

**RAJIV GANDHI PROUDYOGIKI VISHWAVIDYALAYA, BHOPAL**  
**New Scheme Based On AICTE Flexible Curricula**  
**B.Tech. First Year**

**Branch- Common to All Disciplines**

<b>BT101</b>	<b>Engineering Chemistry</b>	<b>3L-0T-2P</b>	<b>4 Credits</b>
--------------	------------------------------	-----------------	------------------

**Course Contents:**

**(i) Water – Analysis, Treatments and Industrial Applications (4 Lectures)**

Sources, Impurities, Hardness & its units, Determination of hardness by EDTA method, Alkalinity & It's determination and related numerical problems.

**(ii) Boiler problem & softening methods (4 Lectures)**

Boiler troubles (Sludge & Scale, Priming & Foaming, Boiler Corrosion, Caustic Embrittlement), Softening methods (Lime-Soda, Zeolite and Ion Exchange Methods) and related numerical problems.

**(iii) Lubricants and Lubrication (4 Lectures)**

Introduction, Mechanism of lubrication, Classification of lubricants, significance & determination of Viscosity and Viscosity Index, Flash & Fire Points, Cloud & Pour Points, Aniline Point, Acid Number, Saponification Number, Steam Emulsification Number and related numerical problems.

**(iv) Polymer & polymerization (4 Lectures)**

Introduction, types of polymerisation, Classification, mechanism of polymerisation (Free radical & Ionic polymerization). Thermoplastic & Thermosetting polymers Elementary idea of Biodegradable polymers, preparation, properties & uses of the following polymers- PVC, PMMA, Teflon, Nylon 6, Nylon 6:6, Polyester phenol formaldehyde, Urea- Formaldehyde, Buna N, Buna S, Vulcanization of Rubber.

**(v) Phase equilibrium and Corrosion (5 Lectures)**

Phase diagram of single component system (Water) Phase diagram of binary Eutectic System ( Cu-Ag.) Corrosion: Types, Mechanisms & prevention.

**(vi) Spectroscopic techniques and application (6 Lectures)**

Principle, Instrumentation & Applications, electronics spectroscopy, Vibrational & Rotational Spectroscopy of diatomic molecules.

**(vii) Periodic properties (4 Lectures)**

Effective Nuclear Charge, Variations: S, P, d & f Orbital energies of atoms in periodic table, Electronics Configuration, atomic & Ionic sizes, electron affinity & electro negativity, Polarizability & Oxidation States.

**Course Outcomes**

The concepts developed in this course will aid in quantification of several concepts in chemistry that have been introduced at the 10+2 levels in schools. Technology is being increasingly based on the electronic, atomic and molecular level modifications.

Quantum theory is more than 100 years old and to understand phenomena at nanometer levels, one has to base the description of all chemical processes at molecular levels. The course will enable the student to:

- Analyse microscopic chemistry in terms of atomic and molecular orbitals and intermolecular forces.
- Rationalise bulk properties and processes using thermodynamic considerations.
- Distinguish the ranges of the electromagnetic spectrum used for exciting different molecular

- energy levels in various spectroscopic techniques
- Rationalise periodic properties such as ionization potential, electronegativity, oxidation states and electronegativity.
- List major chemical reactions that are used in the synthesis of molecules.

### Practical List

NOTE: At least 8 of the following core experiments must be performed during the session.

- Water testing**
  - Determination of Total hardness by Complexometric titration method.
  - Determination of mixed alkalinity
    - OH & CO<sub>3</sub>**
    - CO<sub>3</sub> & HCO<sub>3</sub>**
  - Chloride ion estimation by Argentometric method.
- Fuels & Lubricant testing:**
  - Flash & fire points determination by
    - Pensky Martin Apparatus,
    - Abel's Apparatus
    - Cleveland's open cup Apparatus
    - Calorific value by bomb calorimeter.
  - Viscosity and Viscosity index determination by
    - Redwood viscometer No.1
    - Redwood viscometer No.2
  - Proximate analysis of coal
    - Moisture content
    - Ash content
    - Volatile matter content
    - Carbon residue
  - Steam emulsification No & Anline point determination
  - Cloud and Pour point determination of lubricating oil
- Alloy Analysis**
  - Determination of percentage of Fe in an iron alloy by redox titration using N-Phenyl anthranilic acid as internal indicator.
  - Determination of Cu and or Cr in alloy by Iodometric Titration.
  - Determination of % purity of Ferrous Ammonium Sulphate & Copper Sulphate.

### Reference Books :

- Chemistry in Engineering and Technology - Vol.1 &2 Kuriacose and Rajaram , McGraw Hill Education
- Fundamental of Molecular Spectroscopy C.N. Banwell , McGraw Hill Education
- Engineering Chemistry – B.K. Sharma, Krishna Prakashan Media (P) Ltd., Meerut.
- Basics of Engineering Chemistry – S.S. Dara & A.K. Singh, S. Chand &Company Ltd., Delhi.
- Applied Chemistry – Theory and Practice, O.P. Viramani, A.K. Narula, New Age International Pvt. Ltd. Publishers, New Delhi.
- Elementary Spectroscopy ,Y .R. Sharma , S. Chand Publishing
- Polymer Science, Vasant R. Gowariker, N. V. Viswanathan, Jayadev Sreedhar, New Age International Pvt. Ltd
- Advanced Inorganic Chemistry, G.R. Chatwal, Goal Publishing house
- Engineering Chemistry (NPTEL Web-book ) B.L. Tembe, Kamaluddin and M.S. Krishna

## UNIT I: WATER ANALYSIS, TREATMENTS AND INDUSTRIAL APPLICATIONS

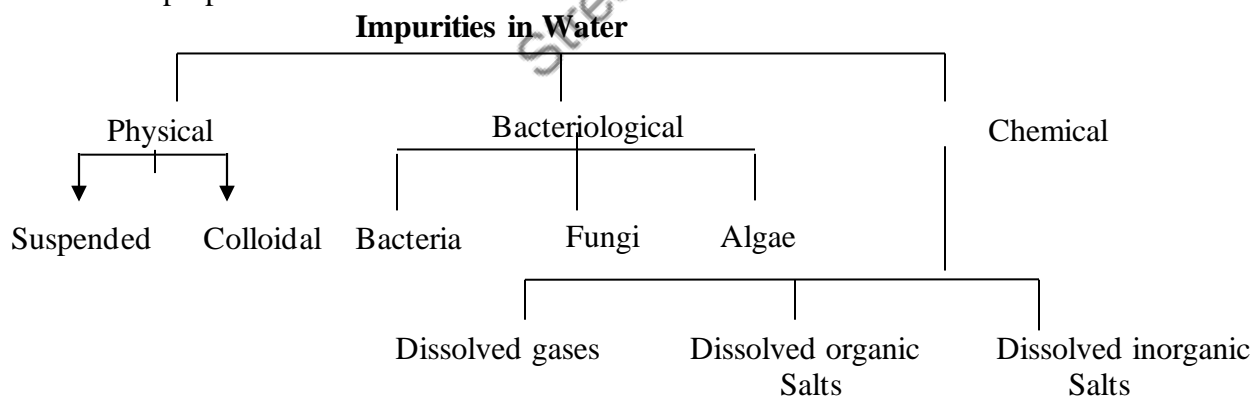
**INTRODUCTION:** For the existence of all living beings, water is very crucial. Almost all human activities – domestic, agricultural and industrial demand use of water. Although water is nature's most wonderful and abundant compound but only less than 1% of the world's water resources is available for ready use. Hence, water has to be used carefully and economically.

### **SPECIFICATIONS OF WATER:**

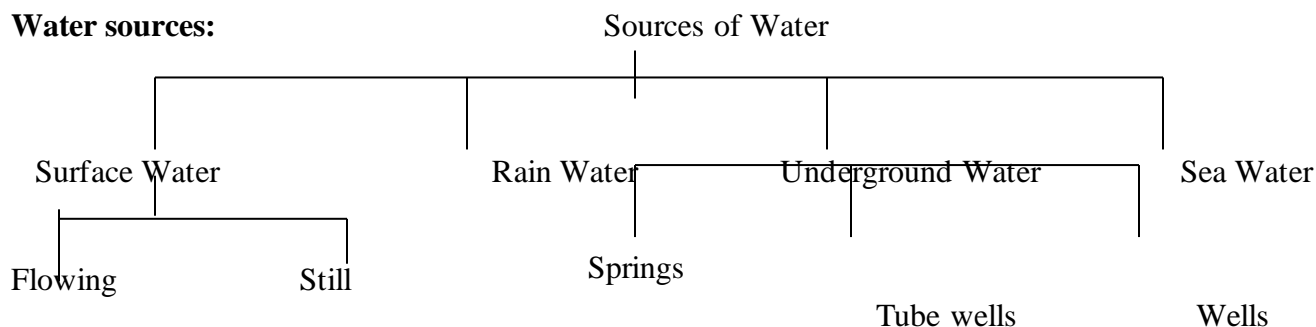
Different uses of water demand different specifications –

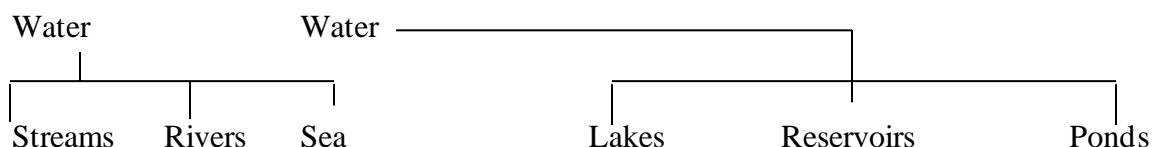
- (i) Textile industry needs frequent dyeing of clothes and the water used by this industry should be soft and free from organic matter. Hard water decreases the solubility of acidic dyes. Organic matter imparts foal smell.
- (ii) Laundries require soft water, free from colour, Mn and Fe, because hardness inc. consumption of soaps, salts of Fe and Mn impart a grey or yellow shade to the fabric.
- (iii) Boilers require eater of zero hardness otherwise efficient heat transfers is prevented by scale formation. Untreated water can lead to corrosion of boiler material.
- (iv) Paper industry requires water free from  $\text{SiO}_2$  as it produces cracks in paper; turbidity as it can affect brightness and colour of paper; alkalinity as it consumes more alum; hardness as  $\text{Ca}^{2+}$  Mg. Salts increases the ash content of the paper.
- (v) Sugar industry requires water free from hardness because hard water causes difficulty in the crystallization of sugar.
- (vi) Dairies and pharmaceutical industry require ultra pure water, which should be colorless, tasteless, odorless and free from pathogenic organisms.

Therefore water needs to be treated to remove undesirable impurities. "Water treatment" is the process by which all types of undesirable impurities are removed from water and making it fit for domestic or industrial purposes.



### **Water sources:**



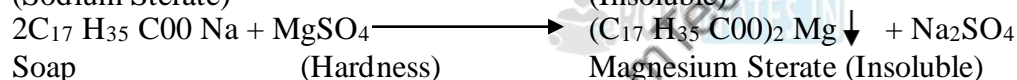
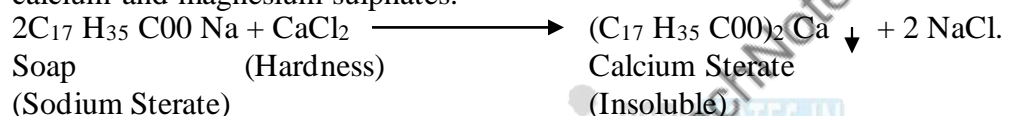


River water contains dissolved minerals like chlorides sulphates, bicarbonates of sodium, magnesium, calcium and iron. Its composition is not constant. Lake water has high quantity of organic matter present in it. Its chemical composition is also constant. Rain water, in the purest form of natural water. When it comes down, it dissolves organic and inorganic suspended particles and some amount of industrial gases.

Underground water is free from organic impurities and is clearer in appearance due to filtering action of the soil. It has large amount of dissolved salts. Sea water is very impure due to continuous evaporation and impurity thrown by rivers as they join sea.

### **HARDNESS OF WATER:**

Hardness is defined as soap consuming capacity of water sample. It is that characteristic “which prevent the lathering of soap.” It is due to presence of certain salts of Ca, Mg and other heavy metal ions like  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  dissolved in it. A sample of hard water, when treated with soap (K or Na salt of higher fatty acids like oleic, palmitic or stearic acid), does not produce lather, but forms insol. white scum or ppt. which does not possess any detergent action, due to formation of insoluble soaps of calcium and magnesium sulphates.



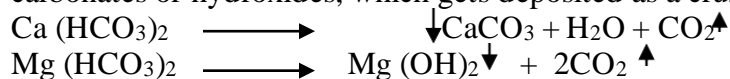
S.No	HARD WATER	SOFT WATER
1.	Water which does not produce lather with soap solution readily, but forms a ppt.	Water which lather easily on shaking with soap solution, is called soft water.
2.	It contains dissolved Ca & Mg salts in it.	It does not contain Ca & Mg salts in it.
3.	Cleansing quality is depressed and lot of soap is wasted.	Cleansing quality is not depressed and so not soap is wasted.
4.	Boiling point of water is elevated, and more fuel and time are required for cooking.	Less fuel and time are required for cooking in soft water.
5.	Water is said to hard when hardness is above 100 mg. / ltr.	In soft water hardness is below 100 mg. / ltr.

### **TYPES OF HARDNESS: It is of following types**

#### **1. Temporary Hardness:**

- (a) It is caused by presence of dissolved bicarbonates of Ca, Mg and other heavy metals and the carbonates of Iron. Example –  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$ .

- (b) It can be removed by boiling of water, when bicarbonates decompose to yield insoluble carbonates or hydroxides, which gets deposited as a crust at the bottom of vessel.

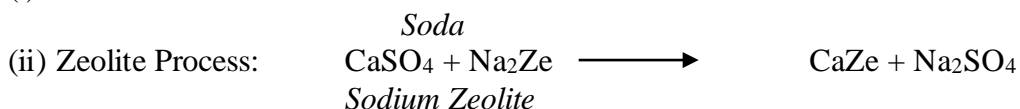
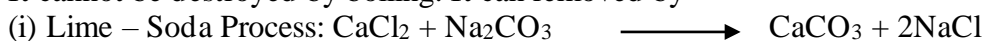


- (c) It is also known as carbonate hardness or alkaline hardness.

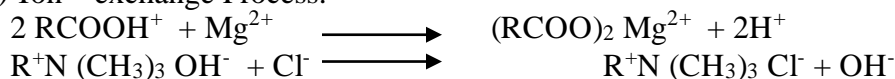
- (d) It is determined by titration with HCl using methyl orange as indicator.

## 2. Permanent Hardness:

- (a) It is due to presence of dissolved chlorides and sulphates of calcium, magnesium, iron and other heavy metals, eg.  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{FeSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$  etc.
- (b) It cannot be destroyed by boiling. It can be removed by-



(iii) Ion – exchange Process:



- (c) Permanent hardness is also known as non-carbonate or non-alkaline hardness.

3. Total Hardness = Carbonate Hardness (Temporary) + Non-carbonate Hardness (Permanent)

## DEGREE OF HARDNESS:

Although hardness of water is never present in form of calcium carbonate because it is insoluble in water and calcium is not the only cation causing hardness but hardness is expressed in terms of equivalent amount (equivalents) of  $\text{CaCO}_3$  i.e., the mg  $\text{CaCO}_3$  / Litre.

The  $\text{CaCO}_3$  is chosen as standard because:

- $\text{CaCO}_3$  is chosen as the standard mainly because it is having great convenience to calculate as the molecular weight is 100 and its equivalent weight is 50.
- It is sparingly soluble salt in water, thus, can be easily precipitated in the lime soda processes of softening water.

Therefore, all the hardness-causing impurities are first converted in terms of their respective weights equivalent to  $\text{CaCO}_3$  and is expressed in parts per million.

**Multiplication factors for different salts are:**

Constituent Salt / ion	Molar Mass	n – factor	Chemical equivalent = $\frac{\text{molar mass}}{\text{n – factor}}$	Multiplication factor for converting into equivalents of $\text{CaCO}_3$
$\text{Ca}(\text{HCO}_3)_2$	162	(divalent) 2	$162/2 = 81$	$100/2 \times 81 = 100/162$
$\text{Mg}(\text{HCO}_3)_2$	146	2	$146/2 = 73$	$100/2 \times 73 = 100/146$
$\text{CaSO}_4$	136	2	$136/2 = 68$	$100/2 \times 68 = 100/136$
$\text{MgSO}_4$	120	2	$120/2 = 60$	$100/2 \times 60 = 100/120$
$\text{CaCl}_2$	111	2	$111/2 = 47.5$	$100/2 \times 47.5 = 100/111$
$\text{MgCl}_2$	95	2	$95/2 = 47.5$	$100/2 \times 50 = 100/95$
$\text{CaCO}_3$	100	2	$100/2 = 50$	$100/2 \times 50 = 100/100$
$\text{MgCO}_3$	84	2	$84/2 = 42$	$100/2 \times 42 = 100/84$
$\text{CO}_2$	44	2	$44/2 = 22$	$100/2 \times 22 = 100/44$
$\text{Mg}(\text{NO}_3)_2$	148	2	$148/2 = 74$	$100/2 \times 74 = 100/148$
$\text{HCO}_3^-$	61	(monovalent) 1	$61/1 = 61$	$100/2 \times 61 = 100/122$
$\text{OH}^-$	17	1	$17/1 = 17$	$100/2 \times 17 = 100/34$
$\text{CO}_3^{2-}$	60	2	$60/2 = 30$	$100/2 \times 30 = 100/60$
$\text{NaAlO}_2$	82	1	$82/2 = 82$	$82/2 \times 82 = 100/164$

$\text{Al}_2(\text{SO}_4)_3$	342	6	$342/6 = 57$	$100/2 \times 57 = 100/114$
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278	2	$278/2 = 139$	$100/2 \times 139 = 100/278$
$\text{H}^+$	1	1	$1/1 = 1$	$100/2 \times 1 = 100/2$

### UNITS OF HARDNESS:

Parts per million (ppm): ppm is the parts of calcium carbonate equivalent hardness per  $10^6$  parts of water.

1. Milligrams per litre (mg/L): It is the number of milligrams of  $\text{CaCO}_3$  equivalent hardness present per litre of water.

$1 \text{ mg / L} = 1 \text{ mg of } \text{CaCO}_3 \text{ eq. Hardness / L of water}$

But 1 L of water weights = 1000 gms.

$= 1000 \times 1000 \text{ mg.}$

$1 \text{ mg / L} = 1 \text{ mg / } 10^6 \text{ mg} = 1 \text{ ppm.}$

2. Clarke's degree ( $^\circ\text{Cl}$ ): It is the number of grains of  $\text{CaCO}_3$  equivalent hardness per gallon of water. It is the parts of  $\text{CaCO}_3$  equivalent hardness per 70,000 parts of water.
3. Degree French ( $^\circ\text{Fr}$ ): It is the parts of  $\text{CaCO}_3$  eq. Hardness per  $10^5$  parts of water.

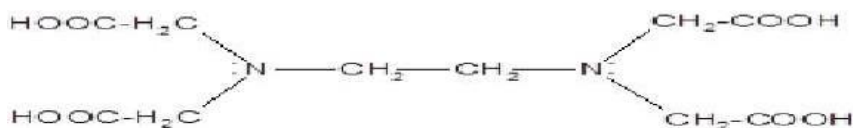
### Relationship between units:

1 PPm	=	1 mg / L	=	0.1 $^\circ\text{Fr}$	=	0.07 $^\circ\text{Cl}$
1 $^\circ\text{Fr}$	=	10 PPm	=	10 mg / L	=	0.7 $^\circ\text{Cl}$
1 $^\circ\text{Cl}$	=	14.3 PPm	=	14.3 mg/L	=	1.43 $^\circ\text{Fr}$

### Determination of Hardness by EDTA Method

- EDTA is abbreviation of Ethylene diamine tetra acetic acid.
- EDTA dissolves in water with great difficulty and in a very very small quantity.
- On the contrary its di-sodium salt dissolves in water quickly and completely. Hence for common experimental purpose, in place of EDTA, its di-sodium derivative is used.
- EDTA is a hexadentate ligand. It binds the metal ions in water i.e  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  to give highly stable chelate complex. (These metal ions are bonded via oxygen or nitrogen from EDTA molecule). Therefore this method is called as **Complexometric Titration**.

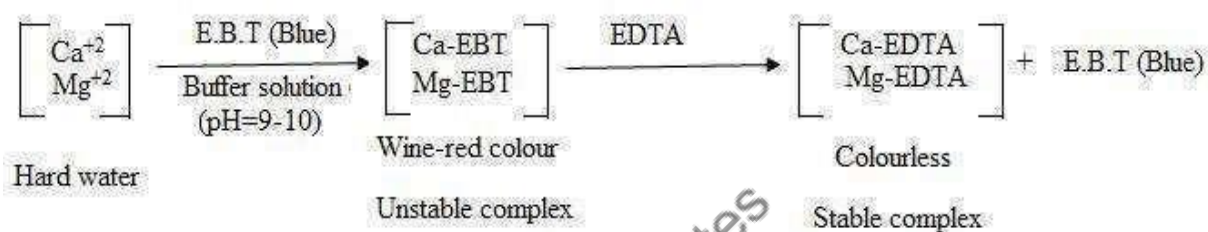
### Structure of EDTA (Ethylene diamine Tetra acetic acid)



### Principle of EDTA Method:

- The di-sodium salt of EDTA forms complexes with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , as well as with many other metal cations, in aqueous solution.

- Thus, the total hardness of a hard water sample, can be determined by titrating  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  present in the sample with di-sodium salt of EDTA ( $\text{Na}_2\text{EDTA}$ ) solution, using ammonical buffer solution containing  $\text{NH}_4\text{Cl-NH}_4\text{OH}$  of  $\text{pH}$  10 using Eriochrome Black-T (EBT) as the metal indicator.
- At  $\text{pH}$  10, EBT indicator from wine red coloured unstable complex with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions in hard water.
- This complex is broken by EDTA solution during titration, giving stable complex with ions and releasing EBT indicator solution which is blue in colour. Hence the colour change is from wine red to blue (EBT's own colour).
- Thus noting the colour change, the point of equivalence can be trapped and hardness of water can be determined by this method.



#### Advantages of EDTA Method:

- Greater accuracy
- Highly rapid
- Highly convenient

#### Alkalinity and its determination:

##### Alkalinity:

- It can be defined as “the concentration of the salts present in water which increases the concentration of  $\text{OH}^-$  ions due to hydrolysis thereby rising  $\text{pH}$  of water to alkaline range”.
- Natural water when found alkaline, it is generally due to the presence of  $\text{HCO}_3^-$ ,  $\text{SiO}_3^{2-}$  and sometimes  $\text{CO}_3^{2-}$  ions. In addition to the above the alkalinity of boiler water is also due to the presence of  $\text{OH}^-$  &  $\text{PO}_4^{2-}$  ions.
- The extent of alkalinity depends on the presence of ions, which broadly can be categorized as presence of
- (i)  $\text{OH}^-$  only (ii)  $\text{CO}_3^{2-}$  only (iii)  $\text{HCO}_3^-$  only (iv)  $\text{OH}^-$  &  $\text{CO}_3^{2-}$  together (v)  $\text{HCO}_3^-$  &  $\text{CO}_3^{2-}$  together.
- Hydroxide and bicarbonates do not exist together because hydroxyl ions react with bicarbonate ions to form carbonate ions. Therefore existence of hydroxyl and bicarbonates ions together is ruled out.

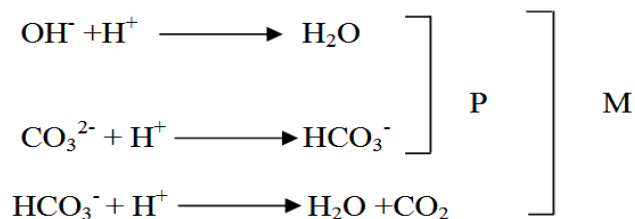


The alkalinity of natural water is due to the presence of hydroxides, carbonates and bicarbonates of Calcium and Magnesium. Alkalinity is a measure of the ability of water to neutralize the acids. The constituents causing alkalinity in natural water are as follows:



This is determined by titrating the sample with a standard solution of a strong acid. When the pH of the sample is above 8.3, titration is first carried out using phenolphthalein indicator. At the end point when the indicator changes from pink to colorless, the pH is lowered to about 4.5 due to addition of HCl. At this point complete neutralization of hydroxide and conversion of all the carbonate into bicarbonate occurs. The alkalinity measured up to this point is called phenolphthalein alkalinity. [P] Titration is continued using methyl orange indicator. The color changes from yellow to red and shows complete neutralization of all the bicarbonate ions.

When standard acid solution is added to alkaline water following reactions takes place:-



The total volume of acid used in both the stages corresponds to the neutralization of hydroxide, carbonate and bicarbonate and is thus, a measure of Total Alkalinity. [M]

**Calculation of Alkalinity of water by following table**

Alkalinity	OH <sup>-</sup> (ppm)	CO <sub>3</sub> <sup>2-</sup> (ppm)	HCO <sub>3</sub> <sup>-</sup> (ppm)
P = 0	0	0	M
P = 1/2M	0	2P	0
P < 1/2M	0	2P	(M-2P)
P > 1/2M	(2P-M)	2(M-P)	0
P = M	P = M	0	0

#### **Significance:**

- 1) For calculating the amounts of lime and soda required for water softening.
- 2) In conditioning boiler feed water, highly alkaline waters may lead to Caustic Embrittlement and also may cause deposition of precipitates and sludge in boiler tubes and pipes.
- 3) Bicarbonates of calcium and magnesium induce temporary hardness in water, which if untreated, causes scale formation in boilers.

#### **Numerical based on Hardness & Strength**

#### **Formula for Determination of Hardness:**

**Hardness = Strength (in mg/l) × Chemical equivalent wt. of CaCO<sub>3</sub>**

**Chemical equivalent wt. of hardness producing salt**



**Formula for Determination of Strength:**

$$\text{Strength} = \text{Hardness (in mg/l)} \times \frac{\text{Chemical equivalent wt. of hardness producing salt}}{\text{Chemical equivalent wt. of CaCO}_3}$$

## **UNIT II: BOILER PROBLEMS & SOFTENING METHODS**

### **BOILER WATER (WATER FOR STEAM GENERATION)**

A boiler is a closed vessel in which water under pressure is transferred into steam by the application of heat. In the boiler furnace, the chemical energy in the fuel is converted into heat, and it is the function of the boiler to transfer this heat to the contained water in the most efficient manner. The boiler should also be designed to generate high quality steam for plant use. A boiler must be designed to absorb the maximum amount of heat released in the process of combustion. This heat is transferred to the boiler water through radiation, conduction and convection.

*Steam utilization.* Steam is generated for the following plant uses:

- (i) Turbine drive for electric generating equipment, blowers and pumps,
- (ii) Heating for direct contact for equipment and comfort,
- (iii) Process for direct contact with products; direct contact sterilization and noncontact for processing temperatures.

Water is mainly used in boilers for the generation of steam (for industries and power houses). For such water all the impurities are not necessarily eliminated, and only those impurities which lead to operational troubles in boilers are eliminated or kept within the tolerable limits.

**Boiler-feed water should correspond with the following composition:**

- (i) Its hardness should be below 0.2 ppm.
- (ii) Its caustic alkalinity (due to  $\text{OH}^-$ ) should be between 0.15 and 0.45 ppm.
- (iii) Its soda alkalinity (due to  $\text{Na}_2\text{CO}_3$ ) should be 0.45–1 ppm.

Excess of impurities, if present, in boiler feed water generally cause the following problems:

**Scale and sludge formation, corrosion, priming and foaming, caustic embrittlement.**

### **BOILER PROBLEM:**

1. SLUDGE & SCALE FORMATION
2. PRIMING & FOAMING
3. CARRY OVER
4. BOILER CORROSION
5. CAUSTIC EMBRITTLEMENT

#### **1. Sludge and Scale Formation in Boilers**

In a boiler, water is continuously evaporated to form steam. This increases the concentration of dissolved salts. Finally a stage is reached when the ionic product of these salts exceeds their solubility product and hence they are thrown out as precipitates.

If the precipitates formed are soft loose and slimy, these are known as *sludges*, while if the precipitate is hard and adhering on the inner walls, it is called as *scale*.

**SLUDGE:** Sludge is a soft, loose and slimy precipitate formed within the boiler. Sludges are formed by substances which have greater solubility in hot water than in cold water, e.g.  $\text{MgCO}_3$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{MgSO}_4$  etc. They are formed at comparatively colder portions of the boiler get collected at places where the flow rate is slow; they can be easily removed (scrapped off) with a wire brush. If sludges are formed along with scales, then former gets entrapped in the latter and both get deposited as scales.

**Disadvantages of sludge formation:-**

---

- (i) Sludges are poor conductors of heat, so they tend to waste a portion of heat generated and thus decrease the efficiency of boiler.
- (ii) Excessive sludge formation disturbs the working of the boiler. It settles in the regions of poor water circulation such as pipe connection, plug opening, gauge-glass connection, thereby causing even choking of the pipes.

#### Prevention of sludge formation:-

- (i) By using softened water
- (ii) By frequently '**blow-down operation**', (i.e. partial removal of concentrated water through a tap at the bottom of boiler, when extent of hardness in the boiler becomes alarmingly high.

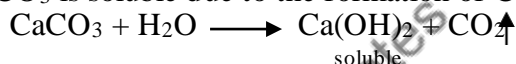
**SCALES:** Scales are hard deposits firmly sticking to the inner surfaces of the boiler. They are difficult to remove, even with the help of hammer and chisel, and are the main source of boiler troubles.

(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,  $\text{CaCO}_3$  is soluble due to the formation of  $\text{Ca(OH)}_2$



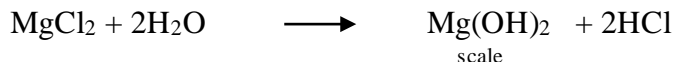
(iii) *Deposition of calcium sulphate:-*

The solubility of  $\text{CaSO}_4$  in water decreases with increase in temperature.  $\text{CaSO}_4$  is soluble in cold water, but almost completely insoluble in super-heated water. It may be due to increase ionization at high temperature so  $k_{sp} < k_{ionic \text{ prod.}}$  and less availability of water molecules for solvation at high temperature.

Consequently,  $\text{CaSO}_4$  gets precipitated as hard scale on the hotter parts, of the boiler. *This type of scale causes troubles mainly in high pressure boilers*. Calcium sulphate scale is quite adherent and difficult to remove, even with the help of hammer and chisel.

(iii) *Hydrolysis of magnesium salts*

Dissolved magnesium salts get hydrolyzed (at prevailing high temperature inside the boiler) forming magnesium hydroxide precipitate, which forms a soft type of scale, e.g.



(iv) *Presence of silica:-*

Even if a small quantity of  $\text{SiO}_2$  is present, it may deposit as calcium silicate ( $\text{CaSiO}_3$ ) and / or magnesium silicate ( $\text{MgSiO}_3$ ). These deposits adhere very firmly on the inner side of the boiler surface and are very difficult to remove. One important source of silica in water is the sand filter.

#### Disadvantages of Scale formation:

(i) *Wastage of fuel.* Scales have a poor thermal conductivity so the rate of heat transfer from boiler to inside water is greatly reduced. In order to provide a steady supply of heat to water, excessive or over-heating is done and these causes increase in fuel consumption.

The wastage of fuel being dependent on the thickness and the nature of scale:

Thickness of scale (mm)	0.325	0.625	1.25	2.5	12
Wastage of fuel	10%	15%	50%	80%	150%

(ii) *Lowering of boiler safety.* Due to scale formation, over-heating of boiler is done in order to maintain a steady supply of steam. It makes the boiler material softer and weaker. This cause distortion of boiler tube and also makes the boiler unsafe to bear the pressure of the steam, especially in high-pressure boilers.

(iii) *Decrease in efficiency.* Deposition of scales in the valves and condensers of the boiler, choke them partially. This results in decrease in efficiency of the boiler.

(iv) *Danger of explosion.* When thick scales crack due to uneven expansion, the water comes suddenly in contact with over-heated portion and large amount of steam is formed instantaneously. This results in development of sudden of sudden high-pressure which may cause explosion of the boiler.

### Removal of Scales:

Scales are removed by mechanical methods (i – iii) and / or by chemical methods (iv)

(i) If the scales are loosely adhering, it can be removed with the help of scraper or piece of wood or wire brush,

(ii) *If the scales are brittle*, it can be removed by giving thermal shocks (i.e., heating the boiler and then suddenly cooling with cold water).

(iii) *If the scales are loosely adhering, they can also be removed* by frequent blow-down operation. Blow-down operation is partial removal of hard water through a ‘tap’ at the bottom of the boiler, when extent of hardness in the boiler becomes alarmingly high. ‘Make-up’ water is addition of fresh softened water to boiler after blow down operation.

(iv) *If the scales are adherent and hard*, they can be removed by dissolving them by adding chemicals e.g.,  $\text{CaCO}_3$  scales can be dissolved by using 5-10% HCl. Calcium sulphate scales can be removed by adding EDTA, since the Ca – EDTA complex is highly soluble in water.

The essential differences between sludges and scales are summarized as follows:

S.No.	Sludges	Scales
1.	Sludges are soft, loose and slimy precipitate.	Scales are hard deposits.
2.	They are non-adherent deposits and can be easily removed.	They stick very firmly to the inner surface of boiler and are very difficult to remove.
3.	Formed by substances like $\text{CaCl}_2$ , $\text{MgCl}_2$ , $\text{MgSO}_4$ , $\text{MgCO}_3$ etc.	Formed by substance like $\text{CaSO}_4$ , $\text{Mg(OH)}_2$ etc.
4.	Formed at comparatively colder portions of the boiler.	Formed generally at heated positions of the boiler.
5.	They decrease the efficiency of boiler but are less dangerous.	Decrease the efficiency of boiler and chances of explosions are also there.
6.	Can be removed by blow-down operation.	Cannot be removed by blow-down operation.

### 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** refers to the propulsion of water into the steam drum by extremely rapid, almost explosive boiling of the water at the heating surfaces.

The moisture contamination in the steam is expressed in percentage by weight of steam.

For example, if steam contains 0.2% moisture, its steam quality will be reported as  $100 - 0.2 = 99.8\%$ .

*Priming is caused by:*

- (i) The presence of considerable quantities of dissolved solids (mainly due to suspended impurities and due to dissolved impurities in water).
- (ii) Steam velocities high enough to carry droplets of water into the steam pipe;
- (iii) Sudden boiling;
- (iv) Faulty design of boiler.

*Priming can be avoided by:*

- (i) Controlling rapid change in steaming velocities,
- (ii) The proper design of boilers (maintaining low water levels in boilers)
- (iii) Ensuring efficient softening and
- (iv) Filtration of the boiler-water carried over to the boiler.
- (v) By blowing off sludge or scales from time to time.

**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 scaps, which greatly lowers the surface tension of water, and thus increase the foaming tendency of the liquid.

With respect to foaming, water can be following grades:

- (i) *Foaming water.* It is that water which produces foam even in two days, if blowing off operation is not done.
- (ii) *Semi-Foaming water.* It is that water which does not produce any foam in locomotive boilers for two days.
- (iii) *Non-Foaming water.* It is that water which does not produce any foam in locomotive boilers for one week.

*Foaming can be avoided by:* (i) the addition of anti-foaming agents, which act by count enacting the reduction in surface tension. For example addition of castor oil (which spreads on the surface of water and therefore) neutralizes the surface tension reduction. (ii) The removal of foaming agent (oil) from boiler water.

Traces oils are generally introduced in boiler feed water through the lubricating materials used for pumps etc. Oils can be removed by the addition of aluminum compounds, like *sodium aluminate* and *aluminium sulphate* which is hydrolyzed to form aluminium hydroxide flocks which entrap oil drops. The flocks of  $\text{Al(OH)}_3$  containing oil droplets are removed by filtration through anthracite filter bed.

**Carry Over:** The phenomenon of carrying of water along with impurities by steam is called “carry over”. This is mainly due to priming and foaming.

*Priming and foaming usually occur together.*

*They are objectionable, usually occur together.*

- (i) Dissolved salts or suspended solids in boiler water are carried by the wet steam to super heater and turbine blades, where they get deposited as water evaporates. This deposit decreases the efficiency of boiler.
- (ii) Dissolved salts may enter the parts of other machinery, thereby decreasing their life;
- (iii) The maintenance of the boiler pressure becomes difficult because of improper judgment of actual height of water column.

## Boiler Corrosion

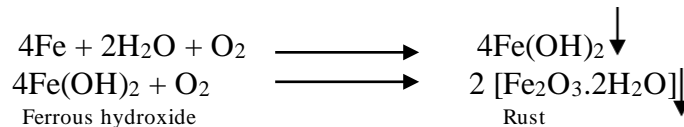
Boiler corrosion is “decay” or “disintegration” of boiler body material either due to chemical or electrochemical reaction with its environment.

The disadvantages of corrosion are:

- (i) Shortening of boiler life,
- (ii) Leakages of the joints and rivets;
- (iii) Increased cost of repairs and maintenance

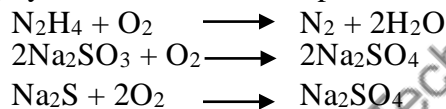
Corrosion in boilers is due to the following reasons:

(1) **Dissolved oxygen.** This is the most usual corrosion causing factor. In Boilers, oxygen is introduced through the raw water supply. Water usually contains about 8 ppm of dissolved oxygen at room temp. As the water is heated, the dissolved oxygen is set free and the boiler starts corroding. Dissolved oxygen reacts with the iron of boiler in presence of water and under prevailing high temperature to form ferric oxide (rust).



*Removal of dissolved oxygen:*

- (i) By adding hydrazine or sodium sulphate or sodium sulphide. Thus:



Hydrazine is an ideal chemical for the removal of dissolved oxygen. It reacts with oxygen, forming nitrogen and water. Nitrogen is harmless. Consequently hydrazine removes oxygen without increasing the conc. of dissolved solids/salts.

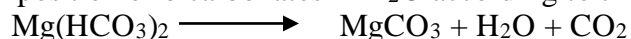
- (a) Pure hydrazine is not used in water treatment because it is an explosive inflammable liquid so 40% aqueous solution of hydrazine is used which is quite safe.
- (b) Excess hydrazine must not be used because excess of it decomposes to give  $\text{NH}_3$ , which causes corrosion of some alloys like brass etc. used in condenser tubes.



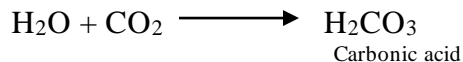
On the other hand, if sodium sulphite or sodium sulphide is used, the sodium sulphate is formed. Under high pressure it decomposes giving  $\text{SO}_2$ . The  $\text{SO}_2$  enters the steam pipes and appears as corrosive sulphurous acid ( $\text{H}_2\text{SO}_3$ ) in steam condensate. So as a rule a very low concentration of 5-10 ppm of  $\text{Na}_2\text{SO}_3$  in the boiler is maintained, rather adding it intermittently.

- (ii) *By mechanical de-aeration.* This process consists of spraying water over preheated perforated plates stacked in a degasifier. Removal of dissolved  $\text{O}_2$  is ensured by applying high temperature and vacuum.

(2) **Carbon dioxide.** There are two sources of  $\text{CO}_2$  in boiler water, viz. dissolved  $\text{CO}_2$  in raw water and  $\text{CO}_2$  formed by decomposition of bicarbonates in  $\text{H}_2\text{O}$  according to the equation:



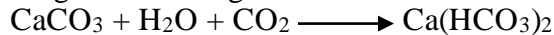
Carbon dioxide in presence of water forms carbonic acid which has a corrosive effect on the boiler material like any other acid.



*CO<sub>2</sub> can be removed by:*

- (i) Mechanical de-aeration along with  $\text{O}_2$ .

(ii) Filtering water through lime-stone



But this method increases hardness

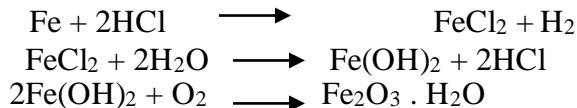
(iii) Addition of appropriate quantity of ammonium hydroxide



(3) **Mineral acids.** Magnesium chloride, if present in boiler feed water, can undergo hydrolysis producing HCl



The liberated acid reacts with iron material of the boiler to form ferrous hydroxide which in turn is converted to rust in the following way:



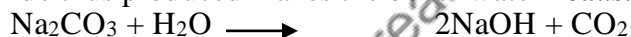
Thus, a small amount of HCl may cause extensive corrosion since HCl is produced in a chain-like manner. Consequently presence of even a small amount of  $\text{MgCl}_2$  causes corrosion of iron to a large extent.

As the boiler water is generally alkaline and hence the acid is usually neutralized. In case the amount of acid is more, calculated quantity of alkali is added from outside to neutralize the acid for preventing this corrosion.

### Caustic Embrittlement

**Caustic embrittlement** is the phenomenon during which the boiler material becomes brittle due to the accumulation of caustic substances. This type of boiler corrosion is caused by the use of highly alkaline water in the high pressure boiler.

During softening by lime-soda process, it is likely that some residual  $\text{Na}_2\text{CO}_3$  is still present in the softened water. In high pressure boilers  $\text{Na}_2\text{CO}_3$  decomposes to give sodium hydroxide and  $\text{CO}_2$ , and sodium hydroxide thus produced makes the boiler water "caustic".



This caustic water flows into the minute hair-cracks, present in the inner side of boiler, by capillary action. On evaporation of water the dissolved caustic soda concentration increases progressively which attacks the surrounding area, thereby dissolving iron of boiler as Sodium ferrote ( $\text{Na}_2\text{FeO}_2$ ).

From its place of formation, sodium ferroate decomposes a short distance away as per the following equation.



Further dissolution of iron takes place because of

- (i) The precipitation of  $\text{Fe}_3\text{O}_4$ , and
- (ii) The regeneration of NaOH.

This causes embrittlement of boiler walls more particularly stressed parts (like bends, joints, rivets, etc.), causing even failure of the boiler.

Mechanically embrittlement arises due to the setting up of a *concentration cell*.

With the iron surrounded by *dil. NaOH* acting as the *Cathode*, while the iron surrounded by *conc. NaOH* acting as the *anode*.

The iron in the anodic part gets dissolved or corroded.

*Caustic embrittlement can be prevented:*

- (i) by using sodium phosphate as softening reagent, instead of sodium carbonate in external treatment of boiler water.
- (ii) by adding tannin or lignin to boiler water which blocks the hair-cracks in the boiler walls thereby preventing infiltration of caustic soda solution into these areas.
- (iii) by adding sodium sulphate to boiler water:



$\text{Na}_2\text{SO}_4$  also blocks hair-cracks, thereby preventing infiltration of caustic soda solution in these. It has been observed that caustic cracking can be prevented if  $\text{Na}_2\text{SO}_4$  is added to boiler water so that the ratio:

$\frac{[\text{Na}_2\text{SO}_4 \text{ conc.}]}{[\text{NaOH conc.}]}$  is kept as 1:1, 2:1 and 3:1 in boilers working respectively at pressures up to 10, 20 and above 20 atmospheres.

## **Softening Methods**

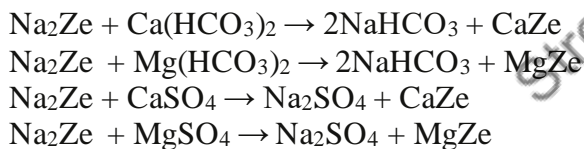
### **Zeolite process**

Zeolite is micro-porous mineral which is used as catalyst in many industrial purposes such as water purification and air purification. The zeolites are hydrated aluminosilicates and general composition  $\text{Al}_x\text{Si}_y\text{O}_{2(x+y)}$  (without water molecules). Zeolites are two types natural and synthetic or artificial. The natural zeolite that is used for water softening is gluconites or greensand. Permutit is the synthetic zeolite that is most used in water softening and its chemical formula is  $\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, n\text{SiO}_2, x\text{H}_2\text{O}$ . These are used as ion exchanger and odor removal in water softener. Permutit are more porous, glassy, and have higher softening capacity than greensand.

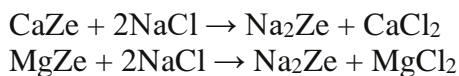
Zeolites are characteristically soft to moderately hard, light in density, insoluble in water but can act as base exchangers in contact with water containing cations. Hence these can remove  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions from water when hard water is passes through.

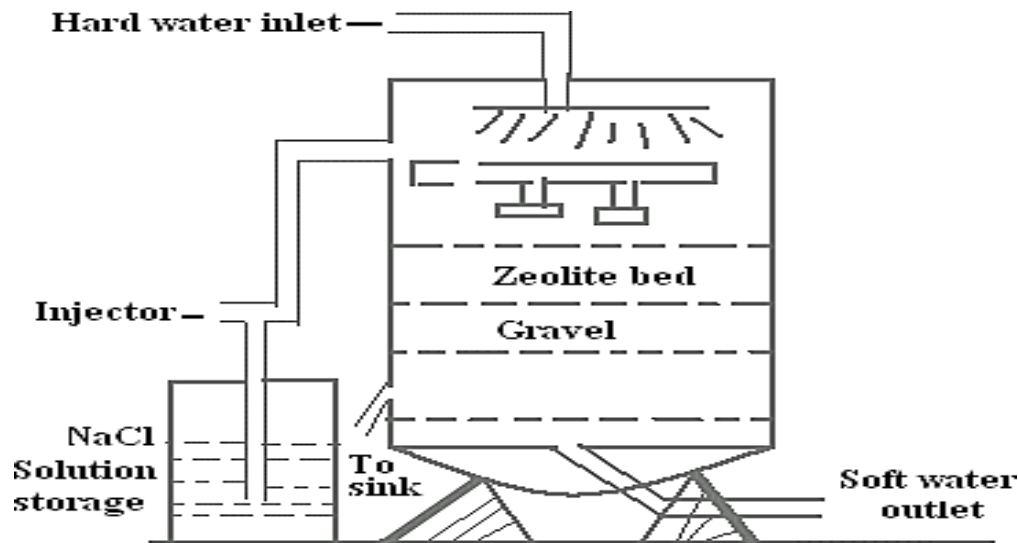
#### **Zeolite process for water softening**

Zeolite process for water softening has become a commercial success for the reason that zeolite can be easily regenerated. When  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions containing hard water is passes through a bed of sodium zeolite, the sodium ions are replace by the calcium and magnesium ions.



When all sodium ions are replaced by calcium and magnesium ions, the zeolite becomes inactive. Then the zeolite needs to be regenerated. Brine solutions are passing through the bed of inactivated zeolite. The following reactions are taken place and form  $\text{Na}_2\text{Ze}$





### Merits of Zeolite Process:

It removes the hardness almost completely (about 10 ppm hardness only).

The process automatically adjust itself for variation in hardness of incoming water.

This process does not involve any type of precipitation, thus, no problem of sludge formation occurs.

### Demerits of Zeolite Process:

The outgoing water (treated water) contains more sodium salts.

This method only replaces  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  ions by  $\text{Na}^{+}$  ions.

High turbidity water cannot be softened efficiently by zeolite process.

### Ion exchange process Or Demineralization process Or Deionization process

Ion exchanger resin are insoluble, cross linked, long chain higher molecular weight organic polymers which are permeable due to their micro porous structure, and the functional groups attached to the chains are involved in the ion-exchanging properties.

#### Types of ion exchanger resins

**Cation exchanger resins ( $\text{RH}^{+}$ )** : These are usually styrene divinyl benzene copolymers which on carboxylation or sulphonation become capable of exchanging their  $\text{H}^{+}$  ions with the cations of the solution. These have acidic functional groups like  $\text{SO}_3\text{H}^{+}$ ,  $-\text{COOH}^{-}$  or  $\text{OH}^{-}$

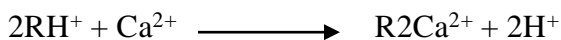
**Anion exchanger resins ( $\text{ROH}^{-}$ )** : These are usually styrene divinyl benzene or amine formaldehyde copolymers which on treatment with dilute  $\text{NaOH}$  solution become capable to exchange their  $\text{OH}^{-}$  anions with anions in water. Which contains basic functional groups like quaternary ammonium or quaternary sulphonium or quaternary phosphonium groups.

#### Ion exchange process

It is a two stage process, the water first passes through the column containing hydrogen exchanger (Cation exchanger) and then through second column containing hydroxyl exchanger

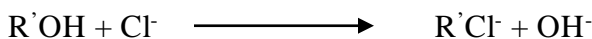
(Anion exchanger).  $\text{H}^+$  and  $\text{OH}^-$  ions released from cation exchanger and anion exchanger columns get combined to produce water molecule.

Cation exchange resins :



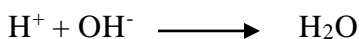
( $\text{RH}^+$  = Cation exchange resin)

Anion exchange resins :

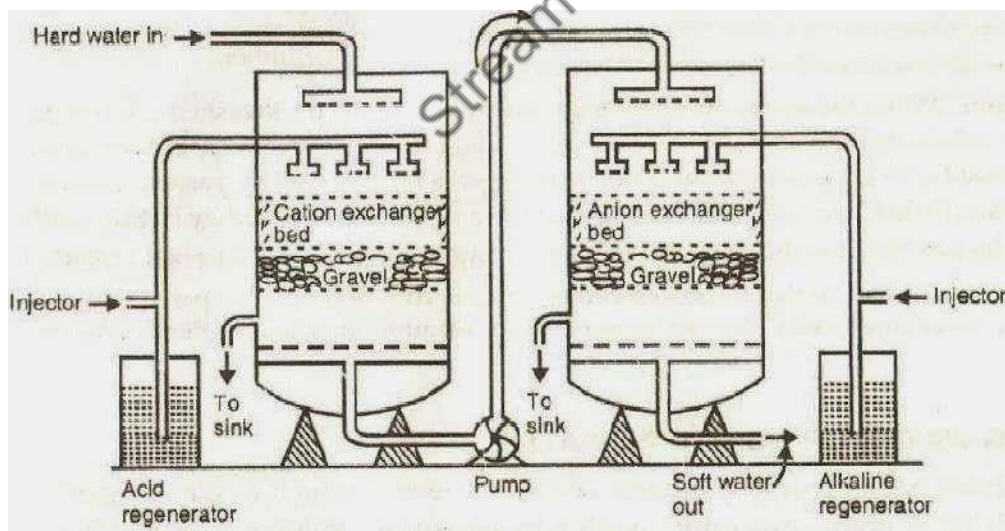


( $\text{R}'\text{OH}^-$  = Anion exchange resin)

$\text{H}^+ + \text{OH}^-$  ions , combine and produce water



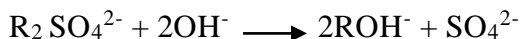
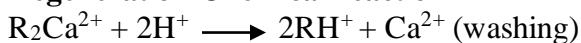
### **Ion exchange process Diagram**



### **Regeneration of exhausted resins**

After some time the cation and anion exchanging resins lose the capacity to remove  $\text{H}^+$  ions and  $\text{OH}^-$  ions respectively, they are then said to be exhausted.

When the resins are exhausted, the supply of water is stopped. The exhausted cation exchanger is regenerated by passing dilute  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  Solution and exhausted anion exchanger resin is regenerated by passing dilute  $\text{NaOH}$  solution.

**Regeneration Chemical reaction**

The columns are washed with deionised water and washing (which contain  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $SO_4^{2-}$ ,  $Na^+$  ions) are passed to sink or drain. The regenerated resins are again used.

**Advantages:**

Highly acidic or alkaline water also can be softened by this process.

It produces water of low hardness (up to 2 ppm).

If the output water is passed through de-gassifier, then the gaseous impurities like  $O_2$ ,  $CO_2$  also get expelled, to get water of distilled water standard.

**Disadvantages:**

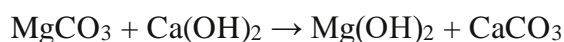
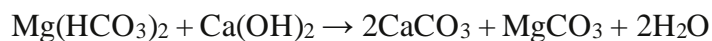
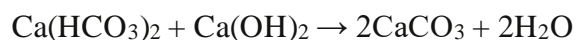
Costly equipment and costly chemicals are needed for regeneration.

Turbid water can not be used as it decreases the efficiency of resins.

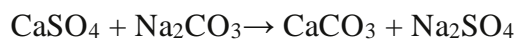
It can be operated only small scale purification of water.

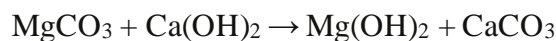
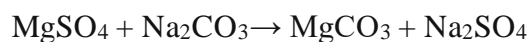
Soda lime is a process used in water treatment to remove **Hardness** from water. This process is now obsolete but was very useful for the treatment of large volumes of hard water. Addition of lime ( $CaO$ ) and soda ( $Na_2CO_3$ ) to the hard water precipitates calcium as the carbonate, and magnesium as its hydroxide. The amounts of the two chemicals required are easily calculated from the analysis of the water and stoichiometry of the reactions. The lime-soda uses lime,  $Ca(OH)_2$  and soda ash,  $Na_2CO_3$ , to precipitate hardness from solution. Carbon dioxide and carbonate hardness (calcium and Magnesium bicarbonate) are complexed by lime. In this process Calcium and Magnesium ions are precipitated by the addition of lime ( $Ca(OH)_2$ ) and soda ash ( $Na_2CO_3$ ).

temporary water hardness the following reactions are take places:



In case of permanent water hardness the following reactions are take places:





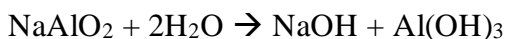
There are two type lime-soda process; cold lime soda process and hot lime soda process.

### **Cold Lime soda process**

When the chemicals (L Or S) are added to hard water at room temperature, the process is known as cold lime soda process.

At room temperature, the precipitates are finely divided and do not settle easily, nor can they be easily filtered.

They help in the formation of coarse precipitates.



Cold lime soda process provides water containing a residual hardness of 50-60 ppm.

### **Hot Lime soda process**

When the chemicals are added to higher temperature (80° C to 150° C) the process is known as Hot lime soda process.

### **Why Hot L-S Method is proffered over the Cold L-S Method**

- In hot lime soda method at higher temperature.
- The reactions are fast.
- Precipitation is more complete.
- Settling rate and filtration rates are increased. As a result the precipitate and sludge formed settle rapidly and coagulants and also chemicals needed are in smaller quantities than that of cold L-S process.
- Dissolved gases are eliminated from water to a certain extent.
- The softened water recovered has hardness of about 15 to 30 ppm.

### **Advantages**

- It is very economical process.
- Less amount of coagulants are required.
- Certain quantity of minerals is reduced from water.
- The level of carbon dioxide can also be reduced using hot L-S Process.
- Fe and Mn are also removed from the water.
- The process increases the PH value of the treated water thereby corrosion of the distribution pipes is reduced.

### **Disdvantages**

- Sludge disposal is problem.
- This can remove hardness only up to 15 ppm, which is not good for boilers.
- Careful operations and skilled supervision are required for economical and efficient softening.

StreamTechNotes

## **UNIT III: LUBRICANTS & LUBRICATION**

### **INTRODUCTION:**

All material surfaces, harder or softer, have many irregularities in the form of asperities (Peaks) and valleys. When two solid surfaces are pressed over each other, the asperities of both the upper surface and lower surface come in contact with each other, it causes some deformation effect on the metal surface which is more in case of ductile metals. This contact causes the weld junction which carries all the loads between the two surfaces. Thus, the true area of contact is only a small fraction of the apparent contact area between the two surfaces. Friction is the relative movement of two surfaces in contact with each other. Generally, there are two types of friction encountered, (i) sliding friction and (ii) rolling friction.

Surface wear during sliding is due to shearing of asperities

**(i) Sliding friction:** The friction caused by the sliding two materials of different hardness over one another. Due to this sliding, the peaks of the softer metal gets broken easily than the peaks of the harder metals.

The effects of the sliding friction are:

(a) Ploughing i.e., cutting out the softer material by the asperities of the harder materials.

(b) The interlocking of the surface irregularities.

**(ii) Rolling friction:** It occurs when a load sphere or cylinder rolls over a flat surface of the other body. The coefficient of the rolling friction is usually very low as compared to the sliding friction. Thus, the effect of rolling friction is much lower than the sliding friction, as the effect of rolling friction is caused by elastic deformation of the two surfaces. In case of sliding friction, the coefficient of friction is much larger in static condition than for the kinetic condition. Therefore, the lubricant plays less important role in case of rolling friction than the sliding friction.

In case of any friction a considerable amount of frictional heat is released at the rubbing surfaces which is more in case of sliding friction as the contact area of this friction is more. The frictional heat is not uniformly distributed over apparent contact area between the rubbing materials but it is highly localized, particularly at the surface asperities. If this frictional heat reaches the melting temperature of the material, welded junction may be formed. The amount of frictional heat depends upon the nature of the sliding material and the speed of the sliding.

**Lubricant- A substance which is introduced between two relatively moving surfaces for reducing friction and wear is called lubricants.** The process of reducing frictional resistance between moving surfaces by the application of lubricants is called lubrication.

Functions of Lubricants:

1. It reduces the loss of energy in the form of heat.
2. It increases the efficiency of machine.
3. It efficiently prevents the interlocking or inter-joints welding at the surface asperities.
4. It increases the smooth motion of the moving parts.
5. It reduces the surface deformation, wear and tear.
6. It reduces the expansion of metal by local frictional heat.
7. It protects the materials from corrosion.
8. Sometimes it stops the leakage of gases or pressures from the cylinder.

### **Mechanisms of Lubrication:-**

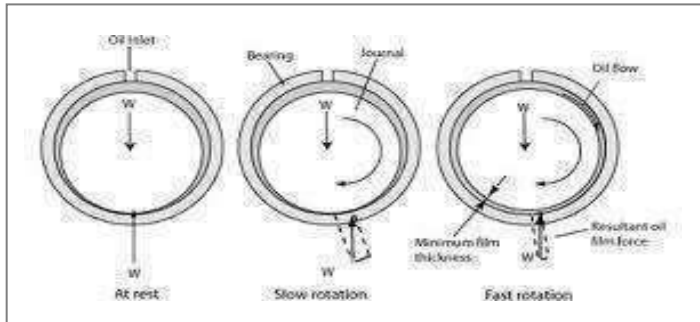
There are mainly three types of mechanism of lubrication. They are:

- 1. Fluid film or hydrodynamic lubrication.**
- 2. Thin film or boundary lubrication.**



### 3. Extreme pressure lubrication.

**(1) Fluid film or hydrodynamic lubrication:** In this lubrication, two moving surfaces are separated from each other by a thick film of lubricating oil (thickness around  $1000\text{\AA}$ ). Hence it prevents the direct contact between these rubbing surfaces and welding of junctions generally does not occur. This happens because, the lubricating oil covers the irregularities of the sliding surfaces & forms a thick layer in between them, so that there is no direct contact between the material surfaces. Actually the shaft floats in the lubricant.



The resistance to movement of moving parts is only due to the internal resistance between the particles of the lubricant moving over each other. Based on this principle, the lubricant chosen should have low viscosity. Selection of lubricant: In order to maintain a suitable viscosity of the oil, ordinary hydrocarbon lubricants are blended with long chain polymers. At operating condition, hydrocarbon petroleum fractions. Generally contain small quantities of unsaturated hydrocarbons, which get oxidized to form gummy products. To reduce the antioxidants like amino phenols are added. This type of hydrodynamic lubrication gives satisfactory results as the coefficient of friction in such cases is very low. Hydrodynamic friction occurs in the case of a shaft running at a fair speed with a low load.

**(ii) Boundary lubrication or thin film lubrication:** It is done when a thick fluid film cannot be maintained between the two moving surfaces so that direct metal to metal contact is possible. This happens when (i) the viscosity of the oil is low (ii) the load is very high (iii) the speed of the movement is very low and (iv) a shaft starts moving from rest. Under such conditions, the lubricant should be adsorbed physically or chemically on both the metallic surfaces. These adsorbed lubricant layers avoid the direct metal to metal contact. The coefficient of friction in these cases is slightly more than hydrodynamic lubrication. In boundary lubrication, surface asperities contact each other even though the lubricant supports much of the load. Friction depends mainly on the shearing forces necessary to cleave these adhering asperities and wear and friction can be reduced by certain additives. Wear inhibitors and lubricity agents are polar materials that adsorb on a metal and provide a film that reduces metal-to-metal contact.

Condition of lubricants: The lubricant used for boundary lubrication should have:

- (1) Long hydrocarbon chains.
- (2) Lateral attraction between the chains.
- (3) Polar groups to promote spreading and orientation over the metallic surfaces at high pressure.
- (4) Active groups to form chemical bonds with metallic surfaces.

In this boundary lubrication the metal surfaces are closer to each other, but still they are well separated by the lubricant. The property of the oil which enhances the adsorption and maintenance of the thin film is called oiliness. High viscosity index, resistance to heat and oxidation, good oiliness and low pour

point are some of the good qualities of boundary lubricants. Boundary lubrication (i.e., the boundary friction) boundary lubrication is the lubricant from the friction surfaces between the molecules and the internal friction between molecules (i.e., liquid lubrication) the transition to direct contact with the surface friction before the critical state. At this time there is a layer of friction interface adsorption film thickness is typically about  $0.1\mu\text{m}$ , with some lubrication. We call this layer of thin boundary film. Boundary lubrication film depends on the nature of the friction surface; depends on the oil lubricant additives, extreme pressure additives on the friction surface of the metal structure of the boundary film formation with the oil viscosity has little mouth. Generally vegetable and animals oils have all the above mentioned good qualities of lubricant. They are adsorbed (physically or chemically) easily on the, metal surfaces with the active group of  $-\text{COOH}$ . But they tend to break down at high temperatures. In order to improve the oiliness of the mineral oils, usually little fatty acids are added.

(iii) **Extreme pressure lubrications:** Extreme pressure lubrication are a special case of boundary lubrication, friction is Deputy Commissioner in the override (or high contact stress), speed, temperature conditions, extreme pressure lubricant additives react with the metal friction surface generate a chemical reaction film, separated the two friction surfaces, and play a lower coefficient of friction, reduce wear and tear (or change the direct contact with the metal surface of serious wear and tear), to the role of lubrication, it is called extreme pressure lubrication. When the moving surfaces are under very high pressure and speed, the lubricant may decompose or vaporize or they may not stick on the surfaces because high local temperature is produced. To meet these extreme pressure conditions, special additives called "extreme pressure additives" are added to the mineral oils. Extreme pressure additives are compounds having active groups such as chlorine (chlorinated esters), sulphur (sulphurised oils) and phosphorus (tricresyl, phosphate). At high temperatures, they react with metal giving surface layers like metallic chlorides, sulphides or phosphides. These surface layers have high melting point and serve as good lubricant under extreme pressure and temperature conditions. Extreme pressure (EP) additives are a special class of boundary lubrication additive which react with the metal surface to form compounds with lower shear strength than the metal.

### **Classification of Lubricants:-**

Lubricants may be broadly classified, on the basis of their physical state as:

1. Liquid Lubricants.
  - (a) Vegetable oils and animals oils.
  - (b) Mineral oils from petroleum.
  - (c) Blended oils or doped oils or compound oils.
  - (d) Synthetic oils.
2. Semi solid lubricants.
3. Solid lubricants.

### **Lubricating Oils/ Liquid lubricants:**

**(a) Vegetable or animal oils:** These are most commonly used lubricants. They possess good oiliness and adsorb themselves on the metallic surfaces. However, they decompose at high temperatures and undergo oxidation easy, forming gummy and -acidic hydrolyzed products and get thickened on coming in contact with air. Thereby restricting the smooth movement of the moving surfaces. To overcome such restrictions, usually they are blended with mineral oils (blending agents).

**(b) Mineral oils:** They are obtained by fractional distillation of petroleum. They are the heavier fractions containing long chain hydrocarbons in petroleum oils ranging between 12 to 50 carbon atoms. The shorter chain oils have lower viscosity than the longer chain hydrocarbons. They are widely used as

lubricants as they possess good stability under service conditions but poor oiliness. The oiliness of these oils can be improved by adding oils like oleic, stearic acids etc. They have impurities like sulphur compounds, gum forming alkenes, asphalt, waxy impurities, other color impurities, reluctant and some other unwanted impurities. All these impurities should be removed to prevent the formation of corrosive and gummy products to decrease the friction.

**Removal of impurities:** A number of processes are used for removing these undesired impurities as follows:

(i) Solvent refining: Sulphur compounds, alkenes and other gum products can be removed by this process. In this process, the oil is mixed with a suitable solvent like phenol which is immiscible with oils. But the undesirable impurities are highly soluble in phenol, thereby the liquid separates into two layers (oil goes up and phenol comes down).

Oil layer is free from impurities but containing some solvents and the solvent layer contains the impurities. Then the oil layer is distilled out and some additives may be added to improve the lubricating quality of the oil.

(ii) Dewaxing: Waxy impurities are removed by treating the lubricants with suitable solvents like propane and then the wax solution is cooled. The wax precipitates, which is removed from the oil by passing the oil wax suspension through a filter. The solvent present in the oil is then recovered by distillation.

(iii) Filtration: The colored impurities can be removed by filtration through bauxite or clay.

(iv) Acid refining: Sometimes the dewaxed oils contain a number of undesirable impurities. To eliminate these impurities, the dewaxed-oil is treated with concentrated  $H_2SO_4$  and then agitated so that the impurities dissolve in acid and it is filtered out. This filtrate is neutralized by adding a calculated amount of a base NaOH.

**(c) Blended lubricating oils:** Single oil cannot possess all the good qualities of the lubrication. Therefore to get the satisfactory lubricant with desirable characteristics, specific additives are blended with the oil. These are called blended oils. An additive is a material that imparts a new or desired properties to the lubricating oil. It may also enhance a desirable property that the lubricating oil already possess to some degree. Broadly, there are two types of additives chemically active additive & chemically inert additives. Chemically active additive are those which chemically interact with metals (to form protective films) .dispersant, detergents, extreme pressure agents, etc. Chemically inert additives are those additives which improve the physical properties that are critical to the effective performance of the lubricant. Like viscosity index improver, foam inhibitors etc.

### **Greases or Semi solid lubricants:-**

The most important semisolid lubricants are Greases and Vaseline.

**Grease:** Grease is used to lubricate journal bearings when cooling of the bearing is not a factor, typically if the bearing operates at relatively low speeds. Grease is also beneficial if shock loading occurs or if the bearing frequently starts and stops or reverses direction. Grease is almost always used to lubricate pins and bushings because it provides a thicker lubricant than oil to support static loads and to protect against vibration and shock-loading that are common in many of these applications. Lithium soap or lithium complex thickeners are the most common thickeners used in greases and are excellent for most journal bearing applications.

Grease is a semisolid combination of a petroleum product and soap. It is obtained by saponification of fat (fatty acids etc.) with alkali like NaOH followed by adding hot Lubricating oil under agitation. The amount of mineral oil added determines the consistency of the finished grease. Soaps are gelling agents which can interconnect with the added oil. Therefore, the structure of the lubricating greases is like gel.

Soaps dissolve in the oil at higher temperatures so that the interconnecting bonds will be broken out and the grease liquefies. To improve the heat resistance of grease; inorganic solid thickening agents like clay, colloidal silica, carbon black etc. are added to it.

#### **Advantages of greases:**

1. Greases have higher frictional resistance than oil.
2. Because of the presence of soap in oil, greases stick well on the surfaces.
3. Greases are used in situations where oil film cannot be remaining in its position i.e. in machine working under high pressures at slow speed.
4. Greases can support heavier load at low speed.
5. Greases can be used in bearing and gears that work at high temperatures.
6. They are used in situations where sealing is necessary against entry of dust, dirt, grit or moisture.
7. Greases are used in situations, where dripping or spurting of oil is undesirable; therefore it can be used in textile and good products manufacturing industries.
8. They also do not require much attention as oils.

#### **Disadvantages of greases:**

1. They have high co-efficient of friction.
2. They have a tendency to separate into oils and soaps.
3. On long use, oil in the grease may evaporate.
4. Greases cannot effectively dissipate heat from the bearing.

Greases are classified based on the soap used in their manufacture as below:

- (a) **Lime or calcium soap grease or cup greases:** They are the emulsions of petroleum oil with calcium soaps. They are insoluble in water, so water resistant. Above 65°C they cannot be used because oil and soap separates out above this temperature. They are widely used as they are the cheapest.
- (b) **Sodium soap greases:** They are sodium soaps dispersed in petroleum oils. They are water soluble, so they are not water resistant. They can be used up to 175°C because of its high melting point and fibrous structure. They are suitable for use where the lubricants get heated due to friction.
- (c) **Lithium soap greases:** They are petroleum oils, thickened by mixing lithium soaps. They are water resistant, high temperature withstanding, good mechanical stability and low oxidation tendency. They are suitable for use at low temperature about 15°C only. They are used in multipurpose.
- (d) **Aluminum soap greases:** They are aluminum soaps dispersed in oils. Due to its low soap content, they are water proof. They cannot be used above 90°C.
- (e) **Axle greases:** They are the resin greases. They are separated by adding slaked lime to the mixture of soluble resin oil and fatty oils. They are allowed to react at 58°C. The mixture is thoroughly mixed and allowed to stand, when grease flats as stiff mass called cold set grease. Filters like talc and mica are also added to these greases. They are water resistant and suitable for use as axle greases and for heavy equipments.

**Solid Lubricants:** Solid lubrication between the friction surface materials into the solid lubricant powder also can play a good lubricating effect. Friction between the two surfaces of solid lubricant, its shear resistance is very small, slight external force, will have a slip between molecules. This put the two outside the friction between the grinding into a solid lubricant in friction between molecules. There are two necessary conditions for solid lubricant, the first is a solid lubricant molecules should have a low shear strength, it is easy to slip; followed with solid lubricant to the friction surface has a strong affinity, in the friction process, always has maintained that the surface friction layer of solid lubricant, and a layer of solid lubricant which does not corrode the surface friction. Generally attached to the metal surface, a mechanical, but there are also form a chemical combination. The nature of the solid material with many, such as graphite, molybdenum disulfide, talc and so on. For non-layered structure for the

solid lubricant, or soft metal, mainly for its low shear stress, play a role of lubrication, then it attached to the friction surface lubricating film. For the already formed solid lubricating film lubrication mechanism of boundary lubrication mechanism can explain the lubrication approximation.

The two most usual solid lubricants employed are graphite and molybdenum disulphide. These lubricants are used either in the dry powder form or mixed with water or oil. The solids fill up the low spots in the surfaces of moving parts and form solid films, which have low frictional resistance. The usual coefficient of friction between solid-lubricants is between 0.005 and 0.01.

Advantages of solid lubricants:

1. They are used in heavy machineries working at very high loads and slow speeds.
2. The operating temperature is too high.
3. Liquid lubricants and greases are easily contaminated with dust which is unaccountable, for example, in commutator blades of electric motors and generators, because proper films cannot be maintained.
4. Combustible lubricants must be avoided.

**1. Graphite:** Graphite is most widely used of all solid lubricants. In graphite, carbon atoms are arranged in hexagons in several flat layers, which are held together by only weak bonds so that the force to shear the crystals parallel to the layers is low.

Each carbon atom in a layer is surrounded by three other carbon atoms.

**Lubricating action of graphite:** It is very soapy, non flammable graphite is mainly used at high temperature in the absence of air and high pressures. Graphite is used either in dry powder form or dispersed in oil (oil dag) or in water (aqua dag) or as graphite grease. Oil dag is found particularly useful in IC engines, because it forms a film between the piston rings and the cylinder and gives a tight fit contact, thereby increasing compression. Water dag is used in food industries, where a lubricant free from oil is needed. Graphite grease is used at high temperature.

Uses: It is used as lubricant in air compressors, lathes, general machine-shop works, food stuffs industry, railway track joints etc.

**2. Molybdenum disulphide:** It has sandwich like structure 'Mo' and 'S' are separately arranged in different layers and are sandwiched alternatively.

**Lubricating action of molybdenum disulphide:** Poor inter laminar attraction is responsible for low shear strength in a direction parallel to the layers. It is stable up to 400°C and is used at high temperatures. It possesses very low coefficient of friction. It can be used as a dry powder or oil-dag or aqua-dag or grease. A solid film made from 70% MoS<sub>2</sub>, 7% graphite and 23% silicate is used in space vehicles which can withstand high temperature and even nuclear radiation. The other commonly used solid lubricants are talc, mica, soap stone etc. Teflon acts as a lubricant in gear pumps, periscope etc.

**Synthetic Lubricants:** These are synthesized specially to meet the severe operating conditions. The synthetic lubricants can perform well over a wide range of temperatures from -50°C upto 260°C. These lubricants possess low freezing points, high viscosity index and non flammable. Polyalkene glycols, silicones, chlorinated and fluorinated hydrocarbons; organic amines, imines and oxides are the important synthetic oils.

**Advantages of synthetic lubricants**

1. They possess high thermal stability at high operating temperatures.
2. They have viscosity index and high flash points.
3. They are chemically stable and having low freezing points.



**(a) Polyalkene glycols:** Polyalkene glycols like polyethylene glycol, poly-propylene glycol etc. can be used as both water soluble and water insoluble lubricants in rubber bearings and joints. They have all the three advantages mentioned above.

**(b) Silicones:** These synthetic lubricants are not oxidized below 200°C and possess high viscosity index. At temperature above 200°C, silicones are oxidized quickly and undergo cracking process at about 230°C. Therefore such lubricants are used for low temperature lubrication purposes but not employed for high temperature applications.

**(c) Chlorinated and fluorinated hydrocarbons:** They are not decomposed by heat, not easily oxidisable and chemically inert and resistant to chemicals etc.

**(d) Organic amines:** They are good synthetic lubricants, since they possess low pour points and high viscosity index. They can be used under temperature conditions of -50°C to 250°C.

**Lubricating Emulsions:** - An emulsion is a heterogeneous system consists of disperse phase and dispersion medium. In this emulsion, the two phases are immiscible liquids. The liquid being dispersed as fine droplets (dispersed phase) into a fairly coarse dispersion medium. The size of dispersed phase should be within the range of 1 micron to 6 micron. As the two immiscible liquids is inherently unstable, it is prepared by vigorous stirring and addition of emulsifier or emulsifying agent to make it more stable. The emulsifying agents contain polar and non- polar groups and they are classified as hydrophilic end and hydrophobic end depending on their affinity towards water molecule. The hydrophilic end emulsions have greater affinity towards water while the hydrophobic ends do not have any affinity towards water, rather they are preferred to wet by oil. The emulsifier molecule is adsorbed at the interface of the two phases, resulting in formation of a protective film around the dispersed droplet. For example, soaps of different types, detergents, long chain sulphonics acids, lyophilic colloids etc. act as emulsifying agents in different cases. A certain large number of droplets of a liquid into another liquid increases the surface area and hence requires large amount of energy. The required energy would be less if the surface tension is decreased. The function of the emulsifying agents is to diminish the surface tension.

Emulsions are broadly classified into two types (1) Oil in water type in which the disperse phase is the oil in water medium (2) Water in oil type in which water droplets are dispersed in oil. The type of emulsion produced depends upon the nature of the emulsifying agents used. For example, when sodium oleate is used as an emulsifier, oil in water emulsion is formed. But if soap with a bivalent cation is employed, say calcium oleate, water in oil type emulsion is obtained. In order to ascertain the type of given emulsion, a small quantity of water is added with stirring and the effect is observed under a microscope. If the emulsion is oil in water type, water would mix freely with the excess medium, the droplets remaining undisturbed. If it is water in oil type, the addition of oil to the emulsion would produce similar effect.

### **Properties and Testing of lubricating oils**

1. Viscosity and Viscosity index
2. Flash Point and Fire Point
3. Cloud Point and Pour Point
4. Aniline Point
5. Steam Emulsion Number
6. Neutralization Number
7. Saponification Number
8. Iodine value
9. Carbon residue

**1. VISCOSITY:** - It is the property of a fluid that determines its resistance to flow. It is an indicator of flowability of a lubricating oil, the lower the viscosity, greater the flowability. It is mainly, due to the forces of cohesion between the molecules of lubricating oil.

*Absolute viscosity* may be defined as "the tangential force per unit area which is required to maintain a unit velocity gradient between two parallel layers; It is denoted by  $\eta$ . Its unit in C.G.S. System is poise and its dimensions are  $ML^{-1}T^{-1}$

*Absolute Kinematic viscosity* is the ratio of absolute viscosity to 'density for any fluid. It is denoted by  $\nu$ . Its unit in C.G.S. system is stokes and its dimensions are  $L^2 T^{-1}$

#### **Effect of temperature on viscosity.**

Like any other fluid, viscosity of lubricating oil is inversely proportional to temperature. *i.e.*, with increase of temperature, viscosity decreases. This is due to the decreases in intermolecular attraction. At higher temperatures oils must have sufficient viscosity to carry loads. Hence, heavier oils are used at higher temperatures. Similarly, light oils are used at low ambient temperatures.

#### **Effect of pressure on Viscosity**

Lubricating oils are subjected to extreme pressure at the interface between gears and between rolling element and race in a rolling bearing.. At such high pressures, viscosity of lubricating oils increases considerably.

#### **Significance of Viscosity.**

Viscosity helps in the selection of good Lubricating oil. For instance, Light oils have low densities and easy flowability. These oils *i.e.*, generally used on parts moving at high speed promotes the formation of a good oil film. Moreover, light oils do not impose much drag on high-speed parts.

#### **Diagram (from manual):**

In contrast, Heavy oils are used on parts moving at slow speed under heavy loads as they resist being squeeze out. Light oils are not suitable in this case as they have low viscosities and it is not possible to maintain lubricant film between the moving surfaces. Subsequently, excessive wear will occur. To sum up, in hydrodynamic lubrication, that lubricant is selected which should have a sufficient high viscosity to adhere to the bearing and resist being squeeze out due to high pressure and get fluid enough to resist excessive friction due to the shearing of oil itself. Thinner oil can easily dissipate the frictional heat because of good oil circulation.

#### **Measurement of viscosity of lubricating oil**

There are many instruments for measuring viscosity and are known as viscometers (or viscosity meters). For examples, Kinematic & Saybolt universal viscometers used in the United States and the Redwood viscometers are commonly used in England.

#### **The Saybolt Viscometer**

It consists of cylindrical brass cup in the bottom of which is an orifice of specified dimension. This cup is surrounded by constant temperature oil bath. A desired bath temperature can be obtained by adjusting the temperature regulator. When the sample of lubricating oil reaches test temperature. The time required for 60 mL of the oil to run through the orifice is measured. The oil sample flows by gravity under a standard falling head and at a temperature of 100°F and 210°F. A calibrated standard flask collects the liquid sample. The time of efflux is measured in seconds and are reported as Saybolt Universal Seconds (SUS); for example, 260 SUS, at 100°F. For heavy lubricating oils with high viscosities, a large orifice is used in the same apparatus, and the results are reported in Saybolt Furol Seconds (SFS) at a Specified temperature.

#### **The kinematic Viscometer**

It is a U-type of glass apparatus having respectively cone and two bulbs at its two sides. At the bottom portion of two bulb side, capillary tube is attached. It is used for the determination of Kinematic



viscosity. The four simple measurements steps are shown. For a fixed volume of sample, time is measured for the sample to flow through a calibrated capillary under an accurately reproducible head of liquid and at a constant temperature. From the measured efflux time, the kinematic viscosity is calculated.

$$\text{Kinematic viscosity in centistokes (CST)} = C \times t$$

Where C = Viscometer constant and.

t = Observed flow time in seconds.

**The Redwood Viscometer:** It is of two types:

**(a) Redwood viscosity No. 1-Universal and (b) Redwood viscosity No.2-Admiralty.**

The essential differences between the two are:

	(a)	(b)
Dimensions of Orifice.	Length: 10 mm Diameter: 1.62 mm	50 mm 3.80 mm
Useful for	Low viscous oils	Higher viscous oils
Receiving flask has	Smaller mouth	Larger mouth

The Redwood No. 1 apparatus consists of a cylindrical brass oil cup (90mm in height and 46.5 mm in diameter) that holds the test sample of lubricating oil. Bottom of the oil cup is fitted with a polished-agate discharge tube containing an orifice of specified dimension. The oil cup is surrounded by water bath for adjusting the temperature. A calibrated receiving flask (known as Kohlrausch flask) is provided for receiving the oil from polished-agate discharge tube. It is shown in when the sample reaches test temperature the time for 50mL of the sample flow through the orifice is measured. Results are reported in seconds.

For example, Redwood Viscosity No. 1 at 140°F, 350 seconds.

#### **Conversion Formulas:**

Let time of efflux = t seconds,

Saybolt:  $cSt = 0.22 t - 180ft$

Redwood:  $cSt = 0.26 t - 171ft$ .

#### **Significance of viscosity measurements.**

Viscosity is the property of lubricating oil that determines its ability to lubricate. Viscosity values are used in evaluating load carrying capacity, in denoting the effect of temperature changes, for establishing uniformity in shipments and for determining the presence of contaminants in used oil during absolute Viscosity values are required for use in all-bearing design calculations and other lubrication Engg. Technical design problems. Kinematic values are applied in oil blending procedures.

**Viscosity Index** -With changes in temperature, the viscosity of lubricating oil varies, the higher the temperature, the lower the viscosity and vice-versa. The rate of variation of Viscosity with temperature is different for different base oils or fluids. For example, in petroleum oils, the viscosities of naphthenic base oils vary more over the same temperature range than those of paraffinic base oils. The rate at which the viscosity of oil changes with temperature is measured by an empirical number, known as the **viscosity-index (V.I.)**. A relatively small change in viscosity with temperature is indicated by high viscosity index. Whereas a low viscosity index shows a relatively large change in viscosity with temperature. The Pennsylvanian oils, consisting mainly of paraffin's, are arbitrarily assigned a viscosity index value of 100 as they exhibit a relatively small change in viscosity with a rise in temperature. Oils of Gulf-coast origin, consists mainly of alicyclic (naphthenic), and are arbitrarily assigned a viscosity index value of 0 as they exhibit a larger change in viscosity with a rise in temperature. In industry, lubricating oils of high viscosity index are preferred since they have practically the same viscosity over a range of temperatures. Determination of Viscosity-index, Viscosity index of test oil is determined with

the help of two types of standard oils viz. Pennsylvanian oils and Gulf oils having V.I.'s 100 and 0 respectively. The V.I. of the test oil is given by the formula:-

$$V.I. = L - U / L - H \times 100$$

V.I. = viscosity index of the oil under-test.

$L$  = viscosity at 100° F of the low-viscosity standard oil having a V.I. of a (i.e., Gulf oil) and also having the same viscosity as the oil under test at 210° F.

$U$  = Viscosity at 100° F of the oil under test.

$H$  = viscosity at 100° F of the high-viscosity standard oil having a Viscosity of 100 (i.e., Pennsylvanian oil) and 50 having the same viscosity as the oil under test 210° F.

Example 1. An oil of unknown viscosity-index has a Saybolt universal viscosity of 60 seconds at 210° F and of 600 seconds at 100° F. The high viscosity index standard (i.e Pennsylvanian) oil has Saybolt viscosity of 60 seconds at 210° F and 500 seconds at 100° F. The low viscosity-index standard (i.e., Gulf oil has a Saybolt universal viscosity

6? Seconds at 210° F and 800 seconds at 100° F. Calculate the viscosity index of unknown oil.

Solution. Here  $L = 800$  s,  $H = 500$  s and  $U = 600$  s

So, viscosity-index of unknown oil  $V.I. = L - U / L - H \times 100$

$$800 - 600 / 800 - 500 \times 100$$

$$V.I. = 66.67$$

Example 2. An oil sample under test has a Saybolt universal viscosity of 64 sec. at 210° F and 564 seconds at 100° F. The low viscosity standard (Gulf oil) possess Saybolt ,viscosity of 64 seconds at 210° F and 774 seconds at 100° F and 414 sec. at 100° F. Calculate the viscosity-index of the oil sample under test.; Solution. Here,  $L = 774$ s,  $H = 414$ s and  $U = 564$ s

So, viscosity index of the oil-sample. Under test,  $V.I. = L - U / L - H \times 100$

$$= 774 - 564 / 774 - 414 \times 100$$

$$V.I. = 774 - 414 \times 100 = 58.33$$

### Viscosity Index and Molecular Structure of Oil

There is a direct co-relation between molecular structure of lubricating oil with its viscosity and viscosity-index. A high V.I. is exhibited, by those lubricating oils which have linear or rod-like shaped molecules of higher molecular weights. This is due to the greater inter-molecular attraction.

### Viscosity-Temperature Curves.

The variation of viscosity with temperature can also be indicated by viscosity- temperature curves: In fact, viscosity index is the numerical expression of the average slope of the viscosity-temperature curve of lubricating oil between 100°F and 210° F. Lubricating oils with small variation in viscosity with temperature exhibit flatter viscosity-temperature plots and they have high VI's.

### GRAF (from manual)

#### 1. Flash and Fire & Point:

The *flash point* of oil is the lowest temperature at which it gives off vapors that will ignite for a moment when a small flame is brought near it. The *fire point* of oil is the lowest temperature at which the vapors of the oil burn continuously for at least 5 seconds when a small flame is brought near it.

The flash points and fire points are used to indicate the fire hazards of petroleum products and evaporation losses under high temperature operations. Knowledge of flash and fire points in lubricating oil aids in precautionary measures against fire hazards. A good lubricant should have flash point at least above the temperature at which it is to be used.

### Measurement of Flash and Fire Points of Lubricating Oil

(i) *The Pensky-Marten Closed cup method.* It is used to determine- the flash Point of lubricating oils, fuel oils, solvents, solvent containing materials and suspension of solids, except cut-back asphalt. It consists of a *cup* made of brass, which is about 5.5 mm deep and 5 cm in diameter. The lid of the cup is provided with four openings of standard sizes. Through one of these openings passes a *stirrer* carrying

two brass blades; while the second opening is meant for admission of air. Through third opening passes a thermometer. While the fourth is meant for introducing test flame. At the top of the cup, a *shutter* is provided. By moving the shutter, opening in the lid opens and flame (from *flame exposure device*) is dipped into this opening. There by bringing the flame over the oil surface. As the test-flame is introduced in the opening, it gets extinguished, but when the test-flame is returned to its original position, it is automatically lighted by the pilot burner. There is also a stove consisting of an air bath and a top plate on which the flange of the cup rests. The air bath may be either a flame-heated metal casting or an electric-resistance element. Pensky-Marten's flash point apparatus is shown in Fig. **DIGRAM (from manual)**

**Procedure.** The oil sample is filled up to the specified filling mark in the cup. It is then covered and positioned properly in the stove. The thermometer is inserted in the sample. The test flame is lighted, while being stirred, the sample is heated at the rate of 9° to 11°F per minute. Upto 220° F, the test flame is applied at every 2° F rise in temperature, thereafter it is applied at every 5° F rise in temperature. When a distinct flash occurs in the interior of the cup at the time of the flame application, the temperature reading on the thermometer is the flash point.

## 2. Cloud and Pour Points.

The **cloud point** of petroleum oil is the temperature at which solidifiable compounds, like paraffin wax, present in the oil begin to crystallize or separate from solution. When the oil is cooled under specified conditions. Naphthenic type of oils that are quite wax-free show no cloud points. The **pour point** of a petroleum oil is the temperature at which the oil ceases to flow or pour.

At the Cloud point, oil becomes cloudy or hazy in appearance. Cloud and pour-points indicate the suitability of lubricants in cold conditions. Lubricants used in a machine working at low temperature should possess low pour-point; otherwise solidification of lubricant will cause jamming of the machine. Pour point is of importance in establishing the lowest temperature at which a diesel fuel is still sufficiently fluid to be pumped or transferred. Oil with a low pour point should be selected whenever the oil must remain fluid at low temperatures.

**Determination of cloud and Pour Points-** These determinations are carried out with help of apparatus. The apparatus consists of a flat-bottomed tube (about 2 cm high and 3 cm in dia.) enclosed in an air-jacket. The air-jacket is surrounded by freezing mixture. (Ice + NaCl) contained in a jar.

To determine cloud point, a sample of the lubricating oil (moisture free) is poured into a test jar and cooled in progressive steps. When inspection first reveals a distinct cloudiness or haze at the bottom of the test jar, the temperature is recorded as the cloud point.

To determine pour point, a sample of oil is cooled in flat-bottomed tube (*i.e.*, test jar) under specified conditions; the temperature is observed in increments of 5° F until no movement is observed at the surface of the oil when the tube is held in a horizontal position for 5 seconds. This temperature is recorded as the solid point. By definition the pour point is 5°F above this temperature.

**Significance.** Cloud point is useful for estimating the temperature at which filter screens in the fuel intake system of diesel engines might become dogged because of wax separation. Filterability depends on type of wax, micro crystalline or amorphous. The amorphous wax is sticky in nature and would more easily clog filter screens. Pour point values of petroleum and non-petroleum lubricants are significant as many operations must function in sub-freezing conditions.

**Aniline Point:** Aniline point is defined as "the minimum equilibrium solution temperature for equal volume of aniline and oil sample." It is determined by thoroughly mixing equal volumes of oil sample af aniline in a test tube and heating the mixture until a homogeneous solution is obtained. Then, the tube is allowed to cool at a controlled rate. The temperature at which the oil and aniline phases separate out is recorded as the aniline point. A lower aniline point of oil means a higher percentage of aromatic hydrocarbons in it. Since aromatic hydrocarbons have a tendency to dissolve natural rubber and certain types of synthetic rubbers. Thus, higher the percentage of aromatic hydrocarbon or lower the aniline

point of an oil, more are the chances of deterioration of an oil when it comes in contact with rubber sealing's, packing, etc. Consequently, low aromatic content in the lubricants or their higher aniline point is desirable.

### 3. Steam Emulsion Number:

When water enters an oil system, as it often does in hot strip mills, turbulence caused by high volume flow results in the formation of emulsions and initiate mixture of oil and water. Depending on the base oil and the refining processes, some oils form emulsions with water more easily than others. Moreover, contamination also contribute to the formation of emulsions. These emulsions have poor lubricating properties thereby causing abrasion and wearing out of the lubricated parts of the machinery. The higher the percentage of water, the worse the lubricating properties. Hence, it is desirable that the lubricating oil should form such an emulsion with water which breaks off readily. This ability of lubricating oil to separate from water is called Demulsibility. Oil that separates readily from water has good demulsibility. Oil that does not has poor demulsibility. The tendency of lubricant Water emulsion to break is determined by following *test*; steam at 100°C is bubbled through a test tube containing 20 mL of oil, till the increases to 90° C and the time is noted when the oil, and water separate out in distinct layers. The time in second in which oil and water emulsion separate out in distinct layers is called '**steam emulsion number**' (SEN) or '**emulsification number**'. The quicker the oil separates out from the emulsion, the lower the steam emulsion number and the better the lubricating oil for most purposes.

**Significance:** To avoid corrosion of polished steel surfaces like roll necks and to ensure proper lubrication, it is important to evaluate the speed of water and oil separation (demulsibility properties) of medium to high viscosity circulating oils used in rolling mills subject to cooling water contamination.

### 4. Neutralization Number

Lubricating Oil's acidity or alkalinity is determined in terms of neutralization number.

Neutralization number represents either the **Total Acid Number (TAN)**. "The number of milligrams of potassium hydroxide (KOH) needed to neutralize any acid in one gram of oil" or the **Total Base Number (TBN)**. The number of milligram of hydrochloric acid (HCl) needed to neutralize any base in one gram of oil. Determination of TAN is more common and its test procedure is given below:

#### **Reagents:**

- (i) 0.1 N alcoholic HCl solution,
- (ii) 0.1 N alcoholic KOH solution,
- (iii) Titration solvent: Made by mixing 500 mL of toluene and 5 mL of distilled water with 495 mL of isopropyl alcohol.
- (iv) Para-Naphtholbenzene indicator solution made by adding 1 g of dry indicator powder in 100 mL of isopropyl alcohol.

#### **Test procedure:**

- (i) Into 300 mL conical flask, take a weighed amount of the sample (20 gm sample for light-colored oil or 2 gm sample for dark-colored oil).
- (ii) Add 100 mL of titration solvent and 30 drops of indicator solution to the flask, then carefully swirl the mixture until the sample is completely dissolved.
- (iii) If the solution turns yellow-orange or deep orange in color, it means the oil sample was acidic [But if it assumes green or green-blue color, it means the oil sample was basic, then titration should be done with HCl.
- (iv) Slowly add the alc. KOH solution from the burette drop by drop with careful swirling until the green or green-blue end point is reached which persist for at least 15 s. The color change is reversed if HCl is the titrating agent].
- (v) Read from the burette the number of mL of solution required to reach the end point.

**Calculations:** - Total mL of titrating solution / weight of sample used  $\times 5.61$

**Significance.** This test shows relative changes in oil due to oxidation. Comparing the TAN or TBN with the values of new oil will indicate the development of harmful products or the effect of additive depletion. In fact, acid number greater than oil is usually taken as an indication of oxidation of the oil. This will consequently lead to corrosion, besides gum and sludge formation.

**Saponification Number:** **Saponification number** is defined as "The number of milligrams of potassium hydroxide required to saponify the fatty material present in one gram of the oil".

**Determination.** Saponification number is determined by refluxing a known quantity of oil with a known excess of potassium hydroxide solution and titrating the unused alkali against an acid.

**Significance.** Mineral oils do not undergo saponification but animal and vegetable oils undergo saponification. Hence, this test gives an indication of the amount of animal and vegetable oils added to mineral oils to improve oiliness. Moreover, most of the animal and vegetable oils possess their own characteristic saponification values. Any deviation from this value in a given sample indicates the probability and extent of adulteration. And last but not the least, this test helps us to ascertain whether the oil under study is animal/vegetable or mineral or compounded oil.

### **Iodine Value**

The **iodine value** is defined as "the number of milligrams of iodine absorbed by one gram of the oil. It is determined by the addition of a measured, excess of a solution of iodine bromide in glacial acetic acid, to a weighed quantity of oil dissolved in  $\text{CCl}_4$  or acetic acid. The addition of the halogenating agent to the double bond ( $s$ ) is allowed to proceed to completion. The unused  $\text{IBr}$  is then back-titrated against standard hypo solution using starch as indicator.

**Importance.** The iodine value is a measure of the degree of unsaturation and hence the tendency of a fatty oil to absorb oxygen. Regardless of composition, any oil exposed to air and heat eventually combines with the oxygen in the air to form chemical compounds unsuitable for use as lubricants. Acids and gummy sludge are typical products of oxidation. Oils with high resistance to oxidation should be used in steam turbines and other large circulating oil systems, in which/oils attain high temperatures and remain in service for extended duration. Oils with lower oxidation resistance are satisfactory in application, where oil remains in service for periods or where makeup is high because of losses.

### **Carbon Residue**

Lubricating oils contain high % of carbon in combined form. On being subjected to high temperatures, they decompose and form a carbonaceous deposit. There are two methods for measuring the amount of carbon residue or deposit remaining after a lubricating oil has been subjected to extreme heat.

(i) **The Conradson method.** It is conducted in the absence of air and is applicable for heavy residuals, crudes and non-volatile stock.

**Procedure:** A weighed amount of sample is placed in a silica crucible (of about 65-85 ml capacity), which in turn is put into a smaller iron crucible having a close-fitting cover with a small horizontal opening. The crucibles are then placed into a larger third crucible also fitted with a cover fitted loosely to shaped iron hood. Heat is supplied from a Meker burner at certain prescribed rates till vapors of all volatile matter are burnt completely. After 30 minutes the silica crucible is removed, cooled in a desiccator, and weighed.

$\% \text{ Carbon Residue} = \text{Weight of residue in crucible} / \text{Weight of original oil sample} \times 100$

(ii) **The Ramsbottom method.** This method is used with the more fluid products.

**Procedure.** A weighed sample is placed in a special glass bulb with capillary opening. (The oil is injected into the bulb through the capillary inlet by means of a syringe). This glass bulb containing



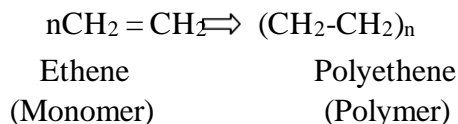
sample is inserted in one of the holes of an electrically heated small furnace (Ramsbottom apparatus) maintained at approximately 550°C. At this temperature, all volatile matter escapes the bulb capillary leaving a residue that undergoes cracking and possible coke formation. After the heating, the bulb is taken out, cooled in a desiccator and weighed.

$\% \text{ Carbon Residue} = \text{Weight of residue in crucible} / \text{Weight of original oil sample} \times 100$

**Significance of carbon-residue tests.** Certain lubricating oils tend to deposit carbon in the combustion chambers of internal combustion engines, due to the carbonizing of the lubricating oil carried up past the piston rings into the combustion chambers. Incomplete combustion of fuel also results in carbon deposition. Excessive buildup of carbon deposits in the combustion chamber results in decreased volume of the charge at the end of the compression stroke giving increasing compression ratio which eventually leads to detonation. The tests are used in the evaluation of base crudes and feed stocks for the formulation of lubricants and fuels to be used in extreme temperature service.

## POLYMERS

The word 'polymer' is derived from the classical Greek words poly meaning 'many' and \_meres' meaning 'parts'. Simply stated, a polymer is a molecular compound with high molecular mass, ranging into thousands and millions of gram. It is composed of a large number of repeating units of identical structure called monomers. For example, polythene is a polymer formed by linking together of a large number of ethene molecules.



Certain polymers, such as proteins, cellulose, and silk are found in nature and hence are called natural polymers, whereas, a number of polymers are produced by synthetic routes and are called synthetic polymers. In some cases, naturally occurring polymers can also be prepared synthetically. For e.g. rubber, which is also known as polyisoprene?

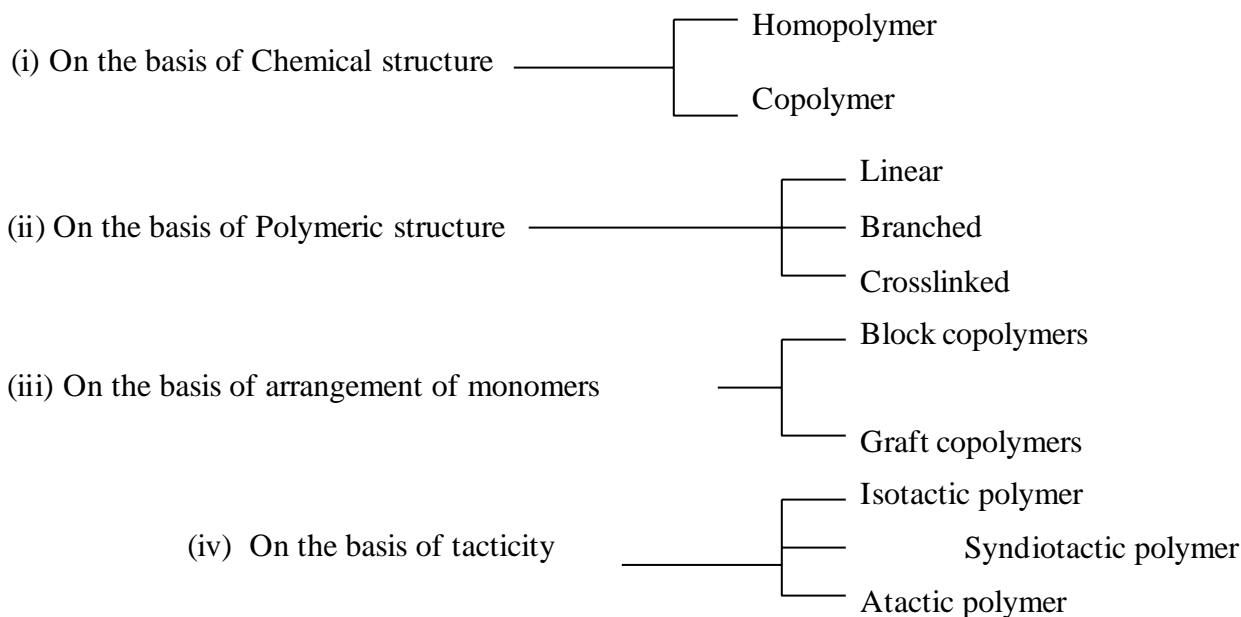
Both natural and synthetic polymers impinge on every aspect of our existence. The idea is often expressed that we live in "a plastic age". The range of polymeric materials is so wide that they have found applications in practically every branch of industry. About 80% of today's chemists, including biochemists, work with polymers.

The number of repeating; units in a chain formed in a polymer, is known as the "degree of polymerization". Polymers with high degree of polymerization are termed as "high polymers" and those with low degree of polymerization are called oligopolymers.

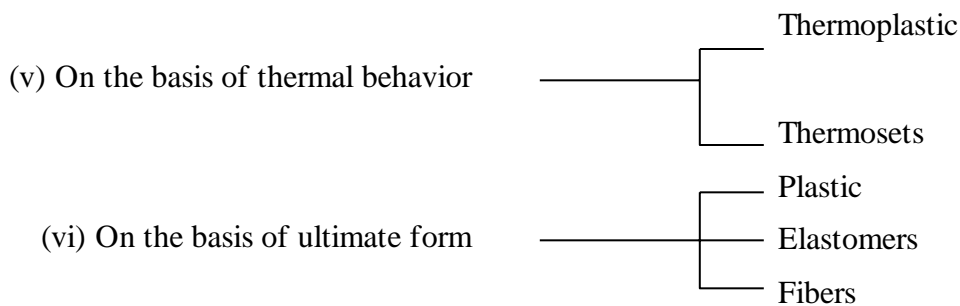
### CLASSIFICATION OF POLYMERS

Synthetic polymers have been classified into various groups, in various manners.

#### CLASSIFICATION OF POLYMERS



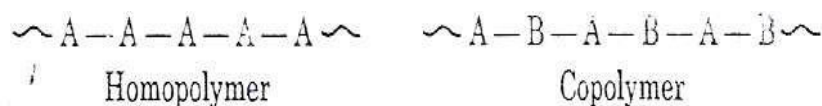




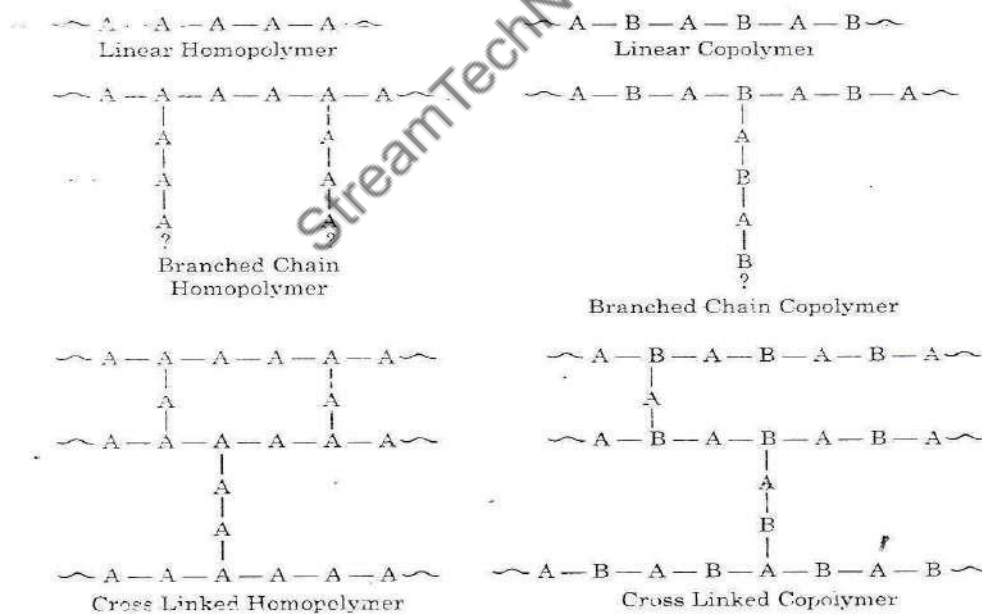
(i) On the basis of the chemical structure of their backbone, polymers are of two types:

**Homopolymer:** If a polymer consists of identical monomer, the polymer is termed as homopolymer.

**Copolymer:** If the polymer is a mixture of more than one type of monomer it is termed as copolymer.

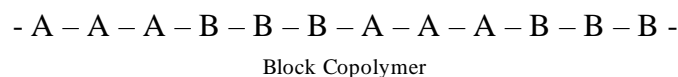


(ii) On the basis of their polymeric structures, the polymers can be classified as linear, branched or Crosslinked.



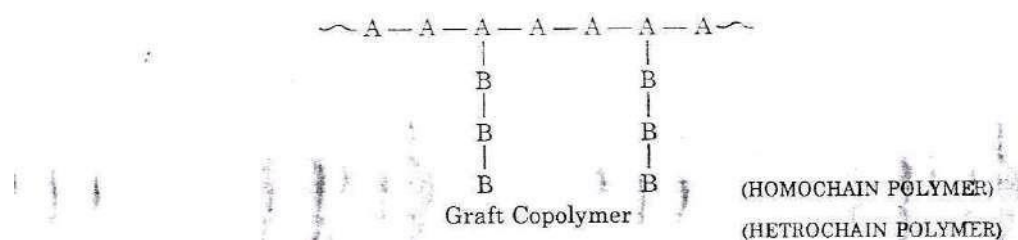
(iii) Depending upon the arrangement of the monomers in the case of copolymers, the polymers are divided into block copolymers and graft copolymers.

**Block Copolymers:** Linear polymers in which the identical monomeric units occur in relatively long sequences are called block co-polymers.



**Graft Copolymers:** Graft copolymers are branched copolymers in which the backbone is formed from one type of monomer and branches are formed of the other, i.e., the monomer

segments on the branches and backbone are not the same.

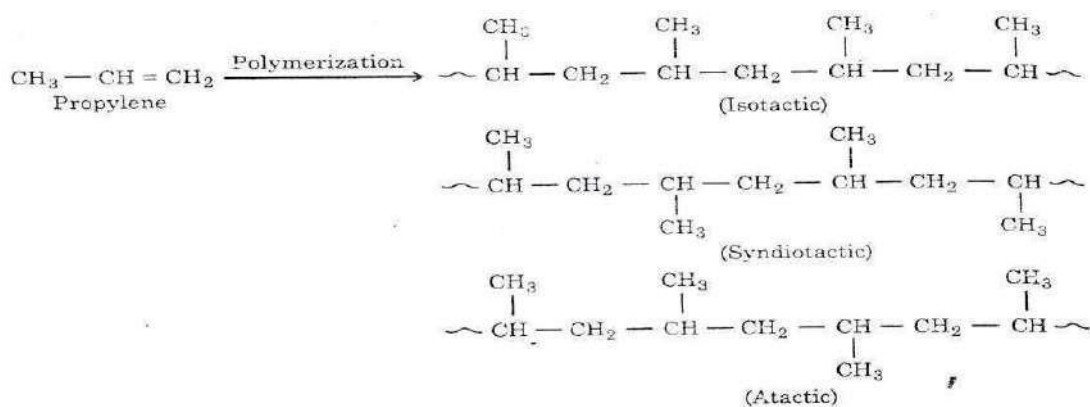


(iv) Depending upon the orientation of monomer units in a polymer molecule: With respect to the main chain the polymers are classified as:

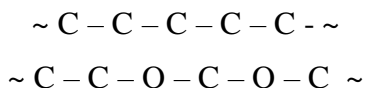
**Isotactic polymer:** If the side groups of the monomers lie on the same side of the chain, it is called an isotactic polymer.

**Syndiotactic polymer:** If the side groups are arranged in an alternate fashion, it is called syndiotactic polymer.

**Atactic polymer:** If the side groups are arranged in irregular fashion on randomly around the main chain, it is called atactic polymer.



(v) If the main chain is composed of the atoms of the same specie, the polymer is called homochain and if the main chain is made up of different atoms then they are called heterochain polymers.



(vi) According to their behavior on heating, the polymers are divided into two groups.

**Thermoplastics:** Those polymers, which soften on heating and become plastic so that they can be converted to any shape by moulding, are known as thermoplastics.

**Thermosets:** Those polymers which change irreversibly into hard and rigid materials on heating and cannot be reshaped, once they are set are called thermosets. They form infusible and insoluble mass on heating.

**Plastics:** All the synthetic polymers (other than elastomers) are usually referred to as plastics. The polymers, which are shaped into hard and tough utility articles by the application of heat and pressure, are called plastics. At some stage of manufacture, these are in plastic condition (Plasticity is the property by virtue of which a material undergoes permanent deformation under stress).

## FUNCTIONALITY

Compound	Chemical Formula	Functionality
Acetic Acid	CH <sub>3</sub> COOH	1
Molonic acid	HOOC CH <sub>2</sub> COOH	2
Ethyl alcohol	C <sub>2</sub> H <sub>5</sub> OH	1
Ethylene glycol	HOCH <sub>2</sub> CH <sub>2</sub> OH	2
Lactic acid	CH <sub>3</sub> CH (OH) COOH	2
Tartaric acid	HOOC (CHOH) <sub>2</sub> COOH	4

Depending on the functionality of the monomers used, we get linear, branched or three dimensional cross-linked polymers.

There are two types of polymerization processes:

- ## Addition Polymerization

Examples:

$$n\text{CH}_2 = \text{CH}_2 \longrightarrow \left[ \text{CH}_2 - \text{CH}_2 \right]_n$$

(ethene)                      (Polyethene)

$$\text{CH}_3\text{CH} + (n+1) \begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O} \end{array} \longrightarrow \text{CH}_3\text{O} - \left[ \text{CH}_2 - \text{CH}_2 - \text{O} \right]_n \text{CH}_2\text{CH}_2\text{OH}$$

Vinyl compound ( $\text{CH}_2 = \text{CHX}$ ), allyl compounds ( $\text{CH}_2 = \text{CH}.\text{CH}_2\text{X}$ ), olefins ( $\text{CH}_2 = \text{CHR}$ ) and dienes ( $\text{CH}_2 = \text{CR}-\text{CH} = \text{CH}_2$ ) typically undergo addition polymerization. Since a majority of these fall under the 'vinyl' category, addition polymerization is also customarily termed as vinyl polymerization.

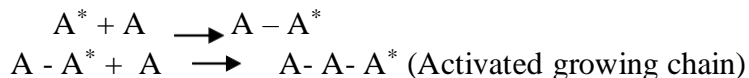
## MECHANISM OF ADDITION POLYMERIZATION

Addition polymerization is a typical chain reaction and consists of three important steps:

(i) Initiation of the formation of active centers.



(ii) Chain propagation



(iii) Chain termination or removal of active centre.



The process of addition polymerization can be brought about by three methods:

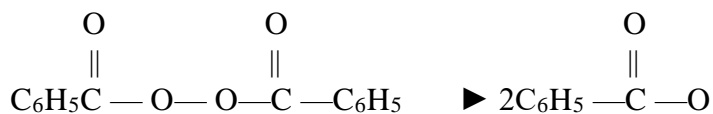
1. Free radical mechanism
2. Ionic mechanism (Anionic and Cationic)
3. Coordination mechanism

The three types of mechanisms for addition polymerization, depending upon the active centres formed, are discussed below.

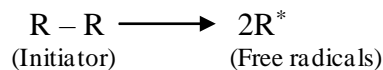
1. Free **Radical Addition** Polymerization: The free radical addition polymerization involves the formation of free radicals in the initiation step, which can be produced by decomposition of compounds called initiators. The free radical polymerization has three principal steps:

(i) Initiation: Initiation in a free radical polymerization consists of two steps. The first is the 'generation of the free radical species, followed by the second step which involves the addition of a single monomer molecule to the free radical.

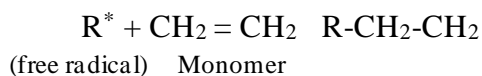
The generation of free radical takes place as a result of homolytic dissociation of an initiator, which may take place in the presence of heat energy, light energy or catalysts. A number of low molecular weight compounds, comprising mainly of azo compounds, peroxides, hydroperoxides, peracids and peresters are useful as initiators. An important example of a free radical initiator is benzoyl peroxide which dissociates as:



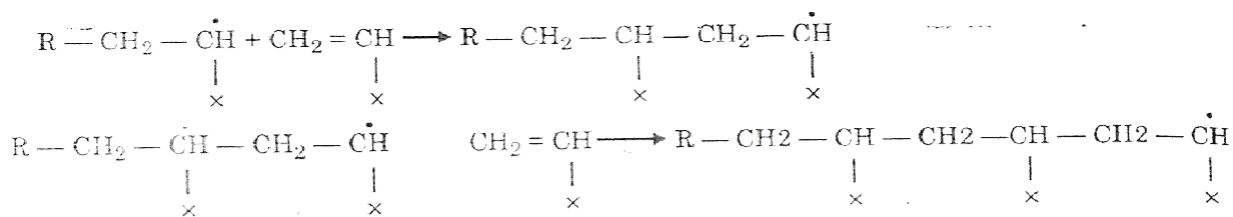
In general, the dissociation of the initiator (R-R) to form free radical specie can be represented as



In the second step of initiation, the free radical so formed gets attached to the monomer molecule (M) to form the chain initiating species



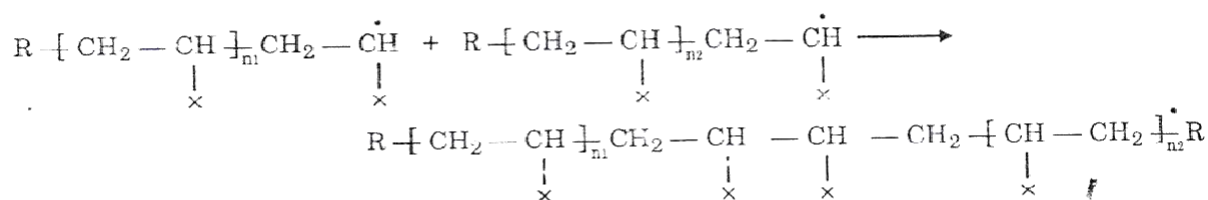
- (ii) **Propagation:** In the next step, additional monomer units are added to the initiated monomer species, as



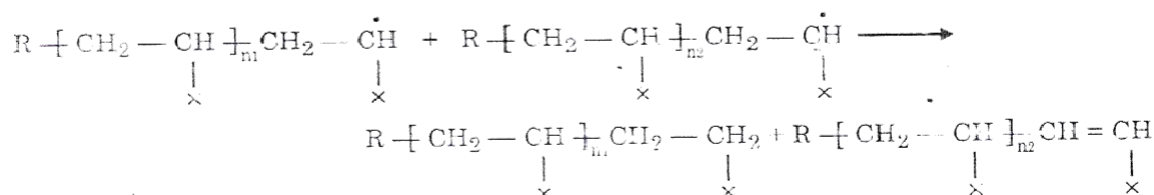
The propagation step involves a continuing attack on fresh monomer molecules which, in turn, keep successively adding to the growing chain one after another.

(iii) **Termination:** Propagation will continue until some termination process takes place. The propagating polymer chain is terminated by any of the following reactions.

(a) *By combination:* Since the decomposition of the initiator produces many free radicals at the same time, each one of them can initiate and propagate the growth of a number of chains simultaneously. The two growing chains may come close and collide with each other and get deactivated.

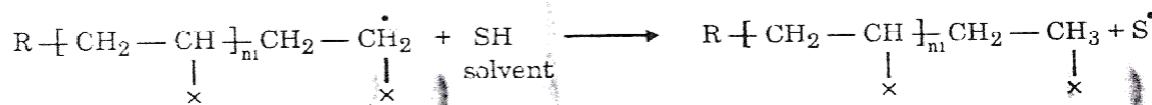


(b) *By disproportionation:* In some cases, one hydrogen atom from one growing chain is abstracted by the other growing chain and results in the formation of two polymer molecules, one saturated and other unsaturated. In this case the termination process results in the formation of two polymer molecules of shorter chain length as against a single molecule of a longer chain length obtained by first method.



Thus the products so formed do not contain any reactive sites and may be termed as dead polymers as these cannot grow further.

(c) In addition to the above two methods of chain termination, chain transfer by hydrogen abstraction from solvent molecule, may also terminate the growing chain.



In this reaction the original growing chain is terminated whereas the new chain gets initiated by the solvent free radical, hence this is called termination by chain transfer.

Certain chemical compounds, which are capable of inhibiting or completely stopping the chain growth process, are called radical inhibitors. Phenolic compounds are widely used as inhibitors, because phenolic hydrogen can be easily abstracted by the polymer chain. The phenolic free radical so formed is highly stabilized and no further reaction is possible. Hydroquinone is often added as inhibitor.

Polythene, polypropylene, styrene etc. are some of the polymers that can prepare by free

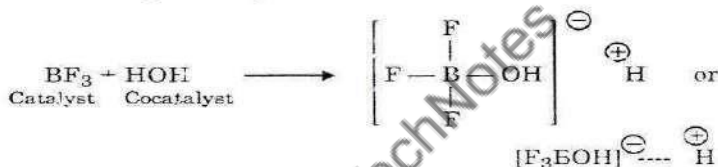
radical polymerization. Branching and cross linking during the free-radical addition polymerization.

**2. Ionic Addition Polymerization:** Ionic polymerization follow the same basic steps as free-radical addition polymerization i.e. initiation, propagation and termination, in this process, the initiation step involves the formation of carbonium ion or the carbanion as the active site and hence the polymerization can be termed as cationic or anionic polymerization respectively.

(i) Cationic Polymerization

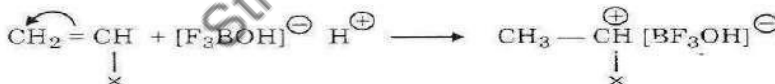
Cationic polymerization takes place in the presence of catalyst that is regenerated at the end of polymerization (in contrast to free radical and anionic polymerization where the catalyst added become incorporated into the terminated Dolymer chain) Polymerization of vinyl monomers with an electron-donating group (such as  $-\text{OC}_2\text{H}_5$  -  $\text{OCH}_3$  -  $\text{C}_6\text{H}_5$  etc.) may take place by a cationic mechanism which involves the following steps.

**Initiation:** This step involves the formation of a carbonium ion by the attack of a proton on the monomer. Any strong Lewis acid like  $\text{BF}_3$ ,  $\text{AlCl}_3$  etc can be used as a catalyst. In this case a cocatlyst like water is required to provide the proton source.

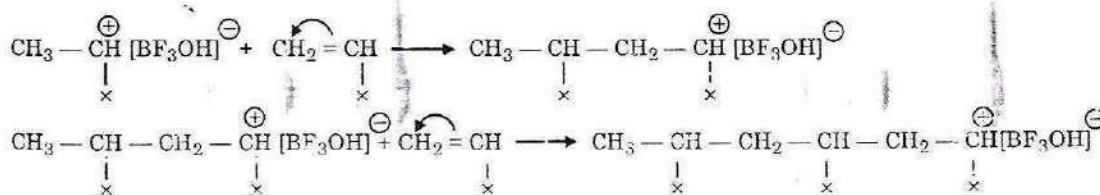


$\text{H}^\oplus$  is the initiator and  $[\text{F}_3\text{BOH}]^\ominus$  is the counter ion.

The  $\text{H}^\oplus$  now attacks the  $\pi$  electron of the monomer and forms the carbonium ion. The counter ion  $[\text{F}_3\text{BOH}]^\ominus$  anion faces the growing chain end.



**Propagation:** The propagation reaction involves the addition of monomer units and simultaneous transfer of the charge to the newly added monomer unit.

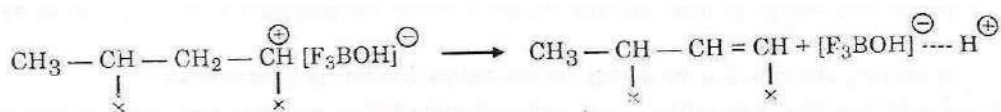


More and more units are added up and the chain keeps on growing. The electron pair of the adding monomer units are pulled in a direction opposite to the growth of the chain and the positive charge keeps on moving in the direction of the chain growth. The counter ion  $[\text{BF}_3\text{OH}]^\ominus$ , moves along the positive charge all the time.

**Termination:** Termination takes place when the growing polymer chain having  $\text{C}^\oplus$  collides with an anion, which may be added deliberately or with the counter ion. The possible reactions may be:

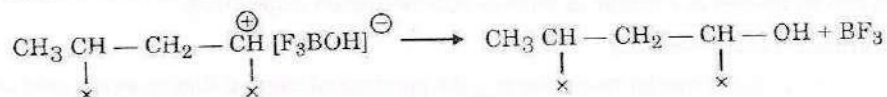
(a) Donation of a portion to the counter by the growing polymer chain. This results in the formation of a double bond at the end of growing polymer molecule.





Thus the initiator or catalyst is regenerated.

(b) Formation of covalent bond between the carbonium ion and the counterion (coupling):

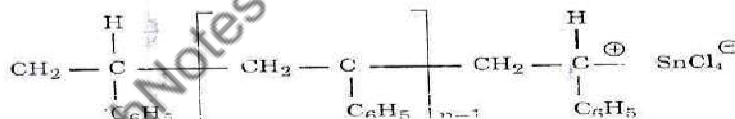
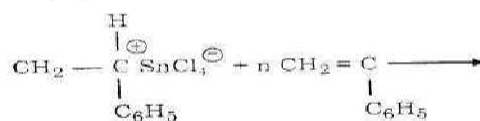


In this case also the regeneration of the initiator takes place.

Examples of the monomers that can undergo cationic polymerization are isobutylene, styrene methyl styrene and many vinyl others. Cationic

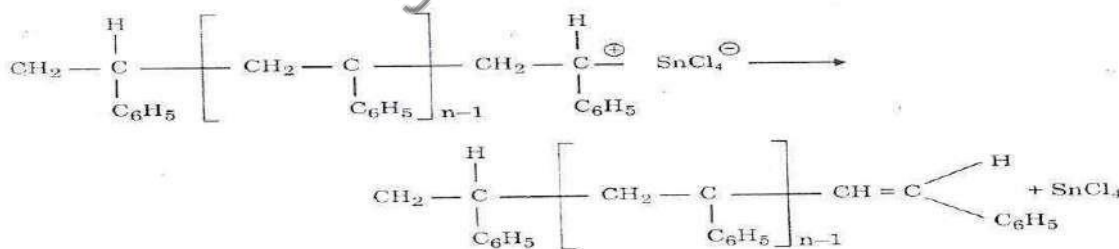


*Propagation:* Carbonium ion attacks the another molecule of styrene.



More and more styrene molecules are added and the charge is simultaneously transferred to the newly added monomer unit.

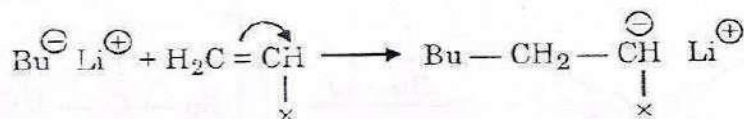
**Termination:** Termination takes places by donation of a proton to the counter ion by growing polymer chain forming a double bond



## (ii) Anionic Polymerization

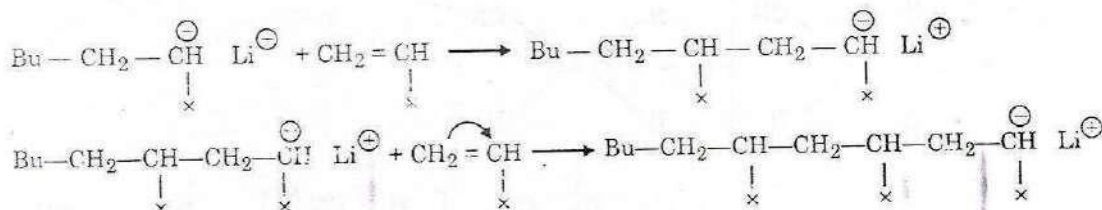
Anionic polymerization involves the formation of the carbanion in the initiation step. Polymerization of vinyl monomers with an electron withdrawing group can proceed by an anionic mechanism, involving the following steps:

**Initiation:** The initiators or the catalysts used in anionic addition polymerization are strong bases such as organo alkali compounds (alkyl or aryl derivatives of alkali metals) like n-butyl lithium, ethyl sodium etc. Alkali metal amides, hydroxides etc. can also be used.



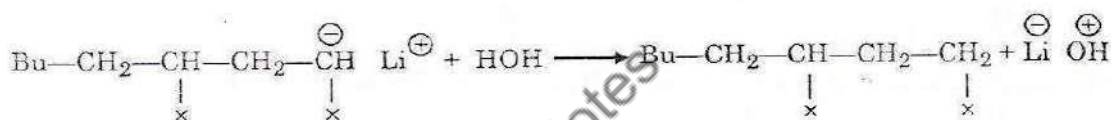
The electron pair in this case is pushed to the end of the molecule forming the carbanion.  $\text{Li}^\oplus$  is the counter ion.

Propagation: The carbanion formed, propagates the chain growth by attacking the second monomer **PAI** unit, pushing its electron pair further away to the end and forming a sigma bond with the new monomer unit.



In the case of anionic polymerization the movement of the **PAI** electrons is towards the direction of the chain growth (in cationic polymerization, the movement of the **PAI** electrons is opposite to the chain growth).

**Termination:** The termination in anionic polymerization is not a spontaneous process. If the starting reagents are pure and no impurities are present, propagation can proceed indefinitely or until all the monomer is consumed. Termination is generally accomplished by the transfer of negative charge to a species which is not directly involved in the reaction. For example CO<sub>2</sub>, methanol, water etc.

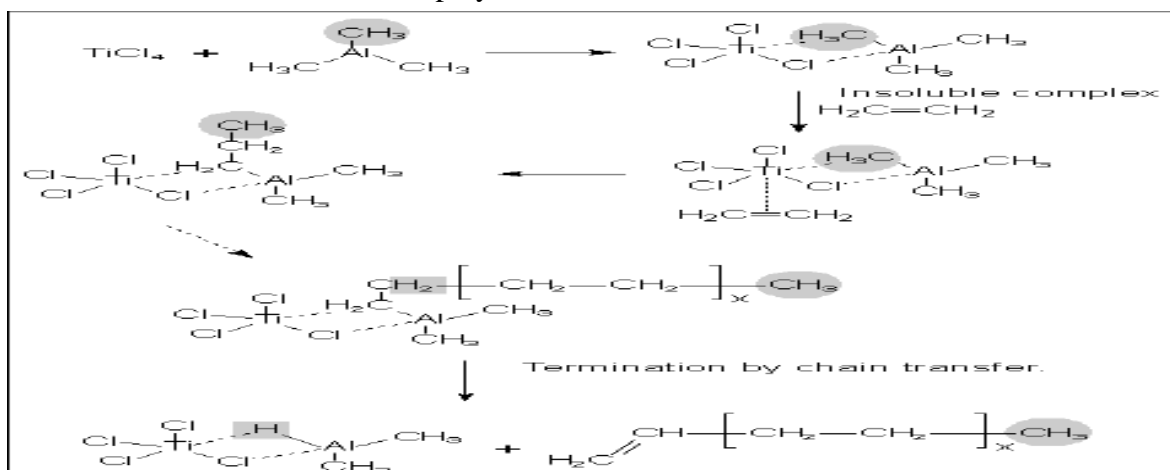


**3. Coordination Polymerization:** Polymerization reactions, taking place in the presence of organometallic compounds as catalysts, are termed as coordination polymerizations.

Zeigler (1953) and Natta (1955) discovered that in the presence of a catalyst which is a combination of a transition metal halide (like  $\text{TiCl}_4$  or  $\text{TiCl}_3$ ) with organo-metallic compounds (like triethyl aluminium), stereoregular polymers can be prepared. The combination is often referred to as, ZeiglerNatta catalyst. The commonly used Zeigler-Natta is triethylaluminium in combination with titanium trichloride.

In the formation of the monomer catalyst complex, a co-ordinate bond is involved between a carbon atom of a monomer and metal atom of the catalyst that is why, this type of polymerization is known as coordination polymerization. The co-ordinate metal-carbon bond formed in the monomer-catalyst complex acts as an active center from where propagation starts.

Mechanism of coordination polymerization can be illustrated as follows:





Coordination polymerization is used to prepare stereospecific polypropylene; polydiene etc. polypropylene of nearly 90% isotacticity can be prepared. The exact mechanism of coordination polymerization is still unclear.

### Condensation Polymerization

Condensation polymerization is brought about by monomers containing two or more reactive functional groups with the elimination of small molecules like  $\text{O}$ ,  $\text{HCl}$  etc. For example, It is seen from the above reaction that the polymer formed still contains both the reactive functional groups at its chain ends and hence, is 'active' and not 'dead'. In the above example, the different type of reactive functional groups, viz.  $-\text{NH}_2$  and  $-\text{COOH}$  are present on two different monomers. In some cases, both the reactive groups may be present on the same monomer and hence lead to self-condensation reaction. For example, polycondensation of amino acids.

Some polycondensation reactions leading to different types of polymers are:

- (i) Polycondensation of dihydric alcohols and dicarboxylic acids leads to the formation of **polyesters**.
- (ii) Polycondensation of dicarboxylic acids and diamines to give **polyamides**.
- (iii) Polycondensation of dihydric alcohols and methyl esters of dicarboxylic acids to give **polyesters**.
- (iv) Self condensation of  $\alpha$ -hydrogen acids yields **polyesters**.
- (v) Self condensation of amides to form **polyamides**.
- (vi) Polycondensation of bisphenol A and phosgene to form **polycarbonate**.

### COPOLYMERIZATION

Commonly available nature and synthetic polymer suffer from many disadvantages and therefore cannot be used for special purposes. However, it is possible to modify a number of natural and commercially available synthetic polymers to give products which can be utilized for performing desired functions.

Copolymerization is the most general and powerful method of affecting modification in polymers and is widely used in the production of commercial polymers. It provides a technique to combine the properties of two or more different polymers into a single polymer. Copolymerization can be defined as any process whereby two or more monomers are copolymerized to form a single polymer. The resulting high molecular weight compound is known as copolymer. For example, butadiene and styrene, copolymerize to form butadiene-styrene rubber.

Depending upon the sequence in which different polymeric units are arranged, copolymers are of following types:

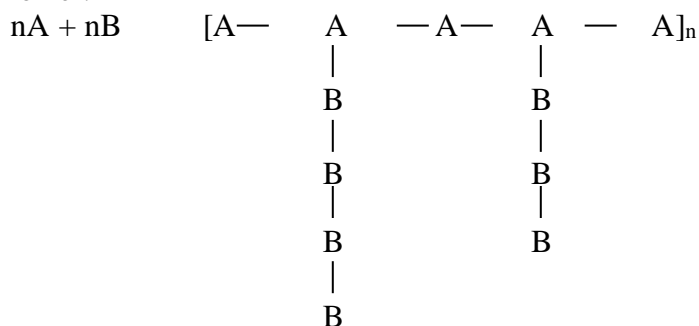
- (a) Random copolymers
  - (b) Alternating copolymers
  - (c) Block copolymers
  - (d) Graft copolymers
- (a) **Random copolymers:** In random copolymers the two monomers A and B are distributed randomly along the polymer chain.  

$$n\text{A} + n\text{B} \quad [\text{A} - \text{A} - \text{B} - \text{B} - \text{A} - \text{B} - \text{A} - \text{A}]_n$$
  - (b) **Alternating copolymers:** In block copolymers, a sequence or block of one monomer is followed by the block of the other monomer.  

$$n\text{A} + n\text{B} \quad [\text{A} - \text{B} - \text{A} - \text{B} - \text{A} - \text{B} - \text{A}]_n$$
  - (c) **Block copolymers:** In block copolymers, a sequence or block of one monomer is followed by the block of the other monomer.  

$$n\text{A} + n\text{B} \quad \underbrace{[\text{A} - \text{A} - \text{A} - \text{A} - \text{A} - \text{A} - \text{A}]}_{\text{Block}} - \underbrace{[\text{B} - \text{B} - \text{B} - \text{B} - \text{B} - \text{B} - \text{B}]}_{\text{Block}}$$
  - (d) **Graft copolymer:** Graft copolymers are branched polymers and contain main chain

or backbone consisting of one monomer and branches formed from the other monomer:



## PLASTICS

As was discussed earlier, plastics are a group of artificially synthesized materials, which can be moulded into any desired form, when subjected to heat and pressure in the presence of a catalyst.

The resins are the basic binding materials, which form the major part of the plastics and determine the type of treatment needed in the moulding operations.

From an engineering point of view there are two types of resins –

- (i) Thermoplastic resins.
- (ii) Thermosetting resins.

(i) **Thermoplastics:** Thermoplastics or resins soften on heating and become plastic so that they can be converted to any desired shape by moulding. On cooling, they become hard and rigid but their hardness is a temporary property subject to change with increase or decrease in temperature. In thermoplastic resins, the chemical structure or the molecular weight are not changed during the heating or moulding operations, because the changes involved are of physical nature. Only the secondary bonds between the individual molecular chains are broken on heating which results in their softening. On cooling, these secondary bonds are again formed and hence they become hard again. Some common examples of thermoplastics are polyethene, polypropylene, polystyrene, polyvinyl chloride, teflon, polyacrylonitrile etc.

**Plasticizer:** Sometimes, the substances called plasticizers are added to improve plasticity and flexibility of the plastics. A variety of organic materials are used as plasticizers including non-drying vegetable oils, tributyl phosphate, triphenyl phosphate, triacetin camphor, esters of oleic or stearic acid.

(ii) **Thermosetting resins:** Thermosetting resins are those, which upon heating, change irreversibly into hard and rigid materials on heating. After cooling, if the set article is again heated, it will not soften again. The thermosetting resins during moulding acquire three-dimensional cross-linked structures with predominantly covalent bonds, which retain their strength even on heating. Thus, the three dimensional network structure joined by strong covalent bonds make the thermosetting resins harder, stronger and more brittle than thermoplastic resins, if heating of a thermoset resin is prolonged, these undergo change in chemical composition to give a hard, infusible and insoluble mass. Some common examples include phenol formaldehyde, malamine formaldehyde, alkyds, epoxy resins etc.

### Difference between Thermoplastics and Thermosetting Resins

	Thermoplastic	Thermosetting Resin
1.	They are generally long chain linear polymers.	They have three dimensional crosslinked network structure joined by strong covalent bonds.
2.	On heating, they soften readily because secondary forces between the chain can be easily broken.	They do not soften on heating because cross links and strong covalent bonds retain their strength on heating. They can, however, be changed on strong heating.
3.	They can be softened, reshaped and even reused by reheating to a suitable temperature.	They can not be reshaped and reused because they do not soften on heating and retain their shape and structure.
4.	They are generally weak, soft and less brittle.	They are usually hard, strong and more brittle.
5.	They can be reclaimed from waste.	They can not be reclaimed from waste.
6.	They can dissolve in some organic solvents.	They are insoluble almost in all organic solvents because of the presence of cross linking and strong covalent bonds.

### COMMERCIALLY IMPORTANT THERMOPLASTICS

1. **Polyethene:** Ethylene, one of the most important petrochemicals, may be polymerized by a number of methods to produce thermoplastic polymer, polyethene.



The starting material (monomer) is obtained either by dehydration of alcohol or by the cracking of petroleum. There are two varieties of polyethylenes, viz., low density polyethylene (LDPE) and high density polyethylene (HDPE).

(a) **LDPE :** Low density polyethylene is prepared by polymerizing ethylene at high pressures (1000-5000 atm) at a temperature of 250<sup>0</sup> C in the presence of oxygen as a free radical initiator. LDPE consists of highly branched structure, which does not allow the polymeric chains to pack close together and hence results in low density (0.91 to 0.925 g/cm<sup>3</sup>) of the polymer.

#### Properties:

- (i) Low-density polyethylene melts at 110-125<sup>0</sup>C and is only 40-50% crystalline.
- (ii) It has low density (0.91 g/cm<sup>3</sup>).
- (iii) It is a transparent polymer having moderate tensile strength and high toughness.
- (iv) It is chemically inert, slightly flexible and poor electrical conductor.
- (v) Its elasticity is preserved even at lower temperatures
- (vi) It is moisture resistant.

#### Uses:

- (i) LDPE films are mainly used for packing and wrapping frozen food, textile products etc because of their flexibility, chemical and moisture resistance.
- (ii) The non-polar nature of the polymer makes it suitable for insulation for electric wires and cables.
- (iii) Its inertness to chemicals and resistance to breakage makes it a useful material for the manufacture of 'squeeze bottles' and in many attractive containers.
- (iv) It is also used for making pipes for agricultural, irrigation and cold water plumbing and chemical plants,

- (b) **HDPE:** High-density polyethylene is prepared by polymerizing ethylene at low pressure (3200-2000atm) and at a temperature of 180-200°C in the presence of metal oxide catalysts. HDPE can also be produced by using Ziegler Natta catalyst by coordination polymerization. In this second method ethylene is heated to 60-200°C under a pressure of 6-7 atmospheres in the presence of a catalyst consisting of triethylaluminium and titanium tetrachloride (Ziegler-Natta catalyst). The polyethene so produced consists of linear chains of polymer molecules which pack close together resulting in high density polyethene (0.97 g/cm<sup>3</sup>).

**Properties:**

- (i) High density polyethene has melting point in the range of 145-150° C and is 90% crystalline,
- (ii) It possesses density in the range of 0.941 to 0.965 g/cm<sup>3</sup>.
- (iii) It is much stiffer than LDPE and has higher tensile strength and hardness.
- (iv) It is chemical resistant and has significantly lower gas permeability.
- (v) Insulating and moisture resistant properties are similar to LDPE.
- (vi) Due to high crystallinity, it has low gas and water vapour permeability.

**Uses:**

- (i) HDPE is used in the manufacture of toys, crates closures, caps, buckets etc because it is more tough and stiffer than LDPE.
  - (ii) Its greaseproof nature and chemical inertness makes it suitable for wrapping material for food products.
  - (iii) Low gas permeability makes it suitable for domestic gas piping.
  - (iv) It is also used for manufacturing bottles for milk, household chemicals and drug packaging.
  - (v) It is used in the manufacture of overhead tanks for water storage.
- Whenever high tensile strength and stiffness are required HDPE finds better use than LDPE.
2. **Polypropylene:** Polypropylene is probably the lightest known industrial polymer and can be prepared in isotactic, syndiotactic or atactic forms. The monomer propylene is obtained as a byproduct from gasoline refineries. Polypropylene (isotactic) is produced by polymerizing propylene in the presence of Ziegler-Natta catalyst [Al (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> – TiCl<sub>4</sub>]

**Properties:**

- (i) Polypropylene is stereoregular (isotactic) and highly crystalline polymer (slightly lower than HDPE).
- (ii) Isotactic polypropylene (IPP) melts at 160-170° C.
- (iii) It exhibits high stiffness, hardness and tensile strength,
- (iv) Its moisture resistance is comparable to that of polyethylene.
- (v) Polypropylene is resistant to many chemicals such as alkalies, acids and oils. But due to presence of methyl groups attached to alternate carbon atoms, it is susceptible to oxidation.
- (vi) Its electrical properties are similar to polyethylene.
- (vii) Films of polypropylene are impermeable to a number of vapours and gases.

**Uses:**

- (i) The higher melting point of polypropylene allows it to be used in products that must be steam sterilized such as baby bottles, flasks etc.
- (ii) Its fibres are extremely strong by weight and hence are used in making ropes and filaments; it is also used for the manufacture of drinking glasses.

- (iii) Polypropylene films are used to: packaging due to high clarity and their impermeable nature to a number of vapours and gases. It is also used for wrapping confectionary items (bread, biscuits etc) and potato chips.
  - (iv) Due to high strength, rigidity and temperature and chemical resistance it is used for the production of chemical process equipments such as pipes and tanks.
  - (v) It is used for the preparation of textile machinery parts (bobbins, spools, spindles etc), when blended with suitable elastomer it is widely used for making bumpers, radiator grills etc.
  - (vi) It is also used as an insulating material for electrical wires.
3. **Polystyrene:** Polystyrene is also known as polyvinyl benzene. The monomer styrene is produced from ethylene and benzene. When ethylene is passed into benzene in the presence of  $\text{AlCl}_3$  catalyst, ethyl benzene is formed, which on passing over iron oxide catalyst at high temperatures is converted into styrene.



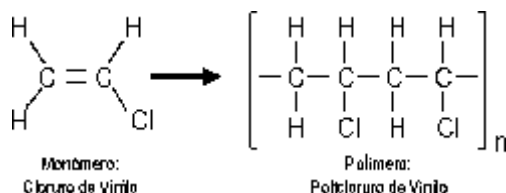
#### Properties:

- (i) Polystyrene is transparent and has high refractive index (1.6) which gives it high brilliance.
- (ii) It has got low heat distortion temperature ( $85^\circ \text{C}$ ) and hence articles made of polystyrene cannot be sterilized with steam.
- (iii) It consists generally of linear chains and is chemically inert and resistant to most alkalies, oxidising and reducing agents and acids.
- (iv) It is susceptible to photooxidative degradation, which results in brittleness and yellowing.
- (v) It has got excellent moisture resistance.
- (vi) It has good electrical insulating properties.
- (vii) It can be dyed to different colors.
- (viii) It has the unique property of transmitting light of all wavelengths through curved sections.
- (ix) Polystyrene is attacked by a number of solvents.

#### Uses:

- (i) Polystyrene is widely used in the manufacture of articles such as lids, jars, bottles, combs, brush handles, radio and television cabinets.
- (ii) It is used for preparing synthetic ion exchange resins in combination with p-divinyl benzene.
- (iii) An important use of polystyrene is the manufacture of foam and bead for insulation and packaging material. The polymer is foamed by using blowing agents, usually pentane.
- (iv) High-impact polystyrene (HIPS), produced by combination of polystyrene with rubbery material such as polybutadiene (SBR). Contributes to improved impact properties and is used for door liners, inner liners of refrigerators, etc.
- (v) Polystyrene copolymerized with acrylonitrile and butadiene (ABS), due to its high impact resistance and high dimensional stability at elevated temperatures is used in the manufacture of door handles, radiator grills, loudspeaker housings etc.
- (vi) Styreneacrylonitrile (SAN) copolymer is a transparent plastic with very good impact strength and is used for moulding crockery items and machine components.

**4. Polyvinyl Chloride (PVC):** Polyvinyl chloride is one of the cheapest and most widely used plastic globally. The monomer vinyl chloride is a gas, boiling at  $-14^{\circ}\text{C}$ . Polyvinyl chloride is prepared by the polymerization of vinyl chloride by heating its water emulsion in presence of a small amount of benzoyl peroxide.



#### Properties:

- (i) It is colourless, odourless and non-inflammable.
- (ii) PVC is partially syndiotactic and has low crystallinity.
- (ii) PVC is thermally not very stable and degrades above  $200^{\circ}\text{C}$ , with the evolution of HCL.
- (iv) It is resistant to atmospheric oxygen, inorganic acids and alkalies.
- (v) It has greater abrasion and flex resistance compared to leather.
- (vi) It is water proof and washable
- (vii) It is less brittle and lighter when compared to glass.

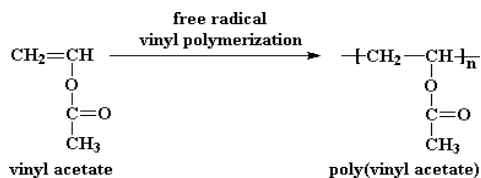
#### Uses: (Rigid PVC)

- (i) Rigid PVC or unplasticized PVC has superior chemical resistance and high rigidity but is brittle. It is used as sheets for tank linings, safety helmets, and mudguards.
- (ii) It is used for making window frames as a substitute for wood because the frames do not corrode.
- (iii) It is used for the manufacture of containers for detergents, cosmetics, mineral water.
- (iv) Because of its oil-resistant property, it is used for storing consumable liquids like edible oils, fruit squashes, table wine etc.

#### (Plasticized PVC)

- (i) Plasticized PVC is used as an insulating material.
- (ii) Because it is washable and has greater abrasion resistance therefore it is used for making ladies-handbags, bathroom curtains, kitchen upholstery.
- (iii) Used for upholstery for seats in public transport vehicles,
- (iv) In the film form it is used in membrane separation technology.

**5. Polyvinylacetate (PVA):** Polyvinyl acetate is produced by heating vinyl acetate In the presence of small amount of benzoyl peroxide.



#### Properties

- (i) Polyvinyl acetate is a solid, clear resin, and has no taste or odour and is soft sticky material.
- (ii) It is insoluble in water and is saponified with great difficulty and hence is not absorbed by the digestive system. Moreover if at all saponification takes place, the products polyvinyl alcohol and acetic acid are not harmful. Due to the above-stated reasons, polyvinyl acetate is used as a basic material for chewing gums and surgical dressings.

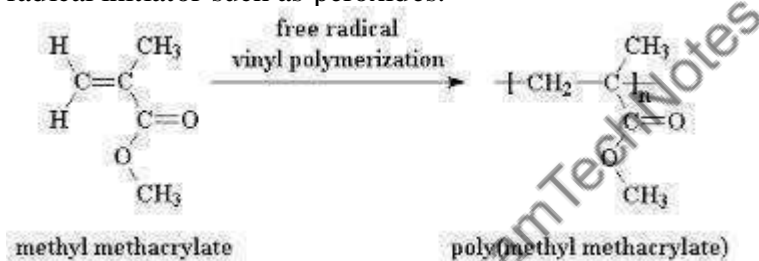
- (iii) It is resistant to atmospheric oxygen, water and chemicals.

#### Uses

- (i) Polyvinyl acetate is used for the manufacture of lacquers, paints and adhesives. Polyvinyl acetate adhesives are-used for bonding of textile to textile, leather to leather/paper to paper, paper to textile, leather to wood etc.
- (ii) It is used as a basic material for chewing gum and surgical dressings.
- (iii) It is also used for finishing of textile fabrics.
- (iv) On copolymerization with polyvinyl chloride, it is converted into a polymer having varying degree of softness. For example, vinylite, which is a copolymer of polyvinyl acetate and polyvinyl chloride, is especially useful as a surface coating material for metals.
- (v) It is mainly used for the manufacture of polyvinyl alcohol.

Polyvinyl butyral is tough and elastic and is used for laminating safety glass. It holds the broken pieces of glass in case of accident and thus minimizes the danger from flying glass fragments.

**5. Polymethylmethacrylate (PMMA):** Polymethyl methacrylate (PMMA) is one of the important thermoplastic from commercial point of view, because of its outstanding optical properties. It is prepared by the polymerization of methylmethacrylate in presence of free radical initiator such as peroxides.



#### Properties

- (i) It is a colorless transparent plastic with an excellent outdoor life period and good strength.
- (ii) Owing to the presence of bulky side groups, it is amorphous in nature.
- (iii) It can be depolymerized to yield back the monomer.
- (iv) It has high softening point of about 130-140°C but it becomes rubber-like at a temperature above 65°C.
- (v) The main feature of this plastic is its high optical transparency and capacity of transmitting light accurately, even in curved sections.
- (vi) It has good mechanical properties but has poor scratch resistance as compared to glass.
- (vii) It has low chemical resistance to hot acids and alkalies.
- (viii) It has excellent weathering properties.

#### Uses

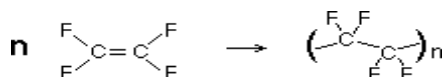
- (i) PMMA is the nearest alternative to glass as it does not shatter and can be moulded into any shape. Infact, PMMA sheets known as plexiglass or lucite are used as an alternative to glass.
- (ii) PMMA finds major use in automotive industry (e.g. housing for rear lamps, profiles, light fittings, ceiling lighting signal-light etc).
- (iii) It is used for making hard contact lenses due to its high transparency.



- (iv) It is used as composite materials for kitchen sinks, basins and bathtubs because it provides wide range of colour and are cheap and light.
- (v) PMMA is also used for making windscreens T. V. screens etc. The fragments formed after cracking are less sharp and hence less harmful.
- (vi) It is also used for decorative purposes such as in jewellery etc. (vii) It is also used in bone splints, artificial eyes, dentures etc.

**6. Polytetrafluoro Ethylene (Teflon) (PTFE):** Polytetra fluoroethylene is prepared by the polymerization of tetrafluoroethylnce (  $\text{CF}_2=\text{CF}_2$  ), under high pressure in presence of benzoyl peroxide as catalyst.

The polymerization is associated with the release of large quantities of heat and if sufficient precautions are not taken, this can result in violent explosions.



### Properties

- (i) PTFE has a highly regular structure and is highly crystalline.
- (ii) Due to the presence of highly electronegative fluorine atoms and regular configuration of PTFE molecule there are very strong attractive forces between different chains, which give the material extreme toughness.
- (iii) PTFE has high softening point of about  $327^\circ\text{C}$ . above  $400^\circ\text{C}$  it decomposes without changing into vapour.
- (iv) It is extremely resistant to attack by chemicals such as strong alkalis and acids. Only hot alkali metals and hot fluorine can attack PTFE.
- (v) PTFE is highly dense polymer (2.1 to 2.3 g/cm) having excellent mechanical properties.
- (vi) It can be machined, punched and drilled.
- (vii) It has a very low coefficient of friction
- (viii) It has extremely good electrical insulating properties.
- (ix) It is slippery and waxy to touch.
- (x) It does not melt like other thermoplastics and hence behaves somewhat like a thermosetting polymer.
- (xi) It has non-adhesive characteristics.

### Uses

- (i) Due to its chemical inertness, it is used in chemical carrying pipes, tubing's, stop-cock for burettes,
- (ii) Its extreme inertness and stability to temperature makes it a suitable material for making gaskets and seals.
- (iii) It is used as an insulating material for transformers, cables, wires, fittings etc.
- (iv) Because of its low coefficient of friction, it is used in non-lubricating bearings.
- (v) Its most important application is, as non-stick coating for Dots and pan;. PTFE is applied as a coating over the rollers and mixing equipments used for preparing sticky materials such as adhesives and jams.
- (vi) Its fiber is used to form belts, filter cloth etc.
- (a) **Polyamides:** Polyamides are a group of polymers which contain the amide(-CONH-) linkage in the main polymer chain.. Polymers of this type are the synthetic

---

linear aliphatic polyamides, which are capable of fibre formation.

**Nylon** is the generic name for synthetic polyamides capable of forming fibres. Polyamides (nylons) are prepared by the polycondensation between dicarboxylic acids and diamines. Nylons are designated by two numbers, the first representing the diamine. Polyamides of commercial importance are Nylon 6,6; Nylon 6, 10, Nylon 6 etc.

- (i) Nylon 6,6: Nylon 6,6 is prepared by the polycondensation of hexamethylene diamine with adipic acid.

#### **Properties of Nylons**

- (i) Nylons are characterized by a combination of high strength, elasticity, toughness and abrasion resistance.
- (ii) They have very good moisture resistance.
- (iii) They are insoluble in common solvents.
- (iv) The molecular chains are held together to each other by hydrogen bonds having linear structure, permitting side-by-side alignment.
- (v) They are very flexible and retain their original shape after use.
- (vi) Nylons provide excellent resistance to wear and abrasion
- (vii) Due to the presence of hydrogen bonding, all nylons are water sensitive. Water acts as plasticizer, which reduces tensile strength and dimensional stability.

#### **Uses**

- (i) Nylon 6,6 is used as a plastic as well as a fibre. Its most important fibre applications include automobile tire cords, ropes, threads, cords having high tenacity and good elasticity.
- (ii) Nylon 6,6 is also used to make textile fibres for use in dresses, undergarments, socks etc.
- (iii) Nylon 6,6 being a tough plastic is used/as a substitute for metals in gears and bearings etc. Nylon 6,6 can be moulded in one piece whereas similar item in metal require assembling of several parts. Moreover, nylon bearings and gears perform quietly and need little or no lubrication.
- (iv) It is also used in making rollers, slides and door latches.
- (v) Nylon 6, 10 is not used much as synthetic fibre, but is used to manufacture articles like brushes and bristles.
- (vi) Nylon 11, is used as textile fibre.
- (vii) Due to its good barrier properties, nylon-6 film is used for packaging some oxygen sensitive food.
- (viii) Due to its high tenacity, nylon is suitably used for parachute fabric.
- (ix) Nylons are also used in making transmission belting, ribbons for electric typewriters, spindle bands on textile spinning machines etc because of its high durability.
- (x) Nylon is also used for making insect screens because of their biological resistance.

Aromatic polyamides, often called aramids have been produced to improve the heat and flame-resistance of nylons. These polymers have very high melting points (greater than 500°C). One such nylon is Kevlar. It is prepared by polycondensation between aromatic dichloride and aromatic diamines.

Kevlar is exceptionally strong and decomposes only above 500° C It is 5 times stronger than steel and it is used as a substitute for steel in belted radial tires as well as in bullet resistant vests. It is also used in making car parts such as tyres, brackets, clutch linings etc.

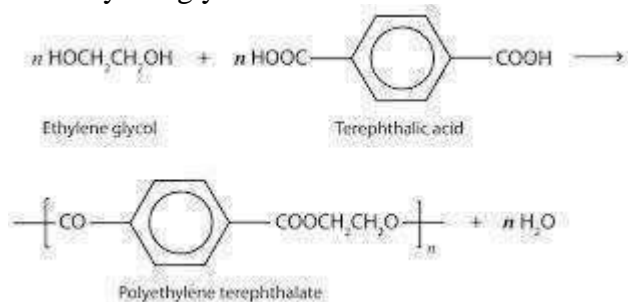
---

## COMMERCIALLY IMPORTANT THERMOSETTING RESINS

1. **Polyesters:** Polyester resins are the condensation products of dicarboxylic acid with dihydroxy alcohols. The industrially most important polyester is poly (ethylene terephthalate) (PET), with the trade name Terylene or Dacron. PET can be prepared from terephthalic acid and ethylene glycol, either by direct esterification or by catalyzed ester interchange.

Nowadays, dimethyl terephthalate is used instead of terephthalic acid. This is because of the fact that terephthalic acid is nonvolatile and is very slightly soluble in most of the solvents. The reaction takes place in two successive stages:

The ethylene glycol so formed is distilled off at such high temperature.



### Properties

- (i) PET is resistant to heat and moisture.
- (ii) It is strongly resistant to both weak acids and bases at room temperature but readily attacked by strong acids and bases.
- (iii) Presence of numerous polar groups results in powerful dipole attractions in it.
- (iv) It has good mechanical strength up to  $175^\circ\text{C}$ .
- (v) It is resistant to almost all kinds of insect attacks.
- (i) It can be dyed at  $100^\circ\text{C}$  or in presence of a carrier.
- (ii) The fibre has good wrinkle resistance due to good elasticity,
- (iii) PET fibres are abrasion and oxidation resistant.

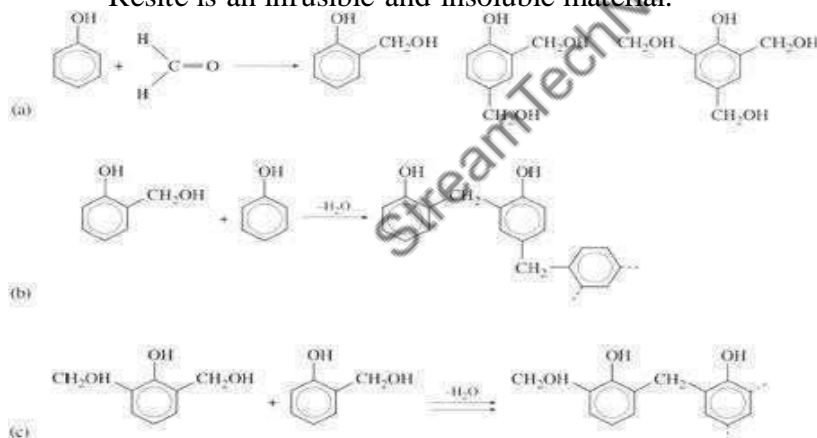
### Uses:

- (i) PET is mostly used for making synthetic fibres like Terylene, Dacron etc. Garments made from its fibres resist the formation of wrinkles and have many desirable properties such as warmth to touch, low moisture absorption (and hence dry rapidly), crease resistance, shape retention, and mildew proof. Moreover, these may be blended with other fibres, such as wool and cotton.
  - (ii) PET is also useful for making films because of its high strength, resistance to tearing durability, transparency etc. PET is used in making the transparencies of overhead projector.
  - (iii) Due to its impermeability to a number of organic and inorganic gases it is used in the manufacture of plastic bottles for carbonated beverages (barrier to  $\text{CO}_2$  and water)
  - (iv) It is also used to make magnetic recording tapes.
  - (v) Due to their high dielectric strength they are used for electrical insulation.
  - (vi) Glass reinforced PET is used for the manufacture of housings-for coffee machines, car heaters, toasters.
2. **Phenolic Resins:** Phenol formaldehyde resins are the most important and extensively used synthetic plastics and perhaps the oldest synthetic plastics. In these resins one of the monomers is always a phenol molecule. One of the most important member of this class is

phenol formaldehyde resin.

The phenol formaldehyde reaction is catalyzed by alkalies and acids. The nature of the product depends on several factors, the major one being the nature of the catalyst and the proportion of the reactants (phenol formaldehyde ratio). The formation of phenol formaldehyde resin comprises of the following steps:

- (i) **Methylation:** When phenol and formaldehyde react together, the first step is the entry of methylol ( $\text{CH}_2\text{OH}$ ) groups in ortho and para positions to the hydroxy group. The reaction takes place in the presence of acid or alkali. Depending upon phenol formaldehyde ratio, various phenol-alcohols may be formed.
- (ii) **Novolac formation:** Depending upon the ratio of phenol formaldehyde (P/F) different resins, namely novolac and resol resins are obtained. In the presence of acid catalyst, when the P/F ratio is greater than unity, the methylol derivatives condense with phenol to form a linear polymer with little methylol groups. The product is thermoplastic in nature and is known as novolac.
- (iii) **Resole formation:** In the presence of alkaline catalysts with P/F ratio less than 3, the methylol phenols condense to form linear structure called resoles. The resoles are soluble in the reaction mixture and have excess of methylol groups capable of further reaction during continued heating. Resoles, therefore have limited shelf-life. However, the reaction may be stopped at the desired step by cooling.
- (iv) **Resin formation:** On further heating, resole is transformed into a three dimensional polymer, called resin, due to the presence of active groups and mobile hydrogens. Resin is an infusible and insoluble material.



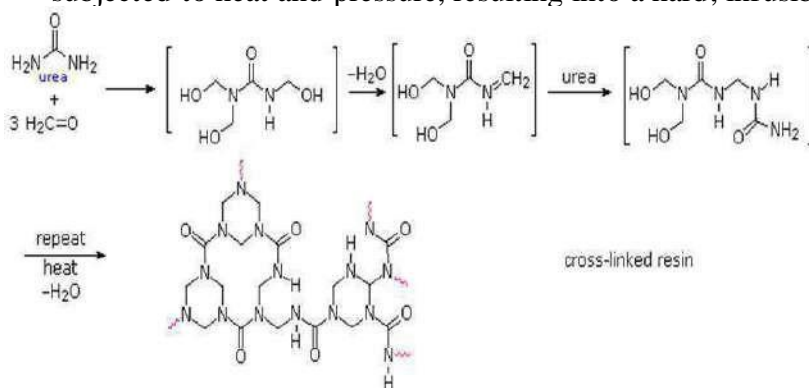
### Properties

- (i) Phenol formaldehyde moulding resins have excellent heat resistance.
- (ii) These have high dimensional stability.
- (iii) To improve the properties further, fillers such as wood, flour, mica, asbestos etc are added to them.
- (iv) Phenolic resins have good dielectric properties.
- (v) These have remarkable adhesive properties and bonding strength.
- (vi) They are however attacked by alkalies, because of the presence of free hydroxy groups.
- (vii) They are hard, rigid and scratch-resistant.

**Uses** Phenolic resins have wide applications.

- (i) The main use of phenolic resin is in moulding applications. They are widely used in making telephone parts, cabinets for radio, television and automobile parts

- (ii) Due to their adhesive properties and bonding strength, they are used for producing brake linings, abrasive wheels and sand paper.
  - (iii) They are used for making electric insulator parts like switches, plugs, switch boards, heater-handles etc,
  - (iv) Phenolic resins are used for impregnating paper, wood and other fillers.
  - (v) These are also used in varnishes, paints and protective coatings.
  - (vi) These are used in the production of ion exchange resin for water softening.
4. **Amine Resins:** Amino resins or amino plastics are prepared by the reactions of formaldehyde with nitrogen compounds such as urea, melamine and other amino compounds. Because of their attractive light colours, these resins have great commercial importance.
- (a) **Urea formaldehyde resins:** This is prepared by the condensation reaction between urea and formaldehyde in neutral or alkaline conditions. The first products formed during the formation of resin are monomethylol and dimethylol ureas.
  - (ii) Polymerization can take place from mono or dimethylol urea, or possibly through both, with the formation of long chains.
  - (iii) Thermosetting of the resin takes place during the moulding process. For moulding, the methylol derivatives are compound with fillers, plasticizers, pigments etc. and then are subjected to heat and pressure, resulting into a hard, infusible product.



### Properties

- (i) The urea formaldehyde resins are light in colour and enable the production of light or pastel coloured objects.
- (ii) Their heat and moisture resistance are lower than those of phenolic resins.
- (iii) They have good electrical insulating properties.
- (iv) They are resistant to oxidation to oil, grease and weak acids.
- (v) They are hard, resist abrasion and scratching.
- (vi) They have good adhesive properties.

### Uses

- (i) Urea-formaldehyde resins are widely used to make moulded articles like vacuum flask cups jugs buttons, bottle caps etc where the darker colour of phenolics may be objectionable.
- (ii) They are also used for adhesive applications for the production of plywood and laminating.
- (ii) They are used for the manufacture of cc .ted abrasive paper and binder for foundry

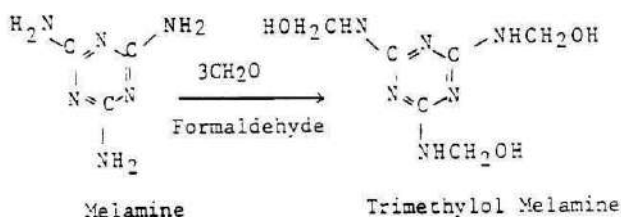
cores.

(iv) They are used for the manufacture of cation exchange resins.

(v) These also find use in the manufacture of electrical switches, plugs and insulating foams,

(vi) Their applications also include the treatment of textile fibers for improving their shrink and crease resistance.

(b) **Melamine-formaldehyde resin:** Melamine formaldehyde resins are another class of amino resins. They are produced by the condensation of melamine (2, 4, 6 triamino – 1, 3, 5 triazine), trimer of dicyandiamide with formaldehyde, exactly in the same manner as in the formation of urea formaldehyde resin. The reaction takes place under mild alkaline or neutral conditions.



### Properties:

(i) The melamine resins have better hardness, heat resistance, and moisture resistance than the urea - formaldehyde resins. However these are expensive. Rest of the properties is similar to urea-formaldehyde resins.

### Uses

(i) Typical applications of urea formaldehyde resins include the production of decorative plastic ware, laminated worktops.

(ii) They are used in electrical fittings.

(iii) They are used for resin bonded grinding wheels.

(iv) They are used for textile finishing providing crease resistance, stiffness, water repellency etc.

(v) They are also used in automotive finishes.

(vi) Melamine resins are also used as a tanning material for leather. The presence of small amount of this resin in the tanning material improves the strength of the leather.

(vii) They are also used for the preparation of lacquer

### RUBBERS (ELASTOMERS)

It was discussed in the beginning of the chapter that depending on the ultimate form and use a polymer can be classified into two broad categories: Plastics and Elastomers (rubbers).

Elastomers are the polymers which are capable of being stretched rapidly at least 150 percent of their original length without breaking and return to their original shape on release of stress. For example, rubber band is a typical elastomeric material. When stretched, it is elongated to many times its length. But when the force is released it gets back to its original length.

The properties of typical elastomers are defined by the following:

- They must stretch rapidly and considerably when stretched, reaching high elongations (500-1000%).
- They must exhibit high tensile strength and high stiffness when fully stretched.
- They must snap back to their original length once the stretching force is withdrawn or the



---

stress is released.

These criteria are met with the materials which:

- Have high molecular mass (high polymers).
- Are above their glass transition temperature.
- Are amorphous.
- Contain a network of crosslinks to restrain gross mobility of its chains.

Columbus on this voyage to America found the native of West Indies were playing with the solid mass collected from the exudate of a tree. Years later, Joseph Priestly showed that this solid mass could rub off pencil marks from paper and hence the material was called rubber. The main source of natural rubber is the species of tree known as 'Hevea Basiliensis' even today, which account for multibillion-dollar rubber industry. Rubber or elastomers can be obtained naturally or synthetically. Consequently we have natural rubber and synthetic rubber.

#### NATURAL RUBBER

Natural rubber of nearly same characteristics occur in the inner bark and to a lesser extent in the leaves and roots of a number of tropical plants But the latex from the tree 'Hevea Basiliensis' is proved to be the main source of rubber. Latex is an emulsion of poly hydrocarbon droplets in an aqueous solution and looks like milk. The negatively charged particles of polyhydrocarbons, a colloidal dispersion, stabilize the emulsion.

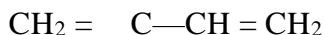
#### Processing

The latex is collected by making small incisions in the trees in such a manner so as to allow the latex to accumulate in small cups. The percentage of rubber in it is 25-35%. A fully grown tree gives about 5 gm of rubber in a day.

The average composition of the latex is:

Water = 60%; Rubber = 35%; Proteins, enzymes and nucleic acid = 3%; fatty acids and esters = 1% and inorganic salts = 0.5%.

In these trees, the rubber is formed from polymerization of isoprene i.e. (2-methyl-1, 3-butadiene) to produce poly-(cis)isoprene by a biochemical reaction in which a particular type of enzyme acts as a catalyst.



Isoprene (2 – methyl – 1, 3 – butadiene )

The latex is first sieved to remove the impurities such as leaves, bark etc. From 25-35% dry rubber content the latex is diluted to contain about 15-20% of rubber content. The rubber is then separated from the latex by the process of coagulation. The acetic acid or formic acid is added as coagulants and the rubber is coagulated to soft white mass. About 1 g of acetic acid/formic acid is added per 200 kg of rubber material. This coagulated mass is the crude rubber and consists of 90-95% rubber, 2-4% proteins and 1-2% resins. The crude rubber is washed and treated for producing the following types of rubber depending upon the process.

- 1. Crepe Rubber:** Crepe rubber is prepared by adding a small amount of sodium bisulphite ( $\text{NaHSO}_3$ ) to the coagulated mass to bleach the rubber. Then the rubber is passed through a creping machine. The creping machine is rolling machine which consists of two rollers having longitudinal grooves. Thus, after passing through it, the spongy rubber is converted into a sheet having a rough surface which resembles the crepe paper and hence the name.
- 2. Smoked Rubber:** The smoked rubber is produced by carrying out the coagulation of latex in the tanks provided with vertical grooves on sides and fitted with metal plates which run



across the width of the tank. First the diluted latex is poured into the tanks, with the metal plates removed. Then the coagulant is added (acetic or formic acid) and the plates are inserted. The tanks are kept undisturbed for 15-16 hours. The tough slabs are formed. These slabs are passed through a series of rolling machines and finally rubber sheets having ribbed pattern are obtained. The ribbed surface prevents the sticking of the rubber with each other. These sheets are then dried in smoke houses at about 50°C in the smoke obtained from burning wood or coconut shells. The smoked rubber so obtained is translucent and ambre coloured.

### GUTTA PERCHA

Gutta percha is another variety of natural rubber; it is obtained from the mature leaves of *Dichopsis gutta* and *palagum gutia* trees. The hevea rubber and gutta percha, both are composed of isoprene units with structures shown in the figure? But **natural rubber** is *cis*-isomer where a bending back of successive isoprene units take place giving the molecule a coiled structure. The gutta percha, on the other hand is a *trans*-isomer which consist of straight chains, giving a rod like structure to the molecule. The rod-like structure results into close packing of adjacent chains. Thus gutta percha is more crystalline.

#### Processing of Gutta Percha

The mature leaves obtained from the trees *Dichopsis gutta* or *palagum gutta* are carefully ground in mills and are then treated with water maintained at 70°C for about half an hour when the gutta percha is extracted in water. The solution is dropped into cold water and gutta percha floats on the surface. Alternatively, gutta percha can be recovered by solvent extraction.

#### Properties of natural (Hevea)rubber and gutta percha:

Natural Rubber (Hevea rubber)	Gutta Percha
1. Natural rubber is highly soft and elastic material 1000°C	Gutta percha is a hard thermoplastic material at room temperature but it softens and becomes tacky at about
2. It is soluble in carbon disulphide and petrol.	It is soluble in petrol,
3. It is <i>cis</i> polyisoprene	It is <i>trans</i> polyisoprene.

**Drawbacks of Raw Rubber:** Raw rubber has a number of drawbacks when put to use. Some of the drawbacks are:

- (i) Crude rubber is soft at high temperatures but becomes brittle at low temperatures. So it can be used in a limited temperature range.
- (ii) It is too weak with a tensile strength of 200 kg/cm<sup>2</sup>
- (iii) It is not resistant to mineral oils, organic solvents.
- (iv) It has large water absorption capacity.
- (v) Due to oxidation in air, it deteriorates and hence its durability is decreased.
- (vi) It is also attacked by the oxidizing agents like nitric acid, Conc. sulphuric acid, chromic acid etc.
- (v) It undergoes permanent deformation when stretched. This may be due to stretching the individual chains slip past each other and get separated resulting in the breakage of the material.
- (vi) However the above drawbacks can be overcome by improving the properties by the addition of suitable materials and further heat treatments.

Some of the processes for improving the properties of rubber are discussed below:

### PROCESSES FOR IMPROVING THE PROPERTIES OF RUBBER

The desired properties in rubber can be obtained by compounding it with certain chemicals. The compounding of rubber is generally facilitated by a process called mastication.

**Mastication:** When rubber is subjected to mechanical stresses arising from say, high-speed stirring or milling, it undergoes considerable molecular degradation or fragmentation. The process is called mastication. The mastication converts hard and tough rubber into a soft, supple and semisolid mass. The  $\text{CH}_2 - \text{CH}_2$  links between the isoprene units in the rubber are weak and hence break when subjected to mechanical stresses. The net effect is that the big molecule is broken into small fragments. After mastication is complete the compounding agents are added to the rubber.

**Compounding:** The process involving the incorporation of chemicals such as plasticizers, vulcanizing agents, stabilizers, fillers, fillers etc., into the rubber industry was discovered by Charles Goodyear in 1839. the process by which a network of crosslinks is introduced into an elastomers is called vulcanization. Charles Goodyear used sulphur to crosslink polyisoprene molecules in natural rubber. The added sulphur combines chemically at the double bonds bringing about changes in its properties profoundly. Vulcanization transforms elastomers which are a weak thermoplastic mass of no use into a strong, elastic and tough rubber. The tensile strength, stiffness, durability, resistance to changes in temperature, elasticity and chemical resistance of a vulcanized rubber are increased manifolds as compared to unvulcanized rubber.

The introduction of sulphur links in between the polymer chains restrict the intermolecular movement which brings about stiffening of rubber.

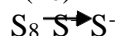
The extent of stiffness of vulcanized rubber depends upon the amount of sulphur added. For example, a rubber may contain 3 to 5% sulphur whereas Vulcanite or ebonite (hard rubber) contains about 32% sulphur. The extensive Crosslinking in hard rubber makes it so stiffer tat there is practically no elasticity in it. Fig. shows the effect of vulcanization on rubber. Ordinary rubber molecules are bent and convoluted (a) When stretched the molecules can slip past one another. But vulcanization introduces crosslinks between these and hence on stretching the molecular chains cannot slip past each other.

(a)	(b)	(c)
Unvulcanized Rubber	Vulcanized Rubber (Unstretched)	Vulcanized Rubber (Stretched)

### Chemistry of Vulcanization

The addition of sulphur develops crosslinks, thereby improving the processibility and utility of rubber. But the mechanism of vulcanization is quite complex and is still not known in detail. Both free radical and ionic intermediates have been postulated. Sulphur exists as  $\text{S}_8$  i.e. cyclo octasulphur. The probable mechanism can be:

- Sulphur ( $\text{S}_8$ ) dissociates into  $\text{S}^+ \text{S}^-$



Where m and n are the numbers of sulphur atoms.

- The sulphur cation  $\text{S}_m^+$  reacts with a diene molecule of rubber to give I.
- This cation adds to other polymer molecule to give II and carbonium ion iii
- The arlylic carbonium ion reacts with  $\text{S}_8$  to form IV which adds to polydiene to form sulphur bridges (V). This can further react with  $\text{S}_8$  and the cycle goes on

It must be emphasized that neither heat nor sulphur is essential for the vulcanization process. Vulcanization can even be carried out by number of other substances. Hence vulcanization can be of two types:

- (a) **Sulphur Vulcanization:** As stated earlier, in this process the rubber is heated with sulphur or  $\text{CS}_2$ .

(b) **Non-sulphur Vulcanization:** Non-sulphur vulcanization is achieved through a free radical.

- ❑ Free radical can be generated from a curing agent such as benzoyl peroxide or as a step in the oxidative degradation of rubber.
- ❑ This free radical abstracts a hydrogen atom from one of the –methylene groups.
- ❑ The rubber free radical so formed attacks a double bond in an adjacent polymer chain resulting into crosslink (vulcanization) and regeneration of a free radical.

This cross linked free radical will further attacks more C=C bonds to form a large number of cross linkages leading to vulcanization.

Further, the compounds such as Se, Te, ZnO, benzoyl, chloride, trinitrobenzene, etc., are also used as vulcanizing agents.

### Advantages of Vulcanization

Vulcanized rubber has got ideal elastomeric properties which increase its utility manifolds. The main advantages of vulcanized rubber are:

1. **Tensile strength:** Tensile strength is the measure of the ability of a polymer to withstand pulling stresses. Vulcanized rubber has got good tensile strength and extensibility. The tensile of the raw rubber is 20 kg/cm<sup>2</sup>, which increases to 2000 kg/cm<sup>2</sup> on vulcanization.
2. **Resilience:** It is the property of a elastomers to return to its original shape on the release of stress. Resilience of vulcanized rubber improves manifolds as compared to raw rubber.
3. **Water Absorption Capacity:** The water absorption capacity of vulcanized rubber is greatly reduced.
4. Vulcanized rubber is resistant to organic solvents such as benzene CCl<sub>4</sub>, fats and oils. Though it swells in these solvents but to a lesser extent than raw rubber.
5. **Insulation Properties:** Vulcanized rubber has better insulation properties than raw rubber. Raw rubber vulcanized with 32% sulphur (ebonite) has extremely good insulating properties.
6. **Elasticity:** The elasticity of vulcanized rubber is greatly reduced. The elasticity of the vulcanized rubber depends upon the extent of vulcanization. If 30-50% of sulphur is present in vulcanized rubber then a rigid, non-elastomeric plastic (ebonite or hard rubber) is formed.
7. The working temperature range for vulcanized rubber is -40°C to 100°C as compared to raw rubber, which has working temperature range of 10°C to 60°C.
8. It is resistant to abrasion, ageing and reactivity with oxygen and ozone.

A comparison of raw rubber and vulcanized rubber is given in the following table:

**Table:** Comparison of properties of Raw, Vulcanized Rubber, Reinforced Vulcanized Rubber.

Property	Raw Rubber	Vercanized Rubber	Reinforced Valcanized Rubber
1. Tensile strength (psi)	300	3000	4500
2. Elongationat break (%)	1200	800	600
3. Elasticity	Very high	Low, depends upon extent of vulcanization	Very low, depends upon extent of vulcanization and reinforcement
4. Water absorption	Large	Small	Small
5. Solvent resistance (hydrocarbons)	Sluble	Swells only	Swells only
6. Chemical resistance	Poor	Much better	Much better

---

### Other Compounding Techniques

Though vulcanization improves the properties of natural rubber to a great extent but even vulcanized rubber do not exhibit satisfactory properties for various utility items. These properties can be enhanced by other compounding techniques discussed below:

- (i) **Reinforcing Fillers:** To give strength and rigidity to the rubber, fillers are added. Fillers are of two types: (a) inert fillers, such as clay which make the rubber mixture easy to handle before vulcanization, but have no effect on the physical properties, and (b) reinforcing fillers which greatly improve the properties of rubber or vulcanized rubber.

Common fillers include carbon black, zinc oxide, magnesium carbonate, barium, sulphate, calcium carbonate etc. Carbon black is remarkable reinforcing filler for both natural and synthetic rubbers. Table gives the comparison of raw rubber and non-reinforced vulcanized rubber and reinforced vulcanized rubber. In vulcanization, though the long range movement of the polymer molecules is restricted, still movement of local chains is high. Reinforcement of vulcanized rubber restricts this local freedom of movement, making the polymer stiffer and tougher.

- (ii) **Plasticizers or Softeners:** Plasticizers are added to rubber to improve flow and therefore, processability-plasticizers also reduce the brittleness of the product. The common plasticizers used are hydrocarbon oils, resins, waxes, etc. The oil serves as a plasticizer and a softener by reducing the melt viscosity of the rubber to the levels required Compounding.
- (iii) **Antioxidants:** Rubbers that retain double bonds in their vulcanized structure are sensitive to heat, light and particularly oxygen. Thus rubber deteriorates in presence of light and air due to oxidation and as a result becomes soft and degrades. Antioxidants" are substances that protect the polymer by preventing oxidation. In many cases these also prevent undesirable reactions promoted by oxygen. Common antioxidant is complex organic amines like phenyl p-naphthylamine, phenolic substances and phosphates. The structures of two common antioxidants are given below:

#### Antioxidants

- (iv) **Accelerators:** Vulcanization takes place by heat and in presence of sulphur, but the process is very slow. The process can be speeded up by addition of small amounts of organic or inorganic compounds known as accelerators. The inorganic accelerators include lime, magnesia and white lead whereas organic accelerators are complex organic compounds such as aldehydes, amines, thicarbonates and 2-mercaptol benzothiozole. Sometimes accelerators require the presence of still other chemicals known as activators or promoters. These activators are usually metallic oxides such as zinc oxide. The best combination for efficient vulcanization include sulphur, an organic accelerator, a metallic oxide and a soap.
- (v) **Colouring Agents:** Several dyes and pigments are used to impart colours to elastomers.

Common colourants for polymers include:

Appearance	Chemical used
White	TiO <sub>2</sub> , BaSO <sub>4</sub>
Yellow	Lead Chromate
Red	Ferric oxide
Crimson	Antimony sulphides
Blue	Ultramarine
Green	Chromium trioxide
Silver metallic effect	Flake Aluminium
Pearlescence	Lead carbonate and mica.

The oil-soluble dyes or which have small particle size and refractive index near that of the

---

plastic (organic pigments such as phthalocyanins) are added to get transparent coloured products from transparent plastics. The inorganic pigments impart opacity to the plastic.

### SYNTHETIC RUBBERS

The polymers possessing similar physical properties as that of natural rubber are called synthetic rubbers. As natural rubber suffers from many disadvantages, attempts to find out a substitute for natural rubber began very early.

Greville William (1860) was first to isolate isoprene as a decomposition product by heating rubber to a high temperature. This gave a clue that rubber can be synthesized by the polymerization of monomers like isoprene. By the end of 19th century the fact was confirmed when polymerization of isoprene yielded rubber like product.

Since then attempts were on to prepare synthetic rubber by other monomers as well. Synthetic rubbers have been produced by the polymerization of a large number of conjugated dienes resembling isoprene. The foremost of all is, Buna Rubber (polymer of butadiene) which was prepared by the action of sodium on butadiene. That is why synthetic rubber is known as Buna rubber—'Bu' for Butadiene and 'Na' for sodium. However, the product prepared had poor tensile strength, and ageing characteristics. Improvements in properties were made by developing copolymers of butadiene. Several types of synthetic rubber are available today and some of them are described below:

#### 1. SBR or Buna-s Rubber

Styrene-butadiene rubber (SBR) is the first commercially made synthetic rubber. It is a copolymer obtained by the free-radical polymerization of two monomers, styrene and butadiene. The two components are allowed to react in a mixing vessel containing an aqueous solution of an emulsifying agent in presence of free radical initiator such as. cumene hydroperoxide or p-menthane hydroperoxide.

According to the temperature used, two processes have been developed, the hot process (at 50°C) and the cold process. In the cold process the temperature is kept in the range -18°C to 5°C. The rubber is known as cold rubber. Cold process is more efficient than the hot process because chain length can be controlled more efficiently. The SBR copolymer contains about 75% butadiene and 25% styrene and is a random copolymer. Both type of rubbers 'cold' as well as 'warm rubbers' can be vulcanized by conventional methods using sulphur. A reinforcing filler is added to achieve good physical properties.

#### Properties

- (i) SBR possesses high abrasion loses resistance and high load bearing capacity,
- (ii) At elevated temperatures SBR almost 2/3 of their tensile strength whereas natural rubber only loses 1/4<sup>th</sup>.
- (iii) Its resilience is poorer than that of natural rubber, which restricts its use in tire industry.
- (iv) The weather ability of SBR is better than that of natural rubber.
- (v) 'Cold' SBR is superior to the standard product because it contains less chain branching and crosslinking.
- (vi) SBR gets easily oxidized in presence of traces of ozone present in atmosphere.
- (vii) It swells in oils and solvents.

#### Uses

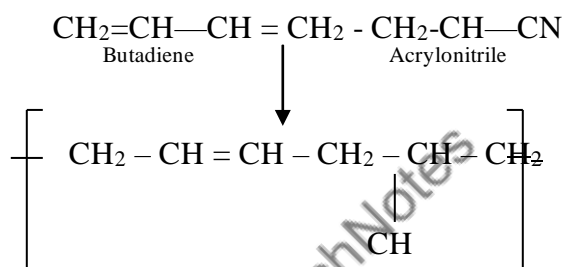
Of all the synthetic elastomers; SBR enjoys the major share of the market. SBR has the

following applications:

- (i) The principal use of SBR is in the production of tires and tire, products which are typically blends of both natural and synthetic rubbers. SBR is used for lighter duty tyres but is inferior to the natural rubber in its use for truck tyres.
- (ii) For many mechanical goods, it is superior to natural rubber and is used because of its easier processing.
- (iii) It is used for making hose, shoe soles, gaskets, floor tiles, carpet backing, tank linings etc.
- (iv) It is widely used for electrical insulation, although its properties are not good as those of butyl rubber.

## 2. Buna-N or Nitrile Rubber (NBR) or GR-A

The nitrile rubbers are polymers of butadiene and acrylonitrile in the ratio of 75% and 25% respectively. It is prepared by emulsion polymerization using cumene hydroperoxide as initiator. Hydrogen peroxide and ferrous sulphate can also be used as initiators. Vulcanization is done by conventional means by adding sulphur.



- (i) Nitrile rubbers are noted for their oil resistance. However the oil resistance varies with composition. If the acrylonitrile content is between 18% then the rubber has fair oil resistance and if it is more than 40% then it is extremely oil resistant.
- (ii) It possesses excellent resistance to heat, sunlight, acids and salts.
- (iii) Because of the presence of cyano groups (-CN), it is less resistant to alkalies than natural rubber.
- (iv) it has good tensile strength and abrasion resistance.
- (v) The rubbers are less resilient than natural rubbers.
- (vi) It has good heat resistance and if properly protected by antioxidants, it shows resistance to oxidative degradation as well.

### Uses

- (i) Nitrile rubber is used primarily for its oil resistance. These are extensively used for fuel tanks, gasoline hoses, gaskets, printing rollers and high altitude aircraft components.
- (ii) They can be used in contact with water and antifreeze solutions.
- (iii) They are also used in the form of latex for impregnating paper, textile and leather.
- (iv) It can also be used as blend component in tyre manufacture.

## 3. Neoprene or GR-M Rubber

This is also known as polychloroprene or polychlorobutadiene or duprene. Neoprene was the first synthetic rubbers developed in the United States.

**Preparation:** Neoprene or polychloroprene is prepared by polymerization of

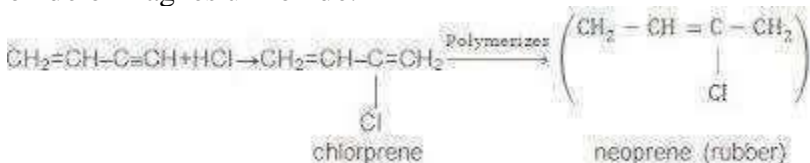


chloroprene, which is 2-chloro-1, 3 butadiene.

The preferred configuration produced during the polymerization is trans 1-4 polychloroprene. The polymerization of chloroprene takes place through emulsion polymerization.

The starting material, chloroprene is manufactured by the addition of hydrogen chloride to vinyl acetylene, which in turn is prepared by dimerization of acetylene.

The vulcanization of neoprene is different from that of other elastomers in that it can be vulcanized by heat alone. Although some types are polymerized in presence of sulphur which introduces crosslinks in the polymer. Neoprene can also be vulcanized using zinc oxide or magnesium oxide.



**Properties:** Neoprene is closely related to the natural rubber and can replace rubber because similarly in the properties of the two. Some of the properties of Neoprene are:

- (i) As H atom in the natural rubber is replaced by Cl atom in Neoprene, Neoprene has superior resistance to vegetable and mineral oils.
- (ii) It is superior to natural rubber as far as ageing and effects of high temperatures are concerned.
- (iii) Neoprene is soluble in polar solvents due to the presence of chloro-group.
- (iv) Vulcanized neoprenes have high tensile strength (3500-4000 psi) in the absence of protection.
- (v) Vulcanized neoprene is extremely resistant to oxidative degradation if suitably protected.
- (vi) It has good weathering and ozone resistance.
- (vii) It has got excellent oil resistance, though inferior to Nitrile rubber but better than natural rubber or SBR.

### Uses

Neoprene is used for:

- (i) It is used in oil resistant wire and cable coatings, industrial hoses, shoe soles.
- (ii) Its latex is used for the manufacture of gloves and coated fabrics.
- (iii) It is used for making tubings for carrying corrosive gases and oils.
- (iv) It is used for the manufacture of sponges, conveyor belts, linings of reaction vessels etc.

## 4. Butyl Rubber (GR-I)

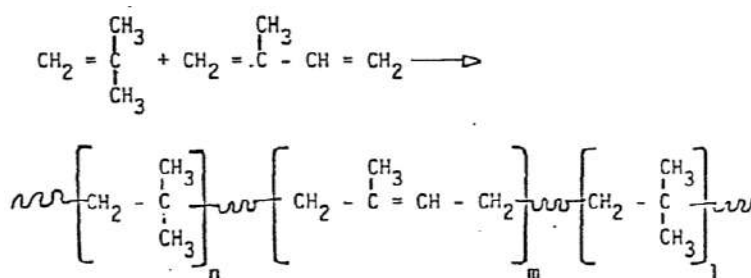
Butyl rubber belongs to the class of elastomers which do not have unsaturated chain structure. However, a small amount of diene monomer that provides a site for vulcanization is included by means of copolymerization.

### Preparation

Butyl rubber or polyisobutylene are prepared by the copolymerization of isobutylene with a small amount (1.5 to 4.5%) of isoprene. Isoprene is added to render them vulcanizable. It is prepared by low temperature cationic polymerization using Friedel-Crafts catalyst at



-80°C.



### Properties

The absence or low concentrations of double bonds in the main chain of butyl rubber results in high resistance to attack by a number of chemicals. It has the following properties.

- (i) Polyisobutylene or butyl rubber is amorphous under normal conditions but crystallizes on stretching.
- (ii) It exhibits outstanding resistance to attack by oxygen and ozone due to low concentration of double bonds. It is less sensitive to oxidative ageing as compared to other elastomers except silicones.
- (iii) Butyl rubber becomes soft on oxidative degradation.
- (iv) It exhibits low gas permeability due to closepacked linear paraffinic chains.
- (v) It has high ozone and acid resistance.
- (vi) Due to very low unsaturation, it cannot be hardened much on vulcanization.
- (vii) Unstabilized polyisobutylenes are degraded by light or heat to sticky low-molecular weight products. Therefore usual rubber antioxidants should be added to stabilize the polymer.
- (viii) It has excellent insulating properties as predicted from its non-polar, saturated nature.
- (ix) It is soluble in hydrocarbons such as benzene.
- (x) The tear resistance of butyl rubber is quite good and is retained well at high temperature and for long times, in contrast to natural rubber.

### Uses

- (i) Butyl rubber is used for inner tubes for tires because of its impermeability to gases.
- (ii) It is used for wire and cable insulation.
- (iii) It is used for linings of tanks, hoses etc.

### 5. Polysulphide Rubber (Thiccol or GR-P)

Polysulphide Rubbers are the condensation products of ethylene dihalides and alkali sulphides. These are linear condensation polymers.

#### Preparation

Polysulphide rubber is obtained by the reaction between sodium polysulphide and ethylene dichloride. Thus sulphur forms the part of the polymer chain. During the reaction NaCl gets eliminated. Vulcanization cannot be achieved by sulphur because polymer chain is not unsaturated. Hence it is not a hard rubber. However vulcanization can be achieved by reacting with ZnO which reacts with sulphur links forcing crosslinks.

#### Properties

The properties of the materials depend on the length of the aliphatic groups and the

number of sulphur atoms present in it. With four sulphur per monomer, the product is rubbery, whereas if only two sulphur atoms are present per monomer, the polymer do not behave as elastomer. In that case at least four methylene groups are needed in the dihalide to induce elastomeric properties to the products. Some of the important properties are:

- (i) Thiokol is resistant to swelling.
- (ii) It is resistant to oils and solvents. Fuel oils, lubricating oils, gasoline and kerosene have no effect on Thiokol.
- (iii) Thiokol films are impermeable to gases to a large extent.
- (iv) It cannot be vulcanized and hence does not form hard rubber.

Thiokol rubbers from many disadvantages:

- (i) It has disagreeable odour (mercaptan odour).
- (ii) It has poor heat resistance, poor abrasion resistance and low tensile strength.
- (iii) It tends to lose its shape under continuous pressure.

However, recent developments of Thiokol have overcome these disadvantages.

#### Uses

- (i) Polysulphides or Thiokol is used to make sealants, gaskets, balloons, fabric coating.
- (ii) Due to low permeability it is used to make gasoline hoses.
- (iii) Liquid Thiokol can be cured at room temperature to tough solvent-resistant rubbers. These liquid compounds are used as gasoline tank sealants and liners for aircraft and in variety of other sealing applications.
- (iv) The liquid polymers, when combined with oxidizers burn with great intensity and generate large volume of gas. Thus it can be used in solid-fuel rocket propellants.

#### 6. Polyurethane (PU)

Polyurethanes are polymers containing the group (carbonate group) these are known as urethane linkages

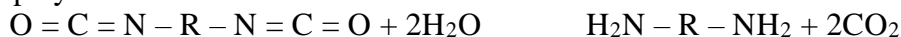
**Preparation:** The polyurethanes are formed through the reaction diisocyanate with the compound containing at least two active hydrogen atoms such as diols or diamines. The reaction of diisocyanate with glycol is represented as:

The properties of the final product depend upon the type of monomers and their chain length. A wide variety of polymers can be prepared ranging from rigid to elastic polymers. Crosslinking takes place through isocyanate groups which are capable of reacting with hydrogen atoms attached to the polymers leading to vulcanization. The polyurethanes can be produced in the form of fibers, elastomers or foams.

The foamed plastic can be obtained by blowing air/gas through molten polyurethane. This foamed plastic is also known as thermocol.

**Note:** Thermocol is also prepared by blowing air/gas through polystyrene.

Alternatively, for the production of foamed polyurethane little water is mixed with the reaction mixture, which reacts with isocyanate group to evolve CO<sub>2</sub>. The CO<sub>2</sub> produced foams the polymer as it sets.



#### Properties

- (i) Polyurethanes have high strength, good resistance to gas and aromatic hydrocarbons.
- (ii) They have excellent resistance to ozone and oxygen but are susceptible to microbial attack.
- (iii) The polyurethanes can be prepared in different forms varying from hard coatings to

flexible rubbers and rigid foams each having different properties.

- Coatings: Coatings are hard, glassy and solvent resistant. They have good flexibility and impact resistance.
- Elastomers: Elastomers have excellent abrasion resistance and are resistant to oils, greases and solvents.
- Fibers: Fibers are obtained by reacting di-isocyanate with long chain glycols which are usually polyesters or polyethers.
- Foams: Foams can be flexible or tough depending upon the polymer and the type of Crosslinking produced. They are light, tough and resistant to heat.

### Uses

- (i) The polyurethane foams have found the widest use. The flexible foams are used as upholstery material for furniture, insulation and crash pads.
- (ii) The rigid polyurethane foams are used as core material as insulation cover in refrigerated appliances and vehicles.
- (iii) Flexible polyurethanes can also be used for coating rubber articles to give them additional resistance to abrasion, such as in gymnasium and dance floors.
- (iv) Polyurethane resin is used to insulate the wires polyurethane coated wires can be soldered directly.
- (v) Polyurethane fibers with unusually high elasticity are used in foundation garments and swim wear. They have replaced rubber latex thread in this use.
- (vi) Flexible urethane foams are used as cushions for furniture and automobiles and have replaced rubber foams in these applications because of improved strength, lower density and easier fabrication.
- (vii) Polyurethanes are also used in making mattresses and pillows.
- (viii) As they are radiation resistant, they are also used in encapsulation for integrated-circuit devices.
- (ix) Its applications in medical field include its use in dental materials, artificial heart and skin.

### 7. Chlorosulphonated Polyethylene Rubber (Hypalon)

**Preparation:** When polyethylene is treated with a mixture of chlorine and sulphur dioxide, chlorosulphonated polyethylene is formed. The chlorosulphonation can be carried out either on the solid material or in solutions.

#### Properties

The chlorosulphonylation of ethane provides two modifications:

- (a) The chlorine atoms break the regularity of polyethylene chain structure changing the crystalline polyethylene to an elastomer.

## UNIT V

### Phase equilibrium and corrosion

**Phase-** It is defined as any homogeneous, physically distinct and mechanically separable portion of a system, which is separated from other such parts of the system by definite boundary surfaces in a system.

**Component-** It is defined as the smallest number of independently variable constituents taking part in the state of equilibrium by means of which the composition of each phase can be expressed directly or in the form of chemical equation.

**Degree of freedom-** It is defined as the minimum number of the independently variable factors such as the temperature, pressure and composition of the phases which must be arbitrarily specified in order to represent perfectly the condition of a system.

#### **PHASE RULE**

**Gibbs' phase rule** was proposed by Josiah Willard Gibbs . The rule applies to non-reactive multi-component heterogeneous systems in thermodynamic equilibrium and is given by the equality .

$$F = C - P + 2$$

where  $F$  is the number of degrees of freedom,  $C$  is the number of components and  $P$  is the number of phases in thermodynamic equilibrium with each other.

The number of degrees of freedom is the number of independent intensive variables, i.e. the largest number of thermodynamic parameters such as temperature or pressure that can be varied simultaneously and arbitrarily without determining one another. An example of one-component system is a system involving one pure chemical, while two-component systems, such as mixtures of water and ethanol, have two chemically independent components, and so on. Typical phases are solids, liquids and gases.

Uses of Phase Rule : -

- With the help of terms phases , components and degrees of freedom the phase rule gives a convenient basis for classification of equilibrium state of system.
- The information about molecular structure is not necessary because It applies to macroscopic systems .
- The phase rule shows that various systems having same degrees of freedom behave in a similar fashion .
- It helps in deciding whether the given number of substances together would exist in equilibrium under a given set of conditions

Limitations of phase rule : -

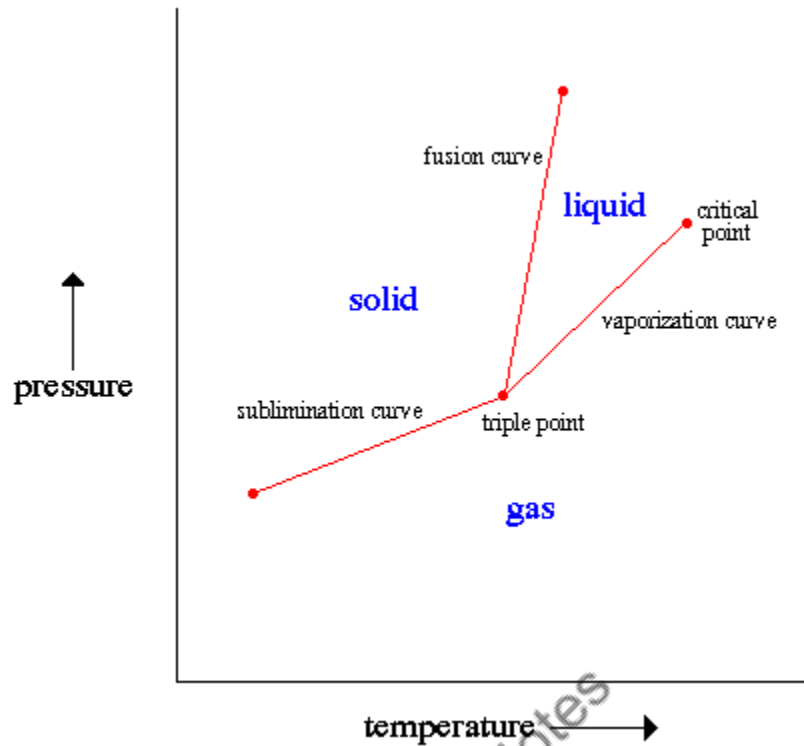
- Not applicable for the systems which are slow in reaching to equilibrium state .
- There is no consideration of magnetic and electric influence since system is defined only the variables like pressure temperature and components force.

- Any liquid or solid present should not be in finally divided state otherwise the value of their vapor pressure will differ from their normal value .

**Phase equilibrium** – it refers to the set of conditions where more than one phase may exist. It can be reflected by constancy with time in the phase characteristics of a system. In most metallurgical and materials systems, phase equilibrium involves just solid phases. However the state of equilibrium is never completely achieved because of very slow rate of approach of equilibrium in solid systems. This leads to non-equilibrium or meta-stable state, which may persist indefinitely and of course, has more practical significance than equilibrium phases. An equilibrium state of solid system can be reflected in terms of characteristics of the microstructure, phases present and their compositions, relative phase amounts and their spatial arrangement or distribution.

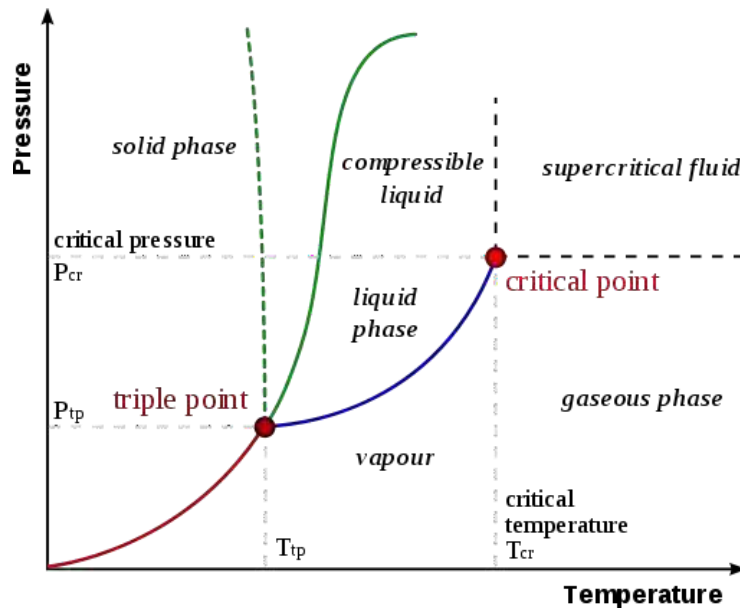
A **phase diagram** in physical chemistry, engineering, mineralogy, and materials science is a type of chart used to show conditions (pressure, temperature, volume, etc.) at which thermodynamically distinct **phases** occur and coexist at equilibrium. Common components of a phase diagram are lines of equilibrium or phase boundaries, which refer to lines that mark conditions under which multiple phases can coexist at equilibrium. Phase transitions occur along lines of equilibrium.

A phase diagram is a graph showing the limiting conditions for solid, liquid, and gaseous phases of a single substance or of a mixture of substances while undergoing changes in pressure and temperature or in some other combination of variables, such as solubility and temperature. The figure shown below displays a typical phase diagram for a one-component system (i.e., one consisting of a single pure substance), the curves having been obtained from measurements made at various pressures and temperatures.



Phase diagrams are specific for each substance and mixture. Complex mixtures may require three-dimensional phase diagrams, which can be represented in two dimensions through use of perspective. Phase diagrams are widely used in studies of mineral equilibria in connection with the conditions of formation of rocks and minerals within the Earth. They also are invaluable when designing industrial equipment and seeking optimum conditions for manufacturing processes, and in determining the purity of substances.

Phase diagrams illustrate the variations between the states of matter of elements or compounds as they relate to pressure and temperatures. The following is an example of a phase diagram for a generic single-component system:



**Figure 1. General Phase diagram**

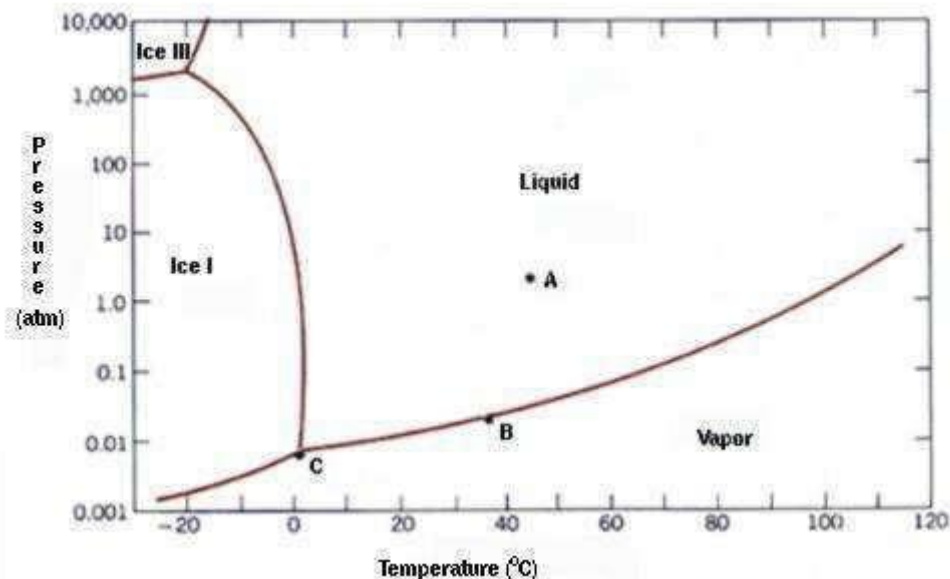
- **Triple point** – the point on a phase diagram at which the three states of matter: gas, liquid, and solid coexist
- **Critical point** – the point on a phase diagram at which the substance is indistinguishable between liquid and gaseous states
- **Fusion(melting) (or freezing) curve** – the curve on a phase diagram which represents the transition between liquid and solid states
- **Vaporization (or condensation) curve** – the curve on a phase diagram which represents the transition between gaseous and liquid states
- **Sublimation (or deposition) curve** – the curve on a phase diagram which represents the transition between gaseous and solid states

**Binary diagrams:** These diagrams constitute two components, e.g.: two metals (Cu and Ni), or a metal and a compound (Fe and Fe<sub>3</sub>C), or two compounds (Al<sub>2</sub>O<sub>3</sub> and Si<sub>2</sub>O<sub>3</sub>), etc. In most engineering applications, as mentioned before, condensed phase rule is applicable. It is assumed that the same is applicable for all binary diagrams, thus the presentation of binary diagrams becomes less complicated. Thus binary diagrams are usually drawn showing variations in temperature and composition only. It is also to be noted that all binary systems consist only one liquid phase i.e. a component is completely soluble in the other component when both are in liquid state. Hence, binary systems are classified according to their solid solubility. If both the components are completely soluble in each other, the system is called isomorphous system. E.g.: Cu-Ni, Ag-Au, Ge-Si, Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>. Extent solid solubility for a system of two metallic components can be predicted based on Hume-Ruthery conditions, summarized in the following: - Crystal structure of each element of solid solution must be the same. - Size of atoms of each two elements must not differ by more than 15%. - Elements should not form compounds with



each other i.e. there should be no appreciable difference in the electro-negativities of the two elements. - Elements should have the same valence.

**Isomorphous system:** Figure-2 depicts a typical phase diagram for an isomorphous system made of two metallic elements A and B. As cited earlier, any phase diagram can be considered as a map. A set of coordinates – a temperature and a composition – is associated with each point in the diagram. If the alloy composition and temperature specified, then the phase diagram allows determination of the phase or phases that will present under equilibrium conditions. There are only two phases in the phase diagram, the liquid and the solid phases. These single-phases regions are separated by a two-phase region where both liquid and solid co-exist. The area in the figure-2 above the line marked liquids (A'bB') corresponds to the region of stability of the liquid phase, and the area below the solidus line (A'dB') represents the stable region for the solid phase.



## CORROSION

Corrosion is defined as “the destruction or deterioration and consequent loss of metals or alloys through chemical or electrochemical attack by the surrounding environment”.

The primary factors that initiate corrosion on metals are atmospheric air, water and also conducting surface of the metal.

Egs: Rusting of iron, green scales are formed on copper vessels

Corrosion of metal occurs either by direct chemical attacks or by electrochemical attack on the metal by the corrosive environment.

If the corrosion takes place due to direct chemical attack (in the absence of moisture ) that type of corrosion is known as dry corrosion.

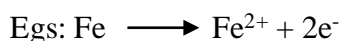
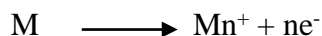
If the corrosion of metal takes place due to electrochemical attack in presence of moisture or a conducting medium such corrosion is known as wet corrosion or electrochemical corrosion.

**Electrochemical theory of corrosion:** Most of the corrosion takes place on the basis of electrochemical reactions on the surface of metal such a type of corrosion is known as wet corrosion. Electrochemical theory of corrosion can be taking iron as an example.

When a metal like iron is exposed to the environment according to electrochemical theory corrosion of metal takes place due to the formation of anodic and cathodic regions on the same metal surface or when the two metals are in contact with each other in a corrosive medium. These anodes and cathodes are formed due to the heterogeneities at the interfaces of the metal and environment. The heterogeneities on a metal surface could develop due to several factors like

1. On a metal surface if the concentration of the oxygen is different (if in the metal the area which is exposed to more oxygen acts as cathode, the area which is exposed to less oxygen concentration acts as anode).
2. Due to contact of two different metals (egs: if copper and iron are in contact with each other, then Fe acts as anode and copper acts as cathode due to change in electrode potential).
3. If metal surface subjected to stress (area under stress acts as anode).

Thus anodic and cathodic area are formed, in presence of corrosion medium ( like moisture etc.) At anode oxidation takes place so that metal is converted into metal ions with the liberation of electrons.

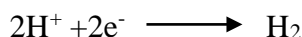


At the cathodic regions, reduction takes place since the metal at cathodic region cannot be reduced further, so some constituents of the corrosive medium take part in the cathodic reaction. Since in the cathodic reaction as the constituents of the corrosion medium are involved, they are more complicated and dependent on the nature of environment. Most common type of cathodic reaction are 1. Liberation of hydrogen 2. Absorption of oxygen.

### **Cathodic reactions:**

#### **(a) Liberation of Hydrogen type**

- (i) If the medium is acidic and in the absence of  $O_2$

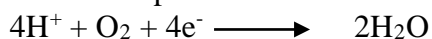


- (ii) If the medium is neutral or alkaline in the absence of  $O_2$ .

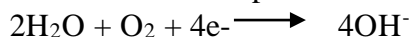


#### **(b) Absorption of oxygen type**

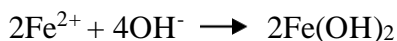
- (i) If the medium is acidic and in the presence of  $O_2$ .



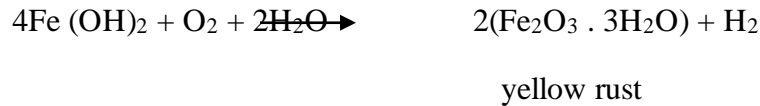
- (ii) If the medium is neutral or alkaline and in the presence of  $O_2$ .



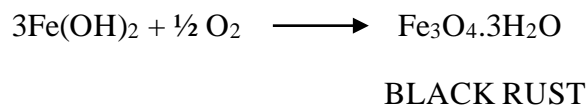
The metal ions ( $Fe^{2+}$ ) liberated at anode and some anions ( $OH^-$ ) formed at cathode diffuse towards each other through the conducting medium and form a corrosion product somewhere between the anode and cathode as



In an oxidizing environment, the insoluble  $\text{Fe(OH)}_2$  oxidised to ferric oxide as following reaction.



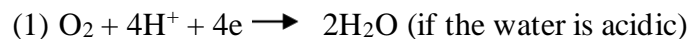
if the concentration of oxygen is limited then  $\text{Fe(OH)}_2$  is converted into magnetic oxide of Fe and is known as black rust.



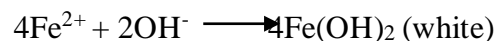
**Mechanism of CORROSION :** - The anodic reaction would be



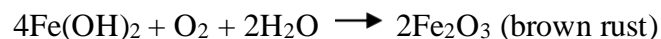
The loss of electrons leaves positively charged ions at the anode which travel from the anode to cathode via the water and carry the positive current. The electrons which are released on the anode travel from the anode to the cathode via the metallic circuit. These electrons are utilized in the reduction of oxygen present in water which is in contact with the cathode. Hence, at the cathode, one of the following reactions may take place.



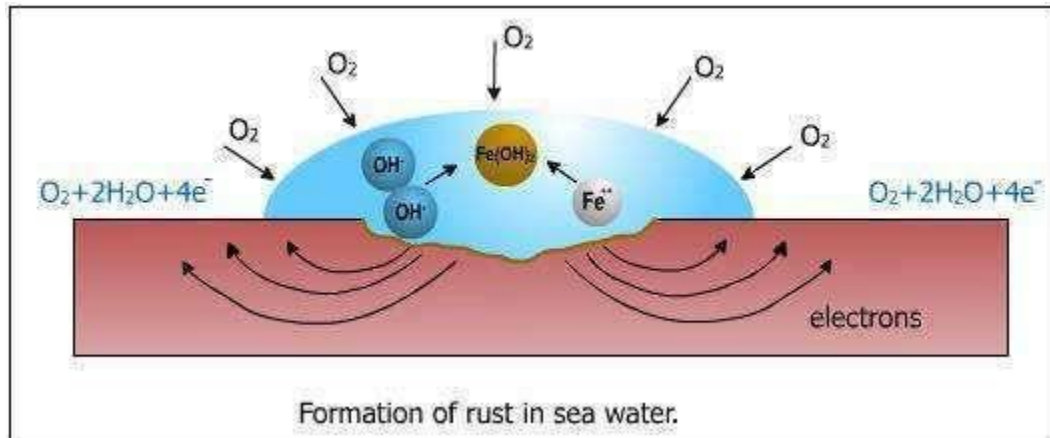
The negatively charged  $\text{OH}^-$  ions react with the positively charged  $\text{Fe}^{2+}$  ions and forms  $\text{Fe(OH)}_2$ .



OR



The end product is  $\text{Fe}_2\text{O}_3$ , which is generally called "rust". The rust is formed a little away from the surface. The mechanism of rust formation is shown in the following figure.



**Types of Corrosion:** Corrosion on the metals taking place depending on the nature of metals and depending on the types of environment by different mechanisms, giving different types of corrosion.

### 1 Galvanic corrosion or differential metal corrosion:

This occurs when two dissimilar metals are in contact with each other in a corrosive conductive medium; a potential difference is set up resulting in a galvanic current. The two metals differ in their tendencies to undergo oxidation. The metal with lower electrode potential or more active metal acts as anode and the metal with higher electrode potential acts as cathode. The potential difference is main factor for corrosion to take place. The anodic metal undergoes corrosion where as cathodic metal gets un-attacked.

Ex: When iron contact with copper iron has lower electrode potential acts as anode and undergoes oxidation as,



Whereas copper which is having higher electrode potential acts as cathode gets unaffected. The rate of galvanic corrosion depends upon potential difference between anodic and cathodic

metals, ratio of anodic and cathodic area and environmental factors and tendency of the metal to undergo passivity etc.

Other example : When Fe contact with Sn then Fe acts as anode and Sn acts as cathode but when Fe contact with Zn, Fe acts as cathode where as Zn acts as anode.

**PITTING CORROSION:** Pitting corrosion is a localized and accelerated corrosion. When a small particles of dust or water etc are get deposited on a metal (like steel). The portion covered by the dust will not be well-aerated area compared to the exposed surface hence the covered surface becomes anodic with respect to the surface exposed. In presence of an conducting medium (moisture) corrosion starts below the dust part and forming a pit. Once pit is formed the ratio of corrosion increases, because of the formation of smaller anodic and larger cathodic area intense corrosion takes place.

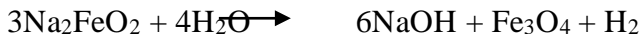
Pitting corrosion is one of the most destructive forms of corrosion. It causes equipment to fail because of perforation with only a small percent weight loss of the entire structure. Because of the small sizes of the pits it is highly difficult to identify the pitting corrosion. Pitting corrosion is an autocatalytic process, and once the corrosion products are formed, it further provides the condition for differential aeration below the corrosion product and surrounding metal parts. The pit grows and ultimately may cause failure of the metal.

Caustic embrittlement: It is a form of stress corrosion takes place in boilers operating at high temperature and pressure. Caustic embrittlement focus at stressed part of boilers such as cracks, rivets, bents, joints etc.

The boiler fed water usually contains some residual sodium carbonate (used for softening process). At high temperature and pressure it undergoes hydrolysis to form sodium hydroxide.



The alkali water sweeps through the minute cracks, crevices between the rivets and joints by capillary action. Inside the cracks water gets evaporated leaving behind NaOH. The concentrations of the NaOH gradually increase on these sites due to poor circulation of water. When concentrations of the NaOH reaches a value of 10% it attacks the metal at the stressed region dissolving it in the form of sodium ferroate (  $\text{Na}_2\text{FeO}_2$  ). Sodium ferroate undergoes hydrolysis-depositing magnetite as follows



So NaOH is regenerated in the process and its concentration is keep on increasing maintaining a required environment. Thus corrosion process develops cracks and making the metal brittle by the deposition of the product.

The corrosion cell can be represented as

Fe (under stress) / conc. NaOH / dil. NaOH/ Fe (stress free)

Anode

Cathode

Caustic embrittlement can be prevented by the addition of compounds like sodium sulphite, tannin, lignin, phosphates etc. which blocks the cracks thereby preventing the infiltration of alkali.

**Factors affecting rate of corrosion:** Several factors affecting the rate of the corrosion, which can be divided into two parts

2. Factors affecting on metal (related to the metal)
3. Factors affecting on corrosive environment.

**Factors affecting the metals:**

1. **Nature of the metal:** The tendency of the metal to undergo corrosion is mainly dependent on the nature of the metal. IN general the metal with lower electrode potential have more reactive and more susceptible for corrosion and metal with high electrode potential are less reactive and less susceptible for corrosion for egs: metals like K, Na, Mg, Zn etc have low electrode potential are undergo corrosion very easily, where as noble metals like Ag, Au, Pt have higher electrode potential, their corrosion rate are negligible but there are few exception for this general trend as some metals show the property of passivity like Al, Cr, Ti, Ta etc.
2. **Surface state of the metal or nature of the corrosion product (passivity):**  
The corrosion product is usually the oxide of the metal; the nature of the product determines the rate of further corrosion process.

If the oxide layer, which forms on the surface, is stoichiometric, highly insoluble and non-porous in nature with low ionic and electronic conductivity then that type of products



layer effectively prevents further corrosion, which acts as a protective film. For egs: Al, Cr, Ti develop such a layer on their surface and become passive to corrosion and some metal like Ta, Zr and Mo not only forms such a protective layers but are capable of self repairing oxide films when it is damaged. Hence these are extremely passive metals.

If the oxide layer forms on the metal surface is non-stoichiometric, soluble, unstable and porous in nature and have an appreciable conductivity, they cannot control corrosion on the metal surface for egs: oxide layer formed on metals like Zn, Fe, Mg etc.

### 3. **Anodic and Cathodic area:**

The rate of the corrosion is greatly influenced by the relative sizes of cathodic and anodic areas.

If the metal has smaller the anodic area and larger the cathodic area exposed to corrosive atmosphere, more intense and faster is the corrosion occurring at anodic area because at anode oxidation takes place and electrons are liberated. At the cathode these electrons are consumed. When anode is smaller and cathode region is larger all the liberated electrons at anode are rapidly consumed. This process makes the anodic reaction to takes place at its maximum rate thus increasing the corrosion rate. If the cathode is smaller and reverse process takes place decrease rate of corrosion.

For egs: If tin (Sn) coated on iron (Fe) and in that some area are not covered or some pin holes are left, there forms smaller anodic area and larger cathodic area because tin is cathodic with respect to iron so intense localized corrosion takes place. On the other hand if Zn coated to Fe then if there are some pin holes are there creates larger anodic area and smaller cathodic area because Fe is cathodic with respect to zinc so that rate of corrosion is very less.

### 4. **Hydrogen over voltage:**

A metal with low hydrogen over voltage on its surface is more susceptible for corrosion. When the cathodic reaction is hydrogen evolution type with low hydrogen over voltage, liberation of  $H_2$  gas is easier so that cathodic reaction is very fast, that makes anodic reaction faster hence overall corrosion process is very fast. If the  $H_2$  over voltage is high so cathodic reaction is slow hence corrosion reaction also slower.

### **Factors related to corrosive environment:**

1. **pH of the medium:** Usually higher acidic nature (low pH) higher is the rate of corrosion. If the pH is greater than 10 corrosion of iron is very less due to the formation of protective coating of hydrous oxides of iron.  
If pH is between 10 and 3, then presence of oxygen is essential for corrosion of iron. If the pH is 3 or lower than 3, severe corrosion occurs in the absence of air due to the continuous evolution of  $H_2$  at cathode. However metals like Al, Zn etc undergo fast corrosion in highly alkaline medium.
2. **Temperature:** On increasing the temp. Rate of corrosion process also gets increases because on increase of temp. Conductance of the aqueous medium increases hence rate of diffusion also.  
In some cases on rise in temp. Decrease the passivity, which again leads to increase in the corrosion rate.
3. **Polarization at anodic and cathodic area:** Polarization of cathode or anode decreases the rate of corrosion. If anodic polarization takes place due to some reaction, then tendency of metal to undergo oxidation decreases hence dissolution of metals as metal ion decreases. This is usually due to increase in conc. Of ions of the dissolved metals in the vicinity of electrode or also due to the anodic passivity. Cathode polarization decreases the cathodic reaction hence hindering the combination of cathode reactant and electron. For the corrosion to continue both anodic and cathodic reaction should take place simultaneously if any one reaction is slower than the rate of corrosion is slower. Use of depolarizers reduces the polarization effect hence the rate of corrosion reaction increases.

### **Galvanic corrosion or Corrosion of Metals due to contact of metals:**

The name of this type of corrosion is indicative that there must be a formation of galvanic cell on metal surface causing corrosion. Such cells get set up all along the surface of metal when it faces the electrolytic environment and two dissimilar metals in contact.

For example:

- If metal iron or brass alloy is used together to join various parts, due to difference in potential, a galvanic cells gets set, leading to corrosion.
- In such cases all along the surface of metal small galvanic cells are set up, where area of high potential acts as an anode and the one with lower potential act as a cathode. The portion of metal acting as an anode deteriorates and at cathode the cathodic product gets evolved/deposited, depending upon the environment, and mechanism of the corrosion, i.e. by absorption of oxygen or evolution of hydrogen.
- When metals are surrounded by aqueous alkaline/acidic/neutral solution, the movement electrons, cations and anions occurs just like as in a typical galvanic cell. But when the

metal is just exposed to moisture or a few drops of certain solution, the movement of electrons, cations and anions takes place through the bulk of metal, thus the metal itself serves as a conducting medium while its outer surface gets corroded.

- If the metal is exposed to acidic medium the mechanism at cathode proceeds to form  $H_2$  gas while anodic reactions remain the same.

**Control of corrosion:** *To avoid the formation of galvanic cells,*

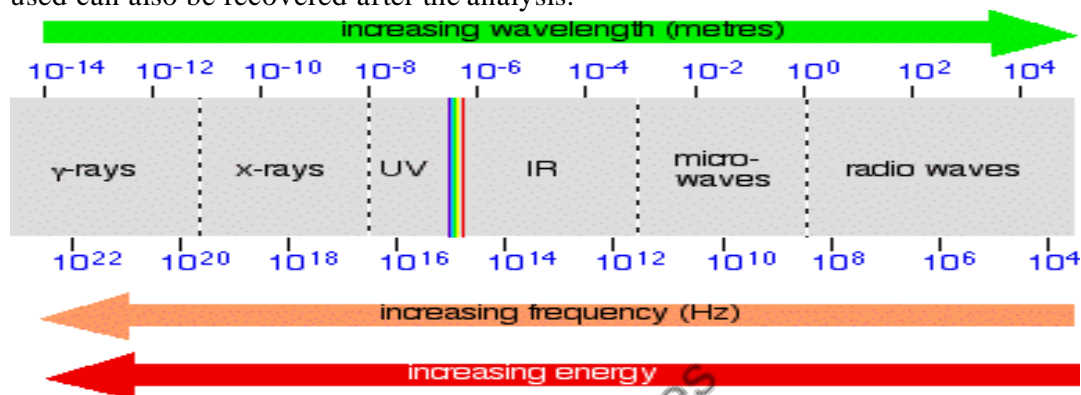
- (a) The metals should be pure.
- (b) The materials used to assemble the different parts should be of same potentials.

## UV SPECTROSCOPY

### INTRODUCTION

The spectroscopic methods have proved to be extensively useful for qualitative analysis identification and structural elucidation of organic compounds. Spectroscopic methods are advantageous over other methods because

- (i) They are quick
- (ii) They are sensitive
- (iii) Information obtained by them is in the form of permanent record
- (iv) The informations obtained by these methods are highly reliable
- (v) Very small quantity of substance is required for the determination of spectra and even the quantity used can also be recovered after the analysis.



**Origin of Electronic Spectra** – Spectroscopy is the term applied for the branch of science which deals with the study of resolution of visible radiations into its component wave lengths. Now, the term is broadened and is applied to studies involving entire electromagnetic spectrum. Electromagnetic radiations consists of waves of energy and their parameters as:

- (i) **Wavelength** – ( $\lambda$ ) It is the distance between two consecutive peaks or crests.
- (ii) **Wave Number** – ( $\bar{\nu}$ ) It is the number of waves per cm.
- (iii) **Frequency** – ( $\nu$ ) It is the number of waves per second.

Different types of electronic spectra are – Emission Spectra, Absorption Spectra.

**Emission spectra**- when a substance is subjected to intense heat or to an electric discharge, its atoms & molecules absorb energy & get excited. These excited species, on returning to the ground state may emit radiation which on passing through a prism gives rise to a spectrum of atoms appears as bright lines on a dark back ground where as spectra of molecules appears as band, when white light is passed through a prism, we get a continuous spectrum of seven colours and sodium light gives a line spectrum [two-D-line] (yellow) of define wave length both are emission spectra.

**Absorption spectra**- when white light is passed through yellow sodium flame before reaching the prism, we get a continuous spectrum with two black lines in place of yellow lines obtained from sodium light. Here sodium flame has absorbed two wavelengths from white light which it itself emits. This is absorption spectrum.

During the absorption, some molecules falling in the path of incident beam colloid with photons of energy exactly equal to the difference in energy between the ground and excited states of the molecules. Thus a spectroscopic technique, qualitative or quantitative if it depends upon the measurement of an absorption spectrum is called absorption spectroscopy or molecular spectroscopy.

**Principle**- consider a molecule of a compound [X] have only two energy levels  $E_1$  and  $E_2$  the energy difference  $\Delta E$  is determined as  $\Delta E = E_2 - E_1 = h\nu$  or  $hc/\lambda$

Energy absorbed by each molecule is given by  $\Delta E = N hc/\lambda$

Where

$h$	=	Plank's constant = $6.63 \times 10^{-34}$
$c$	=	Velocity of electromagnetic radiations = $3 \times 10^8 \text{ ms}^{-1}$
$N$	=	$6.02 \times 10^{23} \text{ mol}^{-1}$

8 = wavelength

The light of wavelength 8 has photon of energy just equal to the energy difference between the two energy levels. In actual practice, molecules of compound have large number of energy levels and very small but definite amounts of energy is needed for transition between some of these while extremely large amounts of energy are involved between some other transitions. The following transitions are brought about by absorption of radiant energy by a molecule –

- (i) **Electronic Transition** – Electrons are jumped to higher energy levels by the absorption of energy.
- (ii) **Vibrational Transition** – Stretching, contracting and bending of covalent bond may occur due to absorption of energy.
- (iii) **Rotational Transition** – Due to the absorption of radiant energy change in the rotational energy of the molecule takes place.

Bond	A	B
Bond Stretching	A	B
Contracting	A	B
Bending	A	B

Any wavelength of radiations absorbed by a molecule is determined by the changes in the electronic, Vibrational or rotational energy levels, permissible for it and its atoms.

- (i) High-energy radiations as uv or visible are required to bring about electronic transition.
- (ii) The low energy radiations as IR are required for Vibrational transitions.
- (iii) The radiation of far infrared regions brings about rotational transitions.

### **ABSORBANCE**

The intensity of absorption is related to the number of photons absorbed by the molecules usually some photons are absorbed by the molecules. The fraction of photon absorbed by the molecules at given frequency depends upon

- (i) The nature of absorbing molecule.
- (ii) The concentration of molecules. The higher the concentration the more molecules are present to absorb the photons.
- (iii) The length of the path of the radiation through the material. The longer path, the larger number of molecules exposed and hence greater is the probability that a given photon will be absorbed.

### **Laws of Absorbance**

- (i) **Lamberts Law** – If a monochromatic light passes through a transparent medium, the rate of decrease in intensity with the thickness of medium is proportional to the intensity of the incident light i.e. the intensity of the emitted light decreases exponentially as the thickness of the absorbing medium increases arithmetically.

$$dI/I = -k \, dx \quad dI/I = -k \, dx$$

$dI$  = Change in transmitted light

$I$  = Intensity of light

$dx$  = Small thickness of medium

$k$  = Proportionality constant

On integrating his equation between  $I = I_0$  limits at  $x = 0$  and  $I = I$  at  $x = L$  we get

- (ii) **Beers Law** – The intensity of beam of monochromatic light decreases exponentially as the concentration of the absorbing substance increases arithmetically.

$$I_t = I_0 10^{-k'c}$$

According to Beers law, the absorbance at any particular wave length is directly proportional to the number of absorbing molecules. If the solution contains more than one type of absorbing species, the total absorbance will be the sum of the absorbance of all the species provided they do not interact chemically.

$$\begin{aligned} I_t &= I_0 10^{-k'c} \\ &= I_0 10^{-0.47343 k'c} \\ &= I_0 10^{-k'c \, 3/4} \text{ (Beer's Law)} \end{aligned}$$

$I_t$	=	Intensity of Transmitted light
$I_o$	=	Intensity of incident light
$k$	=	Proportionality constant
$C$	=	Concentration (Molar) of medium

(iii) **Beer's Lambert's Law** – Electronic spectra of organic compound are most frequently recorded in solution when a monochromatic light of intensity  $I_o$  is passed through a solution of concentration  $C$  Molar, then intensity of Transmitted light  $I_t$  changes. The probability of absorption of  $r$  addition is determined by a mathematical expression given by Beer's lamberts law which expresses the relationship between amount of light absorbed and -

- (i) Concentration of the solution
- (ii) Length of the solution through which light passes

$$\ln \frac{I_o}{I_t} = -K L \text{ or } I_t = I_o e^{-KL} \text{ --- (i) Lambert's Law}$$

From lambert's Law

$$\ln \frac{I_o}{I_t} = -Kcl$$

$$2.303 \log I_o/I_t = -Kcl$$

$$\log I_o/I_t = K / 2.303 cl = \epsilon cl = A$$

$$\epsilon = K/2.303 \text{ and is called molar absorptivity coefficient}$$

From Beer's law

$$\log I_o/I_t = A \text{ Absorbance}$$

$$I_t = I_o e^{-K'C} = I_o 10^{-K'C}$$

By combining equation (i) and (ii) i.e. lambert's law and Beer's law.

$$I_t = I_o \cdot 10^{-\epsilon cl}$$

$$\text{Where } \epsilon = K/2.303$$

$$\log I_o/I_t = \epsilon cl$$

$$\text{Where } I_o/I_t = A$$

$$A = \epsilon \times c \times l \text{ or } \epsilon = A/cl$$

$I_o$  = Intensity of incident light

$I_t$  or  $I$  = Intensity of transmitted light

$C$  = Concentration of absorbing compound in moles per litre

$L$  = Length of sample in cm

$\epsilon$  = (Epsilon) is called molar absorptivity co-efficient

$A$  = Absorbance of the solution

$$A = \log I_o/I_t \text{ or } T = \log I/I_o \text{ or } T = I/A$$

Where  $T$  is transmittance of the solution. The wavelength at which a molecule has highest absorption co-efficient [ $\epsilon_{\max}$ ] is designated as [ $\lambda_{\max}$ ]. a spectrum may have several different maxima each with characteristic value of  $\epsilon_{\max}$ .

### **INSTRUMENT USED FOR MEASUREMENT OF ABSORPTION**

All chemicals interact with the electromagnetic radiations and due to this there occurs decrease in the intensity of radiant beam. This decrease in intensity is measured by absorption spectroscopic methods.

The various instruments used for measurement of absorption are:

- (i) Colorimeter
- (ii) Absorptionmeter
- (iii) Spectro photometer

- (i) **Colorimeter** – It is concerned with the determination of concentration of substance by measurement of relative absorption of light with respect to known concentration of the substance [Absorption in visible region is employed].
- (ii) **Absorptionmeter** – Includes instrument which are useful in other spectral region as well. This measures the ratio of some function of two, of radiant power or two electromagnetic beams.
- (iii) **Spectrometer** – It is an absorption meter used for much narrower bands of wave lengths as produced by monochromator. They can be used in UV, Visible and IR region.

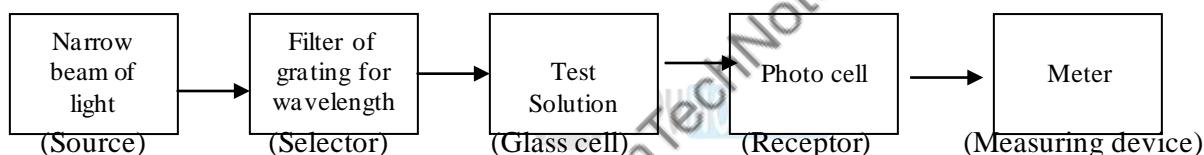
All these instruments have some common features like –

### COLORIMETRIC ANALYSIS

The variation of color of the system with change in concentration is the basis of colorimetry. In colorimetry the concentration of a substance is determined by measurement of relative absorption of light with respect to a known concentration of a substance. In visual colorimetry, natural or artificial white light is generally used as a source of light and determinations are made by colorimeter because the method is convenient for the systems in which substances or their solutions are coloured. The eye is replaced by photoelectric cell and intensity of colour is easily measured by photoelectric colorimeter. If the substance is colourless then a suitable complexing agent is used to get a coloured complex (which absorb light in the visible region) for example for the estimation of cuprous ion, complexing agent ammonium hydroxide, is added to get blue coloured solution.

In a colorimeter, a narrow beam of light (of proper wavelength) passes through the solution under test towards a sensitive photocell. Usually colorimeters are provided with arrangements of filters or diffraction grating. Consequently it is possible to select the most appropriate wavelength by choosing a filter grating.

Signal Indicator



The current generated in the photocell is proportional to the amount of light transmitted by the solution. This depends upon depth of colour of substance under test. Thus current from photocell will be greatest when light transmitted is greatest. This occurs when coloured solution is dilute. The general meter is designed in such a way that it does not show the fraction of light transmitted but it shows the fraction of light absorbed. This is proportional to the concentration of the coloured substance in the test solution.

Thus colorimetric analysis is meant to compare under suitable conditions. The colour produced by a substance in unknown amount with the same colour produced by a known amount of material being determined.

### ULTRAVIOLET SPECTROSCOPY

UV region of electromagnetic radiation lies between 200 – 400 nm and visible region lies between 400 – 800 nm. The UV region of the electromagnetic spectrum is subdivided into two spectral regions as follows –

- (i) Near Ultraviolet      200 to 400 nm
- (ii) Far Ultraviolet      10 to 200 nm

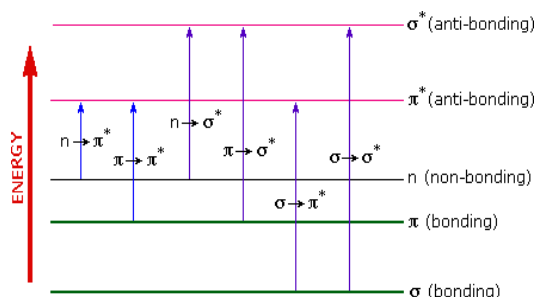
Or Vacuum Ultraviolet

Ultraviolet absorption spectra originates from transition of electron within a molecule or ion from lower electronic energy level to higher electronic energy level. When an electromagnetic radiation in ultraviolet region is made to pass through a compound containing multiple bonds, it is observed that a part of the incident radiation is usually absorbed which causes electronic excitation. The amount of radiation absorbed depends upon the structure of the compound as well as wavelength of the radiation. The energy of the radiation absorbed causes excitation of electron from lower energy level to higher energy level and the difference of energy is given by –  $E = h\nu$ . Thus the actual energy required depends upon the difference in energy between ground state ( $E_0$ ) and the excited state ( $E_1$ ) of the electron.

$$E_1 - E_0 = h\nu$$



**Electronic Transitions** – When UV energy is in the form of quanta the absorption spectrum arising from single electronic transition is expected to consist of a single discrete line, but this does not happen because electronic absorption is super imposed upon Vibrational and rotational sub energy levels. Therefore, the spectra of simple molecules in the gaseous state contain narrow absorption peaks, where in each peak represents a transition from a particular combination of Vibrational and rotational levels in the electronic ground state to a corresponding combination in the excited state. However, in case of polyatomic complex molecules, broad absorption bands are obtained due to coalescence of discrete bands.



When energy is absorbed by a molecule in the UV region, it brings about some changes in the electronic energy of the molecule resulting from transitions of valence electrons. The following three types of electrons are involved in organic molecules.

- (i)  **$\pi$  Electrons** – The electrons which are forming double bonds are called relectrons. These are involved in unsaturated hydrocarbons like trienes and aromatic compounds. In unsaturated systems,  $\pi$  electrons predominantly determine the energy state of electron sheaths which are excited by the absorption of UV or visible light.
- (ii)  **$\sigma$  Electrons** – The electrons which form single bonds are electrons according to molecular notation. They are involved in saturated bonds between 'C' and 'H' in paraffins such bonds are also known as 'S' bonds. The energy required to excite electrons in bond is very higher than the obtained by UV radiation hence electron do not absorb UV radiation and are not excited by UV radiations.
- (iii)  **$n$  Electrons** – These are the unshared or non-bonded electrons and are not involved in the bonding between atoms in molecules. Examples – organic compounds containing N, O, or S, halogens. However  $n$  – electrons can be excited by UV radiation and hence compounds containing atoms like N, O, S, halogen compounds or unsaturated hydrocarbons may absorb UV radiations.

Representation in the electronic energy levels is as follows:

	Antibonding	$\sigma^*$
Energy	Antibonding	$\pi^*$
Level	non bonding	$n$
	Bonding	$\pi$
	Bonding	$\sigma$

### Electronic Energy Levels is Simple Organic Molecule

Energy absorbed in the UV region by complex organic molecules results in transitions of valency electrons in the molecules. These transitions are –

- (a)  **$n \rightarrow \pi^*$  transition** – The general characteristics of  $n \rightarrow \pi^*$  bonds are (a) They have low intensity (b) They are shifted to shorter wave lengths by more polar solvents as well as electron donating groups. In the spectra of simple molecules  $n \rightarrow \pi^*$  transition requires the least energy and the corresponding bonds are of longer wave length. Such transitions are shown by unsaturated compounds which contain atoms like, N, O and S. These show weaker bands in spectrum. In aldehydes and ketones the band due to  $n \rightarrow \pi^*$  transition generally occurs in the range 270-300 nm, while in case of carbonyl compounds, the bands are in the range 300 to 350 nm due to the  $n \rightarrow \pi^*$  transitions. This transition is between non-bonding orbital and

antibonding orbital. In absorption of uV radiation, the nuclei along with electrons held together plays an important role in determining which wavelength of radiation will be absorbed. The nuclei determine the strength with which electrons are bound and influence the energy gaps between the excited and ground states.

- (b)  **$\pi \rightarrow \pi^*$  transition** – These types of transitions are related to the transition of electron from bonding orbital to  $\pi$  antibonding  $\pi^*$ Orbital. In unsaturated molecules, these transitions are possible. Alkenes absorb around 175 nm, alkynes absorb around 170 nm and carbonyl compounds absorb around 188 nm. For example the UV spectrum of ethylene exhibits an intense band at 174 nm and a weak band at 200 nm, both of these are due to  $\pi \rightarrow \pi^*$  transitions. According to selection rules only band at 174 nm represent an allowed transition. This can be represented as given in the figure. This is a transition between bonding orbitals and antibonding orbitals.
- (c)  **$n \rightarrow \sigma^*$  transition** – The energy required for  $n \rightarrow \sigma^*$  transition is generally less than that required for  $\sigma \rightarrow \sigma^*$  transition and their corresponding absorption bands appear at longer wavelengths in the ultraviolet region (180 to 200 nm) saturated compounds with lone pair (non bonding) electrons undergo  $n \rightarrow \sigma^*$  transitions apart from  $\sigma \rightarrow \sigma^*$  transition. In case of saturated molecules which contain atoms having unshared pairs of electrons  $n \rightarrow \sigma^*$  transition becomes be determined by commonly available spectrophotometers. For examples – alcohols and amines (containing –OH and –NH<sub>2</sub> groups) absorb between 175 to 200 nm.
- (d)  **$\sigma \rightarrow \sigma^*$  transition** – Such transitions occur in case of saturated hydrocarbons which do not contain lone pairs of electrons. The energy required for this type of transitions is very large and absorption band occurs in (126 to 135 nm) for ultraviolet region. For example, methane has  $\lambda_{\text{max}}$  at 121.9 nm and ethane at 135 nm corresponds spectrophotometers which generally do not operate at wave lengths below 180 nm. Thus this is a transition between bonding orbital and antibonding orbital.

### Concept of Chromophore and Auxochrome in the UV spectroscopy

**Chromophore-** Chromophore is defined as any isolated covalently bonded group that shows a characteristic absorption in the ultraviolet or visible region (200-800 nm). Chromophores can be divided into two groups-

a) Chromophores which contain p electrons and which undergo  $\pi$  to  $\pi^*$  transitions. Ethylenes and acetylenes are the example of such chromophores.

b) Chromophores which contain both p and nonbonding electrons. They undergo two types of transitions;  $\pi$  to  $\pi^*$  and nonbonding to  $\pi^*$ . Carbonyl, nitriles, azo compounds, nitro compounds etc. are the example of such chromophores.

**Auxochrome-** An Auxochrome can be defined as any group which does not itself act as a chromophore but whose presence brings about a shift of the absorption band towards the longer wavelength of the spectrum. – OH, -OR, -NH<sub>2</sub>, -NHR, -SH etc. are the examples of auxochromic groups.

### Absorption and intensity shifts in the UV spectroscopy

There are four types of shifts observed in the UV spectroscopy-

a) Bathochromic effect- This type of shift is also known as red shift. Bathochromic shift is an effect by virtue of which the absorption maximum is shifted towards the longer wavelength due to the presence of an auxochrome or change in solvents. The nonbonding to  $\pi^*$  transition of carbonyl compounds observes bathochromic or red shift.

b) Hypsochromic shift- This effect is also known as blue shift. Hypsochromic shift is an effect by virtue of which absorption maximum is shifted towards the shorter wavelength. Generally it is caused due to the removal of conjugation or by changing the polarity of the solvents.

c) Hyperchromic effect- Hyperchromic shift is an effect by virtue of which absorption maximum increases. The introduction of an auxochrome in the compound generally results in the hyperchromic effect.

d) Hypochromic effect- Hyperchromic effect is defined as the effect by virtue of intensity of absorption maximum decreases. Hyperchromic effect occurs due to the distortion of the geometry of the molecule with an introduction of new group.

## **INSTRUMENTATION OF UV SPECTROSCOPY**

The instrumentation for UV spectroscopy i.e. UV spectrometer is made up of following important components.

- (i) Source of Radiation
- (ii) Monochromator
- (iii) Beam splitter
- (iv) Sample chamber
- (v) Detector
- (vi) Recorder

In UV spectrometer, a beam of light is split into two equal halves, one half of the beam called sample beam is directed through a transparent cell containing a solution of the compound being analyzed and one half (reference beam) is directed through an identical cell that contains only the solvent. The instrument is so designed that it can compare the intensities of the two beams at each wavelength of the region.

Instrumentation and working of the UV spectrometers can be studied simultaneously. Most of the modern UV spectrometers consist of the following parts-

**Light Source-** Tungsten filament lamps and Hydrogen-Deuterium lamps are most widely used and suitable light source as they cover the whole UV region. Tungsten filament lamps are rich in red radiations; more specifically they emit the radiations of 375 nm, while the intensity of Hydrogen-Deuterium lamps falls below 375 nm.

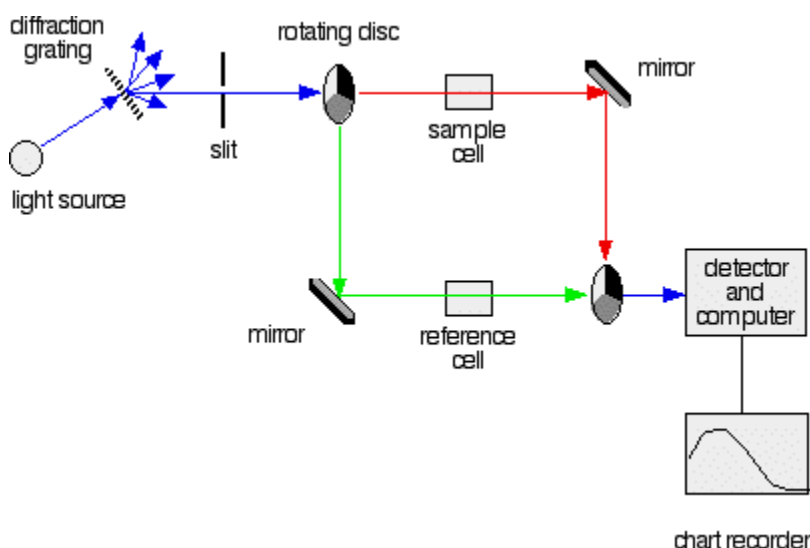
**Monochromator-** Monochromator generally composed of prisms and slits. The most of the spectrophotometers are double beam spectrophotometers. The radiation emitted from the primary source is dispersed with the help of rotating prisms. The various wavelengths of the light source which are separated by the prism are then selected by the slits such the rotation of the prism results in a series of continuously increasing wavelength to pass through the slits for recording purpose. The beam selected by the slit is monochromatic and further divided into two beams with the help of another prism.

**Sample and reference cells-** One of the two divided beams is passed through the sample solution and second beam is passed through the reference solution. Both sample and reference solution are contained in the cells. These cells are made of either silica or quartz. Glass can't be used for the cells as it also absorbs light in the UV region.

**Detector-** Generally two photocells serve the purpose of detector in UV spectroscopy. One of the photocell receives the beam from sample cell and second detector receives the beam from the reference. The intensity of the radiation from the reference cell is stronger than the beam of sample cell. This results in the generation of pulsating or alternating currents in the photocells.

**Amplifier-** The alternating current generated in the photocells is transferred to the amplifier. The amplifier is coupled to a small servometer. Generally current generated in the photocells is of very low intensity, the main purpose of amplifier is to amplify the signals many times so we can get clear and recordable signals.

**Recording devices-** Most of the time amplifier is coupled to a pen recorder which is connected to the computer. Computer stores all the data generated and produces the spectrum of the desired compound.



### **APPLICATION OF UV SPECTROSCOPY**

- (i) **Qualitative Analysis** – UV spectroscopy is used for characterization of aromatic compounds and conjugated olefins. Identification is done by comparing the UV absorption spectrum of the sample with the UV spectra of known compound for reference.
- (ii) **Detection of Impurities** – Detection of impurities in organic compounds can also be done by UV spectroscopy. (a) If benzene is associated in small quantity with cyclohexane it can be detected by UV spectroscopy by the absorption band of benzene at 255 nm. (b) If impure adiponitrile or hexamethylene diamine is used for the preparation of nylon the product will be of poor quality. The impurities present with the raw materials can be detected by UV method. (c) Purification of organic compounds can be continued until the absorption bands characteristic of the impurities disappear in the spectrum.
- (iii) **Quantitative Analysis** – UV spectroscopy is used for the quantitative analysis of compounds which absorb UV radiation. The determination is carried out on the basis of Beer Lamberts law according to which absorbance is determined by the formula

$$A = \log I_0 / I = \log T = \epsilon lc$$

Where  $\epsilon$  is molecular absorptivity co-efficient,  $L$  is length of the path or cell  $C$  is the concentration of solution.

- (iv) **Studying Kinetics of Chemical Reaction** – UV spectroscopy can be used to study the kinetics of chemical reactions by following the change in concentration of a product or a reactant with time during the reaction.
- (v) **Determination of Dissociation Constants of Weak Acids or Bases** – UV spectroscopy can be used to determine the dissociation constants of acids or bases. The dissociation constant of an acid (HA) is determined by determining the ratio  $[HA]/[A^-]$  spectrometrically from the graph plotted between absorbance and wavelengths at different pH.  

$$pK_a = pH + \log [HA] / [A^-]$$
- (vi) **Molecular Weight Determination** – UV Spectroscopy is used in determination of molecular weight of the compound can be converted into a suitable derivative which shows an absorption band in its spectrum for example molecular weight of amine is determined by converting it into picrate. The concentration of amine picrate can be determined by using the formula -

$$C = \frac{\log(I_0 / I_1)}{\epsilon_{\max} \times L}$$

- (vii) **Study of Tautomeric Equilibria** – UV spectroscopy can be used to determine the percentage of keto and enol forms present in compounds such as ethyl acetyl acetate by measuring the strength of the respective absorption bands.
- (viii) **Determination of Calcium in Blood Serum** – Calcium in blood can be indirectly determined by converting the calcium present in 1 ml of serum as its oxalate, redissolving it into sulphuric acid and treating it with dilute ceric sulphate. The absorption of the excess ceric ion is measured at 315 nm. The amount of calcium in the blood serum can thus be indirectly calculated.
- (ix) **Determination of Ozone in Environment** – The ozone concentration present in (Smog.) smoke fog in environment can be calculated by measuring its absorption at 260 nm.
- (x) **Detection of functional groups**- UV spectroscopy is used to detect the presence or absence of chromophore in the compound. This technique is not useful for the detection of chromophore in complex compounds. The absence of a band at a particular band can be seen as an evidence for the absence of a particular group. If the spectrum of a compound comes out to be transparent above 200 nm then it confirms the absence of – a) Conjugation b) A carbonyl group c) Benzene or aromatic compound d) Bromo or iodo atoms.
- (xi) **Identification of an unknown compound**- An unknown compound can be identified with the help of UV spectroscopy. The spectrum of unknown compound is compared with the spectrum of a reference compound and if both the spectra coincide then it confirms the identification of the unknown substance.
- (xii) **Determination of configurations of geometrical isomers**- It is observed that cis-alkenes absorb at different wavelength than the trans-alkenes. The two isomers can be distinguished with each other when one of the isomers has non-coplanar structure due to steric hindrances. The cis-isomer suffers distortion and absorbs at lower wavelength as compared to trans-isomer.

#### Lambert's and Beer's Law

“When a beam of light is allowed to pass through a transparent medium, the rate of decrease of intensity with the thickness of medium is directly proportional to the intensity of light.”

**Mathematically**, the Lambert's law may be expressed as follows.

$$-dl / dt \propto I$$

$$-dl / dt = KI \dots\dots\dots (1)$$

**Where** I = intensity of incident light

t = thickness of the medium

K= proportionality constant

**Beer's law may be stated as follows:**

“Intensity of incident light decreases exponentially as the concentration of absorbing medium increases arithmetically.”

The above sentence is very similar to Lambert's law. So,

$$I_t = I_0 e^{-k' c}$$

$$I_t = I_0 10^{-0.4343 K' c}$$

$$I_t = I_0 10^{K' c} \dots\dots\dots (4)$$

**Where** k' and K'= proportionality constants

c = concentration

By combining equation (3) and (4), we get,

$$I_t = I_0 10^{-act}$$

$$I_0 / I_t = 10^{act}$$

Where, K and K' = a or ε

c = concentration

t or b = thickness of the medium

$$\log I_0 / I_t = \epsilon bc \dots \dots \dots (5)$$

Where ε = absorptivity, a constant dependent upon the λ of the incident radiation and nature of absorbing material. The value of ε will depend upon the method of expression of concentration.

The ratio  $I_0 / I_t$  is termed as transmittance T, and the ratio  $\log I_0 / I_t$  is termed as absorbance A. formerly, absorbance was termed as optical density D or extinction coefficient E. the ratio  $I_0 / I_t$  is termed as opacity. Thus,

$$A = \log I_0 / I_t \dots \dots \dots (6)$$

From equation (5) and (6),

$$A = \epsilon bc \dots \dots \dots (7)$$

Thus, absorbance is the product of absorptivity, optical path length and the concentration of the solution.

Limitations:

The linearity of the Beer-Lambert law is limited by chemical and instrumental factors. Causes of nonlinearity include:

- deviations in absorptivity coefficients at **high concentrations (>0.01M)** due to electrostatic interactions between molecules in close proximity
- **scattering of light due to particulates** in the sample
- **fluorescence or phosphorescence** of the sample
- changes in refractive index at high analyte concentration
- shifts in chemical equilibria as a function of concentration
- non-monochromatic radiation, deviations can be minimized by using a relatively flat part of the absorption spectrum such as the maximum of an absorption band
- stray light

## INTRODUCTION

Infrared spectroscopy is one of the most powerful analytical techniques, which provides a spectrum containing a large number of absorption bands from which a wealth of information can be derived about the structure of an organic compound. The absorption of infrared radiation causes the various bands in a molecule to stretch and bend with respect to one another. After absorption of IR radiations, the molecules of chemical substance vibrate at different frequency of vibrations.

When infrared light is passed through the sample, the vibration and the rotational energies of the molecules are increased. Two types of fundamental vibrations are

### (1) Stretching vibrations (2) Bending vibrations

**(1) Stretching vibrations:** In stretching vibrations the atoms move along the bond axis. As a result, the bond length increases or decreases but bond angle remains unchanged. There are two types of stretching vibrations:

**(1) Symmetric stretching:** In this type the atoms of the molecule move in the same direction.

**(2) Asymmetric stretching:** In this type the atoms of the molecule move in the opposite direction.

**(2) Bending or Deformation vibrations:** Bending vibrations involves a change in the bond angle whereas the bond length remains unchanged.

There are two types of bending vibrations:

**(A) In – plane bending vibrations:**

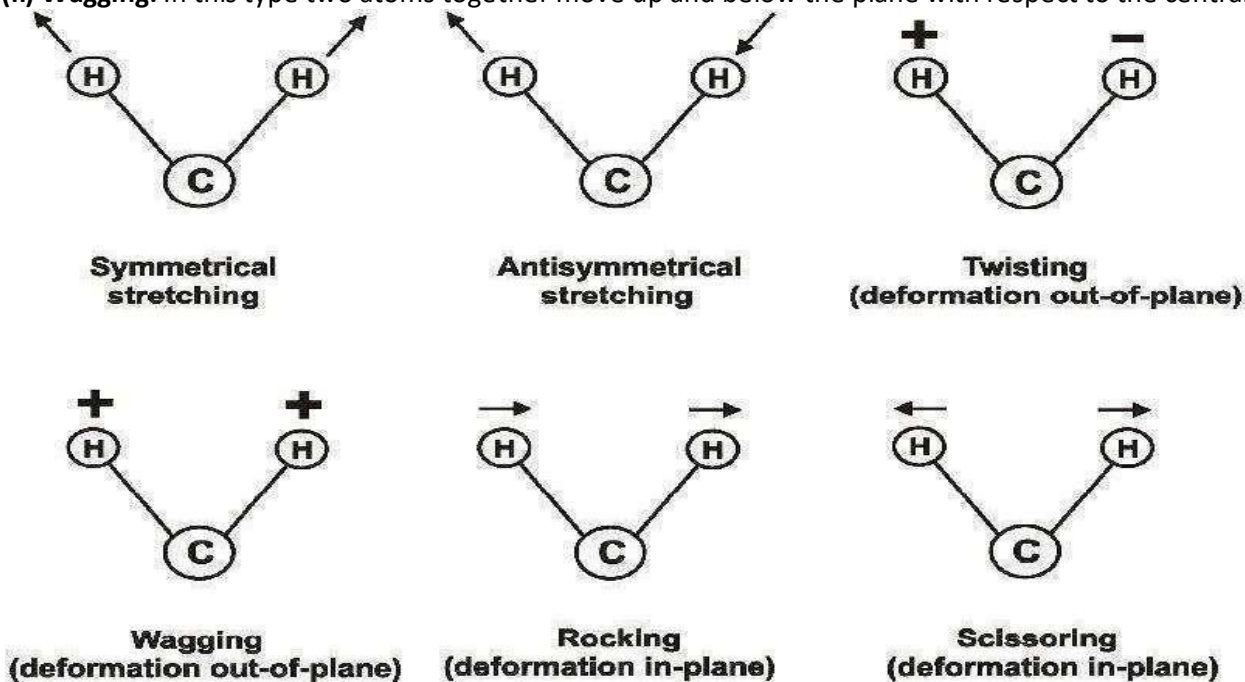
(i) **Scissoring:** In this type, the atoms move away and come close to each other in the same plane just like the blades of a scissor.

(ii) **Rocking:** In this type the movement of atoms takes place in the same direction.

**(B) Out-of-plane bending vibrations:**

(i) **Twisting:** In this type one atom moves up and the other moves down the plane with respect to the central atom.

(ii) **Wagging:** In this type two atoms together move up and below the plane with respect to the central atom.



The number of fundamental vibrational modes of a molecule can be calculated as follows:

A nonlinear molecule containing N atoms has  $(3N-6)$  fundamental vibrational modes. For example water is a nonlinear triatomic molecule, therefore, vibrational degrees of freedom of water =  $(3N-6) = 3 \times 3 - 6 = 3$

So, water is having three fundamental modes of vibration such as symmetrical stretching, asymmetrical stretching and bending vibrations. All the three vibrations are said to be IR active as there is a change in dipole moment during the vibration. So the IR spectrum of water exhibits three absorption bands.

Thus for a vibration to be IR active, there should be a change in dipole moment of the molecule. Homonuclear diatomic molecules like  $O_2$ ,  $N_2$  and  $H_2$  have zero dipole moments and they are IR inactive.

A linear molecule containing N atoms has  $(3N-5)$  fundamental vibrational modes. For example  $CO_2$  is a linear molecule. Therefore, vibrational degrees of freedom of  $CO_2 = (3N-5) = 3 \times 3 - 5 = 4$

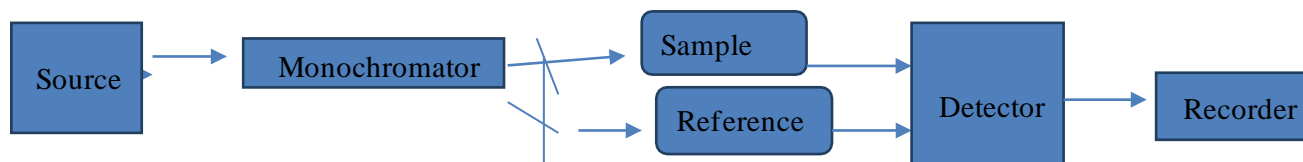
So, Carbon dioxide is having four fundamental modes of vibration such as symmetrical stretching, asymmetrical stretching in plane bending vibrations and out of plane bending vibrations.



### Instrumentation and working of IR spectrometer:

The essential components of an IR spectrometer are as follows:

(1) Radiation source (2) Monochromator (3) Sample holder (4) Detector



- (1) **Radiation source:** The Nernst glower and globar are the most common source of radiation. The Nernst glower consists of a rod of hollow tube about 20 mm long and 1 mm in diameter made by sintering a mixture of oxides of zirconium, thorium and yttrium. Globar is a silicon carbide rod when heated electrically at 1200-2000°C, it glows and produces IR radiations.
- (2) **Monochromator:** The radiation source emits radiations of various frequencies. As the sample absorbs only at certain frequencies, it is therefore necessary to select desired frequencies from the radiation source. This has been achieved by monochromators. Prisms and gratings are commonly used for this purpose.
- (3) **Sample holder:** The sample holder made up of sodium chloride or potassium bromide. It is used to contain sample solutions as well as reference solution because they are transparent to IR radiation.
- (4) **Detector:** The detectors generally convert thermal radiation energy into electrical energy. Thermocouples and bolometer are generally used for this purpose.

**Working of IR spectrometer:** The radiation from source is passed through monochromator.

Light reflected from the monochromator is diffracted to get the light of specific wavelength. The beam of radiation passed out to monochromator is split into two identical beams, out of which one passes through the reference solution and other through the sample solution. If the frequency of vibration of sample molecules falls within the range of the radiation, the molecule may absorb energy of this frequency from the light. Then the intensity of beam coming out of the sample solution is less than that of beam coming out of the reference solution. If  $I$  is the intensity of the sample solution and  $I_0$  that of the reference solution then  $I/I_0$  is called transmittance. A graph is recorded by the instrument which is plot of transmittance versus wave number.

### Applications of IR spectroscopy

1. Identification of functional group and structure elucidation.
2. Identification of substances.
3. Studying the progress of the reaction.
4. Detection of impurities.
5. Quantitative analysis

periodic table can be constructed as follows:

III IV

Mn	Fe	Co	Ni	Cu	Zn
Tc	Ru	Rh	Pd	Ag	Cd
Re	Os	Ir	Pt	Au	Hg

The elements are arranged in rows and columns. Elements with one shell are placed in the first row (ie H and He), Elements with two shells are placed in the second row (Li to Ne) and so on.

In addition, the elements are aligned vertically (in columns) with other elements in different rows, if they share a similar outer-shell electronic configuration. For example, elements with outer-shell configuration  $ns^1$  are all placed in the same column (Li, Na, K, Rb, Cs, Fr).

According to these principles, the periodic table can be constructed as follows:

[illegible]

He is placed in group 0 on this basis, but hydrogen does not behave like any other element and so is placed in a group of its own.

All elements belong to one of four main blocks: the s-block, the p-block, the d-block and the f-block.

**The p-block elements are all those with at least one p-electron in the outer shell.**

**The d-block elements are all those with at least one d-electron and at least one s-electron but no f or p electrons in the outer shell.**

The f-block elements are all those with at least one f-electron and at least one s-electron but no d or p electrons in the outer shell.

I	II													III	IV	V	VI	VII	0		
		H																		He	
Li	Be													B	C	N	O	F	Ne		
Na	Mg													Al	Si	P	S	Cl	Ar		
K	Ca	Sc												Ga	Ge	As	Se	Br	Kr		
Rb	Sr	Y												In	Sn	Sb	Te	I	Xe		
Cs	Ba	La	Ce - Lu											Tl	Pb	Bi	Po	At	Rn		
Fr	Ra	Ac	Th - Lw																		

Elements colored green are in the s-block

Elements colored blue are in the p-block

Elements colored red are in the d-block

Elements colored black are in the f-block

The physical and chemical properties of elements in the Periodic Table show clear patterns related to the position of each element in the Periodic Table. Elements in the same group show similar properties, and properties change gradually on crossing a Period.

As atomic number increases, the properties of the elements show trends which repeat themselves in each Period of the Periodic Table. These trends are known as **Periodic Trends** and the study of these trends is known as **Periodicity**.

### Atomic Radius

The distance from the center of an atom's nucleus to its outermost energy level is its atomic radius. An atom's radius is determined by the size of the electron cloud that surrounds it.

Moving from top to bottom (moving down a group), with each new energy level, the size of the radius increases.

Generally, the radii of atoms decrease in size as you move from left to right on each period. Even though one electron is added to each successive atom (moving left to right on the table), the atomic radius still gets smaller, or "tighter." This happens because of atoms' strong nuclear charge. Each additional proton pulls even tighter to "pull electrons in" closer to the nucleus. Even though the charges are opposite and equal, a proton has almost 2x the attractive power of an electron.

The shell where an electron is added (s, p, d or f) also affects the atomic radius. When electrons are added to the s or p in the outermost shell, the nuclear charge (positive charge from protons in the nucleus) pulls on the outer shell the most.

When electrons are added to a d or f in the inner shell, the outermost electrons have a “shield” from the positive nuclear charge, so they are not as affected as inner electrons.

To summarize:

In general, atomic radius *decreases* from left to right along a period and it *increases* when moving from top to bottom down a group.

# INCREASING ATOMIC RADIUS

INCREASING ATOMIC RADIUS

1  
**H**  
Hydrogen  
(1.00794)

2  
**He**  
Helium  
(4.003)

3 <b>Li</b> <small>Lithium (6.941)</small>	4 <b>Be</b> <small>Beryllium (9.012182)</small>																	5 <b>B</b> <small>Boron (10.811)</small>	6 <b>C</b> <small>Carbon (12.0107)</small>	7 <b>N</b> <small>Nitrogen (14.00643)</small>	8 <b>O</b> <small>Oxygen (15.9994)</small>	9 <b>F</b> <small>Fluorine (18.9984032)</small>	10 <b>Ne</b> <small>Neon (20.1797)</small>												
11 <b>Na</b> <small>Sodium (22.989770)</small>	12 <b>Mg</b> <small>Magnesium (24.304)</small>																	13 <b>Al</b> <small>Aluminum (26.981538)</small>	14 <b>Si</b> <small>Silicon (28.0855)</small>	15 <b>P</b> <small>Phosphorus (30.973761)</small>	16 <b>S</b> <small>Sulfur (32.066)</small>	17 <b>Cl</b> <small>Chlorine (35.4527)</small>	18 <b>Ar</b> <small>Argon (39.948)</small>												
19 <b>K</b> <small>Potassium (39.0983)</small>	20 <b>Ca</b> <small>Calcium (40.078)</small>	21 <b>Sc</b> <small>Scandium (44.955910)</small>	22 <b>Ti</b> <small>Titanium (47.867)</small>	23 <b>V</b> <small>Vanadium (50.9415)</small>	24 <b>Cr</b> <small>Chromium (51.996)</small>	25 <b>Mn</b> <small>Manganese (54.938044)</small>	26 <b>Fe</b> <small>Iron (55.845)</small>	27 <b>Co</b> <small>Cobalt (58.933200)</small>	28 <b>Ni</b> <small>Nickel (58.6934)</small>	29 <b>Cu</b> <small>Copper (63.546)</small>	30 <b>Zn</b> <small>Zinc (65.39)</small>	31 <b>Ga</b> <small>Gallium (69.723)</small>	32 <b>Ge</b> <small>Germanium (72.61)</small>	33 <b>As</b> <small>Arsenic (74.92160)</small>	34 <b>Se</b> <small>Selenium (78.96)</small>	35 <b>Br</b> <small>Bromine (79.904)</small>	36 <b>Kr</b> <small>Krypton (83.80)</small>	37 <b>Rb</b> <small>Rubidium (85.4678)</small>	38 <b>Sr</b> <small>Strontium (87.62)</small>	39 <b>Y</b> <small>Yttrium (88.90585)</small>	40 <b>Zr</b> <small>Zirconium (91.224)</small>	41 <b>Nb</b> <small>Niobium (92.90638)</small>	42 <b>Mo</b> <small>Molybdenum (95.94)</small>	43 <b>Tc</b> <small>Technetium (98)</small>	44 <b>Ru</b> <small>Ruthenium (101.07)</small>	45 <b>Rh</b> <small>Rhodium (102.90550)</small>	46 <b>Pd</b> <small>Palladium (106.42)</small>	47 <b>Ag</b> <small>Silver (107.8682)</small>	48 <b>Cd</b> <small>Cadmium (112.41)</small>	49 <b>In</b> <small>Indium (114.818)</small>	50 <b>Sn</b> <small>Tin (118.710)</small>	51 <b>Sb</b> <small>Antimony (121.760)</small>	52 <b>Te</b> <small>Tellurium (127.60)</small>	53 <b>I</b> <small>Iodine (126.90447)</small>	54 <b>Xe</b> <small>Xenon (131.29)</small>
55 <b>Cs</b> <small>Cesium (132.90545)</small>	56 <b>Ba</b> <small>Barium (137.327)</small>	57 <b>La</b> <small>Lanthanum (138.90547)</small>	58 <b>Hf</b> <small>Hafnium (178.49)</small>	72 <b>Ta</b> <small>Tantalum (180.9479)</small>	73 <b>W</b> <small>Tungsten (183.84)</small>	74 <b>Re</b> <small>Rhenium (186.207)</small>	75 <b>Os</b> <small>Osmium (190.23)</small>	76 <b>Ir</b> <small>Iridium (192.217)</small>	77 <b>Pt</b> <small>Platinum (195.078)</small>	78 <b>Au</b> <small>Gold (196.96655)</small>	79 <b>Hg</b> <small>Mercury (200.59)</small>	80 <b>Tl</b> <small>Thallium (204.3833)</small>	81 <b>Pb</b> <small>Lead (207.2)</small>	82 <b>Bi</b> <small>Bismuth (208.98038)</small>	83 <b>Po</b> <small>Polonium (209)</small>	84 <b>At</b> <small>Astatine (210)</small>	85 <b>Rn</b> <small>Radon (222)</small>																		
87 <b>Fr</b> <small>Francium (223)</small>	88 <b>Ra</b> <small>Radium (226)</small>	89 <b>Ac</b> <small>Actinium (227)</small>	104 <b>Rf</b> <small>Rutherfordium (261)</small>	105 <b>Db</b> <small>Dubnium (262)</small>	106 <b>Sg</b> <small>Seaborgium (263)</small>	107 <b>Bh</b> <small>Bohrium (264)</small>	108 <b>Hs</b> <small>Hassium (265)</small>	109 <b>Mt</b> <small>Meitnerium (266)</small>	110 <b>Ds</b> <small>Darmstadtium (271)</small>	111 <b>Rg</b> <small>Roentgenium (272)</small>	112 <b>Cn</b> <small>Copernicium (277)</small>	113 <b>Nh</b> <small>Nihonium (284)</small>	114 <b>Fl</b> <small>Flerovium (289)</small>	115 <b>Mc</b> <small>Moscovium (288)</small>	116 <b>Lv</b> <small>Livermorium (293)</small>	117 <b>Ts</b> <small>Tennessine (289)</small>	118 <b>Og</b> <small>Oganesson (294)</small>																		

## Forming Ions

An ion is an atom that has lost or gained electrons.

An atom that loses electrons is positively charged and is called a cation.

An atom that gains extra electrons is negatively charged and is called an anion.

The atomic radius of a cation is smaller than the parent atom's radius, because they have fewer electrons to pull against the positive nuclear charge. With fewer electrons, the positive nuclear charge pulls the remaining electrons tighter, making a smaller atomic radius.

The atomic radius of anions is increased compared to the parent atom. Excess electrons help shield other electrons from the positive nuclear charge. They also act to repel other electrons, pushing them away; this makes the electron cloud “stretch” to a bigger size.

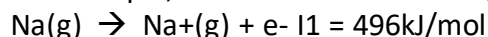
Some atoms easily lose electrons; these are atoms that are unstable until they get rid of some electrons. Other atoms quickly grab extra electrons to become stable.

The ease with which electrons donate or accept electrons (becoming “ionized”) is important for predicting how different elements will react chemically.

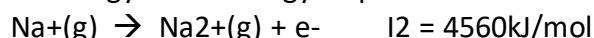
### **Ionization Energy**

“Ionization energy” is the minimum amount of energy required to remove one electron from the ground state (lowest energy state) of the gaseous-state atom.

The first ionization energy is the amount of energy required to remove the first electron from a neutral atom. For example, the first ionization energy of sodium:



Second ionization energy is the energy required to remove the second electron.



The higher the ionization energy, the more difficult it is to remove an electron; in other words, the less likely the atom will give up an electron.

For every atom, ionization energy increases as each electron is removed, because the atom becomes increasingly more positive causing a stronger pull on the remaining electrons.

Ionization energy depends also on atomic radius. When the radius is bigger (and electrons are further away from the nucleus) the ionization energy is lower.

Generally, ionization energy *increases* going left to right along each row and it *decreases* as you go top to bottom down a group. (This is the opposite of the trend for atomic radii)

Factors affecting: -

#### **1. Size of the positive nuclear charge**

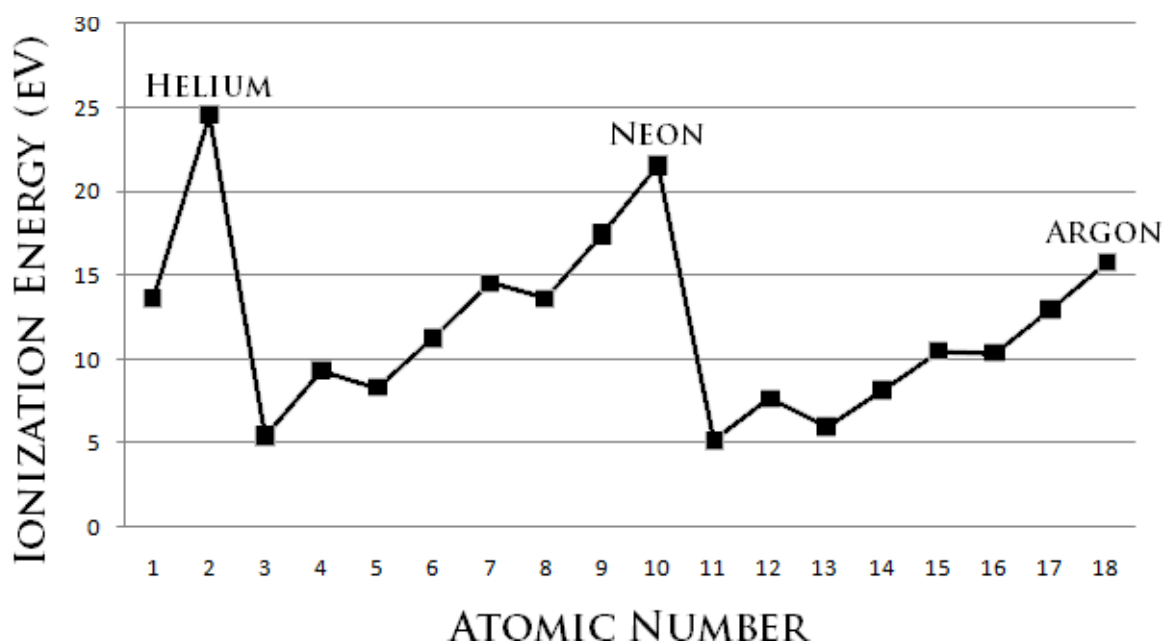
As the nuclear charge increases, its attraction for the outermost electron increases and more energy is required to remove an electron. This means that the ionization energy increases.

#### **2. Size of atom (distance of outermost electron from the nucleus)**

As atomic size increases, the attraction of the positive nucleus for the negative electron decreases and less energy is required to remove an electron. This means that the ionization energy decreases.

#### **3. Screening (shielding) effect of inner shell electrons**

The outermost electron is screened (shielded) from the attraction of the nucleus by the repelling effect of the inner electrons. As shielding increases, the attraction of the positive nucleus for the negative electron decreases and less energy is required to remove an electron. This means that the ionization energy decreases.



### Electron Affinity

Affinity: "a natural liking for, or attraction to a thing."

The energy involved in the addition of an electron to an atom is its electron affinity. This energy is a measure of the attraction (or "affinity") of the atom for the added electron. Usually, when an electron is added (creating an anion), energy is released, so the value is negative.

Example of electron affinity for Chlorine:  $\text{Cl(g)} + \text{e}^- \rightarrow \text{Cl}^-(\text{g}) \quad \Delta E = -349 \text{ J}$

In general, electron affinity *increases* from left to right along a period and *decreases* from top to bottom in a group. (Similar to ionization energy and opposite of atomic radii)

Exception: This is NOT true for noble gases. They do not want extra electrons, because that takes more energy.

Remember: Ionization energy is a measure of the energy required to *remove* an electron while electron affinity is a measure of the energy involved in *adding* an electron.

**Electro negativity:** The tendency for an atom to attract electrons to itself when forming a bond with another element.

The vertical and horizontal trends for electro negativity (and their explanations) are the SAME as those for ionization energy. There is an exception: fluorine, not helium has the highest electro negativity on the periodic table and similarly the halogens are the group with the highest electro negativity, not the noble gases. This is because the noble gases have a full outer

shell of electrons and do not tend to attract additional electron density. The halogens, on the other hand strongly attract electrons in order to fill their outer shell (remember that they have seven valence electrons, but would be most stable with eight)

- **From left to right across a period of elements, electro negativity increases.** If the valence shell of an atom is less than half full, it requires less energy to lose an electron than to gain one. Conversely, if the valence shell is more than half full, it is easier to pull an electron into the valence shell than to donate one.
- **From top to bottom down a group, electro negativity decreases.** This is because atomic number increases down a group, and thus there is an increased distance between the valence electrons and nucleus, or a greater atomic radius.
- **Important exceptions of the above rules include the noble gases, lanthanides, and actinides.** The noble gases possess a complete valence shell and do not usually attract electrons. The lanthanides and actinides possess more complicated chemistry that does not generally follow any trends. Therefore, noble gases, lanthanides, and actinides do not have electro negativity values.
- **As for the transition metals, although they have electro negativity values, there is little variance among them across the period and up and down a group.** This is because their metallic properties affect their ability to attract electrons as easily as the other elements.

According to these two general trends, the *most electronegative element is fluorine*, with 3.98 Pauling units.

# INCREASING ELECTRONEGATIVITY

1 <b>H</b> Hydrogen (1.00794)																	2 <b>He</b> Helium (4.003)						
3 <b>Li</b> Lithium (6.941)	4 <b>Be</b> Beryllium (9.012182)																	5 <b>B</b> Boron (10.811)	6 <b>C</b> Carbon (12.0107)	7 <b>N</b> Nitrogen (14.0064)	8 <b>O</b> Oxygen (15.9994)	9 <b>F</b> Fluorine (18.9984032)	10 <b>Ne</b> Neon (20.1797)
11 <b>Na</b> Sodium (22.989770)	12 <b>Mg</b> Magnesium (24.3050)																	13 <b>Al</b> Aluminum (26.981538)	14 <b>Si</b> Silicon (28.0855)	15 <b>P</b> Phosphorus (30.973761)	16 <b>S</b> Sulfur (32.066)	17 <b>Cl</b> Chlorine (35.4527)	18 <b>Ar</b> Argon (39.948)
19 <b>K</b> Potassium (39.0983)	20 <b>Ca</b> Calcium (40.078)	21 <b>Sc</b> Scandium (44.955910)	22 <b>Ti</b> Titanium (47.867)	23 <b>V</b> Vanadium (50.9415)	24 <b>Cr</b> Chromium (51.9961)	25 <b>Mn</b> Manganese (54.938049)	26 <b>Fe</b> Iron (55.845)	27 <b>Co</b> Cobalt (58.933200)	28 <b>Ni</b> Nickel (58.6934)	29 <b>Cu</b> Copper (63.546)	30 <b>Zn</b> Zinc (65.39)	31 <b>Ga</b> Gallium (69.723)	32 <b>Ge</b> Germanium (72.61)	33 <b>As</b> Arsenic (74.92160)	34 <b>Se</b> Selenium (78.96)	35 <b>Br</b> Bromine (79.904)	36 <b>Kr</b> Krypton (83.80)						
37 <b>Rb</b> Rubidium (85.4678)	38 <b>Sr</b> Strontium (87.62)	39 <b>Y</b> Yttrium (88.90585)	40 <b>Zr</b> Zirconium (91.224)	41 <b>Nb</b> Niobium (92.90638)	42 <b>Mo</b> Molybdenum (95.94)	43 <b>Tc</b> Technetium (98)	44 <b>Ru</b> Ruthenium (101.07)	45 <b>Rh</b> Rhodium (102.90550)	46 <b>Pd</b> Palladium (106.42)	47 <b>Ag</b> Silver (107.8682)	48 <b>Cd</b> Cadmium (112.41)	49 <b>In</b> Indium (114.818)	50 <b>Sn</b> Tin (118.710)	51 <b>Sb</b> Antimony (121.760)	52 <b>Te</b> Tellurium (127.60)	53 <b>I</b> Iodine (126.90547)	54 <b>Xe</b> Xenon (131.29)						
55 <b>Cs</b> Cesium (132.90545)	56 <b>Ba</b> Barium (137.327)	57 <b>La</b> Lanthanum (138.9055)	58 <b>Ce</b> Cerium (140.12)	59 <b>Pr</b> Praseodymium (140.90768)	60 <b>Nd</b> Neodymium (144.24)	61 <b>Pm</b> Promethium (144.9126)	62 <b>Sm</b> Samarium (150.36)	63 <b>Eu</b> Europium (151.964)	64 <b>Gd</b> Gadolinium (157.25)	65 <b>Tb</b> Terbium (158.92534)	66 <b>Dy</b> Dysprosium (162.5001)	67 <b>Ho</b> Holmium (164.93032)	68 <b>Er</b> Erbium (167.259)	69 <b>Tm</b> Thulium (168.93032)	70 <b>Yb</b> Ytterbium (173.054)	71 <b>Lu</b> Lutetium (174.967)	72 <b>Hf</b> Hafnium (178.49)						
73 <b>Ta</b> Tantalum (180.9479)	74 <b>W</b> Tungsten (183.84)	75 <b>Re</b> Rhenium (186.207)	76 <b>Os</b> Osmium (190.23)	77 <b>Ir</b> Iridium (192.222)	78 <b>Pt</b> Platinum (195.078)	79 <b>Au</b> Gold (196.96657)	80 <b>Hg</b> Mercury (200.59)	81 <b>Tl</b> Thallium (204.3833)	82 <b>Pb</b> Lead (207.2)	83 <b>Bi</b> Bismuth (208.98038)	84 <b>Po</b> Polonium (209)	85 <b>At</b> Astatine (210)	86 <b>Rn</b> Radon (222)										
87 <b>Fr</b> Francium (223)	88 <b>Ra</b> Radium (226)	89 <b>Ac</b> Actinium (227)	90 <b>Th</b> Thorium (232.0377)	91 <b>Pa</b> Protactinium (231.03688)	92 <b>U</b> Uranium (238.02891)	93 <b>Np</b> Neptunium (237.04817)	94 <b>Pu</b> Plutonium (244.0642)	95 <b>Am</b> Americium (243.0613)	96 <b>Cm</b> Curium (247.0703)	97 <b>Bk</b> Berkelium (247.0703)	98 <b>Cf</b> Californium (251.0833)	99 <b>Es</b> Einsteinium (252.0833)	100 <b>Fm</b> Fermium (257)	101 <b>Md</b> Mendelevium (258)	102 <b>No</b> Nobelium (259)	103 <b>Lr</b> Lawrencium (262)	104 <b>Rf</b> Rutherfordium (261)						
105 <b>Db</b> Dubnium (262)	106 <b>Sg</b> Seaborgium (266)	107 <b>Bh</b> Bohrium (264)	108 <b>Hs</b> Hassium (277)	109 <b>Mt</b> Meitnerium (268)	110 <b>Ds</b> Darmstadtium (271)	111 <b>Rg</b> Roentgenium (272)	112 <b>Cn</b> Copernicium (285)	113 <b>Nh</b> Nihonium (284)	114 <b>Fl</b> Flerovium (289)	115 <b>Mc</b> Moscovium (288)	116 <b>Lv</b> Livermorium (293)	117 <b>Ts</b> Tennessine (289)	118 <b>Og</b> Oganesson (294)										

# INCREASING ELECTRONEGATIVITY

**Figure . Periodic Table showing Electro negativity Trend**



**Effective nuclear charge** – The attractive positive charge of nuclear protons acting on valence electrons.

1. The effective nuclear charge is always less than the total number of protons present in a nucleus due to shielding effect.
2. Effective nuclear charge is behind all other periodic table tendencies.

**Shielding effect** – the lessening of attractive electrostatic charge difference between nuclear protons and valence electrons by partially or fully filled inner shells.

1. Shielding effect increases with the number of inner shells of electrons.
2. Electrons sharing the same shell do not shield one another from the attractive pull of the nucleus.

### Calculating the effective nuclear charge:

An estimate of effective nuclear charge can be obtained from  $Z_{\text{eff}} = Z - S$ , where  $Z_{\text{eff}}$  = effective nuclear charge,  $Z$  = atomic number, and,  $S$  = the screening constant. Consider aluminum:  $[\text{Ne}]3s^23p^1$   $Z = 13$   $S = 10$   $Z_{\text{eff}} = Z - S = 13 - 10 = 3+$

*Don't forget that  $Z_{\text{eff}}$  is only an estimate. Actual shielding effect is always greater than the screening constant  $S$  because core electrons are much closer to the nucleus than are valence electrons.*

### Trends

The periodic table tendency for effective nuclear charge:

1. Increase across a period (due to increasing nuclear charge with no accompanying increase in shielding effect).
2. Decrease down a group (although nuclear charge increases down a group, shielding effect more than counters its effect).

### ELECTRONIC CONFIGURATION

The **electron configuration** is the distribution of electrons of an atom or molecule (or other physical structure) in atomic or molecular orbital. Electronic configurations describe each electron as moving independently in an orbital, in an average field created by all other orbital.

Atomic number	Symbol	Electron configuration	Atomic number	Symbol	Electron configuration	Atomic number	Symbol	Electron configuration
1	H	1s <sup>1</sup>	37	Rb	[Kr]5s <sup>1</sup>	73	Ta	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>3</sup>
2	He	1s <sup>2</sup>	38	Sr	[Kr]5s <sup>2</sup>	74	W	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>4</sup>
3	Li	[He]2s <sup>1</sup>	39	Y	[Kr]5s <sup>2</sup> 4d <sup>1</sup>	75	Re	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>5</sup>
4	Be	[He]2s <sup>2</sup>	40	Zr	[Kr]5s <sup>2</sup> 4d <sup>2</sup>	76	Os	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>6</sup>
5	B	[He]2s <sup>2</sup> 2p <sup>1</sup>	41	Nb	[Kr]5s <sup>1</sup> 4d <sup>4</sup>	77	Ir	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>7</sup>
6	C	[He]2s <sup>2</sup> 2p <sup>2</sup>	42	Mo	[Kr]5s <sup>1</sup> 4d <sup>5</sup>	78	Pt	[Xe]6s <sup>1</sup> 4f <sup>14</sup> 5d <sup>9</sup>
7	N	[He]2s <sup>2</sup> 2p <sup>3</sup>	43	Tc	[Kr]5s <sup>2</sup> 4d <sup>5</sup>	79	Au	[Xe]6s <sup>1</sup> 4f <sup>14</sup> 5d <sup>10</sup>
8	O	[He]2s <sup>2</sup> 2p <sup>4</sup>	44	Ru	[Kr]5s <sup>1</sup> 4d <sup>7</sup>	80	Hg	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup>
9	F	[He]2s <sup>2</sup> 2p <sup>5</sup>	45	Rh	[Kr]5s <sup>1</sup> 4d <sup>8</sup>	81	Tl	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>1</sup>
10	Ne	[He]2s <sup>2</sup> 2p <sup>6</sup>	46	Pd	[Kr]4d <sup>10</sup>	82	Pb	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>2</sup>
11	Na	[Ne]3s <sup>1</sup>	47	Ag	[Kr]5s <sup>1</sup> 4d <sup>10</sup>	83	Bi	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>3</sup>
12	Mg	[Ne]3s <sup>2</sup>	48	Cd	[Kr]5s <sup>2</sup> 4d <sup>10</sup>	84	Po	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>4</sup>
13	Al	[Ne]3s <sup>2</sup> 3p <sup>1</sup>	49	In	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>1</sup>	85	At	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>5</sup>
14	Si	[Ne]3s <sup>2</sup> 3p <sup>2</sup>	50	Sn	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>2</sup>	86	Rn	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>6</sup>
15	P	[Ne]3s <sup>2</sup> 3p <sup>3</sup>	51	Sb	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>3</sup>	87	Fr	[Rn]7s <sup>1</sup>
16	S	[Ne]3s <sup>2</sup> 3p <sup>4</sup>	52	Te	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>4</sup>	88	Ra	[Rn]7s <sup>2</sup>
17	Cl	[Ne]3s <sup>2</sup> 3p <sup>5</sup>	53	I	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>5</sup>	89	Ac	[Rn]7s <sup>2</sup> 6d <sup>1</sup>
18	Ar	[Ne]3s <sup>2</sup> 3p <sup>6</sup>	54	Xe	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>6</sup>	90	Th	[Rn]7s <sup>2</sup> 6d <sup>2</sup>
19	K	[Ar]4s <sup>1</sup>	55	Cs	[Xe]6s <sup>1</sup>	91	Pa	[Rn]7s <sup>2</sup> 5f <sup>6</sup> 6d <sup>1</sup>
20	Ca	[Ar]4s <sup>2</sup>	56	Ba	[Xe]6s <sup>2</sup>	92	U	[Rn]7s <sup>2</sup> 5f <sup>6</sup> 6d <sup>1</sup>
21	Sc	[Ar]4s <sup>2</sup> 3d <sup>1</sup>	57	La	[Xe]6s <sup>2</sup> 5d <sup>1</sup>	93	Np	[Rn]7s <sup>2</sup> 5f <sup>6</sup> 6d <sup>1</sup>
22	Ti	[Ar]4s <sup>2</sup> 3d <sup>2</sup>	58	Ce	[Xe]6s <sup>2</sup> 4f <sup>1</sup> 5d <sup>1</sup>	94	Pu	[Rn]7s <sup>2</sup> 5f <sup>6</sup>
23	V	[Ar]4s <sup>2</sup> 3d <sup>3</sup>	59	Pr	[Xe]6s <sup>2</sup> 4f <sup>3</sup>	95	Am	[Rn]7s <sup>2</sup> 5f <sup>7</sup>
24	Cr	[Ar]4s <sup>1</sup> 3d <sup>5</sup>	60	Nd	[Xe]6s <sup>2</sup> 4f <sup>4</sup>	96	Cm	[Rn]7s <sup>2</sup> 5f <sup>6</sup> 6d <sup>1</sup>
25	Mn	[Ar]4s <sup>2</sup> 3d <sup>5</sup>	61	Pm	[Xe]6s <sup>2</sup> 4f <sup>5</sup>	97	Bk	[Rn]7s <sup>2</sup> 5f <sup>9</sup>
26	Fe	[Ar]4s <sup>2</sup> 3d <sup>6</sup>	62	Sm	[Xe]6s <sup>2</sup> 4f <sup>6</sup>	98	Cf	[Rn]7s <sup>2</sup> 5f <sup>10</sup>
27	Co	[Ar]4s <sup>2</sup> 3d <sup>7</sup>	63	Eu	[Xe]6s <sup>2</sup> 4f <sup>7</sup>	99	Es	[Rn]7s <sup>2</sup> 5f <sup>11</sup>
28	Ni	[Ar]4s <sup>2</sup> 3d <sup>8</sup>	64	Gd	[Xe]6s <sup>2</sup> 4f <sup>7</sup> 5d <sup>1</sup>	100	Fm	[Rn]7s <sup>2</sup> 5f <sup>12</sup>
29	Cu	[Ar]4s <sup>1</sup> 3d <sup>10</sup>	65	Tb	[Xe]6s <sup>2</sup> 4f <sup>9</sup>	101	Md	[Rn]7s <sup>2</sup> 5f <sup>13</sup>
30	Zn	[Ar]4s <sup>2</sup> 3d <sup>10</sup>	66	Dy	[Xe]6s <sup>2</sup> 4f <sup>10</sup>	102	No	[Rn]7s <sup>2</sup> 5f <sup>14</sup>
31	Ga	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>1</sup>	67	Ho	[Xe]6s <sup>2</sup> 4f <sup>11</sup>	103	Lr	[Rn]7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>1</sup>
32	Ge	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>2</sup>	68	Er	[Xe]6s <sup>2</sup> 4f <sup>12</sup>	104	Rf	[Rn]7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>2</sup>
33	As	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>3</sup>	69	Tm	[Xe]6s <sup>2</sup> 4f <sup>13</sup>	105	Db	[Rn]7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>3</sup>
34	Se	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>4</sup>	70	Yb	[Xe]6s <sup>2</sup> 4f <sup>14</sup>	106	Sg	[Rn]7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>4</sup>
35	Br	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>5</sup>	71	Lu	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>1</sup>	107	Bh	[Rn]7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>5</sup>
36	Kr	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>6</sup>	72	Hf	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>2</sup>	108	Hs	[Rn]7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>6</sup>
						109	Mt	[Rn]7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>7</sup>
						110	Ds	[Rn]7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>9</sup>
						111	Rg	[Rn]7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>10</sup>

## CLASSIFICATION OF ELEMENTS AS s , p , d , f block elements

### s block elements :-

The **s-block** is one of four blocks of elements in the periodic table. The element of s- group have a common property. The electron in their most outward electron shell are in the s-orbital. Elements in the s- are in the first two periodic table groups. The elements in group one are called the alkali metals. The elements in group two are called the alkaline earth metals.

### Properties:-

- All of the s- elements are metals (except Hydrogen).
- In general, they are shiny, silvery, good conductors of heat and electricity.
- They lose their valence electrons easily. In fact, they lose their trademark s orbital valence electrons so easily that the s- elements are some of the most reactive elements on the periodic table.
- The elements in group 1, known collectively as the alkali metals (except hydrogen), always lose their one valence electron to make a +1 ion. These metals are characterized by being silvery, very soft, not very dense and having low melting points.
- The elements in group 2, known as the alkaline earth metals (except helium), always lose their two valence electrons to make a +2 ion. Like the alkali metals, the alkaline earth metals are silvery, shiny and relatively soft.
- S- elements are famous for being ingredients in fireworks. The ionic forms of potassium, strontium and barium make appearances in firework displays as the brilliant purples, reds and greens.
- The first element in group one, Lithium, and the first in group two, Beryllium, behave differently to other members of their groups. Their behavior is like the second element of the next group. So lithium is similar to magnesium, and beryllium is similar to aluminum.
- In the periodic table this is known as a 'diagonal relationship'. The diagonal relationship is because of similarities in ionic sizes and charge/radius ratio of the element. The similarity between lithium and magnesium is because of their similar sizes Radii, Li=152pm Mg=160pm

s-Block		d-Block										p-Block						
H													He					
Li	Be											B	C	N	O	F	Ne	
Na	Mg											Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub							
		f-Block																
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			

**p Block elements :** - Elements having a place within the group 13 (i.e. group IIIA) to group 17 (i.e. group VIIA) of the periodic table alongside the group 18 i.e. the zero group elements together frame the p-block of the periodic table.

### Position of P Block Elements in the Periodic Table

In the elements of p-block, the last electron enters the furthest p orbital. They have 3 to 8 electrons in the peripheral shell. Consequently, there are six groups of p-block elements in the periodic table numbering from **13 to 18**.

First group: group IIIA called as **Boron group**

Second group: group IVA called as **Carbon group**.

Third group: group VA called as **Nitrogen group**.

Fourth group: group VIA called as **Chalcogens**.

Fifth group: group VIIA called as **Halogens**.

Sixth group: zero group or group 18 called as **Inert** or **Noble gases group**.

**Characteristics of p block elements:** -

- The general valence shell electronic design of p-block elements is  $ns^2 np^{1-6}$  (with the exception of He).
- The p-block is the main locale of the periodic table to contain metalloids. The nonmetallic character diminishes down the group though there is a progressive increment in non-metallic character from left to right in the p-block. The metallic character tends to increment down every group while it diminishes as we go from left to right over a period.
- The Atomic Density of elements in p-block increments down the group, this is because of increment in the atom's size down the group. Though it diminishes as we move from left to right over the period, this is because of the lessening in nuclear size of all elements in the p-block over the period.
- The Melting and Boiling points slowly increment down the group in light of the fact that the atomic mass increments down the group and thus the intermolecular forces also increase.

The p-block elements demonstrate a variable oxidation state. The oxidation states increments as we move from left towards right in the periodic table. Boron family (Group 13): - + 3 Carbon family (Group 14): - + 4 Nitrogen family (Group 15): - + 5, Oxygen family (Group 16): - + 6, Halogen family (Group 17): - + 7, Noble gases (Group 18): - + 8

**d Block Elements :** -

Transition metals are defined as those elements that have (or readily form) partially filled *d* orbitals. The *d*-block elements in groups 3–11 are transition elements. The *f*-block elements, also called *inner transition metals* (the lanthanides and actinides), also meet this criterion because the *d* orbital is partially occupied before the *f* orbitals.

The *d*-block elements are divided into the **first transition series** (the elements Sc through Cu), the **second transition series** (the elements Y through Ag), and the **third transition series** (the element La and the elements Hf through Au). Actinium, Ac, is the first member of the fourth transition series, which also includes Rf through Rg.

## CHARACTERISTICS

1. **Metallic nature:** As the number of electrons in the outermost shell is very less i.e. All the transition elements are metals. They show the characteristics of metals such as malleability and ductile in nature and form alloys with several other metals. They also serve as good conductors of heat and electricity. The hard and brittle nature of these elements indicates the presence of covalent bond which is due to the presence of unfilled d-orbital. They are said to form covalent bonding as well as the metallic bonding.
2. **Melting and boiling points:** They show very high melting and boiling points. This can be attributed to the presence of strong metallic bonding due to the overlapping of (n-1) d orbital and covalent bonding of the unpaired d orbital electrons. Since Zn, Cd and Hg have completely filled (n-1)d orbital they are not expected to form covalent bonds. Hence, they show comparatively lower melting point than other d-block elements.
3. **Atomic radii:** A great degree of variation is seen in the atomic radii across each transition series. The atomic radii of the d-block elements within a given series decreases with increase in the atomic number. This is due to the increase in the nuclear charge that attracts the electron cloud inwards resulting in decrease in size. However, the decrease a uniform decrease in atomic radius is not observed across a period. The decrease in atomic radii is small compared to the S and P block elements. This is due to the screening effect caused by the electrons of the (n-1)d sub shell on the outermost shell. The atomic radius increases on descending the group. In a given series, the atomic radius decreases to a minimum for the group VIII elements and then it increases towards the end of the series. This increase in radius towards the end of the series is due to the force of repulsion among the added electrons. A close similarity is observed in the radii of the elements of the second and third transition series due to the filling of 4f subshells.
4. **Ionic radii:** The ionic radius is similar to the pattern of atomic radii. Thus, for ions of a given charge the radius decreases slowly with increase in atomic number.
5. **Atomic volume and Densities:** The atomic volume of transition elements is much lower than those of s and p block elements. This is because of the filling of the (n-1)d orbital that cause an increase in the nuclear charge and pulls the electrons inward. This results in decrease in atomic volume. With the decrease in the atomic volume, the atomic density

these elements increases. Osmium is having a maximum density.

6. **Ionization potentials:** Transition elements have high ionization energy due to their small size. Their ionization potentials lie between those of s and p block elements. Thus, they are less electropositive than the s-block elements. Hence, they do not form ionic compounds readily like the alkali and alkaline earth metals. They also have the ability to form covalent compounds.

The ionization potentials of d-block elements increase as we move across each series from left to right. However, the increase is not as much as in case of s and p blocks elements. This is due to the screening effect caused by the new electrons that are added into the (n-1) d subshell.

The second ionization energies of the first transition series also increases with the increase in atomic number. However, Cr and Cu are sufficiently higher than those of their neighbors. This is due to their stable electronic configuration.

7. **Electronic configuration:** The outer electronic configuration remains constant. But, an electron is added to the penultimate shell till the d-sub shell reaches its full capacity. There are three series of elements depending on the n-1 d orbital that is being filled. The orbitals are filled in order of their increasing energy i.e. an orbital of lower energy is filled first. Thus 4s orbital with lesser energy is filled first to its full extent then the 3d orbital with higher energy is filled. The exactly half-filled and completely filled d-orbitals are extra stable.

The electronic configuration of the first series is given as  $1s^2 2s^2 p^6 3s^2 p^6 d^{1-10} 4s^2$

The electronic configuration of the second series is given as  $1s^2 2s^2 p^6 3s^2 p^6 d^{1-10} 4s^2 p^6 d^{1-10} 5s^2$

The electronic configuration of the third series is given as  $1s^2 2s^2 p^6 3s^2 p^6 d^{1-10} 4s^2 p^6 d^{1-10} 5s^2 p^6 d^{1-10} 6s^2$

Transition elements also show variable oxidation states, tendency to form complexes, magnetic nature and other properties.

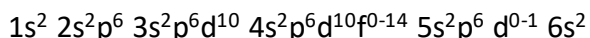
8. **f Block elements :** - These elements have an incomplete f-orbital of the anti-penultimate shell i.e. inner to the penultimate shell in addition to the incomplete d-orbital of the penultimate shell. f-block elements are also termed as inner transition elements as they are transition elements within the transition elements i.e. d-block elements. An f-orbital can accommodate 14 electrons. This means f-block series can be said to include 14 elements. The general electronic configuration of the f-block elements is given as

$(n-2) f^{1-14}, (n-1) s^2 (n-1) p^6 (n-1) d^{10}, ns^2$ . The f-block elements are grouped into two series basing on the nature of the f-orbital of the anti-penultimate shell (4f or 5f) into which the differentiating electron enters.

## General Characteristics:

1. **Electronic Configuration of Lanthanides:** as the 4f and 5d electrons are so close in energy it is not possible to decide whether the electron has entered the 5d or 4f orbital. However, it is considered that the 5d orbital remains vacant and the electrons enter into the 4f orbital except for gadolinium, Gd (Z=64) where the electron enters into the 5d orbital due to the presence of half filled d-orbital. At Ytterbium (z=70) all the 4f orbital's are completely filled and hence, the differentiating electron of the next element that is lutetium (z=71) enters in to the 5d orbital.

2. The complete electronic configuration of Lanthanides can be given as



3. **Oxidation States:** Lanthanides show variable oxidation states but the degree of variability is less compared to the transition elements. The most stable oxidation state of Lanthanides is +3. In addition to the most stable +2 state, Lanthanides also show +2 and +4 oxidation states. These additional oxidations states also show stability due to presence of either half filled or completely filled or empty 4f subshell. It should be noted that the +2 and +4 oxidation states are unstable in aqueous solutions except for  $Ce^{+4}$  salts such as the ceric sulphate which acts as an oxidising agent in volumetric analysis.

4. **Ionic Radii and Lanthanide contraction:** the atomic size decreases with the increase in atomic number as we move across from La to Lu. Thus, among lanthanides, lanthanum has the largest atomic radius and lutetium has the smallest atomic radius. This gradual decrease in the size of an atom is said as lanthanide contraction.

5 **Color:** All lanthanide metals are silver white. The trivalent lanthanide ions are colored both in solid state and in aqueous solution. It should be noted that the color change is seen only in case of cations. The color of a cation depends on the number of unpaired f electrons. Lanthanides with either half-filled or completely filled orbitals are colorless.

- 6 **Oxidation States:** Unlike lanthanides which show the +3 oxidation states, actinides show a variety of oxidation states from +3 to +6. However, +3 and +4 are the principal oxidation states. The +3 oxidation state is the most stable in Ac and all the other elements of the series. The +4 oxidation state is the most stable in Th and Pu. +5 in Pa and Np and +6 is seen in U.



7 **Ionic radius:** In actinides, the ionic radius decreases as we move down the series. This decrease in ionic radius is termed as actinide contraction. This effect is due to poor screening offered by f electrons.

8 **Complex formation:** Unlike lanthanides, they have the tendency to form complexes. Complex formation with ligands such as thio-ethers is also seen.

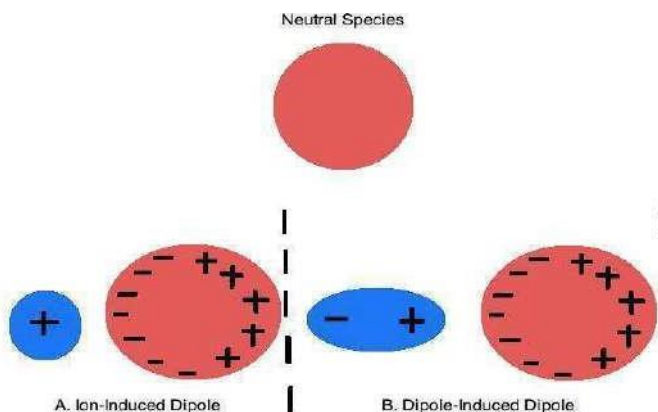
**POLARIZABILITY:** - **Polarizability** is a measure of how easily an electron cloud is distorted by an electric field. Typically the electron cloud will belong to an **atom** or molecule or ion. The electric field could be caused, for example, by an electrode or a nearby cation or anion.

Neutral non polar species have spherically symmetric arrangements of electrons in their electron clouds. When in the presence of an electric field, their electron clouds can be distorted. The ease of this distortion is defined as the **polarizability** of the atom or molecule. The created distortion of the electron cloud causes the originally non polar molecule or atom to acquire a dipole moment. This induced dipole moment is related to the polarizability of the molecule or atom and the strength of the electric field by the following equation:

$$\mu_{\text{ind}} = \alpha E$$

Where

- $E$  denotes the strength of the electric field and
- $\alpha$  is the polarizability constant with units of  $\text{C m}^2\text{V}^{-1}$ .



### Factors that Influence Polarizability

The relationship between polarizability and the factors of electron density, atomic radii, and molecular orientation is as follows:

1. The greater the number of electrons, the less control the nuclear charge has on charge distribution, and thus the increased polarizability of the atom.
2. The greater the distance of electrons from nuclear charge, the less control the nuclear charge has on the charge distribution, and thus the increased polarizability of the atom.
3. Molecular orientation with respect to an electric field can affect polarizability (labeled Orientation-dependent), except for molecules that are: tetrahedral, octahedral or icosahedral (labeled Orientation-independent). This factor is more important for unsaturated molecules that contain areas of electron dense regions, such as 2,4-hexadiene. Greatest polarizability in these molecules is achieved when the electric field is applied parallel to the molecule rather than perpendicular to the molecule.

### **Polarizability Influences Dispersion Forces**

The dispersion force is the weakest intermolecular force. It is an attractive force that arises from surrounding temporary dipole moments in non polar molecules or species. These temporary dipole moments arise when there are instantaneous deviations in the electron clouds of the non polar species. Surrounding molecules are influenced by these temporary dipole moments and a sort of chain reaction results in which subsequent weak, dipole-induced dipole interactions are created. These cumulative dipole-induced dipole interactions create the attractive dispersion forces. Dispersion forces are the forces that make non polar substances condense to liquids and freeze into solids when the temperature is low enough.

### **Polarizability affects dispersion forces in the following ways:**

- As polarizability *increases*, the dispersion forces also become *stronger*. Thus, molecules attract one another more *strongly* and melting and boiling points of covalent substances *increase* with *larger* molecular mass.
- Polarizability also affects dispersion forces through the molecular shape of the affected molecules. Elongated molecules have electrons that are easily moved increasing their polarizability and thus strengthening the dispersion forces. In contrast, small, compact, symmetrical molecules are less polarizable resulting in weaker dispersion forces.