

Molecular Orbital Theory

Postulates:

1. When nuclei of two atoms come close to each other, their atomic orbitals combine leading to the formation of molecular orbitals (MO) and electrons in them belong to the molecule as a whole.
2. The atomic orbitals of same energy and symmetry will combine to form molecular orbitals (MO).
3. The number of molecular orbitals (MOs) formed is equal to the number of atomic orbitals that are combined. The MO thus formed is associated with a definite energy level and the total energy of the molecule is the sum of energies of occupied molecular orbitals.

When two atomic orbitals are combined, one of the resulting MOs is at a lower energy than the original atomic orbitals; this is a bonding orbital (BMO). The other MO is at a higher energy than the original atomic orbitals; this is an antibonding orbital (ABMO).

Difference between a BMO and an ABMO

- a. BMO is formed by addition overlap of atomic orbitals (AO). ABMO is formed by subtraction overlap of AOs.
 - b. BMO has lower energy and hence greater stability than the AOs from which it is formed. ABMO has a higher energy and lower stability than the AOs.
 - c. The electron charge density in between the nuclei is high resulting in lesser repulsion between the nuclei and this causes greater stability of the BMO. In ABMO, the electron charge density is low in between the nuclei which causes greater repulsion and hence destabilizes the ABMO.
4. The atomic orbitals of the atoms in a molecule completely lose their identity after the formation of MOs.
 5. Electrons fill the molecular orbitals in the same way as they fill the atomic orbitals, following the Aufbau principle, Pauli Exclusion Principle and the Hund's rule of maximum multiplicity.

Aufbau principle:

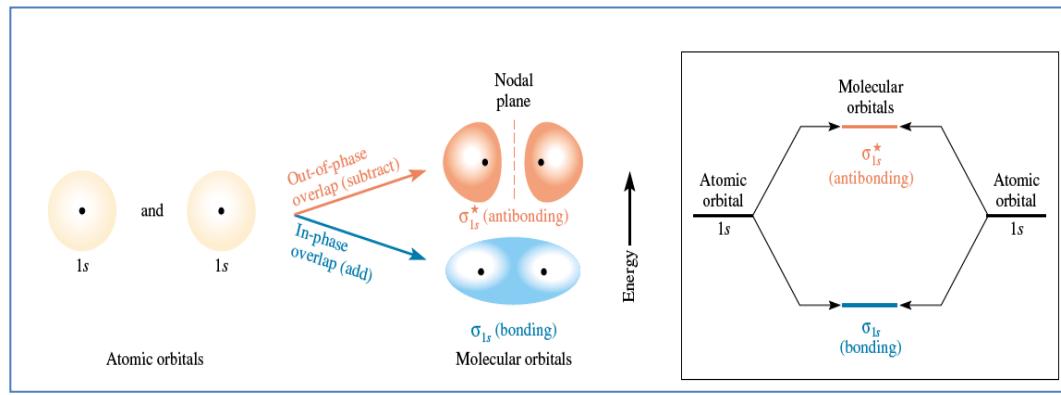
- Orbitals of lowest energy are filled up first.
- Each orbital will hold a maximum of two electrons, provided that they have opposite signs.

Pauli Exclusion Principle

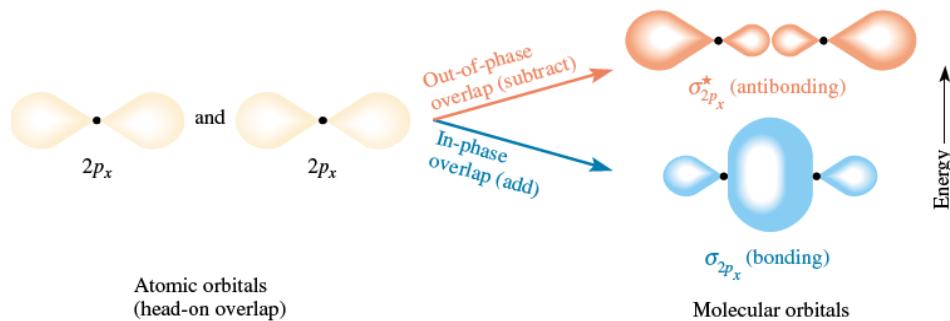
- in a given atom orbital, no two electrons can have all four quantum numbers the same.
- when applied for MO, the principle states that no two electrons in the same molecule can have all four quantum numbers the same.

Hund's rule:

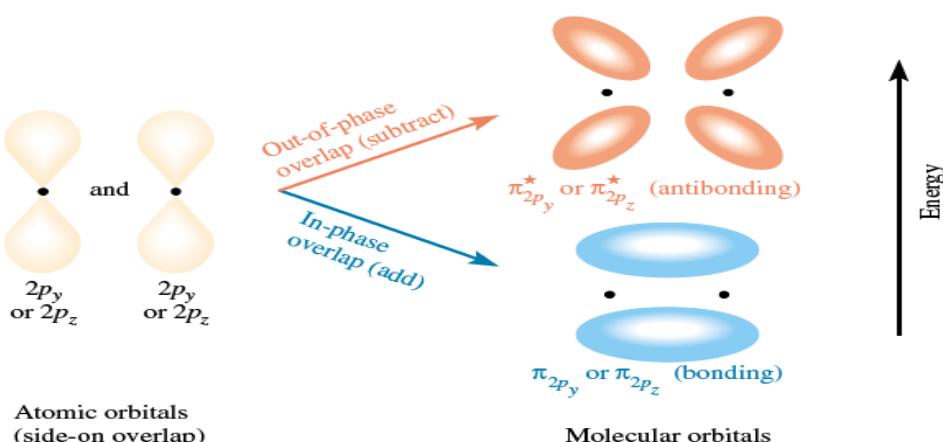
- Several orbitals have the same energy (degenerate orbitals of d, f)
- Electrons will be arranged so as to give maximum number of unpaired spins.



(MO) diagram for the combination of the 1s atomic orbitals on two identical atoms (*at the left*) to form two MOs: a *bonding* orbital, 1s (blue), resulting from addition of the 1s orbitals. The other is an *antibonding* orbital, 1s* (red), at higher energy resulting from subtraction of the combining 1s orbitals. Nuclei are represented by dots.



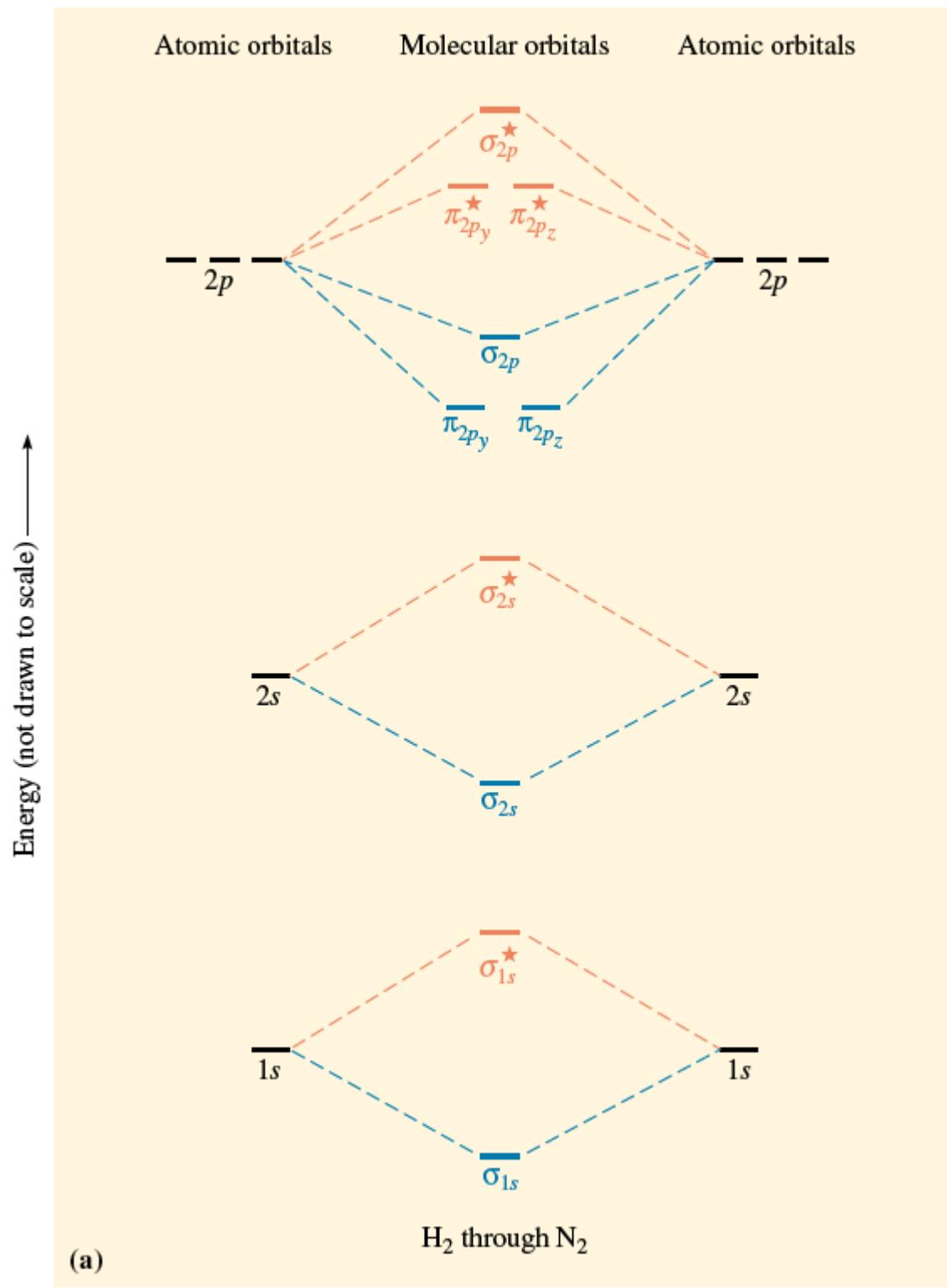
Production of σ_{2p_x} and $\sigma^*_{2p_x}$ MO by overlap of σ_{2p_x} AO on two atoms.



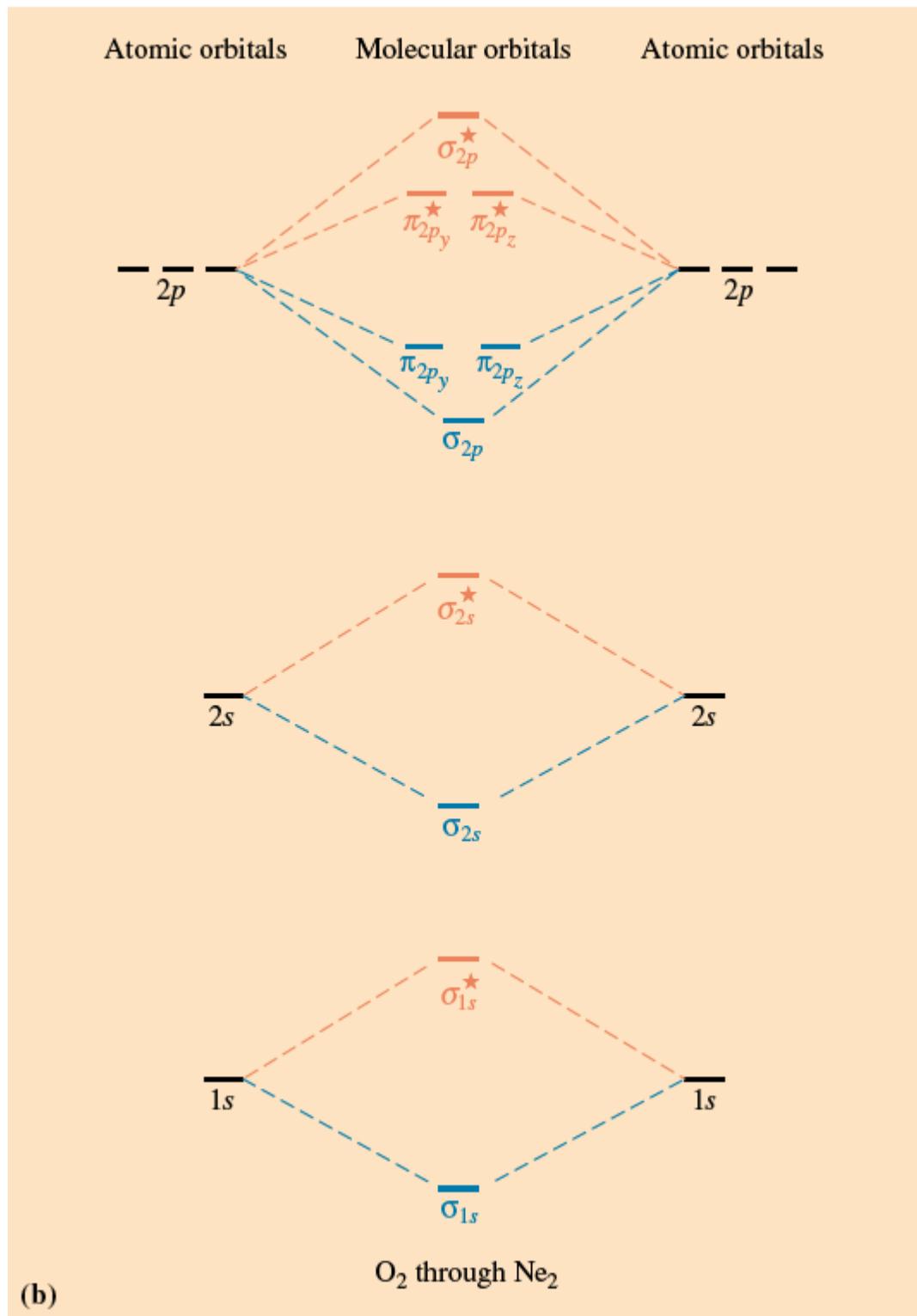
The $\Pi 2p$ and $\Pi^* 2p$ MO from overlap of one pair of 2p AO (for instance, $2p_y$ orbitals)

6. The order of energy of molecular orbitals

In simple homonuclear diatomic molecules (H_2 , He_2 , Li_2 , Be_2 , B_2 , C_2 , N_2) the order is



$$(\sigma 1s), (\sigma^* 1s), (\sigma 2s), (\sigma^* 2s), (\pi 2p_y) = (\pi 2p_z), (\sigma 2p_z), (\pi^* 2p_y) = (\pi^* 2p_z), (\sigma^* 2p_z)$$



For diatomic molecules like O_2 , F_2 and hypothetical Ne_2 , the order is $(\sigma 1s)$, $(\sigma^* 1s)$, $(\sigma 2s)$, $(\sigma^* 2s)$, $(\sigma 2p_x)$, $(\pi 2p_y) = (\pi 2p_z)$, $(\pi^* 2p_y) = (\pi 2p_z)$ $(\sigma^* 2p_x)$

7. Bond order and stability:

If N_b represents the number of electrons present in the BMO and N_a the number of electrons present in the ABMO.

$$\text{Then Bond Order (BO)} = \frac{[\text{BMO} - \text{ABMO}]}{2}$$

- a. If $\text{BO} > 1$; i.e BMO $>$ ABMO; then the molecule is stable
- b. If $\text{BO} < 1$; then the molecule is unstable
- c. If $\text{BO} = 0$; the molecule is unstable.
- d. For diatomic molecules, the stability is directly proportional to the bond order. Thus a molecule with a bond order 3 is more stable than a molecule with a bond order 2.
- e. Bond length is found to be inversely proportional to the bond order. Greater the bond order, shorter is the bond length.

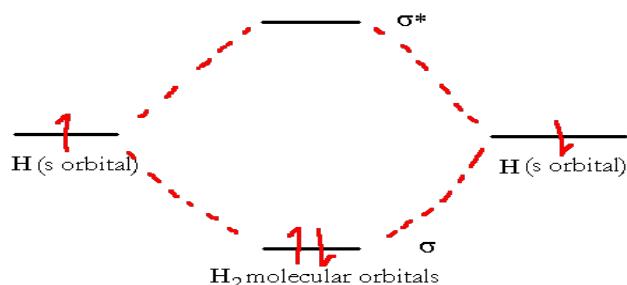
8. Diamagnetic and paramagnetic nature of the molecules

If all the electrons in the molecule are paired, it is diamagnetic in nature.

On the other hand, if the molecule has some unpaired electrons, it is paramagnetic in nature.

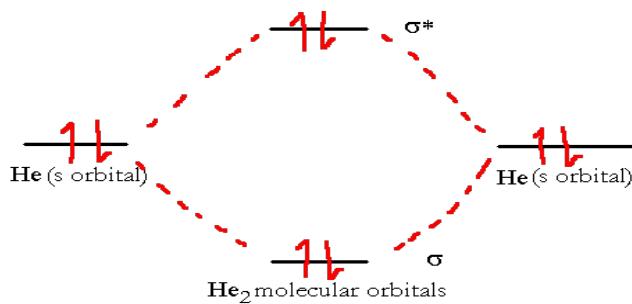
Molecular orbital diagrams of homonuclear diatomic molecules

1. H_2

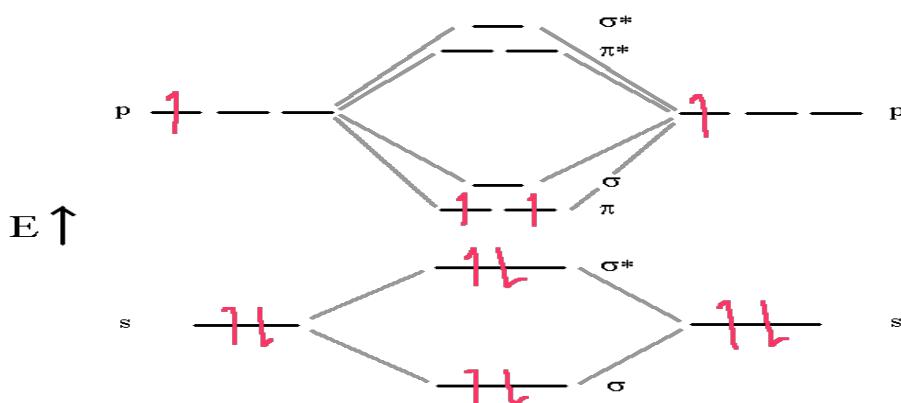


- The Molecule H_2 has an electron configuration $(\sigma_{1s})^2$.
- Bond order = [bonding electrons-Anti-bonding electrons]/2 = $2/2 = 1$.

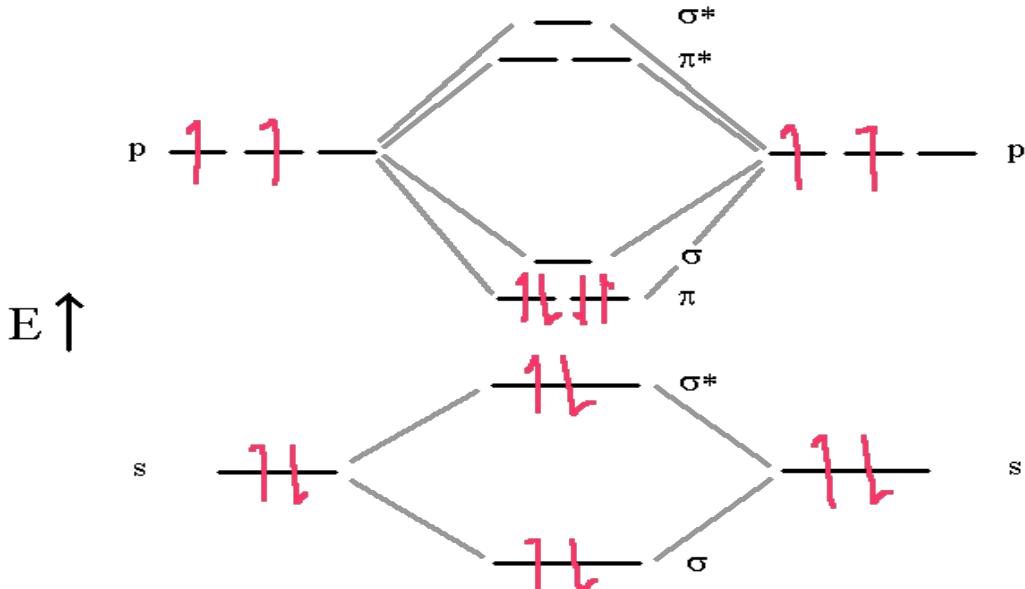
2. He_2



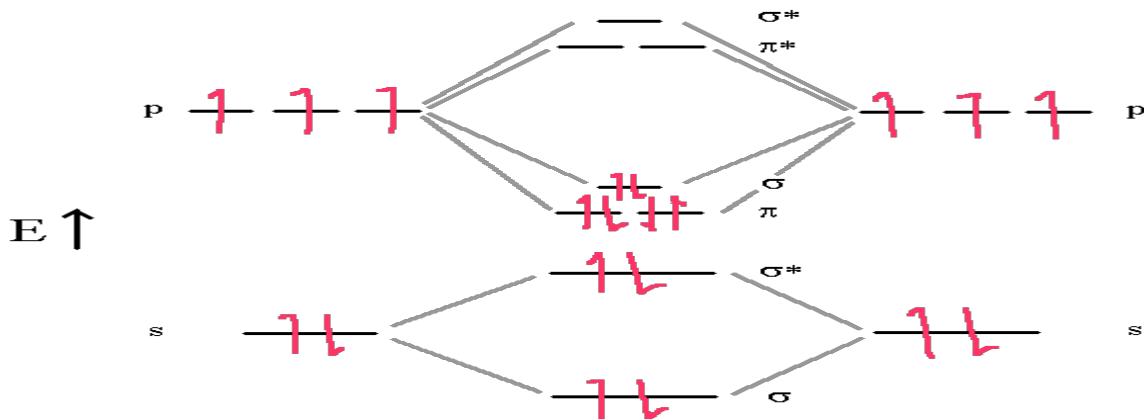
- The MO electronic configuration is $(\sigma_{1s})^2(\sigma_{1s}^*)^2$, i.e., one bonding orbital having 2 electrons and one antibonding orbital having 2 electrons.
- Bond order = $[2-2]/2 = 0$
- Thus the He_2 molecule does not exist.

3. B₂

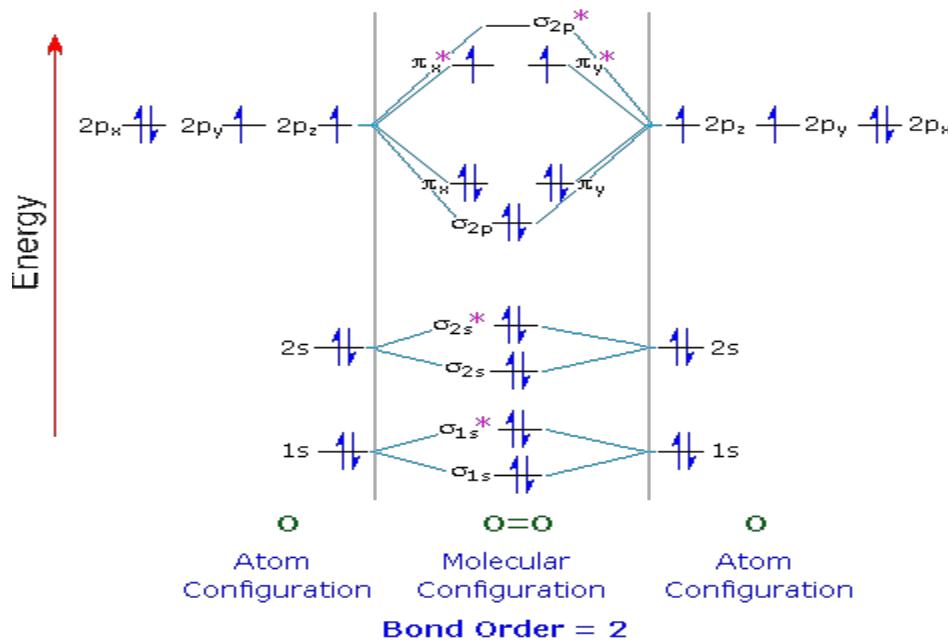
- Atomic Number of B = 5; Number of electrons in Boron molecule = 10
- The MO electronic configuration is $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 [(\pi 2p_y)^1 (\pi 2p_z)^1]$, **π2p orbitals have lower energy than σ2p_x orbital.**
- Since the π_{2p_y} , π_{2p_z} orbitals are degenerate (identical energy) Hund's rule applies and each orbital is singly filled.
- The inner shell does not participate in bonding. Stability occurs due to filling of π_{2p} orbitals
- Bond order = $[6-4]/2 = 1$; hence B₂ exists

4. C₂

- Atomic Number of C = 6; Number of electrons in C₂ molecule = 12
- The MO electronic configuration is $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 [(\pi 2p_y)^2 (\pi 2p_z)^2]$
- Bond order = $[8-4]/2 = 2$; hence C₂ exists

5. N₂

- Atomic Number of N = 7; Number of electrons in N₂ molecule = 14
- The MO electronic configuration is $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 [(\pi 2p_y)^2 (\pi 2p_z)^2] (\sigma 2p_x)^2$
- The inner shell do not participate in bonding, the bonding and antibonding 2s orbitals cancel each other, so only one σ2px and 2 π2p orbitals remain giving a
- Bond order = $[10-4]/2 = 3$; hence 3 bonds exist in N₂ molecule

O₂

- Atomic Number of O = 8; Number of electrons in O₂ molecule = 16
- The MO electronic configuration is $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 [(\pi 2p_y)^2 (\pi 2p_z)^2] (\sigma 2p_x)^2 [(\pi^* 2p_y)^1 (\pi^* 2p_z)^1]$

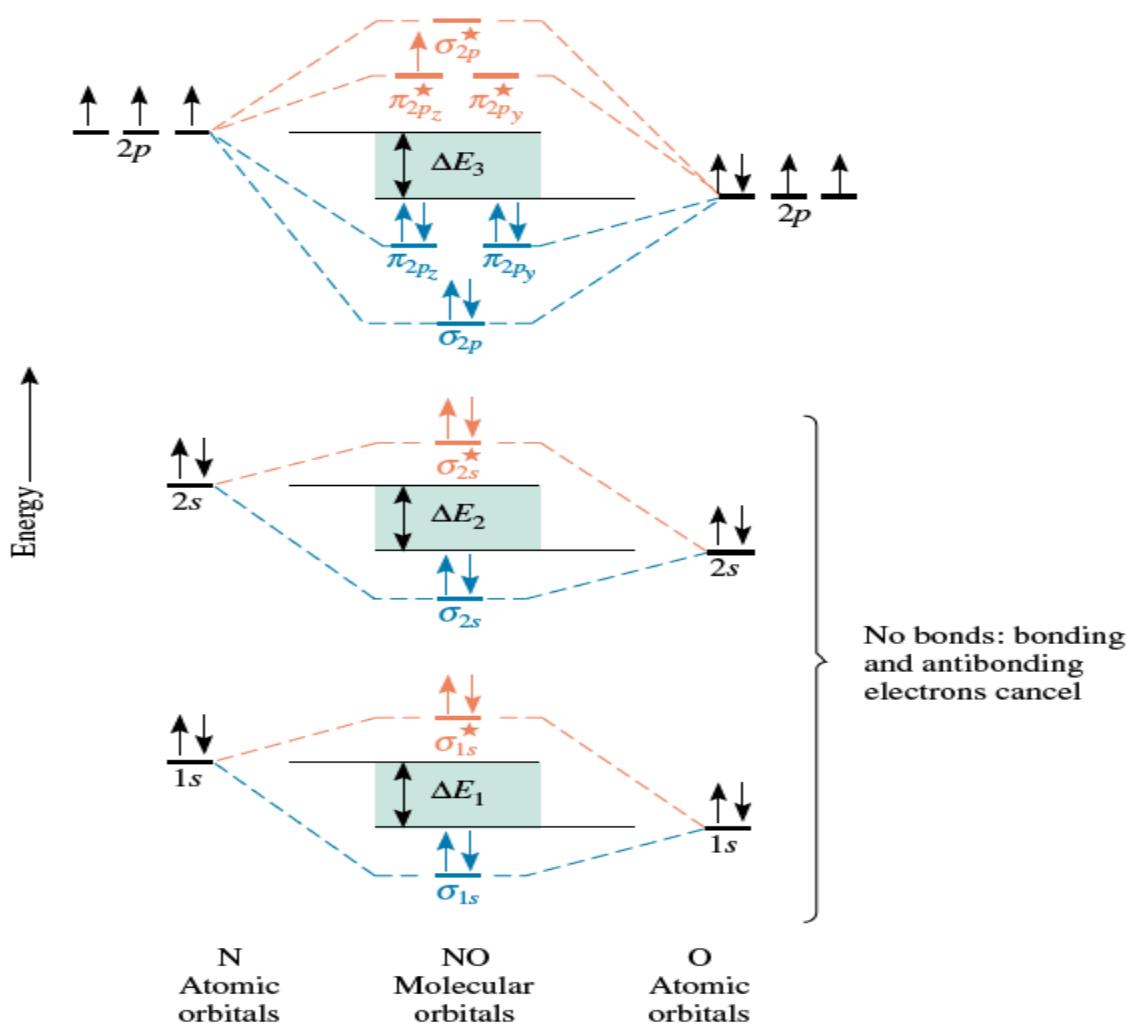
- The antibonding $\pi^*_{2p_y}$ and $\pi^*_{2p_z}$ orbitals are singly occupied in accordance to Hund's rule.
- Unpaired electrons give rise to paramagnetism. Since there are two unpaired electrons with parallel spins, this explains why oxygen is paramagnetic.
- Bond order = $[10-6]/2 = 2$; hence a double bonds exist in O₂ molecule

Molecular Orbitals for First- and Second-Period (Row) Diatomic Molecules^a

	H ₂	He ₂ ^c	Li ₂ ^b	Be ₂ ^c	B ₂ ^b	C ₂ ^b	N ₂	O ₂	F ₂	Ne ₂ ^c
Increasing energy (not to scale)	σ_{2p}^* $\pi_{2p_y}^*, \pi_{2p_z}^*$ σ_{2p} π_{2p_y}, π_{2p_z} σ_{2s}^* σ_{2s} σ_{1s}^* σ_{1s}	— — — — — — — —	— — — — — — — —	— — — — — — — —	— — — — — — — —	— — — — — — — —	π_{2p_y}, π_{2p_z} σ_{2p}	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$
Paramagnetic?	no	no	no	no	yes	no	no	yes	no	no
Bond order	1	0	1	0	1	2	3	2	1	0
Observed bond length (Å)	0.74	—	2.67	—	1.59	1.31	1.09	1.21	1.43	—
Observed bond energy (kJ/mol)	436	—	110	9	≈270	602	945	498	155	—

^aElectron distribution in molecular orbitals, bond order, bond length, and bond energy of homonuclear diatomic molecules of the first- and second-period elements. Note that nitrogen molecules, N₂, have the highest bond energies listed; they have a bond order of three. The species C₂ and O₂, with a bond order of two, have the next highest bond energies.

^bExists only in the vapor state at elevated temperatures.

Molecular orbital diagrams of heteronuclear diatomic molecules1. NO

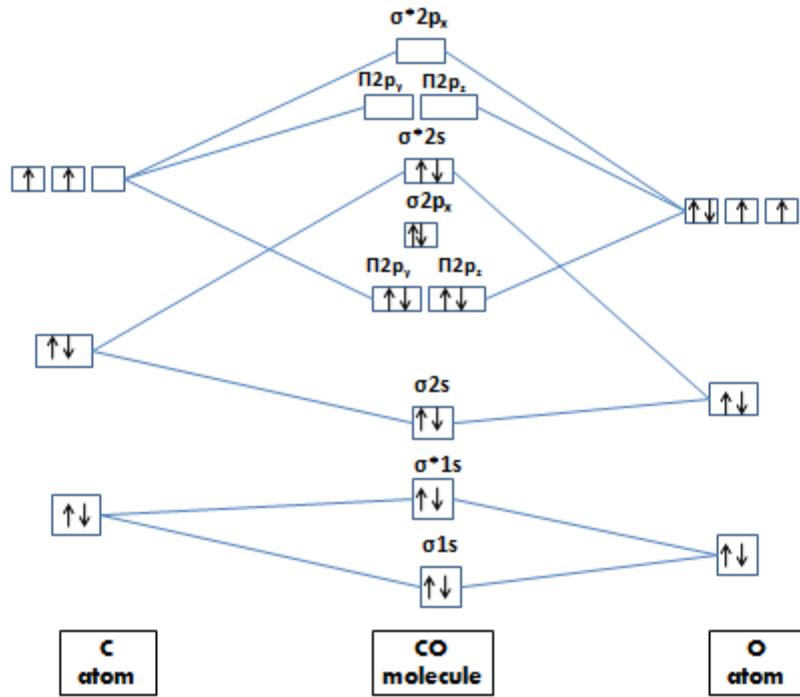
MO energy level diagram for nitrogen oxide, NO, a slightly polar heteronuclear diatomic molecule

- Atomic Number of N = 7; Atomic Number of O = 8; Number of electrons in NO = 15
- The MO electronic configuration is $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_x)^2 [(\pi 2p_y)^2 (\pi 2p_z)^2 ((\pi^* 2p_y)^1 (\pi^* 2p_z)^0) (\sigma^* 2p_x)]$
- The AO of oxygen, the more electronegative element, are a little lower in energy than the corresponding AOs of nitrogen, the less electronegative element.
- Bond order = $[10-5]/2 = 2.5$; hence NO is stable.
- NO is paramagnetic since it contains one unpaired electron.

2. CO

- Atomic Number of C = 6; Atomic Number of O = 8; Number of electrons in CO = 14
- The MO electronic configuration is

$$(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 [(\pi 2p_y)^2 (\pi 2p_z)^2] (\sigma 2p_x)^2 (\sigma^* 2s)^2$$
- The AO of oxygen are a little lower in energy than the corresponding AOs of Carbon, the less electronegative element.
- Bond order = $[10-4]/2 = 3$; thus CO contains a triple bond.
- CO is diamagnetic because there are no unpaired electrons.



Metallic Bonding

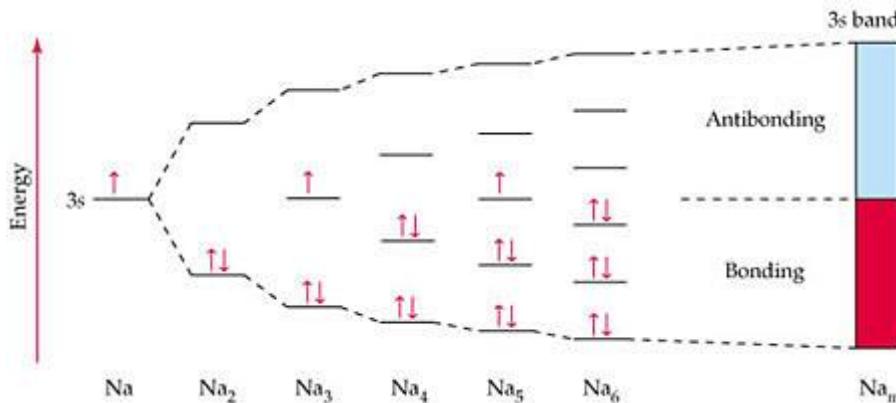
- The force of attraction which binds a metal atom to a number of electrons within its sphere of influence is known as metallic bond
- The attractive force that holds the atoms of two or more metals together in a metal crystal or in an alloy is known as metallic bond.
- Characteristics of metals:
 1. They are good conductors of heat
 2. They are good conductors of electricity.
 3. They have high density
 4. they have high melting point and high boiling point
 5. They have metallic luster
 6. they are hard and have high elasticity
 7. They have the tendency to crystallize
 8. They form alloys with other metals easily
 9. They can be drawn into wires (ductility) and can be hammered into sheets (malleability)

Molecular Orbital theory in metals or Band Theory

1. Band theory is a quantitative model of applying the MO theory to bonding in metals.
2. Postulates:
 - Each atomic orbital of two metal atoms interact giving rise to two molecular orbital.
 - Atomic orbitals combining to form MO need to have same energy and same symmetry.
 - Each MO is associated with a separate energy level and each has capacity to accommodate 2 electrons.
 - Bonding molecular orbitals result from constructive interference.
 - Antibonding molecular orbitals result from destructive interference.
 - Bonding orbitals are at a lower energy level than the antibonding MO
 - The number of molecular orbitals formed equals the number of atomic orbitals involved.
 - For every bonding molecular orbital formed, one antibonding molecular orbital is also formed.
 - For odd number of bonding atoms, a nonbonding molecular orbital is formed.
 - The molecular orbitals formed belong to the entire set of atoms
 - As the number of atoms increase in a metallic crystal, more will be the number of atomic orbitals which may overlap to give more MO each having a distinct energy level. The energy separation between any two adjacent MO energy levels would go on decreasing with increase in the number of overlapping atomic orbitals.
 - Consequently if the overlapping atomic orbitals are very large, there is virtually no energy difference from one MO to the next. At this point, the MO has merged into a band of continuous energy, and this is the origin of the term band theory.

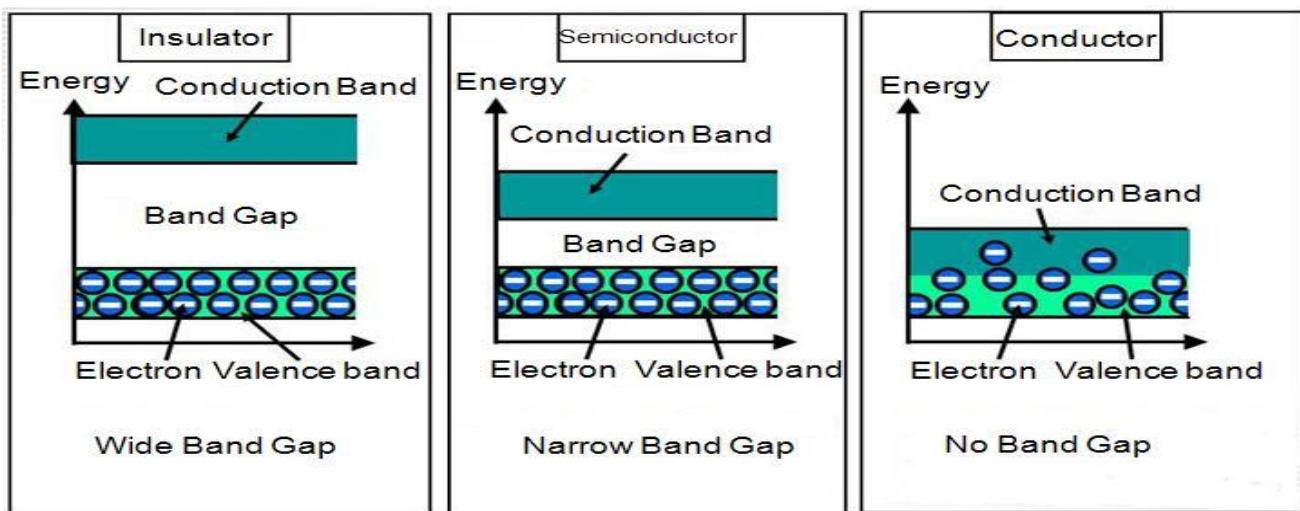
3. Let's consider sodium metal: The electronic configuration of Na atom is [Ne] 3s¹.

- a. In Na₂, the 3s orbitals of the two Na atoms combine to give a bonding MO (σ 3s) and an antibonding MO (σ 3s*). Each sodium atom has just one 3s valence electron, so the lower-energy bonding orbital is filled and the higher-energy antibonding orbital is empty.
- b. Suppose there are 3 Na atoms joined to form Na₃. Three 3s atomic orbitals combine to form 3 MOs-one bonding, one non bonding and one antibonding. The energy of non-bonding MO is in between that for bending and anti-bonding MO. The three valence electrons from the 3 Na atoms would occupy the bonding and non-bonding MO.
- c. In Na₄, 4 atomic orbitals combine to form four MOs- two bonding and two anti-bonding. The 4 valence electrons would occupy the two lowest bonding MOs. Thus half of the total number of MO is vacant.
- d. As the number of atoms increase, the spacing between the energy levels of various orbitals decrease. And when the number of atoms is very large, the energy levels of the orbitals are so close that a band of closely spaced MO is formed. This band which is half full with valence electrons and constituting the bonding MO is called the valence band (VB). The anti-bonding MO constituting the other half of the band and which is empty is called the conduction band (CB).



- In the case of Na metal, the gap between the valence band and conduction band is negligible and the band is half filled, slight excitation can move the valence electrons from valence band to conduction band. Hence sodium metal has high thermal and electrical conductivity.

4. Band theory helps to explain the properties of metals but also helps to classify metals into 3 categories: conductors, insulators and semi-conductors depending on the energy gap between the valence and conduction band.
- Conductors: Either the valence band and conduction band overlap (Magnesium metal) or there is half filled valence band (sodium metal).
 - Insulator: there is large gap between the filled valence band and empty conduction band (diamond). There is hence no electron movement of electrons from valence band to conduction band.
 - Semiconductors: when there is a small gap between the valence band and conduction band (Si or Ge) sufficient to promote an electron from VB to CB thereby contributing to conductivity.



Semiconductors are of two types:**Intrinsic semiconductors**

Intrinsic semiconductors are basically insulators at zero temperatures, but their conductivity increases with increase in temperature.

Extrinsic semiconductors

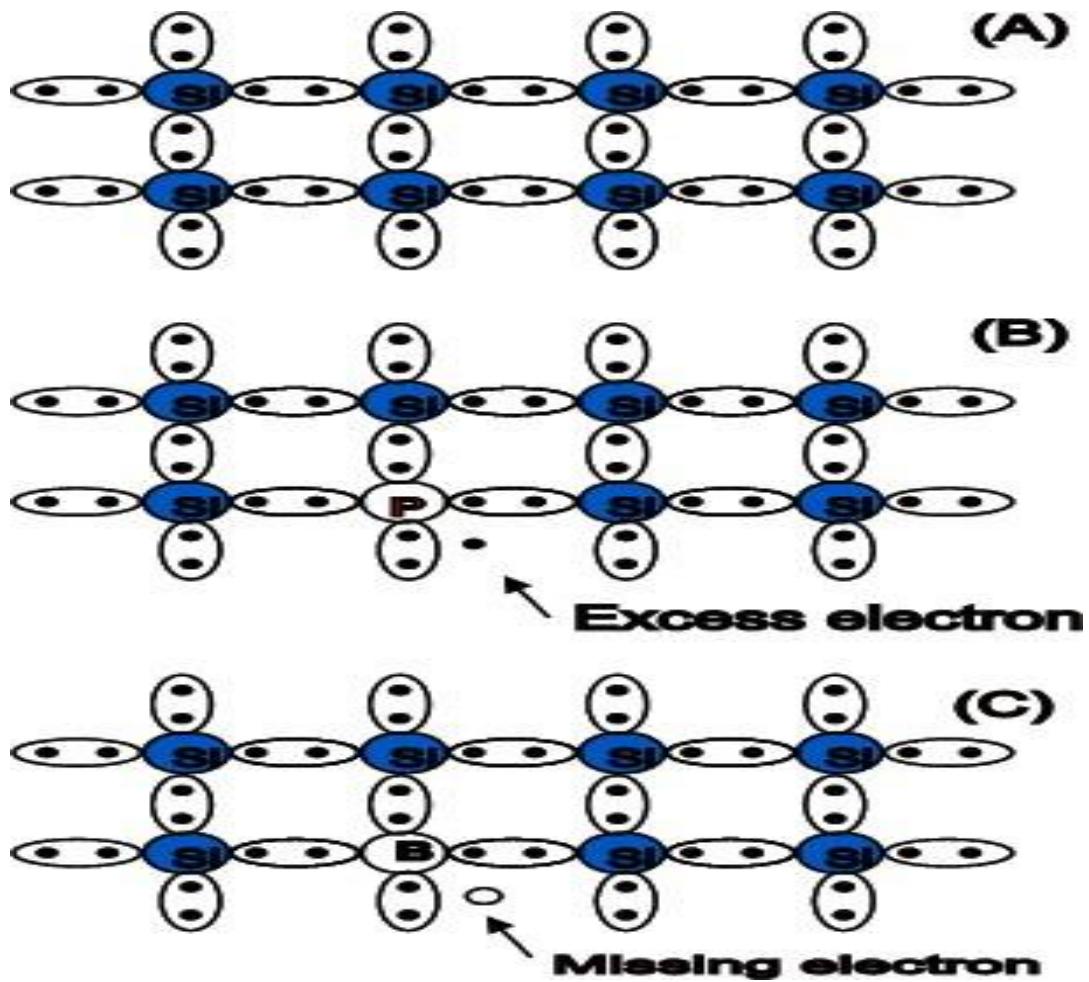
Semiconductors are produced by doping an insulator with a suitable impurity. Such types are called as extrinsic semiconductors. These are of two types: n-type and p-type semiconductor. Let us take our well-known silicon as an example. We know that silicon is covalently bonded with four silicon atoms. It suggests that there are no free electrons available for conduction [A].

n-type doping

Group 15 elements in the periodic table are, in general, considered for n-type doping. Typically, Phosphorous, Arsenic and Antimony are the elements from group V [B]. They have five electrons in the outermost shell and if it replaces an intrinsic silicon atom, one electron will remain as excess. Such kind of elements are called Donors. This excess (additional) electron is loosely bounded, and therefore it behaves more like a free-electron. In the band diagram, the energy levels of these donor atoms lie in the forbidden gap, slightly below the conduction band of intrinsic semiconductor.

p-type doping

Group 13 of periodic table elements is suitable for p-type doping. They are Boron, Gallium and Indium so on. The outermost shell contains three electrons, if such elements replace a Silicon atom one bonding remains vacant. Hence the dopant is ready to accept one electron and thus called an Acceptor [C]. The Acceptor energy level are close to valence band.



Hydrogen Bonding

The attractive electrostatic force which binds hydrogen atom (positive end) of one molecule with an electronegative atom (F, O, N) (negative end) of another molecule is known as hydrogen bond. The strength of a hydrogen bond varies from 10-40kJ/mol while that of a covalent bond is 400kJ/mol. Thus, hydrogen bond is much weaker than a covalent bond.

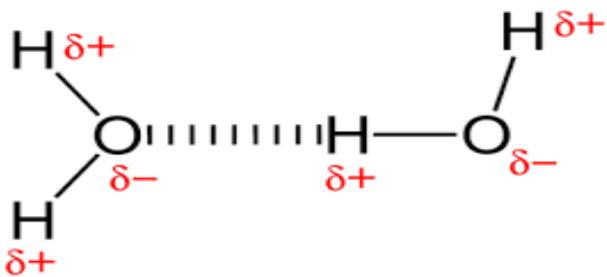
Example of molecules exhibiting hydrogen bonding are HF, H₂O, NH₃

In HF, F atom is highly electronegative; hence it pulls the covalently bonded electron pair towards the nucleus and away from the hydrogen atom. The hydrogen atom is then left with a partial positive charge and the F atom with a slight negative charge. This phenomenon of charge separation makes the HF molecule polar and the molecule behaves as a dipole. The electrostatic force of attraction causes one molecule of HF to get attached to another HF molecule. This attractive force between H atom of HF molecule and F atom of another HF molecule is hydrogen bond.

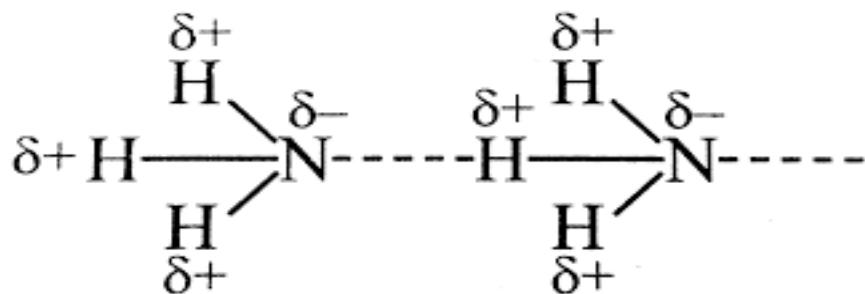


hydrogen bonding in HF (dotted line shows hydrogen bonding)

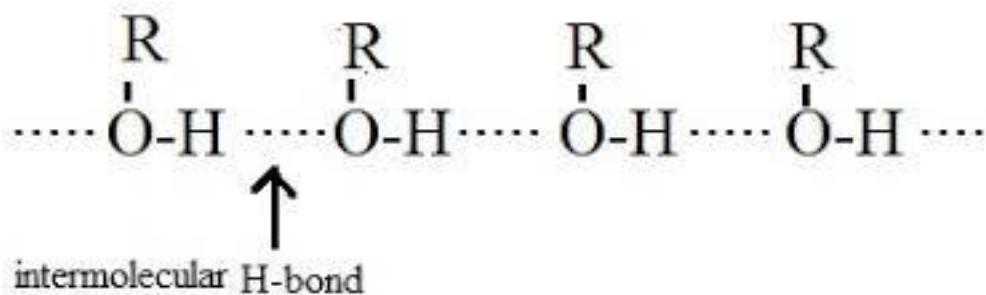
H₂O molecule too exhibits hydrogen bonding because it is polar molecule and because of its bent shape, is also a dipole; Oxygen end carrying a negative charge and hydrogen end carrying a positive charge.



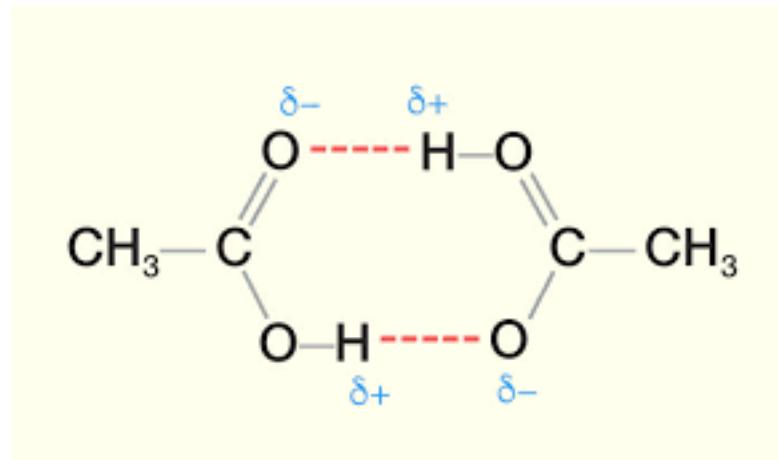
Hydrogen bonding in H₂O (dotted line shows hydrogen bonding)



Hydrogen bonding in NH_3 (dotted line shows hydrogen bonding)



Hydrogen bonding in alcohols (dotted line shows hydrogen bonding)



Hydrogen bonding in carboxylic acids (dotted line shows hydrogen bonding)

Types of hydrogen bonds

Hydrogen bonds can occur within one single molecule, between two like molecules, or between two unlike molecules.

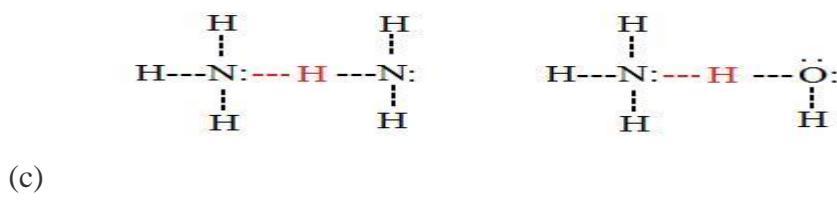
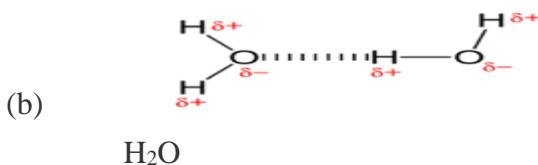
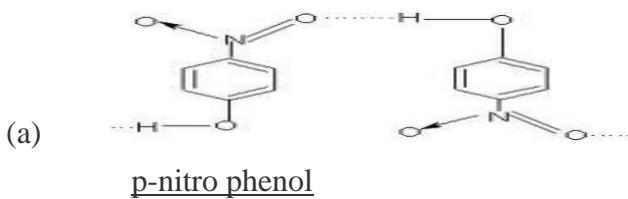
1. Intramolecular hydrogen bonds:

- Intramolecular hydrogen bonds are those which occur within one single molecule.
- This occurs when hydrogen and an electronegative element like O, N, F is present in the same molecule.
- Example is o-nitro phenol, o-Cl-phenol



2. Intermolecular hydrogen bonds

- Intermolecular hydrogen bonds occur between hydrogen atom of one molecule and an electronegative atom of another molecule of the same substance.
- Example, NH₃, H₂O molecules alone, or between NH₃ and H₂O molecules.



Consequences of hydrogen bonding

1. Melting and boiling points:

Compounds exhibiting hydrogen bonding have strong intermolecular force of attraction and hence require high energy to break the bonds in order to separate the molecules. Consequently such molecules have high melting point and boiling point.

Also, boiling point of liquids increases because hydrogen bonding leads to increase in intermolecular attractions which lead to increase in heat of vaporization.

The abnormal boiling point of water is due to hydrogen bonding.

2. Association of molecules:

Due to hydrogen bonding, two or more molecules of a compound get associated to form bigger units. For example, 2 molecules of carboxylic acid get associated to form a dimer.

3. Solubility

The solubility of organic compounds in water is attributed to hydrogen bonding.

For example, a. CH_3OCH_3 (dimethyl ether) is completely miscible in water but CH_3SCH_3 (dimethyl sulphide) is partially miscible. This is because dimethyl ether is capable of hydrogen bonding with H_2O molecule.

The high solubility of sugar in water is due to hydrogen bonding.

4. Viscosity:

Intermolecular hydrogen bonding increases attraction between molecules in different layers of hydrogen bonded liquids. This results in increase in viscosity. Compounds exhibiting strong hydrogen bonding are highly viscous and have high surface tension.

Example: concentrated sulphuric acid, glycerol etc are highly viscous due to extensive hydrogen bonding

5. Unique properties of water:

- Density of water in solid state is less than that in liquid state. This is unusual because in most substances, density in solid state is more than in liquid state. This is due to intermolecular hydrogen bonding.
- Water contracts when heated between 0°C and 4°C . This is again unusual because most substances expand when heated in all temperature ranges.
- Water is liquid over wide temperature range (0 - 100°C)
- known as universal solvent: can dissolve many substances

- water has high heat of evaporation thereby sweating leads to cooling
- adhesion and cohesion: strong forces of attraction between molecules allows water to rise up inside plants from roots to leaves
- water conducts heat more easily than any other liquid except mercury

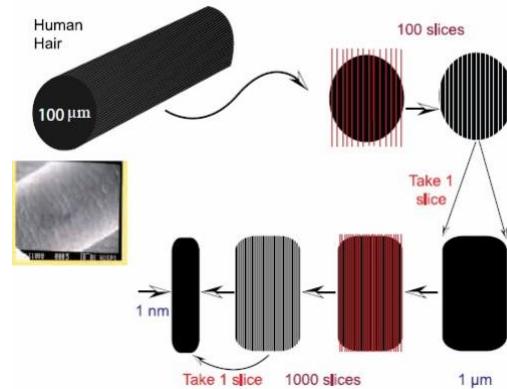
NANOMATERIALS

- A. Basics*
- B. Classification of nanomaterials*
- C. Properties of nanomaterials*

A. Basics of nano-materials and nano-chemistry

- Nanoscience: Scientific study of nanomaterials or objects having size in the 1 – 100 nm range in at least one dimension.
- Nanotechnology: Technology of using nanomaterials to develop products with possible practical application.

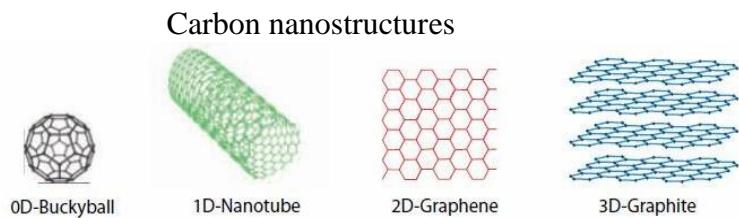
The term nano is derived from the Greek word for dwarf. It is used as a prefix for any unit (sec or meter). A nano represents a billionth of a unit. A Nanoscale is considered to span from 1nm to 100 nm.



Cross-sectional area of human hair

Nanomaterials are typically categorized as zero dimensional (0D), one dimensional (1D), two dimensional (2D) and three dimensional (3D). This classification is based on the number of dimensions which are not confined to the nanoscale range (1-100nm). This means that in 0D nanomaterials, no dimensions are outside the nanoscale range. In 1D nanomaterial, 1 dimension is outside the nanoscale. In 2D and 3D, two and three dimensions are outside the nanoscale range respectively.

Common examples of 0D nanomaterials are nanoparticles. 1D nanomaterial includes nanotubes, nanorods and nanowires. 2D nanomaterials include nanofilms, nanolayers, and nanocoatings. 3D nanomaterials are known as bulk nanomaterials; none of its dimension exists in the nanoscale range. The reason for their inclusion in the nanomaterials is because: such materials posses a nanocrystalline structure or involve the presence of features at the Nanoscale. Bulk nanomaterials can be composed of a multiple arrangement of nanosized crystals in different orientations. 3D nanomaterials can contain dispersed nanoparticles, bundles of Nanowires, nanotubes as well as multi nanolayers. The different nanostructures existing in carbon nanomaterials are 0D-Buckyball, 1D-nanotube, 2D-graphene and 3D-graphite



B. Difference between nanomaterials and bulk materials (micro-sized)

1. Surface effects (Surface-to Volume Ratio versus Shape)

One of the fundamental differences between nanomaterials and large-scale materials is that nanoscale materials have an extraordinary ratio of surface area to volume. The large surface area of nanomaterials as compared to their volumes plays a significant role in dictating their properties.

2. Quantum effects

In bulk crystalline materials, the electrons are delocalized within the entire particle. The atomic energy levels spread out into continuous valence and conduction bands. While band gap is minimal in conductors, the same is maximum in insulators. In semiconductors, the band gap is very small resulting in requirement of a minimum energy to excite the valence band electrons to conduction band. This overall behavior changes when the dimension of the bulk materials are reduced to Nanoscale.

For 0D nanomaterials, where all the dimensions are in Nanoscale, the electrons are confined in 3D space. Therefore no electron displacement occurs. For 1D, electron confinement is restricted to 2D, whereas delocalization takes place across the long axis of nanowire/nanorod/nanotube. In the case of 2D nanomaterials, the conduction electrons are confined to the 1d, whereas delocalization takes place across the plane of the sheet.

Thus, for 0D nanomaterials, the electrons are fully confined. For 3D nanomaterials, the electrons are fully delocalized. In 1D and 2D nanomaterials, electron confinement and delocalization coexist.

With decrease in the size of the material to nanoscale, electron movement is restricted within the dimension of the nanostructure. Also, the atomic energy levels within valence and conduction band become discrete. The band gap is also shifted to higher energy levels.



C. Properties of nanomaterials as compared to bulk materials

1. Mechanical properties: Increased hardness, yield strength, elastic modulus, toughness
2. Magnetic properties of nanostructured materials are distinctly different from that of bulk materials. Ferromagnetism disappears and transfers to superparamagnetism in the nanometer scale due to the huge surface energy.
3. Reduced Melting Point -- Nanomaterials may have a significantly lower melting point or phase transition temperature and appreciably reduced lattice constants (spacing between atoms is reduced), due to a huge fraction of surface atoms in the total amount of atoms.
4. Metal nanoparticles have unique light scattering properties and exhibit Plasmon resonance
5. Optical properties of nanomaterials can be significantly different from bulk crystals.
 - Semiconductor Blue Shift in absorption and emission due to an increased band gap
 - Metallic Nanoparticles Color Changes in spectra due to Surface Plasmons Resonances
6. Electrical conductivity decreases with reduced dimension
7. Self-purification is an intrinsic thermodynamic property of nanostructures and nanomaterials due to enhanced diffusion of impurities/defects/dislocations to the nearby surface.
8. Increased perfection enhances chemical stability.

Bulk (e.g.Gold)	Nano (e.g.Gold)
<p>1. Is a pure metal having metallic properties Like metallic lustrous, malleability, ductility, better heat and electrical conductivity, high density, high melting point (1080°C), high tensile strength and is chemically inert</p> <p>2. Yellow or golden color when in a mass</p>	<p>1. Is not a metal but is a semiconductor</p> <p>2. Color is never yellow or golden</p> <p>3. Color depends on its size and shape For example; Gold particles in glass: 25 nm — Red reflected 50 nm — Green reflected</p> <p>4. Are very good catalysts.</p> <p>5. Melts at relatively low temperature (~940° C).</p> <p>6. Unexpected visible properties & they are small enough to scatter visible light rather than absorb)</p>

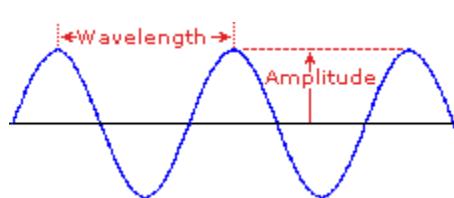
SPECTROSCOPY

Spectroscopy deals with the transitions that a molecule undergoes between its energy levels upon absorption of suitable radiation as determined by quantum mechanical selection rules. It is the study of electromagnetic radiation scattered, absorbed or emitted by molecules.

The structure of organic compounds can be determined by the study of their interaction with light (electromagnetic radiation). Spectroscopic techniques are non-destructive and generally require small amounts of sample. They help in fast analysis of sample.

Light is uniform or homogeneous in color, it is actually composed of a broad range of radiation having wavelengths in the ultraviolet (UV), visible and infrared (IR) portions of the spectrum. Different regions of the electromagnetic spectrum provide different kinds of information as a result of such interactions. Light may be considered to have both wave-like and particle-like characteristics. Like all wave characteristics, it is characterized by a wavelength or frequency.

Wavelength is defined, as the distance between adjacent peaks (or troughs), and may be designated in meters, centimeters or nanometers (10^{-9} meters).



- **Violet:** 400 - 420 nm
- **Indigo:** 420 - 440 nm
- **Blue:** 440 - 490 nm
- **Green:** 490 - 570 nm
- **Yellow:** 570 - 585 nm
- **Orange:** 585 - 620 nm
- **Red:** 620 - 780 nm

Frequency is the number of wave cycles that travel past a fixed point per unit of time, and is usually given in cycles per second, or hertz (Hz).

Frequency and wavelength are inversely related but has a direct relationship to energy.

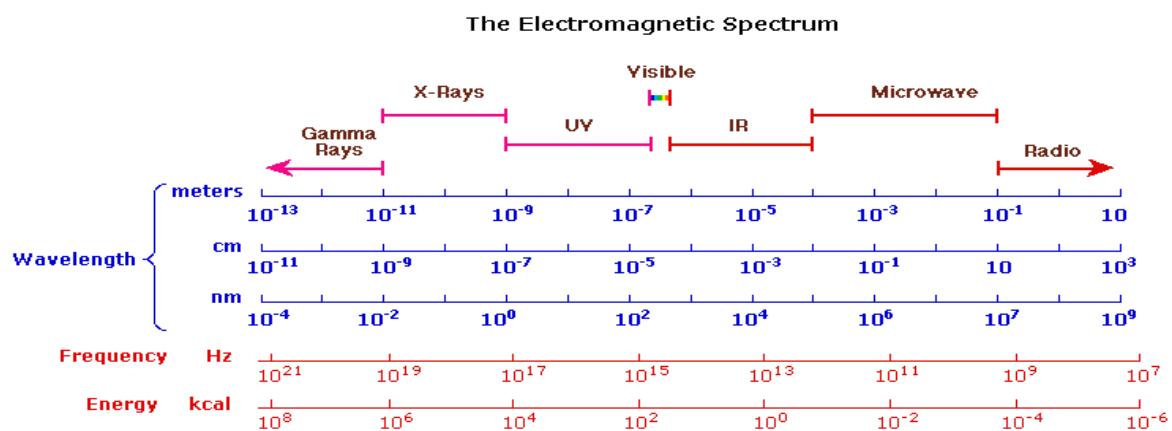
$$\nu = c/\lambda \quad \nu = \text{frequency}, \lambda = \text{wavelength}, c = \text{velocity of light} (c = 3 \cdot 10^{10} \text{ cm/sec})$$

$$\Delta E = h\nu \quad E = \text{energy}, \nu = \text{frequency}, h = \text{Planck's constant} (h = 6.6 \cdot 10^{-27} \text{ erg sec})$$

Visible wavelengths cover a range from approximately 400 to 800 nm. The longest visible wavelength is red and the shortest is violet.

The Electromagnetic Spectrum

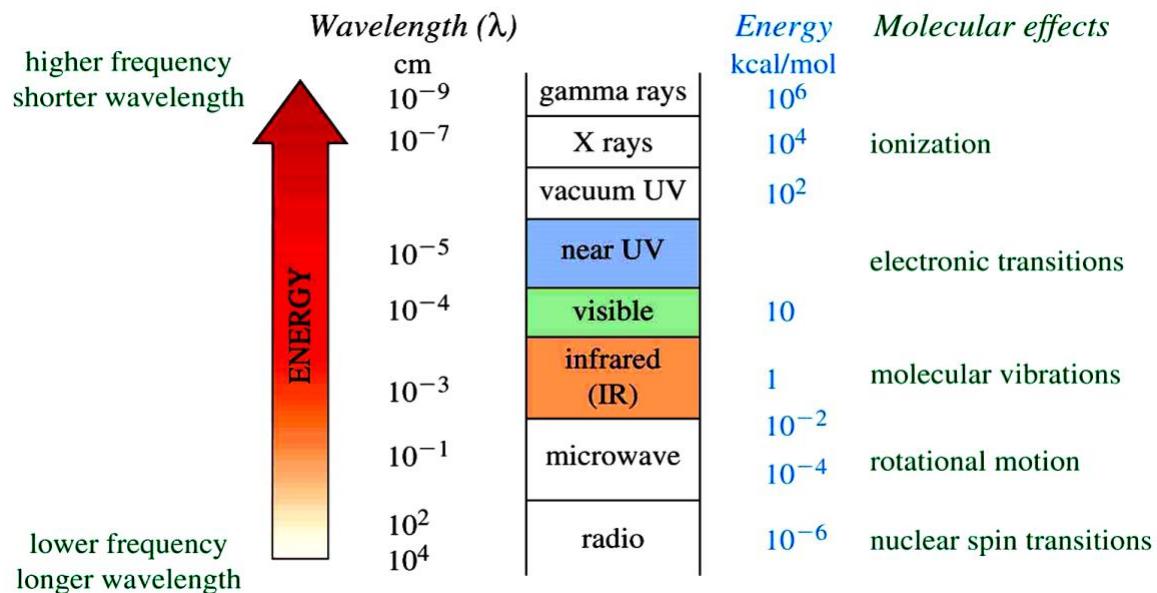
The visible spectrum constitutes but a small part of the total radiation spectrum. Most of the radiation that surrounds us cannot be seen, but can be detected by dedicated sensing instruments. This electromagnetic spectrum ranges from very short wavelengths (including gamma and x-rays) to very long wavelengths (including microwaves and broadcast radio waves). The following chart displays many of the important regions of this spectrum, and demonstrates the inverse relationship between wavelength and frequency.



$$v = c/\lambda \quad v = \text{frequency}, \lambda = \text{wavelength}, c = \text{velocity of light} (c=3 \cdot 10^{10} \text{ cm/sec})$$

$$\Delta E = h\nu \quad E = \text{energy}, \nu = \text{frequency}, h = \text{Planck's constant} (h=6.6 \cdot 10^{-27} \text{ erg sec})$$

Effect of electromagnetic radiation on molecules



Spectra	Transitions	Region of electromagnetic spectrum
Infrared	Between the vibrational energy levels	Infrared (500-4000cm ⁻¹)
UV-Vis	Between the electronic energy levels	Visible (12,500-25,000cm ⁻¹) UV (25,000 – 70,000cm ⁻¹)
NMR	Between the magnetic energy levels of nuclei	Radiofrequency

UV-Vis. Spectroscopy

- It involves transitions of electrons within a molecule from a lower to higher energy level or vice-versa by the absorption or emission of energy or radiations.
- The frequency of the radiations fall in the UV-Visible range of the electromagnetic spectrum. The Visible range is $12,500\text{-}25,000\text{cm}^{-1}$ (400-750nm) and the UV region is $25,000\text{-}72,000\text{ cm}^{-1}$ (190-400 nm)
- They have limited use in sample identification but are highly useful in quantitative measurements.

For quantitative measurement,

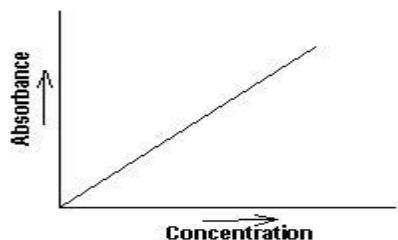
The concentration of an analyte in solution can be determined by measuring the absorbance at a specific wavelength and applying the Beer Lambert law.

When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting spectrum is presented as a graph of absorbance (A) versus wavelength.

$$\text{Beer Lambert law: } A = \epsilon C l$$

Where A= absorbance (no units, since $A = \log_{10} P_0 / P$); C= sample concentration in mole/L, l= length of light passing through the sample in cm; ϵ is the molar absorbtivity with units of $\text{L mol}^{-1} \text{ cm}^{-1}$

The law tells us that absorbance depends on the total quantity of the absorbing compound in the light path through the cuvette. If we plot absorbance against concentration, we get a straight line passing through the origin (0,0).



Principle of UV-Vis Spectroscopy:

Electronic transitions

The absorption of UV or visible radiation corresponds to the excitation of outer most valence electrons. When an atom or molecule absorbs energy, electrons are promoted from their ground state to an excited state. In a molecule, the atoms can rotate and vibrate with respect to each other. These vibrations and rotations also have discrete energy levels, which can be considered as being packed on top of each electronic level. Thus each electronic level in a molecule is associated with a number of vibrational sub-level (with smaller energy separation) and each vibrational sub-level is again associated with a number of rotational sub-levels (with still smaller energy separation).

Thus in its transition to a higher energy level, an electron can go from any of the sub-levels (corresponding to various vibrational and rotational states) in the ground state to any of the sub-levels in the excited state (diag below). The spectrum of a molecule containing these chromophores is complex. This is because the superposition of rotational and vibrational transitions on the electronic transitions gives a combination of overlapping lines. This appears as a continuous absorption band.



Absorbing species containing π , σ , and n electrons

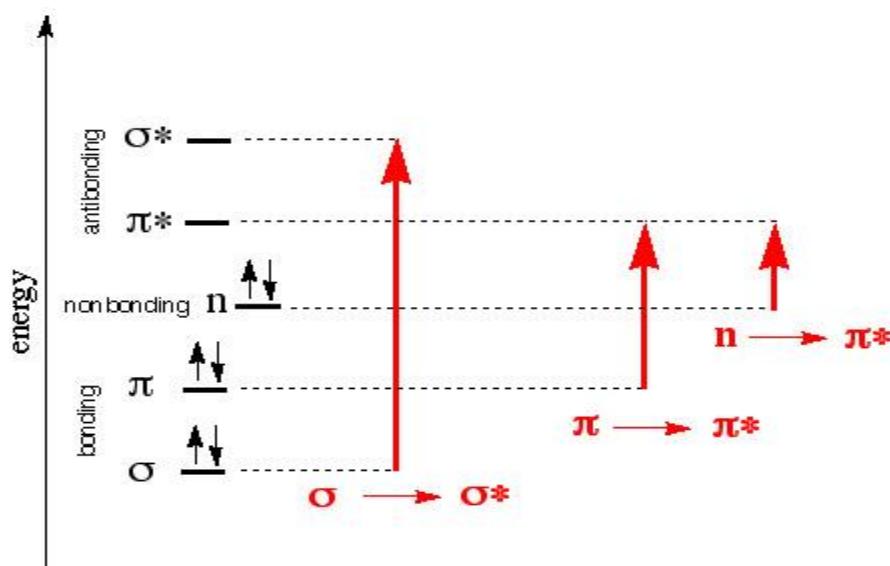
Absorption of ultraviolet and visible radiation in organic molecules is restricted to certain functional groups (chromophores) that contain valence electrons of low excitation energy.

SPECTROSCOPY

Classification of electronic transitions:

1. $\sigma \rightarrow \sigma^*$ transition: As (σ) electrons are held more firmly in the molecule, this transition takes place in the UV region.
2. $\pi \rightarrow \pi^*$ transition: This transition takes place in the near UV and the Vis region.
3. $n \rightarrow n^*$ transition: This transition takes place in the Vis region.

The relative energies of the molecular orbitals showing such transitions are shown:



The position of bands for different electronic transitions is summarized:

Organic compound	Electronic transitions	Position of bands
Alkanes	$\sigma \rightarrow \sigma^*$ transition	150 nm (requires high energy which does not lie in the UV region)
Alkenes	$\pi \rightarrow \pi^*$ transition	170-190nm
Aliphatic ketones	$n \rightarrow \pi^*$ transition	280 nm (forbidden and of low intensity)
	$n \rightarrow \sigma^*$ transition	185 nm (allowed and of high intensity)
	$\pi \rightarrow \pi^*$ transition	160 nm (allowed and of high intensity)
Conjugated dienes	$\pi \rightarrow \pi^*$ transition	217 nm (transition is of low energy and is due to conjugation)

SPECTROSCOPY

Chromophores: A chromophore is the part of a molecule responsible for its color. The color arises when a molecule absorbs certain wavelengths of visible light and transmits or reflects others. The chromophore is a region in the molecule where the energy difference between two different molecular orbitals falls within the range of the visible spectrum. Visible light that hits the chromophore can thus be absorbed by exciting an electron from its ground state into an excited state.

Auxochrome: An auxochrome is a group of atoms attached to a chromophore which modifies the ability of that chromophore to absorb light. They themselves fail to produce the colour; but when present along with the chromophores in an organic compound intensifies the colour of the chromogen.

Examples include the hydroxyl group (-OH), the amino group (-NH₂), and an aldehyde group (-CHO).

Terminology for absorption shifts

The solvent in which the absorbing species is dissolved also has an effect on the spectrum of the species. Peaks resulting from $n \rightarrow \pi^*$ transitions are shifted to shorter wavelengths (*blue shift*) with increasing solvent polarity. This arises from increased solvation of the lone pair, which lowers the energy of the n orbital. Often (but *not always*), the reverse (i.e. *red shift*) is seen for $\pi \rightarrow \pi^*$ transitions. This is caused by attractive polarization forces between the solvent and the absorber, which lower the energy levels of both the excited and unexcited states. This effect is greater for the excited state, and so the energy difference between the excited and unexcited states is slightly reduced - resulting in a small red shift. This effect also influences $n \rightarrow \pi^*$ transitions but is overshadowed by the blue shift resulting from solvation of lone pairs.

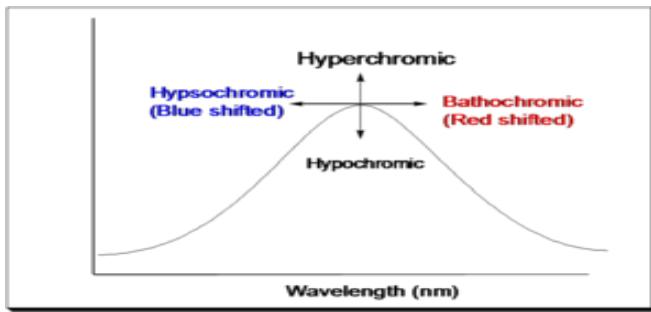
Bathochromic: a shift of a band to lower energy or longer wavelength (often called a red shift).

Hypsochromic: a shift of a band to higher energy or shorter wavelength (often called a blue shift).

Hyperchromic: an increase in the molar absorptivity.

Hypochromic: a decrease in the molar absorptivity.

SPECTROSCOPY



Applications of UV-Vis. Spectroscopy

1. For the identification of aromatic compounds and conjugated dienes or other olefins.
2. Detection of impurities
3. Quantitative determination of analyte
4. Determination of molecular weight
5. Study of kinetics of chemical reaction
6. Dissociation constant for weak acids and bases can be determined.

Infra-Red Spectroscopy

Theory or Principle of Infrared Absorption Spectroscopy

- a. IR photons have low energy (1-15kcal/mol); hence are not large enough to excite electrons (electronic transitions do not occur) but may induce vibrational excitation of covalently bonded atoms and groups in organic molecules.
- b. The covalent bonds in molecules are not rigid sticks or rods, but are more like stiff springs that can be stretched and bent. Thus, in addition to the facile rotation of groups about single bonds, molecules experience a wide variety of vibrational motions, characteristic of their component atoms. Consequently, virtually all organic compounds will absorb infrared radiation that corresponds in energy to these vibrations.
- c. There are three types of molecular transitions that occur during IR irradiation:
 - 1) Rotational transitions:
 - 2) Vibrational-rotational transitions
 - 3) Vibrational transitions
- d. Conditions for IR absorbance to occur:
 - The frequency of vibration must satisfy the equation: $E=hc\nu$.
 - The intensity of absorption must be proportional to square of the rate of change of dipole.
 - The natural frequency of vibration of the molecule must be equal to the frequency of incident radiation.
 - Changes in the vibration must stimulate changes in the dipole moment of the molecule. Hence Symmetric molecules (or bonds) do not absorb IR radiation since there is no dipole moment.

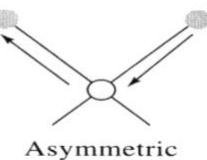
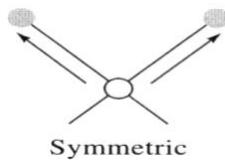
Thus Infra red inactive molecules-

- a. do not show vibrational spectra.
- b. Do not have a permanent dipole moment
- c. Do not exhibit a change in dipole moment
- d. Eg - O₂, H₂, N₂ etc

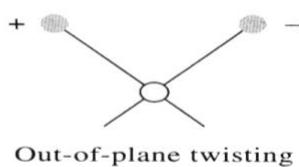
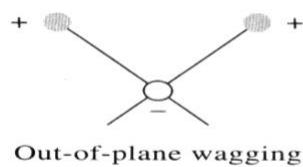
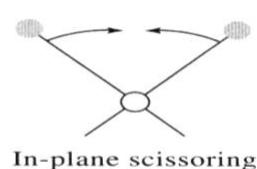
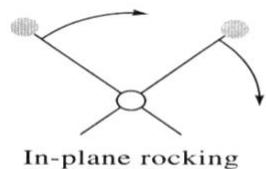
SPECTROSCOPY

Infra red active molecules –

- a. Show vibrational spectra
- b. Have a permanent dipole moment
- c. Exhibit a change in the dipole moment
- d. CO₂ is a molecule which does not have a permanent dipole moment but still is IR active.
- e. The IR region is divided into three regions: the near, mid, and far IR. The mid IR region is of greatest practical use to the organic chemist. This is the region of wavelengths between 3×10^{-4} and 3×10^{-3} cm. In wave numbers, the mid IR range is 4000–400 cm⁻¹. An increase in wave number corresponds to an increase in energy.
- f. The different Vibrational Modes occurring as a result of IR absorption:
 - i. **Stretching** -the rhythmic movement along a bond axis with a subsequent increase and decrease in bond length



- ii. **Bending** - a change in bond angle or movement of a group of atoms with respect to the rest of the molecule.



- g. It is not necessary that all fundamental vibrations will exist in the IR spectrum. Some vibrations are inadequate and are called degenerate bonds. Since different bonds and functional groups absorb at different wavelengths, an IR spectrum is used in the identification of a compound or establishing the structure of an unknown substance.

SPECTROSCOPY

Regions of IR spectra

1. **Functional group region:** is the high frequency region between **5000-1300cm⁻¹**. It is particularly useful in the identification of important functional groups present in the organic molecule.
2. **Finger print region:** is the middle frequency region between **1300-650cm⁻¹**. This region helps in the identification of unknown organic substance. No two compounds, however closely related can have identical or superimposable bands in this region.

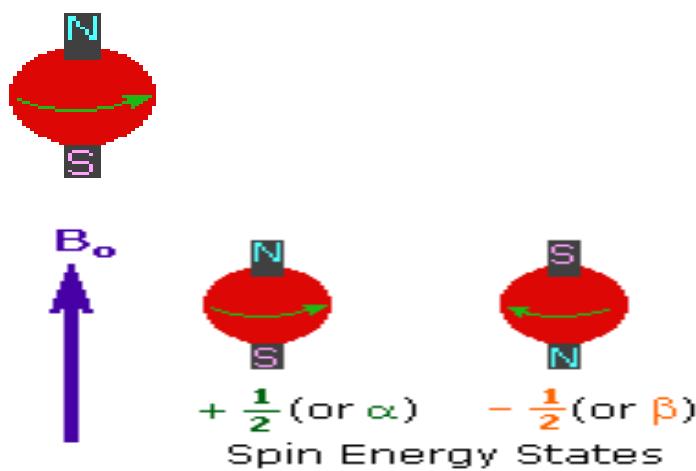
Applications of IR Spectroscopy

1. **Identification of an unknown compound**
2. **Identification of functional groups in organic molecules.**
3. **To distinguish between inter and intra molecular hydrogen bonding**
4. **To determine the structure of an organic compound**

NMR-Spectroscopy (Nuclear Magnetic Resonance Spectroscopy)

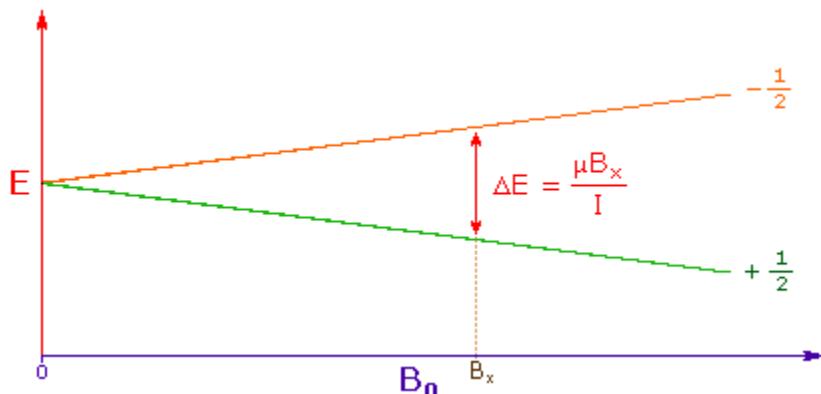
- The nuclei of many elemental isotopes have a characteristic spin (I).
- Some nuclei have integral spins (e.g. $I = 1, 2, 3 \dots$), some have fractional spins (e.g. $I = 1/2, 3/2, 5/2 \dots$), and a few have no spin, $I = 0$ (e.g. $^{12}\text{C}, ^{16}\text{O}, ^{32}\text{S}, \dots$).
- Isotopes of particular interest and use to organic chemists are $^1\text{H}, ^{13}\text{C}, ^{19}\text{F}$ and ^{31}P , all of which have $I = 1/2$.

The theory behind NMR comes from the spin, I of a nucleus. Just as electrons have a $+1/2, -1/2$ spin, certain nuclei also experience charged spins that create a magnetic field (called the magnetic moment), which allows chemists to study them using NMR. Nuclei with even numbers of both neutrons and protons experience NO spin and nuclei with odd numbers of both neutrons and protons have integer spins. Nuclei that have the sum of protons and neutrons equal to an odd number (like ^1H and ^{13}C) have half-integer spins. When there is no external or applied magnetic field (B_0), the nuclear spins orient randomly; however, when there is an applied magnetic field, the nuclei orient themselves with or against the larger applied field. The α -spin state is parallel to the applied force and has lower energy than the β -spin state that is antiparallel to the applied force. The energy difference (ΔE) between the α - and β -spin states depends on the strength of the applied magnetic field. The greater the strength of the applied magnetic field, the greater is the ΔE between the between the α - and β -spin states. This (ΔE) is $\sim 0.02 \text{ cal mol}^{-1}$, which lies in the radio frequency region. The emitted energy in this region produces an NMR signal.



SPECTROSCOPY

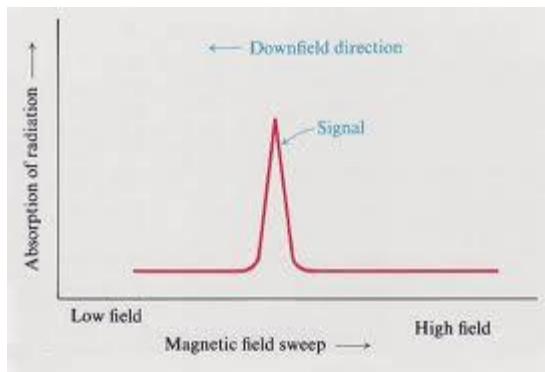
Addition of energy results in a spin flip



As the applied magnetic field increases, so does the energy difference between α - and β -spin states

NMR Spectrum

The NMR spectrum is a plot of the intensity of NMR signal versus the magnetic field (frequency) in reference to a standard (TMS).



NMR Applications

Today, NMR has become a sophisticated and powerful analytical technology that has found a variety of applications in many disciplines of scientific research, medicine, and various industries. Modern NMR spectroscopy has been emphasizing the application in biomolecular systems and plays an important role in structural biology. With developments in both methodology and instrumentation in the past two decades, NMR has become one of the most powerful and versatile spectroscopic techniques for the analysis of biomacromolecules, allowing characterization of biomacromolecules and their

SPECTROSCOPY

complexes. Together with X-ray crystallography, NMR spectroscopy is one of the two leading technologies for the structure determination of biomacromolecules at atomic resolution. In addition, NMR provides unique and important molecular motional and interaction profiles containing pivotal information on protein function. The information is also critical in drug development.

Hardness: Water which does not produce lather with soap solution readily, but forms a white scum (mass) is called hard water. The soap consuming capacity of water is called hard water.

Hard water consumes a lot of soap: This is due to the presence of salts of metal ions like Ca^{2+} , Mg^{2+} , Al^{3+} , Fe^{3+} , Mn^{2+} dissolved in water. Such metal salts react with soap (sodium or potassium salt of higher fatty acid like oleic acid, palmitic acid, stearic acid) to form insoluble white scum.



Difference between hard water and soft water:

S.No	Hard Water	Soft water
1	Water which does not produce lather with soap solution readily but forms a white scum is called hard water	Water which easily lathers with soap solution is called soft water
2	The presence of calcium and magnesium salts in water forms hard water	The absence of calcium and magnesium salts in water leads to soft water
3	Hard water causes wastage of soap due to depressed cleansing and detergent action Presence of calcium and magnesium salts results in elevated boiling point of water; thus more fuel and time are required for cooking	Soft water lathers easily and does not result in wastage of soap. It also does not result in wastage of fuel and time during cooking due to absence of calcium and magnesium salts.

Classification of hard water:

Hardness is of two types:

1. Temporary hardness: This type of hardness is caused by the presence of dissolved bicarbonates of calcium and magnesium and other heavy metals and the carbonate of iron.

Thus the salts responsible for temporary hardness are $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$. It is also known as carbonate hardness or alkaline hardness. Alkaline hardness is due to presence of bicarbonate, carbonate and hydroxides of the hardness producing metal ions. Temporary hardness can be removed by boiling of water when bicarbonates are decomposed yielding insoluble carbonates or hydroxides which are deposited as a crust at the bottom of the vessel.



2. Permanent hardness: It is due to the presence of dissolved chlorides and sulphates of calcium and magnesium, iron and other heavy metals. Hence the salts responsible for permanent hardness of water are CaCl_2 , MgCl_2 , CaSO_4 , MgSO_4 , FeSO_4 , $\text{Al}_2(\text{SO}_4)_3$ etc. Permanent hardness cannot be removed by boiling. It is also known as non-carbonate or non-alkaline hardness. It can be removed by following processes:

- (i) Lime-soda process:
- (ii) Zeolite process:
- (iii) Ion-exchange process
- (iv) Reverse Osmosis

3. Total hardness: Temporary hardness + Permanent hardness

Advantages and disadvantages of hard water:

S.No	Advantages of hard water	Disadvantages of hard water
1	Hard water tastes better. The dissolved calcium in water is beneficial for stronger bones and teeth in children.	Hard water produces scum with soap. Washing and detergent efficiency of soap decreases and the economy decreases. Cooking with Hard water results in more fuel consumption and more time consumption due to elevated boiling point of hard water.

Degree of hardness

Hardness of water is expressed in equivalents amounts of CaCO_3 because it forms the insoluble precipitate which can be removed easily in water treatment and also because its molecular mass is 100 (which makes calculations easier).

Equivalent of CaCO_3 (mg/L) or (ppm) =

$$\frac{(\text{Strength of hardness producing substance mg/L}) \times (\text{Molecular weight of CaCO}_3/2)}{\text{Molecular weight of substance}/2}$$

Units of Hardness:

- i. **Part per million (ppm)** It is defines as the number of parts by weight of calcium carbonate (CaCO_3) present per million (10^6) parts by weight of water.
1 ppm= 1 part of CaCO_3 equivalents hardness in (10^6) parts of water
- ii. **Milligrams per litre (mg/L)**. It is defines as the number of milligrams of CaCO_3 present in one litre of water.
1 ppm= 1mg/L
- iii. **Degree Clarke (${}^\circ\text{Cl}$)**. It is defines as the parts of CaCO_3 equivalent hardness per 70,000 parts of water.
 ${}^\circ\text{Cl} = 1$ part of CaCO_3 per 70000 parts of water
- iv. **Degree French (${}^\circ\text{Fr}$)**. It is defines as the parts of CaCO_3 equivalent hardness per 10^5 parts of water.
 ${}^\circ\text{Fr} = 1$ part of CaCO_3 per 10^5 parts of water

Relationship between various units of hardness:

$$1\text{ppm} = 0.1{}^\circ\text{Fr} = 0.07{}^\circ\text{Cl} = 1\text{mg/L}$$

Water Softening

Processes involved in removal of temporary and permanent hardness is called as “softening of water”. It is very essential process since hard water is unsuitable for domestic and industrial use. Use of hard water for generating steam in boilers so as to generate electricity results in problems like sludge formation, priming, foaming, boiler corrosion and caustic embrittlement.

Boiler Hard water can be removed by two ways:

1. **External Treatment:** Treatment of hard water is done before its entry into the boiler. This involves lime-soda, zeolite and ion exchange process. All are preventive methods.
2. **Internal treatment:** Treatment of raw water is done inside the boiler by two processes.
 - a. Appropriate chemicals are added to the boiler water to precipitate the scale forming impurities in the form of sludges which can be later removed.
 - b. Cations causing hardness are converted into compounds which will stay in dissolved form in water and thus do not cause any harm.

The processes involved are Colloidal conditioning, carbonate conditioning, phosphate conditioning and calgon conditioning.

Difference b/w Internal and Colloidal conditioning

S.No	Internal Treatment	External Treatment
1.	These are corrective methods	These are preventive methods
2.	It is carried out inside the boiler	It is carried out outside the boiler, before the entry of water into the boiler.
3.	Includes Colloidal conditioning, carbonate conditioning, phosphate conditioning and calgon conditioning	Includes lime-soda, zeolite and ion exchange process

Lime soda process:

- The basic principle of this process is to chemically convert all the soluble hardness causing salts of calcium and magnesium into insoluble precipitates which can then be removed by settling and filtration.
- Lime $[\text{Ca}(\text{OH})_2]$ and soda ash (Na_2CO_3) is added to facilitate precipitation. The precipitates thus formed are CaCO_3 , $\text{Mg}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, and $\text{Al}(\text{OH})_3$. These are then filtered off.
- But the precipitates formed at room temperature are not coarse and hence do not settle down and thereby cause difficulty in filtration.
- To facilitate precipitation, addition of lime is done at high temperature. This is followed by addition of Coagulants like Alum $[\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}]$, Aluminum sulphate $[\text{Al}_2(\text{SO}_4)_3]$ or Sodium aluminate $[\text{NaAlO}_2]$. By this process coarse precipitate are formed which can then be filtered off.
- Thus there are two methods of Lime soda: Cold Lime process and Hot Lime process. Both operate under the same principle but their difference is as follows:

Difference

Cold lime process	Hot lime process
<ul style="list-style-type: none"> (i) It operates at room temperature (25°C to 30°C) (ii) It is a slow process. (iii) Coagulants are required like $\text{Al}_2(\text{SO}_4)_3$. (iv) Dissolved gases are not removed. (v) Softened water contains hardness of about 60 ppm. (vi) Filtration of ppt's is a difficult task. 	<ul style="list-style-type: none"> (i) It operates at 90°–100°C. (ii) It is a fast process. (iii) No coagulant is required. (iv) Dissolved gases are removed due to high temperature. (v) Softened water contains hardness of about 15–30 ppm. (vi) Filtration at raised temperature is easy because viscosity of liquid to be filtered becomes low.

- Following are the reactions that takes place in this process when the following substituent is present in hard water:

Constituent	Reactions	Lime/Soda required
$\text{Ca}(\text{HCO}_3)_2$	$\text{Ca}(\text{OH})_2 + \text{Ca}(\text{HCO}_3)_2 \rightarrow 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$	1Lime
$\text{Mg}(\text{HCO}_3)_2$	$2\text{Ca}(\text{OH})_2 + \text{Mg}(\text{HCO}_3)_2 \rightarrow \text{Mg}(\text{OH})_2 + 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$	2Lime
Mg^{2+}	$\text{Ca}(\text{OH})_2 + \text{Mg}^{2+} \rightarrow \text{Mg}(\text{OH})_2 + \text{Ca}^{2+}$ $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{Na}^+$	L S
MgCl_2	$\text{MgCl}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 + \text{CaCl}_2$ $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{NaCl}$	
MgSO_4	$\text{MgSO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 \downarrow + \text{CaSO}_4$ $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{Na}_2\text{SO}_4$	1lime+1Soda
Ca^{2+} CaSO_4	$\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{Na}_2\text{SO}_4$	1Soda
CaCl_2	$\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{NaCl}$	1Soda
HCO_3^- [NaHCO_3]	$\text{NaHCO}_3 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O} + \text{Na}_2\text{CO}_3$	L-S

Advantage of L-S Process:

- It is very economical
- Treated water is alkaline and has less corrosion tendencies
- It removes not only hardness causing salts but also minerals.
- Iron and magnesium are also removed from water to some extent

Disadvantage of L-S Process:

- The process results in sludge formation
- The process cannot be used for high pressure boilers

Calculation for Lime/ Soda Requirement:

$$\text{Lime requirement} = \frac{\text{MW of lime}}{\text{MW of CaCO}_3} [\text{Hardness in ppm}] \times \text{Volume of water (L)}$$

$$\text{Soda requirement} = \frac{\text{MW of soda}}{\text{MW of CaCO}_3} [\text{Hardness in ppm}] \times \text{Volume of water (L)}$$

MW of lime= 74, MW of soda= 106

NUMERICALS on L-S Process:

- Q1.** Calculate the amount of lime required for softening of 5000L of hard water containing 72ppm of MgSO₄.

Ans: 72 ppm of MgSO₄ = 72x100/120 = 60ppm of CaCO₃ equivalent.

Lime requirement = 74/100x60x5000 mg = 222g.

- Q2.** Calculate the amount of lime required for softening 50,000L of hard water containing Mg(HCO₃)₂ = 144ppm, Ca(HCO₃)₂ = 25ppm, MgCl₂ = 95 ppm, CaCl₂ = 111ppm, Fe₂O₃ = 25 ppm, Na₂SO₄ = 15 ppm

Ans:

Constituent	Reactions	Lime/Soda required
Ca(HCO ₃) ₂	$\text{Ca(OH)}_2 + \text{Ca(HCO}_3)_2 \rightarrow 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$	1Lime
Mg(HCO ₃) ₂	$2\text{Ca(OH)}_2 + \text{Mg(HCO}_3)_2 \rightarrow \text{Mg(OH)}_2 + 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$	2Lime
CaCl ₂	$\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{NaCl}$	1Soda
MgCl ₂	$\text{MgCl}_2 + \text{Ca(OH)}_2 \rightarrow \text{Mg(OH)}_2 + \text{CaCl}_2$	1Lime

Fe₂O₃ and Na₂SO₄ do not cause hardness and hence do not require L or S

Hardness causing salt	Amount (ppm)	Multiplication factor	CaCO ₃ equivalent
Mg(HCO ₃) ₂	144	100/146	144x100/146 = 98.6ppm
Ca(HCO ₃) ₂	25	100/162	25x100/162 = 15.4 ppm
MgCl ₂	95	100/95	95x100/95 = 100 ppm

Lime requirement = 74/100 (2x98.6 + 15.4 + 100) mg/L x 50,000L = 1156200mg = 11.57kg

Q3. A water sample on analysis gave the following results:

$\text{Ca}^{2+} = 30\text{mg/L}$; $\text{Mg}^{2+} = 18\text{mg/L}$, $\text{K}^+ = 19.5\text{mg/L}$, $\text{HCO}_3^- = 122\text{mg/L}$, $\text{Cl}^- = 35.5\text{mg/L}$, $\text{SO}_4^{2-} = 48\text{ mg/L}$

Calculate the total hardness and alkalinity present in water sample.

Also, calculate the lime soda required for softening 1L sample of the hard water.

Ans: Total hardness = $[\text{Ca}^{2+} + \text{Mg}^{2+} + \text{HCO}_3^-] = 30 \times 100/40 + 18 \times 100/24 + 122 \times 100/122 = 250\text{ ppm}$

Alkalinity = $[\text{HCO}_3^-] = 122 \times 100/122 = 100\text{ppm}$

Lime required = $74/100[\text{Mg}^{2+} + \text{HCO}_3^- \text{ in CaCO}_3 \text{ equiv.}] \text{ mg/L} \times V (\text{L}) = 74/100[18 \times 100/24 + 122 \times 100/122] \times 1 \text{ L} = 129.5\text{mg}$

Soda required = $106/100[[\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^- \text{ in CaCO}_3 \text{ equiv.}] \text{ mg/L} \times V (\text{L}) = 106/100[30 \times 100/40 + 18 \times 100/24 - 122 \times 100/122] \times 1 \text{ L} = 53\text{mg}$

Q4. Calculate the amount of lime and soda needed for softening a water sample containing 36ppm Mg^{2+} , 20ppm Ca^{2+} and 183ppm HCO_3^-

Ans:

Lime required = $74/100[\text{Mg}^{2+} + \text{HCO}_3^- \text{ in CaCO}_3 \text{ equiv.}] \text{ mg/L} = 74/100[36 \times 100/24 + 183 \times 100/122] \text{ mg/L} = 222\text{ppm}$

Soda required = $106/100[[\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^- \text{ in CaCO}_3 \text{ equiv.}] \text{ mg/L} = 106/100[36 \times 100/40 + 20 \times 100/24 - 183 \times 100/122] \text{ mg/L} = 53\text{ppm}$

Q5. A water sample contains the following impurities:

$\text{Ca}^{2+} = 20\text{ppm}$, $\text{Mg}^{2+} = 18\text{ppm}$, $\text{HCO}_3^- = 183\text{ppm}$, $\text{SO}_4^{2-} = 24\text{ppm}$

Calculate the lime and soda required for softening

Ans:

Lime required = $74/100[\text{Mg}^{2+} + \text{HCO}_3^- \text{ in CaCO}_3 \text{ equiv.}] \text{ mg/L} = 74/100[18 \times 100/24 + 183 \times 100/122] \text{ mg/L} = 166.5\text{ppm}$

Soda required = $106/100[[\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^- \text{ in CaCO}_3 \text{ equiv.}] \text{ mg/L} = 106/100[20 \times 100/40 + 18 \times 100/24 - 183 \times 100/122] = - 26.5\text{ppm}$

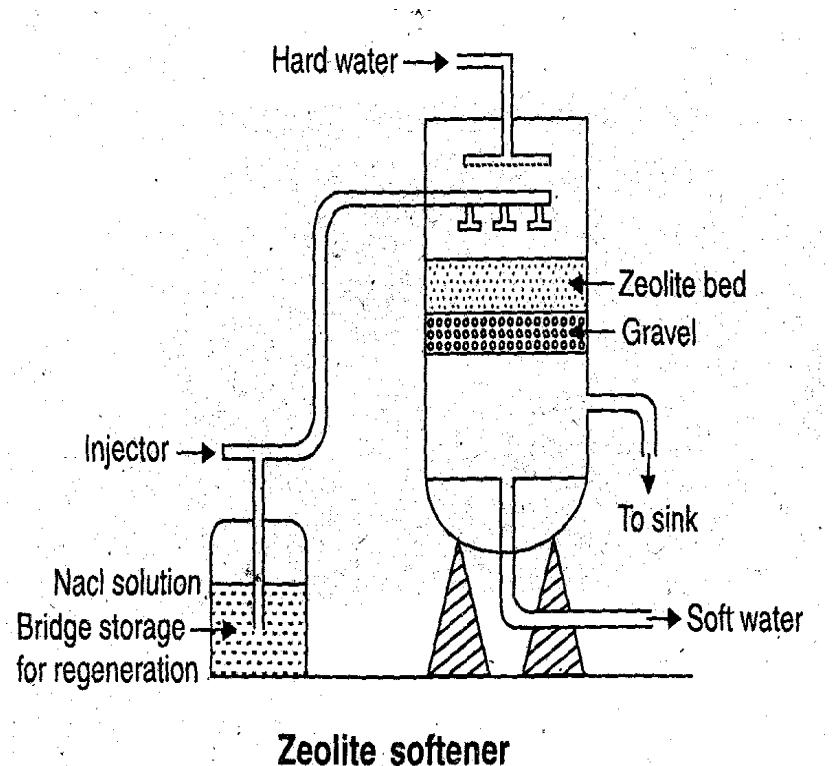
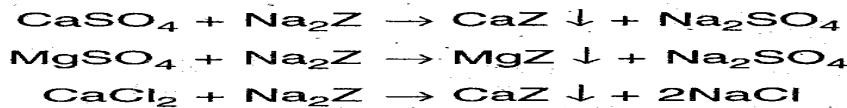
Soda is hence not required

Zeolite or permutite process:

- Zeolites are naturally occurring hydrated sodium alumino silicate minerals capable of exchanging reversibly its sodium ions for the ions present and responsible of formation of hard water.
- Permutite-is the trade name given to sodium zeolites.
- Chemical formula of zeolite is $\text{Na}_2\text{O Al}_2\text{O}_3 \text{ ySiO}_2 \text{ xH}_2\text{O}$. $y=2-10$, $x=2-6$
When $y = 2$, we get $\text{Na}_2\text{OAl}_2\text{Si}_2\text{O}_8.x\text{H}_2\text{O}$.
- For simplicity, we can write zeolites as Na_2Z Where $\text{Z} = \text{OAl}_2\text{Si}_2\text{O}_8.x\text{H}_2\text{O}$
- Zeolites are of two types: Natural zeolites and synthetic zeolites.

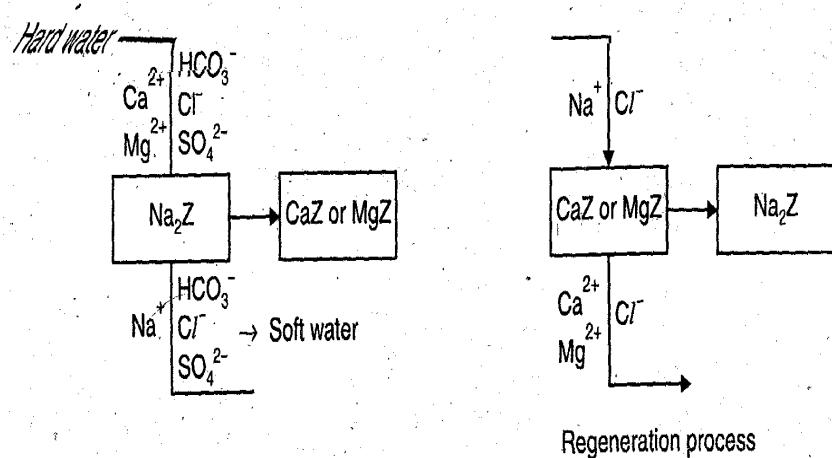
Process involved:

In this method, hard water is passed through a bed of permutite contained in a cylindrical vessel. The water percolates at a specified rate through the bed. The loose sodium ions of the zeolite are exchanged for Ca^{2+} and Mg^{2+} ions of hard water. Thus calcium and magnesium salts get removed in the form of the insoluble zeolites and soft water is collected.



This process removes both temporary and permanent hardness. After long use, the zeolite bed gets exhausted. It can be regenerated by using chemicals, such as brine solution, NaCl or sodium nitrate or sodium sulphate. However, NaCl is preferred on account of its

cheapness, easy availability and low molecular weight. The products 'calcium chloride and magnesium chloride are highly soluble in water and can be easily washed out. The softening and regeneration process can be represented as follows:



Merits of Zeolite Process

1. The equipment used is compact. So time saving process.
2. No impurities are precipitated. So no sludge formation occurs.
3. Requires less time for softening
4. Requires less skill for maintenance.

Demerits

- a. Treated water contains more number of Na ions
- b. This method leaves acidic ions (HCO_3^- and CO_3^{2-} ions) in soft water which if enters a boiler, generates CO_2 which leads to corrosion.
- c. Turbid water can't be made soft by this process because it leads to clogging of the holes of zeolite bed.

Numericals on Zeolite process

Q1. The hardness of 1000L of a sample of water was removed by passing it through a zeolite softener. The zeolite softener required 30L of NaCl containing 1.5g/L of NaCl for regeneration. Find the hardness of water sample.

Ans:

Quantity of NaCl in 30L of NaCl solution = $1.5\text{g/L} \times 30\text{L} = 45\text{g}$

CaCO_3 equivalent of NaCl = $45 \times [(100/2)/(58.5/1)] = 45 \times 50/58.5 = 38.46\text{gm equiv.}$

1000L of water sample is contains 38.46gm equiv of CaCO_3 equiv.

1L of water sample contains $38.46 \times 1000\text{mg}/1000\text{L} = 38.46 \text{ ppm}$

Hardness of water sample = 38.46ppm

Q2. An exhausted zeolite softener was regenerated by passing 150L of NaCl solution having strength of 1.5g/L of NaCl. Find the total volume of water that can be softened by this zeolite softener, if the hardness of water is 600 ppm.

Ans:

Quantity of NaCl in 150L of NaCl solution = $1.5\text{g/L} \times 150\text{L} = 225\text{g}$

CaCO_3 equivalent of $\text{NaCl} = 225 \times [(100/2)/(58.5/1)] = 2255 \times 50/58.5 = 192.308\text{g equiv.}$

Hardness of water = 600ppm

i.e 600mg of CaCO_3 equiv is present in 1L of water

$192.308 \times 1000 \text{ mg of } \text{CaCO}_3 \text{ is present in } 192308/600 = 320.5 \text{ L}$

Q3. A zeolite softener was 90% exhausted by removing the hardness completely when 10,000L of hard water sample was passed through it. The exhausted zeolite bed required 200L of 3% NaCl solution for its complete regeneration. Calculate the hardness of water solution.

Ans:

Quantity of NaCl in 200L of 3% NaCl solution = $3/100 \times 1000 \times 200\text{L} = 6000\text{g}$

CaCO_3 equivalent of $\text{NaCl} = 6000 \times [(100/2)/(58.5/1)] = 6000 \times 50/58.5 = 5128\text{g equiv.}$

90% of 10000 L of water = 5128g equiv = $5128 \times 1000\text{mg equiv}$

1L of water = $[5128 \times 1000]/[90/100 \times 10000] = 569.8 \text{ mg/L} = 569.8 \text{ ppm}$

Hardness = 569.8 ppm

Ion –exchange method

Ion exchange is a process by which ions held on a porous, essentially insoluble solid (resin) are exchanged for ions in solution that is brought in contact with it.

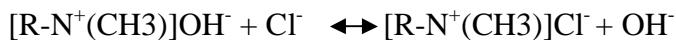
Ion exchange resins are insoluble, cross linked, high molecular weight organic polymers having a porous structure. The functional groups attached to the chains are responsible for the ion exchange properties.

Process:

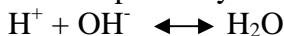
The hard water is passed through a cation exchange column. All cations like Ca^{2+} , Mg^{2+} etc are removed by the resin and equivalent amount of H^+ ions are released from the column to the water.



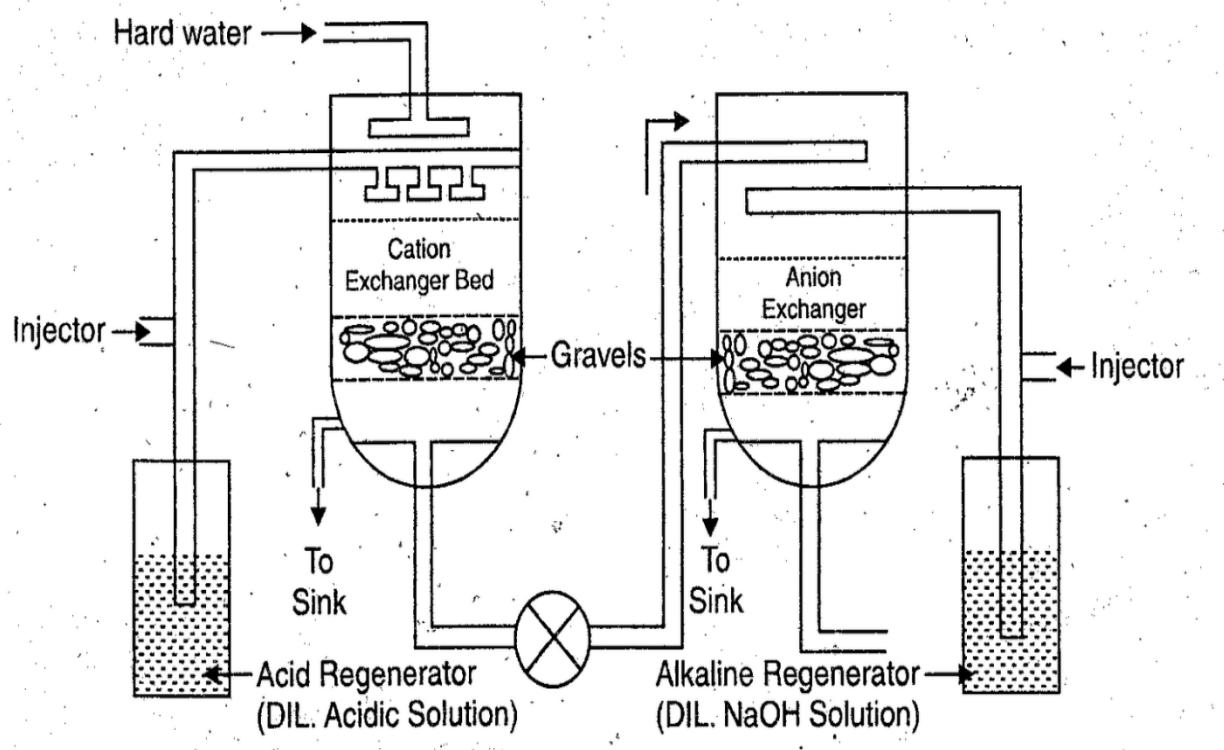
After passing through the cation exchange column, the hard water is passed through anion exchange column, when all the anions like SO_4^{2-} , Cl^- etc present in hard water are removed and taken up by the resin. An equivalent amount of OH^- is released from this column to the water.



The H^+ and OH^- ions released from the cation exchange resin and the anion exchange resin respectively combine to give water molecule.



Such water produced is free from any ions; hence is known as demineralised water. Since it is free from any ions, acidity or alkalinity, it is pure like distilled water.



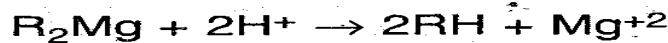
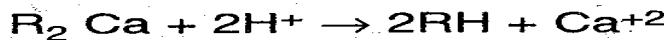
Demineralization of water by ion exchange process

Regeneration

During process, both cation and anion exchange the resins get exhausted i.e capacity to exchange H^+ and OH^- ions is lost.

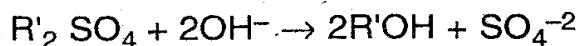
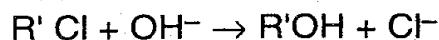
The cationic resins can be regenerated by passing solution of dil. HCl or H_2SO_4 through first the 1st column.

The regeneration reactions are:



Washing the column with deionized water releases the Ca^{2+} , Mg^{2+} ions or Cl^- , SO_4^{2-} ions into the sink.

Similarly the anion exchange resins can be regenerated by passing solution of dil. NaOH through the second column and regeneration is represented as:



The column is washed with deionized water and ions like Na^+ , Cl^- , SO_4^{2-} are released into the sink.

Advantages and disadvantages of ion exchange process are:

Advantages	Disadvantages
The ion exchange process can be used to soften highly acidic or alkaline waters	Very costly process as equipment and chemicals are costly
The process produces water of very low hardness (<2ppm). Very good for use in high pressure boilers	Presence of turbidity reduces the efficiency of the process

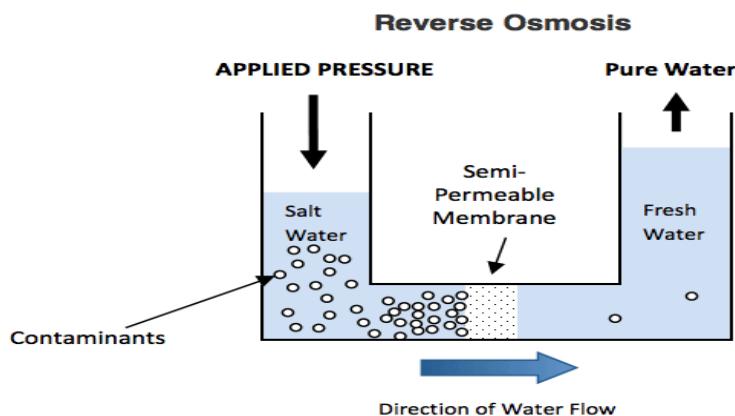
For water to be used for domestic purpose, water softening by ion exchange process will include only cation exchange resin. This is because, only cations responsible for hardness like Ca^{2+} , Mg^{2+} etc need to be removed. Regeneration is carried out by using inexpensive brine or NaCl solution.

Reverse Osmosis (RO):

Reverse Osmosis is a process where water is demineralized using a semi permeable membrane at high pressure. Reverse osmosis is osmosis in reverse.

A semi permeable membrane is a selective membrane which does not permit the passage of dissolved solute particles.

Osmosis is the phenomenon by which water or any solvent starts to flow from a region of low concentration to high concentration when the two solutions are separated by a semi permeable membrane. The flow continues till the concentration is equal on both sides of the membrane. This is most commonly observed in plants. If you don't water your plants they wilt. A plant cell is a semi permeable (water flows through the membrane but salts don't) membrane with the living stuff on the inside in a salt solution. Water is drawn into the cell from the outside because pure water will move across a semi permeable membrane to dilute the higher concentration of salt on the inside. This is how water is drawn in from the ground when you water your plants. If you salt your plants (over fertilize or spill some salt on the grass), the plant will wilt because the salt concentration on the outside of the cell is higher than the inside and water then moves across the membrane from the inside to the outside. To reverse this process, you must overcome the osmotic pressure equilibrium across the membrane because the flow is naturally from dilute to concentrate. We want more pure water so we must increase the salt content in the cell (concentrate side of the membrane). To do this we increase the pressure on the salty side of the membrane and force the water across. The amount of pressure is determined by the salt concentration. As we force water out, the salt concentration increases requiring even greater pressure to get more pure water.



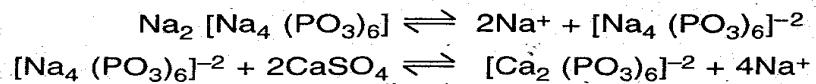
Diagrammatic representation of Reverse Osmosis

Advantage:

1. It is simple and reliable process of water softening.
2. It is not expensive.
3. It is energy efficient
4. It operates at low temperature.
5. The life of semi permeable membrane is 2 years and can be replaced within minutes.

What is calgon conditioning of a boiler feed water?

Ans: It is addition of calgon i.e.: sodium hexa metaphosphate in boiler water to prevent the formation of scale and sludge. Calgon removes scale forming Ca^{2+} , Mg^{2+} .



Q 7. Calculate the amount of lime (84% pure) and soda (92% pure) required for treatment of 20000 litres of water whose analysis is as follows :

$$\text{Ca}(\text{HCO}_3)_2 = 40.5 \text{ ppm}; \text{Mg}(\text{HCO}_3)_2 = 36.5 \text{ ppm}$$

$$\text{MgSO}_4 = 30 \text{ ppm}; \text{CaSO}_4 = 34 \text{ ppm}$$

$$\text{CaCl}_2 = 27.75 \text{ ppm}; \text{NaCl} = 10 \text{ ppm}$$

Also calculate temporary and permanent hardness of water sample [Given atomic masses H = 1, Na = 23, Ca = 40, Mg = 24, O = 16, C = 12, S = 32, Cl = 35.5].

(PTU, May 2007 ; Dec. 2006 ; 2005)

$$\text{Ans. Hardness due to } \text{Ca}(\text{HCO}_3)_2 = 40.5 \times \frac{100}{162} \\ = 25 \text{ ppm}$$

$$\text{Hardness due to } \text{Mg}(\text{HCO}_3)_2 = 36.5 \times \frac{100}{146} = 25 \text{ ppm}$$

$$\text{Hardness due to } \text{MgSO}_4 = 30 \times \frac{100}{120} = 25 \text{ ppm}$$

$$\text{Hardness due to } \text{CaSO}_4 = 34 \times \frac{100}{136} = 25 \text{ ppm}$$

$$\text{Hardness due to } \text{CaCl}_2 = 27.75 \times \frac{100}{111} = 25 \text{ ppm}$$

$$\text{Amount of lime required} = \frac{74}{100} (25 + 2 \times 25 + 25) \times \frac{100}{84} \times 20000 \\ = \frac{74}{100} (100) \times \frac{100}{84} \times 20000 \\ = 1.76 \text{ Kg}$$

$$\text{Amount of soda required} = \frac{106}{100} \times [25 + 25 + 25] \times \frac{100}{92} \times 20000 \\ = \frac{106}{100} (75) \times \frac{100}{92} \times 20000 = 1.752 \text{ Kg}$$

$$\text{Temporary hardness} = [\text{i.e. due to } \text{Ca}(\text{HCO}_3)_2 \text{ and } (\text{HCO}_3)_2] \\ = 25 + 25 = 50 \text{ ppm}$$

$$\text{Permanent hardness} = (\text{due to } \text{SO}_4^{2-} \text{ or } \text{Cl}^- \text{ of } \text{Ca}^{2+} \text{ and } \text{Mg}^{2+}) \\ = 25 + 25 + 25 = 75 \text{ ppm.}$$

Q 4. Calculate amount of lime (91% pure) and soda (97.2%) required to soften one million litres of water containing :

$$\text{H}^+ (\text{Free acidity}) = 1.5 \text{ ppm}, \text{HCO}_3^- = 396.5 \text{ ppm.}$$

$$\text{Mg}^{+2} = 42 \text{ ppm}, \text{Ca}^{+2} = 90 \text{ ppm}, \text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 14 \text{ ppm.} \quad (\text{PTU, Dec. 2007})$$

$$\text{Ans. Hardness due to } \text{H}^+ = 1.5 \times \frac{100}{2} = 75 \text{ ppm}$$

$$\text{Hardness due to } \text{HCO}_3^- = 396.5 \times \frac{100}{122} = 325 \text{ ppm}$$

$$\text{Hardness due to } \text{Mg}^{+2} = 42 \times \frac{100}{24} = 175 \text{ ppm}$$

$$\text{Hardness due to } \text{Ca}^{+2} = 90 \times \frac{100}{40} = 225 \text{ ppm}$$

$$\text{Hardness due to } \text{FeSO}_4 = 14 \times \frac{100}{278} = 5 \text{ ppm}$$

$$\text{Amount of lime required} = \frac{74}{100} [175 + 75 + 325 + 5] \times \frac{100}{91} \times 10^6 \\ = 487.9 \text{ kg}$$

$$\text{Amount of soda required} = \frac{106}{100} [225 + 75 + 175 - 325 + 5] \times \frac{100}{97.2} \times 10^6 \\ = 169 \text{ kg}$$

Q. A sample of water has the following impurities in mg/liter. Find the temporary and permanent hardness in ppm.

$$\text{Ca}(\text{HCO}_3)_2 = 10.0 \text{ ppm}$$

$$\text{Mg}(\text{HCO}_3)_2 = 8 \text{ ppm}$$

$$\text{CaSO}_4 = 12.00 \text{ ppm}$$

$$\begin{aligned}\text{Ans. Hardness due to } \text{Ca}(\text{HCO}_3)_2 &= 10 \times \frac{100}{162} \\ &= 6.2 \text{ ppm}\end{aligned}$$

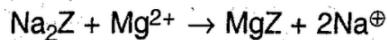
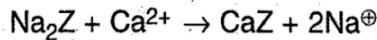
$$\begin{aligned}\text{Hardness due to } \text{Mg}(\text{HCO}_3)_2 &= 8 \times \frac{100}{146} \\ &= 5.5 \text{ ppm.}\end{aligned}$$

$$\text{Hardness due to } \text{CaSO}_4 = 12 \times \frac{100}{136} = 8.8 \text{ ppm}$$

$$\text{Temporary hardness} = \text{Hardness due to } \text{Ca}(\text{HCO}_3)_2 + \text{Mg}(\text{HCO}_3)_2$$

Q. What are zeolites? Why is water softened by zeolite process unfit for use in Boilers?

Ans. Zeolites are hydrated sodium aluminosilicates $\text{Na}_2\text{OAl}_2\text{O}_3\text{xSiO}_2\text{yH}_2\text{O}$ (Na_2Z) or we can say sodium zeolite. Where $Z = \text{Al}_2\text{Si}_2\text{O}_8\text{yH}_2\text{O}$. Na^+ ions present in it, can exchange the Ca^{2+} and Mg^{2+} ions of hard water and thus soften it.



In this process although Ca^{2+} and Mg^{2+} ions are removed, but yet water contains a number of Na^+ ions and anions like HCO_3^- , SO_4^{2-} , Cl^- . So these ions will lead to formation of scale and sludges in the boilers, so water is still unfit for use in boilers.

Q. Give specifications of boiler feed water.

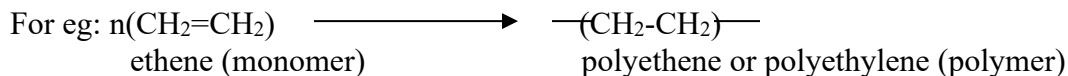
Ans The specifications of boiler feed water are as follows

- i. Water for boilers: Boiler feed water should be free from soluble salts of Mg^{2+} and Ca^{2+} . It should not contain any organic matter.
- ii. Boiler feed water should be free from suspended impurities.
- iii. Boiler feed water should not be acidic or alkaline.

Polymer: A polymer is a long molecule formed by joining together of thousands of small molecules by chemical bonds. A polymer is called a macromolecule because of its large size.

Polymerization: The chemical process leading to the formation of polymer from its monomer is called polymerization.

Monomers: The small molecules which combine to form large molecules or polymer are known as monomers.



n is the degree of polymerization.

Degree of polymerization (DP): It is the number of repeat units or monomer units in a polymer. DP in cellulose is 250 and in vinyl polymers are 400.

It is the long chain that gives the polymer its unique properties.

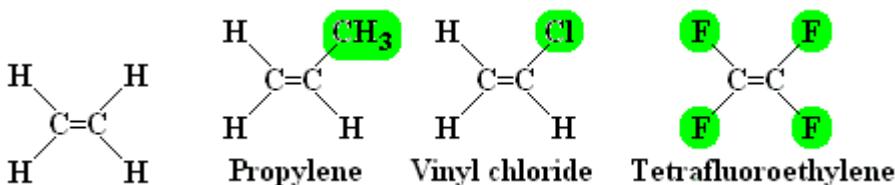
Ethane, $\text{CH}_3\text{-CH}_3$, is a gas molecule at room temperature. Because of their small size, ethane molecules are very mobile and can run almost anywhere they want without interacting with other molecules.

Now, if we double the chain length or the total number of carbons to four, we get butane, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$. It is a liquid fuel. In liquids, atoms or molecules can no longer act as independent units. Because of their larger size, butane molecules are less mobile than ethane molecules. Their lowered mobility allows them to run into or interact with one another more frequently.

When the chain length increases 6 fold, as in paraffin, $\text{CH}_3(\text{CH}_2\text{CH}_2)_{10}\text{CH}_3$, we get a waxy substance. In this case, the solid-like property of paraffin is a reflection of the entanglement of its long molecules when they move. If we keep increasing the number of repeating carbon units to, say, 2000, i.e., $\text{CH}_3(\text{CH}_2\text{CH}_2)_{2000}\text{CH}_3$, we have a polyethylene polymer, which is a very strong, brittle solid. The polymer molecules have become so long and so entangled that their movement becomes almost completely restricted.

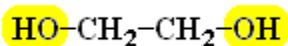
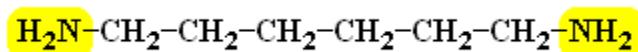
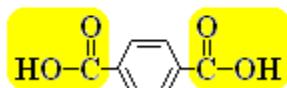
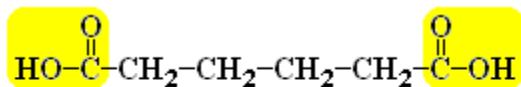
Functionality: It is the number of bonding or reactive sites in a monomer. Reactive sites can be double bond, a triple bond, $-\text{NH}_2$, $-\text{OH}$, $-\text{COOH}$, $-\text{SH}$ etc. For a molecule to behave as a monomer, minimum two functional groups must be present. Hence molecules like acetic acid, benzoic acid, ethyl alcohol, aniline, methyl isocyanate etc cannot act as monomer since they are mono-functional.

Vinyl monomer is bifunctional because the double bond in it is considered as a site for two free valencies. When the double bond is broken, two single bonds become available for combination.



The double bond is the vital feature that allows these monomers to form the long polymer chains. The highlighted areas show the side groups on these monomer molecules. These groups give the polymer chain some of its properties.

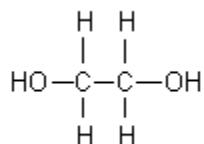
In the following examples, the functional groups are highlighted in yellow. Each molecule has two functional groups.



It is the presence of two functional groups that allow such molecules to behave as monomer giving them ability to form chains and polymerize.

Classify the following on the basis of their functionality:

- a. Ethylene glycol: Its chemical formula is:

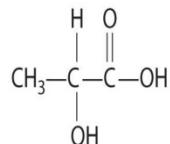


Functional groups present are 2 hydroxyl groups. Hence it is bifunctional.

- b. Vinyl chloride. Its chemical formula is $\text{CH}_2=\text{CHCl}$

Number of double bonds is one. Hence it is bifunctional.

- c. Lactic acid: Chemical formula is



Lactic acid

Functional groups present are 1hydroxyl group and 1 carboxylic acid group. Hence it is bifunctional.

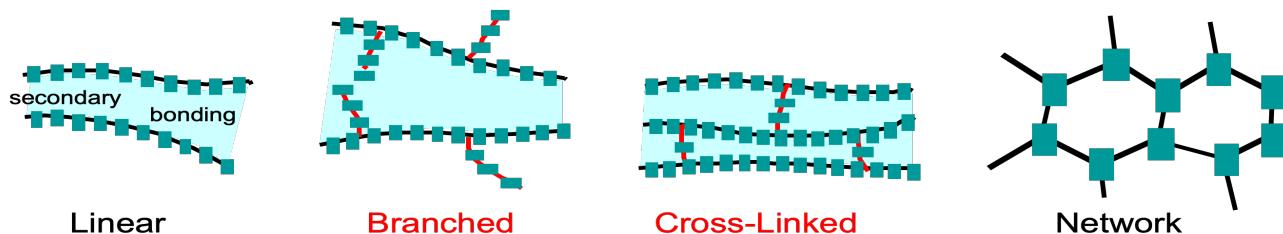
Significance of functionality:

- When the functionality of monomer is two, linear or straight chain polymer molecule is formed. Example of bifunctional monomer is vinyl monomers, adipic acid, ethylene glycol, amino acid, hexamethylene diamine etc.
- When the functionality of monomer is three, a three dimensional network polymer is formed. Example is phenol, melamine etc.
- When a trifunctional monomer is mixed with a bifunctional monomer, a branched chain polymer is formed.
- When a bifunctional monomer is mixed with a trifunctional monomer, a three dimensional network polymer is formed.

Classification of Polymers

1. Based on Structure/Shape of polymer

Polymers can be linear, branched, cross linked or networked.



- Linear polymers have monomeric units joined end to end in single chains. There may be extensive van der Waals and hydrogen bonding between the chains. Examples: polyethylene, PVC, nylon.
- In branched polymers, side-branch chains are connected to main chains. HDPE – high density polyethylene is primarily a linear polymer with minor branching, while LDPE – low density polyethylene contains numerous short chain branches. Greater chain linearity and chain length tend to increase the melting point and improve the physical and mechanical properties of the polymer due to greater crystallinity.
- In cross-linked polymers, adjacent linear chains are joined to one another at various positions by covalent bonding of atoms. Examples are the rubber elastic materials.
- Small molecules that form 3 or more active covalent bonds create structures called network polymers. Examples are the epoxies and polyurethanes.

2. Based on number of monomers:

Polymers can be homopolymers when only one type of monomer is present (eg: polyethylene, polypropylene, polyvinyl chloride).

Polymers can be co-polymer when two or more types of monomeric units are present (eg: styrene, acrylonitrile etc)

Homopolymers – only one monomer (repeating unit): - A – A – A – A – A – A – A -

Copolymer – more than one monomer

Statistical Copolymers Also called random copolymers. Here the monomeric units are distributed randomly, and sometimes unevenly, in the polymer chain: ~ABBAABABAABBBAABA~.

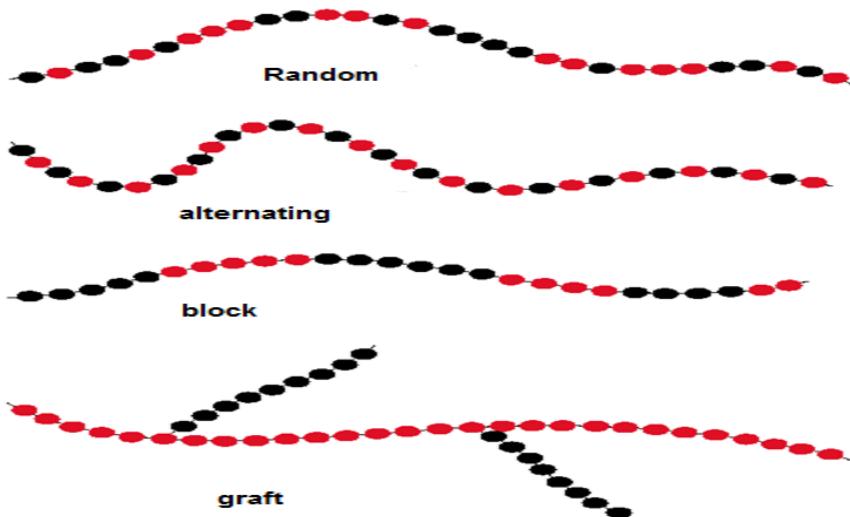
Alternating Copolymers Here the monomeric units are distributed in a regular alternating fashion, with nearly equimolar amounts of each in the chain: ~ABABABABABABAB~.

Block Copolymers

Instead of a mixed distribution of monomeric units, a long sequence or block of one monomer is joined to a block of the second monomer: ~AAAAA-BBBBBBB~AAAAAAA~BBB~.

Graft Copolymers

As the name suggests, side chains of a given monomer are attached to the main chain of the second monomer:
~AAAAAAA(BBBBBBB~)AAAAAAA(BBB~)AAA~.



Red Dot: A; Black Dot: B

3. Based on Origin:

Synthetic organic polymers
Biopolymers (proteins, polypeptides, polynucleotide, polysaccharides, natural rubber)
Semi-synthetic polymers (chemically modified synthetic polymers)
Inorganic polymers (siloxanes, silanes, phosphazenes)

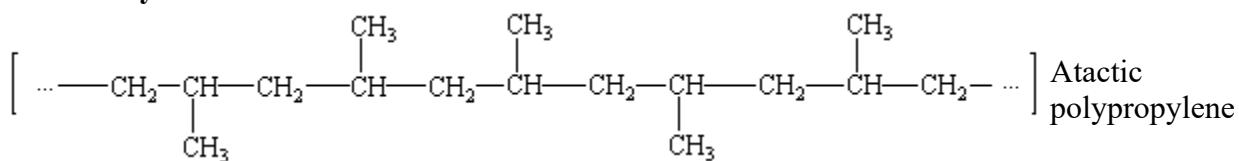
4. Based on Tacticity:

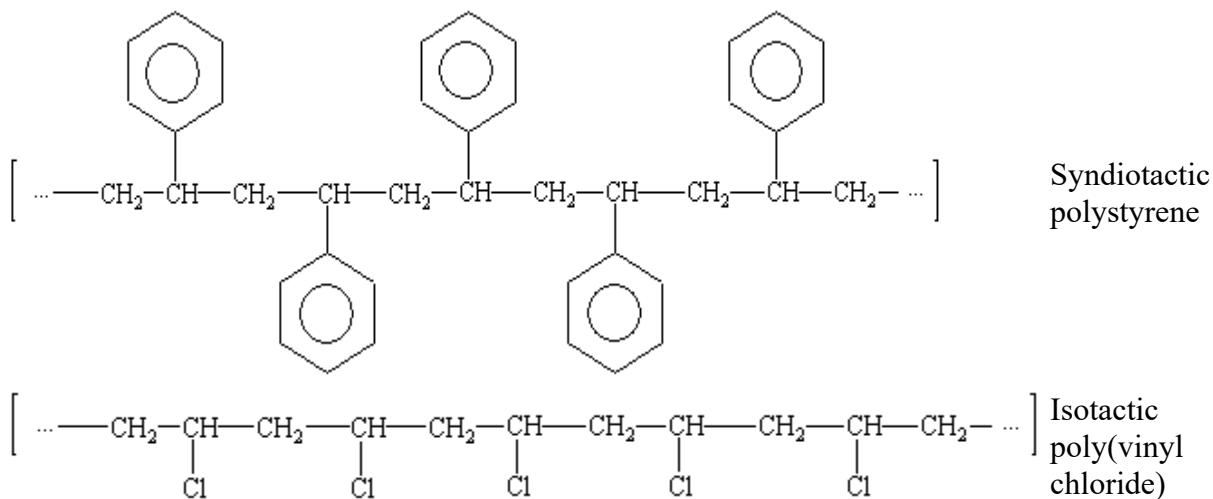
Polymers with regular substituents on the polymer chain possess a property known as **tacticity**. Tacticity results from the different ways in which the substituents can be arranged on the polymer backbone.

When the substituents are arranged in an irregular, random fashion, the polymer is **atactic** (literally, no arrangement).

When the substituents are all on the same side of the chain, the polymer is **isotactic** (literally, the same arrangement).

If the substituents alternate regularly from one side of the chain to the other, the polymer is **syndiotactic**.





5. Based on its behavior to heat

Polymers may be classified according to the mechanical response at elevated temperatures: Thermoplasts and Thermosets.

Difference b/w thermoplast and thermoset polymer

	Thermoplastic polymer	Thermoset polymer
1.	They are low molecular weight and are soluble in suitable solvent	They are high molecular weight and are insoluble in any solvent.
	Linear and branched polymer are thermoplastics	They have three dimensional, cross-linked structures.
2	Adjacent polymer chains are held together by either Van-der-Waals forces or by dipole-dipole forces or by H-bonds	Adjacent polymer chains are held together by strong covalent bonds or cross-links.
3	They are formed by either addition or by condensation polymerization reactions.	They are formed by condensation polymerization reactions.
4.	They soften on heating and stiffen on cooling	They do not soften on heating
5.	They can be remoulded, reshaped and reused	They cannot be reused.
6.	They can be recycled	They cannot be recycled
7.	They are tough	They are brittle
8.	There is no change of chemical composition during remoulding	There is change of chemical composition during remoulding
9	Thermoplastics are very soft and ductile	Thermoset polymers are harder, stronger, more brittle and have better dimensional stability.
10.	Example: PE, PP, PVC,PMMA, PS, PTFE, Nylon, Polyester	Example: vulcanized rubber, Epoxy, phenolic resins, XLPE etc.

Addition and Condensation Polymerization:

Addition Polymerization: Addition polymers are formed when an unsaturated organic compound (presence of double/triple bond) react to form long chain polymer molecule and when no small molecules are eliminated during the reaction.

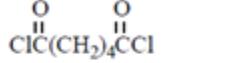
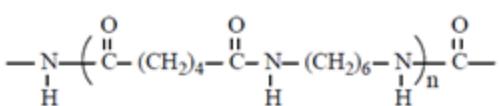
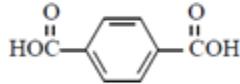
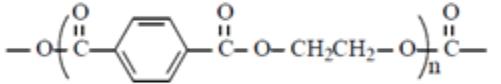
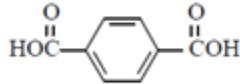
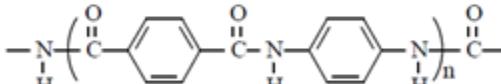
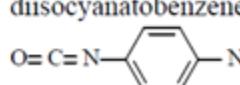
Some Common Addition Polymers

Name(s)	Formula	Monomer	Properties	Uses
Polyethylene low density (LDPE)	$-(\text{CH}_2-\text{CH}_2)_n-$	ethylene $\text{CH}_2=\text{CH}_2$	soft, waxy solid	film wrap, plastic bags
Polyethylene high density (HDPE)	$-(\text{CH}_2-\text{CH}_2)_n-$	ethylene $\text{CH}_2=\text{CH}_2$	rigid, translucent solid	electrical insulation bottles, toys
Poly(vinyl chloride) (PVC)	$-(\text{CH}_2-\text{CHCl})_n-$	vinyl chloride $\text{CH}_2=\text{CHCl}$	strong rigid solid	Pipes, siding, flooring
Polystyrene (PS)	$-[\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)]_n-$	styrene $\text{CH}_2=\text{CHC}_6\text{H}_5$	hard, rigid, clear solid soluble in organic solvents	toys, cabinets packaging (foamed)
Polyacrylonitrile (PAN, Orlon, Acrilan)	$-(\text{CH}_2-\text{CHCN})_n-$	acrylonitrile $\text{CH}_2=\text{CHCN}$	high-melting solid soluble in organic solvents	rugs, blankets clothing
Polytetrafluoroethylene (PTFE, Teflon)	$-(\text{CF}_2-\text{CF}_2)_n-$	tetrafluoroethylene $\text{CF}_2=\text{CF}_2$	resistant, smooth solid	non-stick surfaces electrical insulation
Poly(methyl methacrylate) (PMMA, Lucite, Plexiglas)	$-[\text{CH}_2-\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3]_n-$	methyl methacrylate $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$	hard, transparent solid	lighting covers, signs skylights
Poly(vinyl acetate) (PVAc)	$-(\text{CH}_2-\text{CHOCOCH}_3)_n-$	vinyl acetate $\text{CH}_2=\text{CHOCOCH}_3$	soft, sticky solid	latex paints, adhesives

Condensation Polymerization: The process of formation of polymer via condensation of two different bi-or poly functional monomers having functional groups which have affinity to each other. Condensation polymers form when:

- bifunctional monomers combine to form a long chain polymer molecule.
- small molecules like water is eliminated during the reaction.

Some Common Condensation Polymers and Their Monomers

Monomers Names and Formulas	Polymer Name and formula	Typical Uses
1,6-diaminohexane $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$ hexandioic acid (adipic acid) 	Nylon 66, a polyamide 	Women hose, rope, fabric carpeting
Terephthalic acid  Ethylene glycol $\text{HOCH}_2\text{CH}_2\text{OH}$	Dacron or Mylar (polyesters) 	Clothing, films, tapes
Terephthalic acid  1,4-diaminobenzene 	Kevlar, a polyamide 	Bullet proof vests
diisocyanatobenzene  Ethylene glycol $\text{HOCH}_2\text{CH}_2\text{OH}$	Polyurethane 	foams

Difference between addition and condensation polymerization

S.No	Addition Polymerization	Condensation Polymerization
1.	Requires the presence of double bond in the monomer	Requires the presence of minimum two functional groups in a single monomer which are of close proximity to each other
2.	No by product is formed	A byproduct like H_2O , HCl etc is formed
3.	Polymer formed is homopolymer	Polymer formed is heteropolymer
4.	Polymer is thermoplastic	Polymer formed is thermosetting
5.	Example: a. Ethylene polymerizing to polyethylene b. Vinyl chloride polymerizing to PVC c. styrene polymerizing to polystyrene	Example: a. Hexamethylene diamine and adipic acid polymerizing to nylon 66 b. Caprolactum polymerizing to Nylon 6 c. Terephthalic acid and ethylene glycol polymerizing to polyethylene terephthalate

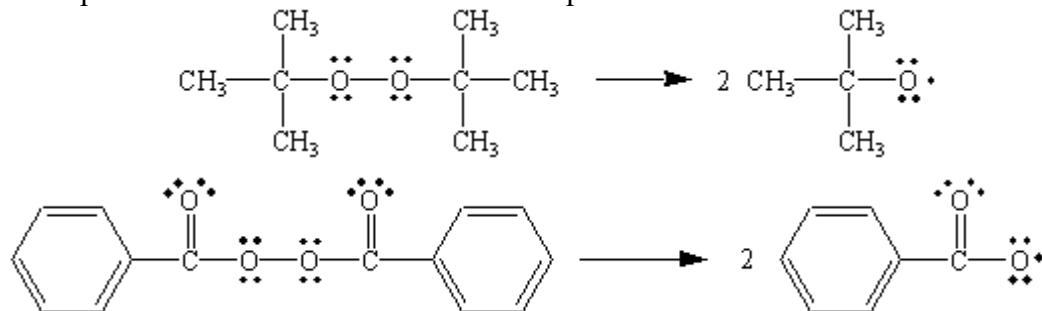
The Mechanism of Addition Polymerization

Depending on the initiator used to start the polymerization process, the mechanism can be classified as:

1. Free Radical Addition Polymerization
 2. Anionic or Carbanion Addition Polymerization
 3. Cationic or Carbonion Addition Polymerization
1. Free Radical Polymerization mechanism: The simplest way to catalyze the polymerization reaction that leads to an addition polymer is to add a source of a **free radical** to the monomer. The term *free radical* is used to describe a family of very reactive, short-lived components of a reaction that contain one or more unpaired electrons. In the presence of a free radical, addition polymers form by a chain-reaction mechanism that contains chain-initiation, chain-propagation, and chain- termination steps.

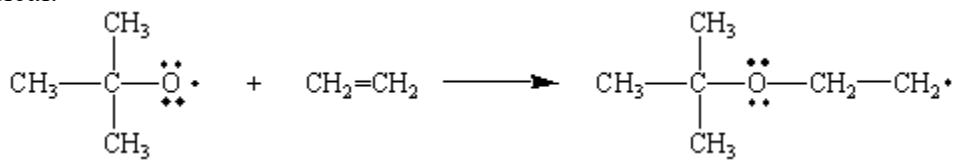
Chain Initiation

A source of free radicals is needed to initiate the chain reaction. These free radicals are usually produced by decomposing a peroxide such as di-*tert*-butyl peroxide or benzoyl peroxide, shown below. In the presence of either heat or light, these peroxides decompose to form a pair of free radicals that contain an unpaired electron.

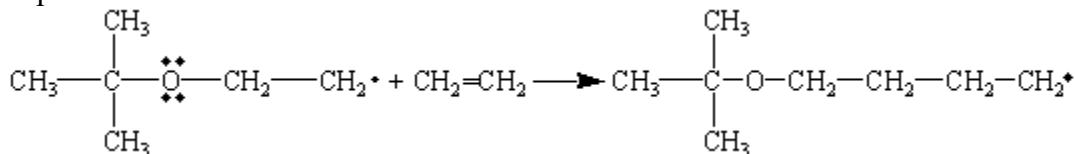


Chain Propagation

The free radical produced in the chain-initiation step adds to an alkene to form a new free radical.

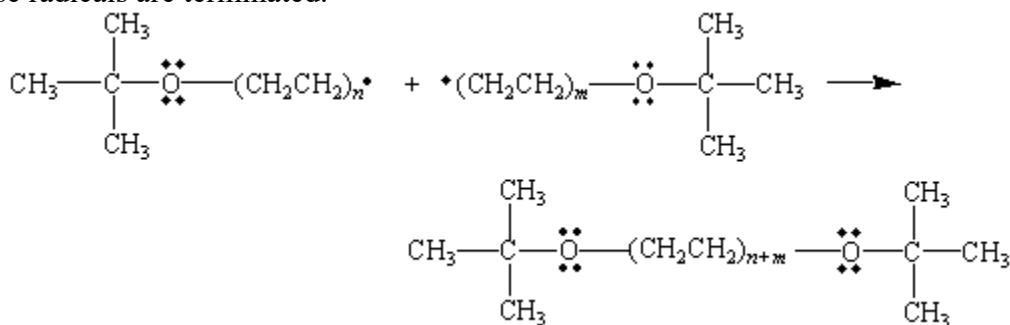


The product of this reaction can then add additional monomers in a chain reaction.



Chain Termination

Whenever pairs of radicals combine to form a covalent bond, the chain reactions carried by these radicals are terminated.

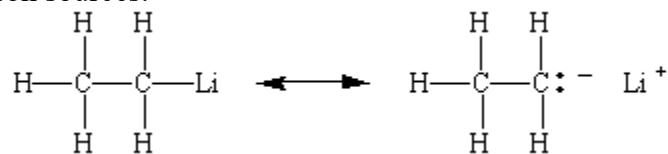


2. Anionic Polymerization

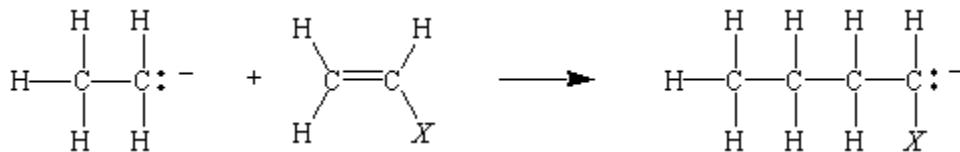
Addition polymers can also be made by chain reactions that proceed through intermediates that carry either a negative or positive charge.

When the chain reaction is initiated and carried by negatively charged intermediates, the reaction is known as **anionic polymerization**. Like free-radical polymerizations, these chain reactions take place via chain-initiation, chain-propagation, and chain-termination steps.

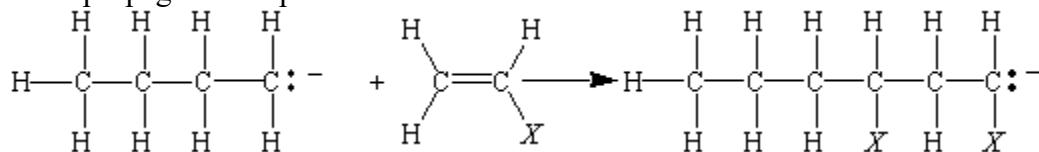
The reaction is initiated by a Grignard reagent or alkyl lithium reagent, which can be thought of a source of a negatively charged CH_3^- or CH_3CH_2^- ion. Species that have been used to initiate anionic polymerization include alkali metals, alkali amides, alkyl lithium and various electron sources.



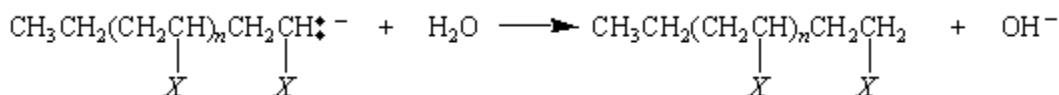
The CH_3^- or CH_3CH_2^- ion from one of these metal alkyls can attack an alkene to form a carbon-carbon bond.



The product of this chain-initiation reaction is a new carbanion that can attack another alkene in a chain-propagation step.

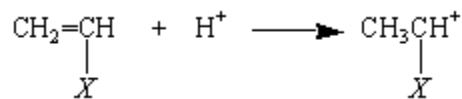


The chain reaction is terminated when the carbanion reacts with traces of water in the solvent in which the reaction is run.

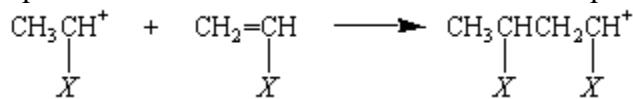


3. Cationic Polymerization

The intermediate that carries the chain reaction during polymerization can also be a positive ion, or cation. In this case, the **cationic polymerization** reaction is initiated by adding a strong acid to an alkene to form a carbocation.



The ion produced in this reaction adds monomers to produce a growing polymer chain.



The chain reaction is terminated when the carbonium ion reacts with water that contaminates the solvent in which the polymerization is run.

Monomers bearing cation stabilizing groups, such as alkyl, phenyl or vinyl can be polymerized by cationic processes. These are normally initiated at low temperature in methylene chloride solution. Strong acids, such as HClO_4 , or Lewis acids containing traces of water (as shown above) serve as initiating reagents

Difference between Mechanism of Free radical and Ionic Polymerization

	Free radical	cationic	anionic
Monomers involved	Ethylene, butadiene, isoprene, acrylates, vinyl chloride,	Monomers with electron releasing substituents like methoxy, ethoxy substituents	Monomers with electron attracting substituents like vinyl cyanide, methyl methacrylate etc
Initiator	Benzoyl peroxide	Lewis acids, Friedel Craft catalyst like AlCl_3 , BF_3 , SnCl_4 etc	Strong bases like alkali metals, sodium or potassium amide, Grignard reagent
Intermediates involved	Free radical	Carbocation intermediate	Carbanionic intermediates
Reaction conditions	Temperature $\geq 50^\circ\text{C}$	Temperature=0°C	
Solvent conditions	Not sensitive to polarity of solvent	Highly sensitive to changes in polarity of solvent	

PLASTICS AND FIBERS

Plastics:

- ▶ Plastics are semi-synthetic materials
- ▶ Monomers of plastics are either natural or synthetic organic compounds
- ▶ Depending on the arrangement of monomer units, plastics are classified as two types
 - Thermoplastics: linear or lightly cross linked monomers
 - Thermosetting plastics: heavily cross linked monomers

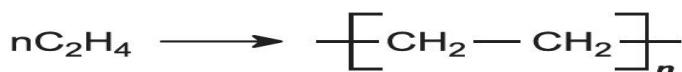
1. Thermoplastics-Polyethylene:

Use: Poly(ethene) is produced in two main forms: low density (LDPE) ($< 0.930 \text{ g/cc}$) and high density (HDPE) ($0.940\text{-}0.965 \text{ g/cc}$).

The LDPE form is preferred for film packaging and for electrical insulation.
HDPE is used to make containers for household chemicals such as washing-up liquids and drums for industrial packaging. It is also used for domestic and gas pipe.

Preparation:

LDPE is prepared from ethylene at high pressure of 1000 to 5000 atmospheres at 250°C in the presence of free radical initiator (O_2)



Two types of catalyst are used principally in the manufacture of HDPE:

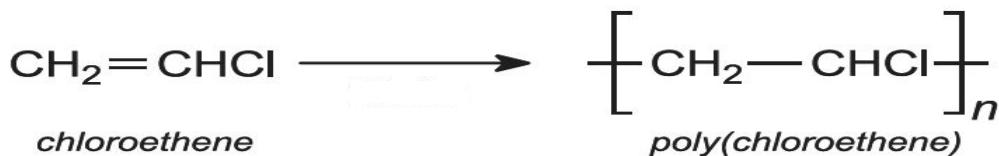
- a. Using Ziegler-Natta organometallic catalyst (titanium compounds with an aluminium alkyl), ethylene is polymerized under 6-7 atmospheres at $60\text{-}70^\circ\text{C}$
- b. Using supported metal oxide catalyst like CrO_3 supported on silica-alumina, ethylene is polymerized at 35 atm at $160\text{-}200^\circ\text{C}$

2. Thermoplastics-Polyvinyl chloride (PVC):

Uses:

- a. wirings and cables
- b. bottles for drinks, oils, cosmetics, detergents
- c. building and construction (window frames), floorings, pipes for drainage
- d. coated fabrics
- e. films and sheets
- f. vinyl records

Preparation: This is an example of addition polymerization. PVC is made by free-radical polymerization (in the form of emulsion) in the presence of benzoyl peroxide as catalyst under pressure.



3. Thermoplastics-PMMA:

Uses:

Poly(methyl 2-methylpropenoate) is better known as Lucite, Perspex and Altuglas (when in sheet form) and as Diakon (when in powder form).

The sheet form is used in baths and other sanitary ware. High molecular mass cast sheet (Perspex) is also used as a lightweight replacement for glass.

Lower molecular mass products, made by suspension or solution polymerization (Diakon), are used in car lights and domestic lighting.

Special grades are used in diverse applications such as false teeth and eyes and as a major component of bone cements.

The monomer is used in adhesives, surface coatings and in paints.

The monomer is used in adhesives, surface coatings and in paints.

Preparation: PMMA is prepared by addition polymerization of methyl methacrylate in the presence of acetyl peroxide as catalyst.



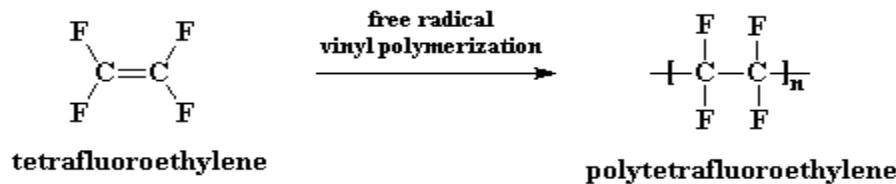
4. Thermoplastics-Teflon (Poly tetra fluoroethylene) [PTFE]

The uses of poly (tetrafluoroethylene) (PTFE) are a function of its resistance to chemical attack, unreactivity (even above 500 K), low friction, non-stick properties and high electrical resistance.

Uses of Teflon

- a. cable insulation
 - b. reactor and plant equipment linings, when reactants or products are highly corrosive to ordinary materials such as steel
 - c. semi-permeable membranes in chlor-alkali cells and fuel cells
 - d. bearings and components in mechanical devices such as small electrical motors and pumps
 - e. permeable membrane for clothing and shoes, which allows water vapor to diffuse away from the skin but prevents liquid water (rain) from soaking in
 - f. non-stick domestic utensils, e.g. frying pans
 - g. medical - catheter tubing
 - h. hose and tubing
 - i. solid lubricants

Preparation: Teflon is prepared by addition polymerization of tetrafluoroethylene in the presence of benzoyl peroxide as catalyst.

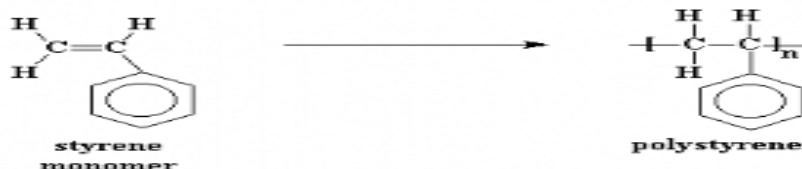


5. Thermoplastics-Polystyrene

Use: Its largest use is for packaging, particularly for foods such as poultry and eggs, for cold drinks and take-away meals.

- a. making audiocassettes, TV housing, refrigerators, vacuum cleaners
 - b. talcum powder containers,
 - c. small jars and containers for food packaging, bottle caps
 - d. combs, brush handles

Preparation: Polystyrene is prepared by addition polymerization of styrene monomer in the presence of benzoyl peroxide as catalyst

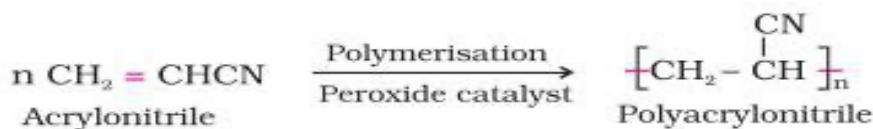


6. Thermoplastics-Polyacrylonitrile (ORLON) (PAN)

Uses:

- a. Used as tough fabric for example a soft top of a car or in brake linings.
 - b. It is even used to reinforce concrete and in road construction.
 - c. Co-polymerization of propenonitrile with ethenyl ethanoate (vinyl acetate) and propenonitrile with methyl propenoate (methyl acrylate) leads to softer variety of 'acrylic' fibers. These are often mixed with cotton fibers to produce a light fabric, used in women's clothes.

Preparation: ORLON is prepared by addition polymerization of acrylonitrile in the presence of acetyl peroxide as catalyst



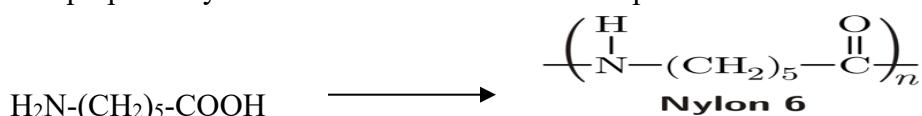
Fibers:

- ▶ Thin, long, threadlike material having high tensile strength
- ▶ High strength is due to strong intermolecular force of polymer chain
- ▶ Intermolecular forces can be Vander Waals force (polypropylene), dipole-dipole interaction (Dacron, terylene), or hydrogen bonding (nylon, spandex)
- ▶ Example:
 (SYNTHETIC): polyamide (Nylon); polyester (polyethylene terephthalate or Terylene or Dacron), acrylics (polyacrylonitrile), elastomeric (Spandex, Lycra)
 (NATURAL): Cellulose fiber (Cotton, linen, jute, coir), protein fiber (wool, silk), mineral fiber (asbestos)

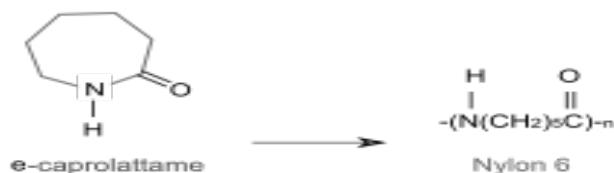
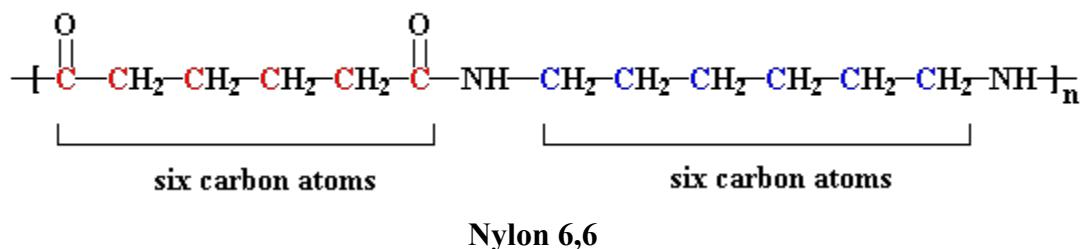
1. Thermoset-Nylon 6: Nylon 6 is a synthetic fiber having a polyamide functional group.

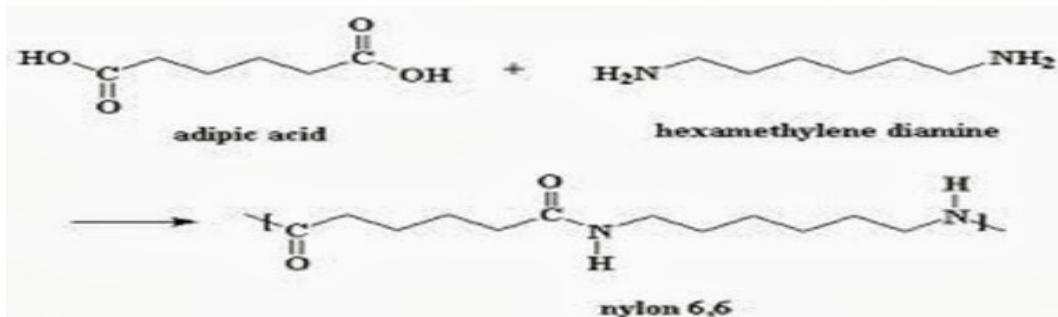
Preparation:

- a. It is prepared by self condensation of ε-amino caproic acid



- b. or by ring opening of caprolactum

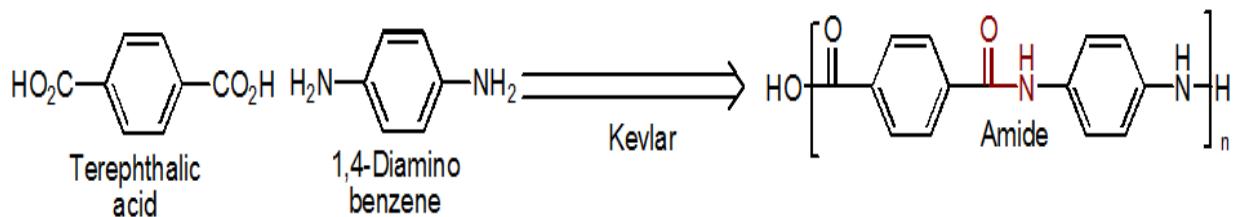
**2. Thermoset-Nylon 6,6:** It is made by the condensation polymerization of hexamethylene diamine and adipic acid.



Uses:

- Nylon 6 and Nylon 6,6 are used primarily as fibres in making socks, undergarments, carpets etc.
- Used in making hair combs.
- Nylon 6 is used mainly for making tyre cords.
- Nylon 6, 6 is used in making gears, bearings etc.
- Nylon 6, 6 is used for jacketing electrical ware to provide tough abrasion resistant outer cover to protect the primary electrical insulation.

3. **Thermoset-Kevlar:** It is a polyamide and is prepared by condensation polymerization of Terephthalic acid and 1, 4 di-amino benzene.



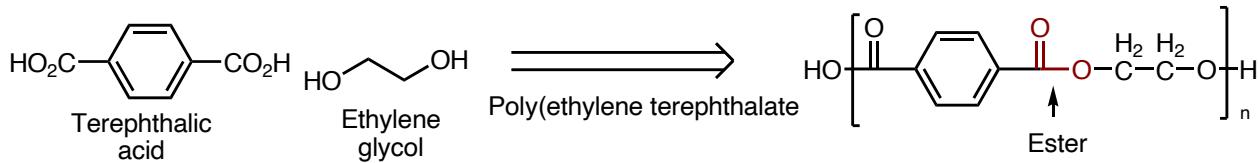
Uses:

Typically it is spun into ropes or fabric sheets that can be used as such or as an ingredient in composite material components. Currently, Kevlar has many applications, ranging from bicycle tires and racing sails to body armor because of its high tensile strength-to-weight ratio. It is also used to make modern drumheads that hold up withstanding high impact. When used as a woven material, it is suitable for mooring lines and other underwater applications.

4. **Thermoset-Polyethylene Terephthalate (PET) (also known as Terylene or Decron)**

It is polyester, prepared by heating dimethyl terephthalate and ethylene glycol in basic medium.

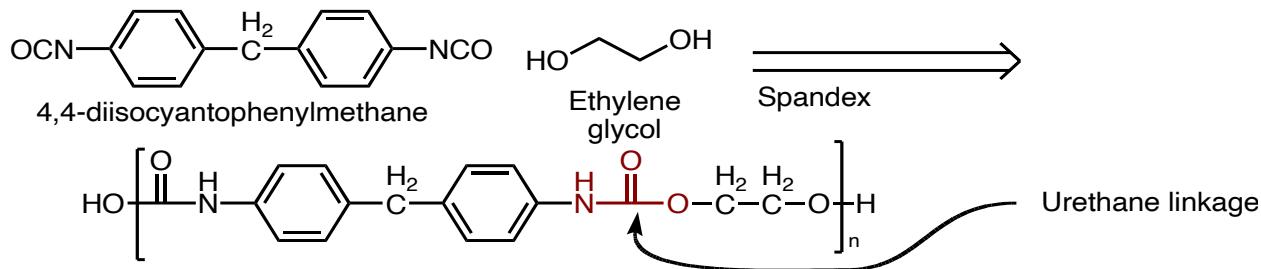
Monomer



Uses:

- It is used for making magnetic recording tapes.
- It is sued for making bottles for Cola drinks, fruit juice, sauces etc.
- It is used for making wide necked jars for coffee.
- It is used for making films of overhead projector.
- Glass filled PET moldings are used for housings for toasters, coffee machines, car heaters and water meter.

5. Thermoset-Polyurethane: It has a urethane linkage and is prepared by heating 4, 4 di-isocyanato-phenylmethane and ethylene glycol

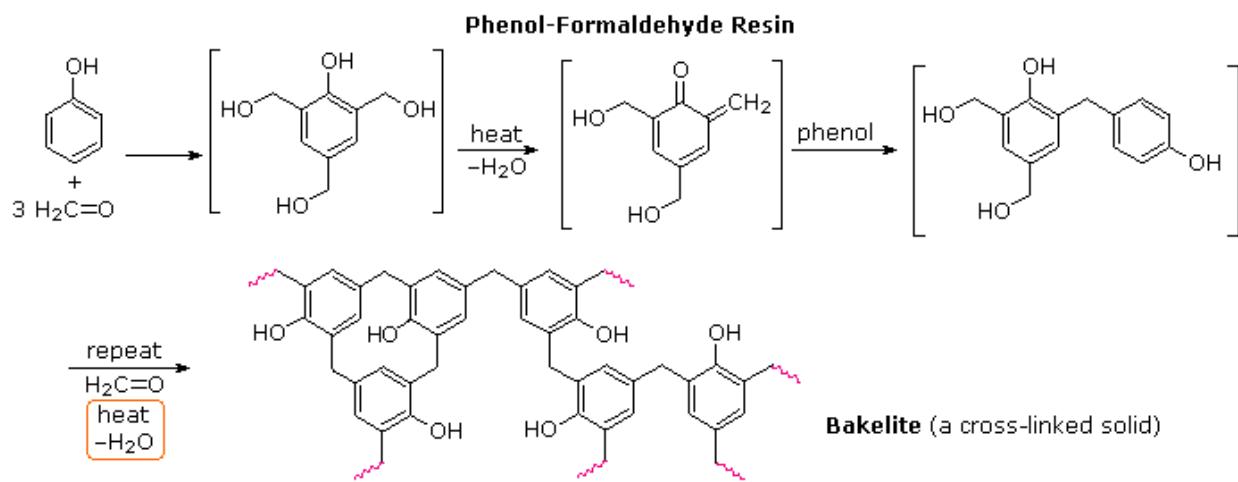


Uses:

- Apparel
- Appliances. The most common use for polyurethanes in major appliances is rigid foams for refrigerator and freezer thermal insulation systems. The good thermal insulating properties of rigid polyurethane foams result from the combination of a fine, closed-cell foam structure and cell gases that resist heat transfer.
- Automotive
Polyurethanes are used throughout cars. In addition to the foam that makes car seats comfortable, bumpers, interior "headline" ceiling sections, the car body, spoilers, doors and windows all use polyurethanes.
- Building and Construction
- Composite Wood
- Electronics
- Flooring
- Furnishings
- Medical
Polyurethanes are commonly used in a number of medical applications, including catheter and general purpose tubing, hospital bedding, surgical drapes, wound dressings and a variety of injection-molded devices.
- Packaging

6. Thermoset-Bakelite (Phenol-Formaldehyde Resin)

Preparation:

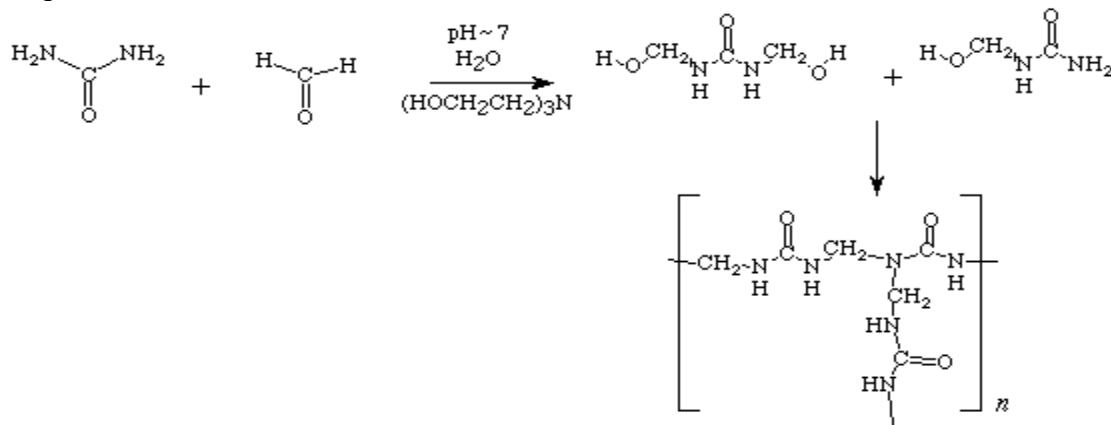


Use:

- Bakelite is used for the emerging electrical and automobile industries because of its extraordinarily high resistance – not only to electricity, but to heat and chemical action. It is used for all non-conducting parts of radios and other electrical devices, such as bases and sockets for light bulbs and vacuum tubes, supports for electrical components, automobile distributor caps and other insulators.
- Bakelite is used today for wire insulation, brake pads and related automotive components, and industrial electrical-related applications. It is used in myriad applications including saxophone mouthpieces, whistles, cameras, solid-body electric guitars, telephone housings and handsets, early machine guns, pistol grips, and appliance casings. In the pure form it was made into such articles as pipe stems, buttons, etc.

7. Thermoset-Urea-Formaldehyde Resin

Preparation:

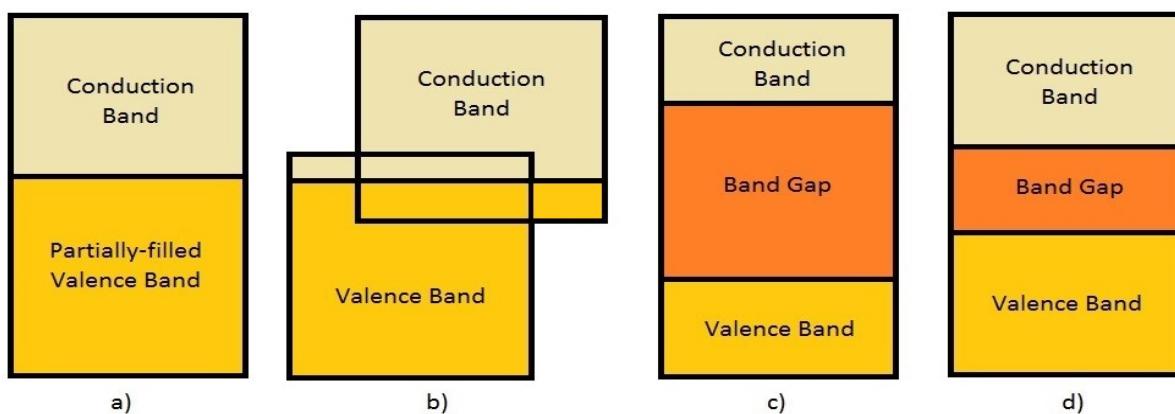


Uses:

Urea-Formaldehyde is used in many manufacturing processes due to its useful properties. Examples include decorative laminates, textiles, paper, foundry sand molds, wrinkle resistant fabrics, cotton blends, rayon, corduroy, etc. It is also used to glue wood together. Urea formaldehyde is also commonly used when producing electrical appliances casing (e.g. desk lamps).

CONDUCTING POLYMERS

Polymers are organic macromolecules, a long carbonic chain, composed by structural repeat entities, called monomer. The majority of polymers are insulators, due to an unavailability of free electrons to create conductivity. The poor conductivity of polymers is explained by the band theory. Band theory explains the existence of valence and conduction band. While valence band are continuous energy levels placing the valence electrons; conduction band are continuous higher energy levels that are empty. The band gap determines the conducting nature of materials. The Fig below shows the band structure of monovalent metallic conductors (a), for divalent metallic conductors (b) for insulators (c) and for semiconductors (d).



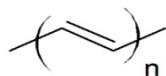
Band Structure for Conductors, Semiconductors, and Insulators: a) for monovalent metals; b) divalent metal; c) Insulators; and d) Semiconductors

Polymers were considered as insulators. But in 1970, the first intrinsic conductive polymer was discovered by Shirakawa, Heeger, and MacDiarmid, for which they were awarded the Nobel prize in 2000. The polymer was produced by the exposure of the polyacetylene to dopant compounds: oxidizing or reducing agents; electron-donor or electron-receptor of electrons.

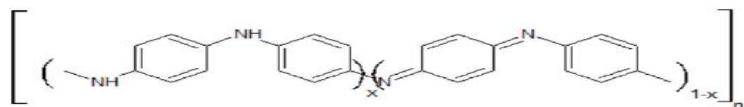
Conducting Polymers

Polymers which conduct electricity are known as conducting polymers. Conducting polymers are classified as Intrinsic and Extrinsic Conducting polymers

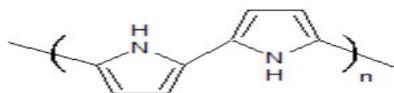
Intrinsically Conducting polymers have inherent double or triple bonds in conjugation. Extensive delocalization of π electrons over the entire polymeric backbone results in the formation of valence and conduction bands. Significant band gap exists in such polymers. Such polymers exhibit semiconducting properties. Electrical conductivity in such polymers results only after appropriate thermal or photolytic activation. The electrons in valence band get sufficient energy to jump the gap and reach the lower energy level of the conduction band. Examples are polyacetylene, Polyaniline and polypyrrole



Structure of a polyacetylene



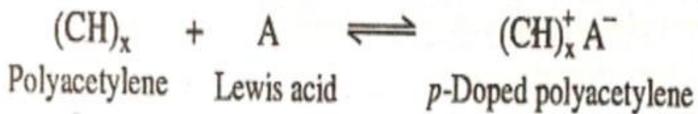
Structure of Polyaniline



Structure of polypyrrole

Doping i.e addition of external agent into the conjugated polymer can lead to a dramatic increase in electrical conductivity to values as high as 10^5 S/cm (Cu has an electrical conductivity of 10^6 S/cm). In the presence of a dopant, positive or negative charges are created on the polymer backbone as a result of oxidation or reduction. Doping is of two types: p type and n type

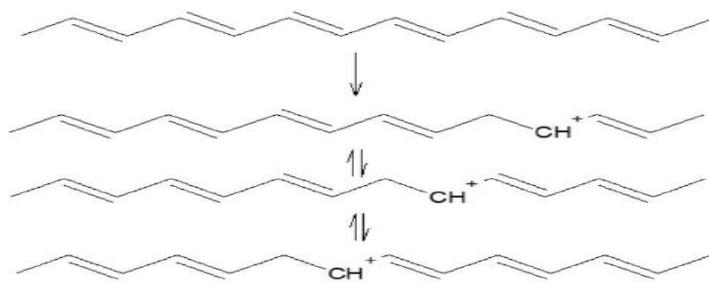
In p type, conducting polymers are exposed to Lewis acid. Oxidation occurs and positive charges are developed on polymer backbone.



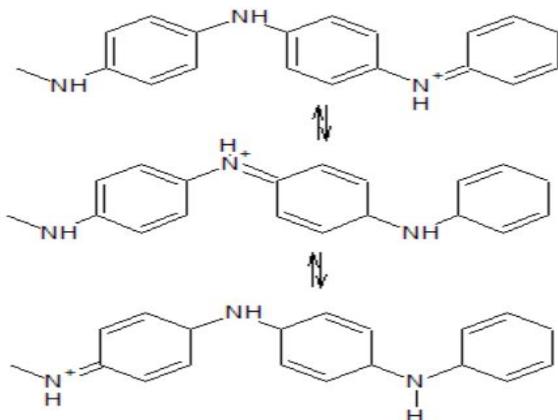
In n type, Lewis base causes reduction to occur and negative charges are developed on polymer chain.



The movement of such charges as a result of resonance in the presence of an externally applied field give rise to enhanced conductivity.



Resonance in polyacetylene in the presence of Lewis acid



Resonance in Polyaniline in the presence of Lewis base

Disadvantage of such Intrinsically Conducting Polymers is low conductivities, improcessabilities, poor mechanical strength and poor stability.

Extrinsically Conducting Polymers are of two types:

- Conductive element filled polymer: Conducting elements like carbon black, metallic fibers, metallic oxides etc. are filled into the polymer to form a solid entity. Such polymers are low in cost, possess high conductivity, light in weight, mechanically durable, strong and are easily processable in different forms, shapes and sizes. Disadvantages include reduction in tensile strength
- Blended conducting polymer: a conventional polymer that is insulator is blended with a conducting polymer. Such polymers possess better physical, chemical, electrical and mechanical properties and can easily be processed.

Application

Conducting polymers are widely used

- In rechargeable batteries.
- In making analytical sensors for pH, O₂, SO₂, NH₃, glucose, etc.
- In the preparation of ion exchangers.
- In controlled release of drugs.
- In optical filters.
- In photo voltaic devices.
- In telecommunication systems.
- In micro-electronic devices.
- In bio-medical applications.

Synthesis

There are three ways to produce conductive polymers: reactional chemistry, electrochemical, and photoelectrochemical, being the first one the most used, due to its high profitability and efficiency.

The chemical process consists in the union of monomers by the addition of the oxidizing or reducing agents that makes the neutral polymer to a cationic or anionic ionic complex, ending the reaction by the bonding of this complex to the counter-ion of the redox agent. This process requires a high control, since the reaction is very exothermic and emits gases, requiring proper treatment and equipment of protection.

The electrochemical method consists in the electronic deposition of the polymer in the electrode. The solution that the electrode is immersed has the monomers and the dopants. When a voltage or a current strong enough is applied, the monomers oxidize resulting in the polymerization. This process results in polymers with shape of the electrode, requiring a posterior processing to get the shape desired.

The photoelectrochemical process is based on photoexcitation of the polymer or in compounds that have catalyst properties in presence of light, oxidizing the monomers resulting in a polymerization. Even though this process is simple and environmentally friendly, the mechanical properties of the resulting polymer are not good.

BIODEGRADABLE POLYMERS

- Polymers which get degraded by the process of biodegradation
- Biodegradation is the process which involves biological organisms like fungi or bacteria for degrading or cleaving of a polymer
- Requirements for biodegradation are
 - biological organisms,
 - appropriate environmental conditions (temperature, pH, moisture, O₂, light, pressure etc.)
 - Substrate i.e the polymer
- Types of Biodegradable Polymers are:
 - Natural Biodegradable Polymers: Natural Rubber, collagen, lignin
 - Synthetic Biodegradable Polymers: Polyvinyl alcohol, polyanhydrides, poly (3 hydroxy butyrate), polylactic acid, β-hydroxy butyrate-β-hydroxy valerate)
- Applications of Biodegradable Polymers
 - a. Poly (β-hydroxy butyrate) or PHB is used in the manufacture of shampoo bottles
 - b. β-hydroxy butyrate- β-hydroxy-valerate are suitable as matrices for controlled release of drugs due to their favorable biocompatibility and biodegradation properties. It is also used as a packaging material, in orthopaedic devices etc.
 - c. Poly (lactic acid) or PLA is used widely in medical applications like sutures, drug delivery systems and wound clips. It is also used in some agricultural applications like “timed-release coatings for fertilizers and pesticides”
 - d. Dextron is the 1st bioabsorbable suture made from biodegradable polyester for post operative stitches
- Need for Biodegradable polymers are
 - Environmental friendly as they do not cause solid waste and pollution problems

FUEL

Definition:

Whenever a substance is burnt in air or oxygen with the evolution of heat, the process is called combustion and the substance which is burnt is called combustible substance. In the process of combustion, the chemical energy of fuel is converted into heat energy and light energy.

The heat evolved during combustion can be used for household purposes or economically for industrial purposes. All combustible substances which contain carbon as the main constituent are called fuels. Thus fuel can be defined as any combustible substance, containing carbon as the main constituent which on proper burning produces heat that can be used economically for domestic and industrial purposes and in the generation of power.

**Classification:**

The fuels are broadly classified in two ways, depending on the state of matter

1. Primary Fuels: These include the naturally occurring fuels that are found free on the earth's crust. These are classified as
 - i. Solid fuels for eg wood, peat, lignite, coal etc
 - ii. Liquid Fuels for eg. Petroleum, crude oil etc.
 - iii. Gaseous Fuels like natural gas etc.
2. Secondary or Derived Fuels: These are artificially derived or manufactured from primary fuels. These are further classified into
 - i. Solid fuels for eg coke, charcoal, petroleum coke, pulverized coal etc.
 - ii. Liquid Fuels for eg. Gasoline, diesel oil, kerosene, coal tar, LPG, alcohol etc.
 - iii. Gaseous Fuels like coal gas, water gas, biogas, blast furnace gas etc.

Natural Fuels	Manufactured Fuels
Solid Fuels	
Wood Coal Oil shale	Tanbark, Bagasse, Straw Charcoal Coke Briquettes
Liquid Fuels	
Petroleum	Oils from distillation of petroleum Coal tar Shale-oil Alcohols, etc.
Gaseous Fuels	
Natural gas	Coal gas Producer gas Water gas Hydrogen Acetylene Blast furnace gas Oil gas

Characteristics of a good fuel

While selecting an ideal fuel for domestic or industrial purpose we should keep in mind that the fuel selected must possess the following characteristic properties.

1. It should possess high calorific value.
2. It should have low moisture content as moisture reduces the heating value of fuel
3. It should have low non-combustible substance as its presence reduces heating value and produces more ash
4. It should have proper ignition temperature. The ignition temperature of the fuel should neither be too low nor too high. Very low ignition temperature is harmful for storage and transport while high ignition temperature causes difficulty in igniting the fuel.
5. It should be easy to handle, store and transport.
6. It should not produce poisonous products during combustion. In other words, it should not cause pollution.
7. It should burn with more efficiency and less smoke.
8. It should be easily available in plenty.
9. It should be cheap.
10. It should have moderate rate of combustion.
11. Combustion should be easily controllable i.e., combustion of fuel should be easy to start or stop as and when required.

Relative Merits of Solid, Liquid and Gaseous Fuels

Fuel Characteristics	Solid Fuels	Liquid Fuels	Gaseous Fuels
1. Calorific Value	least	higher	highest
2. Cost	cheap	Costly than solid fuels	costliest
3. smoke	Is produced	Is produced from higher carbon and aromatic components but burning is clean	Is not produced
4. ash	Always produced	Not produced	Not produced
4. environmentally friendly	no	no	yes
5. storage	easy	Should be stored in closed containers	Must be stored in closed containers
6. handling cost	high	low	low
7. safety	highest	least	least
8. Ignition temperature	high	low	least

Calorific Value of a Fuel

It is defined as the amount of heat produced by the complete combustion of a given mass of a fuel, usually expressed in joules per kilogram. It is expressed in two forms:

Gross Calorific Value (GCV) or High Calorific Value (HCV):

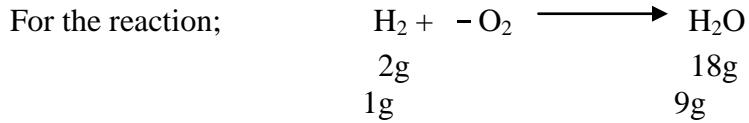
It is the total amount of heat generated when a unit mass of fuel is completely burnt and the products of combustion are allowed to cool down to room temperature.

When a fuel containing hydrogen is burnt, the hydrogen present in fuel produces steam. If the products of combustion are allowed to cool to room temperature, the latent heat of condensation of steam gets included in the measured heat. This is called the gross calorific value (GCV)

Net Calorific Value (NCV) or Low Calorific value (LCV)

It is the net amount of heat produced when unit mass of fuel is completely burnt and the products are allowed to escape.

Net Calorific Value = Gross Calorific Value – Latent heat of condensation of steam
 = Gross Calorific Value – Latent heat of vaporization of water vapor
 = Gross Calorific Value – (Mass of hydrogen per unit weight of fuel burnt x 9/100 x Latent heat of vaporization of water vapor)



One part by weight of hydrogen gives nine parts by weight of H_2O .

Let H% be the hydrogen content in a fuel.

Thus 1 g of fuel contains H/100 g of H_2

H/100 g of H_2 will produce 9*H/100 g of H_2O (because 1g of H_2 produces 9g of H_2O)

$$= 0.09\text{H} \times (\text{latent heat of steam}) = 0.09\text{H} \times 587 \text{ cal/g}$$

Latent heat of steam = 587cal/g of water vapor produced.

Thus,

$$\boxed{\text{NCV} = \text{HCV} - 0.09 \times \text{H} \times 587}$$

where H = mass of hydrogen in fuel

Units of calorific value of fuel:

Calorific values of solid and liquid are expressed in Calories/g (cal/g) or kilocalories/kg (kcal/kg) or British Thermal unit/pound (BTU/lb)

Calorific values of gaseous fuels are expressed in kilocalories/m³ kg (kcal/m³) or British Thermal unit/ft³ (BTU/ ft³)

Determination of Calorific Value (Bomb calorimeter)

The gross calorific value of solid and liquid fuels is determined by Bomb Calorimeter.

Principle: A known unit mass of fuel is burnt completely and the quantity of heat produced is absorbed in water and measured. Then the quantity of heat produced by burning unit mass of fuel is calculated. According to principle of calorimetry, heat liberated by fuel = heat absorbed by water, apparatus.

Construction: It consists of the following parts:

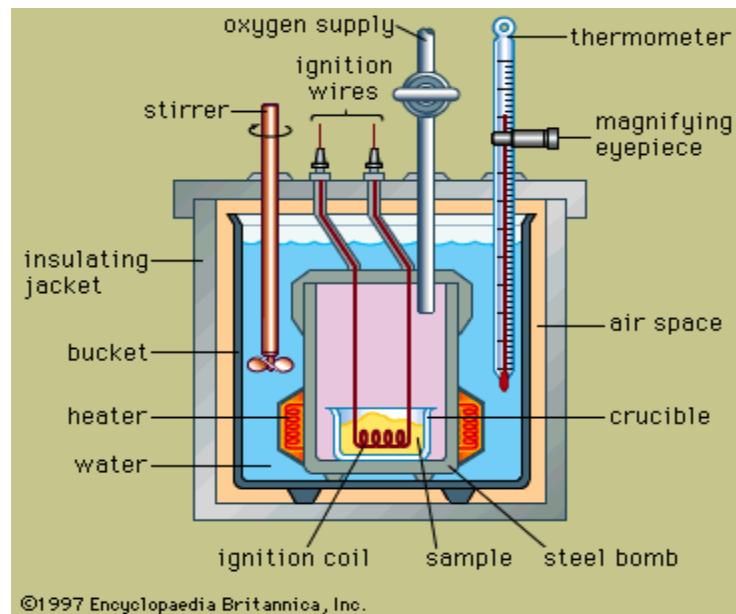
1. A strong cylindrical bomb made of stainless steel, resistant to corrosion and capable of withstanding high pressure up to 50 atmospheres. It is provided with a lid which can be

screwed firmly to the bomb. The lid is provided with two electrodes and an oxygen inlet valve. A small ring is attached to one of the electrodes which act as a support for the crucible.

2. A copper calorimeter vessel is used which contains a known weight of water and in which the bomb is placed.
3. The calorimeter is surrounded by an air jacket and a air jacket to prevent loss of heat due to radiation.
4. The calorimeter is provided with an electrical stirrer for stirring water and a Beckman Thermometer to measure temperature.
5. The crucible in which the sample is kept is made of stainless steel or fused silica

Design of Bomb Calorimeter:

The design of a typical bomb calorimeter is shown in the picture below:



A Bomb Calorimeter

Working:

A weighed amount of sample (fuel) is placed in the silica crucible supported over the ring. A fine magnesium wire touching the sample of the fuel is stretched across the electrodes. About 10mL of distilled water is introduced into the bomb to absorb vapors of sulphuric acid and nitric acid formed during the combustion. Oxygen supply is forced into the bomb to a pressure of 25-30 atmosphere. The bomb is then carefully placed in the calorimetric vessel containing a known

amount of water. Water is stirred with the stirrer and temperature is recorded. The electrodes are connected to a battery and the circuit is completed. The combustion of fuel takes place with the evolution of heat. The heat produced by burning is transferred to water which is stirred throughout the experiment with the stirrer. Maximum temperature is recorded and the gross calorific value is calculated as follows;

Let x = mass of fuel sample taken in crucible (g)

W = mass of water in the calorimeter (g)

w = water equivalent of calorimeter, stirrer, bomb, thermometer etc (g)

= mass x specific heat of apparatus = $W' \times S$

T_1 = initial temperature of water in calorimeter ($^{\circ}\text{C}$)

T_2 = final temperature of water in calorimeter ($^{\circ}\text{C}$)

L = Gross Calorific Value of fuel (cal/g)

S = specific heat

Heat liberated by burning of fuel = xL cal

Heat absorbed by water = $[W \times S \times (T_2 - T_1)]$ cal

Heat absorbed by apparatus = $[W' \times S \times (T_2 - T_1)]$ cal = $w(T_2 - T_1)$ cal

Specific heat of water = 1 cal/g $^{\circ}\text{C}$ and 1 cal = 4.2J

Therefore, total heat absorbed by water, apparatus =

$[W \times 1 \times (T_2 - T_1) + w \times 1 \times (T_2 - T_1)] = [(W+w) \times 1 \times (T_2 - T_1)]$ cal

According to principle of calorimetry, heat liberated by fuel = heat absorbed by water, apparatus

$xL = [(W+w)(T_2 - T_1)]$

$$\mathbf{L = Gross calorific value of fuel = HCV = GCV = \underline{\hspace{10cm}} \text{ cal/g}}$$

LCV = Low calorific value = $(HCV - 0.09 H \times 587)$ cal/g

Corrections

Accurate reading of calorific value requires the following corrections:

1. Fuse wire Correction: The heat liberated as GCV includes the heat given out by ignition of the fuse wire used. Hence it must be subtracted from total value.

2. Acid Correction: Fuels containing S and n are oxidized during combustion producing H_2SO_4 and HNO_3 respectively. Such reactions are exothermic and hence the measured heat includes the heat given out during the acid formation. Such heat is subtracted from total value.
3. Cooling correction: Time is required to cool the water in the calorimeter from maximum temperature to room temperature is noted. This time is recorded and the cooling correction is calculated by multiplying it by rate of cooling. The cooling correction is then added to rise in temperature.
4. Cotton Thread correction: As the cotton thread is used for igniting the fuel, its burning thus liberates heat which is then subtracted from total heat.

Gross calorific Value = GCV =

Advantage of liquid Fuels:

1. They have higher calorific value than solid fuels.
2. They burn without ash, smoke
3. They are easy to transport, store and handle.
4. They can be easily used in internal combustion engines.
5. Liquid fuels can be easily kindled. Combustion can be started and stopped at once.

Conventional source of energy

The energy sources which cannot be compensated, once these are used (after their exploitation) are termed as conventional energy sources. Examples are coal, wood, petroleum, natural gas and nuclear energy.

Non-Conventional source of energy

The conventional energy sources discussed above are exhaustible and, in some cases, installation of plants to get energy is highly expensive. In order to meet the energy demand of increased population, the scientists developed alternate nonconventional natural Resources sources of energy which should be renewable and provide a pollution free environment.

Some examples of non-conventional source of energy are

1. solar energy
2. wind energy
3. tidal energy
4. geo-thermal energy
5. Biomass based energy
6. Biogas
7. Bagasse based plants
8. energy from urban waste (sewage and municipal solid waste)

Liquefied Petroleum gas (LPG) is a liquid fuel naturally derived from crude oil and natural gas. About 60% of the world's LPG is obtained from natural gas, and the remaining 40% is achieved from refining crude oil. When natural gas is pulled from the ground, the resulting hydrocarbon is a mix of several gases and liquids. About 90% of what is recovered is methane, or natural gas. The other 10% is made up of propane, butane and ethane -- or LPG.

LPG used for cooking purpose is made up of Propane and Butane, or a combination of the two. It is labeled as "liquefied gas" because LPG is very easily converted to a liquid state. LPG requires only slight pressure or refrigeration to transform it from its natural gaseous state into a liquid. As a gas, LPG occupies 274 times its volume as a liquid, making the liquid state much preferred for transportation and storage.

LPG is considered a clean-burning fossil fuel. This is because LPG burns completely, leaving no waste and emitting significantly less pollutants into the environment than other hydrocarbons.

Easily stored in massive tanks, LPG is many times used as a fuel source in remote areas where obtaining other products via pipeline or transport would be impossible.

Compressed natural gas (CNG) is a gaseous fuel which can be used in place of petrol, diesel and LPG. Its composition is methane and is compressed to less than 1% of the volume that it occupies at standard atmospheric pressure. CNG is stored in cylindrical or spherical containers at very high pressure of 20–25 MPa.

Advantages of CNG

1. Combustion of CNG produces fewer undesirable gases (e.g., carbon dioxide (CO_2), unburned hydrocarbons (UHC), carbon monoxide (CO), nitrogen oxides (NO_x), sulfur oxides (SO_x) and PM (particulate matter) than the petroleum derived fuels. Due to lower carbon dioxide emissions, switching to CNG can help reduce greenhouse gas emissions and hence is environmentally safe.
2. It is safer than other fuels in the event of a leak or spill, because CNG is lighter than air and disperses quickly when released.
3. Being a gaseous fuel, its calorific value is higher as compared to liquid or solid fuels. Hence its efficiency as a fuel is higher.
4. CNG does not contain lead and does not react with metals; hence the maintenance cost of engines of transportation vehicles is increased.

Disadvantage of CNG

The drawback is that being a gaseous fuel, CNG occupies greater amount of space for fuel storage than liquid fuels like petrol, diesel or conventional gasoline.

Coal:

Coal is formed from the fossilized remains of animals and plants; hence it is a fossil fuel.

The factors responsible for usage of coal as a fuel are:

High calorific value; Low cost; least risk of fire hazards and easy storage

Classification of coal:

- Soft coals: have low % of C. example-peat (57% C), lignite (67% C)
- Hard coal: have very high % of C. example- bituminous coal (83%), anthracite (93% C)

Analysis of Coal

Coal Analysis techniques are specific analytical methods designed to measure the particular physical and chemical properties of coals. There are two methods to analyze coal which are called proximate analysis and ultimate analysis.

The proximate analysis determines only the fixed carbon, volatile matter, moisture and ash percentages and it can be determined with a simple apparatus.

The ultimate analysis determines all coal component elements like C, H, N, S, O and ash. It needs properly equipped laboratory with skilled chemists.

The proximate analysis of coal determines the following aspects:

1. *Measurement of moisture*

The moisture content is determined by placing a known weight of sample of powdered raw coal of size 200- micron (A gms) in an uncovered crucible which is placed in the oven kept at $105\pm 2^\circ\text{C}$ along with the lid for 1 hr. After that sample is cooled to room temperature and weighed again (B gms). The loss in weight represents moisture.

$$\% \text{ moisture} = \frac{A - B}{A} \times 100 = \text{---} \times 100$$

High Moisture content in coal is undesirable because it decreases the calorific value and hence quality of coal. It increases the cost of coal as well as transportation charges

2. *Measurement of volatile matter*

B gms of moisture free coal is taken in a silica crucible and covered with a lid. It is then heated in a furnace at $925\pm 20^\circ\text{C}$ for 7 mins. After that sample is cooled and weighed (C gms). Loss of weight represents the volatile matter on a percentage basis.

$$\% \text{ volatile matter} = \frac{B - C}{B} \times 100 = \text{---} \times 100$$

Volatile matter present in coal may be combustible gases (H_2 , CO , CH_4 and other lower hydrocarbons) or non-combustible gases (CO_2 and N_2). Presence of volatile matter does not add to heat/calorific value and hence is undesirable. Coal having high volatile matter burns with a long flame, emits smoke and has less calorific value. A large proportion of coal distills over as gas or vapor while a significant proportion of it escapes unburnt.

3. Measurement of carbon and ash

A weighed amount of dry coal (A gms) is burnt in an open crucible in the presence of air or oxygen at $700-750^\circ C$ for 30 mins in a muffle furnace. The residue after cooling is weighed, which is the incombustible ash (D gms).

$$\% \text{ ash} = \frac{\text{Weight of ash}}{\text{Weight of coal}} \times 100 = \frac{D}{A} \times 100$$

Ash is the non-combustible, useless matter in the coal. It is undesirable because its presence in coal decreases its calorific value. Ash causes the hindrance to the flow of air or heat and thereby, decreases the efficiency of burning of coal. It also increases the cost of transportation, handling and storage. There is additional cost of disposal of ash.

4. Fixed Carbon

After the determination of moisture, volatile matter and ash content, the remaining matter is known as fixed carbon. Higher the % of fixed carbon, higher is the calorific value of coal. It is determined indirectly by deducting the sum total of moisture, ash and volatile matter from 100

$$\% \text{ fixed Carbon} = 100 - \% \text{ of (moisture+volatile matter + ash)}$$

CRACKING AND KNOCKING

Cracking is the process whereby complex organic molecules are converted to simpler molecules by the breaking of carbon-carbon bonds. The rate of cracking and the end products are strongly dependent on the temperature and presence of any catalysts.

Knocking, technically known as detonation is a term used in internal combustion engines and occurs when fuel/air mixture in the cylinder has been ignited by the spark plug and the smooth burning is interrupted by the unburned mixture in the combustion chamber. See, gasoline is a liquid with different hydrocarbons together for example $C_4 - C_{12}$ such as benzene C_6 , butane C_4 , pentane C_5 etc. (Higher the auto ignition temperature higher the octane number) Normally, when gasoline is used in an engine, due to its composition of different hydrocarbons, each get ignited at different time. So, due to the irregular ignition in closed chamber, the force of

combustion may damage the piston head, intake, exhaust valves, etc. These kind of problems also occur when the autoignition temperature is low. So in order to overcome these problems, anti knocking agents are used. So What are Anti Knock agents? Anti Knock agents are those with higher octane number. For example, Tetraethyl lead (TEL) has an octane number of 100+ where as for gasoline it is usually around 87–90. But one drawback of TEL is it is poisonous, so in order to replace TEL, ethanol (Octane number 104~), a biofuel, Methyl tert-butyl ether (MTBE) and Ethyl tert-butyl ether (ETBE) has been encouraged to be blended with gasoline (Petrol).

Octane number: Octane rating or octane number is a measure of the resistance of gasoline and other fuels to detonation (engine knocking) in spark-ignition internal combustion engines. The octane number of a fuel is measured against a mixture of iso-octane and heptane. If a gasoline sample has the same antiknock quality as that of a mixture containing 90% iso-octane and 10% heptane, then the octane number for that sample is defined as 90.

Biomass and Bioenergy

Biomass—renewable energy from plants and animals

Biomass is organic material that comes from plants and animals, and it is a renewable source of energy.

Biomass contains stored energy from the sun. Plants absorb the sun's energy in a process called photosynthesis. When biomass is burned, the chemical energy in biomass is released as heat. Biomass can be burned directly or converted to liquid biofuels or biogas that can be burned as fuels.

Examples of biomass and their uses for energy:

- Wood and wood processing wastes—burned to heat buildings, to produce process heat in industry, and to generate electricity
- Agricultural crops and waste materials—burned as a fuel or converted to liquid biofuels
- Food, yard, and wood waste in garbage—burned to generate electricity in power plants or converted to biogas in landfills
- Animal manure and human sewage—converted to biogas, which can be burned as a fuel

Biogas

Biogas is produced by the degradation of organic matter by the action of bacteria or fungi in the absence of oxygen (anaerobic). The cheapest and easily obtainable biogas is obtained from cattle dung and is known as gobar gas.

The process of formation of gobar gas is carried out in steel chambers placed above or below the ground into which a slurry made by mixing equal parts of fresh cattle dung and water is poured. Anaerobic bacteria present in the dung digests this sludge generating carbon dioxide and methane. The optimum temperature for fermentation is 34-48°C. The gas generated is collected in a steel gas holder placed on top of the digestion tank.

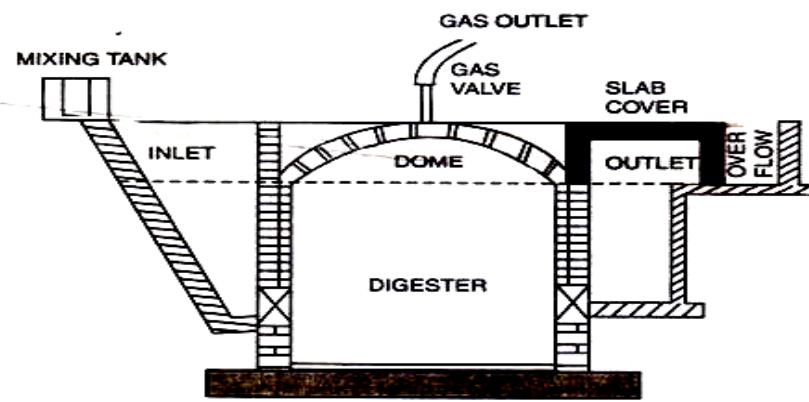


FIG. 4.3 : FIXED DOME TYPE BIOGAS PLANT

The average composition of the gobar gas is

$\text{CH}_4 = 55\%$, $\text{H}_2 = 7.4\%$, $\text{CO}_2 = 35\%$, $\text{N}_2 = 2.6\%$ and traces of H_2S

Its gross calorific value = 1200kcal/m^3 .

Advantages of Gobar Gas:

1. It has been found that 4.25kg of fresh cow dung (1 kg of dry cow dung) gives 160L of gobar gas which can supply 188kcal of heat. On the other hand 1kg of dry dung on direct heating gives 23.4kcal of effective heat. Thus gobar gas production is very economical.
2. The gas has all advantages of gaseous fuel like flexibility, optimum utilization, of waste, cleanliness, absence of dust, smoke, dirt etc.
3. It does not emit poisonous gas like CO.
4. It provides flame temperature of 540°C
5. Gobar gas simultaneously produces excellent yield of manure (N_2 content is 2% as farm manure which is 0.75%)

Limitation of Gobar gas: The gas stove or burner needs to be placed around 10m of the plant

Numerical on Calorific Value

1. On burning 0.83g of a solid fuel in a Bomb Calorimeter, the temperature of water (3500g) inside the calorimeter increased from 25.5°C to 29.2°C. Water equivalent of calorimeter and latent heat of steam are 385g and 587cal/g respectively. If the fuel contains 0.7% H, calculate the GCV and NCV of the fuel?

ans:

$$\text{GCV} = (3500+385)(29.2-25.5^\circ\text{C})/0.83 = 17,318.6 \text{ cal/g}$$

$$\text{NCV} = 17318.6 - (0.09*587*0.7) = 17318.6 - 36.981 = 17,281.6 \text{ cal/g}$$

2. A sample of coal containing 89%C, 8%H and 3% ash. When this coal was tested in the laboratory for its Calorific value in the Bomb Calorimeter, the following data was obtained.

Weight of coal burnt = 0.85g

Weight of water = 650g

Water equivalent of bomb calorimeter = 2500g

Rise in temp= 2.5°C

Cooling Correction = 0.03°C

Fuse wire Correction = 10 calories

Acid Correction = 50 Calories

Assuming the latent heat of condensation of steam = 580 cal/g

Calculate the GCV and LCV of coal in cal/g

ans:

$$\text{GCV} = [(650+2500)(2.5+0.03) - (10+50)]/0.85 = 9305.29 \text{ cal/g}$$

$$\text{LCV} = 9305.29 - (0.09*8*580) = 9305.29 - 417.6 = 8887.69 \text{ cal/g}$$

3. Calculate LCV of a fuel which has 8.9% hydrogen and its HCV is 6500 cal/g (given latent heat of steam =580 cal/g).

ans:

$$\text{LCV} = 6500 - (0.09*8.9*580) = 6500 - (464.58) = 6035.42 \text{ cal/g}$$

4. A 0.80g of sample of solid fuel was completely combusted in excess of oxygen using bomb calorimeter. The rise in temperature of water in calorimeter was 2.5°C. Calculate the High Calorific value of the fuel, if water taken in calorimeter is 2000g and water equivalent of calorimeter is 2200g. Also calculate Low calorific value (given % hydrogen in fuel = 2.2)

ans:

$$\text{HCV} = (2000+2200)(2.5)/0.80 = 13,125 \text{ cal/g}$$

$$\text{LCV} = 13125 - (0.09*2.2*580) = 13125 - 114.84 = 13010.16 \text{ cal/g}$$

5. 0.72 g of fuel containing 80% carbon when burnt in a bomb calorimeter increased the temperature of water from 27.3°C to 29.1°C. If the calorimeter contains 250g of water and if its water equivalent is 150g, Calculate the HCV of fuel.

$$\text{Ans: HCV} = (250+150)(1.8)/0.72 = 1000 \text{ cal/g}$$

ELECTROCHEMISTRY

Electrochemistry is the study of chemical processes that cause electrons to move. This movement of electrons is called electricity. In other words, it is the study of relationship between chemical energy and electric energy or the interconversion of the two. The movements of electrons from one element to another occur as a result of a reaction known as an oxidation-reduction ("redox") reaction.

Electrode: A metal (M) in contact with its salt solution (M^{n+}) is defined as an electrode. The metal either undergoes oxidation (loss of electrons) or reduction (gain of electrons).

During oxidation process, $M \longrightarrow M^{n+} + ne^-$

the metal acquires a net negative charge while the M^{n+} ions goes into the solution. The negative charge developed on the metal attracts the positive M^{n+} ; thereby a layer of positive charge is developed around the metal. Thus an electrical double layer is formed (Helmoltz double layer).

Similarly, during reduction, $M^{n+} + ne^- \longrightarrow M$

The metal acquires a net positive charge due to the accumulation of M^{n+} from the solution. The positive charge developed on the metal attracts the negative electrons from the solution; thereby a layer of negative charge is developed around the metal, Thus an electrical double layer is formed (Helmoltz double layer).

Irrespective of the nature of reaction taking place on the electrode, because of the exchange of ions between the metal and its solution, a potential difference is developed. This potential difference becomes constant at equilibrium and is then known as the electrode potential.

Electrode potential: It is the measure of the tendency of the metal to lose electrons (oxidation potential) or gain electrons (reduction potential) when it is in contact with its salt solution. It is denoted by E and its unit is Volt.

Standard electrode potential: It is the measure of the tendency of the metal to lose electrons (oxidation potential) or gain electrons (reduction potential), when it is in contact with its salt solution (having a concentration of 1M) maintained at a temperature of 25°C. It is denoted by E° and its unit is Volt.

Factors on which Electrode potential depends:

- Nature of the electrode
- Concentration of electrolyte
- Temperature

ELECTROCHEMISTRY

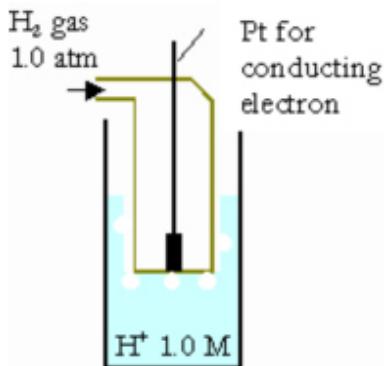
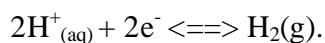
Nernst equation is used to derive the relation between electrode potential and the electrolyte concentration as well as the temperature

Standard Hydrogen Electrode

A Standard Hydrogen Electrode (SHE) is an electrode that scientists use for reference on all half-cell potential reactions. The value of the standard electrode potential of SHE is zero, which forms the basis one needs to calculate cell potentials using different electrodes or different concentrations.

What is a SHE made of?

SHE is composed of an inverted containing 1.0 M H⁺(aq) solution in which a Pt wire coated with Pt black is dipped. The setup is maintained at 25°C. During the reaction, hydrogen gas maintained at 1 atmosphere is then passed through the tube and into the solution causing the reaction:



Standard Hydrogen Electrode (SHE)

The SHE is represented as: Pt, H₂ (g) (1atm)/H⁺ (1M).

The SHE can act as the anode or the cathode depending on the nature of the other electrode to which it is attached. Since the E° of SHE is zero, the electrode potential of the other electrode will be equal to E°_{cell}.

It is a common practice to express the electrode potential as reduction potential.

Standard reduction potential of an electrode is defined as the reduction potential of an electrode as determined with respect to a standard hydrogen electrode.

ELECTROCHEMISTRY

Electrochemical Series (importance of Reduction Electrode Potential)

A series in which the standard reduction potentials of various electrodes have been arranged in the increasing order (downwards) is called electrochemical series.

The standard reduction potential of hydrogen electrode is zero. The electrodes above hydrogen have negative reduction potential while those placed below it have positive reduction potential.

Table 1: Electrochemical Series

Equilibrium (Oxidants \leftrightarrow Reductants)	E° (volts)
Lithium: $\text{Li}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Li}(\text{s})$	-3.03
Potassium: $\text{K}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{K}(\text{s})$	-2.92
Calcium: $\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Ca}(\text{s})$	-2.87
Sodium: $\text{Na}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Na}(\text{s})$	-2.71
Magnesium: $\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Mg}(\text{s})$	-2.37
Aluminum: $\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \leftrightarrow \text{Al}(\text{s})$	-1.66
Zinc: $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Zn}(\text{s})$	-0.76
Iron: $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Fe}(\text{s})$	-0.44
Lead: $\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Pb}(\text{s})$	-0.13
Hydrogen: $2\text{H}^+(\text{aq}) + 2\text{e}^- \leftrightarrow \text{H}_2(\text{g})$	0.00
Copper: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Cu}(\text{s})$	+0.34
Silver: $\text{Ag}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Ag}(\text{s})$	+0.80
Gold: $\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \leftrightarrow \text{Au}(\text{s})$	+1.50

Metal Reducing Activity Increasing

Metal Oxidizing Activity Increasing

Application of Electrochemical Series:

1. To predict the oxidizing and reducing powers:

In an electrochemical series, the species placed above hydrogen are more difficult to be reduced and their standard reduction potential is negative. Li is the strongest reducing agent.

The species placed below hydrogen are easily reduced and their E° values are positive. Gold is a very strong oxidizing agent.

ELECTROCHEMISTRY

In general oxidizing agents have $+E^\circ$ values. Higher the positive value, stronger is the oxidizing agent. Similarly, reducing agents have $-E^\circ$ values. Higher the negative value, stronger is the reducing agent.

2. To predict whether a metal will react with acid to give hydrogen gas.

Metals placed above hydrogen in the series have great tendency for oxidation so they will displace hydrogen from acids.

3. To predict the spontaneity of any redox reaction.

For any spontaneous reaction, free energy change (ΔG) should be negative

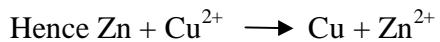
$$\Delta G = -nFE_{\text{cell}}$$

Hence E_{cell} should be positive for spontaneous reaction.

4. To predict the replacement tendency:

If a metal has lower values of reduction potential, it shows a great tendency to assume the oxidized form and it will displace another metal (with higher reduction potential) from the solution of the latter.

$$\text{For example: } E^\circ (\text{Zn}^{2+}/\text{Zn}) < E^\circ (\text{Cu}^{2+}/\text{Cu})$$



Zinc will displace Cu^{2+} from the solution of Cu^{2+} spontaneously

5. To predict correct metallurgical methods:

E° values of Cu, H₂O and Al are +0.34, -0.83 and -1.66V. It means Cu gets easily reduced than water and water gets easily reduced than Al. Hence Cu can be produced by electrolysis of aqueous CuSO₄ but not Al. This is due to the fact that when $\text{Al}^{3+}_{(\text{aq})}$ is electrolyzed, water will be electrolyzed but not $\text{Al}^{3+}_{(\text{aq})}$

6. for calculation of equilibrium constants (K_{eq})

$$\Delta G = -RT \ln K_{\text{eq}}$$

$$\Delta G = -nFE^\circ$$

$$E^\circ = \frac{RT}{nF} \ln K_{\text{eq}}$$

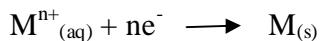
$$\ln K_{\text{eq}} = \frac{nFE^\circ}{RT}$$

Nernst Equation

The *Nernst Equation* helps to determine the electrode potential under non-standard conditions. It also tells us the effect of electrolyte concentration and temperature on the electrode potential.

Derivation of Nernst Equation of an electrode:

Consider the following electrode reaction:



Let the free energy change of the above reaction be (ΔG) and free energy under standard condition be (ΔG°), activity of product (M) be $a_{product}$ and activity of reactant (M^{n+}) be $a_{reactant}$

From thermodynamics, the Gibbs energy change under non-standard conditions can be related to the Gibbs energy change under standard Equations via

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_{product}}{a_{reactant}} \quad (\text{eq 1})$$

Where R is the Gas Constant and T is the temperature in K

ΔG is also related to electrode potential (E) and under standard conditions ΔG° is related to E° via

$$\Delta G = -nFE \quad \text{and} \quad \Delta G^\circ = -nFE^\circ$$

where

- n is the number of electrons transferred in the reaction (from balanced reaction),
- F is the Faraday constant (96,500 Coulombs/mol), and

Hence, putting the value of ΔG and ΔG° in eq 1, we get:

$$\begin{aligned} nFE &= nFE^\circ + RT \ln \frac{a_{product}}{a_{reactant}} \\ \text{Thus, } E &= E^\circ - \frac{RT}{nF} \ln \frac{a_{product}}{a_{reactant}} = E^\circ - \frac{2.303RT}{nF} \log \frac{a_{product}}{a_{reactant}} \quad (\text{eq 2}) \end{aligned}$$

Eq 2 is the Nernst equation under non standard conditions

Under standard conditions ($T=298K$) and putting the value of $R = 8.314 \text{ J/K/mol}$ and $F = 96500\text{C}$, we get:

$$E = E^\circ - \frac{0.0591}{n} \log \frac{a_{product}}{a_{reactant}} \quad (\text{eq 3})$$

Under dilute concentrations, activity of reactant and product can be replaced by molar concentration terms:

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[M]_{(s)}}{[M^{n+}]_{(aq)}} \quad (\text{eq 4})$$

For pure solid $[M]_s = 1$; eq 4 reduces to:

ELECTROCHEMISTRY

$$E = E^\circ - \frac{0.0591}{n} \log \frac{1}{[M^{n+}](aq)} \quad (\text{eq } 5)$$

Eq 5 represents the Nernst equation of the electrode M at 298 K (under standard condition)

Under non-standard conditions, at temp T,

$$\text{Nernst equation of the electrode is: } E = E^\circ - \frac{2.303 RT}{nF} \log \frac{1}{[M^{n+}](aq)} \quad (\text{eq } 6)$$

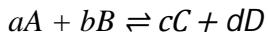
From eq 6, it can be concluded that

- E increases as $[M^{n+}]$ is increased
- E decreases with increase in temperature)

Nernst equation of a cell

An anode and a cathode connected by an electrical circuit is known as the cell.

Consider a redox reaction occurring in a cell:



$$E = E_{\text{cell}}^\circ - \frac{2.303 RT}{nF} \log \left(\frac{C^c D^d}{A^a B^b} \right)$$

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$$

Application of Nernst equation

1. *Nernst equation can be used to study the effect of electrolyte concentration on electrode potential*

Numerical

Calculate the electrode potential of a copper wire dipped in 0.1M CuSO₄ solution at 25°C. The standard electrode potential of copper is 0.34V.

Solution: Cu²⁺_(aq) + 2e⁻ ⇌ Cu(s)

$$E = E^\circ - \frac{2.303 RT}{nF} \log \left(\frac{1}{Cu^{2+}} \right) = 0.34 - \frac{2.303 * 8.314 * 298}{2 * 96500} \log \left(\frac{1}{0.1} \right) = -0.31V$$

2. *Nernst equation is used for the calculation of potential of a cell under non-standard condition*

Numerical

Calculate the potential of the following electrochemical cell at 25°C:

Cu(s) | Cu²⁺(aq)(0.50M) | | H⁺(0.01M) | H₂ (0.95atm); Pt

Given: E[°]_{cathode} = 0.00V and E[°]_{anode} = 0.34V

Solution: E[°]_{cell} = E[°]_{cathode} - E[°]_{anode} = 0.00 - 0.34V = -0.34V

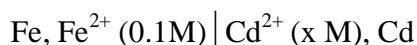
ELECTROCHEMISTRY

$$\text{Potential of cell} = E_{\text{cell}} = E^{\circ}_{\text{cell}} - 0.059/2 \log \frac{[\text{Cu}^{2+}]P_{\text{H}_2}}{[\text{H}^+]^2} = -0.34 - 0.059/2 \log \frac{0.50 \times 0.95}{0.01^2} = -0.449 \text{ V}$$

3. Determination of unknown concentration of one of the ionic species in a cell is possible with the help of Nernst equation provided E°_{cell} and concentration of other ionic species is known

Numerical

Determine the concentration of Cd^{2+} in the following electrochemical cell:



Given: emf of cell $E = -0.02 \text{ V}$ and $E^{\circ} = 0.04 \text{ V}$ at 25°C

Solution: overall cell reaction: $\text{Fe(s)} + \text{Cd}^{2+} \rightleftharpoons \text{Fe}^{2+} + \text{Cd(s)}$

$$E = E^{\circ} - 0.059/2 \log \frac{[\text{Fe}^{2+}]}{[\text{Cd}^{2+}]} = -0.02 - 0.059/2 \log \frac{0.1}{x}$$

$$x = 0.00093 = 0.001 \text{ M}$$

Electrochemical Cell

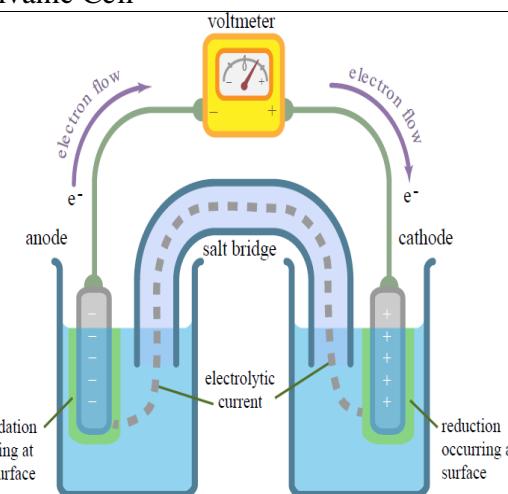
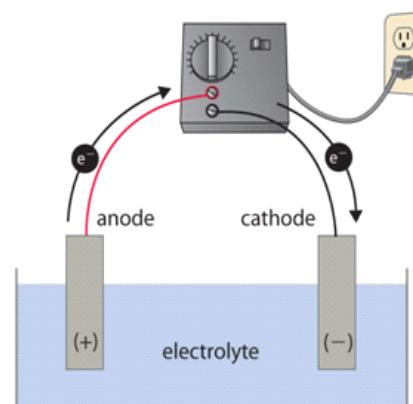
An electrochemical cell is a device for the conversion of electrical energy into chemical energy or vice versa

There are two types of electrochemical cell: Galvanic/Voltaic Cell and electrolytic cell.

Electrolytic cells are very similar to voltaic (galvanic) cells in the sense that both have a cathode and anode side, and both have a consistent flow of electrons from the anode to the cathode. However, there are also striking differences between the two cells. The main differences are outlined below:

ELECTROCHEMISTRY

Difference between Galvanic cell and Electrolytic Cell

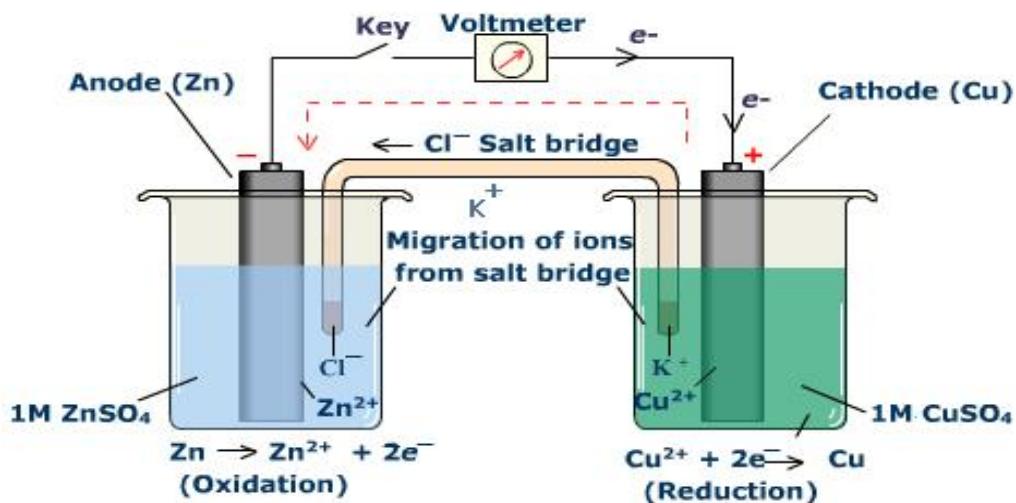
S.No	Galvanic Cell	Electrolytic Cell
1	 <p>Diagram of a Galvanic Cell:</p> <ul style="list-style-type: none"> Anode: oxidation occurring at surface. Cathode: reduction occurring at surface. Electron flow: electrons flow from anode to cathode through an external circuit. Voltmeter: measures the potential difference between the anode and cathode. Salt bridge: connects the two half-cells to allow ion exchange. Electrolytic current: ions move from the cathode compartment to the anode compartment through the salt bridge. 	 <p>Diagram of an Electrolytic Cell:</p> <ul style="list-style-type: none"> Anode: oxidation reaction $X \rightarrow X^+ + e^-$ Cathode: reduction reaction $Y^+ + e^- \rightarrow Y$ Electrolyte: contains ions (X^+ and Y^-) that move towards the electrodes. Electron flow: electrons flow from the cathode (-) to the anode (+) through an external circuit. Power source: provides electrical energy to drive the redox reaction.
2	<p>Anode and cathode are placed in separate containers. Both containers are connected via an external circuit for the flow of electrons from anode to cathode.</p> <p>A second connection (salt bridge) brings about a flow of ions between the two electrolytic solutions so as to maintain electrical neutrality.</p>	<p>Anode and cathode are placed in same container having the same electrolytic solution i.e both electrodes are dipped in the same salt solution.</p> <p>Salt bridge is absent.</p>
3	<p>Anode is the negative electrode where oxidation takes place.</p> <p>Anodic reaction: $X \rightarrow X^+ + e^-$</p> <p>Cathode is the positive electrode where reduction takes place</p> <p>Cathodic reaction: $Y^+ + e^- \rightarrow Y$</p> <p>Overall redox reaction: $X + Y^+ \rightarrow X^+ + Y$</p> <p>Redox reaction is spontaneous ($\Delta G < 0$)</p>	<p>Anode is the positive electrode where oxidation takes place</p> <p>Anodic reaction: $X \rightarrow X^+ + e^-$</p> <p>Cathode is the negative electrode where reduction takes place</p> <p>Cathodic reaction $Y^+ + e^- \rightarrow Y$</p> <p>Overall redox reaction: $X + Y^+ \rightarrow X^+ + Y$</p> <p>Redox reaction is non-spontaneous ($\Delta G > 0$)</p>
4	<p>The potential difference generated is due to redox reaction taking place between cathode and anode and causes the electrons to flow from anode to cathode and hence causes current to flow when circuit is completed</p>	<p>The potential difference generated is due to the electric energy from an external source and causes the electrons to flow from anode to cathode and hence causes the redox reaction to take place.</p>
5	<p>Energy from redox reaction is converted to electrical energy</p>	<p>Electrical energy from external source is converted to chemical energy to drive the redox reaction.</p>
6	<p>Example: dry cell or Daniel Cell</p>	<p>Example: electrolytic purification of metals</p>

Galvanic Cell

It's a device which converts chemical energy from a spontaneous redox reaction to electrical energy.

Example of galvanic cell is Daniel Cell. It consists of a separate anodic compartment (Zn electrode dipped in ZnSO_4 solution) and a separate cathodic compartment (Cu electrode dipped in CuSO_4 solution). Both compartments are connected externally by a wire and a salt bridge. The wire allows for the flow of electrons from the anode to the cathode; while the salt bridge is required for maintaining electrical neutrality between the two electrolytic solutions.

Schematic diagram of a Daniel cell is:



The **cell diagram** is a shorthand notation to represent the redox reactions of a galvanic cell. For the Daniel cell described, the cell diagram is as follows: $\text{Zn(s)}|\text{Zn}^{2+}(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu(s)}$

- A double vertical line (||) is used to separate the anode half reaction from the cathode half reaction. This represents the salt bridge.
- The anode (where oxidation occurs) is placed on the left side of the ||.
- The cathode (where reduction occurs) is placed on the right side of the ||.
- A single vertical line (|) is used to separate different states of matter on the same side, and a comma is used to separate like states of matter on the same side.

ELECTROCHEMISTRY

EMF of a Galvanic Cell

EMF is the maximum potential difference between two electrodes of a cell. It is the EMF that causes current to flow from the electrode of higher potential to the one of lower potential.

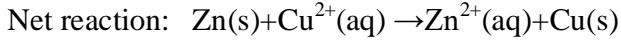
$$\text{EMF of a cell} = E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

For a cell to operate spontaneously, $\Delta G < 0$ (negative) and since $\Delta G = -nFE_{\text{cell}}$, E_{cell} is positive.

$$\text{If the cell operates under standard conditions, } E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

For a Daniel Cell,

- Oxidation half reaction: $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + e^-$ $E^{\circ} = -0.763\text{V}$
- Reduction half reaction: $\text{Cu}^{2+}(\text{aq}) + e^- \rightarrow \text{Cu(s)}$ $E^{\circ} = +0.342\text{V}$



$$\text{Therefore: } E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = 0.340\text{V} - (-0.763\text{V}) = +1.103\text{V}$$

Role of the salt bridge:

Salt bridge is an inverted U-tube containing an aqueous solution of electrolyte (KCl, KNO₃, K₂SO₄). The electrolyte should not react chemically with the redox reaction. Agar-agar or gelatin is added to the aqueous solution of the electrolyte to convert it into a semi-solid paste.

Salt bridge helps to

1. Maintain electrical neutrality of the two electrolytic solutions in the two half cells (anode and cathode)
2. It helps to provide cations and anions to replace the ions that are lost or produced in the two half cells
3. It helps to allow the flow of current by completing the electrical circuit
4. It helps to prevent the intermixing of the two electrolytic solution in the two half cells

Numericals:

Q1. Given:



Give the cell diagram and find the emf of the cell

Solution:

Cell diagram: Cd(s)|Cd²⁺(aq)||Ag⁺|Ag(s)

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = +0.78\text{V} - (-0.40\text{V}) = 1.18\text{V}$$

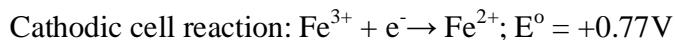
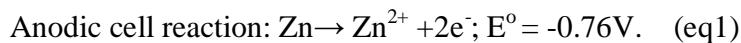
ELECTROCHEMISTRY

Q2. For the cell: $\text{Zn}|\text{Zn}^{2+}(1\text{M})||\text{Fe}^{2+}(1\text{M})|\text{Fe}^{3+}(1\text{M})$

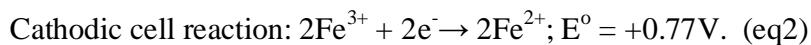
$$E^\circ(\text{Fe}^{3+}|\text{Fe}^{2+}) = +0.77\text{V} \text{ and } E^\circ(\text{Zn}|\text{Zn}^{2+}) = +0.76\text{V}$$

Write the cell reaction and calculate the value of E_{cell}° for the above cell

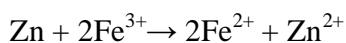
Solution:



Cathodic cell reaction has to be multiplied by 2;



Adding eq 1 and eq2



$$E_{cell}^\circ = E_{cathode}^\circ - E_{anode}^\circ = +0.77\text{V} - (-0.76\text{V}) = +1.53\text{V}$$

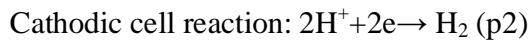
Concentration Cells

In concentration cells, the emf arises due to the changes in the concentration of either the electrolytes or the electrodes. This is in contrast to galvanic cells in which the emf arises due to decrease in free energy of the chemical reaction taking place in the cell.

Concentration cells are of two types.

a. **Electrode concentration cell:** concentration of electrode is different. Example: gas electrode concentration cell. This cell consists of two hydrogen electrodes maintained at different partial pressures of the hydrogen gas (p_1 and p_2) and are dipped in the same electrolyte HCl solution.

Cell representation: $\text{Pt}, \text{H}_2(\text{g})(p\text{H}_2 = p_1) \mid \text{H}^+ \mid \text{H}_2(\text{g})(p\text{H}_2 = p_2)$



$$E_{cell} = \frac{2.303RT}{2F} \log_{10} \frac{p_1}{p_2}$$

b. **Electrolyte concentration cell:** these cells consist of two identical electrodes dipped in two solutions of the same electrolyte at different concentrations.

Cell representation: $\text{M}|\text{M}^{n+}(\text{C}_1)||\text{M}^{n+}(\text{C}_2)|\text{M}$

Where C_1 and C_2 are concentration of the M^{n+} ions and $\text{C}_2 > \text{C}_1$

$$E_{cell} = E_{cathode} - E_{anode} = (E^\circ - \frac{2.303RT}{nF} \log 1/\text{C}_2) - (E^\circ - \frac{2.303RT}{nF} \log 1/\text{C}_1) = \frac{2.303RT}{nF} \log_{10} \frac{\text{C}_2}{\text{C}_1}$$

ELECTROCHEMISTRY

Corrosion: It is the process of chemical or electrochemical interaction of metal with its environment. As a result of corrosion, useful properties of metal such as ductility, malleability and electrical conductivity is lost.

Example is the rusting of iron or tarnishing of silver

Cause of Corrosion: Metals exist in nature in the form of ores i.e the oxides, sulphides, sulphates or carbonates. The existence of metals in ore state is thermodynamically stable and has less energy as compared to the metals. Thus, it is the natural tendency of metals to interact chemically or electrochemically with their environment to form ore and thus undergo corrosion.

Effect of corrosion:

- i. Loss of useful properties of metal and hence loss in its efficiency
- ii. Increase in maintenance and production cost
- iii. Contamination of product
- iv. Unpredictable failure of machinery
- v. Contamination of water due to corroded pipes
- vi. Leakage of toxic liquid or gas from corroded pipes and tubes

Electrochemical theory or Wet theory of Corrosion

When corrosion occurs under wet conditions (in the presence of moisture in the atmosphere), transfer of electrons takes place from anodic parts of metal surface to the cathodic parts through the conducting aqueous medium. The phenomenon is similar to a galvanic cell. Such phenomenon is known as electrochemical corrosion and is more common than dry corrosion.

Mechanism of wet corrosion:

Electrochemical corrosion involves:

- a) Formation of separate anodic and cathodic areas with current flowing through the conducting aqueous medium
- b) Oxidation occurs at the anode with the generation of metallic ions (corrosion occurs at the anode)
- c) while reduction occurs at the cathode with the formation of non-metallic ions like OH^- or O^{2-}
- d) The metallic and non-metallic ions diffuse towards each other through the conducting aqueous medium and corrosion products are formed in between the anode and cathode areas.

ELECTROCHEMISTRY

Rusting of iron in aqueous medium in the presence of oxygen or in acidic environment is an example of electrochemical corrosion.

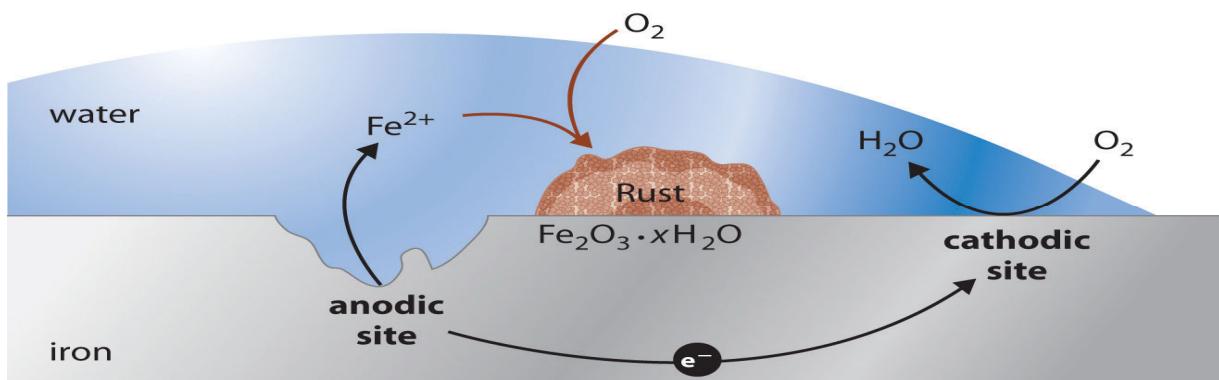
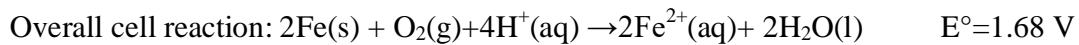
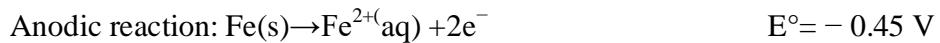
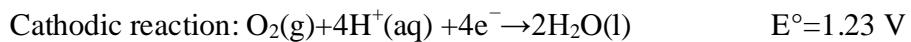


Illustration of the mechanism of electrochemical corrosion of iron

Iron is oxidized to $\text{Fe}^{2+}(\text{aq})$ at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons are transferred from the anode to the cathode through the electrically conductive metal. Water is a solvent for the Fe^{2+} that is produced initially and acts as a salt bridge. Rust ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) is formed by the subsequent oxidation of Fe^{2+} by atmospheric oxygen.



The sign and magnitude of E° for the corrosion process indicate that there is a strong driving force for the oxidation of iron by O_2 under standard conditions (1 M H^+)

The Fe^{2+} ions produced in the initial reaction are then oxidized by atmospheric oxygen to produce the insoluble hydrated oxide containing Fe^{3+} as represented in the following equation:



Factors affecting rusting of iron:

- a) Presence of water
- b) Presence of oxygen

ELECTROCHEMISTRY

Difference between dry corrosion (chemical corrosion) and wet corrosion (electrochemical corrosion):

S. No	Dry corrosion	Wet Corrosion
1	It occurs in dry conditions	It occurs in wet condition in the presence of electrolyte or moisture
2	It involves direct chemical attack of metal with its environment	It involves the formation of innumerable number of galvanic cells and corrosion occurs by electrochemical mechanism
3	It occurs on both homogenous as well as heterogenous surfaces	It occurs only on heterogenous metal surface.
4	Corrosion is uniform	Corrosion is not uniform
5	It is a slow process	It is a fast process
6	Corrosion products accumulate at the same place where corrosion occurs	Corrosion occurs at the anode but products accumulate in between the anode and cathode