



CHEMISTRY

B.Tech (1st year)

Notes

Prepared By:



UNIT I

Molecular Orbital Theory (MOT)

- Molecular orbital theory was given by **Hund** and **Mulliken** in 1932.
The main ideas of this theory are:
- When two atomic orbitals combine or overlap, they lose their identity and form new orbitals. The new orbitals thus formed are called **molecular orbitals**.
- Molecular orbitals are the energy states of a molecule in which the electrons of the molecule are filled just as atomic orbitals are the energy states of an atom in which the electrons of the atom are filled.
- In terms of probability distribution, a molecular orbital gives the electron probability distribution around a group of nuclei just as an atomic orbital gives the electron probability distribution around the single nucleus.
- Only those atomic orbital can combine to form molecular orbital which have comparable energies and proper orientation.
- The number of molecular orbitals formed is equal to the number of combining atomic orbitals.
- When two atomic orbitals combine, they form two new orbitals called bonding molecular orbital and antibonding molecular orbital.
- The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.
- The bonding molecular orbitals are represented by σ , π etc, whereas the corresponding antibonding molecular orbitals are represented by σ^* π^* etc. (Figure 1)
- The shapes of the molecular orbitals formed depend upon the type of combining atomic orbitals.
- The filling of molecular orbitals in a molecule takes place in accordance with **Aufbau principle**, **Pauli's exclusion principle** and **Hund's rule**.
- Electrons are filled in the increasing energy of the MO which is in order
- Bond order \propto Stability of molecule \propto Dissociation energy \propto (1/Bond Length).
- If all the electrons in a molecule are paired then the substance is a diamagnetic on the other hand if there are unpaired electrons in the molecule, then the substance is paramagnetic. More the number of unpaired electrons in the molecule greater are the paramagnetism of the substance.

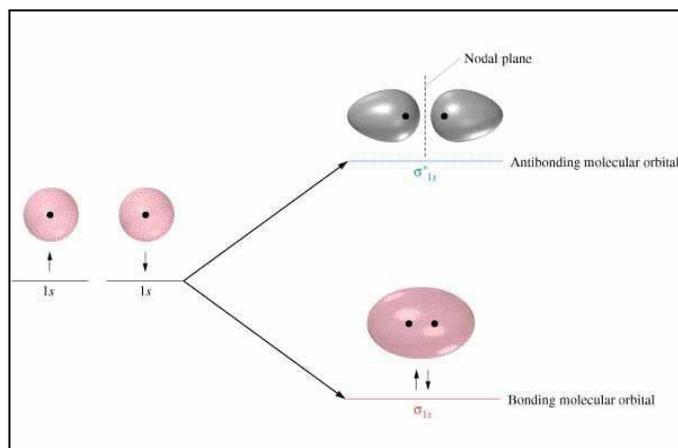


Figure 1

Bond Order

In molecular orbital theory, we calculate bond orders by assuming that two electrons in a bonding molecular orbital contribute one net bond and that two electrons in an antibonding molecular orbital cancel the effect of one bond.

The stability of the molecule can be determined from the parameter called Bond Order. Bond order may be defined as half the difference between number of electrons in bonding molecular orbitals and number of electrons in antibonding molecular orbitals.

$$BO = \frac{Nb - Na}{2}$$

Molecular orbital diagrams of Homodiatomic molecules

MO Diagrams for O_2 and N_2 as shown in Figure 2.

MO diagrams – Contains same number of MOs as the number of atomic orbitals. The more electronegative element is kept on the right - lower in energy. Homoatomic means “of the same atom”—such a molecule contains only one kind of atom. Examples include: H_2 , N_2 , O_2 , F_2 , P_4 , S_8 , Cl_2 , Br_2 , I_2 .

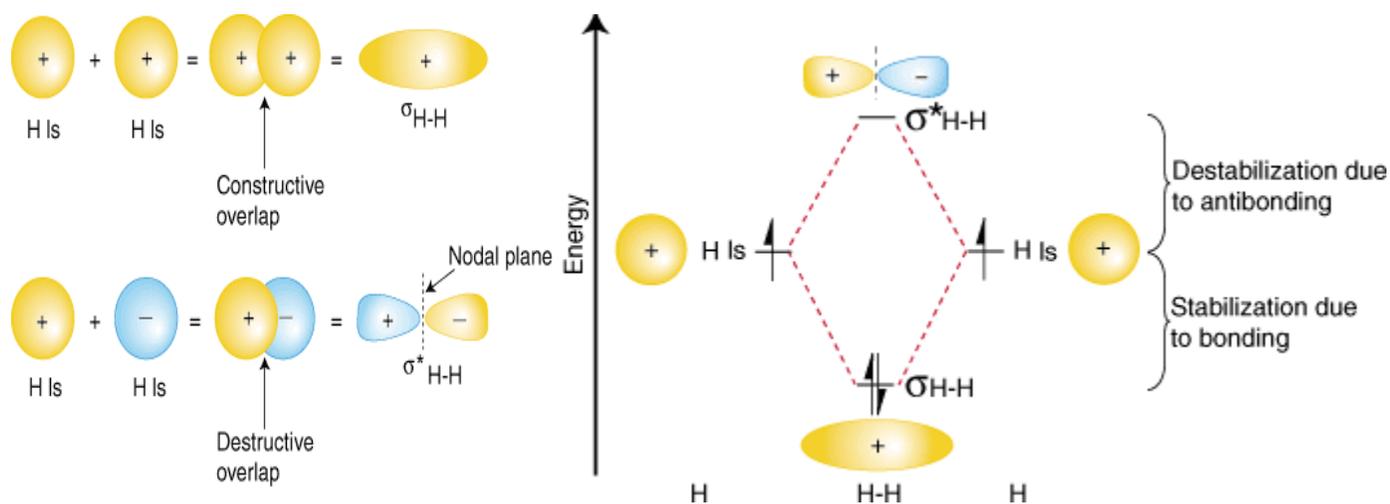


Figure 2: Two 1s Orbitals combine to form a bonding and an antibonding M.O

The orbitals of the separated atoms are written on either side of the diagram as horizontal lines at heights denoting their relative energies shown in Figure 2. The electrons in each atomic orbital are represented by arrows. In the middle of the diagram, the molecular orbitals of the molecule of interest are written. Dashed lines connect the parent atomic orbitals with the daughter molecular orbitals.

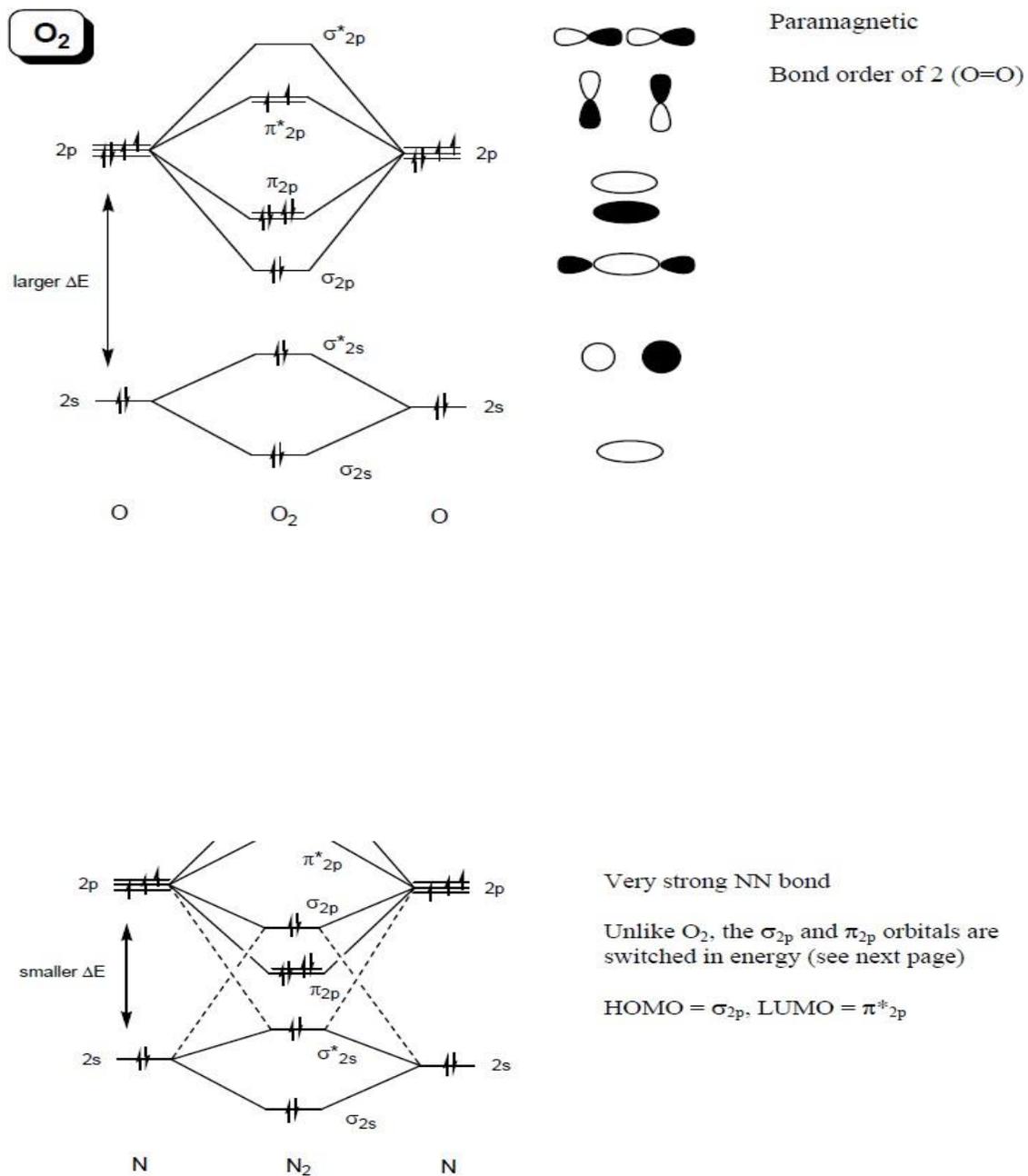


Figure 3: MO diagram of O₂ and N₂

Molecular orbital diagrams of Homodiatomic molecules

In general, bonding molecular orbitals are lower in energy than either of their parent atomic orbitals. Similarly, antibonding orbitals are higher in energy than either of its parent atomic orbitals. Because we must obey the law of conservation of energy, the amount of stabilization of the bonding orbital must equal the amount of destabilization of the antibonding orbital, as shown in figure 4.

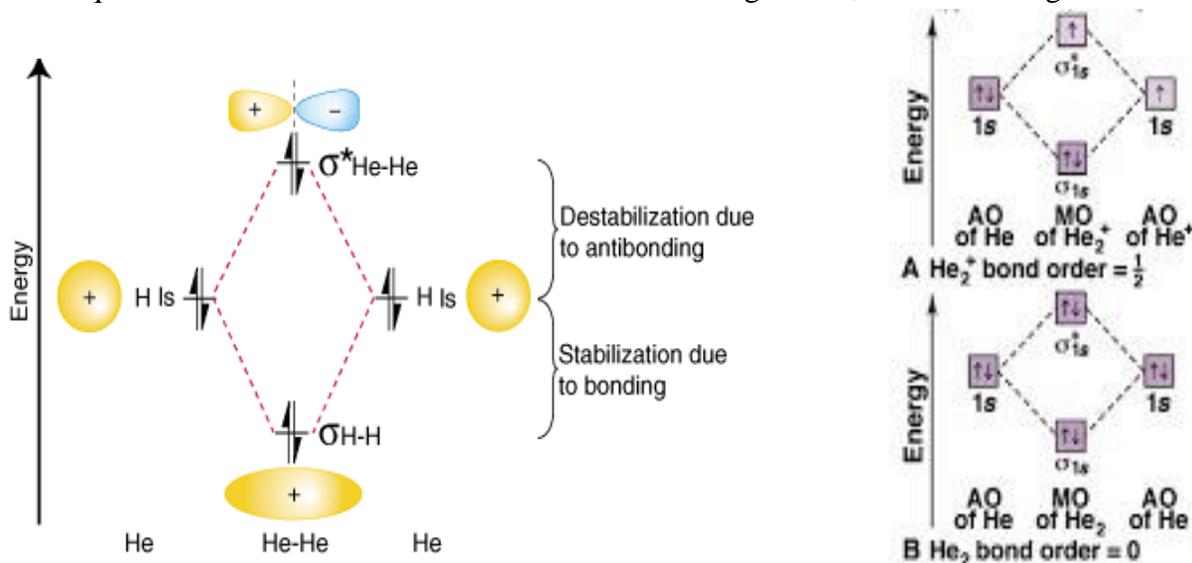


Figure 4: An orbital correlation diagram for a hypothetical He-He molecule, He₂⁺ and He⁺

The orbital correlation diagram for diboron, however, is not generally applicable for all homonuclear diatomic molecules as shown in figure 5. It turns out that only when the bond lengths are relatively short (as in B₂, C₂, and N₂) can the two p-orbitals on the bonded atoms efficiently overlap to form a strong p bond. Some textbooks explain this observation in terms of a concept called s-p mixing.

For any atom with an atomic number greater than seven, the p bond is less stable and higher in energy than is the s bond formed by the two end-on overlapping s orbitals. Therefore the following orbital correlation diagram for molecules with atomic numbers greater than:

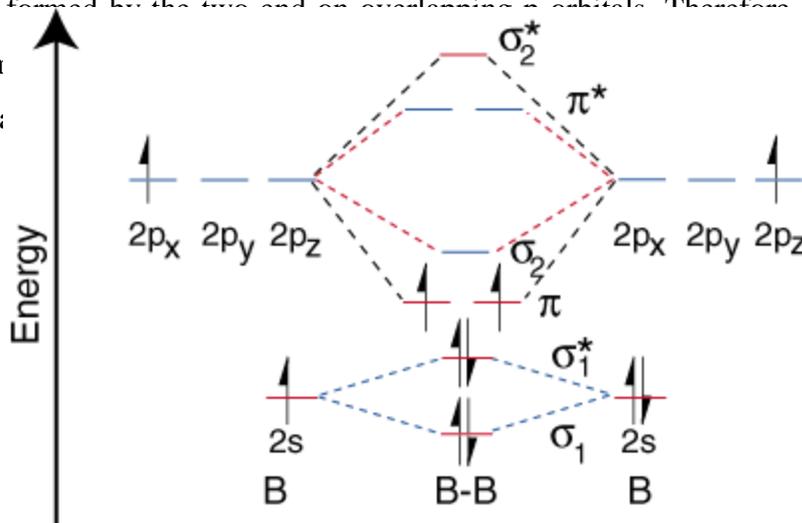


Figure 5: Orbital correlation diagram for diboron

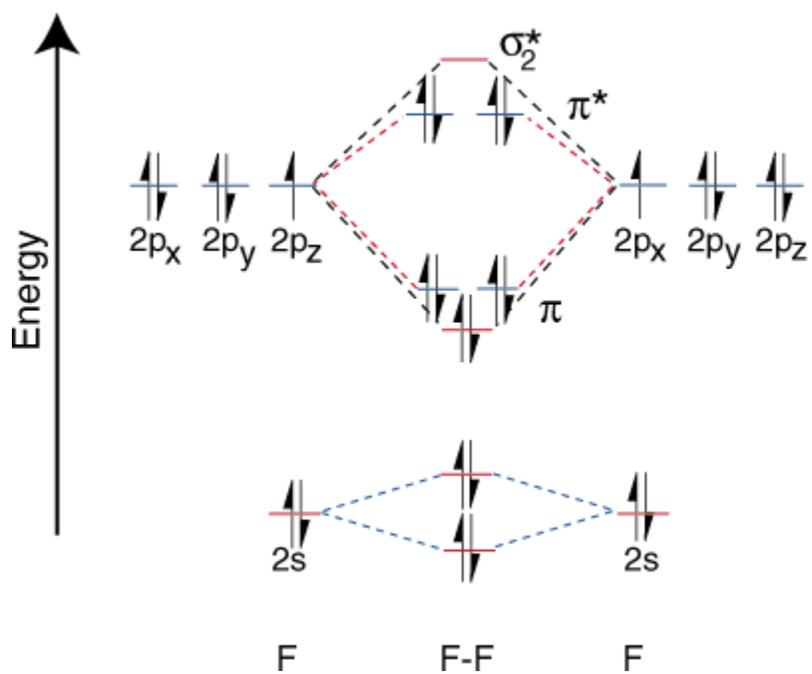


Figure 6: Orbital correlation diagram for difluorine

Molecular orbital diagrams of Heterodiatomic molecules

Heteroatomic molecules are **molecules** that do not have the same atoms making up the **molecule**. For example: HF (hydrogen fluoride) Hydrogen is a different atom than fluorine, and hydrogen fluoride is a **molecule**. Therefore, it is a **heteroatomic molecule**.

To draw the correlation diagrams for heteronuclear diatomic molecules, we face a new problem: where do we place the atomic orbitals on an atom relative to atomic orbitals on other atoms? For example, how can we predict whether a hydrogen 1s or fluorine 2p orbital is lower in energy? The answer comes from our understanding of electronegativity. Fluorine is more electronegative than hydrogen. Then electrons are more stable, i.e. lower in energy, when they are lone pairs on fluorine rather than on hydrogen. The more electronegative element's orbitals are placed lower on the correlation diagram than those of the more electropositive element.

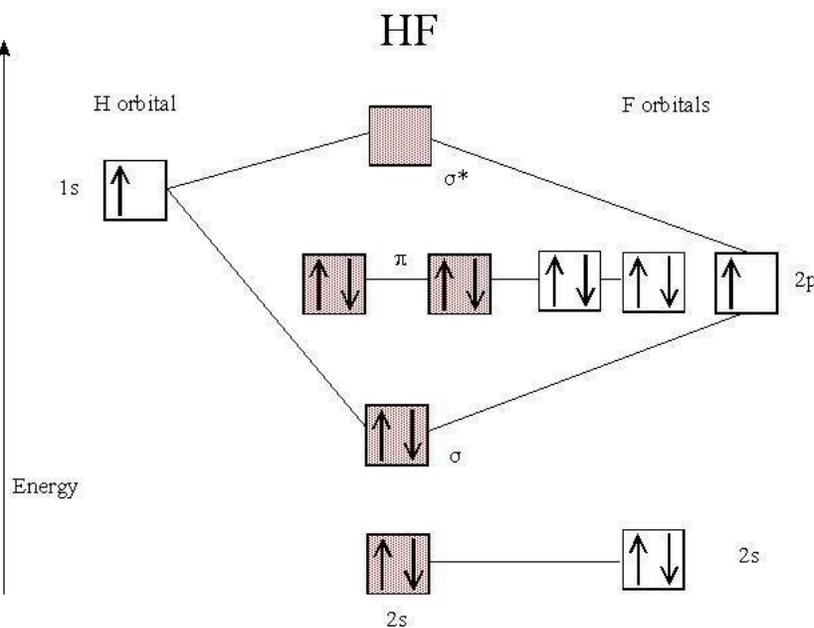


Figure 7: Orbital correlation diagram for HF

Since hydrogen only has one occupied valence orbital, only one bonding and one antibonding orbital are possible. Furthermore, the electrons in orbitals on F that cannot bond with hydrogen are left on F as lone pairs. As seen in Figure 7, the electrons in the H-F bond are quite close in energy to fluorine's 2p orbitals. Then the bonding orbital is primarily composed of a fluorine 2p orbital, so the M.O diagram

predicts that the bond should be polarized toward fluorine--exactly what is found by measuring the bond dipole.

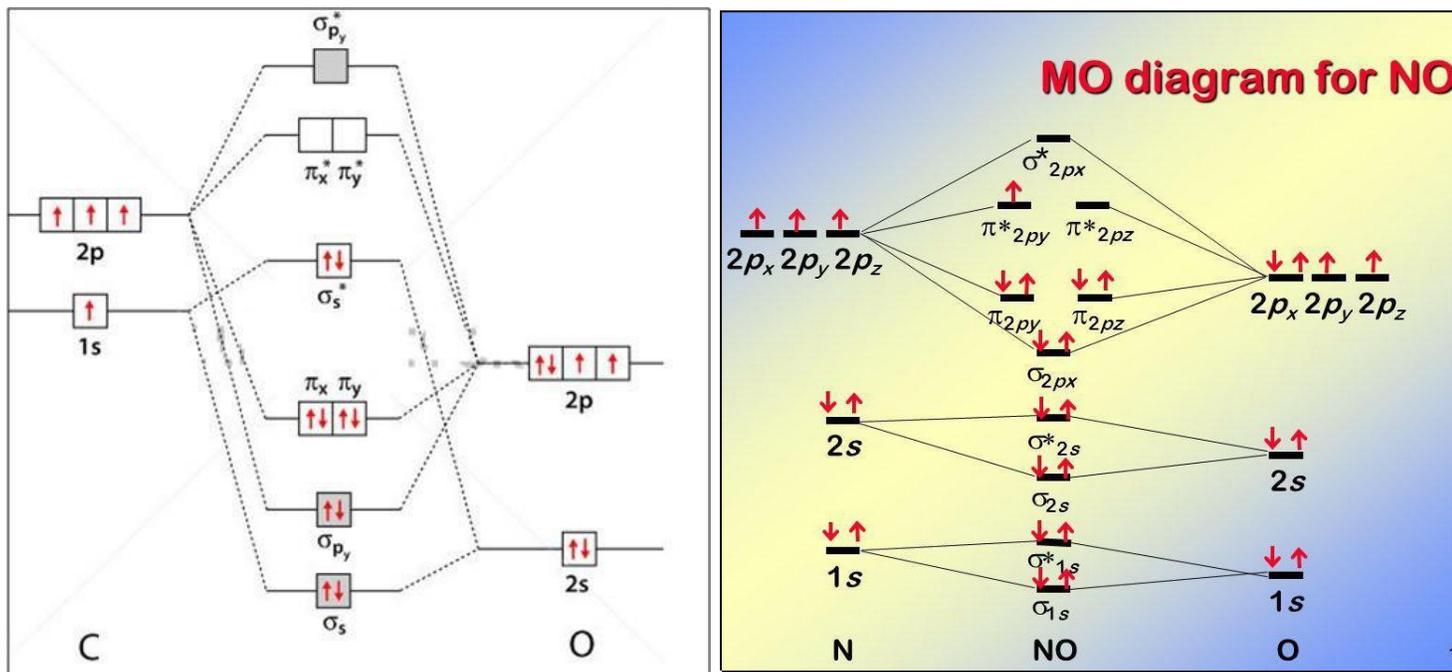


Figure 8: Orbital correlation diagram for CO and NO

Metallic Bonding

In metallic bonds, the valence electrons from the s and p orbital of the interacting metal atoms delocalize. That is to say, instead of orbiting their respective metal atoms, they form a "sea" of electrons that surrounds the positively charged atomic nuclei of interacting metal ions. The electrons then move freely throughout the space between the atomic nuclei.

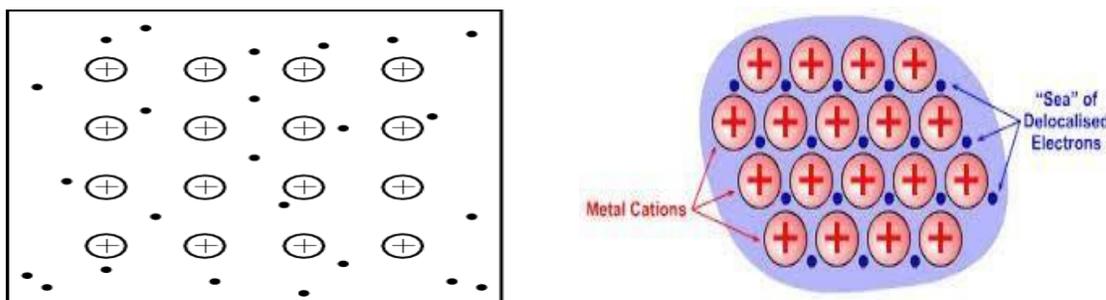


Figure 4: Metallic Bonding: The Electron Sea Model

Positive atomic nuclei are surrounded by a sea of delocalized electrons (the dots) (Figure 4).

The characteristics of metallic bonds explain a number of the unique properties of metals such as:

- Metals are good conductors of electricity because the electrons in the electron sea are free to flow and carry electric current.
- Metals are ductile and malleable because local bonds can be easily broken and reformed.
- Metals are lustrous. Light cannot penetrate their surface; the photons simply reflect off the metal surface. However, there is an upper limit to the frequency of light at which the photons are reflected.

The Band Structure of Metals

In solids, bands result from the overlap of atomic orbitals, much as molecular orbitals result from the overlap of atomic orbitals in small molecules. According to the MO theory of diatomic molecules, molecular orbitals form when an atomic orbital from one atom overlaps with an atomic orbital from a second atom. A lower-energy bonding molecular orbital is formed by the in-phase addition

(constructive interference) of the two atomic orbitals, and a higher-energy antibonding molecular orbital is formed by addition of two atomic orbitals of opposite phase. This idea can be applied to larger molecules. However, because one molecular orbital is generated for each atomic orbital used in its construction, *three or more* molecular orbitals are created when of three or more atomic orbitals overlap. The general idea of how bands arise is illustrated in Figure 5, which shows how the 3s valence atomic orbitals of sodium (Na) overlap to form molecular orbitals in linear Na_n molecules ($n = 2, 3, 4, \dots$) of increasing size.

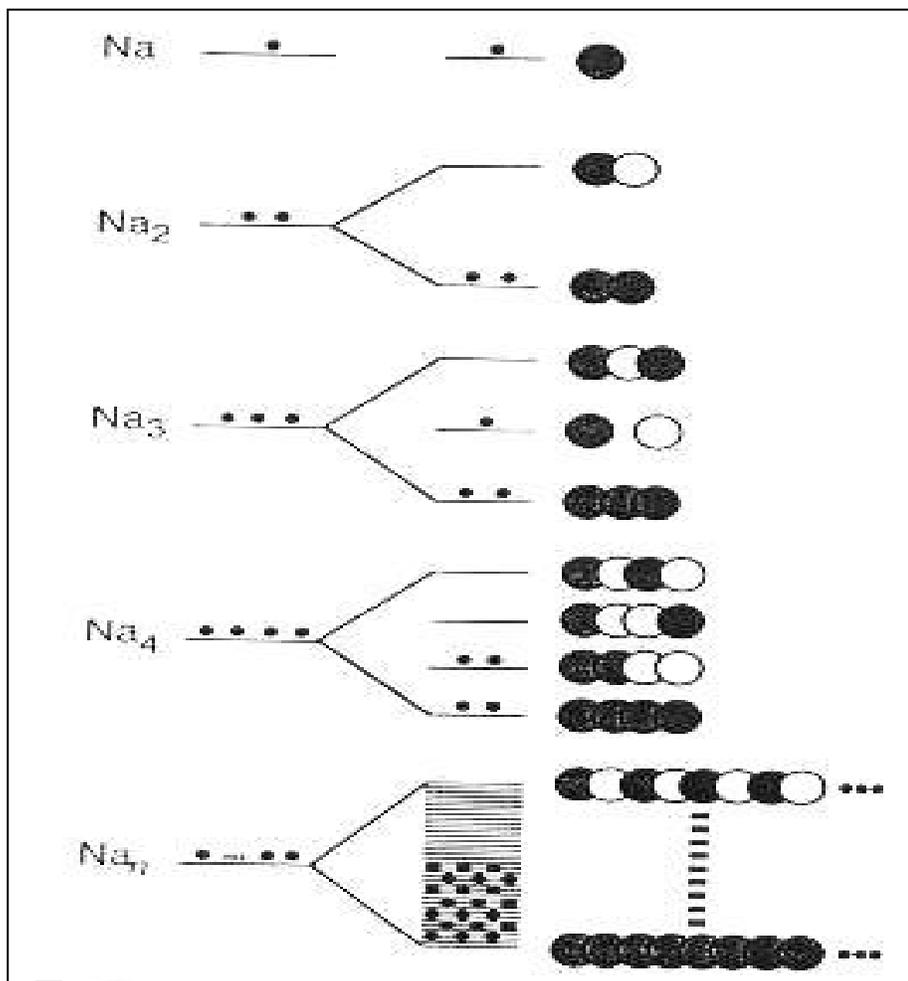


Figure 5

Application of Band Theory

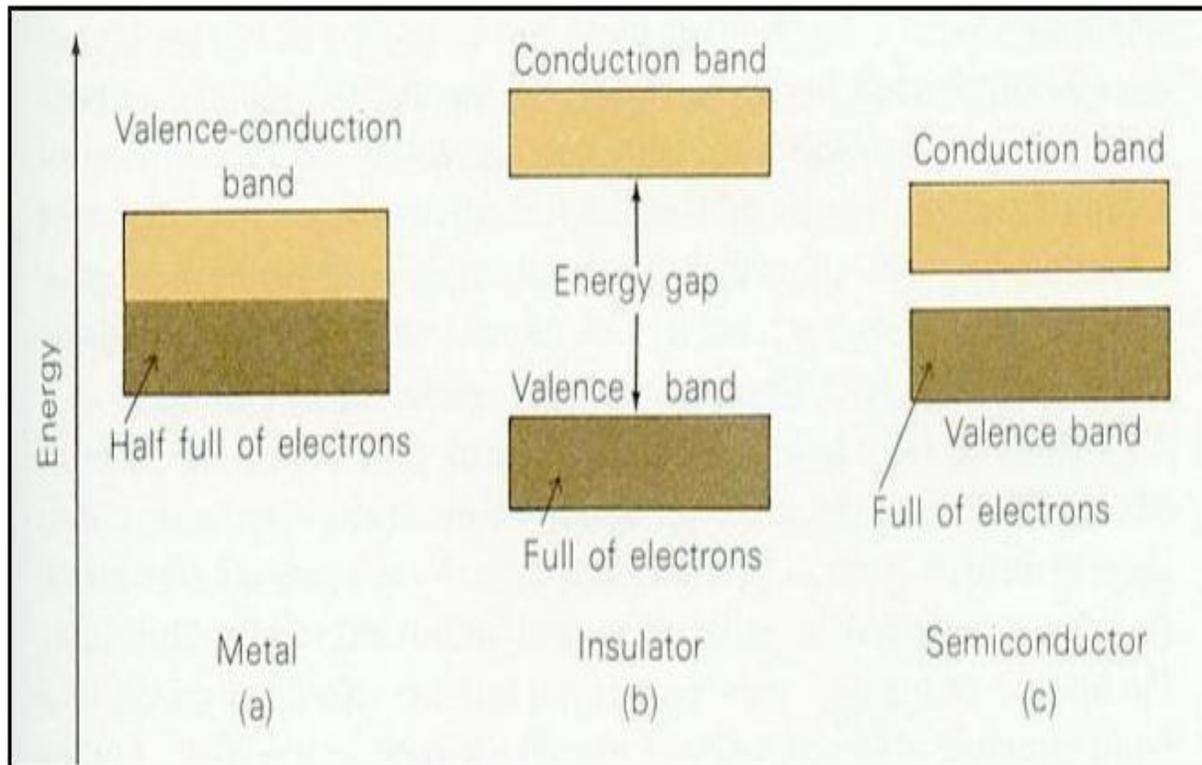


Figure 6

Defects in solids (Point defects)

Imperfections or defects: Any deviation from the perfect atomic arrangement in a crystal is said to contain imperfections or defects. In fact, using the term “defect” is sort of a misnomer since these features are commonly used to manipulate the mechanical properties of a material. There are three types of point defects as:

1. Stoichiometric defects
2. Non-Stoichiometric defects
3. Impurity defects

1. Stoichiometric defects

The compounds in which the number of positive and negative ions is exactly in the ratios indicated by their chemical formulae are called stoichiometric compounds. The defects do not disturb the stoichiometry (the ratio of numbers of positive and negative ions) and hence, are called stoichiometric defects. Such defects are of following types:

(a) **Schottky defect:** This type of defect when equal number of cations and anions are missing from their lattice sites so that the electrical neutrality is maintained as shown in Figure 6. This type of defect occurs in highly ionic compounds which have high co-ordination number and cations and anions of similar sizes. e.g., NaCl, KCl, CsCl and KBr etc.



Figure 7: Schottky defect

(b) **Frenkel defect:** This type of defect arises when an ion is missing from its lattice site and occupies an interstitial position. The crystal as a whole remains electrically neutral because the number of anions and cations remain same. Since cations are usually smaller than

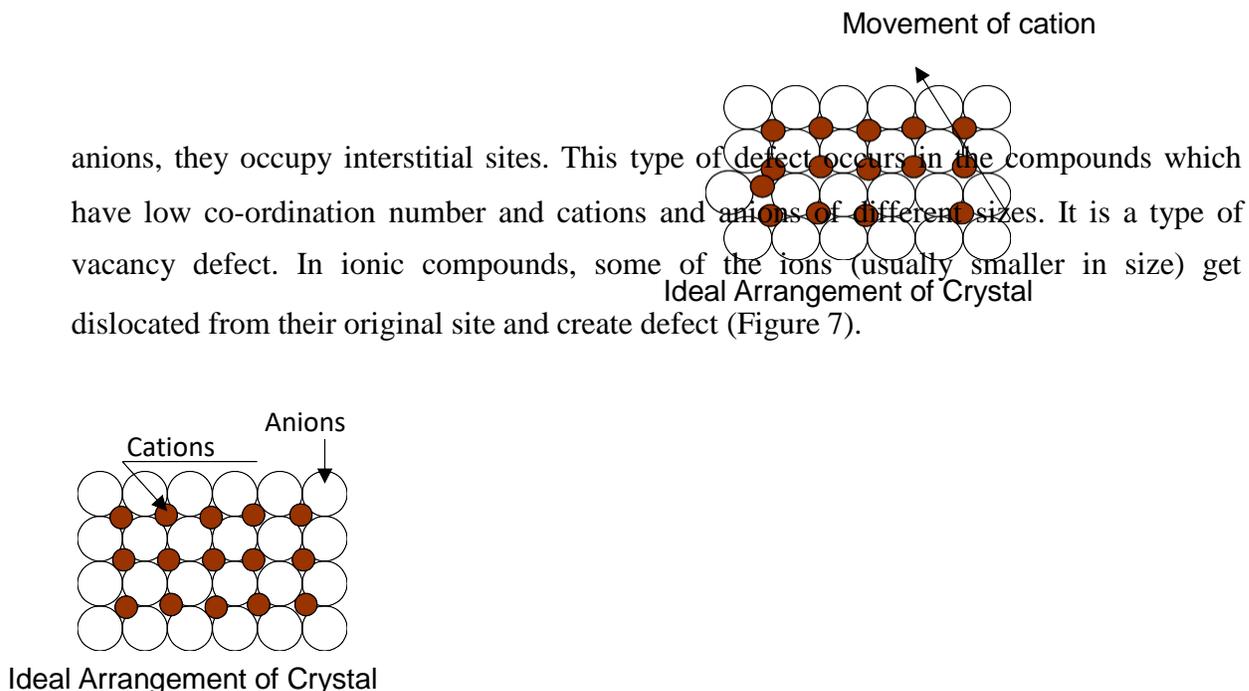


Figure 8: Frenkel defect

2. Non-Stoichiometric defects: Non-stoichiometric compounds are chemical compounds, almost always solid inorganic compounds, having elemental composition whose proportions cannot be represented by integers; most often, in such materials, some small percentage of atoms are missing or too many atoms are packed into an otherwise perfect lattice work.

These defects are either due to the presence of excess metal ions or deficiency of metal ions.

(a) Metal excess defects due to anion vacancies: A compound may have excess metal anion if a negative ion is absent from its lattice site, leaving a 'hole', which is occupied by electron to maintain electrical neutrality. This type of defects are found in crystals which are likely to possess Schottky defects. Anion vacancies in alkali metal halides are reduced by heating the alkali metal halides crystals in an atmosphere of alkali metal vapors. The 'holes' occupy by electrons are called F-centres (or colour centres).

(b) Metal excess defects due to interstitial cations: Another way in which metal excess defects may occur is, if an extra positive ion is present in an interstitial site. Electrical neutrality is maintained by the presence of an electron in the interstitial site. Such type of defects are exhibit by the crystals which are likely to exhibit Frenkel defects e.g., when ZnO is heated, it loses oxygen reversibly (Figure 8). The excess is accommodated in interstitial sites, with electrons trapped in the neighborhood. The yellow color and the electrical conductivity of the non-stoichiometric ZnO is due to these trapped electrons.

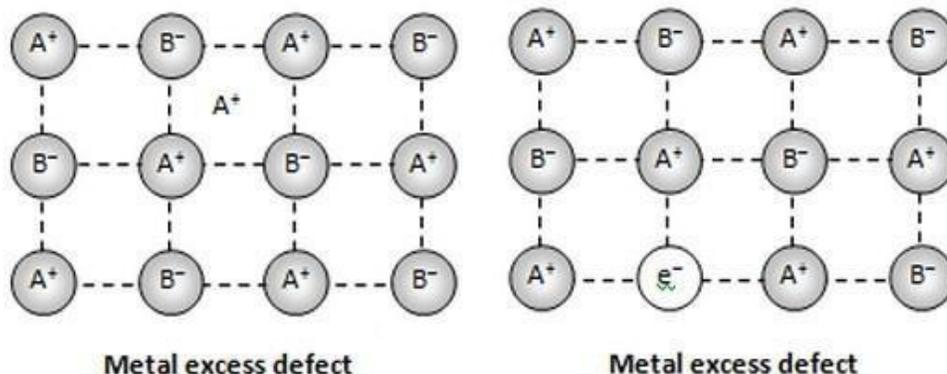


Figure 9: Metal excess defect

Consequences of Metal excess defects

The crystals with metal excess defects are generally coloured due to the presence of free electrons in them. The crystals with metal excess defects conduct electricity due to the presence of free electrons and are semiconductors. As the electric transport is mainly by “excess” electrons, these are called n-type (n for negative) semiconductor.

The crystals with metal excess defects are generally paramagnetic due to the presence of unpaired electrons at lattice sites.

When the crystal is irradiated with white light, the trapped electron absorbs some component of white light for excitation from ground state to the excited state. This gives rise to colour. Such points are called F-centres. (German word Farbe which means colour) such excess ions are accompanied by positive ion vacancies. These vacancies serve to trap holes in the same way as the anion vacancies trapped electrons. The colour centres thus produced are called V-centres.

(c) **Metal deficiency defect by cation vacancy:** In this a cation is missing from its lattice site. To maintain electrical neutrality, one of the nearest metal ion acquires two positive charge. This type of defect occurs in compounds where metal can exhibit variable valency. e.g., Transition metal compounds like NiO, FeO, FeS etc.

(d) **By having extra anion occupying interstitial site:** In this, an extra anion is present in the interstitial position. The extra negative charge is balanced by one extra positive charge on the adjacent metal ion. Since anions are usually larger it could not occupy an interstitial site. Thus, this structure has only a

theoretical possibility. No example is known so far.

Consequences of metal deficiency defects

Due to the movement of electron, an ion A^+ changes to A^{+2} ions. Thus, the movement of an electron from A^+ ion is an apparent of positive hole and the substances are called p-type semiconductor

Liquid crystals (LC) are substances that exhibit long-range order in one or two dimensions, but not all three. Liquid crystals are substances that exhibit a phase of matter that has properties between those of a conventional liquid, and those of a solid crystal.

A large number of organic molecules with long chain such as cholesteryl acetate ($\text{CH}_3\text{COOC}_{27}\text{H}_{45}$), cholesteryl benzoate ($\text{C}_6\text{H}_5\text{COOC}_{27}\text{H}_{45}$), etc show LC behavior. A liquid crystal (LC) may flow like a ordinary liquid, but have the molecules in the liquid arranged and/or oriented in a crystal-like way or they show anisotropy and double refraction like crystalline solids.

A liquid crystal is a thermodynamic stable phase characterized by anisotropy of properties without the existence of a three-dimensional crystal lattice, generally lying in the temperature range between the anisotropic solid and isotropic liquid phase, hence the term mesophase. Both small molecules and polymers may exist in the liquid crystalline state, but generally special spatial structures like rigid rod like or disc like molecules are required. Here define a new term mesogen, is rigid rod like or disc like molecules which are components of liquid crystalline materials.

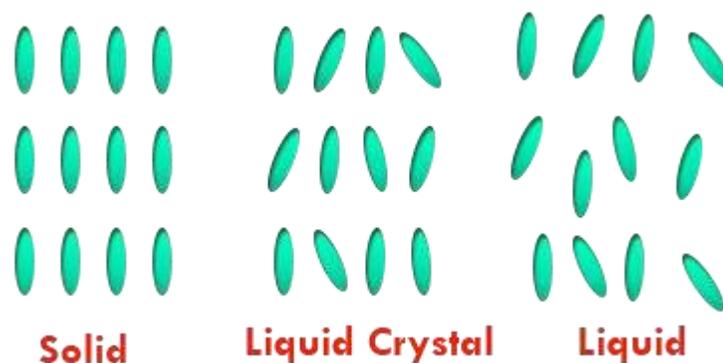


Figure 10: Distribution of molecules in Liquid crystal

Liquid substances are more or less entirely disordered and crystalline materials are ordered in all three dimensions, the LCs lie in-between in properties. Liquid crystals are ordered in one or two dimensions only. Liquid crystals all exhibit some degree of fluidity. The formation of liquid crystals is a direct consequence of molecular asymmetry (Figure 9). It arises because two molecules cannot occupy the same space at the same time and is largely entropically derived.

Crystalline materials demonstrate long range periodic order in three dimensions. By definition, an isotropic liquid has no orientational order.

Characterizing Liquid Crystals: The following parameters describe the liquid crystalline structure:

[1] Orientational Order

[2] Positional Order.

Each of these parameters describes the extent to which the liquid crystal sample is ordered.

Orientalional order: Measure of the tendency of the molecules to align along the director on a long-range basis.

Positional order: The extent to which the position of an average molecule or group of molecules shows translational symmetry.

Most liquid crystal compounds exhibit polymorphism or a condition where more than one phase is observed in the liquid crystalline state. The term mesophase is used to describe the "subphases" of liquid crystal materials. Mesophases are formed by changing the amount of order in the sample, either by imposing order in only one or two dimensions, or by allowing the molecules to have a degree of translational motion. The following section describes the mesophases of liquid crystals in greater detail.

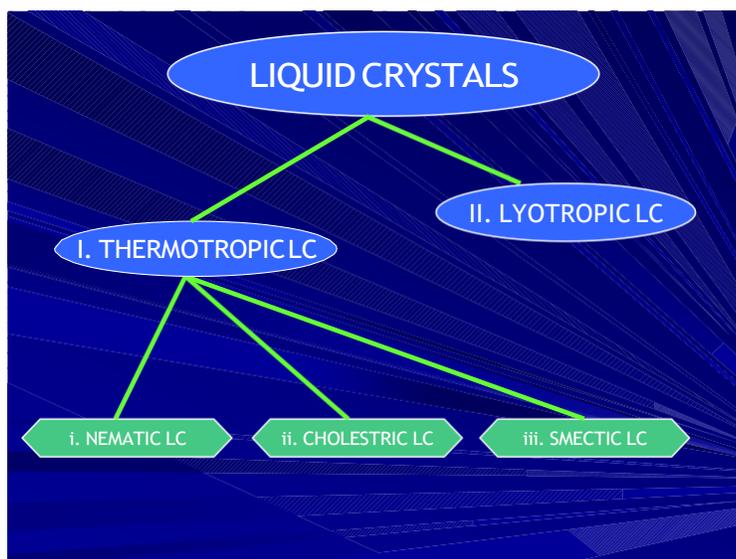


Figure 11: Types of liquid crystals

1. THERMOTROPIC LIQUID CRYSTALS: Liquid crystals are said to be thermotropic if the liquid crystalline properties depend on temperature (Figure 10).

Nematic liquid crystals

It is most common phases in which the molecules (mesogens) have no positional order, but they have long-range orientational order. (Most nematics are uniaxial: they have one axis that is longer and preferred, with the other two being equivalent (can be approximated as cylinders). In Greek ‘nematic’ means thread hence, the thread- like structure of nematic crystals.

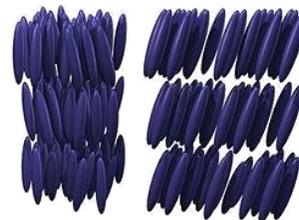
Nematics have fluidity similar to that of ordinary (isotropic) liquids but they can



be easily aligned by an external magnetic or electric field. An aligned nematic has the optical properties of a uniaxial crystal and this makes them extremely useful in liquid crystal displays (LCD).

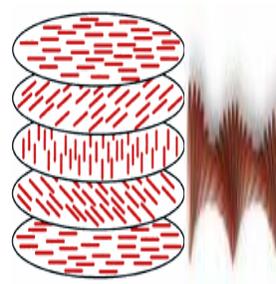
Smectic liquid crystals

In the case of Smectic type LC, the mesogens have both positional order and orientational order. The smectic phases, which are found at lower temperatures than the nematic, form well-defined layers that can slide over one another like soap.



Cholestric liquid crystals

The cholestric phase can be defined as a special type of nematic LC in which the thin layers of parallel mesogens have their longitudinal axes rotated in adjacent layers at certain angle.



2. LYOTROPIC LIQUID CRYSTALS

Liquid crystals which are prepared by mixing two or more substances, of which one is a polar molecule, are known as lyotropic liquid crystals.

Eg. Soap in water.

Discontinuous cubic phase (micellar cubic phase), Hexagonal phase (hexagonal columnar phase) (middle phase), Lamellar phase.

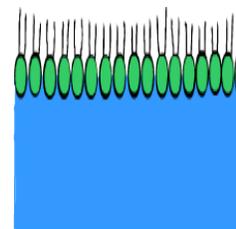


Figure 12: Types of thermotropic LC

Applications of Liquid Crystals:

Liquid crystal technology had a major effect many areas of science and engineering, as well as device technology. Liquid crystals consume very little electrical power. Hence they find use in many electronic devices.

1. Liquid Crystal Displays: Used in display devices (LCDs) such as Laptops, watches, calculators, clocks, etc.
2. Liquid Crystal Thermometers: Chiral nematic (cholesteric) liquid crystals reflect light and the color reflected also is dependent upon temperature.
3. Optical Imaging: An application of liquid crystals that is only now being explored is optical imaging and recording.
4. Some of the liquid crystals are used in hydraulic break/clutch system due to their high viscosity values.
5. Liquid Crystals are also used in medical applications.
6. Cholesteric liquid crystals are used in thermography in the testing of radiations in those devices which convert radiation energy into heat energy(tumor detection).

Graphite: Structure and applications

Graphite: exists as layers of carbon atoms each held in place by three strong covalent bonds. Each layer is held to the one above it by weak bonds. In graphite each C-atom is covalently bonded to three C-atom to give trigonal geometry. Bond angle in graphite is 120° . Each C-atom in graphite is sp^2 -hybridized. Three out of four valence electrons of each C-atom are used in bond formation while the fourth electrons free to move in the structure of graphite. Basic trigonal units unite together to give basic hexagonal ring. In hexagonal ring C-C bond length is 1.42\AA . In graphite these rings forms flat layers. These layers are arranged is parallel, one above the other. These layers 3.35\AA apart and are held together by weak *vander waals* forces only. These layers can slide over one another. Thus it is very soft. Forth electron of each c-atom forms delocalized p-system.

Physical properties of giant covalent structures

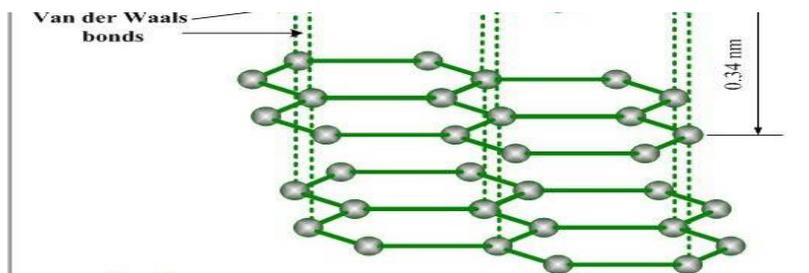


Figure 13: Structure of graphite

Giant molecular structures have very high melting points because all atoms are held firmly in place by strong covalent bonds. In graphite each carbon atom is held in place by three strong covalent bonds which gives graphite a high melting point. In diamond four strong covalent bonds holds each atom in place. This also gives diamond a very high melting point. The four bonds make diamond very hard. Graphite has weak bonds between layers so the layers slip over each other making graphite soft.

They do not usually conduct electricity even when molten because there are no charged particles to carry the current. There are free electrons between layers in graphite so it conducts electricity.

Explaining differences between properties Simple molecular substances like water have weak bonds between molecules so melt at low temperatures because little energy is needed to separate the molecules. Giant covalent structures like diamond have strong covalent bonds holding each atom in place. They melt at high temperatures because a lot of energy is needed to break these strong bonds (Figure 12).

Applications

Refractory Materials: Due to its high temperature stability and chemical inertness graphite is a good candidate for a refractory material. It is used in the production of refractory bricks and in the production of “Mag-carbon” refractory bricks (Mg-C.). Magnesia carbon refractories or Carbon containing Magnesite refractories have been extensively used by steel makers in ladles that are containers for the secondary treatment of steel. MgO-C refractory bricks are widely used in slag lines of BOF (Basic Oxygen Furnace) because of their superior wear resistance.

Chemical Industry: There are many high temperature uses for graphite in the chemical industry such as in the production of phosphorus and calcium carbide in arc furnaces. Graphite is used as anodes in some aqueous electrolytic processes such as in the production of halogens (chlorine and fluorine.)

Nuclear Industry: High purity electrographite is used in large amounts for the production of moderator rods and reflector components in nuclear reactors. Their suitability arises from their low absorption of neutrons, high thermal conductivity and their high strength at temperature.

Electrical Applications: The main application for graphite as an electrical material is in the manufacture of carbon brushes in electric motors. In this application the performance and lifetime of the component is very dependent on grade and structure.

Mechanical Applications: Graphite is used widely as an engineering material over a variety of applications. Applications include piston rings, thrust bearings, journal bearings and vanes. Carbon based seals are used in the shafts and fuel pumps of many aircraft jet engines.

Due to its increased porosity synthetic graphite tends not be used in refractory applications.

Fullerene

Apart from the carbon allotropes of diamond and graphite, third form of carbon exists as fullerenes, also known as *'buckyball'*". Allotropes possess different atomic, molecular arrangements of the same element in the same physical state.

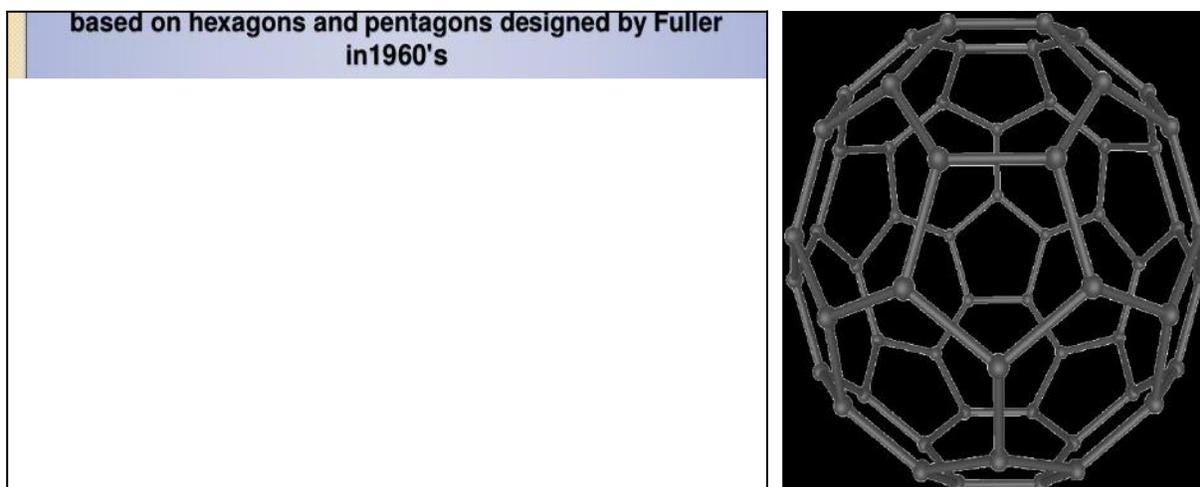


Figure 14: Fullerene

Structure

Fullerenes consist of hexagonal rings of carbon atoms (like in graphite or graphene) and alternating pentagonal carbon rings to allow curvature of the surface (Figure 13).

They are a sort of a hollow 'cage' or 'ball' or 'closed tube' shaped molecules of pure carbon atoms. Fullerenes are not nanoparticles but they are smaller molecular versions equating to sections of the tiny molecular carbon tubes called carbon nanotubes, and they are very interesting molecules in themselves and provide a way into studying carbon nanotubes in terms of their molecular structure and applications in nanotechnology.

These fullerenes (and carbon nanotubes) are quite different from other forms of carbon e.g. in the form of soot, graphite or diamond.

Applications and Examples

Fullerene molecules can be used for drug delivery into the body, as lubricants, as catalysts and in the form of carbon nanotubes can be used for reinforcing composite materials, eg sports equipment like tennis rackets.

They have many chemical synthetic and pharmaceutical applications.

They may be used as vehicles to carry drugs into cells, the cage like fullerene molecules could contain a drug, and the combination can pass easily through the wall of a target cell.

Chemical derivatives of fullerenes have fascinating electrical and magnetic behaviour including superconductivity and ferromagnetism.

C₆₀ is an optical limiter. When light is shone on it, a solution of fullerene-60 turns darker instantly and the more intense the light, the darker it gets, so the intensity of transmitted light is limited to a maximum value. This limiting light transmittance property can be used in the design of safety goggles in intense light situations e.g. people working with laser beams.

Fullerenes may be used in certain medical applications – nanomedicine.

The idea is to use the very small fullerene molecules to easily deliver drugs directly into cells in a highly controlled manner. This is possible because the extremely small diameter of the nanoparticle fullerenes (which act like a cage to hold the drug) allows them to readily pass through cell membranes.

Fullerenes are being developed that have excellent lubricating properties (maybe superior to lubrication oils) and these lubricants significantly reduce friction in moving metal parts of machines

from cog wheels to ball bearings and maybe artificial joints after orthopedic operations on hips and knees!

Fullerenes are mentioned here to illustrate the different forms of carbon and they can be formed into continuous tubes to give very strong fibres of 'pipe like' molecules called 'nanotubes'.

These nanotube molecules-particles behave differently compared to bulk carbon materials like graphite and the much smaller fullerene molecules.

Fullerenes are used in many applications because of their unique chemistry and, especially in materials science, electronics, and nanotechnology. Many examples are obvious which totally explains the popularity of fullerene. Some famous examples are buckyball clusters, nanotubes, megatubes, polymers, nano onions and fullerene rings. All these structures are used in fields of work to extract more improved form of products from existing materials.

Nanomaterials and its concepts

Nanomaterials are defined as engineered materials with a least one dimension in the range of 1-100nm. Particles of “**nano**” size have been shown to exhibit enhanced or novel properties including reactivity, greater sensing capability and increased mechanical strength.

The nanotechnology offers simple, clean, fast, efficient, and economic for the synthesis of a variety of organic molecules, have provided the momentum for many chemists to switch from traditional method. In the present article an attempt was made to focus on what is nanomaterials, how is it generated and what importance may it have.

Nanotechnology

The term "Nanotechnology" was first defined by Norio Taniguchi of the Tokyo Science University in 1974. Nanotechnology, shortened to "Nanotech", is the study of manipulating matter on an atomic and molecular scale. Nanoscience and nanotechnologies are revolutionizing our understanding of matter and are likely to have profound implications for all sectors.

Synthesis of Nanoparticles

Synthesis methods can be classified according to the strategy applied (bottom-up or top-down approach), the nature of the process (physical, chemical, biological, e.g. biomineralization), the energy source (laser, plasma, ion sputtering, electron beam, microwave, hydrothermal, freeze drying, high-energy ball milling, combustion, flame, supercritical) or by the media (synthesis in gas, in liquid or in solid).

- (1) **Bottom-up approach:** Nanoparticles are built up atom by atom or molecule by molecule as shown in Figure 14 e.g. flame synthesis of TiO_2 from gaseous TiCl_4 or flame synthesis of SiO_2 from gaseous SiCl_4 , chemical vapor reactions using resistant heating, laser or plasma, aerosol pyrolysis (spray pyrolysis, vapor pyrolysis) applied to produce nanosized BaTiO_3 from hydrolyzed TiCl_4 and BaCl_2 ; further examples are chemical (reactive) precipitation or coprecipitation, e.g. the wet-chemical precipitation of needle-shaped hydroxyapatite nanocrystals, hydrothermal synthesis (thermal hydrolysis), forced hydrolysis, solvo-thermal synthesis, supercritical hydrothermal processing or supercritical fluid processing, sol-gel synthesis, microwave heating synthesis, synthesis in microemulsions or reverse micelles synthesis.

- (2) **Top-down approach:** Nanoparticles are synthesized by breaking down bulk materials gradually into smaller sizes, e.g. synthesis of nanocrystalline $\alpha\text{-Al}_2\text{O}_3$ (surface area up to $100\text{ m}^2/\text{g}$) by high-energy ball milling (mechanical milling) of $\gamma\text{-Al}_2\text{O}_3$ (by this route nanocrystalline high-temperature phases can be obtained without going through extreme heat treatment for long times, which would promote grain growth and surface area loss), mechanochemical processing (mechanical activation) for the preparation of nanosized (50-100 nm) BaTiO_3 by milling BaCO_3 and TiO_2 with a large amount of NaCl for several hours, cryochemical processing, combustion synthesis (self propagating high-temperature synthesis) for BaTiO_3 – note that it is extremely difficult to produce nanosized BaTiO_3 directly via solid-state synthesis ($\text{BaCO}_3 + \text{TiO}_2 \rightarrow \text{BaTiO}_3 + \text{CO}_2$); synthesis of nanosize yttrium-stabilized zirconia (Y-ZrO_2) by selective leaching of bulky yttrium-doped BaZrO_3 or Na_2ZrO_3 (produced via conventional solid state reactions).

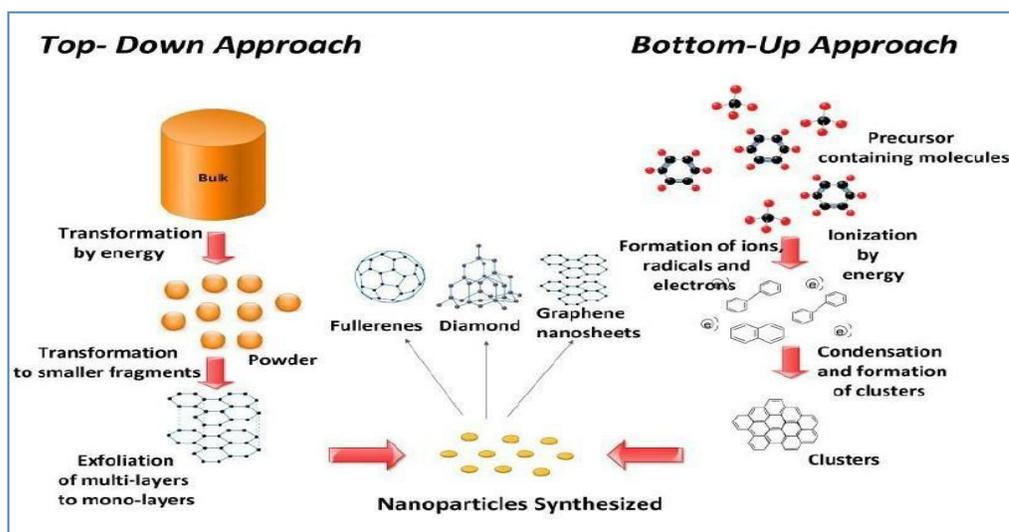


Figure 14: Synthesis of nanomaterials

Applications of Nanomaterials: Nanomaterials are of potential importance in

1) Sunscreens and Cosmetics: A sunscreen based on mineral nanoparticles such as titanium dioxide offer several advantages. Titanium oxide nanoparticles have a comparable UV protection property. Nanosized titanium dioxide and zinc oxide are currently used in some sunscreens, as they absorb and reflect ultraviolet (UV) rays and yet are transparent to visible light and so are more appealing to the consumer. Nanosized iron oxide is present in some lipsticks as a pigment.

2) Paints: Incorporating nanoparticles in paints could improve their performance, for example by making them lighter and giving them different properties. Thinner paint coatings ('light weighting'), used for example on aircraft, would reduce their weight, which could be beneficial to the environment.

3) Batteries: With the growth in portable electronic equipment (mobile phones, laptop computers, remote sensors), there is great demand for lightweight, high energy density batteries. Nanocrystalline

materials synthesized by sol–gel techniques are candidates for separator plates in batteries because of their foam-like (aerogel) structure, which can hold considerably more energy than conventional ones. Nickel–metal hydride batteries made of nanocrystalline nickel and metal hydrides are envisioned to require less frequent recharging and to last longer because of their large surface area.

4) Catalysis: In general, nanoparticles have a high surface area, and hence provide higher catalytic activity. Catalysis is important for the production of chemicals. Nanoparticles serve as an efficient catalyst for some chemical reaction, due to the extremely large surface to volume ratio. Platinum nanoparticles are now being considered in the next generation of automotive catalytic converters because the very high surface area of nanoparticles could reduce the amount of platinum required. Some chemical reactions are also carried out using nanomaterials. For example: reduction of nickel oxide to the base metal Ni.

5) Medicine: Nanotechnology has been a boon in medical field by delivering drugs to specific cells using nanoparticles. The overall drug consumption and side effects can be lowered significantly by depositing the active agent in the morbid region only and in no higher dose than needed. This highly selective approach reduces costs and human suffering. Nanotechnology can also help to reproduce or to repair damaged tissue. “Tissue engineering” might replace today's conventional treatments like organ transplants or artificial implants. For example, bones can be regrown on carbon nanotubes scaffolds. . Gold is also added in certain medical preparations for babies in order to enhance their mental capability.

6) Sensors of gases: The gases like NO_2 and NH_3 can be detected on the basis of increase in electrical conductivity of nanomaterials. This is attributed to increase in hole concentration in nanomaterials due to charge transfer from nanomaterials to NO_2 as the gas molecules bind the nanomaterials.

7) Food: Nanotechnology can be applied in the production, processing, safety and packaging of food. A nanocomposite coating process could improve food packaging by placing anti-microbial agents directly on the surface of the coated film.

8) Construction: Nanotechnology has the potential to make construction faster, cheaper and safer. Automation of nanotechnology construction can allow for the creation of structures from advanced homes to massive skyscrapers much more quickly and at much lower cost. The Silica (SiO_2) is present

in conventional concrete as part of the normal mix. When nano silica is added to concrete the particle packing can be improved mechanical properties.

9) Lubricants: Nanospheres made of inorganic materials can be used as lubricants by acting as nanosized “ball bearing”. Nanoparticles reduce friction between metal surfaces particularly at high loads.

10) Magnetic materials: The magnets made of nano crystalline yttrium- samarium-cobalt grains have useful magnetic properties due to extremely large interface area. This property leads to applications in analytical instruments such as MRI used in hospitals, motors, data storage devices and in micro sensors.

UNIT-II**Electromagnetic Radiation**

- Radiation is absorbed and emitted in photons. The defining characteristic of a photon is that its energy cannot be split into smaller pieces.
- Each photon's energy is defined by its frequency (ν) or wave length (λ) or wave number (Figure 15).

$$E_{\text{photon}} = h\nu = hc/\lambda$$

- Two constants appear in these formulas i.e. h = plank's constant, 6.63×10^{-34} J s and c = speed of light, 3.00×10^8 m s⁻¹
- Wave number = $1/\lambda$

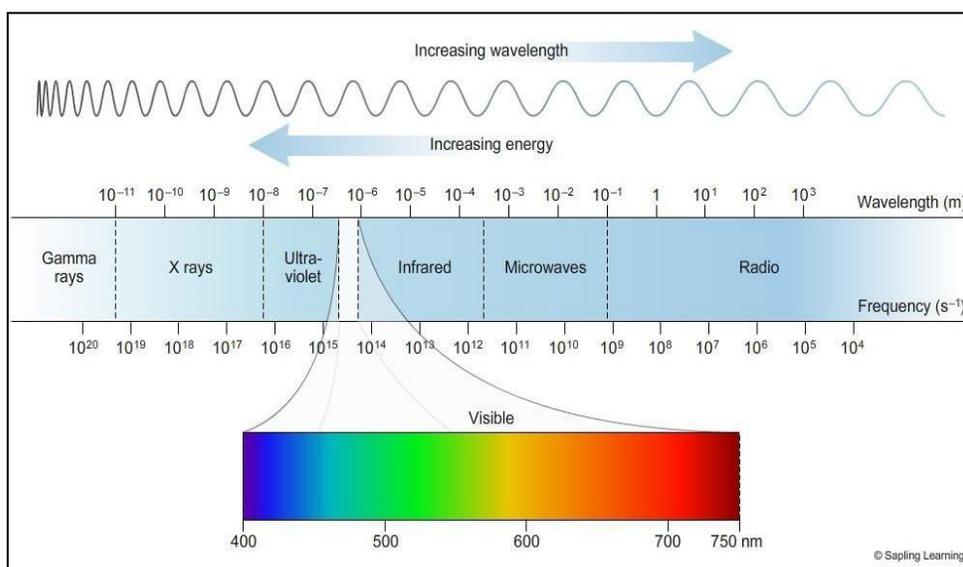


Figure 15: Electromagnetic spectrum

Beer-Lambert Law

The **Beer-Lambert law (or Beer's law)** is the linear relationship between absorbance and concentration of absorbing specie. The general Beer-Lambert law is usually written as:

$$A = \epsilon * b * c$$

where A is the measured absorbance, ϵ is a wavelength-dependent absorptivity coefficient, b is the path length, and c is the analyte concentration. Data are frequently reported in percent transmission ($I/I_0 * 100$) or in absorbance [$A = \log (I/I_0)$].

Instrumentation: Experimental measurements are usually made in terms of **transmittance** (T), which is defined as:

$T = I / I_0$ where I is the **light intensity** after it passes through the sample and I_0 is the **initial light intensity** as shown in Figure 16. The relation between A and T is:

$$A = -\log T = -\log (I / I_0)$$

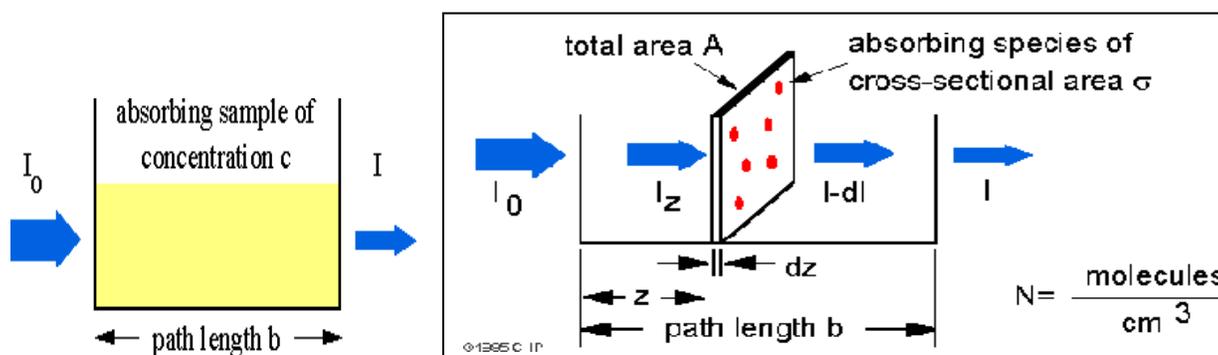


Figure 16: Absorption of light by sample solution and change in intensity

Electronic transitions

The absorption of UV or visible radiation corresponds to the excitation of outer electrons. There are three types of electronic transition which can be considered;

1. Transitions involving σ , Π and n electrons
2. Transitions involving charge-transfer electrons
3. Transitions involving d and f electrons (not covered in this Unit)

When an atom or molecule absorbs energy, electrons are promoted from their ground state to an excited state (Figure 17). 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

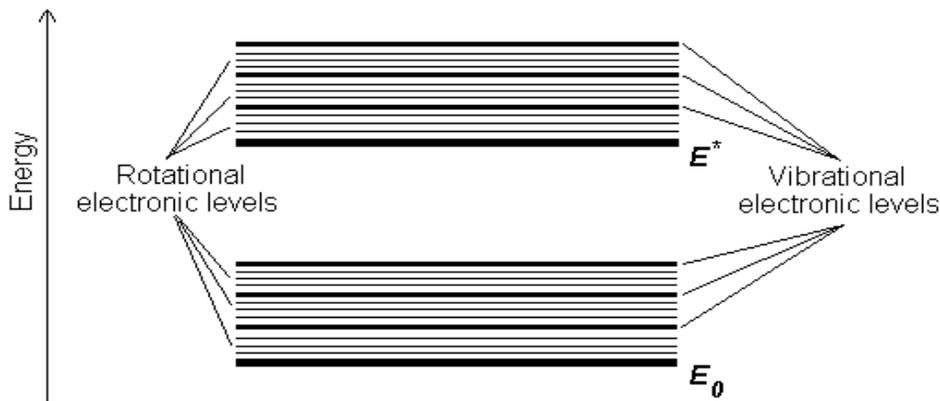


Figure 17: Absorbing species containing σ , Π and n electrons

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

Possible *electronic* transitions of σ , Π and n electrons are;

$\sigma - \sigma^*$ Transitions

An electron in a bonding σ orbital is excited to the corresponding antibonding orbital. The energy required is large. For example, methane (which has only C-H bonds, and can only undergo $\sigma - \sigma^*$ transitions) shows an absorbance maximum at 125 nm. Absorption maxima due to $\sigma - \sigma^*$ transitions are not seen in typical UV-Vis. spectra (200 - 700 nm) as shown in Figure 18.

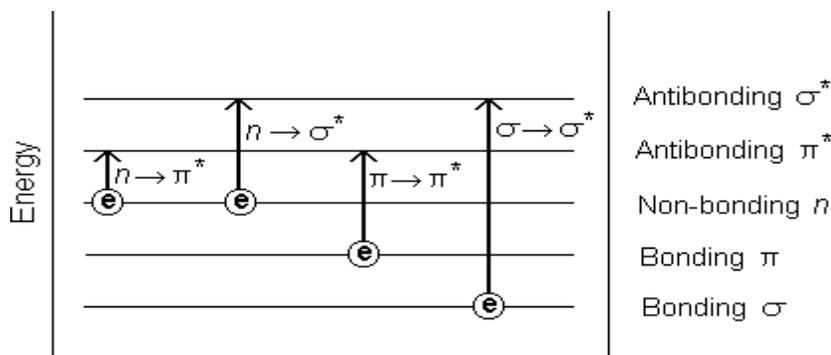


Figure 18: Possible electronic transitions of σ , Π and n electrons

$\Pi - \Pi^*$ Transitions

Saturated compounds containing atoms with lone pairs (non-bonding electrons) are capable of $n - \Pi^*$ transitions. These transitions usually need less energy than $n - \Pi^*$ transitions. They can be initiated by light whose wavelength is in the range 150 - 250 nm. The number of organic functional groups with $n - \Pi^*$ peaks in the UV region is small.

$n - \Pi^*$ and $\Pi - \Pi^*$ Transitions

Most absorption spectroscopy of organic compounds is based on transitions of n or Π electrons to the Π^* excited state. This is because the absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200 - 700 nm). These transitions need an unsaturated group in the molecule to provide the Π electrons.

Molar absorptivity from $n - \Pi^*$ transitions are relatively low, range from 10 to 100 $\text{L mol}^{-1} \text{cm}^{-1}$. $\Pi - \Pi^*$ transitions normally give molar absorptivity between 1000 and 10,000 $\text{L mol}^{-1} \text{cm}^{-1}$.

Solvent Effect:

The solvent in which the absorbing species is dissolved also has an effect on the spectrum of the species. Peaks resulting from $n - \Pi^*$ 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 n orbital. Often the reverse (i.e. *red shift*) is seen for $\Pi - \Pi^*$ 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 $n - \Pi^*$ transitions but is overshadowed by the blue shift resulting from solvation of lone pairs.

Application of UV-Spectroscopy

- **Detection of Impurities:** UV absorption spectroscopy is one of the best methods for determination of impurities in organic molecules. Additional peaks can be observed due to impurities in the sample and it can be compared with that of standard raw material. By also measuring the absorbance at specific wavelength, the impurities can be detected. Benzene appears as a common impurity in cyclohexane. Its presence can be easily detected by its absorption at 255 nm.
- **Structure elucidation of organic compounds:** UV spectroscopy is useful in the structure elucidation of organic molecules, the presence or absence of unsaturation the presence of hetero atoms.
From the location of peaks and combination of peaks, it can be concluded that whether the compound is saturated or unsaturated, hetero atoms are present or not etc.
- **Quantitative analysis:** UV absorption spectroscopy can be used for the quantitative determination of compounds that absorb UV radiation. This determination is based on Beer's law which is as follows:

$$A = \log I_0 / I_t = \log 1/T = -\log T = \epsilon bc$$

Where ϵbc is extinction co-efficient, c is concentration, and b is the length of the cell that is used in UV spectrophotometer.

- **Qualitative analysis:** UV absorption spectroscopy can characterize those types of compounds which absorb UV radiation. Identification is done by comparing the absorption spectrum with the spectra of known compounds. UV absorption spectroscopy is generally used for characterizing aromatic compounds and aromatic olefins.
- **Dissociation constants of acids and bases.**

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

From the above equation the pK_a value can be calculated if the ratio of $[A^-] / [HA]$ is known at a particular PH. and the ratio of $[A^-] / [HA]$ can be determined spectrophotometrically from the graph plotted between absorbance and wavelength at different PH values.

- **Chemical kinetics:** Kinetics of reaction can also be studied using UV spectroscopy. The UV radiation is passed through the reaction cell and the absorbance changes can be observed.
- **Quantitative analysis of pharmaceutical substances:** Many drugs are either in the form of raw material or in the form of formulation. They can be assayed by making a suitable solution of the drug in a solvent and measuring the absorbance at specific wavelength. Diazepam tablet can be analyzed by 0.5% H₂SO₄ in methanol at the wavelength 284 nm.
- **Molecular weight determination:** Molecular weights of compounds can be measured spectrophotometrically by preparing the suitable derivatives of these compounds. For example, if we want to determine the molecular weight of amine then it is converted in to amine picrate. Then known concentration of amine picrate is dissolved in a litre of solution and its optical density is measured at λ_{max} 380 nm. After this the concentration of the solution in gm moles per litre can be calculated by using the following formula

Infrared spectroscopy exploits the fact that molecules absorb frequencies that are characteristic of their structure. These absorptions occur at resonant frequencies, i.e. the frequency of the absorbed radiation matches the vibrational frequency. The energies are affected by the shape of the molecular potential energy surfaces, the masses of the atoms.

In order for a vibrational mode in a sample to be "IR active", it must be associated with changes in the dipole moment. A permanent dipole is not necessary, as the rule requires only a change in dipole moment.

A molecule can vibrate in many ways, and each way is called a *vibrational mode*. For molecules with N number of atoms, linear molecules have $3N - 5$ degrees of vibrational modes, whereas nonlinear molecules have $3N - 6$ degrees of vibrational modes (also called vibrational degrees of freedom). As an example H₂O, a non-linear molecule, will have $3 \times 3 - 6 = 3$ degrees of vibrational freedom, or modes.

Simple diatomic molecules have only one bond and only one vibrational band. If the molecule is symmetrical, e.g. N₂, the band is not observed in the IR spectrum, but only in the Raman spectrum. Asymmetrical diatomic molecules, e.g. CO, absorb in the IR spectrum. More complex molecules have many bonds, and their vibrational spectra are correspondingly more complex, i.e. big molecules have many peaks in their IR spectra. The atoms in a CH₂X₂ group, commonly found in organic compounds and where X can represent any other atom, can vibrate in nine different ways. Six of these vibrations involve only the CH₂ portion:

symmetric and asymmetric stretching, scissoring, rocking, wagging and twisting, as shown in Figure 19. Structures that do not have the two additional X groups attached have fewer modes because some modes are defined by specific relationships to those other attached groups. For example, in water, the rocking, wagging, and twisting modes do not exist because these types of motions of the H represent simple rotation of the whole molecule rather than vibrations within it.

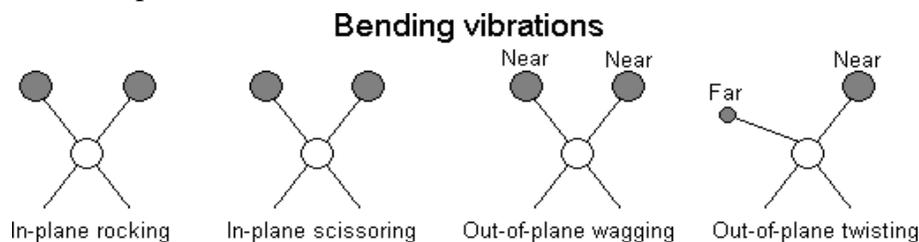
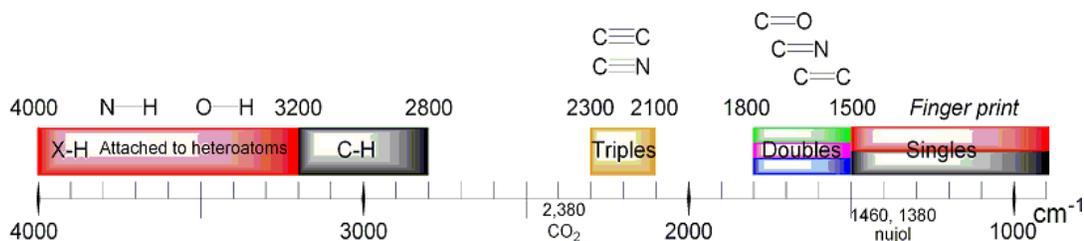


Figure 19: Bending vibrations in a molecule

Summary of absorptions of bonds in organic molecules



Finger Print Region: The region to the right-hand side of the diagram (from about 1500 to 500 cm^{-1}) usually contains a very complicated series of absorptions. These are mainly due to all manner of bending vibrations within the molecule. This is called the *fingerprint region*. It is much more difficult to pick out individual bonds in this region than it is in the "cleaner" region at higher wavenumbers. The importance of the fingerprint region is that each different compound produces a different pattern of troughs in this part of the spectrum.

Using the fingerprint region: Compare the infra-red spectra of propan-1-ol and propan-2-ol. Both compounds contain exactly the same bonds. Both compounds have very similar troughs in the area around 3000 cm^{-1} - but compare them in the fingerprint region between 1500 and 500 cm^{-1} .

Infrared spectroscopy is widely used in industry as well as in research. It is a simple and reliable technique for measurement, quality control and dynamic measurement. It is also employed in forensic analysis in civil and criminal analysis.

Some of the major applications of IR spectroscopy are as follows:

1. Identification of functional group and structure elucidation

Entire IR region is divided into group frequency region and fingerprint region. Range of group frequency is $4000-1500\text{ cm}^{-1}$ while that of fingerprint region is $1500-400\text{ cm}^{-1}$.

In group frequency region, the peaks corresponding to different functional groups can be observed. According to corresponding peaks, functional group can be determined.

Each atom of the molecule is connected by bond and each bond requires different IR region so characteristic peaks are observed. This region of IR spectrum is called as fingerprint region of the molecule. It can be determined by characteristic peaks.

Identification of substances

IR spectroscopy is used to establish whether a given sample of an organic substance is identical with another or not. This is because large number of absorption bands is observed in the IR spectra of organic molecules and the probability that any two compounds will produce identical spectra is almost zero. So if two compounds have identical IR spectra then both of them must be samples of the same substances.

IR spectra of two enantiomeric compounds are identical. So IR spectroscopy fails to distinguish between enantiomers.

For example, an IR spectrum of benzaldehyde is observed as follows.

C-H stretching of aromatic ring-	3080 cm^{-1}
C-H stretching of aldehyde-	2860 cm^{-1} and 2775 cm^{-1}
C=O stretching of an aromatic aldehyde-	1700 cm^{-1}
C=C stretching of an aromatic ring-	1595 cm^{-1}
C-H bending-	745 cm^{-1} and 685 cm^{-1}

No other compound than benzaldehyde produces same IR spectra as shown above.

3. Studying the progress of the reaction

Progress of chemical reaction can be determined by examining the small portion of the reaction mixture withdrawn from time to time. The rate of disappearance of a characteristic absorption band of the reactant group and/or the rate of appearance of the characteristic absorption band of the product group due to formation of product is observed.

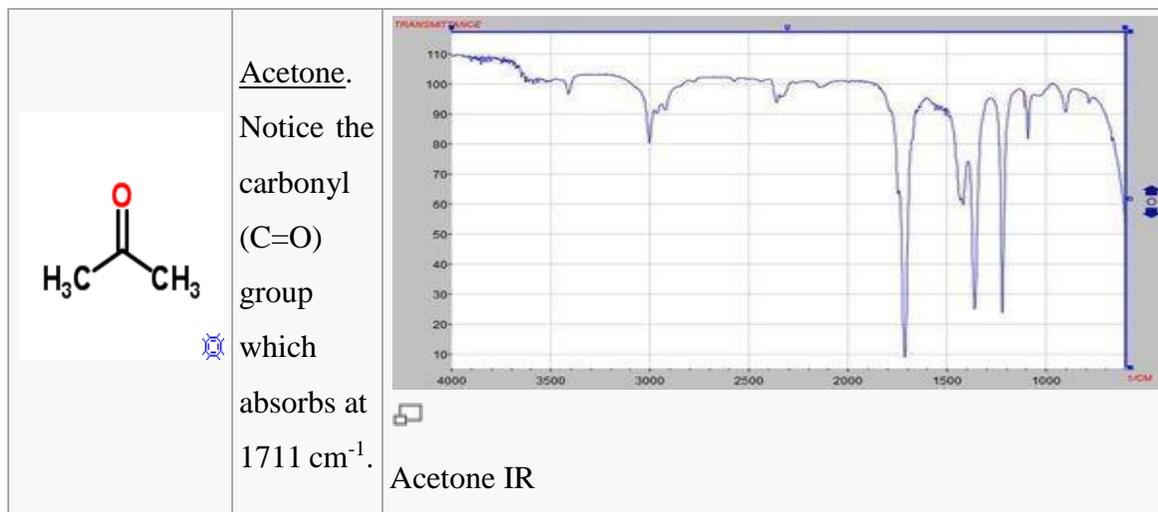
4. Detection of impurities

IR spectrum of the test sample to be determined is compared with the standard compound. If any additional peaks are observed in the IR spectrum, then it is due to impurities present in the compound.

5. Quantitative analysis

The quantity of the substance can be determined either in pure form or as a mixture of two or more compounds. In this, characteristic peak corresponding to the drug substance is chosen and $\log I_0/I_t$ of peaks for standard and test sample is compared. This is called base line technique to determine the quantity of the substance.

Acetone



Raman Spectroscopy

Raman spectroscopy (Named after Indian physicist Sir C. V. Raman) is spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system.^[1] Raman spectroscopy is commonly used in chemistry to provide a structural fingerprint by which molecules can be identified.

Raman spectra relate to vibrational and /or rotational transitions in molecules but in different manner. In this case we measure the scattering and not the absorption of radiation. An intense beam of monochromatic radiation in the visible region is allowed to fall on a sample and the intensity of scattered light is observed at right angles to the incident beam.

Raman spectroscopy reveals the chemical and structural composition of samples. Generally, all materials produce Raman spectra, with the exception of pure metals.

Raman scattering

Raman scattering occurs when light interacts with molecular vibrations. This is similar to the more widely known infrared absorption spectroscopy, but different rules apply. A change in molecular polarisability is required during the vibration for the Raman effect to occur.

You will see some vibrations in the Raman spectrum that are not visible in the infrared spectrum, and vice-versa, because of the different selection rules. For example, Raman spectroscopy is superb for studying the carbon atoms that make up the structure of diamond, unlike infrared absorption spectroscopy.

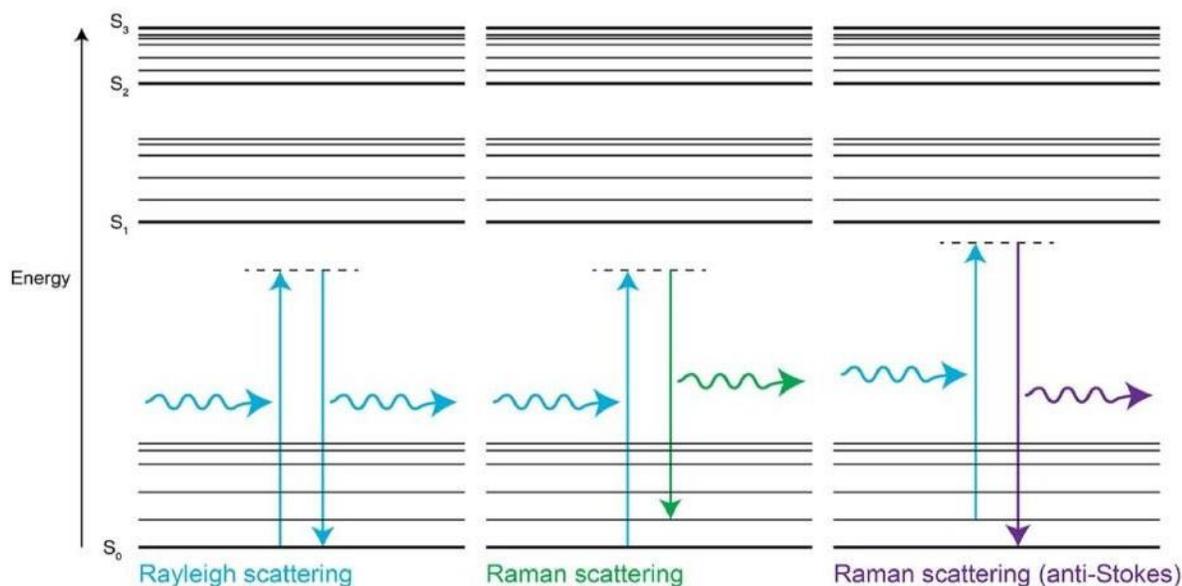
Scattered light

The first step in producing a Raman spectrum is to illuminate your sample with a monochromatic light source, such as a laser.

Most of the light that scatters off is unchanged in energy ('Rayleigh scattered'). A minute fraction—perhaps 1 part in 10 million—has lost or gained energy ('Raman scattered'). This Raman shift occurs because photons (particles of light) exchange part of their energy with molecular vibrations in the material.

Where energy is lost the Raman scattering is designated as 'Stokes'; where energy is gained the Raman scattering is designated as 'anti-Stokes'. We rarely use anti-Stokes Raman light as it is less

intense than the Stokes, however it does represent equivalent vibrational information of the molecule.



Vibrating atoms

The change in energy depends on the frequency of vibration of the molecule. If it is very fast (high frequency)—light atoms held together with strong bonds—the energy change is significant. If it is very slow (low frequency)—heavy atoms held together with weak bonds—the energy change is small.

Raman spectrometers

It consist of:

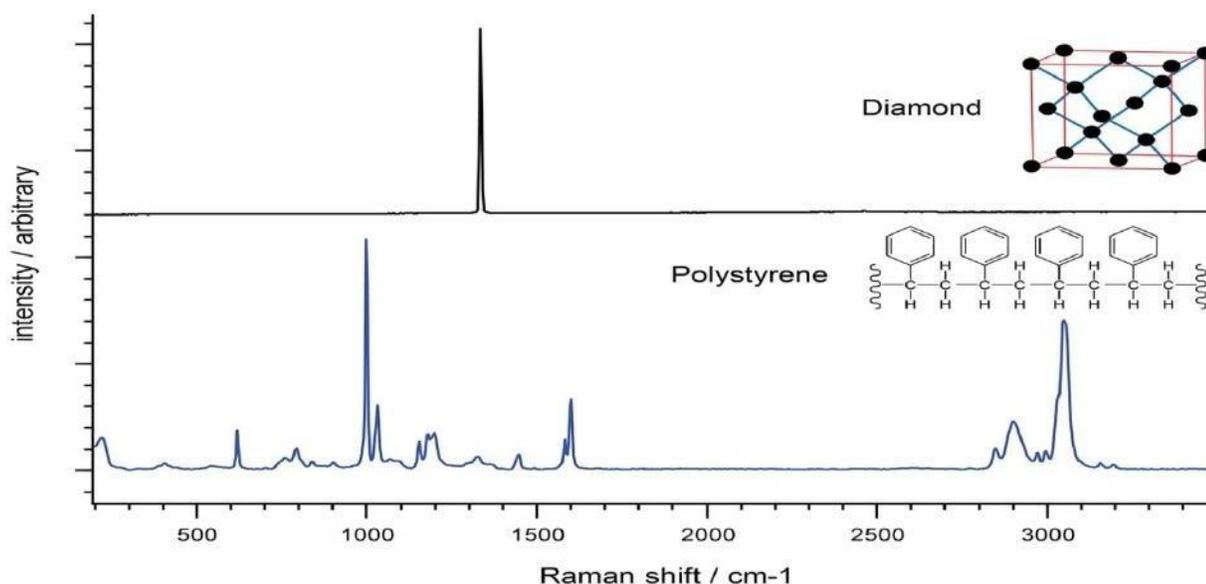
- single or multiple lasers, from UV (244 nm) to IR (1064 nm) – switch with a single click
- high quality objective lenses, from high confocal 100× to long working distance and immersion options
- custom designed motorised spectrometer lenses - automatically align for each configuration
- laser-line-specific Rayleigh filters with a dual filter arrangement to optimise sensitivity
- highest quality master diffraction gratings provide exceptional dispersion and longevity
- thermoelectrically cooled (- 70 °C) CCD detector – stable and sensitive
- high specification multi-core PC for data collection and analysis

Vibration frequencies

The frequencies of vibration depend on the masses of the atoms involved and the strength of the bonds between them. Heavy atoms and weak bonds have low Raman shifts. Light atoms and strong bonds have high Raman shifts.

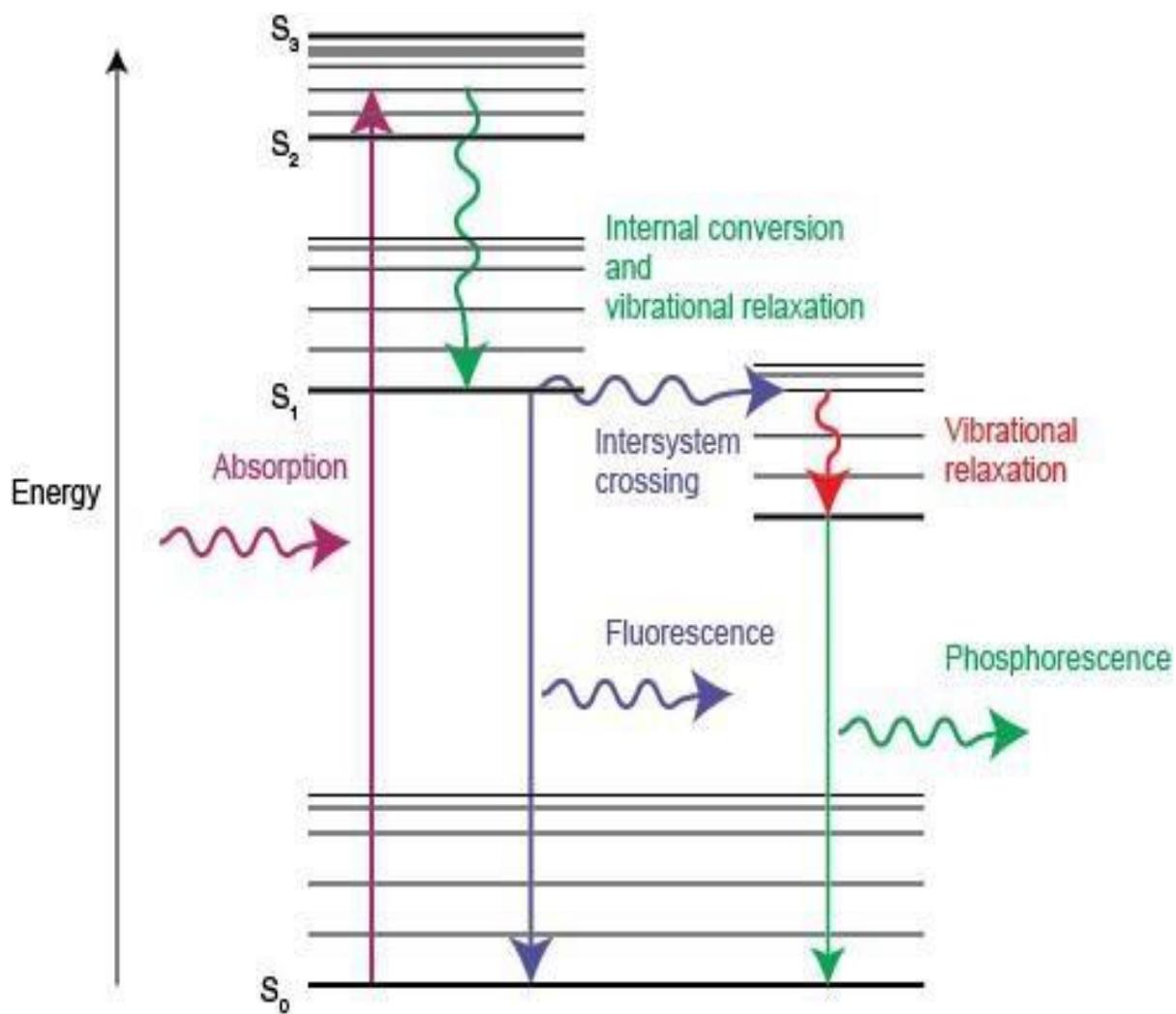
We see the high frequency carbon-hydrogen (C-H) vibrations in the polystyrene spectrum at about 3000 cm^{-1} . The low frequency carbon-carbon (C-C) vibrations are at around 800 cm^{-1} . The C-H vibrations have a higher frequency than the C-C vibrations because hydrogen is lighter than carbon.

We see the vibrations of two carbon atoms linked by strong double bonds (C=C) at around 1600 cm^{-1} . This is at a higher frequency than two carbon atoms lined by a weaker single bond (C-C, 800 cm^{-1}).



When a sample is illuminated by a laser, both Raman scattering and photoluminescence (PL) can occur. The latter can be many times stronger than the former and can prevent successful Raman analysis.

PL comprises both fluorescence and phosphorescence processes and originates from an absorption/emission process between different electronic energy levels in the material. The amount and type of PL depends on which material you are studying and which laser wavelength you are using. Unwanted fluorescence interference can normally be avoided by choosing an appropriate laser wavelength.



- Energy diagram showing absorption of light and the processes involved in the emission of light as fluorescence and phosphorescence

Applications of Raman Spectroscopy

1 Carbon Materials

- Purity of Carbon nanotubes(CNTs)
- sp^2 and sp^3 structure in carbon materials and Diamond like carbon coating properties
- Defects and disorder analysis in carbon materials

2 Pharmaceuticals and Cosmetics

- Compound distribution in tablets.
- Polymorphic forms
- Contaminant identification and Powder content and purity

3 Life Sciences

- Bio-compatibility and DNA/RNA analysis
- Drug/cell interactions and Disease Diagnosis
- Bone Structure

4 Geology and Minerology

- Gemstone and Mineral identification
- Mineral behaviour under extreme conditions.
- Phase Transitions and Fluid inclusion

5 Semiconductors

- Alloy composition
- Defect analysis
- Contamination identification and Doping effects

Microwave Spectroscopy (Rotational Spectroscopy)

Free atoms do not rotate or vibrate. For an oscillatory or a rotational motion of a pendulum, one end has to be tied or fixed to some point. In molecules such a fixed point is the center of mass. The atoms in a molecule are held together by chemical bonds. The rotational and vibrational energies are usually much smaller than the energies required to break chemical bonds. The rotational energies correspond to the microwave region of electromagnetic radiation (3×10^{10} to 3×10^{12} Hz; energy range around 10 to 100 J/mol) and the vibrational energies are in the infrared region (3×10^{12} to 3×10^{14} Hz; energy range around 10 kJ/mol) of the electromagnetic radiation. For rigid rotors (no vibration during rotation) and harmonic oscillators (wherein there are equal displacements of atoms on either side of the center of mass) there are simple formulae characterizing the molecular energy levels. In real life, molecules rotate and vibrate simultaneously and high speed rotations affect vibrations and vice versa

Rotational Spectra of diatomic molecules

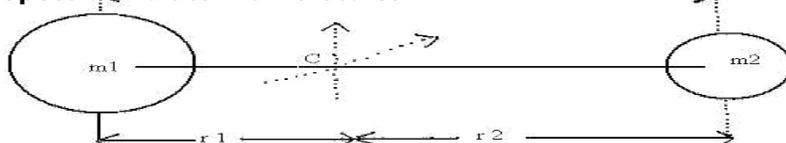


Fig. A rigid diatomic with masses m_1 and m_2 joined by a thin rod of length $r = r_1 + r_2$. The center of mass is at C.

The two independent rotations of this molecule are with respect to the two axes which pass through C and are perpendicular to the “bond length” r . The rotation with respect to the bond axis is possible only for “classical” objects with large masses. For quantum objects, a “rotation” with respect to the molecular axis does not correspond to any change in the molecule as the new configuration is indistinguishable from the old one.

The center of mass is defined by equating the moments on both segments of the molecular axis.

$$m_1 r_1 = m_2 r_2 \tag{1}$$

The moment of inertia is defined by

$$I = m_1 r_1^2 + m_2 r_2^2 \tag{2}$$

$$= \frac{m_1 r_1 r_2}{r_1 + r_2} + \frac{m_2 r_1 r_2}{r_1 + r_2} = \frac{(m_1 + m_2) r_1 r_2}{r_1 + r_2} \tag{3}$$

Since $m_1 r_1 = m_2 r_2$, $m_2 = \frac{m_1 r_1}{r_2}$ (if $m_1 \neq m_2$) Therefore,

$$r_1 = \frac{m_2 r}{m_1 + m_2} \quad r_2 = \frac{m_1 r}{m_1 + m_2}$$

Substituting the above equation in (3), we get

$$I = \frac{m_1 m_2 r^2}{(m_1 + m_2)} = \mu r^2, \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \tag{4}$$

Where μ , the reduced mass is given by

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

The rotation of a diatomic is equivalent to a "rotation" of a mass μ at a distance of r from the origin C.
The kinetic energy of this rotational motion is $\text{K.E.} = \frac{L^2}{2I}$ (5)

where L is the angular momentum, $I\omega$ where ω is the angular (rotational) velocity in radians/sec.

The quantized rotational energy levels for this diatomic are

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \quad (6)$$

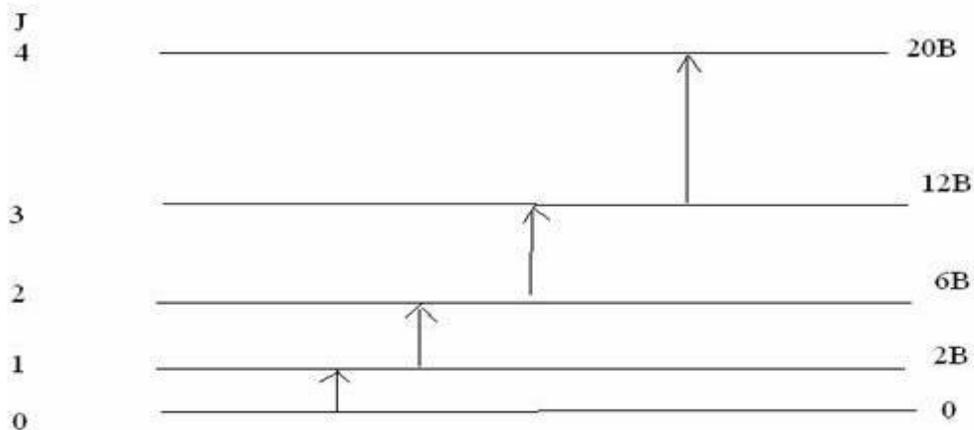
The energy differences between two rotational levels is usually expressed in cm^{-1} . The wave number corresponding to a given ΔE is given by

$$\nu = \Delta E / hc, \text{ cm}^{-1}$$

The energy levels in cm^{-1} are therefore,

$$E_J = B J(J+1) \text{ where } B = \frac{h}{8\pi^2 Ic}$$

The rotational energy levels of a diatomic molecule are shown in Fig.



The selection rule for a rotational transition is, $\Delta J = \pm 1$

$\Delta J = + 1$ absorption

$\Delta J = - 1$ emission

In addition to this requirement, the molecule has to possess a dipole moment, $\mu \neq 0$. A molecule gives a rotational spectrum only if it has a permanent dipole moment. As a dipolar molecule rotates, the rotating dipole constitutes the transition dipole operator μ . Molecules such as HCl and CO will show rotational spectra while H_2 , Cl_2 and CO_2 will not.

For rigid rotor, $J \rightarrow J + 1$, $E_J = BJ(J + 1)$

For the transition; $J = 0 \rightarrow J = 1$

$$\Delta E_j = E_{j=1} - E_{j=0} = 2B - 0 = 2B \text{ cm}^{-1}$$

= position of the first line in the spectrum = $\nu_{j=0 \rightarrow j=1}$

For the transition; $J = 1 \rightarrow J = 2$

$$\Delta E_j = E_{j=2} - E_{j=1} = 6B - 2B = 4B \text{ cm}^{-1}$$

= position of the second line in the spectrum = $\nu_{j=1 \rightarrow j=2}$

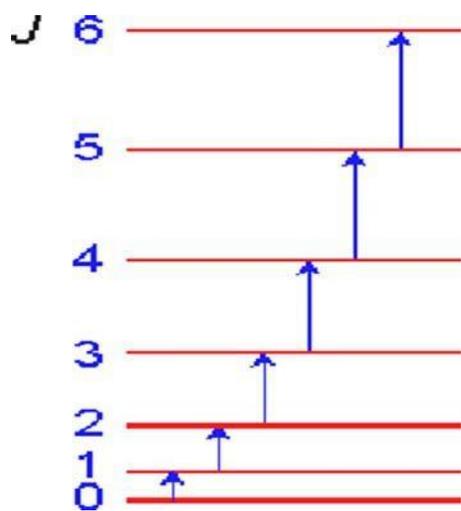
= position of the third line in the spectrum = $\nu_{j=2 \rightarrow j=3}$

Since, The allowed rotational energies are given by; $\nu = BJ(J + 1)$

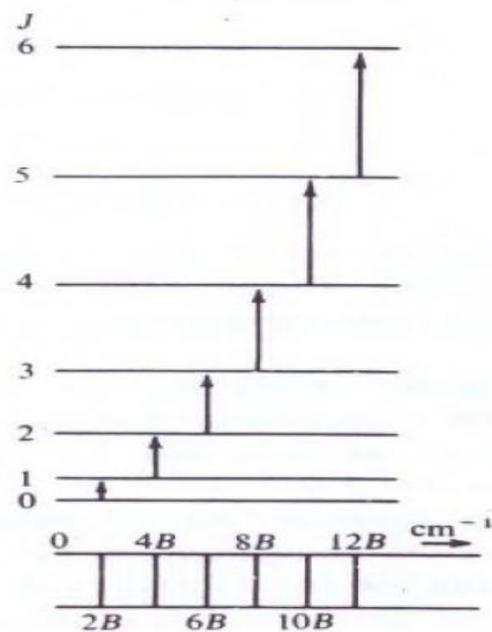
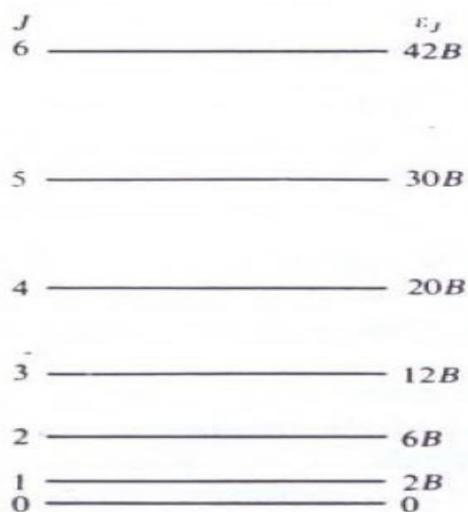
The wave numbers of the different rotational levels will be; 0, 2B, 6B, 12B, 20B, 30B (cm^{-1}),... and so on. And the various lines in the rotational spectra will be equally spaced (separation between lines = 2B).

And for two adjacent rotational states, the energy difference is given by;

$$\Delta E_j = E_{j+1} - E_j = 2B(j+1) \text{ cm}^{-1}$$



Allowed Transition



(i) The allowed rotational energy levels of a rigid diatomic molecule

(ii) Allowed transitions between the energy levels of a rigid diatomic molecule and the spectrum

1. Write the Lambert-Beers' law (absorption law) of UV-VIS spectroscopy. The solution of a compound having concentration 0.1g/L gave 0.2 absorbance value when measured using one cm cell. Calculate its molar absorptivity values. Given M.W of compound is 200.
2. Explain various absorption and intensity shift citing suitable examples.
3. Calculate the value of I and r of CO. $B = 1.92118 \text{ cm}^{-1}$.
4. What do you understand by fingerprint region in IR spectrum?
5. A sample was excited by the 4358 \AA line of mercury. A Raman line was observed at 4447 \AA . Calculate the Raman shift in cm^{-1} .

UNIT III

Electrochemistry

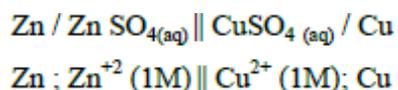
Electrochemistry is the branch of chemistry which deals with the transformation of electrical energy into chemical energy and vice versa.

Electrode Potential: Electrode Potential of a metal is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of unit molar concentration at 25⁰C. Consequently, the tendency of an electrode to lose electrons is a direct measure of its tendency to get oxidized: and this tendency is called, oxidation potential, similarly, the tendency of an electrode to gain electrons is a direct measure of its tendency to get reduced and this tendency is known as reduction potential.

The moment the two electrodes are connected by a wire, the following reactions occur at different electrodes.

Oxidation, takes place at the anode and reduction taken place at the cathode. The electrons flow from anode to cathode.

Representation of Galvanic cell:



- (i) On the left hand side anode is written and on the right hand side cathode is written.
- (i) Anode is written by writing the metal first and then the electrolyte. The two are separated by vertical line or semicolon.
- (ii) Cathode is written by first writing the electrolyte and the metal thereafter. These two are separated by vertical line (or) semicolon.
- (iii) The electrolyte may be represented as complete formula of the whole compound (or) by ionic species.
- (iv) The two half cells, anode and cathode, are separated by double vertical lines which indicate —salt bridge |.

NERNST EQUATION

In the electrochemical series, an electrode or half Cell is said to have a standard value of reduction potential if the concentration of electrolyte is 1M at 298K. Nernst found that the single electrode potential (Reduction potential) varies with the change in concentration of ions and temperature and hence the EMF of the cell also varies. Walter Nernst (1889) derived a mathematical relationship between the standard electrode potential, temperature and the concentration of ions. This relationship is known as the Nernst equation. For a general reduction reaction occurring at an electrode Nernst equation can be written as follows:

At cathode:



$$E_{\text{Cell}} = E_{\text{Cell}}^0 - \frac{2.303}{nF} \log \frac{1}{(M^{n+})}$$

$$E_{\text{Cell}} = E_{\text{Cell}}^0 + \frac{2.303RT}{nF} \log (M^{n+})$$

$$E_{M^{n+}/M} = E_{M^{n+}/M}^0 + \frac{2.303RT}{nF} \log(M^{n+})$$

Where E = Electrode potential of the metal E^0 = Standard EMF of the cell for 1M solution at 298K.
 R = Gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$) T = Kelvin temperature (298K (or) 25°C) n = Number of electrons involved in the cell reaction F = Faraday of electricity, i.e., 96500C.

Substituting the values, $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$; $T = 298\text{K}$; $F = 96500\text{C}$ in the above relation, we get

Let us consider a Daniel Cell in which the concentrations of Zn^{2+} ions and Cu^{2+} ions are different from 1M. In this Cell, zinc acts as anode while copper acts as cathode. Their electrode potentials can be written as:

We know that, $E_{\text{Cell}} = E_{\text{Cathode}} - E_{\text{anode}}$

Substituting the values, we get $E_{\text{Cell}} = E_{\text{Cu}^{2+}/\text{Cu}} - E_{\text{Zn}^{2+}/\text{Zn}}$

$$E_{\text{Cell}} = E_{\text{Cu}^{2+}/\text{Cu}}^0 - \frac{0.0591}{2} \log [\text{Cu}^{2+}] - E_{\text{Zn}^{2+}/\text{Zn}}^0 - \frac{0.0591}{2} \log [\text{Zn}^{2+}]$$

$$E_{\text{Cell}} = E_{\text{Cu}^{2+}/\text{Cu}}^0 - E_{\text{Zn}^{2+}/\text{Zn}}^0 - \frac{0.0591}{2} \log [\text{Cu}^{2+}] - \log [\text{Zn}^{2+}]$$

$$\therefore E_{\text{Cell}} = E_{\text{Cell}}^0 - \frac{0.0591}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]}$$

Electromotive Force (OR) Cell potential (EMF)

The EMF of a cell is a qualitative measurement of the tendency of a net reaction to occur within the cell. Since the net cell reaction is a redox reaction, the EMF of a cell in a way measures relatively the tendency of oxidation reaction to occur at the anode and the tendency of reduction reaction to take place at the cathode of the cell:

Mathematically: EMF OF CELL or $E_{\text{Cell}} = \text{oxidation potential of the anode} + \text{Reduction potential of the cathode}$ Since oxidation takes place at anode and reduction takes place of cathode.

$$E_{\text{Cell}} = E_{\text{anode}} (\text{oxidation}) + E_{\text{cathode}} (\text{Reduction})$$

and $E_{\text{Cell}} = E_{\text{cathode}} (\text{Reduction}) - E_{\text{anode}} (\text{Reduction})$

$$E_{\text{Cell}} = \text{oxd}^{\text{n}} \text{ potential of anode} - \text{oxd}^{\text{n}} \text{ potential of cathode}$$

Applications of Nernst Equation

1. One of the major application of Nernst equation is in determining ion concentration
2. It is also used to calculate the potential of an ion of charge “z” across a membrane.
3. It is used in oxygen and the aquatic environment.
4. It is also used in solubility products and potentiometric titrations.
5. It is also used in pH measurements.

Numerical Problems Based on Nernst Equation

Q1. A copper- silver cell is set up. The copper ion concentration in it is 0.10 M. The concentration of silver ion is not known. The cell potential measured 0.422 V. Determine the concentration of silver ion in the cell. Given:

$$E^{\circ}_{\text{Ag}^+/\text{Ag}} = +0.80 \text{ V}, E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$$

Ans

$$0.422 = 0.46 - 0.029 \left\{ \log[0.1] - \log[\text{Ag}^+]^2 \right\}$$

$$\log[0.1] - 2\log[\text{Ag}^+] = 1.310$$

$$\left(\log 10^{-1} \right) - 2\log[\text{Ag}^+] = 1.310$$

$$-1 - 2\log[\text{Ag}^+] = 1.310$$

$$-2\log[\text{Ag}^+] = 2.310$$

$$\log[\text{Ag}^+] = -1.155$$

$$[\text{Ag}^+] = \text{Antilog}(-1.155)$$

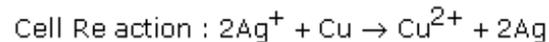
$$[\text{Ag}^+] = 0.0699 \text{ M}$$

$$E_{\text{cell}} = 0.422 \text{ V}$$

Since $E^{\circ}_{\text{Ag}^+/\text{Ag}} > E^{\circ}_{\text{Cu}^{2+}/\text{Cu}}$

So, Ag^+/Ag is cathode and Cu^{2+}/Cu is the anode.

$$\begin{aligned} E_{\text{cell}} &= E_{\text{reduction}} - E_{\text{oxidation}} \\ &= 0.80 - 0.34 \\ &= 0.46 \text{ V} \end{aligned}$$



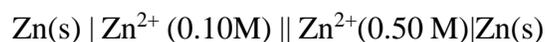
$$E_{\text{cell}} = E_{\text{cell}} - \frac{0.059}{n} \log \frac{[\text{Cu}^{2+}][\text{Ag}]^2}{[\text{Ag}^+]^2[\text{Cu}]^2}$$

$$E_{\text{cell}} = 0.46 - \frac{0.059}{2} \log \frac{[0.1]}{[\text{Ag}^+]^2}$$

Q2. $\text{Zn(s)} | \text{Zn}^{2+}(0.01\text{M}) || \text{Pb}^{2+}(1.0\text{M}) | \text{Pb(s)}$

Given: $E^{\circ}_{\text{Pb}^{2+}/\text{Pb}} = -0.12\text{V}$ and $E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V}$, what is the cell potential of the cell?

Q3. What is the cell potential of the concentration cell described by



Thermodynamic aspect of Electrochemistry and Numerical

1. Work done by the Cell

Let n faraday charge be taken out of a cell of emf E; then work done by the cell will be calculated as:

$$\text{Work} = \text{Charge} \times \text{Potential} = nFE$$

Work done by the cell is equal to decrease in free energy.

$$G = -nFE$$

Similarly, maximum obtainable work from the cell will be

$$W_{\max} = -nFE^{\circ}$$

Where, E° = standard emf or standard cell potential.

$$G = -nFE$$

Concept of Equilibrium in Electrochemical Cell

Let n Faraday charge flows out of a cell of emf E,

$$\text{Then } G = -nFE \dots\dots\dots (i)$$

Gibbs-Helmholtz equation from thermodynamics may be given as

$$\partial G = \partial H + T \partial S \dots\dots\dots (ii)$$

Here ∂S = Entropy

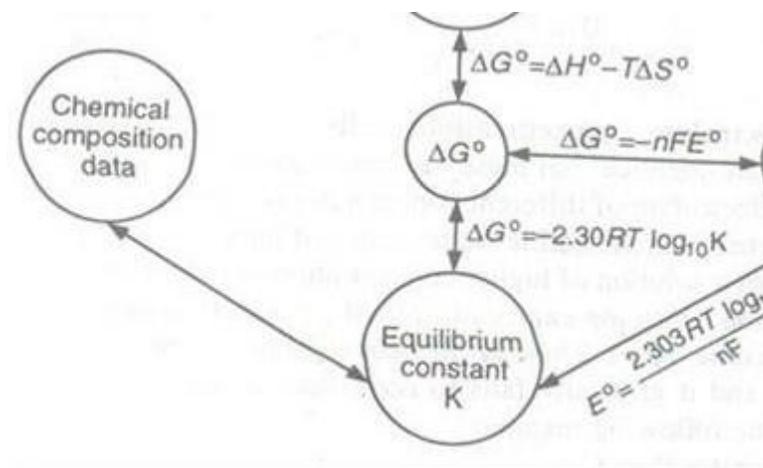


Figure 21

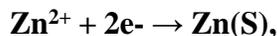
Case I: When $\partial S = 0$, then $\partial H = -nFE$

Case II: When $\partial S > 0$, then $nFE > \partial H$, i.e., process inside the cell is endothermic.

Case III: When $\partial S < 0$, then $nFE < \partial H$, i.e., process inside the cell is exothermic

Numerical Based on EMF of Cell

Q1. Derive Nernst equation. Calculate the half-cell potential at 298 K for the reaction.



if $[\text{Zn}^{2+}]$ is 5.0 M and $E^0_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$

Q2. Calculate the Emf of the cell:



The standard potential of Ag/Ag+ half cell is +0.80 V and Zn/Zn²⁺ is -0.76 V.

Q3. What is the Emf of the following cell at 25°C.



The standard Emf of the cell is 1.54 V.

Q4. Two half cell reactions with their oxidation potentials are



Write the cell reaction and calculate its emf.

Q5. Calculate the Emf of the cell at 25°C.



Batteries

A battery is a storage device used for the storage of chemical energy and for the transformation of chemical energy into electrical energy. It consists of group of two or more electric cells connected together electrically in series. Batteries are of 3 types:

- Primary Batteries (or) Primary Cells or Dry Cells
- Secondary Batteries (or) Secondary Cells
- Fuel Cell

Secondary batteries

- **Lead-Storage or Lead acid Cells**

LEAD ACID BATTERY

In lead acid battery there is a group of cells and in each cell there is one group of positive plates and one group of negative plates. The positive plates are made of lead peroxide (PbO_2) and negative plate is made of spongy lead.

Main parts of lead acid battery

1. Separator

It is most important part of lead acid battery. The separators must be porous so that the electrolyte may circulate between the plates. The separators must have higher insulating resistance and mechanical strength. The material used for separators are wood, rubber, glass wood mate, PVC.

2. Electrolyte

In lead acid battery dilute sulphuric acid (20% H_2SO_4) is used as an electrolyte. The concentration of H_2SO_4 decreases with discharge and is regained on charging as shown in Figure 22.

3. Container

Container is a box of vulcanized rubber, molded rubber, molded plastic, glass or ceramic. On the base of this box there are supports block on which the positive and negative plates are

established. Thus between this supports there are grooves which works like a mud box. The active material separated from the plates get collected in this mud box and it cannot make the contact with the plates thus the internal faults due to the mud are avoided.

4. Vent plug

The vent plug are provide in the cover plate of the cell which are used to fill up the electrolyte in the cell or the inspection of internal condition of the cell the vent plugs are also use for to exhaust the gases generated in the cell to the atmosphere.

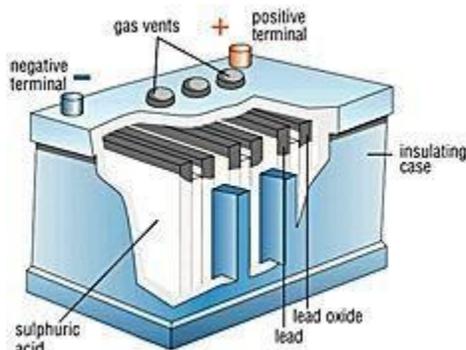


Figure 22

Working

- At the **positive** plate:

$$PbO_2 + 4H^+ + SO_4^{2-} \rightarrow PbSO_4 + 2H_2O + 2e^-$$
- At the **negative** plate: $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$
- Total **Cell Reaction**: $PbO_2 + Pb + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$

Note: Active materials include lead dioxide, lead and sulfuric acid.

Dilute sulfuric acid used for lead acid battery has ratio of acid:water = 1:3. This lead acid storage battery is formed by dipping lead peroxide plate and sponge lead plate in dilute sulfuric acid. A load is connected externally between these plates. In diluted sulfuric acid the molecules of the acid split into positive hydrogen ions and negative sulfate ions.

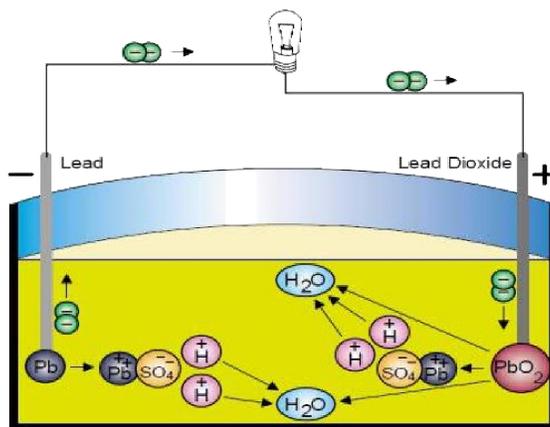
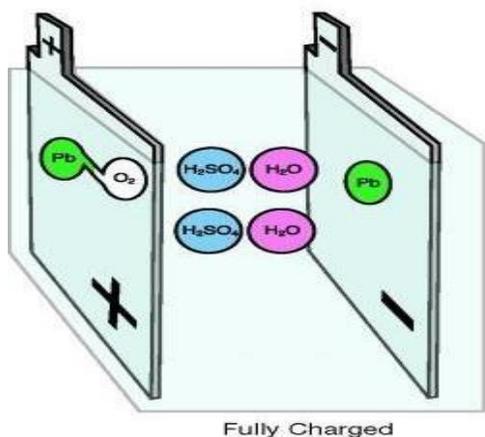


Figure 23

There are 4 stages in discharging-charging process as shown in Figure 23:

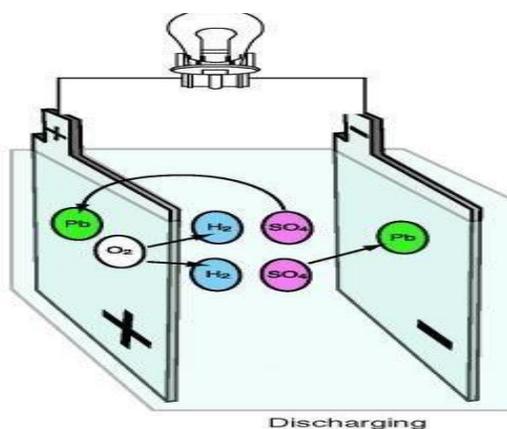
1. Fully charged
2. Discharging
3. Fully discharged
4. Charging



Negative plate covered with lead oxide

Positive plate covered with spongy lead

Fully Charged



Current flows in cell from negative to positive plates

Electrolyte separate into H_2 and SO_4

Discharging

Figure 24

Corrosion

Cause of corrosion

During extraction of metals considerable amounts of energy is required. Consequently, isolated pure metals can be regarded an excited state (higher energy state) than their corresponding ores, and they have a natural tendency to revert back to combined state (lower energy state). Hence when metals are put into use, in various forms, they are exposed to environment (such as dry gases, moisture, liquids etc) and the exposed metal surfaces begin to decay (i.e. conversion into more stable metal compounds) more or less rapidly. In other words, destruction of metal starts at its surface. This type of metallic destruction may be due to direct chemical attack (by the environment) or electrochemical attack.

EFFECTS OF CORROSION: The economic and social consequences of corrosion include.

- (i) Plant shutdown due to failure
- (ii) Replacement of corroded equipment
- (iii) Preventive maintenance (such as painting)
- (iv) Necessity for over design to allow for corrosion.
- (v) Loss of efficiency
- (vi) Contamination or loss of the product (e.g. from a corroded container)
- (vii) Health (e.g. from pollution) due to a corrosion product or due to an escaping chemical from a corroded equipment.

Types of corrosion

Several types of corrosion are often distinguished as follows:

(1) Galvanic Corrosion: This is the most common form of corrosion and can be dry (chemical) or wet (electrochemical). Galvanic corrosion may take place when two different metals incontact (or) (connected by an electrical conductor) are exposed to an electrolytic solution.

The difference in electrical potential between the two metals provides the driving force to pass current through the corroder and results in corrosion of the anodic metal close to the junction of the two metals. The larger the potential difference between the two metals, the greater may be the galvanic corrosion. The relative areas of the cathodic and anodic metals are also important. A much larger area of the more noble metal compared to the active metal, accelerates the attack. When two dissimilar metals (e.g. Zn, Cu) are electrically connected and exposed to an electrolyte the metal higher in electrochemical series (Low E^0 values) undergoes corrosion. This type of corrosion is called galvanic corrosion. In the above example, Zn (higher in electrochemical series or low E^0 value forms the anode and is attacked and gets dissolved, whereas Cu (lower in electrochemical series) acts as cathode. $Zn = -0.763 E^0$ $Cu = +0.153 E^0$

(2) Water – line corrosion: This type of corrosion results from differential aeration leading to the formation of oxygen concentration cells. When water is stagnant in a steel tank for long time, it is observed that corrosion takes place just below the water level.

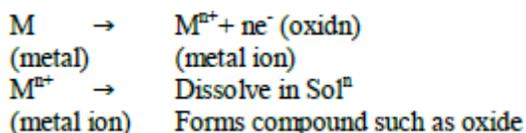
(3) Pitting corrosion: It is a localized attack resulting in the formation of holes in an otherwise relatively unattacked surface. Pitting is generally due to heterogeneity in the metallic surface in presence of a corroding environment, particularly chloride solutions in presence of a depolarizer. A pure and homogeneous metal with a highly polished surface will be much more resistant to pitting than the one with many inclusions, defects on a rough surface. .

(4) Intergranular corrosion: This corrosion is observed in case of alloys. The corrosion product is observed at the boundaries of the grains. Externally, it is not seen. There is sudden failure of material due to this corrosion. For example, during the welding of stainless steel chromium carbide is precipitated at the grain boundaries becomes depleted of chromium composition and is made anodic with respect to solid solution within the grains richer in chromium. Rapid quenching after heat treatment of a metal is the remedy of intergranular corrosion.

(5) Electrochemical or Wet Corrosion: This type of corrosion occurs where a conducting liquid is in contact with metal or when two dissimilar metals or alloys are either immersed or dipped partially in a solution. This corrosion occurs, due to the existence of separate — anodic and cathodic areas, between which current flows through the conducting solution. At anodic area, oxidation reaction (i.e. liberation of free e-s) takes place, so anodic metal is destroyed by

either dissolving in combined state (such as oxide etc). Hence, corrosion always occurs at anodic areas.

At anode :



On the other hand, at cathodic areas, reduction reaction (i.e gain of electrons) takes place. Usually, cathodic reactions do not affect the cathode, since most metals cannot be further reduced.

So at cathodic part, dissolved constituents in the conducting medium accepts the electrons to form some ions (like OH⁻, O₂⁻). The metallic ions (at anodic part) and non – metallic ions (formed at cathodic part) diffuse towards each other through conducting medium and form a corrosion product somewhere between anode and cathode. The electrons set free at the anode flow through the metal and are finally consumed in the cathodic reaction.

The electrochemical corrosion involves:

- (i) Presence of a conducting medium
- (ii) The formation of anodic and cathodic areas in contact with each other
- (iii) Corrosion of anodic areas only
- (iv) Formation of corrosion product somewhere between anodic and cathodic areas.
- (v) Electrochemical corrosion is of two types.
 - (a) Galvanic type corrosion (or) bimetallic corrosion
 - (b) Differential aeration (or) Concentration cell Corrosion

(6) Concentration Cell Corrosion (or) differential aeration corrosion: This type of corrosion is due to electrochemical attack on the metal surface exposed to an electrolyte of varying concentrations (or) of varying aeration. Differential aeration occurs when one part of metal is exposed to a different air concentration from the other part. This causes a difference in potential between differently aerated areas.

Ex: If a Zn metal is partially immersed in a dilute solution of NaCl and the solution is not agitated properly then the parts above and closely adjacent to the water line are more strongly aerated (because of the easy access of oxygen) and hence become cathodic (Figure 25).

On the other hand, parts immersed to greater depth (which have less access of oxygen) show a smaller oxygen concentration and thus become anodic. So, a difference of potential is created, which causes a flow of current between the two differentially aerated areas of the same metal. Zn will dissolve at the anodic areas and oxygen will take up electrons at the cathodic areas to form hydroxyl ions.

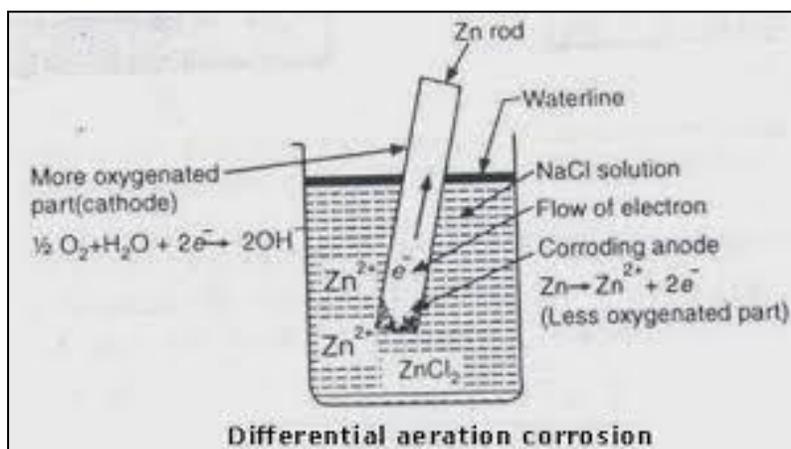
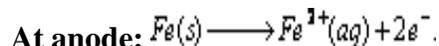


Figure 25

Mechanism of rusting of iron: Electrochemical theory of rusting.

The overall rusting involves the following steps,

(i) Oxidation occurs at the anodes of each electrochemical cell. Therefore, at each anode neutral iron atoms are oxidised to ferrous ions.



Thus, the metal atoms in the lattice pass into the solution as ions, leaving electrons on the metal itself (Figure 26). These electrons move towards the cathode region through the metal.

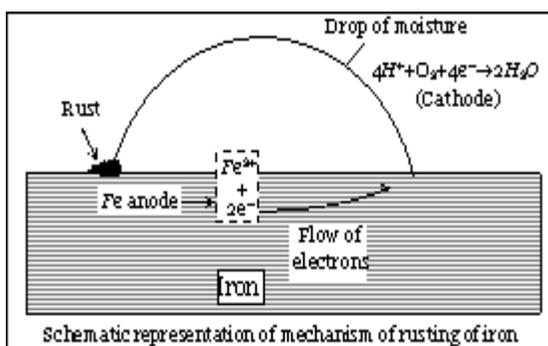
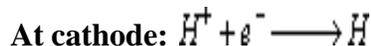


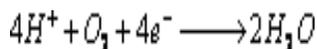
Figure 26

(ii) At the cathodes of each cell, the electrons are taken up by hydrogen ions (reduction takes place). The H^+ ions are obtained either from water or from acidic substances (e.g. CO_2) in water



The hydrogen atoms on the iron surface reduce dissolved oxygen. $4H + O_2 \longrightarrow 2H_2O$

Therefore, the overall reaction at cathode of different electrochemical cells may be written as,



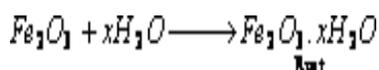
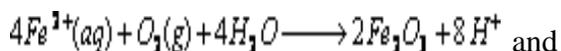
(iii) The overall redox reaction may be written by multiplying reaction at anode by 2 and adding reaction at cathode to equalize number of electrons lost and gained i.e.

Oxidation half reaction: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^- \times 2$ ($E = -0.44V$)

Reduction half reaction: $4H^+ + O_2 + 4e^- \rightarrow 2H_2O$ ($E = 1.23V$)

Overall cell reaction: $2Fe(s) + 4H^+ + O_2 \rightarrow 2Fe^{2+}(aq) + 2H_2O$ ($E_{cell} = 1.67V$)

The ferrous ions are oxidized further by atmospheric oxygen to form rust.



Factors affecting corrosion

The rate and extent of corrosion depends mainly upon two factors—

1. Nature of the metal
2. Nature of the environment

1. Nature of the metal

- **Position in Galvanic Series:** Metal higher in the galvanic series are more likely to undergo corrosion.
- **Relative anodic and cathodic areas:** Corrosion is more rapid if the anodic area is small.
- **Purity of the metal:** Impurities in a metal form minute electrochemical cells and the anodic part gets corroded.
- **Physical state of metal:** The smaller the size of metal greater will be the corrosion and the stressed part of the metal also undergoes faster corrosion.
- **Nature of corrosion product**
- **Solubility of corrosion product:** the corrosion proceeds at a faster rate.

2. Nature of the environment

- **Temperature:** Rise of temperature increases the rate of corrosion.
- **Humidity:** Humidity air is directly related to the rate of corrosion.
- **Effect of pH:** Generally acidic media is $pH < 7$ is more corrosive than alkaline and neutral media.

Corrosion Control Methods Some of the corrosion control methods are described as follows:

1. **Cathodic protection:** The principle involved in this method is —to force the metal to be protected to behave like a cathode, thereby corrosion does not occur. There are two types of cathodic protections. (i) sacrificial anodic protection (ii) impressed current cathodic protection.
2. **Sacrificial anodic protection method:** In this protection method, the metallic structure (to be protected) is connected by a wire to a more anodic metal, so that all the corrosion is concentrated at this more active metal. The more active metal itself gets corroded slowly; while the parent structure (cathodic) is protected. The more active metal so employed is called sacrificial anode. The corroded sacrificial anode block is replaced by a fresh one, when consumed completely.

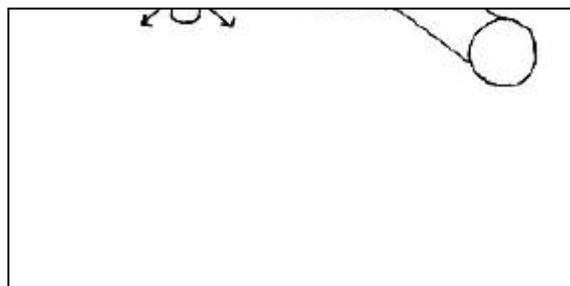


Figure 27

(ii) Impressed current cathodic protection: In this method, an impressed current is applied in opposite direction to nullify the corrosion current and convert the corroding metal from anode to cathode.

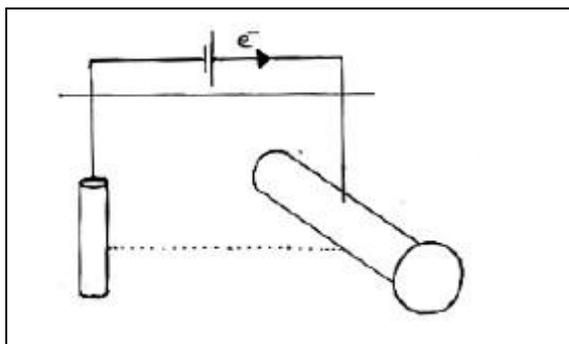


Figure 28

Usually, the impressed current is derived from a direct current source (like battery or rectifier on a.c. line) with an insoluble anode (like graphite, high silica iron, scrap iron, stainless steel or platinum).

3. Coatings A brief description of two important protective coatings (metallic coatings) is given below:

(i) anodic coatings (ii) cathodic coatings:

(i) Anodic Coatings: These are produced from coating metals which are anodic to the base metal (i.e. which is to be protected). Coating of Zn on steel are anodic, because their electrode potentials are lower than that of the base metal iron. If any pores, breaks and discontinuities occur in such an anodic coating, a galvanic cell is formed between the coating metal and the exposed part of the base metal. **Cathodic Coatings:** These are obtained by coating a more noble metal (i.e. having higher electrode potential) than the base metal. They protect the base metal, by their higher corrosion resistance than the base metal.

(ii) Cathodic coating provides effective protection to the base metal only when they are completely continuous and free from pores, breaks or discontinuities. If such coatings are punctured, much more corrosion damages can be done to the base metal than to the coating metal.

Methods of application of metal coating: There are few methods applied for the application of metallic coatings on base metal, namely (1) Hot dipping (2) Metal cladding (3) Electroplating or electrodeposition

(1) Hot dipping: It is used for producing a coating of low melting metal such as Zn (m.p = 4190c) Pb, Al, etc, on iron, steel and copper, which have relatively higher melting points. The process in general consists of immersing the base metal in a bath of the molten coating metal, covered by a molten flux layer. The flux cleans the base metal surface and prevents the oxidation of the molten coating metal. For good adhesion, the base metal surface must be very clear otherwise it cannot be properly wetted by the molten metal. Three most widely applied hot dipping methods are,

- (a) Galvanizing
- (b) Tinning

(a) Galvanizing: The process of coating iron or steel sheets with a thin coat of Zn to prevent them from rusting is called as galvanizing.

(b) Tinning: It is a coating of tin over the iron or steel articles. This process consists of first treating steel sheet in dilute H_2SO_4 acid to remove any oxide film. After this it is passed through a bath of ZnCl_2 flux. The flux helps the molten tin to adhere to the metal sheet. Next, the sheet passes through a tank of molten tin and finally through a series of rollers from underneath the hot tin coated surface of a layer of palm oil. The palm oil protect the hot tin coated surface against oxidation. The rollers remove any excess of Sn and produce a thin film of uniform thickness on the steel sheet.

(2) Metal cladding: It is a process by which a dense, homogenous layer of coating metal is bonded firmly and permanently to the base metal on one or both sides. The choice of cladding material depends on the corrosion resistance required for any particular environment. Nearly all existing corrosion resisting metals (like, Ni, Cu, Pb, Ag, Pt etc.) and alloys (like stainless steel, nickel alloys, copper alloys, lead alloys etc.) can be used as cladding materials and the base metal on which cladding is done are mild steel, aluminum, copper, nickel and their alloys.

(3) Electroplating: Electroplating is the application of electrolytic cells in which a thin layer of metal is deposited onto an electrically conductive surface. A simple example of the electroplating process is the electroplating of copper in which the metal to be plated (copper) is used as the anode and the electrolyte solution contains the ion of the metal to be plated (Cu^{2+} in this example). Copper goes into solution at the anode as it is plated at the cathode. A constant concentration of Cu^{2+} is maintained in the electrolyte solution surrounding the electrodes

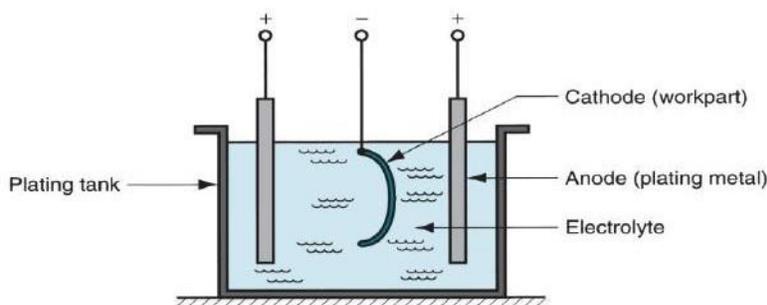
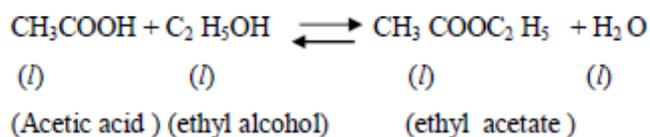
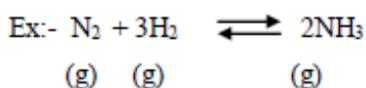


Figure 29

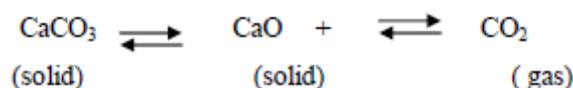
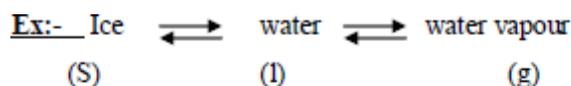
Phase Rule

Phase diagrams are of considerable significance both industrially and commercially, particularly for steels, ceramics, semiconductors. They are basic of separation procedures in petroleum industry, food formulation and in the preparation of cosmetics. Phase rule predicts quantitatively the equilibrium existing between different phases of a heterogeneous system. **System:-** A system refers to a part of space filled with a substance (or) mixture (or) substances and isolated from the surrounding medium. It may include only one phase (or) more than one phases. System is divided into 2 types depending upon the chemical reaction

(a) **Homogeneous system:** A system consisting of only one phase at equilibrium it is called homogeneous system.



(b) **Heterogeneous system:** A system consisting of 2 or more phases at equilibrium, it is called Heterogeneous system.



The phase rule requires a careful use of terms, it contains mainly the 3 important terms namely phase, component and degree of freedom (or) degree of variance.

(A) Phase (P):- A phase is defined as a homogenous, physically distinct and mechanically separable portion of system, which is separated from other homogeneous parts of the system by definite boundary surfaces.

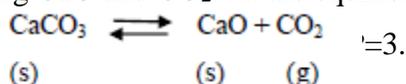
Ex:- (1) In a beaker, the freezing water system contains 3 phases, viz ice(solid), water (liquid) and water vapor (gas) in equilibrium.

(2) Air is the most common example of one phase system, (air which is a mixture of N₂, O₂, CO, water vapor, noble gases).

(3) Mixture of two or more gases and a mixture of two or more miscible liquids is homogeneous, so in such systems, phase is one i.e, P=1. A system consisting of only one phase is said to be homogeneous. Glucose in water, NaCl in water and ethanol in water possess one phase.

(4) Two immiscible liquids, two solids, solid + gas, solid + liquid and liquid + gas constitute two different phases. For example when C₆H₆ and water are mixed, they form two distinct layers, which are physically distinct and mechanically separable, so in such systems, phases are two ;i.e, P=2.

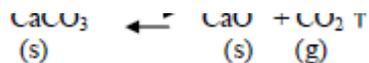
(5) In case of solids each solid constitute one phase. For a mixture of solids, there will be as many phases as the number of solids present in a system at equilibrium; for example, when CaCO₃ is heated it decomposes, giving CaO and CO₂. At the equilibrium, we have 2 solid phases and one gaseous phase. So, in st



(B) Components (C):- It is defined as —Number of components in a system. It is the smallest number of independently variable constituents by means of which the composition of every possible phase in the system can be expressed with a chemical formula. It is denoted by "C". To express the composition of the phases, coefficients like +, — or Zero can be used before the components. **Eg-** In water system , the composition of each phase namely ice, water, (or) water

vapor is given by a single formula H₂O. So the number of components of water system is —one i.e. C=1 and it belongs to single (or) one component system.

Consider another heterogeneous equilibrium.



In the above chemical equilibrium, there are 3 phases, i.e, 2 solid phases and one gaseous phase. The number of independently variable constituents are 3 but the composition of each phase can be expressed in terms of any two of the constituents in taking the quantity of one of the 3 either zero according to need. Hence it is a two component system, i.e, C=2.

(a) If the constituents chosen are CaO and CO₂

Phase	Composition
CaCO ₃	CaCO ₃ + CO ₂
CaO	CaO + CO ₂
CO ₂	“0” CaO + CO ₂

(d) If the constituents chosen are CaCO₃ and CaO

CO ₂	CaCO ₃ - CaO
-----------------	-------------------------

Since at least 2 out of 3 constituents are required to represent the composition of all the phases, the system is a two component system, i.e., C=2.

(C) Degree of freedom (or) degree of variance (F):

Pressure, temperature and concentration (composition) of the phase are the factors which can affect the equilibrium of a system. The minimum number of the variable factors, such as T, P and composition of the phase, which must be arbitrarily fixed in order to define condition of the system completely is termed as degree of freedom (or) variance. The degree of freedom of a system may be one, two, three (or) zero and are known as univariant (mono variant), bi-variant, tri-variant & non-variant system respectively.

Ex:- in case of water system, Ice (s) water (l) water vapor (g) if all the 3 phases are present in equilibrium, then no condition need to be specified, as the 3 phases can be in equilibrium, only at particular temperature (0.00980c) and pressure (4.58 mm). The system is therefore, **zero variant (or) non-variant (or) invariant (or) has no degree** of freedom, i.e., $F=0$. If condition (Ex: Temp, pressure) is altered, three phases will not remain in equilibrium and one of the phase disappears.

For a system consisting of water in contact with its vapor, Water vapor (g) Water (l) We must state either the temperature (or) pressure to define it completely. Hence, degree of freedom is one(or) system is univariant, i.e., $F=1$. (iii) For a gaseous mixture of N_2 and H_2 we must state the pressure and temperature, because if P and T are fixed, the volume automatically becomes definite. Hence, for a gaseous system, two factors must be stated in order to define it completely and thus, it has two degrees of freedom (or) system is bivariant i.e. $F = 2$.

Phase Rule: For the study of the behavior of the heterogeneous systems an important generalization was put forward by **J. William Gibbs** (American Physicist) known as — phase rule, is applicable to all heterogeneous systems in equilibrium without any exception. It states that — when the heterogeneous equilibrium between different phase is not influenced by gravitational forces, electrical forces or by magnetic force, but only by temperature, pressure and composition, the sum of the number of phases (P) and the number of degree of freedom (F) always exceeds the number of component (c) by 2. The relation is as follows. $F + P = C + 2$ (or) $F = C - P + 2$

Uses of phase rule

- (1) Phase rule provides a convenient basis for classification of systems with the help of phases, components, degrees of freedom.
- (2) The phase rule indicates that different systems having same degrees of freedom behave in a similar fashion.
- (3) It is applied to macroscopic systems here information about molecular structure is not required.

Limitations

- (1) The phase rule can be applied only for systems in equilibrium. It is not applicable to system which attain equilibrium at a later stage.
- (2) All the phases must be present under same conditions of temperature and pressure.
- (3) Only three degrees of freedom are allowed to influence the equilibrium system.

Phase Diagram: It may be defined as a plot showing the conditions of pressure and temperature (or temperature and composition) under which two or more physical states of a system can exist together in a state of dynamic equilibrium.

One component system (Water system)

Under normal conditions the system water is a three phase, one component system. In this system ice= water = vapor exists in equilibrium. All the 3 phases can be represented by one chemical formula H_2O . Hence it is a one component system.

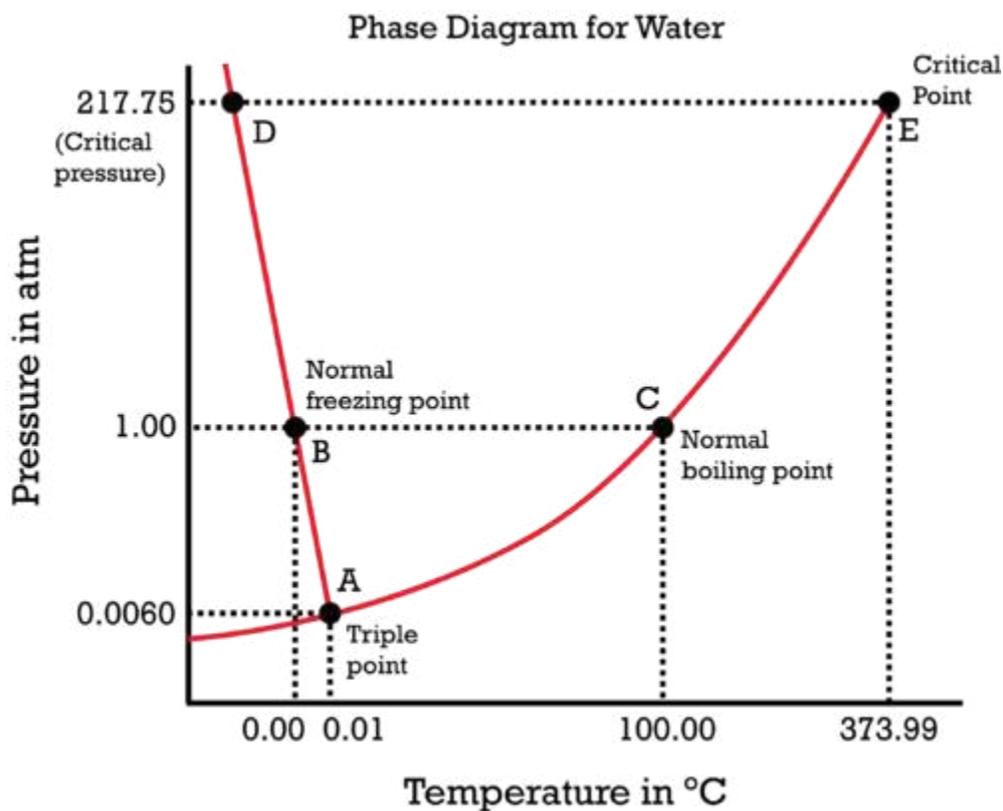


Figure 30: Phase diagram

The phase diagram of water system consists of three important features, namely lines (or) curves, regions (or) areas and triple point (Figure 30).

1. Line (or) curves: The phase diagram of water system consists of 4 curves OA, OB, OC and OA1.

(A) OA CURVE: This is the vapor pressure curve of water. It represents the equilibrium between liquid water and water vapor at different temperatures. The starting point of the curve is “O” and ends at “A” to analyze the curve, consider any point on the curve. For a fixed value of pressure, temperature has also a fixed value. So to define the system, completely at any time, it is necessary to mention either pressure (or) temperature. Thus water vapor system is univariant (or) has one degree of freedom. It may also be shown by phase rule equation.

$$P = 2 \text{ (water vapour); } C = 1 \text{ } F = C - P + 2 = 1 - 2 + 2; F = 1$$

(B) OB Curve: This is the sublimation curve of Ice. It represents the equilibrium between ice and vapor at different temperatures. The starting point of the curve is “O” and ends at “B” from the diagram it is obvious that for a particular temperature there can be one and only one pressure. Similarly, for each pressure, there is only one temperature at which both the phases co- exist. Thus, ice, vapor system is univariant or has one degree of freedom. It may also be shown by the phase rule equation.

$$P = 2; C = 1 \text{ } F = C - P + 2 = 1 - 2 + 2; F = 1.$$

(C) OC curve: This is the melting point curve of ice. It represents the equilibrium between ice and water. The starting point of the curve is “O” and ends at “C”. It is to be noted that the line inclines towards the pressure axis which shows that expansion takes. Place on freezing of water and melting point of ice is increased by increase of pressure. At any point of the curve two phases are in equilibrium this system is univariant system or has one degree of freedom. It may also be shown by phase rule equation.

$$P=2; C=1 \text{ } F=C-P+2 = 1-2+2; F=1.$$

(D) OA curve: The dotted curve OA is a continuation of the OA curve and represents the vapor pressure (Vaporization) curve of super cooled water. This curve is known as Meta stable curve. When slight disturbance is there the super cooled phase at once change to solid, ice and the curve merges into OB.

(2) Areas (or) Regions: The phase diagram of water system has 3 regions namely AOB, AOC and BOC.

(a) AOB Curve: Represents water vapor phase only.

(b) AOC Curve: Represents liquid water phase only.

(C) BOC Curve: Represents ice phase only.

Consider a point “D” in the area AOC, by increasing both “T” and “P” simultaneously it moves to another point “E” in the same area (AOC).there is no change in the number of phases even though two variables are changed simultaneously. Thus “P” and “T” are the 2 quantities to define the system completely at any point in area, so the system represented by area has two degree of freedom or bivariant. According to phase rule:

$$C = 1 \quad P = 1 \quad F = C - P + 2 = 1 - 1 + 2; \quad F = 2.$$

3 Triple point: In water system, it is the point where the 3 curves OA, OB and OC meet together. At this point, all the 3 phases are in equilibrium. At point ‘O’ temperature and pressure are fixed at 0.00980c and 4.58 mm respectively. Since on changing either, temperature or pressure, one of the phase disappears. So the system has Zero degree of freedom, or invariant at the point “O” this can be shown by phase rule equation also,

$$C = 1 \quad P = 3 \quad F = C - P + 2 = 1 - 3 + 2; \quad F = 0.$$

UNIT IV

WATER AND ITS TREATMENT

Hardness of water

Causes of hardness of water

Hardness of water is that characteristic, which prevents the lathering of soap. This is due to presence of Ca and Mg salts in water. Water passes through rocks and flows on the ground. The calcium and magnesium salts that are present in the rocks are dissolved in water and make it hard. A sample of hard water, when treated with soap (sodium stearate) doesn't produce lather, but forms a white scum or precipitate. This precipitate is formed, due to the formation insoluble soaps of calcium and magnesium. Typical reactions of soap (sodium stearate) with calcium chloride and magnesium sulphate are depicted as follows:

Sodium stearate

Magnesium stearate

Thus, water which does not produce lather with soap solution readily, but forms white precipitate, is called hard water. On the other hand water which lathers easily on shaking with soap solution, is called soft water. Such water, consequently, does not contain dissolved calcium and magnesium salts in it.

Types of Hardness

Hardness of water is of two types:

- (a) Temporary hardness (carbonate hardness)
- (b) Permanent hardness (non – carbonate hardness)

(a) **Temporary hardness (carbonate hardness):** The hardness that can be removed simply by boiling is called the temporary hardness. It is due to the presence of dissolved bicarbonates, Temporary hardness is mostly destroyed 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. Thus,

(b) **Permanent (or) Non – carbonate hardness:** Permanent hardness cannot be removed by boiling. It is due to the presence of chlorides and sulphates of calcium, magnesium ions and other heavy metals. These salts cannot be removed by boiling. They are removed by different other methods.

Measurement of Hardness: To estimate hardness, it is essential to know the various units to measure it. Hardness of water is measured in terms of CaCO_3 because it is highly insoluble in water and also its molecular weight is 100 that make the calculation easier.

Units of Hardness:

(i) Parts per million (ppm)

It is defined as the number of parts of equivalent CaCO_3 per 10^6 part of water i.e. $1\text{ppm} = 1\text{part of } \text{CaCO}_3 \text{ equivalent hardness in } 10^6 \text{ parts of water.}$

(ii) Milligrams per liter (mg/L)

It is the number of milligrams of equivalent CaCO_3 present per liter of water.

$1\text{mg} / 1 = 1 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness per liter of hard water.}$

$1\text{mg} / 1 = 1\text{mg of } \text{CaCO}_3\text{eq per } 10^6 \text{ mg of water.} = 1 \text{ part of } \text{CaCO}_3\text{eq per } 10^6 \text{ parts of water} = 1\text{ppm}$

(iii) Degree Clarke (°Cl)

It is the number of grains of equivalent CaCO_3 per gallon of water (or) it is parts of CaCO_3

per gallon of water.

It is thus, parts of CaCO_3 equivalent hardness per 70,000 parts of water. Thus,

$10^\circ\text{Clarke (}10^\circ\text{Cl)} = 1$ grain of CaCO_3 eq. hardness per gallon of water or

$10^\circ\text{Cl} = 1$ part of CaCO_3 equivalent hardness per 70,000 parts of water.

(iv) Degree French (°Fr)

It is the number of parts of CaCO_3 per 10^5 parts of hard water thus,

$10\text{Fr} = 1$ part of equivalent CaCO_3 per 10^5 parts of hard water

Relation among units of hardness

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

Numerical Problems based on hardness of water

Although hardness of water is never present in the form of CaCO_3 because it is insoluble in water, hardness of water is conveniently expressed in terms of equivalent amount of CaCO_3 . The reason for choosing CaCO_3 as the standard for reporting – hardness of water is the ease in calculations as its molecular weight is exactly 100. Moreover, it is the most insoluble salt that can be precipitated in water treatment.

$$\text{Equivalents of CaCO}_3 = \frac{\left[\text{Mass of hardness producing substance in mg/l} \right] \times \left[\text{Chemical Equivalent of CaCO}_3 (50) \right] \times 2}{\left[\text{Chemical equivalent of hardness producing substance} \right] \times 2}$$

$$\text{Equivalents of CaCO}_3 = \frac{\left[\text{Mass of hardness producing substance in mg/l} \right] \times \text{g. mol wt. of CaCO}_3 \times 100}{\left[\text{Chemical equivalent of hardness producing substance} \right]}$$

1	Ca(HCO ₃) ₂	162	81	100/162
2	Mg(HCO ₃) ₂	146	73	100/146
3	CaSO ₄	136	68	100/136
4	CaCl ₂	111	55.5	100/111
5	MgSO ₄	120	60	100/120
6	Mg Cl ₂	95	47.5	100/95
7	CaCO ₃	100	50	100/100
8	MgCO ₃	84	42	100/84
9	Mg ((NO ₃) ₂	148	74	100/148

1. A water sample contains 408mg of CaSO₄ per litre. Calculate the hardness in terms of CaCO₃ equivalents.

Solution : Hardness = [Mass of hardness producing substance] × M
 Hardness = [Mass of CaSO₄ in mg/ l] × M
 Hardness = 408 × 100/136
 Hardness = 300 mg/ l (or) 300 ppm

2. A sample of water analysis was found to contain the following impurities.

Impurity	Ca (HCO ₃) ₂	Mg (HCO ₃) ₂	CaSO ₄	MgSO ₄
M.Wt	162	146	136	120
Quantity(amount)	4	6	8	10

Calculate the temporary, permanent and total hardness of water in ppm, °Cl and °Fr

Solution :

Constituent	Amount (A) mg/l	Multification Factor(M)	CaCO ₃ Equivalent = [A] × [M]
Ca(HCO ₃) ₂	4	100/162	4 × 100/162 = 2.47 mg / l
Mg(HCO ₃) ₂	6	100/146	6 × 100/146 = 4.11 mg / l
CaSO ₄	8	100/136	8 × 100/136 = 5.88 mg / l

Step : II – Determination of temporary hardness

As temporary hardness is due to bicarbonates of Ca and Mg therefore temporary hardness.

$$\text{Temporary hardness} = 2.47 + 4.11 = 6.58 \text{ mg / l}$$

Hence, Temporary hardness = 658 mg / l = 6.58 ppm

$$= 6.58 \times 0.07 = 0.46^{\circ}\text{Cl}$$

$$= 6.58 \times 0.1 = 0.658^{\circ}\text{Fr}$$

Step – III : Determination of permanent hardness

As permanent hardness in this case is due to CaSO_4 and MgSO_4

$$\text{Permanent Hardness} = 5.88 + 8.33 = 14.21 \text{ mg/l}$$

$$= 14.21 \text{ ppm}$$

$$= 14.21 \times 0.07 = 0.995^{\circ}\text{Cl}$$

$$= 14.21 \times 0.1 = 1.421^{\circ}\text{Fr}$$

Total Hardness = Temp Hardness + Permanent Hardness

$$= 6.58 + 14.21$$

$$= 20.79 \text{ mg/l (or) ppm}$$

$$= 20.79 \times 0.07 = 1.4553^{\circ}\text{Cl}$$

$$\text{Total Hardness} = 20.79 \times 0.1 = 2.079^{\circ}\text{Fr}$$

3. Calculate the carbonate hardness and non-carbonate hardness of a sample of water containing the dissolved salts in one liter of hard water as given below also calculate the total hardness/ $\text{Ca}(\text{HCO}_3)_2 = 32.4\text{mg}$; $\text{CaSO}_4 = 13.6\text{mg}$; $\text{MgCl}_2 = 19.00\text{mg}$; $\text{Mg}(\text{HCO}_3)_2 = 14.6\text{mg}$

Hardness Producing Salts	Amount	Minimization Factor	Equivalent of CaCO_3 - hardness
$\text{Ca}(\text{HCO}_3)_2$	32.4mg	100/162	$32.4 \times 100/162 = 20\text{mg/l}$
CaSO_4	13.6mg	100/136	$13.6 \times 100/136 = 10\text{mg/l}$
MgCl_2	19.0mg	100/95	$19.0 \times 100/95 = 20\text{mg/l}$
$\text{Mg}(\text{HCO}_3)_2$	14.6mg	100/146	$14.6 \times 100/146 = 10\text{mg/l}$

Carbonate hardness due to $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2 = 20 + 10 + 30 \text{ mg / l (or) ppm}$
 Non carbonate hardness (permanent hardness) due to CaSO_4 & $\text{MgCl}_2 = 10+20 = 30 \text{ mg/ l (or) ppm}$
 Total Hardness = $30 + 30 = 60 \text{ mg / l (or) ppm}$.

Disadvantages of Hard Water

Boiler troubles

Boiler troubles are mainly caused by the impurities present in the boiler feed water. The total removal of salts in boiler feed water is not made use of the scales produced in the boilers can act as insulators of heat. As a result of it more heat has to be supplied from outside of the boilers. The major boiler troubles are:

- (1) Scales and sludge formation
- (2) Caustic embrittlement
- (3) Boiler corrosion
- (4) Priming and foaming

(1) Scales and sludge formation:

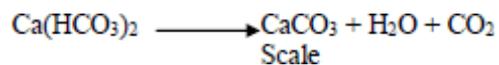
When water is evaporated in boilers to produce steam continuously the concentration of the salts present in the water increases progressively. As the concentration reaches a saturation point the salts are thrown out of water as precipitates either as sludge or as scale adhering to the walls of the boiler. If the precipitate formed is soft, loose and slimy, it is called sludge. If the precipitate produced is hard and adheres very strongly to the walls of the boilers, it is known as scale.

Reasons for scale and sludge formation

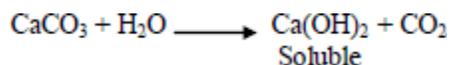
- (a) The solubility product of the salt must be exceeded by the product of concentration of constituent ions.
- (b) The solubility of the salt decreases with rise of temperature
- (c) The increase in the temperature can lead to reactions that results in the formation of insoluble.

Scales: Scales are hard deposits, which stick very firmly to the inner surface of the boiler. Scales are difficult to remove even with the help of hammer and chisel. Scales are the main source of boiler troubles. Scales may be formed inside the boiler due to :

(i) Decomposition of calcium bicarbonate

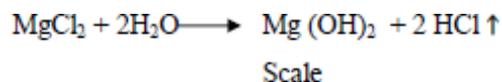


However scale composed chiefly of calcium carbonate is soft and is the main cause of scale formation in low – pressure boilers but in high pressure boilers, CaCO₃ is soluble



(ii) Deposition of calcium sulphate: The solubility of CaSO₄ in water decreases with rise of temperature. Thus, solubility of CaSO₄ is 3200ppm at 15⁰C and it reduce to 55ppm at 30⁰C and 27 ppm at 32⁰C. In other words, CaSO₄ is soluble in cold water, but almost completely insoluble in super-heated water. Consequently, CaSO₄ gets precipitated as hard scale on the boiler. This is the main cause of scales in high – pressure boilers.

(iii) Hydrolysis of Magnesium salts. Dissolved Mg salts undergo hydrolysis forming magnesium hydroxide precipitate, which forms a soft type of scale.



(iv) Presence of Silica (SiO₂) Even present in small quantities, deposits as calcium silicate (CaSiO₃) and / or Magnesium silicate (MgSiO₃), these deposits stick very firmly on the inner side of boiler surface and is very difficult to remove. One important source of silica in water is the sand filter.

Sludge: Sludge is a soft, loose and slimy deposit formed within the boiler as shown in Figure Sludge can easily scrapped off with a wire brush. It is formed at comparatively colder portions of the boiler and collects in areas of the system, where the flow rate is slower or at bends. Sludge is formed by substances which have greater solubility in hot water than in cold H₂O. ex: MgCO₃, MgCl₂, CaCl₂, MgSO₄ etc.

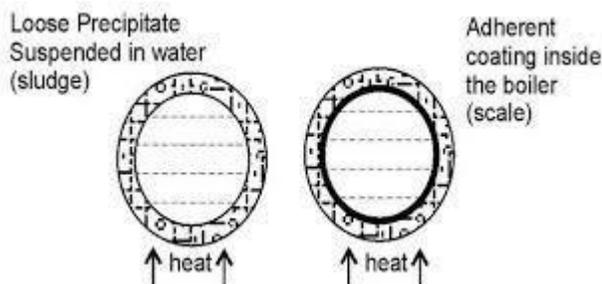


Figure: Scale and sludge

Disadvantages of sludge formation

- (1) Sludge is poor conductor of heat, so they tend to waste a portion of heat generated.
- (2) If sludge are formed along with scales, then former gets entrapped in the latter and both get deposited as scales.
- (3) Excessive sludge formation disturbs the working of the boiler. It settles in the regions of poor water circulation, such as pipe connection, plug opening, thereby causing even choking of the pipes.

Prevention of sludge formation

- (1) By using well softened water.
- (2) By frequently blow – down operation

(2) Caustic embrittlement:

Caustic embrittlement is a type of boiler corrosion, caused by using highly alkaline water in the boiler. During softening process by lime – soda process, free Na_2CO_3 is usually present in small proportion in the softened water. In high pressure boilers, Na_2CO_3 decomposes to give NaOH and CO_2 and this makes the boiler water —Caustic



The iron surrounded by dilute NaOH behaves as cathode while the iron in contact with concentrated NaOH becomes anode which is consequently dissolved or corroded.

Prevention of Caustic embrittlement:

- (1) By using sodium phosphate (Na_3PO_4) as softening reagent, instead of sodium carbonate (Na_2CO_3)
- (2) Neutralizing alkali (NaOH) with a very small amount of acid
- (3) By adding tannins or lignin to boiler water since these blocks the hair cracks, thereby preventing infiltration of caustic soda solution in these.

(4) By adding small amount of Na_2SO_4 to boiler water in order to block small hair cracks at stressed areas.

(3) Boiler Corrosion:

Boiler corrosion is —decay of boiler material by a chemical or electrochemical attack of its environment. The main reasons for boiler corrosion are:

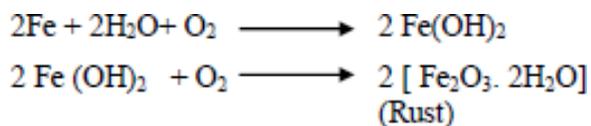
(a) Dissolved Oxygen

(b) Dissolved CO_2

(c) Acids produced by the hydrolysis of dissolved salts

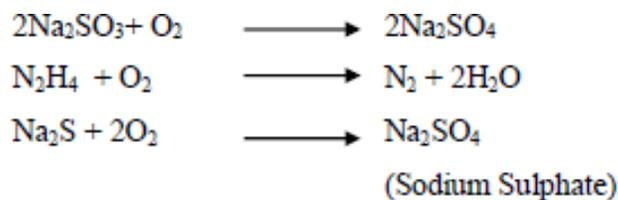
(d) Dissolved oxygen: Water usually contains about 8ml of O_2 in presence of prevailing high temperature attacks boiler material.

(a) Dissolved oxygen: Water usually contains about 8ml of O_2 in presence of prevailing high temperature attacks boiler material.



Removal of Dissolved oxygen

(i) By adding calculated quantity of sodium sulphite (Na_2SO_3) or hydrazine (N_2H_2) or sodium sulphide. Thus,



(ii) By mechanical de-aeration i.e. water sparging in a perforated plate fitted tower heated from side and connected to vacuum pump. High temperature, low pressure and large exposed surface (provided by perforated plates) reduce dissolved oxygen in water.

(4) Priming and foaming:

When steam is produced rapidly in the boilers, some droplets of the liquid water are carried along with the steam. This process of wet steam formation is called priming. Priming is caused due to:

- (a) The presence of considerable quantities of dissolved solids (mainly – due to suspended impurities and due to dissolved impurities in water)
- (b) Steam velocities high to carry droplets of water into the steam pipe.
- (c) Sudden boiling
- (d) Improper or faulty design of boiler
- (e) Sudden increase in steam production rate.

Priming can be avoided by:

- (i) Controlling rapid change in steaming velocities.
- (ii) The proper design of boiler
- (iii) By blowing off sludge and scales from time to time
- (iv) Maintaining low water levels in boilers

Foaming: Foaming is the formation of small but persistent foam or bubbles at the water surface in boilers, which do not break easily. Foaming is caused by the presence of oil and alkalis in boiler feed water. Actually oils and alkalis react to form soaps which greatly lower the surface tension of water and thus increase the foaming tendency of the liquid.

Foaming can be avoided by:

- (a) The addition of anti-foaming agents, like castor oil which acts by counteracting the reduction in surface tension.

(b) Removal of oil from boiler water by adding compounds like sodium aluminate (NaAlO_2)

Zeolite process

Zeolites are hydrated sodium aluminosilicates capable of exchanging its sodium ions with hardness producing cations in water.

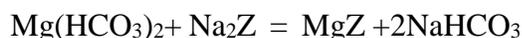
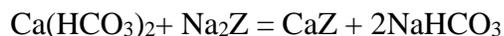


Zeolites are of two types:

- (i) **Natural Zeolites:** These are amorphous and non porous in nature. They are derived from green sand by washing, heating and treating with NaOH. E.g. Natrolite- $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
- (ii) **Synthetic Zeolites:** These are porous and are prepared by heating together solutions of sodium silicate, sodium aluminate and aluminium sulphate.

Principle and working of Zeolit/Permutit process:

Zeolites can be represented as Na_2Z from which Na can easily be replaced by Ca and Mg ions present in hard water.



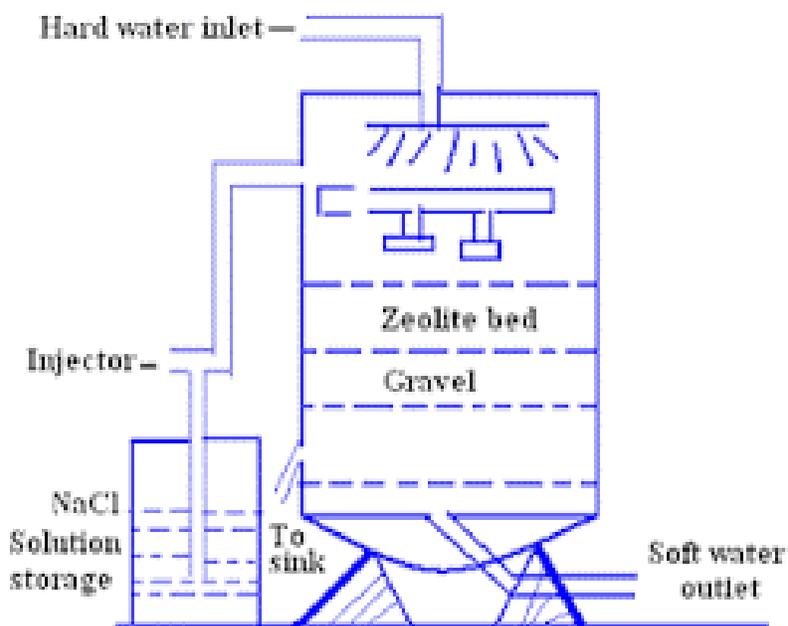
Hard water is percolated through Zeolite bed in a cylindrical tank. Sodium ions are replaced by Ca^{2+} and Mg^{2+} ions to form CaZ and MgZ. After sometimes the bed gets exhausted. At this stage supply of water is stopped and regeneration is carried out by passing 10% brine solution.

Advantages of Zeolite process

1. Water of about 15 ppm hardness is obtained.
2. Mineral acids destroy the zeolite bed so they must be neutralised before hand.
3. Acid radicals which are not removed during softening cause caustic embrittlement and boiler corrosion.



4. If large quantities of Fe^{2+} and Mn^{2+} are present in water it converts zeolite into iron and manganese zeolite which cannot be regenerated.



Disadvantages of zeolite process:

1. Turbid water cannot be used-the suspended impurities will clog the pores of zeolite.
2. Mineral acids should be removed/neutralized mineral acids destroy the zeolite.
3. If water contains large amounts of coloured ions such as Mn^{2+} and Fe^{3+} it must be pretreated because the corresponding manganese and iron zeolite cannot be easily regenerated.
4. Zeolite treatment replaces only the cations like Mg^{2+} and Ca^{2+} , leaving all the anions like HCO_3^- and CO_3^{2-} in the soft water

5. HCO_3^- ions will decompose in boiler and release CO_2 corrode the boiler

Ion exchange (or) de-ionization (or) de-mineralization process

Ion – exchange resins are insoluble, cross – linked, long chain organic polymers with a micro porous structure, and the functional groups attached to the chains are responsible for the ion – exchanging properties. Resins containing acidic functional groups ($-\text{COOH}$, SO_3H etc.) are capable of exchanging their H^+ ions with other cations, which comes in their contact, whereas those containing basic functional groups ($-\text{OH}$) are capable of exchanging their anions, which comes in their contact. The ion – exchange resins may be classified as:

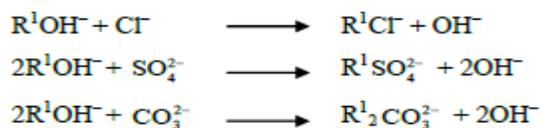
(i) **Cation Exchange resins (RH^+):** These are mainly sulphonated styrene copolymers. These are capable to exchange their hydrogen ions with the cations, in the water (Figure 32).

(ii) **Anion Exchange Resin**

Process: The hard water is passed first through cation exchange column, which removes all the cations as Ca^{+2} , Mg^{+2} etc. from it, and equivalent amount of H^+ ions are released from this column to water. Thus:



After cation exchange column the hard water is passed through anion exchange column, which removes all the anions like etc. present in the water and equivalent amount of OH^- ions are released from this column to water, thus; SO_4^{2-} , CO_3^{2-}



H^+ and OH^- ions (released from cation exchange and anion exchange columns respectively) get combined to produce water molecule. Thus, water coming out from the exchanger is free from cations as well as anions. Ion free water is known as deionized or demineralised water.



Regeneration: When ion exchange capacities of cation and anion exchangers are lost, they are then said to be exhausted. The exhausted cation exchange column is regenerated by passing a solution of dil. HCl (or) dil. H₂SO₄. The column is washed with deionized water and washing (which contains Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻ ions) is passed to sink or drain. The exhausted anion exchange column is regenerated by passing a solution of dil. NaOH. The regeneration can be represented as:



The column is washed with deionized water and washing (which contains Na⁺ and SO₄²⁻ or Cl⁻ ions) is passed to sink or drain. The regenerated ion exchange resins are then used again.

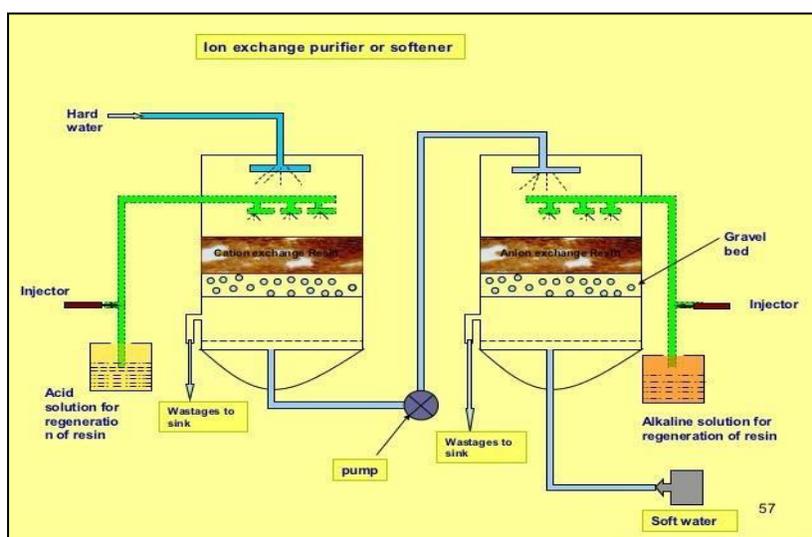


Figure 32: Diagrammatic representation of Ion exchange column

Advantages:

- (a) The process can be used to soften highly acidic or alkaline water.
- (b) It produces water of very low hardness (say 2ppm). So it is very good for treating water for use in high pressure boilers.
- (c) The softened water is completely free from salts.

Disadvantages:

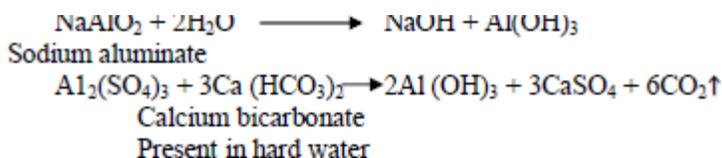
- (a) The equipment is little expensive.
- (b) If water contains turbidity then the output of the process is reduced. The turbidity must be below 10ppm.

Lime Soda Process

Lime $[\text{Ca}(\text{OH})_2]$ and soda $[\text{Na}_2\text{CO}_3]$ are the reagents used to precipitate the dissolved salts of Ca^{+2} and Mg^{+2} as CaCO_3 and $\text{Mg}(\text{OH})_2$.

- The precipitated CaCO_3 and $\text{Mg}(\text{OH})_2$ are filtered off.
- Lime reacts with temporary hardness, CO_2 , acids, bicarbonates and alums.
- Lime cannot remove the calcium permanent hardness which should be removed by soda.
- The precipitation reactions with lime and soda are very slow.
- Only calculated amounts of lime and soda are to be added. Excess amount of lime & soda causes boiler troubles like caustic embrittlement.
- Calculation of lime & soda required for the process:

(A) **Cold Lime – Soda Process** : In this method, calculated quantities of lime and soda are mixed with water at room – temperature. The precipitates formed are very fine and hence cannot be removed by filtration immediately. Normally it takes about 24hrs for setting. To hasten setting, coagulants like sodium aluminate, aluminum sulphate or Alum (potash alum) have to be added. These coagulants get hydrolyzed to gelatinous precipitates of aluminum hydroxide which easily entrap the fine particles of solids and help them to settle.



The residual hardness of cold L-S process treated water is generally 50-60 ppm. Cold lime – soda process can be carried out by 2 methods:

(1) Batch process (intermittent type)

(2) Continuous Process

(1) Batch process: This process is carried out in tank provided with mechanical stirrers for thorough mixing. Calculated quantities of lime and soda are added to the water tank and thoroughly mixed. Required amount of a coagulant is also added to facilitate settling down of the precipitate. It takes about 2 hrs for the precipitate to settle down completely at the bottom of the tank, when it kept undisturbed. The softened water from the top is drawn out using pump and passed through sand filters. The sludge formed at the bottom is removed and cleaned with water. Now the tank is ready for another batch of operation.

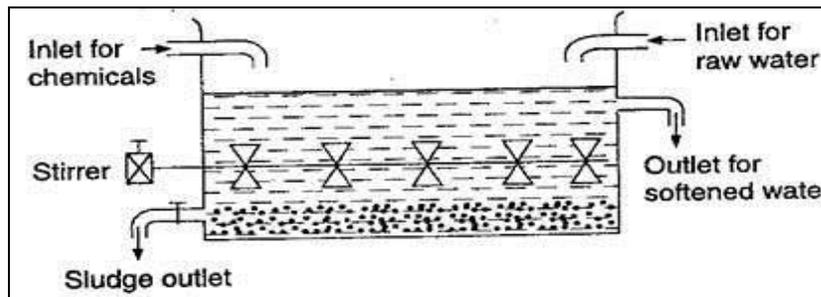


Figure 33

(2) Continuous Process: Raw water and calculated quantities of chemical (lime + Soda+ Coagulants) are fed from the top into the inner vertical chamber, fitted with a vertical rotating stirrer carrying a number of blades. As the raw water and chemical flow down, there is a vigorous stirring and continuous mixing, whereby softening of water takes place. As the softened water comes into the outer co – axial chamber, it rises upwards. The heavy sludge settles down in the outer chamber by the time the softened water reaches up. The softened water then passes through a filtering media (usually made of wood) to ensure complete removal of sludge. Filtered soft water finally flows out continuously through the outlet at the top. Sludge settling at the bottom of the outer chamber is drawn off occasionally.

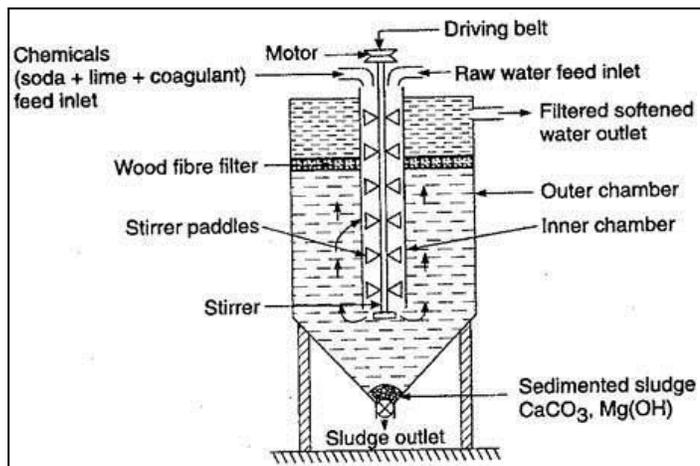


Figure 34

(B) **Hot Lime – Soda Process:** This process is operated at a higher temperature of 90 – 100°C. The following advantages result from the use of the high temperature of operation.

- (i) The reaction rate is increased and the softening reaction is completed in about 15 minutes.
- (ii) Sludge settles faster and the addition of coagulants is not required.
- (iii) Dissolved gases like CO₂ are expelled.
- (iv) Viscosity is decreased and so filtration is faster. These advantages increase softening capacity of Hot L-S process to several more times than that of cold L-S Process.

The softening unit consists essentially of a reaction cum settling tank and a filtering set up. The filtering bed consists of sand/ gravels anthracite coal, calcite or magnesite. The use of sand beds in alkaline water will result in contamination of dissolved silica. If slight excess of chemical are used over that theoretically required, not only the process is fasted bed also complete removal of hardness is achieved.

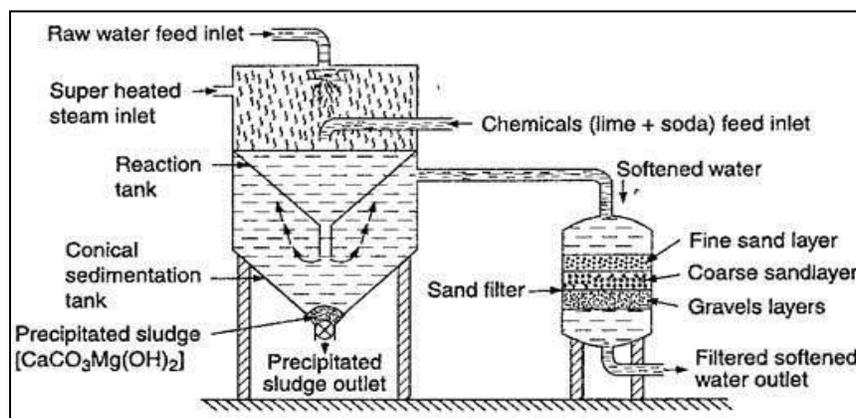


Figure 35

If on other hand, a larger excess of chemicals is used they will be carried through to the softened water and hence decreases its quality. The L-S plants do not completely – remove the hardness and the residual hardness is generally 15 – 30ppm.

Difference between Cold and Hot lime soda process

Sl.No	Cold L-S Process	Hot L - S Process
1	It done at room temp ($25^{\circ} - 30^{\circ}\text{c}$)	It is done at elevated temp ($90^{\circ} - 100^{\circ}\text{c}$)
2	It is a slow process	It is a rapid process
3	The use of coagulants is must	Coagulants not needed
4	Filtration is not easy	Filtration is easy as the viscosity of water becomes low at elevated temperature
5	Softened water has residual hardness around 60ppm	Softened water has residual hardness of 15-20 ppm
6	Dissolved gases are not removed	Dissolved gases such as CO_2 are removed to some extent

CALCULATIONS OF THE REQUIREMENT OF LIME AND SODA

Rules for solving numerical problems on lime-soda requirements for softening of hard water:

- The units in which the impurities are analyzed and expressed are to be noted.
- Substances which do not contribute towards hardness (KCl, NaCl, SiO₂, Na₂SO₄ etc.) should be ignored and explicitly stated.
- A substances causing "hardness should be converted into their respective CaCO₃equivalents.
- CaCO₃ equivalent of hardness causing impurity. = $100 \times \text{wt. of the impurity} / 2 \times \text{chemical equivalent of impurity}$ = Multiplication factor x wt. of impurity.

Salt	Molecular weight	Chemical equivalent	Multiplication Factor
Ca(HCO ₃) ₂	162	81	100/162
Mg(HCO ₃) ₂	146	73	100/146
CaSO ₄	136	68	100/136
CaCl ₂	111	55.5	100/111
MgSO ₄	120	60	100/120
MgCl ₂	95	47.5	100/95
CaCO ₃	100	50	100/100
MgCO ₃	84	42	100/84
CO ₂	44	22	100/44
Mg(NO ₃) ₂	148	74	100/148
HCO ₃	61	61	100/122
OH	41	17	100/34
CO ₃ ²⁻	60	30	100/60
NaAlO ₂	82	82	100/164
Al ₂ (SO ₄) ₃	342	57	100/114
FeSO ₄ .7H ₂ O	278	139	100/278
H ⁺	1	1	100/2
HCl	36.5	36.5	100/73

- If the impurities are given as CaCO_3 or MgCO_3 , these should be considered due to $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$ respectively and they must only be expressed in terms of CaCO_3 and MgCO_3
- The amount expressed as CaCO_3 does not require any further conversion. However, the amount expressed as MgCO_3 should be converted into its CaCO_3 equivalents by multiplying with 100/84
- The amount of lime and soda required are calculated as follows. Lime = $(74/100) \{ \text{temporary calcium hardness} + (2 \times \text{temporary magnesium hardness}) + \text{Perm Mg hardness} + \text{CO}_2 + \text{HCl} + \text{H}_2\text{SO}_4 + \text{HCO}_3^- + \text{salts of Fe}^{2+}, \text{Al}^{3+} - \text{NaAlO}_2 \}$
- Soda = $(106/100) \{ \text{Perm Ca hardness} + \text{Perm Mg hardness} + \text{salts of Fe}^{2+}, \text{Al}^{3+} + \text{HCl} + \text{H}_2\text{SO}_4 + \text{HCO}_3^- - \text{NaAlO}_2 \}$
- If Ca^{2+} and Mg^{2+} is given, 1 equivalent of lime and 1 equivalent of soda is required for Mg^{2+} whereas 1 equivalent of soda is required for Ca^{2+} . The ions Ca^{2+} and Mg^{2+} are treated as permanent hardness due to Ca and Mg.
- If the lime and soda used are impure and if the percentage purity is given, then the actual requirements of the chemicals should be calculated accordingly. Thus, if lime is 90% pure, then the value obtained in step (6) must be multiplied by 100/90 to get actual lime requirement. Similarly, if the soda is 95% pure then the value obtained in step (6) is multiplied by 100/95 to get actual soda requirement.
- The value obtained in step (6) is also multiplied by the volume of water which has to be purified.

Thus, the final formula for calculating the amount of lime or soda required is given as:

Lime = $(74/100) \{ \text{temporary calcium hardness} + (2 \times \text{temporary magnesium hardness}) + \text{Perm Mg hardness} + \text{CO}_2 + \text{HCl} + \text{H}_2\text{SO}_4 + \text{HCO}_3^- + \text{salts of } 100 \text{ Fe}^{2+}, \text{Al}^{3+} - \text{NaAlO}_2 \} \times 100/\% \text{ purity} \times \text{volume of water}$

Soda = $(106/100) \{ \text{Perm Ca hardness} + \text{Perm Mg hardness} + \text{salts of } \text{Fe}^{2+}, \text{Al}^{3+} + \text{HCl} + \text{H}_2\text{SO}_4 - \text{HCO}_3^- - \text{NaAlO}_2 \} \times 100/\% \text{ purity} \times \text{volume of water}$.

Treat

6. Removal of bicarbonates of Na and K



7. Removal of alums



- Amount of lime required for softening = $\frac{74}{100}$ [temp. hardness of Ca^{+2} + 2 x temp. hardness of Mg^{+2} + permanent hardness of Mg^{+2} + CO_2 + $\frac{1}{2}$ HCl + H_2SO_4 + $\frac{1}{2}$ NaHCO_3 + $\frac{1}{2}$ KHCO_3 + FeSO_4 + {3 x $\text{Al}_2(\text{SO}_4)_3$ } - $\frac{1}{2}$ NaAlO_2]

Amount of soda required for softening = $\frac{106}{100}$ [permanent hardness of Ca^{+2} + permanent hardness of Mg^{+2} + $\frac{1}{2}$ HCl + H_2SO_4 + FeSO_4 + {3 x $\text{Al}_2(\text{SO}_4)_3$ } - $\frac{1}{2}$ NaHCO_3 - $\frac{1}{2}$ KHCO_3]

LIME- SODA PROCESS BASED NUMERICALS

1. Calculate the amount of lime and soda required to soften 25,000 litres of water having following analysis.
 $\text{Ca}(\text{HCO}_3)_2$ 4.86 ppm; $\text{Mg}(\text{HCO}_3)_2$ = 7.3 ppm; CaSO_4 = 6.8 ppm; MgCl_2 = 5.7 ppm; MgSO_4 = 9.0 ppm; SiO_2 = 3.5 ppm; NaCl = 5.85 ppm.
2. Calculate the quantity of lime and soda required for softening 50,000 litres of water containing the following salts per litre
 $\text{Ca}(\text{HCO}_3)_2$ = 8.1 mg; $\text{Mg}(\text{HCO}_3)_2$ = 7.5 mg; CaSO_4 = 13.6 mg; MgSO_4 = 12.0 mg MgCl_2 = 2.0 mg; and NaCl = 4.7mg.
3. Calculate the amount of lime (84% pure) and soda (92% pure) required for treatment of 20,000 litres of water, whose analysis is as follows:
 $\text{Ca}(\text{HCO}_3)_2$ 40.5 ppm; $\text{Mg}(\text{HCO}_3)_2$ = 36.5 ppm; MgSO_4 = 30.0 ppm; CaSO_4 = 34.0 ppm; CaCl_2 = 27.75 ppm; and NaCl = 10.00 ppm. Also calculate the temporary & permanent hardness of water sample. (L = 1.762 Kg; S = 1.728 Kg; temp. 50 ppm; p = 75 ppm).
4. Calculate the amounts of lime and soda needed for softening 100,000 litres of water containing **HCl = 7.3 mg/L; Al = 34.2 mg/L; MgCl_2 9.5 mg/L ; NaCl 29.25 mg/L .**
5. A water sample using FeSO_4 as a coagulant at the rate of **278 ppm**, gave following data on analysis for raw water:
 Ca^{2+} = 240 ppm; Mg^{2+} = 96 ppm; CO_2 = 44 ppm HCO_3^- = 732 ppm,
 Calculate the lime and soda required to soften **250,000 litres** of water.
6. Calculate the quantities of lime and soda required for softening **300,000 litres** of water, using **20 ppm** of sodium aluminate as a coagulant. Impurities in water are as follows
 Ca^{2+} = 160 ppm; Mg^{2+} = 96 ppm; HCO_3^- = 403 ppm, dissolved CO_2 34 ppm.
7. Calculate the amount of lime and soda required to soften 10,000 litres of water containing the following ions per litre.
 Mg^{2+} 4.8 mg Ca^{2+} = 16.0 mg; HCO_3^- = 73.2 mg.
8. Calculate the cost of lime and soda required for softening 1 million litres of water containing:
 $\text{Mg}(\text{HCO}_3)_2$ = 73 mg/L; MgSO_4 = 120 mg/L; CaSO_4 = 68 mg/L; CaCl_2 = 111 mg/L. The cost of lime of 80% purity is Rs. 200 per 100kg and that of soda of 90% purity is Rs. 120 per 100kg.
9. Explain with chemical equation and calculate the amount of **lime (94% pure)** and **soda (80% pure)** needed for softening 20,000L of water containing the following salts: **CaSO_4 = 40.8mg/L, MgCl_2 = 19.0mg/L, $\text{Mg}(\text{HCO}_3)_2$ = 14.6mg/L, $\text{Ca}(\text{HCO}_3)_2$ = 16.2mg/L.** If 10% of chemicals are to used in excess in order to complete the reaction quickly.\

Reverse osmosis

The flow of solvent from a region of low concentration to region of high concentration when two solutions of different concentrations are separated by a semi permeable membrane is known as osmosis. Osmotic pressure is the hydrostatic pressure which must be applied to the solution of higher concentration, in order to just prevent osmosis.

Reverse osmosis: If a hydrostatic pressure in excess of osmotic pressure is applied to the high concentration side, the flow of solvent gets reversed and this process is called Reverse osmosis.

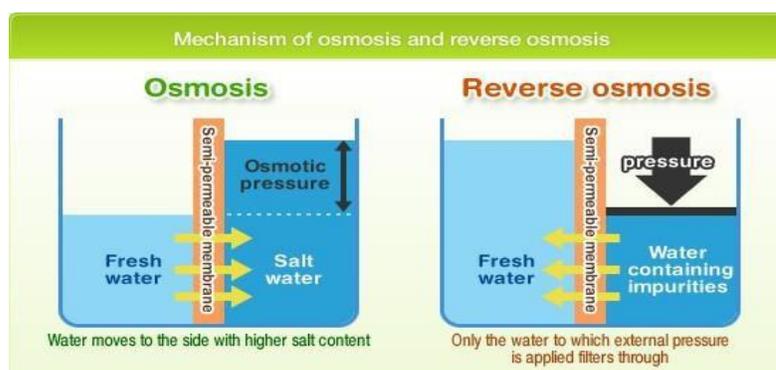


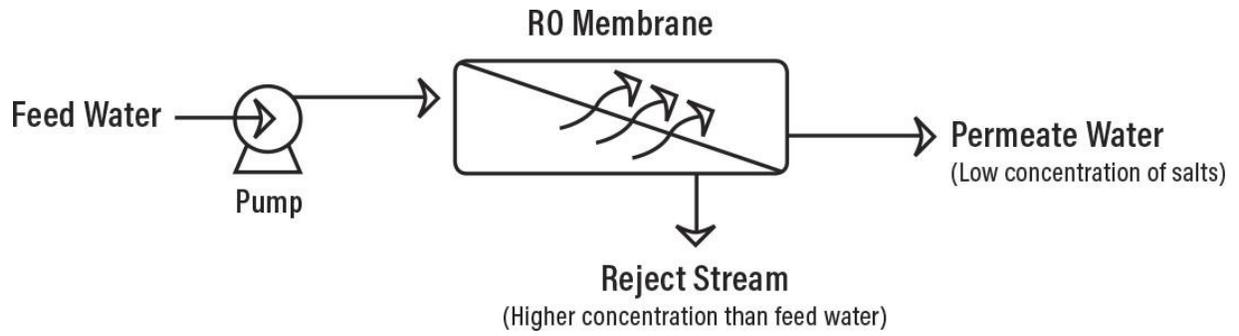
Figure 36

How Does Reverse Osmosis Works

Reverse osmosis is one of the processes that makes desalination (or removing salt from seawater) possible. Beyond that, reverse osmosis is used for recycling, wastewater treatment, and can even produce energy.

Water treatment plants and systems are now adapting reverse osmosis to address some of these concerns. In Perth, Australia (notably dry and arid, yet surrounded by sea), nearly 17 percent of the area's drinking water is desalinated sea water that comes from a reverse osmosis plant. Worldwide, there are now over 13,000 desalination plants in the world, according to the International Desalination Association. But while knowing that reverse osmosis can convert seawater to drinking water is useful, what we really need to understand is how the heck the

processoccurs



FUELS

Fuel is a combustible substance which during combustion gives large amount of heat. There are chemical fuels, nuclear fuels and fossil fuels.

Classification of Fuels

These can be classified on the basis of their occurrence and physical state

On the basis of occurrence they are of two types:

Primary Fuels: Fuels which occur in nature as such are called primary fuels. E.g. wood, peat, coal, petroleum and natural gas.

Secondary Fuels: The fuels which are derived from the primary fuels by further chemical processing are called secondary fuels. E.g., coke, charcoal, kerosene, coal gas, producer gas etc.

(ii) On the basis of physical state these may be classified as: Solid Fuels, Liquid Fuels, Gaseous Fuels

Calorific value: It is defined as the total quantity of heat liberated when a unit mass of a fuel is burnt completely.

Units of Calorific value:

The quantity of heat can be measured in the following units:

(i) **Calorie:** It is defined as the amount of heat required to raise the temperature of 1gm of water by 1°C
 $1 \text{ calorie} = 4.184 \text{ Joules}$

(ii) **Kilo Calorie:** $1 \text{ k cal} = 1000 \text{ cal}$

(iii) **British thermal unit:** (B. T. U.) It is defined as the amount of heat required to raise the temperature of 1 pound of water through 1°F, $1 \text{ B.T.U.} = 252 \text{ Cal} = 0.252 \text{ k cal}$

(IV) Centigrade heat unit (C.H.U): It is defined as the amount of heat required to raise the temperature of 1 pound of water through 1°C., $1\text{kcal} = 3.968 \text{ B.T.U.} = 2.2 \text{ C.H.U.}$

Characteristics of Good Fuel:

- (i) **Suitability:** The fuel selected should be most suitable for the process. E.g., coke made out of bituminous coal is most suitable for blast furnace.
- (ii) High Calorific value.
- (iii) **Ignition Temperature:** A good fuel should have moderate ignition temperature.
- (iv) **Moisture content:** Should be low.
- (v) Non combustible matter content should be low.
- (vi) **Velocity of combustion:** It should be moderate.
- (vii) Nature of the products,
- (viii) Low cost of fuel,
- (ix) Smoke should be low.
- (x) Control of the process

Determination of Calorific value by Bomb Calorimeter

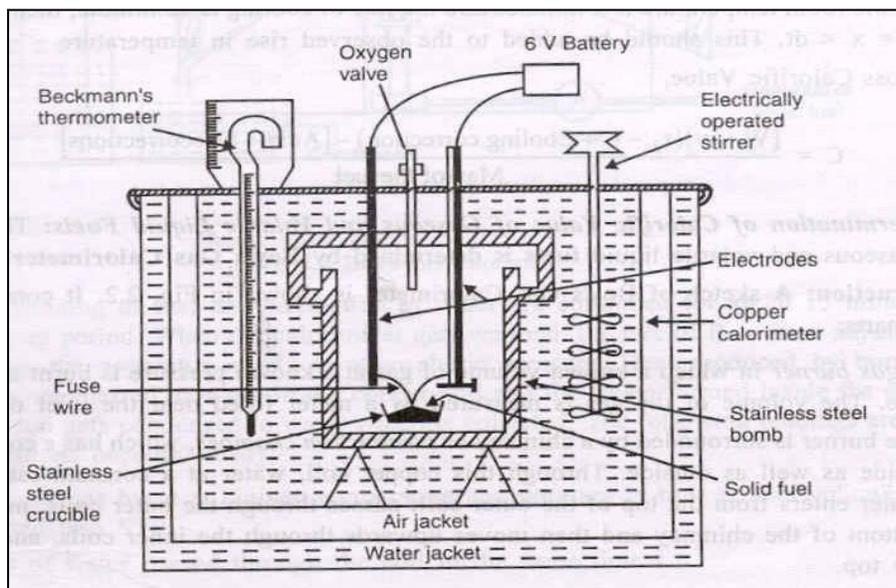


Figure 37

Calculations

Let weight of the fuel sample taken = x g

Weight of water in the calorimeter = W g

Water equivalent of the Calorimeter, stirrer, bomb, thermometer = w g

Initial temperature of water = $t_1^\circ\text{C}$

Final temperature of water = $t_2^\circ\text{C}$

Higher or gross calorific value = C cal/g

Heat gained by water = $W \times \Delta t \times \text{specific heat of water} = W (t_2 - t_1) \times 1$ cal

Heat gained by Calorimeter = $w (t_2 - t_1)$ cal

Heat liberated by the fuel = $x C$ cal

Heat liberated by the fuel = Heat gained by water and calorimeter

Heat gained by Calorimeter = $w (t_2 - t_1)$ cal

Heat liberated by the fuel = $x C$ cal

Heat liberated by the fuel = Heat gained by water and calorimeter

$$x C = (W+w) (t_2 - t_1) \text{ cal, } C = \frac{(W+w)(t_2 - t_1) \text{ cal/g}}{X}$$

- (a) **Fuse wire correction:** As Mg wire is used for ignition, the heat generated by burning of Mg wire is also included in the gross calorific value. Hence this amount of heat has to be subtracted from the total value.
- (b) **Acid Correction:** During combustion, sulphur and nitrogen present in the fuel are oxidized to their corresponding acids under high pressure and temperature. $DH = - 144,000 \text{ Ca, } DH = -57,160 \text{ Cal}$

A temperature correction is therefore necessary to get the correct rise in temperature.

If the time taken for the water in the calorimeter to cool down from the maximum temperature attained, to the room temperature is x minutes and the rate of cooling is dt/min , then the cooling correction = $x \times dt$. This should be added to the observed rise in temperature.

Therefore, Gross calorific value (GCV)

$$GCV = (W+w)(t_2 - t_1 + \text{Cooling correction}) - [\text{Acid} + \text{fuse wire corrections}] / \text{Mass of the fuel.}$$

Q1. Following data obtained in a bomb calorimeter experiment.

Wt. of coal burnt = 0.994gm, Wt. of water in calorimeter = 2592gm,

Wt. of bomb calorimeter = 3940gm, Rise in temp. = 2.732⁰C,

Specific heat of apparatus = 0.098.

Find GCV, if fuel contain 8% hydrogen & calculate NCV if Latent heat of condensation = 587cal/gm.

Ans. weight of the fuel sample taken(W) = 0.994g

Weight of water in the calorimeter = 2592 g

Water equivalent of the Calorimeter (w)=Wt. of water x Specific heat of apparatus gram

$$= 2592 \times 0.098$$

$$=254.01 \text{ gram}$$

Rise in Temp. = 2.732⁰C

$$\text{GCV} = \frac{(W+W)(t_2-t_1) \text{ cal/g}}{X}$$

$$= \frac{(3940+254.01) \times 2.732}{0.994}$$

$$=11527.20 \text{ cal/gm}$$

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

$$=11527.20 - 0.09 \times 8 \times 587$$

$$=11527.20 - 422.64$$

$$= \mathbf{11104.56} \text{ cal/gm}$$

Analysis of Coal

Coal is analyzed in two ways:

1. Proximate analysis
2. Ultimate analysis

The results of analysis are generally reported in the following ways: As received basis, air dried basis, moisture free basis (oven dried), moisture and ash free basis

Proximate Analysis-The data varies with the procedure adopted and hence it is called proximate analysis. It gives information about the practical utility of coal. Proximate analysis of coal determines the moisture, ash, volatile matter and fixed carbon of coal.

1. **Moisture Content:** Air dried moisture is determined by heating a known amount of coal to 105-110°C in an electric hot air oven for about one hour. After one hour, it is taken out from the oven and cooled in a desiccator and weighed.

$$\text{Percentage of moisture} = \frac{\text{Loss in weight} \times 100}{\text{Weight of coal taken}}$$

- Excess of moisture is undesirable in coal.
- Moisture lowers the heating value of coal and takes away appreciable amount of the liberated heat in the form of latent heat of vaporization.
- Excessive surface moisture may cause difficulty in handling the coal.
- Presence of excessive moisture quenches fire in the furnace.

2. **Volatile Matter:** consists of a complex mixture of gaseous and liquid products resulting from the thermal decomposition of the coal.

It is determined by heating a known weight of moisture free coal sample in a covered platinum crucible at $950 \pm 20^\circ\text{C}$ for 7 minutes.

$$\text{Percentage of volatile matter} = \frac{\text{Loss of weight due to volatile matter} \times 100}{\text{Weight of coal taken}}$$

Significance

- A high percent of volatile matter indicates that a large proportion of fuel is burnt as a gas.
- The high volatile content gives long flames, high smoke and relatively low heating values.
- For efficient use of fuel, the outgoing combustible gases has to be burnt by supplying secondary air.
- High volatile matter content is desirable in coal gas manufacture because volatile matter in a coal denotes the proportion of the coal which will be converted into gas and tar products by heat.

3. **Ash:** Coal contains inorganic mineral substances which are converted into ash by chemical reactions during the combustion of coal. Ash usually consists of silica, alumina, iron oxide and small quantities of lime, magnesia etc. Ash content is determined by heating the residue left after the removal of volatile matter at $700 \pm 50^\circ\text{C}$ for $\frac{1}{2}$ an hour without covering

$$\text{Percentage of ash} = \frac{\text{Weight of the residue left} \times 100}{\text{Weight of coal taken}}$$

4. **Fixed Carbon:** Fixed carbon content increases from lignite to anthracite. Higher the percentage of fixed carbon greater is its calorific value and better is the quality of coal.

The percentage of fixed carbon is given by:

$$\% \text{ of fixed carbon} = 100 - [\% \text{ of moisture} + \text{volatile matter} + \text{ash}]$$

Significance:

- Higher the percentage of fixed carbon, greater its calorific value

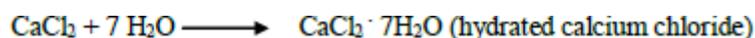
- The percentage of fixed carbon helps in designing the furnace and shape of the fire-box because it is the fixed carbon that burns in the solid state.

Ultimate Analysis

This analysis includes percentage of C, H, O, S, N and ash content in coal.

(a) Carbon and hydrogen determination

A known weight (1-2g) of coal is taken and burnt in an apparatus. The carbon change to CO₂ and hydrogen changes to H₂O. Vapors of CO₂ and H₂O are then passed through KOH and CaCl₂. The CO₂ is absorbed by KOH in the tube while H₂O is absorbed by CaCl₂, because of the absorption, the weight of KOH and CaCl₂ increases, which is measured



$$\text{Percentage of carbon} = \frac{\text{increase in weight of KOH}}{\text{weight of Coal (1-2 gr)}} \times \frac{12}{44} \times 100$$

$$\text{Percentage of carbon} = \frac{\text{increase in weight of CaCl}_2}{\text{weight of Coal (1-2 gr)}} \times \frac{2}{18} \times 100$$

Significance: The higher the percentage of carbon and hydrogen, the better is the quality of coal and higher its calorific value. Percentage of carbon helps in assessing the rank of coal.

b) Nitrogen determination

The estimation of nitrogen is done by Kjeldahl's method (i) About 1 gr of accurately weight powdered coal is heated with conc. H₂SO₄ along with K₂SO₄ (ii) When clear solution is obtained (i.e, when whole nitrogen is converted into ammonia sulphate) it is treated with excess of NaOH to liberate ammonia. (iii) The ammonia thus produced is distilled over and absorbed in a known

volume of standard H₂SO₄ solution. (iv) The volume of unused H₂SO₄ acid is then determined by back titration with standard NaOH solution [un used H₂SO₄ means unreacted H₂SO₄]

$$\text{Percentage of Nitrogen} = \frac{\text{Volume of H}_2\text{SO}_4 \text{ acid} \times \text{Normality} \times 1.4}{d \times \text{Weight of coal taken (1gr)}}$$

Significance: Nitrogen does not have any calorific value. It has no significance, thus a good quality coal should have very little nitrogen content.

Sulphur determination: A known amount of coal is burnt completely in bomb calorimeter in a current of oxygen, by which sulphur present in coal is oxidized to sulphates. The ash from the bomb calorimeter is extracted with dil. HCl. The acid extract is then treated with BaCl₂ solution to precipitate sulphate as BaSO₄ is filtered, washed, dried and heated to constant weight.

$$\text{Percentage of sulphur} = \frac{\text{weight of BaSO}_4 \times 32 \times 100}{\text{weight of Coal} \times 233}$$

Significance: (a) sulphur increases calorific value. (b) The product of combustion SO₂, SO₃ have corrosive effect on equipment, and cause air pollution.

Calculation of Air for Combustion

Substances always combine in definite proportions. These proportions are determined by their molecular masses.



- 1) 22.4 L of any gas at 0°C and 760mm pressure (STP) has a mass equal to its 1 mol.
- 2) Air contain 21% of oxygen by volume and 23% of oxygen by mass.
- 3) 28.94 g/mol is taken as molar mass of air.
- 4) O_2 required for combustion = theoretical O_2 required - O_2 present in the fuel.
- 5) Dry flue gases means products of combustion except moisture.

For solid or Liquid fuels:

$$\text{O}_2 \text{ quantity} = \left(\frac{32}{12} \text{C} + 8 \text{H} + \text{S} - \text{O} \right) \text{ kg.}$$

where C, H, S and O are amounts of elements in Kg.

$$\text{Air quantity} = \frac{\text{Oxygen quantity} \times (100 + \% \text{ excess air})}{23} \text{ Kg.}$$

For Gaseous fuels:

O_2 volume required = volume gas component in m^3 x volume of O_2 per volume of gas.

$$\text{Air volume required} = \frac{\text{Oxygen volume} \times (100 + \% \text{ excess air})}{21} \text{ m}^3.$$

!

Numerical based on Combustion

Q1. A petrol sample contains 14 % H and 86 % carbon. Calculate the quantity of air required for complete combustion of 1 kg petrol.

Soln. : Given : Weight of petrol fuel = 1 kg. C % = 86 and H % = 14,

$$C = \text{Weight of carbon in 1 kg petrol} = \frac{86}{100} \times 1 = 0.86 \text{ kg}$$

$$H = \text{Weight of hydrogen in 1 kg petrol} = \frac{14}{100} \times 1 = 0.14 \text{ kg.}$$

$$O_2 \text{ quantity} = \left(\frac{32}{12} C + 8 H + S - O \right) \text{ kg.}$$

$$= \left(\frac{32}{12} \times 0.86 + 8 \times 0.14 + 0 + 0 \right) \text{ kg.}$$

$$= 2.293 + 1.12 = 3.413 \text{ kg oxygen}$$

Excess air used = zero

$$\text{Air quantity} = \frac{\text{Oxygen quantity} \times (100 + 0 \text{ excess})}{23}$$

$$= \frac{3.413 \times 100}{23} = 14.839 \text{ kg air} \quad \dots\text{Ans.}$$

Q2. Volumetric analysis of producer gas is, H₂ = 20 % CO = 22 % N₂ = 50 %, CH₄ = 2 % and CO₂ = 6 %. Find volume of air required for complete combustion of 1 m³ of the gas

$$\text{Volume of H}_2 \text{ in } 1 \text{ m}^3 \text{ gas} = \frac{20}{100} \times 1 \text{ m}^3 = 0.2 \text{ m}^3$$

$$\text{Similarly, Volume of CO} = 0.22 \text{ m}^3$$

$$\text{Volume of CH}_4 = 0.02 \text{ m}^3$$

(N₂ and CO₂ are not combustible)

Reaction	Volume of O ₂ required
$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$ 1 vol. 1/2 vol.	$\frac{1}{2} \times \text{volume of H}_2 = \frac{1}{2} \times 0.2 = 0.1 \text{ m}^3$
$\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$	$\frac{1}{2} \times 0.22 = 0.11 \text{ m}^3$
$\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}$	$2 \times \text{volume of CH}_4 = 2 \times 0.02 = 0.04 \text{ m}^3$

$$\text{Total volume of O}_2 \text{ required} = 0.25 \text{ m}^3$$

$$\text{Volume of air required} = \frac{\text{Volume of O}_2 \times (100 + 0)}{21}$$

$$= \frac{0.25 \times 100}{21} = 1.19 \text{ m}^3$$

...Ans.

Q3. A gas has following composition by volume, H₂ = 20 %, CH₄ = 6 %, CO = 18 %, O₂ = 5 %, N₂ = 43 %. If 25 % excess air is used. Find volume of air actually supplied per m³ of the gas.

Soln. : 1 m³ of the gaseous fuel contains,

$$\text{CO} = \frac{18}{100} \times 1 = 0.18 \text{ m}^3, \text{O}_2 = \frac{5}{100} \times 1 = 0.05 \text{ m}^3.$$

Reaction	Volume of O ₂ required
$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$ 1 vol. $\frac{1}{2}$ vol.	Volume of gas $\times \frac{1}{2} = 0.2 \times \frac{1}{2} = 0.1 \text{ m}^3$
$\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ 1 vol. 2 vol.	Volume of gas $\times 2 = 0.06 \times 2 = 0.12 \text{ m}^3$
$\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$ 1 vol. $\frac{1}{2}$ vol.	Volume of gas $\times \frac{1}{2} = \frac{0.18}{2} = 0.09 \text{ m}^3$
	Total O ₂ required = 0.1 + 0.12 + 0.09 = 0.31 m ³
	Less O ₂ present in fuel = - 0.05
	Net O ₂ required = 0.26 m ³

$$\text{Volume of O}_2 = 0.26 \text{ m}^3$$

Volume of air with 25 % excess

$$= \frac{\text{Volume of oxygen} \times (100 + 25)}{21} = \frac{0.26 \times 125}{21}$$

$$= 1.548 \text{ m}^3. \quad \dots\text{Ans.}$$

$$\text{H}_2 = \frac{20}{100} \times 1 = 0.2 \text{ m}^3, \text{CH}_4 = \frac{6}{100} \times 1 = 0.06 \text{ m}^3,$$

∴ Actual volume of air supplied with 25 % excess for combusting 1 m³ of the gaseous fuel is 1.548 m³.

Q4. A gas has following composition by volume :H₂ = 20 %; CH₄ = 6% ; CO = 22% CO₂and O₂= 4%, N₂=44% Find the volume of air actually supplied per m³ of this gas.

Soln. :

$$\text{Volume of H}_2 \text{ in } 1\text{m}^3 \text{ gas} = \frac{20}{100} \times 1 = 0.2 \text{ m}^3$$

$$\text{Volume of CH}_4 \text{ in } 1\text{m}^3 \text{ gas} = \frac{6}{100} \times 1 = 0.06 \text{ m}^3$$

$$\text{Volume of CO in } 1\text{m}^3 \text{ gas} = \frac{22}{100} \times 1 = 0.22 \text{ m}^3$$

$$\text{Volume of O}_2 \text{ in } 1\text{m}^3 \text{ gas} = \frac{4}{100} \times 1 = 0.04 \text{ m}^3$$

(CO₂ and N₂ do not burn and do not require air).

Reaction	Volume of O ₂ required = Volume of gas × Volume of O ₂ per molecule
$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$	$0.2 \times \frac{1}{2} = 0.1 \text{ m}^3$
$CH_4 + 2 O_2 \longrightarrow CO_2 + 2 H_2O$	$0.06 \times 2 = 0.12 \text{ m}^3$
$CO + \frac{1}{2} O_2 \longrightarrow CO_2$	$0.22 \times \frac{1}{2} = 0.11 \text{ m}^3$
	Total O ₂ = 0.33 m ³
	Less O ₂ in fuel = 0.33 - 0.04 = 0.29

Q15. A sample of coal was found to have the following composition: C = 75%, H = 5.2%, S = 1.2%, O = 12.8%, ash = 2.1%. Calculate the minimum amount of air necessary for complete combustion of 1 kg of coal

Soln. :

$$\text{Amount of C in 1 kg coal} = \frac{75}{100} \times 1 \text{ kg} = 0.75 \text{ kg}$$

$$\text{Amount of H in 1 kg coal} = \frac{5.2}{100} \times 1 \text{ kg} = 0.052 \text{ kg}$$

$$\text{Amount of O in 1 kg coal} = \frac{12.8}{100} \times 1 \text{ kg} = 0.128 \text{ kg}$$

$$\text{Amount of S in 1 kg coal} = \frac{1.2}{100} \times 1 \text{ kg} = 0.012 \text{ kg}$$

(N and ash do not get burnt, do not require air, during combustion of coal).

$$O_2 \text{ quantity} = \left[\frac{32}{12} C + 8 H + S - O \right] \text{ kg}$$

$$\text{Weight of coal} = 250 \text{ gm}$$

$$\text{Weight of carbon in 250 gm coal} = \frac{81}{100} \times 250 \text{ gm} = 202.5 \text{ gm}$$

Q6. A
for 250
= 9.35

$$\text{Weight of hydrogen in 250 gm coal} = \frac{4}{100} \times 250 \text{ gm} = 10 \text{ gm}$$

$$\text{Weight of sulphur in 250 gm coal} = \frac{1.2}{100} \times 250 \text{ gm} = 3 \text{ gm}$$

e weight of air
6, O = 3%, ash

Soln. :

$$\text{Weight of oxygen in 250 gm coal} = \frac{3}{100} \times 250 = 7.5 \text{ gm}$$

(N and ash do not burn, do not require oxygen)

$$O_2 \text{ quantity} = \left[\frac{32}{12} C + 8 H + S - O \right] \text{ gm}$$

(C, H, S, O are the weights of elements in gms)

$$\therefore O_2 \text{ quantity} = \frac{32}{12} \times 202.5 + 8 \times 10 + 3 - 7.5 \text{ gm}$$

$$= 615.5 \text{ gm oxygen}$$

$$\text{Quantity of air} = \frac{O_2 \text{ quantity} (100 + \% \text{ excess air})}{23}$$

$$= \frac{615.5 (100 + 20)}{23}$$

$$= 3211.3 \text{ gm air}$$

$$= 3.2113 \text{ kg air}$$

Q7. A gas used in internal combustion engine contains, $H_2 = 45\%$, $CO = 15\%$, $CH_4 = 35\%$, $N_2 = 5\%$. Find the minimum quantity (volume) of air required per 1 m^3 of the gas for complete combustion.

Soln. Volume of H_2 in 1 m^3 gas = $45 \times 1 / 100 = 0.45\text{ m}^3$

Similarly, Volume of $CH_4 = 35 \times 1 / 100 = 0.35\text{ m}^3$

Volume of $CO = 15 \times 1 / 100 = 0.15\text{ m}^3$

(N_2 is not combustible)

UNIT V

POLYMERS

Introduction: The word polymer is derived from Greek word (*Poly = many; mere = units or parts*). Polymer is a large molecule which is formed by repeated linkage of small molecules, known as monomers.

The process by which monomer molecules are linked is called as polymerization. Eg. Polyethylene (polythene is a polymer formed by linking together of a large number of ethene (C₂H₄) molecules. Thus:

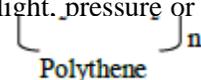


The number of repeating units in the chain is called the —degree of polymerization (D.P). Polymers with high degree of polymerization are called high polymers and those with low degree of polymerization are called oligopolymers. High polymers have very high molecular weights (10^4 to 10^6) and hence are called — macromolecules. These polymers have high strength, good flexibility, special electrical properties, resistance to chemicals, fabrication into complex shapes in a wide variety of colors. Polymers can be used for manufacture of strong articles, flexible rubber like masses, soft and resistant foams, smooth and fine fibres, swollen jelly-like food materials to fill cavities, to seal joints, etc.

Types of Polymerization: Two types of polymerization are generally distinguished. (1) Addition or chain polymerization (2) Condensation polymerization or step polymerization

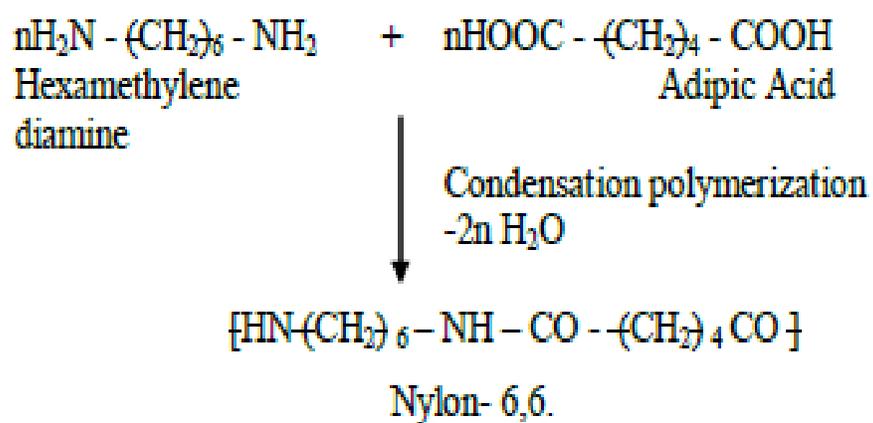
(1) Addition or chain polymerization: In such type of polymerization the polymer is formed from monomer without the loss of any molecule (as HCl, H₂O, NH₃) and the product is an exact multiple of original monomeric molecule. The monomer usually contains one or more double bonds. In general, such polymerization proceeds by formation of some reactive species initially with the regeneration of reactive feature.

The addition polymerization reaction must be initiated by application of heat, light, pressure or a catalyst for breaking



(2) **Condensation or step polymerization:** It is defined as the reaction that occurs between monomers with simple polar group and elimination of small molecules like H₂O, HCl, NH₃ etc. Eg.

(i) Hexamethylene diamine and adipic acid condense to form a polymer, nylon – 6,6.



Polymer Blends

It is defined as the mixture of at least two macromolecular substances, polymers or copolymers in which the ingredient content is above 2 wt%.

Advantages of blending and properties of blends:

Blending may **improve** resin or product **performance** by:

- Producing materials having all desired properties at lowest cost.
- Extending the engineering resins' performance by incorporation of less expensive polymers.
- Improvement of specific properties such as:

Brittleness: Toughening brittle polymers, thus eliminating the need to use low molecular weight additives (e.g. plasticizer in the flexible PVC formulations).

Modulus and Dimensional Stability: Blending with more rigid and more heat resistant resin.

Improve Solvent and Chemical Resistance: Incorporation of semi crystalline polymer into an amorphous resin (e.g., blends of PC with PEST)

Improve Flame Resistance: Incorporation of non-flammable resin into a flammable (e.g., styrenics or acrylics with PVC)

Permanently Anti-Static blends: Blends with polymers having either –OH or –SH functionality (e.g. ethylene oxide-epichlorohydrin with ABS/PC blend).

Biodegradability: Incorporation of a biodegradable resin. Blending makes it possible to produce integrated **multi-layer** structures

- Providing means for recycling of industrial and/or municipal plastics waste.
- The blending technology makes it possible to rebuild high molecular weights of partially degraded polymers, thus to produce high performance articles from the plastics waste.

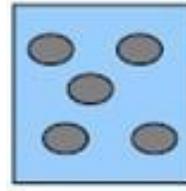
Types of polymer blends

Miscible polymer blend: These are homogenous up to the molecular level. They have negative value of free energy of mixing. It is a single –phase structure that has properties values between the values of properties of its components.

Immiscible polymer blend: It is a blend that exhibits more than two phases. In this system the two components are phase separated.



Miscible polymer blend



Immiscible polymer blend

Most compatible blends are immiscible and can be made compatible by a variety of compatibilization techniques.

Polymer alloy: When the interface and/or the morphology of an immiscible blend is modified a polymer *alloy* is obtained. These are immiscible, compatible polymer blend with modified interface and morphology.

Comparison between Polymer Blend and Polymer Alloy

The properties of many plastics can be greatly modified by blending or alloying two or more polymers. Technically, blends are mixtures that are not fully compatible whereas alloys are mixtures that are fully compatible.

Polymer alloy constitutes a specific sub-class of polymer blend; virtually all high performance engineering blends are alloys.

At present polymer alloys, blends and composites consume over 80 wt% of all plastics. This has resulted in:

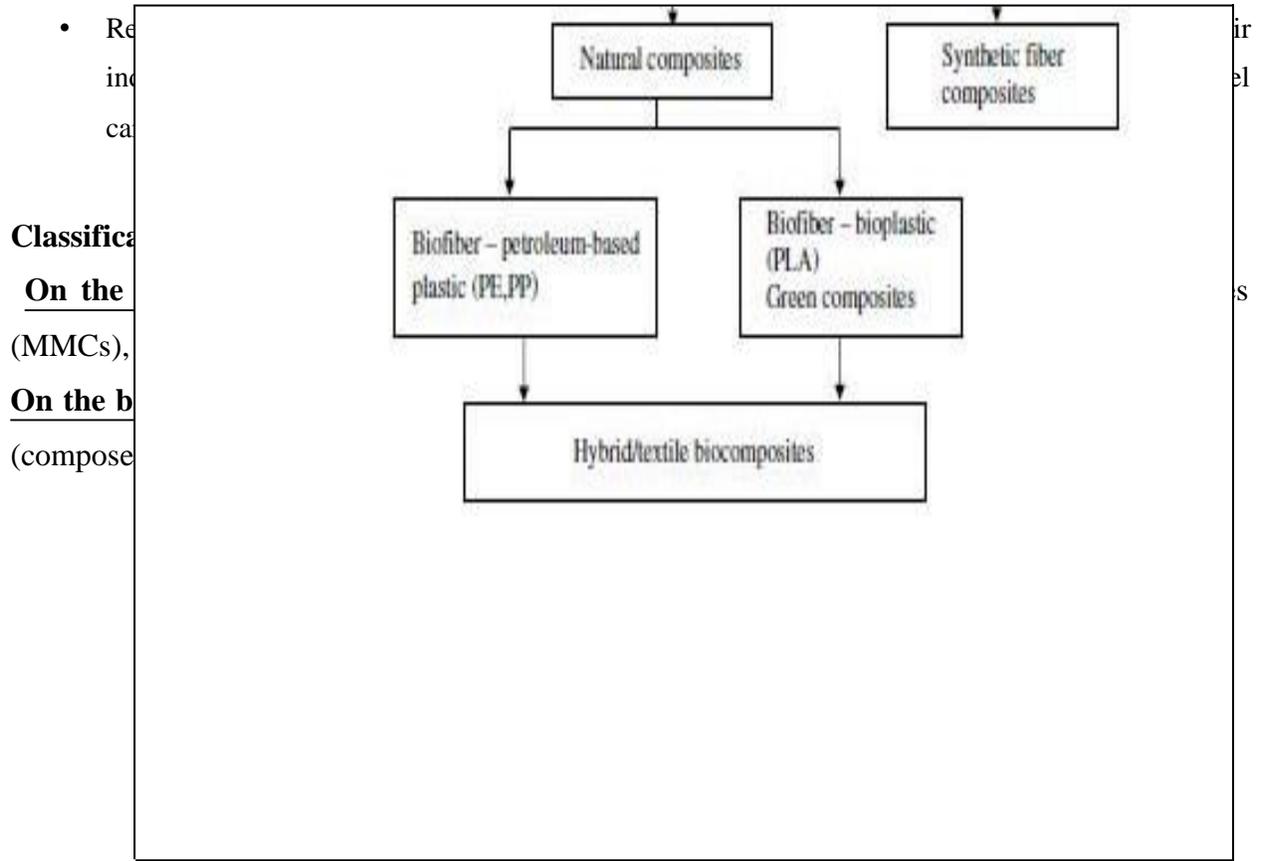
- Increased scale of production.
- Use of multi-component and multiphase materials.
- New processing methods.

Polymer Composites

Composites can be defined as materials that consist of two or more chemically and physically different phases separated by a distinct interface. Composites are combinations of materials differing in composition, where the individual constituents retain their separate identities. These separate constituents act together to give the necessary mechanical strength or stiffness to the composite part. Composite material is a material composed of two or more distinct phases (matrix phase and dispersed phase) and having bulk properties significantly different from those of any of the constituents. Matrix phase is the primary phase having a continuous character. Matrix is usually more ductile and less hard phase. It holds the dispersed phase and shares a load with it. Dispersed (reinforcing) phase is embedded in the matrix in a discontinuous form. This secondary phase is called the dispersed phase. Dispersed phase is usually stronger than the matrix, therefore, it is sometimes called reinforcing phase.

Characteristics of Composites in structural applications

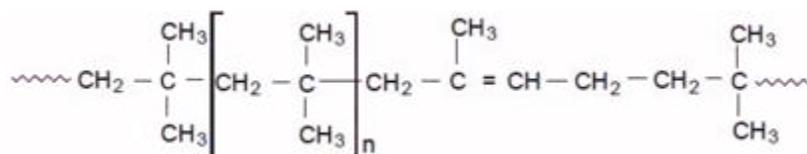
- They generally consist of two or more physically distinct and mechanically separable materials.
- They are made by mixing the separate materials in such a way as to achieve controlled and uniform dispersion of the constituents.
- They have superior mechanical properties and in some cases uniquely different from the properties of their constituents. Wood is a natural composite of cellulose fibers in a matrix of lignin. Most primitive man-made composite materials were straw and mud combined to form bricks for building construction.
- Most visible applications pave our roadways in the form of either steel and aggregate reinforced Portland cement or asphalt concrete.



Some industrially Important Polymers: Preparation and Applications

BUTYL RUBBER: Butyl rubber is a synthetic rubber, a copolymer of isobutylene with isoprene. The abbreviation IIR stands for isobutylene isoprene rubber. Polyisobutylene IS also known as "PIB" or polyisobutene, $(C_4H_8)_n$ is the homopolymer of isobutylene (2-methyl-1-propene) on which butyl rubber is based. Butyl rubber is produced by polymerization of 98% of isobutylene with 2% of isoprene.

Butyl rubber is a great option for shock absorption. But it is not recommended for use when in contact with petroleum oils and fluids. It can be made from the monomer isobutylene $[CH_2=C(CH_3)_2]$ only via cationic addition polymerization.



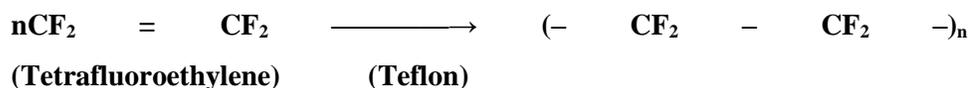
Properties:

- It is impermeable to most common gasses.
- It has exceptionally low gas and moisture permeability.
- It possess high damping capabilities
- It is resistant to heat, aging, weather, ozone, chemical attack, flexing, abrasion, and tearing.
- It is resistant to phosphate ester based hydraulic fluids, and has excellent electrical insulation performance.

Applications:

- It is used as a sealant for rubber roof repair.
- It is used in tubeless tire liners, inner tubes.
- Stoppers for glass bottles, medicine bottles, and pharmaceuticals.
- It is used as construction sealants, hoses, and in mechanical goods.

TEFLON OR (PTFE): PTFE is produced by free-radical polymerization of tetrafluoroethylene.



Properties:

- Teflon is one of the chemically inert substances not affected by strong acids and aqua- regia.

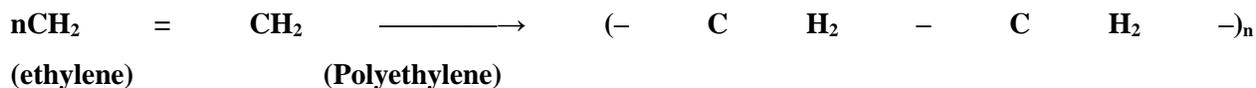
- It is stable at high temperatures.
- It is a thermoplastic polymer that appears as a white solid at room temperature.
- It has density of about 2200 kg/m³. It has a melting point of 600K (327°C; 620°F).
- Alkali metals and most highly reactive fluorinating agents are the only chemicals that can affect its property.
- It has a coefficient of friction of 0.05 to 0.10 which is the third-lowest of any known solid material. It has one of the proficient dielectric properties.

Applications:

- PTFE is usually used to coat non-stick frying pans as it has the ability to resist high temperatures.
- It is mostly used as a film interface patch for sports and medical applications due to pressure-sensitive adhesive backing.
- It is used in high friction areas of footwear as in soles.
- It is widely used in medical synthesis, test and many more medicines.

HDPE: HDPE can be made by following methods:

1. Using Zeigler- Natta catalyst [TiCl₄ + Al (C₂H₅)₃], ethylene is polymerized under 6-7 atm. at 60-70⁰ C.
2. Using metal oxide catalyst, like CrO₃ supported on silica alumina, ethylene is polymerized at 35 atm. and 160-200⁰ C.



Properties:

- It has low cost
- Impact resistant from -40°C to 90°C
- It is moisture resistant and possess good chemical resistance.
- It can be readily processed by all thermoplastic methods.

Applications:

HDPE is resistant to many different solvents and has a wide variety of applications:

- It is used in swimming pool installation, 3-D printer filament and banners.
- It is used in bottle caps, folding chairs and tables.
- Chemical-resistant piping, Coax cable inner insulator
- It is used in Food storage containers as well as fuel tanks for vehicles
- It is used as corrosion protection for steel pipelines
- It is used in Far-IR lenses

DACRON (PET): It can be prepared by the condensation of ethylene glycol and terephthalic acid.

(Ethane-1, 2 - diol)

(Benzene-1,4 - di
carboxylic acid)

REAGENT OF DACRON

Properties:

- It is a hard, stiff, strong, dimensionally stable material that absorbs very little water.
- It has good gas barrier properties and chemical resistance except to alkalis (which hydrolyze it).
- Its crystallinity varies from amorphous to fairly high crystalline.

Applications:

- It is an excellent water and moisture barrier material used for soft drinks, fruit juice concentrates and sauces and wide-necked jars for coffee.
- It is also used as a substrate in thin film solar cells.
- PET is used for making magnetic recording tape.
- Glass filled PET moldings are used for toasters, coffee machines, car heater and water meter.

POLYAMIDES [Nylons]

Polyamides are the polymers, which contain many repeating amide groups in the main polymer chain.

1. Nylon – 6, 6: Nylon – 6;6 is obtained by the polymerization of adipic acid with hexamethylene diamine.

Applications of Nylon:

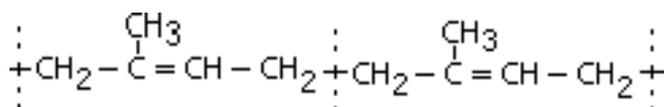
- Nylon 6, 6 is used for making socks, under garments, dresses, carpets, etc.
- Nylon 6 and Nylon 11 are used for moulding purposes for gears, bearings, electrical mountings, etc. Nylon bearings and gears work quietly without any lubrication.
- They are also used for making filaments for ropes, bristles for tooth brushes and films, tyre cords, etc.

Elastomers

Polymers that exhibit extreme elastic extensibility when subjected to relatively low mechanical stress. They are also known as rubber. Some elastomers can be stretched by a factor of 10 and yet completely recover to their original shape. Although their properties are quite different from thermosets, they share a similar molecular structure that is different from the thermoplastic.

Natural Rubber (NR):

Natural rubber is extracted in the form of latex from the bark of the *Hevea* tree.



- 99.99% cis Polyisoprene
- Good low temperature flexibility.
- Low Tg (-65 C). Low heat buildup.
- 200,000 to 400,000 MW. Easy Processing.
- Has high tensile and tear properties. Stress crystallizes.
- Excellent dynamic fatigue
- Poor resistance to oxygen, ozone, hydrocarbon solvents and heat.

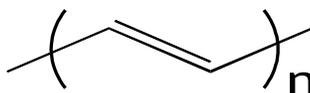
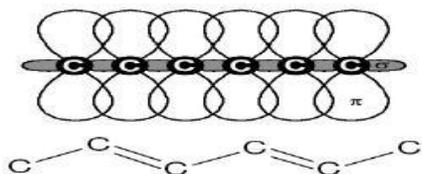
Conducting Polymers

The polymeric materials, which possess electrical conductivities on par with metallic conductors, are called conducting polymers. Conductivities as high as $1.5 \times 10^{-1} \text{ ohm}^{-1} \text{ m}^{-1}$ have been attained in these polymeric materials.

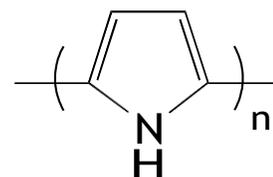
Different types of conducting polymers are listed below:

- (1) Intrinsically conducting polymer (ICP) (or) Conjugated – Electrons conducting polymer
- (2) Doped conducting polymer
- (3) Extrinsicly conducting polymer
- (4) Coordination conducting polymer (inorganic polymer)

(1) Intrinsically conducting polymer (ICP) or Conjugated – Electrons conducting polymer It is a polymer whose backbones or associated groups consist of delocalized electron – pair or residual charge. Such polymers essentially contain conjugated – electrons backbone, which is responsible for electrical charge. In an electric field, conjugated electrons of the polymer get excited, thereby can be transported through the solid polymeric material. Overlapping of orbitals (of conjugated electrons) over the entire backbone results in the formation of valence bands as well as conduction bands, which extends over the entire polymer molecule. Presence of conjugated electrons in a polymer increases its conductivity to a larger extent.



Polyacetylene



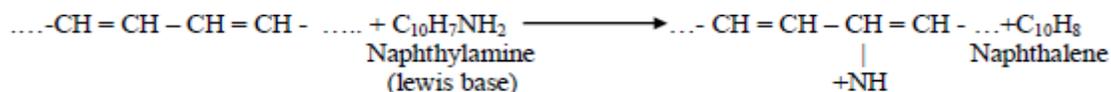
Polypyrrole

(2) Doped conducting polymer

It is obtained by exposing a polymer to a charged transfer agent in either gas phase or in solution. Intrinsically conducting polymers possess low conductivity but these possess low ionization potential and high electron affinities, so these can be easily oxidized or reduced. Consequently, the conductivity of ICP can be increased by creating either positive (or) negative charges on the polymer backbone by oxidation or reduction. This technique, called doping. Doping is classified into 2 types.

(a) **p – doping:** P – doping involves treating an ICP with a Lewis acid, there by oxidation process takes place and positive charges on the polymer backbone are created. Some of the common p – dopant used are I₂, Br₂, AsF₅, PF₆, Naphthylamine, etc, used.

(b) **n – doping:** It involves treating an intrinsically conducting polymer with a lewis base thereby reduction process takes place and negative charges on the polymer backbone are created. Some of the common N – dopant used are Li, Na, Ca, tributyl ammonium, FeCl₃, etc. for example.



(3) **Extrinsically conducting polymers:** Extrinsically conducting polymers are those polymers whose conductivity is due to the presence of an externally added ingredient in them. These are of the following two types.

(a) **Conductive element filled polymer:** It is a resin or polymer filled with conducting elements such as carbon black, metallic fibres, metal acids, etc. In this, the polymer acts as the binder to hold the conducting elements together in the solid entity.

(b) **Blended conducting polymer:** It is the product obtained by blending a conventional polymer with a conducting polymer either by physical or chemical change.

Applications:

Some of the important applications of conducting polymers are:

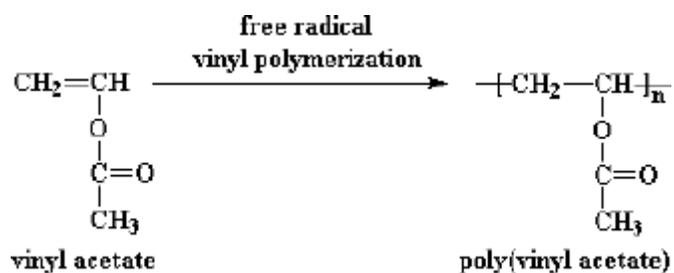
- In rechargeable light weight batteries based on perchlorate doped polyacetylene – lithium system. These are about 10 times, lighter than conventional lead storage batteries.
- In optically display devices based on polythiophene. When the structure is electrically based, the optical density of the film changes, i.e., color changes. Such electrochromic systems produce colored displays with faster switching time and better viewing than conventional liquid crystal display devices.
- It is used in wiring in aircrafts and aerospace components
- It is used in telecommunication systems
- It is used in antistatic coatings for clothing.

Biodegradable polymers

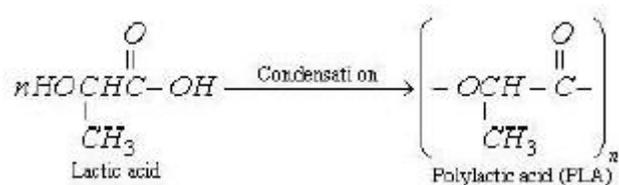
These are those polymers which get decomposed under aerobic or anaerobic conditions, as a result of the action of microorganism/enzymes.

Some biodegradable polymers are listed below

Properties: Polyvinyl acetate is a colorless, transparent material, resistant to water, atmospheric oxygen and chemicals. It is soluble in organic acids and organic solvents. It has a good heat resistance. It is harmless if taken orally. **Uses:** It is used for making records, chewing gums, surgical dresses, paints, plastic emulsions, wrapping papers, leather and textiles etc.

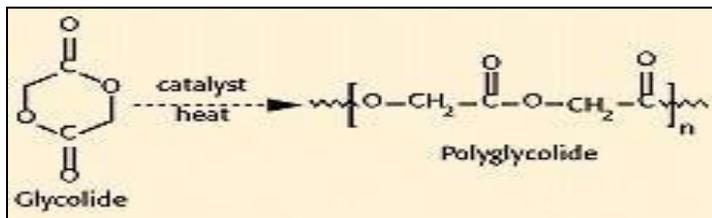


II. Polylactic acid (PLA): Polylactic acid (PLA) is obtained by polymerisation of the cyclic dimer of lactic acid or by microbiological synthesis of lactic acid followed by the polycondensation and removal of water by evaporation.



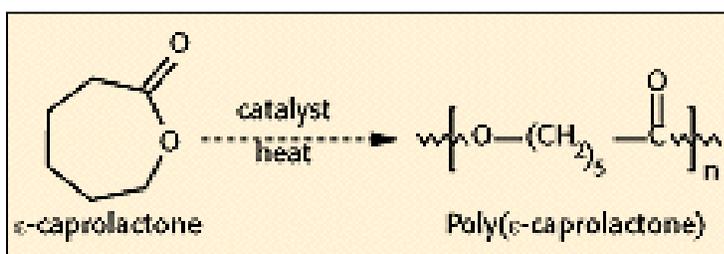
Applications: it breaks down in the environment back to lactic acid which can be metabolized which has application in medical field such as sutures, drug delivery systems and wound clips. it has also agriculture applications such as time release coatings for fertilizers and pesticides.

PGA: It is used in fishing industry, controlled release of pesticides, egg cartons, Razor handles, toys and in the medical field.



PCL (Poly caprolactone)

It is thermoplastic biodegradable polyester synthesized by chemical Conversion of crude oil, followed by ring opening polymerisation. PCL has good water, oil, solvent and chlorine resistance. It is manufactured under trade name "Tone Polymer".



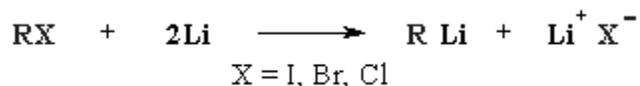
LECTURE-52Organometallic Compounds

Compounds that contain a metal-carbon bond, **R-M** are known as "*organometallic*" compounds. Organometallic compounds of Li, Mg (Grignard reagents) are amongst some of the most important organic reagents.

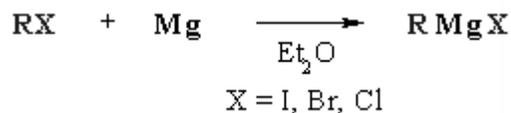
Organometallic compounds provide a source of **nucleophilic carbon** atoms which can react with electrophilic carbon to form a new carbon-carbon bond. This is very important for the synthesis of complex molecules from simple starting materials.

To rationalise the general reactivity of organometallics it is **convenient** to view them as ionic, so **R-M = R⁻M⁺**

The most important reactions in this chapter are the reactions of organolithiums, **RLi**, and Grignard reagents, **RMgX**, with the carbonyl groups in aldehydes, ketones and esters to give alcohols. However, we will also look at some useful reactions involving Cu, Zn and Hg (mercury).

Preparation of Organolithium Reagents

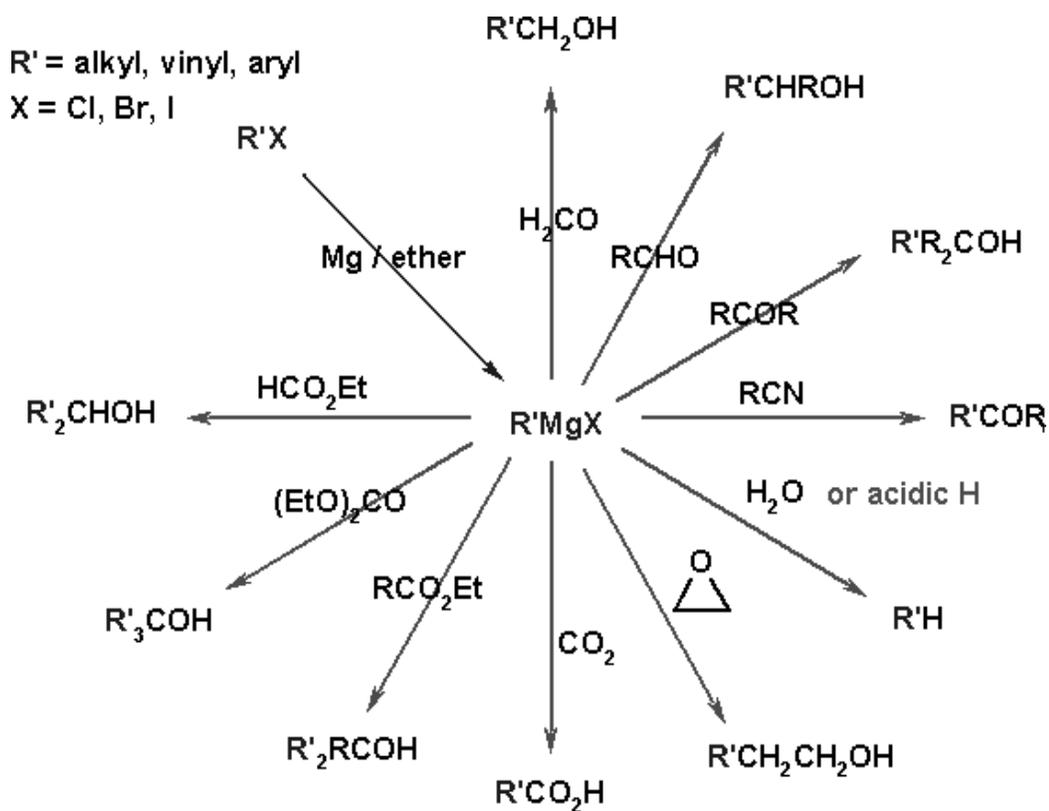
- They are formed by the reaction of alkyl halides with lithium metal.
- Typical solvents are normally anhydrous diethyl ether but pentane or hexane can also be used.
- The alkyl group can be primary, secondary or tertiary.
- Halide reactivity : I > Br > Cl
- **R** can be alkyl, vinyl or aryl
- Other Group I metals (Na, K) can be used instead of Li.

Preparation of Organomagnesium Reagents**Reaction type: oxidation - reduction**

- Organomagnesiums are formed by the reaction of alkyl halides with magnesium metal.

- Typical solvents are normally anhydrous diethyl ether or tetrahydrofuran.
- The alkyl group can be primary, secondary or tertiary.
- Halide reactivity : $I > Br > Cl$
- **R** can be alkyl, vinyl or aryl.

Applications of Grignard Reagent



Typical work-up for these reactions:

1. Dilute aqueous acid or
2. Aqueous ammonium chloride