is known as adsorbent.

Example: Charcoal, Silica gel, clay, Fuller's earth, alumina gel, Ni. Pt, Pd etc…

Adsorbate :The substances that get adsorbed or attached on the surface of the solid is known as adsorbate. E.g : Gas (H_2, N_2), Liquid (NH_3) etc...

3. What is chemisorption? Give an example.

When a gas is held on the surface of a solid by forces similar to that of a chemical bond, the type of adsorption is known as chemical adsorption or chemisorption.

E.g: Adsorption of H_2 on Ni

4. Differentiate between absorption and adsorption?

S.No	Physisorption	Chemisorption
1	Caused by intermolecular Vander Waal's forces (weak)	Caused by chemical bond formation (strong)
2	Heat of adsorption is low (20 – 40 kcal/mol)	Heat of adsorption is high (40 – 400 kcal/mol)
3	Occurs in gases, which are easily liquefiable.	Occurs in gases, which have potentiality to form compound.
4	No appreciable energy of activation.	Energy of activation may be involved.
5	Does not show any specificity.	Highly specific.
6	Rate of adsorption increases with increase of pressure.	Change of pressure has no such effect.

7	Adsorption is completely reversible	Adsorption is irreversible
8	Adsorption decreases with increase in Temperature	Adsorption increases with Temperature
9	Multilayer adsorption is possible	Only monolayer adsorption
10	Equilibrium is established rapidly.	Requires time
11	No surface compound formation	Surface compound is formed
12	The amount of adsorption depends only on adsorbate alone	Depends on adsorbate and adsorbent.

5. What is an adsorption isotherm?

The graphical relation between the amounts of gas adsorbed with pressure at constant temperature" is known as adsorption isotherm.

6. What is Freundlich's adsorption isotherm?

Freundlich proposed an empirical relation in the form of a mathematical equation

$$\frac{x}{m} = kP^{1/n}$$

Where, x – amount of the gas adsorbed on a mass 'm' of adsorbent at a pressure 'P'. k and n are constants at a particular temperature for a particular adsorbent and a gas.

7. Write a suitable equation commonly applied to the adsorption of liquids on solids?

For adsorption from solutions, the amount of the solute adsorbed on the adsorbent depends on the concentration of solute in the solution. The Freundlich isotherm, using concentration 'C', instead of pressure.

$$\frac{x}{m} \propto C^{1/n}$$

$$\frac{x}{m} = KC^{1/n}$$

8. What are the limitations of FAI?

It is an empirical formula, there is no theoretical foundation.

It is valid only for certain range of pressure (not applicable to high pressures).

The constant k and n are temperature dependent, they vary with increase or decrease in temp.

It fails, when the concentration of adsorbate is very high.

9. Multilayer adsorption is possible in physisorption. Justify.

The adsorbate is held on adsorbent by vander vaals forces (inter molecular).

In physical adsorption, the adsorbate molecules are held by comparatively weak vander Waal's forces.

10. Mention any two solid adsorbents.

Charcoal, Silica gel, clay, Fuller's earth, alumina gel, Ni. Pt, Pd etc..

11. Define the term catalyst.

A Catalyst is a substance which alters the rate of a chemical reaction without undergoing any chemical change and can be recovered after the completion of the reaction. *The process is called catalysis.*

12. Mention the two different types of catalysts. Give two examples for each.

i. Positive catalyst

A catalyst which enhances the rate of a reaction is called positive catalyst.

E.g: Decomposition of $KClO_3$ in presence of manganese dioxide.

$$2KClO_3 \xrightarrow[\Delta]{MnO_2} 2KCl + 3O_2$$

ii. Negative catalyst

A catalyst which retards the rate of a reaction is called negative catalyst.

E.g:Oxidation of sodium sulphite by air is retarded by alcohol.

$$2Na_2SO_3 + O_2 \xrightarrow{C_2H_5OH} 2Na_2SO_4$$

13. Distinguish between Homogeneous catalysis and Heterogeneous catalysis.

S. No	Homogeneous catalysis	Heterogeneous catalysis
1	Reactants, products and catalyst are in same phase. Either in solid, liquid and gaseous phases.	Reactants, products and catalyst are in different phases.
2	Catalyst cannot be regenerated.	Catalyst can be regenerated and reused.
3	Thermal stability of catalyst is low.	Thermal stability of catalyst is high.
4	Catalyst performs under low temperature and low pressure.	Catalyst performs under high temperature and high pressure.
5	Temperature can increase the rate of the reaction.	Temperature can increase the rate of the reaction.
6	Selectivity of the catalyst does not depend on the physical nature.	Selectivity of the catalyst depends on the physical nature.

14. What are enzymes (or) biological catalyst? Give examples.

Enzymes are a type of catalysts which are responsible for increasing the rate of reaction in plants and animals. The catalysis in which enzymes act as a catalyst is called enzyme catalysis.

Eg. Diastase acts as catalysts in the conversion of starch into maltose.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Diastase}} \underset{\text{Maltose sugar}}{nC_{12}H_{22}O_{11}}$$

15. What is acid-Base catalysis? Give examples.

A number of homogeneous catalytic reactions which are catalyzed by acids or bases, or both acids and bases. These are often referred as Acid-Base catalysis.

E.g: Decomposition of the sucrose into glucose and fructose in sulfuric acid (or) Inversion of cane sugar.

$$C_{12}H_{22}O_{11\,(l)} + H_2O_{(l)} \xrightarrow{H^+} C_6H_{12}O_{6\,(l)} + C_6H_{12}O_{6\,(l)}$$

16. What is turn over number (K_3)?

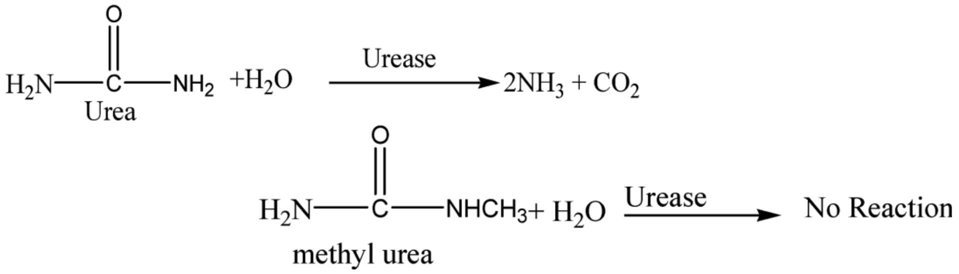
It is defined as the number of molecules converted into products in unit time by one molecules of enzyme. Mathematically,

$$d[P]dt= k3E0[S]km$$

Where, the constant k3 in the above equation is known as Turn over number.

17. Enzyme is highly selective-justify.

Enzymes are highly specific, i.e. the same catalyst cannot be used in more than one reaction. E.g: Urease enzyme catalyses the hydrolysis of urea only and not the hydrolysis of any other amide



18. List out the application area of surface active agents

Surface active agents play an important role as cleaning, wetting, dispersing, emulsifying, foaming and anti-foaming agents in many practical applications and products, including: paints, emulsionsadhesives, inks, biocides (sanitizers), shampoos, toothpastes, firefighting (foams), detergents, insecticides, deinking of recycled papers, ski waxes, spermicides.

19. Define : Detergency

Process by which soil is removed from a surface and undergoes solubilization or dispersion. Result of several physicochemical phenomenons taking place at the interface of three phases : surface/soil/detergent.

20. Mention the action of detergency

The phenomenons are :

i. Wetting of surface.
ii. Removal of soil from surface.
iii. Avoiding re-deposition of soil on surface.

21. How will you define wetting?

Wetting is the ability of liquids to form interfaces with solid surfaces.

22. Differentiate de-foaming and anti-foaming

The term de-foaming agent and anti-foaming are two different terms. The term de-foamer describes a product that is added to destroy existing foam; whereas anti-foaming agent is a product that is added to a system in order to prevent the foam from occurring.

PART-B

1. Differentiate physisorption and chemisorption?
2. Explain the factors affecting adsorption of solutes from solutions.
3. Derive Langmuir adsorption isotherm.
4. Bring out the role of adsorption in heterogeneous catalyst?
5. What are the common applications of adsorption?
6. Describe the effects of catalyst with diagram.
7. Write the characteristics of catalyst.
8. Explain the following the terms with suitable examples: Acid base catalysis.
9. Discuss the characteristics of enzyme catalysis.
10. Derive Michaelis Menten equation. Mention its importance.
11. Derive Langmuir- Hinshelwood mechanism
12. Explain the action detergency
13. Discuss wetting and its application

PART -A

2 MARK QUESTIONS AND ANSWERS

1. What is Nano chemistry (or) Nanoscience?

Nano chemistry is defined as the study of phenomena and manipulation of materials at

atomic, molecular and macromolecular scales

2. What is Nano Technology?

The design ,characterization and application of structures,devices and systems by

controlled manipulation of materials at nano scales is known as Nano Technology

3. What are Nano particles?

Nano particles are particles, the size of which ranges from 1-50 nm.

4. Define nano wires.

Nano wires is a materials having an aspect ratio, length to width ratio greater than 20.

Nano wires are also referred to as quantum wires.

5. What are the characteristics of Nano wires?

- Nano wires are one dimensional material.
- Conductivity of a nano wire is less than that of the corresponding bulk materials.
- It exhibits distinct optical, chemical, thermal and electrical properties due to this large surface area.

6. What are nano rods?

Nano rod is a material having an aspect ratio in the range 1 to 20 with short dimension of the materials being 10-100 nm.

7. **What are nano clusters?**

Nano clusters constitute an intermediate state of matter between molecules and bulk materials .these are fine aggregates of atoms or molecule.

8. **What is magic number?**

It is the number of atoms in the clusters of critical sizes with higher stability.

9. **How are nanomaterials classified?**

1.Zero-dimensional (0D) nanomaterials 2.One-dimensional (1D) nanomaterials.

3.Two-dimensional (2D) nanomaterials 4.Three-dimensional (3D) nanomaterials

10.Distinguish between bulk and nanoparticles

Nano particles	Bulk particles
1. Size is less than 100nm	Size is larger in micron size
2. Collection of few molecules	Collection thousands of molecules
3. Surface area is more	Surface area is less
4. Strength, hardness are more	Strength, hardness are less.

11. **What are size dependent properties? Give examples.**

On a nanometre scale, materials behave differently when compared to larger scales. Chemical and physical properties of a nanomaterial become size-dependent. Some of the major size dependent properties include

(i) Thermal properties – melting temperature
(ii) Optical properties – absorption and scattering of light
(iii) Chemical properties – reactivity, catalysis
(iv) Mechanical properties – mechanical strength
(v) Electronic properties – conductance behaviour
(vi) Magnetic properties – superparaagnetic effect.

12. **What are the advantages of sonochemical method?**

- Decrease of reaction time and increase of yield
- More uniform, smaller and pure crystals with minimal agglomerations are formed

- No chemical reducing agent is necessary for reaction
- Possible switching of reaction pathway
- Use of less or avoidance of phase transfer catalyst

13. State the advantages of electrodeposition

- It is relatively cheap and fast and allows complex shapes.
- It can be performed at low temperatures which will minimize inter diffusion of materials in the case of a multilayered thin film preparation.
- The film thickness can be controlled by monitoring the amount of charge delivered
- The composition and defect chemistry can be controlled by the magnitude of the applied potential, which can be used to deposit non-equilibrium phases.

14.List out the advantages of ball milling method of nanoparticle synthesis

- Few mg to several kgs of nanoparticle can be synthesized in a short time.
- This technique can be operated at large scale.
- It is useful in preparation of elemental and metal oxide nano crystals like Co, Cr, Al-Fe, Ag-Fe and Fe.
- Variety of intermetallic compounds of Ni and Al can be formed.
- Ball milling method is useful in producing new type building materials, fire – proof materials, glass ceramics, etc.

15. What are carbon Nanotubes?

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure.

Nanotubes have been constructed with length-to-diameter ratio of greater than 1,000,000.

These cylindrical carbon molecules have unusual properties and wide range of applications.

16. How is carbon Nanotubes classified?

Carbon nanotubes are classified into two types,

1. Single-walled nanotubes 2. Multi-walled nanotubes.

17. Mention some important applications of CNTs.

- It is used in storage devices.
- It is used as a catalyst.
- It is used as protective shield.
- As a good reinforcing element in composites.

18. List out the advantages and disadvantages of solvothermal process

Advantages

- Products obtained are in crystalline form. So no purification required.
- Can be used for preparing nanomaterials of different morphology (powder, rod, wire, tube, single crystals and nanocrystals).
- Precise control over the size, shape distribution and crystallinity of nanoparticles by varying experimental conditions.

Disadvantages:

- Inability to monitor crystals in the process of their growth.
- The need to expensive autoclave.
- Safety issues during the reaction process.

19. What is biogenic synthesis of nano particles?

The synthesis in which employ biological systems like bacteria, fungi, viruses, yeast, actinomycetes, plant extracts, etc used as reducing agent to producef metal and metal oxide nanoparticles..

20.Differentiate between biogenic and chemically synthesized nanoparticles

Properties	**Chemical**	**Biological**
Nature	Expensive, toxic	Cost effective, nontoxic
Reducing agent	Dimethylformamide, ethylene glycol, hydrazine hydrate, sodium borohydride, polyol, sodium citrate and N,N-dimethyformamide	Biomolecules include phenolics, polysaccharides, flavones, terpenoids, alkaloids, proteins, amino acids, enzymes, predominantly, nitrate reductase
Method	Stabiliser (surfactant) is added to the first solution to prevent the agglomeration of nanoparticles	There is no need to add a stabilising agent
Environmental impact	Environmental pollution is a disadvantage of the chemical method and the chemical reduction methods are energy-intensive	Synthesis carried out in environmental conditions and they are safe enough, and consume no energy

21. List out the drawbacks of bio synthesis

- Time consuming – Rate of production is slow
- Difficulty in control over size distribution, shape and crystallinity.
- The nanoparticles are also not mono dispersed.

PART-B

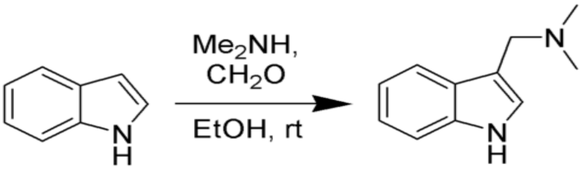
1. Distinguish between molecules, nanoparticles and bulk materials.
2. Discuss the solvothermal method of synthesis of nanomaterials.
3. Explain how nanomaterials are synthesized by the chemical vapour deposition.
4. Discuss the various size dependent properties of nanomaterials.
5. Explain how nanomaterials are synthesized by the electro deposition.
6. Give an account on sonochemical method of synthesis of nanomaterials.
7. Write short notes on photochemical synthesis of nanomaterials.
8. Write note on i.Nanowire ii.nanoclusters

Heterocyclic compounds

Part-A

1. What happened when indole treated with formaldehyde and dimethylamine?

Ans:



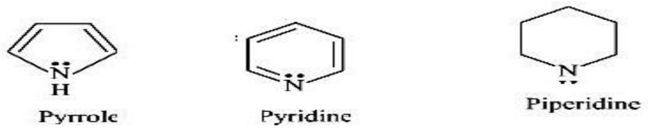
Gramine

2. Compare the basicity of pyrrole, pyridine and piperidine?

Ans:

Increasing Order of basicity of pyrrole, pyridine and piperidine is:
pyrrole< pyridine <piperidine.

Structure of pyrrole, pyridine and piperidine



Pyrrole is least basic as lone pair is not free for donation as it it is in resonance while in pyridine it is not in resonance and free for donation , and piperidine is most basic as lone pair is in sp^3 hybrid orbital while in pyridine it is in sp^2 hybrid orbital , and greater the s-character , more strongly it will be bonded and less available for donation.

3. Five membered rings are less stable than 6 membered rings- Justify.

Ans:
6-membered rings can have 3D conformations, such as the chair conformation (the more stable) and the boat conformation. These conformations relax the angles, getting them closer to the tetrahedral angle. Thus, cycle gains stability. That is why 5-membered rings are less stable than 6-membered.

4. Why thiopheneis most resonance stabilized?

Ans:
As thiophenehasSulphur and least electronegativity ring than nitrogen and oxygen in pyrrole and furan respectively.

5. Five membered rings come under which category of heterocycle classification on the basis of chemical behavior?

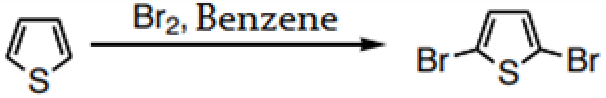
Ans:
In five membered ring, 6 π electrons are distributed between 5 atoms, each atom shares more than 1 e^- (1.2e^-). So, it falls under the category of excessive heterocyclic behaviour

6. What is the reactivity order of five membered heterocyclic compounds?

Ans:
Pyrrole is more reactive than furan and thiophene in electrophilic reactions. Therefore; pyrrole is more prone to electrophilic substitution than furan. The nitrogen atom in pyrrole can conjugate with the π-electrons on the ring, so the density of the π-electrons on the ring will increase.

7. What is the product when thiophene reacts with Br2 in benzene?

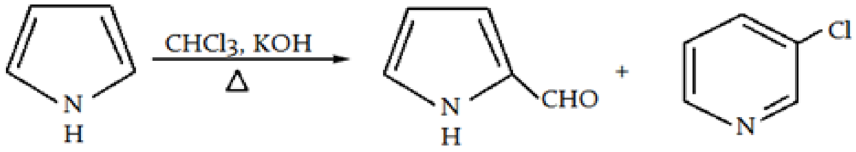
Ans:
This is electrophilic substitution reaction, bromination of thiophene in presence of benzene leads to formation of 2,5-dibromothiophene.



8. What is the product when pyrrole reacts with Br_2 in ethanol?

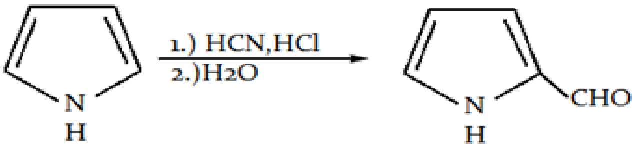
Ans:
This is electrophilic substitution reaction, bromination of pyrrole in presence of ethanol leads to formation of 2,3,4,5-tetrabromopyrrole.

9. What is the name of the following reaction?



Ans:
This is a Riemertiemann reaction, in which boiling pyrrole will react with aqueous or alcoholic potash and chloroform.

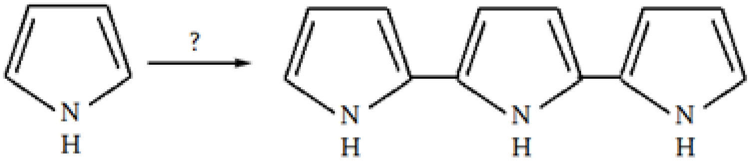
10. What is the name of the following reaction?



Ans:

This is a Gattermann reaction, in which boiling pyrrole will react with HCN and HCl followed by addition of water and leads to formation of pyrole-2-carbaldehyde.

What will be the reagent used for the completion of the following reaction?

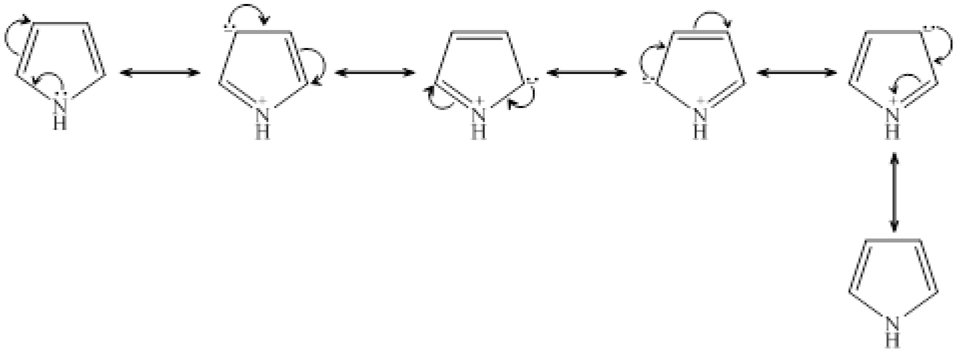


In dilute acid for a brief time, pyrrole form trimer.

11. Pyrrole is acidic in character like phenol. Why?

Ans:

The electron pair in the pyrrole is delocalization from nitrogen makes it positively charged and increases the possibility of proton abstraction giving pyrrole anion.

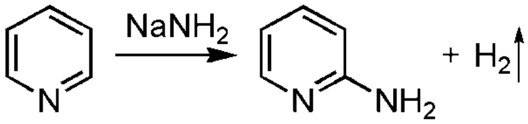


Furthermore, the pyrrole anion is stabilized by delocalization of the negative charge over the ring.

12. What is Chichibabin reaction? Give one example.

Ans:

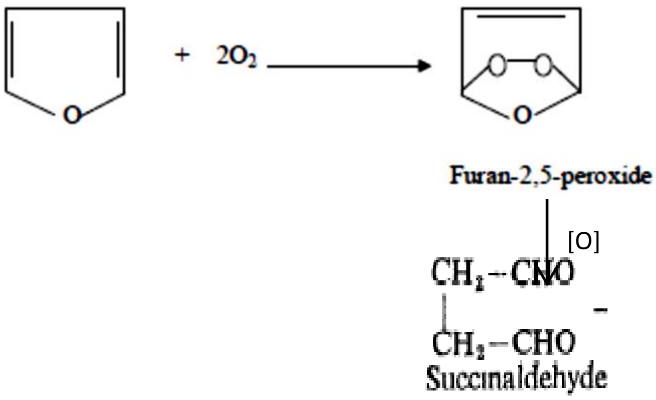
The general process of the reaction involves taking pyridine (an aromatic molecule) and mixing it with NH_2^-. The introduction of the NH_2^- replaces a hydrogen on the pyridine next to the N.



Because this reaction involves substitution on an aromatic ring, you would think this reaction would be EAS. However, NH_2^- is a nucleophile which makes the pyridine the electrophile so this reaction is not actually EAS.

13. How will you convert furan into succinaldehyde?

Ans:



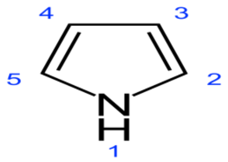
14. Write a note on Skraup synthesis?

Ans:

- The **Skraup synthesis** is a chemical reaction used to synthesize quinolines.
- It is named after the Czech chemist Zdenko Hans Skraup.
- In the reaction, aniline is heated with sulfuric acid, glycerol, and an oxidizing agent such as nitrobenzene to yield quinolines.
- The glycerol undergo the dehydration to form acrolein.
- The attack ognucleophilic amine group on the acrolein lead to formation of intermediate which undergo further reaction and cyclization to form quinioline.

15. Write structure of pyrrole?

Ans:



PART-B

1. Explain the synthesis and electrophilic substitution reactions of pyrrole

2. Write down the structural formula of the reactants and the products obtained in the following reactions

   (i) Tetra hydro furan with ammonia
   (ii) Pyrrolewith benzenediazonium chloride.
   (iii) Furan with maleic anhydride
   (iv) Catalytic reduction of thiophene in presence of nickel

3. Discuss about the electrophilic and nucleophilic substitution reactions of pyridine.

4. Explain i. Fischer indole synthesis, ii.Skaurp synthesis.

5. What do you understand by heterocyclic compounds? Give the preparation, properties and uses of quinolone.

6. Pyridine, though aromatic like benzene, can undergo nucleophilic substitution easily, while benzene cannot. Explain.

7. How will you synthesize Isoquinoline? Give its resonance structures. What are the oxidation products of Isoquinoline.

8. (a) Discuss the structure of quinolone and isoqunioline.

(b) How will your convert isoquinoline into phthalic acid and cinchomeronic acid?

9. How will you proceed to bring following conversions/

(a) Pyrrole into 3-chloropyridine

(b) Furan into 2-acetyl furan

(c) Thiophene into thiophene-2-carboxylic acid

(d) Furfural into furoin

(e) Indole into 3-Iodoindole?

10. Discuss the importance of heterocyclic compounds in medicine and biochemistry.

UNIT V
PART A

1.Define Polymers
2. What is degree of polymerization?
3. Explain functionality of a monomer with suitable example
4. Explain condensation polymerization with suitable example
5.What are additional polymers? Give an example
6. What is copolymerization? Give an example
7. Differentiate additional and condensation polymerization
8.Mention the preparation and uses of PVC
9. List ou the various ways by which polymers can be classified
10. What do you understand by disproportionation of polymer chains?
11. What are the advantages of green polymers?
12. How polycarbonate is prepared?
13. Mention the properties of Kevlar.
14. What are the advantages of green polymers?
15. Give the chemical structure of polyurethane and polycarbonate.

PART B
1.Explain the mechanism of free radical polymerization
2. Discuss the effect of structure on polymer properties

3. Explain the preparation and properties of KEVLAR.
4. Describe a method of preparation of Nylon 6,6 and mention its properties and uses.
5. How polycarbonate is prepared? Mention its properties and uses.
6. Explain the preparation, properties and uses of polyurethane.
7. How PET is prepared? Mention its properties and uses.
8. Differentiate between addition and condensation polymerization.
9. What are green polymers? Discuss the synthesis and application of PLA.
10. Explain how polymers are classified on the basis of their thermal behavior and method polymerization. Give one example for each case.