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Engineering Chemistry-II (BS-104)

# Water Treatment

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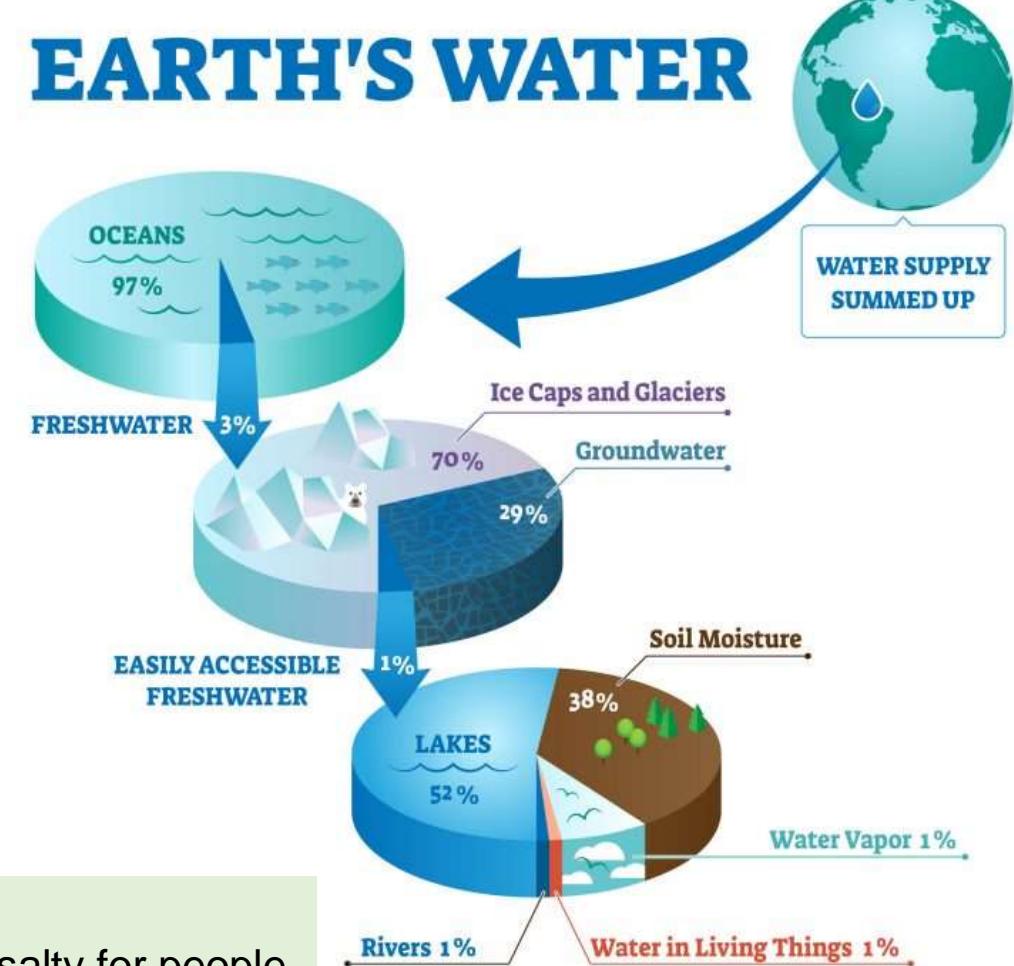


- Water is a vital and precious natural resource
- It is an essential source for the existence of life on the planet earth
- It is present in abundance. The total volume of water on Earth is estimated at 1.386 billion km<sup>3</sup>
- About 70 % of the human body is water
- Even animals and plants require water to complete their daily metabolic activities (Photosynthesis)
- On average, an individual uses 600 to 700 litres in a day
- It is widely used for various purposes such as drinking, washing, bathing, cleaning, cooking, irrigation, and other industrial and domestic uses



Water covers 75% of the earth's surface:

- 97% of this water is in oceans and is too salty for people, animals or plants to use
- 2% is frozen at the north and south poles, in glaciers and on snowy mountain ranges





## Sources of Water:

### A. Surface waters

(i). **Rain water:** purest form of natural water, since it is obtained as a result of evaporation from the surface water. However, it dissolves a considerable amount of industrial gases (like CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>2</sub>, etc.) and suspended solid particles.

(ii). **River water:** Rivers are fed by rain and spring waters. Water from these sources flow over the surface of land, dissolves the soluble minerals of the soil and finally falls in rivers. It thus contains dissolved minerals of the soil such as chlorides, sulphates, bicarbonates of sodium, calcium, magnesium and iron. River water also contains the organic matter, derived from the decomposition of plants, and small particles of sand and rock suspension. Thus, river water contains considerable amounts of dissolved as well as suspended impurities.

(iii). **Lake water:** has a more constant chemical composition. It, usually, contains much lesser amount of dissolved minerals than well water, but quantity of organic matter present in it is quite high.





(iv). **Sea water:** is the **most impure form** of the water. Rivers join sea and throw in the impurities carried by them. Moreover, continuous evaporation of water from the surface of sea makes sea water continuously richer in dissolved impurities. Sea water contains, on an average, about 3.5% of dissolved salts, out of which about 2.6% is sodium chloride. Other salts present are sulphates of sodium; bicarbonates of potassium, magnesium and calcium; bromides of potassium and magnesium and a number of other compounds.

**B. Underground waters:** A part of the rain water, which reaches the surface of the earth, percolates into the earth. As this water journeys downwards, it comes in contact with a number of mineral salts present in the soil and dissolves some of them. Water continues its downwards journey, till it meets a hard rock, when it retreads upwards and it may even come out in the form of 'spring'.

**C. Spring and well water (underground water):** In general, it is clearer in appearance due to the filtering action of the soil, but contain more of dissolved salts. Thus, water from these sources contains more hardness. Usually, underground water is of high organic purity.

Surface water generally, contains suspended matter, which often contains the disease-producing (or pathogenic) bacteria's and hence, are not considered to be safe for human consumption.



## Impurities in Water

### Physical

- Color
- Odor
- Taste
- Turbidity

### Chemical

- Inorganic and organic chemicals
- Pesticides
- Acidity
- Industrial effluents
- Dissolved gases

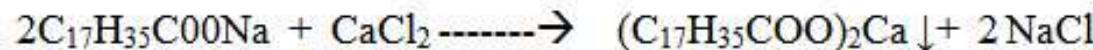
### Biological

- Bacteria
- Algae
- Viruses
- Parasite worms

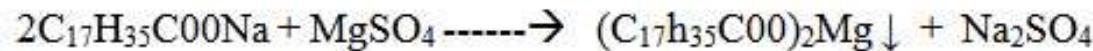


## Hardness of Water

- **Hard water:** Does not produce lather with soap solution => characteristic feature
- Salts like chlorides, bicarbonates and sulfates of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$  make water hard
- On treatment with soap, which is stearic or palmitic acid salts of sodium or potassium causes the formation of white precipitate



Sodium stearate    (Hardness)    Calcium stearate  
(Sodium soap)                         (insoluble)



Magnesium stearate

- **Soft water:** produces lather readily with soap solution





## Types of hardness:

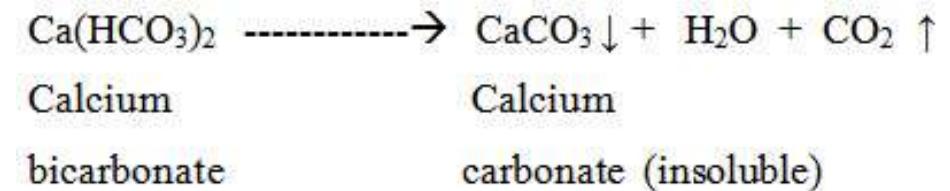
**(1) Temporary or carbonate hardness** is due to the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals and the carbonate of iron.

➤ It is mostly destroyed by mere boiling of water, when bicarbonates are decomposed, yielding insoluble carbonates or hydroxides, which are deposited as a crust at the bottom of vessel.

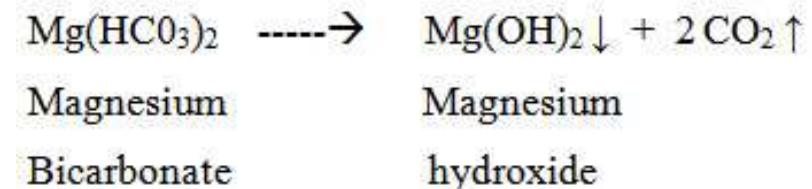
**(2) Permanent or non-carbonate hardness** is due to the presence of chlorides and sulphates of calcium, magnesium, iron and other heavy metals.

➤ Unlike temporary hardness, permanent hardness is not destroyed on boiling.

Heat



Heat



Removal of temporary hardness

Total hardness = temporary hardness + permanent hardness



## Units of hardness:

- Both temporary and permanent hardness are expressed in ppm as  $\text{CaCO}_3$
- Equivalent of  $\text{CaCO}_3$  =

$$\begin{aligned} &= \frac{(\text{Mass of hardness producing substance}) \times (\text{Chemical equivalent of } \text{CaCO}_3)}{\text{Chemical equivalent of hardness producing substance}} \\ &= \frac{\text{Mass of hardness producing substance} \times 50}{\text{Chemical equivalent of hardness producing substance}} \end{aligned}$$

- Hardness is principally expressed in ppm units
- Milligrams per liter (mg/L) are the number of milligrams of  $\text{CaCO}_3$  equivalent hardness present per liter of water

## Other units:

$$1 \text{ Fr. degree of hardness} = \frac{1 \text{ part of hardness}}{10^5 \text{ parts of water}}$$

$$1 \text{ Clark} = \frac{1 \text{ grain of hardness}}{1 \text{ gallon or } 70,000 \text{ grains}} = \frac{1}{7 \times 10^4}$$

$$1 \text{ USA degree of hardness} = \frac{1 \text{ grain}}{1 \text{ USA gallon}} = \frac{1 \text{ grain}}{58,300 \text{ grains}} = \frac{1}{5.83 \times 10^4}$$

$$1 \text{ German degree of hardness} = \frac{1 \text{ grain}}{1 \text{ German grain}} = \frac{1 \text{ grain}}{56,000 \text{ grains}} = \frac{1}{5.6 \times 10^4}$$

### Relation between various units of hardness

1 ppm	= 1 mg/l	= 0.1° Fr	= 0.07° Cl
1 mg/l	= 1 ppm	= 0.1° Fr	= 0.07° Cl
1° Cl	= 1.43° Fr	= 14.3 ppm	= 14.3 mg/l
1° Fr	= 10 ppm	= 10 mg/l	= 0.7° Cl.



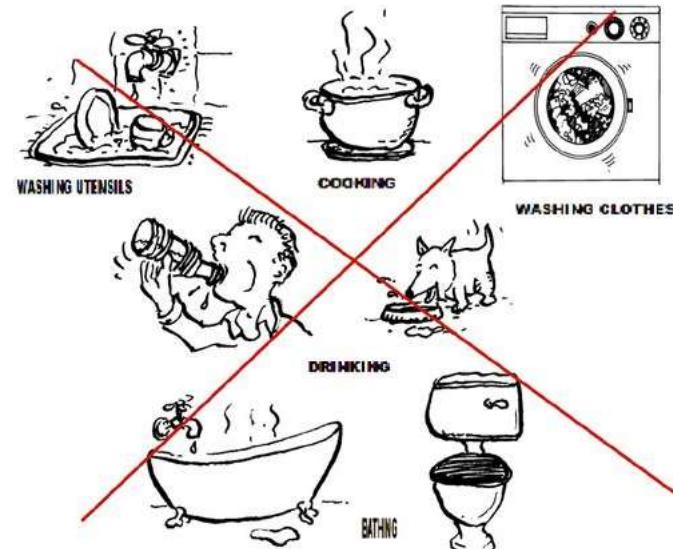
### Disadvantages of Hard Water

(a) *In domestic uses.* For *washing* and *bathing*, hard water creates difficulties, since it does not form lather freely with soap. It also creates sticky precipitates that deposit on bath tub, body, clothes etc. until all the Ca/Mg salts get precipitated. Thus a lot of soap get wasted also.

For *cooking* hard water creates similar difficulties by producing scum on the bottom of the vessels. Due to the presence of hardness producing salts in hard water, boiling point gets elevated and during cooking a lot of fuel is wasted. Pulses etc. do not cook in hard water. Taste of tea, coffee becomes unpleasant. *Drinking* of hard water is also problematic since it affects the digestive system and at the same time the possibility of deposition of calcium oxalate crystals in the urinary tract is alarming.

(b) *In industrial uses.* For *textile industry* and *dyeing industry*, hard water causes the usual problem of deposition of insoluble salts that interfere with the proper dyeing and printing of the fabrics. The stains of iron salts also are undesirable on fabrics. Hard water also hampers the economy by wastage of soap as it does not form good lather.

- For *sugar industry*, the salts responsible for hardness create difficulties in sugar refining and crystallization of sugar and the sugar becomes deliquescent.
- Calcium and magnesium salts also interfere with the smooth and glossy finish of the papers in the *paper industry*. Iron salts interfere with the colour of the paper.
- In *laundry*, hard water causes wastage of costly soap and also interferes with the coloration due to the staining of iron salts.
- The hydration of cement and final hardening of cement are affected by use of hard water in *concrete making*.
- Hard water is not suitable for preparing drug solutions in *pharmaceutical industry*.
- For *steam generation in boilers*, hard water creates many problems like (i) scale formation, (ii) corrosion, (iii) priming and foaming and (iv) caustic embrittlement.



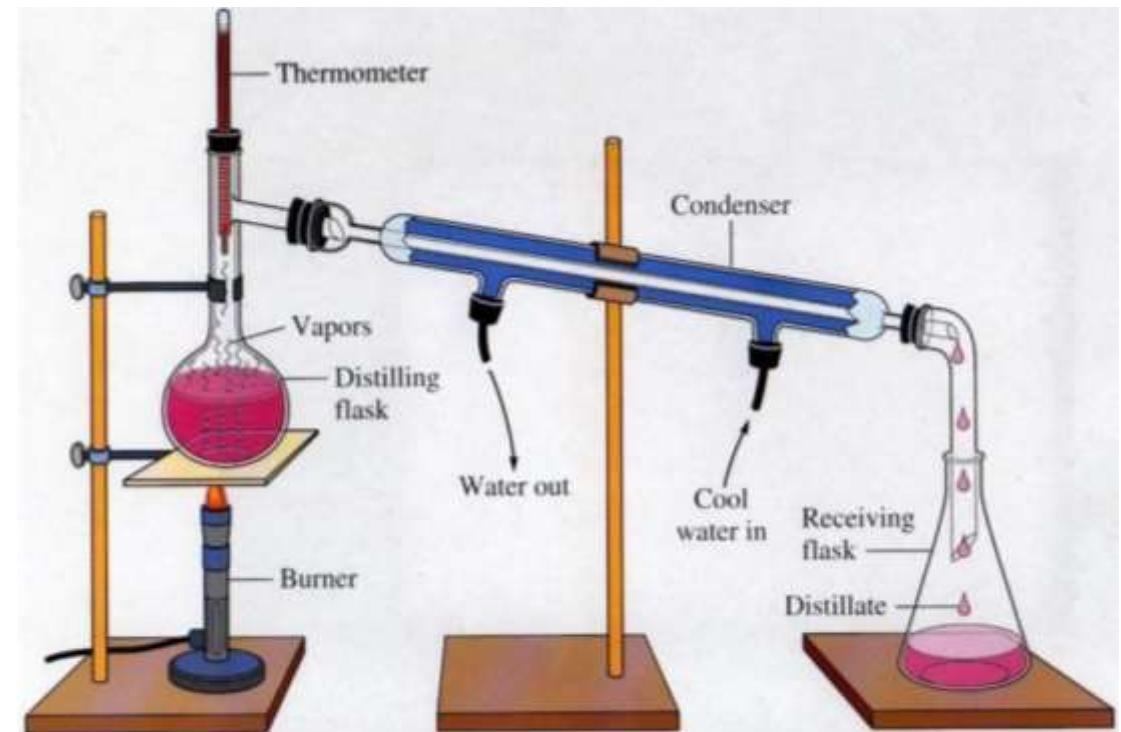
HARD WATER IS NOT  
SUITABLE FOR ALL THESE  
PURPOSES





- **Water treatment:** Any process that improves the quality of water to make it appropriate for a specific end-use
- **Softening of water:** The process of removing hardness producing salts from water i.e. removal of calcium, magnesium, iron salts and other metallic ions
- **Distillation:** widely used non-chemical method for softening of water
  - Relies on evaporation to purify water

- Three important industrial methods for softening of water:
  - I. Lime-soda process
  - II. Ion-exchange or demineralization process
  - III. Zeolite or Permutit process

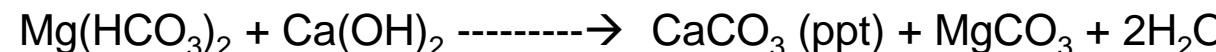


Distillation



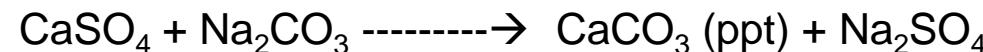
## I. Lime-soda process

- In this method, the soluble calcium and magnesium salts in water are chemically converted into insoluble compounds, by adding calculated amounts of lime ( $\text{Ca}(\text{OH})_2$ ) and soda ( $\text{Na}_2\text{CO}_3$ )
- Extra addition of  $\text{Ca}(\text{OH})_2$  causes hardness, so calculated amounts to be added after determination of actual hardness
- Calcium carbonate ( $\text{CaCO}_3$ ) and Magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ) are precipitated and are filtered off
- Both temporary and permanent hardness can be removed
- For temporary hardness,



⇒ to remove equivalent quantities of Ca and Mg hardness, the amount of lime required is in the ratio of 1:2

- For permanent hardness,



=> Lime is not required for removal of permanent hardness due to Ca-salts, but is necessary for Mg-salts

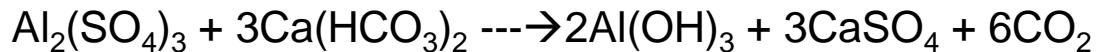


## I. Lime-soda process

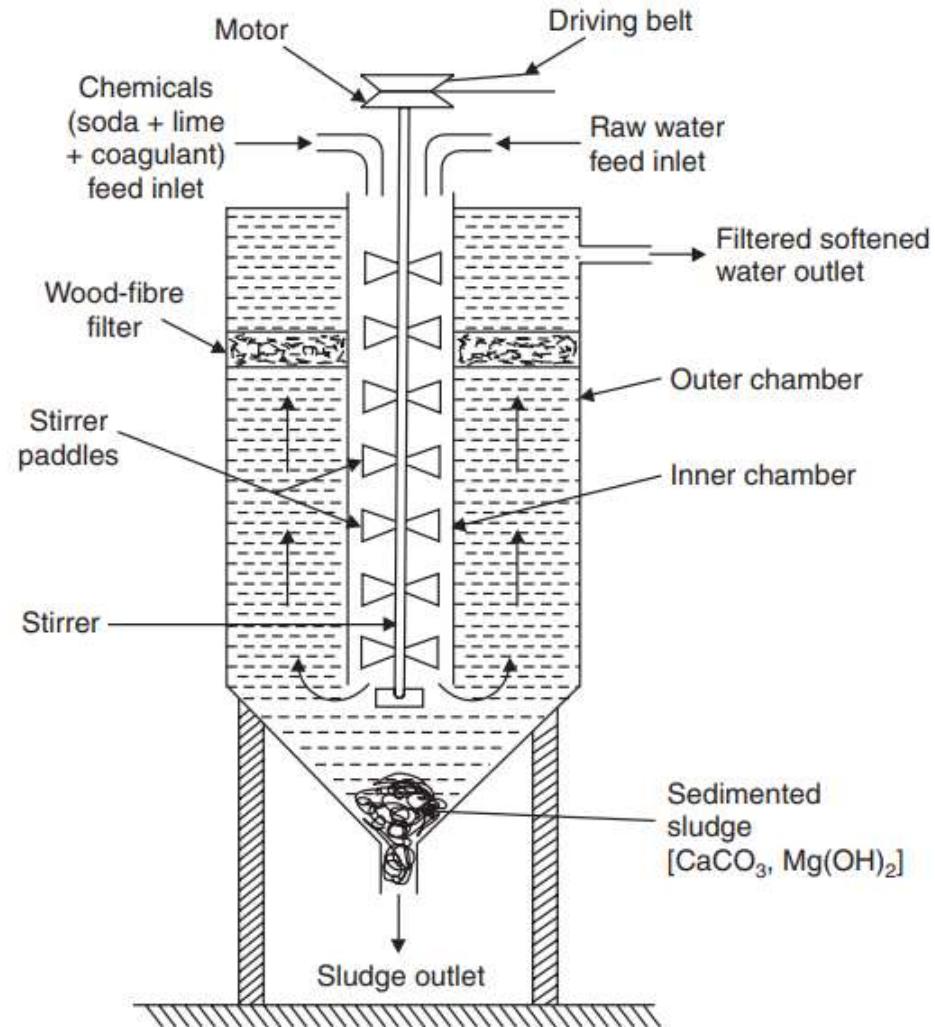
- Types of lime-soda processes:
  - Cold lime-soda process
  - Hot lime-soda process

### a) Cold lime-soda process:

- Calculated quantity of chemicals (lime and soda) is mixed with water at room temperature
- Activated charcoal is acted as activator
- Small amounts of coagulants such as alums (sodium aluminates, aluminum sulfate) are added, which themselves hydrolyze to flocculants and entraps the fine precipitates



- Used for partial softening of municipal water, for softening of cooling water
- It provides water containing a residual hardness of 50 to 60 ppm, which is due to calcium hardness while magnesium hardness is brought down to almost zero

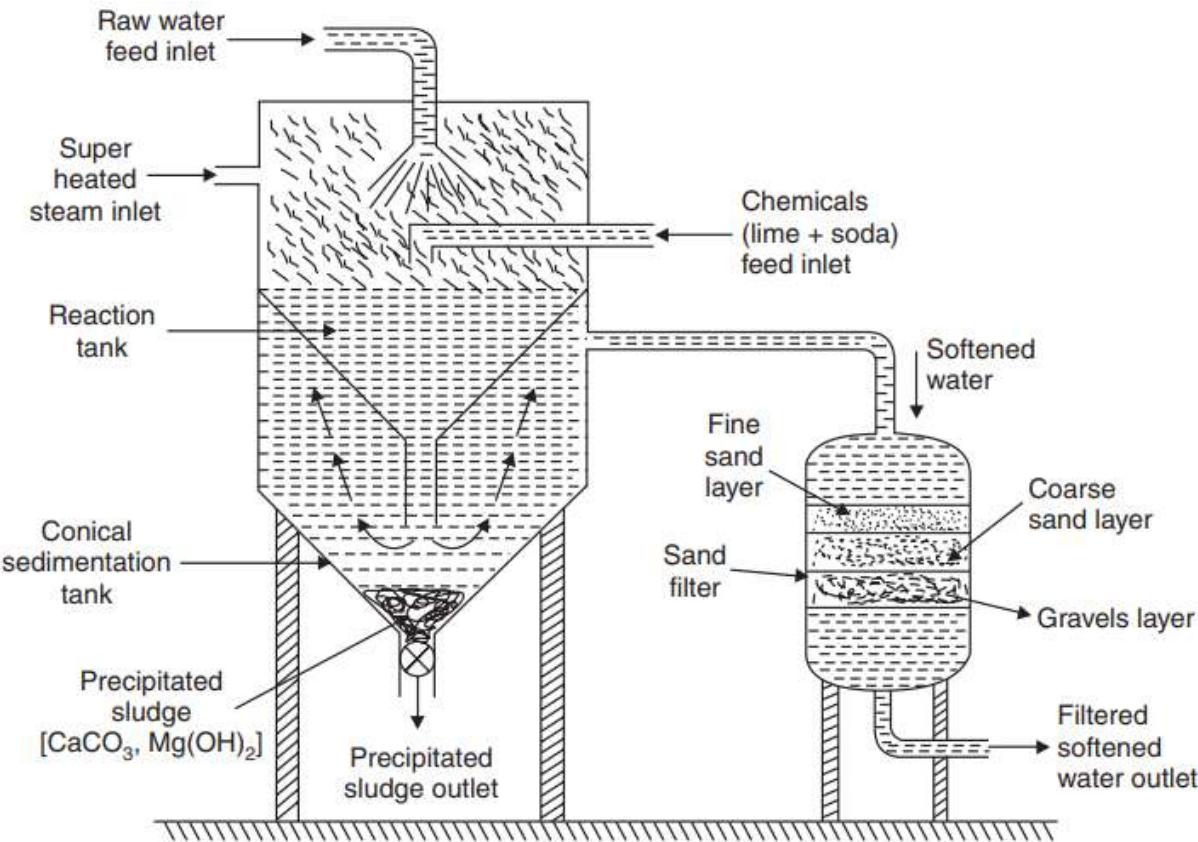


Continuous cold lime-soda softener



**b) Hot lime-soda process:**

- It involves the treatment of water with softening chemicals at a temperature of 80 to 150 °C maintained by exhaust steam
- Hot lime-soda process consists of three parts:
  - i. **Reaction tank:** complete mixing of ingredients
  - ii. **Ionical sedimentation vessel:** sludge settles down
  - iii. **Sand filters:** complete removal of sludge
- Advantages:
  - i. the reaction proceeds faster, the precipitation reaction becomes almost complete
  - ii. the softening capacity of hot process is increased to many fold
  - iii. the precipitate and sludge formed settle down rapidly and hence, no coagulants are needed
  - iv. much of the dissolved gases (such as CO<sub>2</sub> and air) are removed
  - v. viscosity of softened water is lower, so filtration of water becomes much easier. This in-turn increases the filtering capacity of filters.
  - vi. residual hardness is low compared to that in cold process: 15 to 30 ppm.
- Soft water from this process is used for feeding the boilers



Continuous hot lime-soda softener



- **Advantages of Lime-Soda process :**

- (i) It is very economical
- (ii) The process increases the pH value of the treated-water; thereby corrosion of the distribution pipes is reduced
- (iii) Besides the removal of hardness, the quantity of minerals in the water is reduced
- (iv) To certain extent, iron and manganese are also removed from the water
- (v) Due to alkaline nature of treated-water, amount of pathogenic bacteria in water is considerably reduced

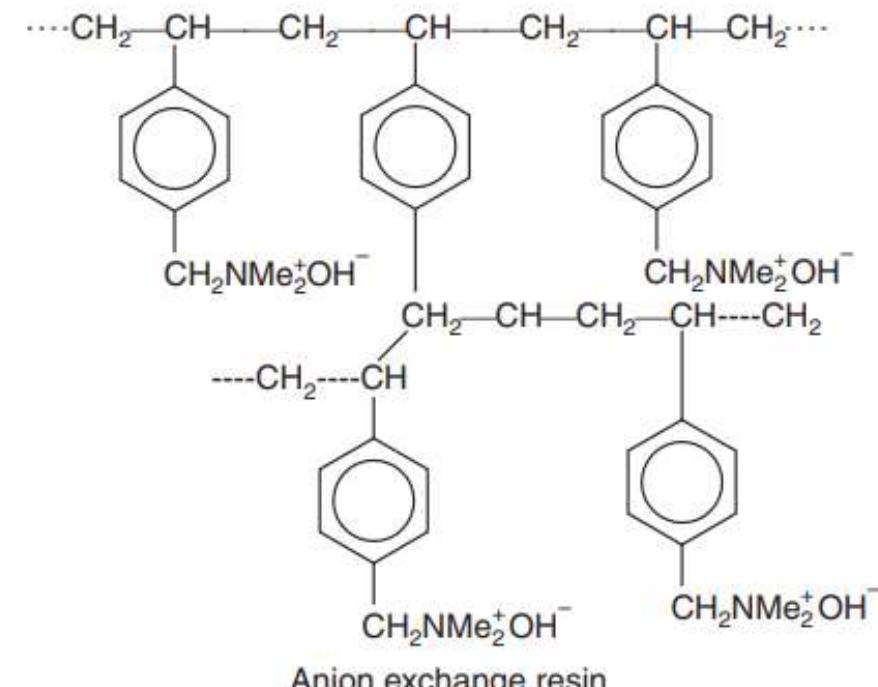
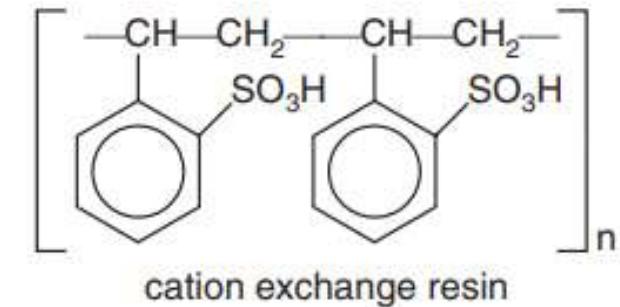
- **Disadvantage of Lime-Soda process:**

- (i) For efficient and economical softening, careful operation and skilled supervision is required
- (ii) Disposal of large amounts of sludge (insoluble precipitate) poses a problem. However, the sludge may be disposed off in raising low-lying areas of the city
- (iii) This can remove hardness only up to 15 ppm, which is not good for high pressure boilers



## II. Ion-exchange or demineralization process

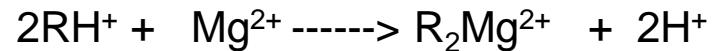
- This process removes almost all the ions present in water
- Ion-exchange resins are insoluble, cross-linked, long chain organic polymers with a microporous structure, and the "functional groups" attached to the chains are responsible for the ion-exchanging properties
- Resins containing acidic functional groups ( $-COOH$ ,  $-SO_3H$  etc.) are capable of exchanging their  $H^+$  ions with other cations; whereas those containing basic functional groups ( $-NH_2$ ,  $-OH$  groups) are capable of exchanging their anions with other anions.
- Classification of ion-exchange resins:
  - Cation exchange resins ( $RH^+$ ):** mainly phenol-sulfonic acid-formaldehyde resin and styrene-divinyl benzene copolymers, which exchange their hydrogen ions with the cations in the water e.g.  $Ca^{2+}$  and  $Mg^{2+}$
  - Anion exchange resins ( $ROH^-$ ):** styrene-divinyl benzene or amine formaldehyde copolymers, which contain amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an integral part of the resin matrix. These, after treatment with dil.  $NaOH$  solution, become capable to exchange their  $OH^-$  with anions in water e.g.  $Cl^-$ ,  $SO_4^{2-}$





- **Process:**

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



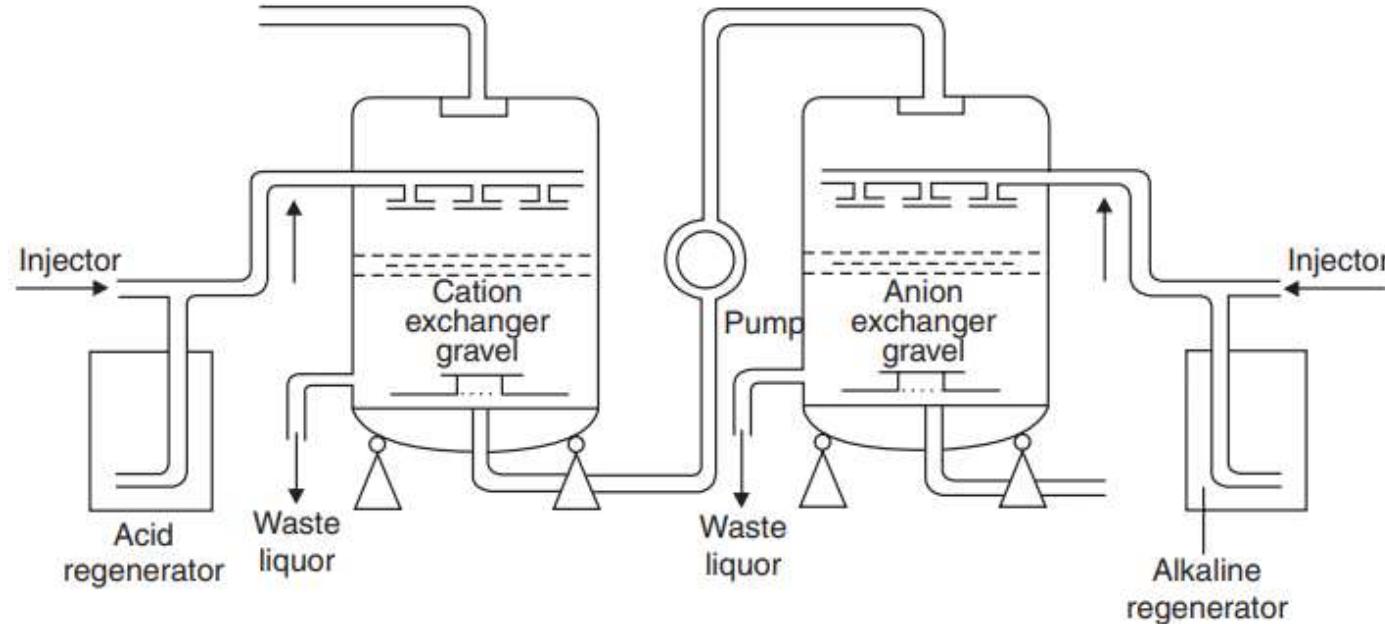
- After cation exchange column, the hard water is passed through anion exchange column, which removes all the anions like  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , etc. present in the water and equivalent amount of  $\text{OH}^-$  ions are released from this column to water.



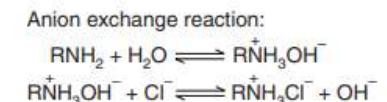
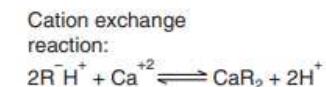
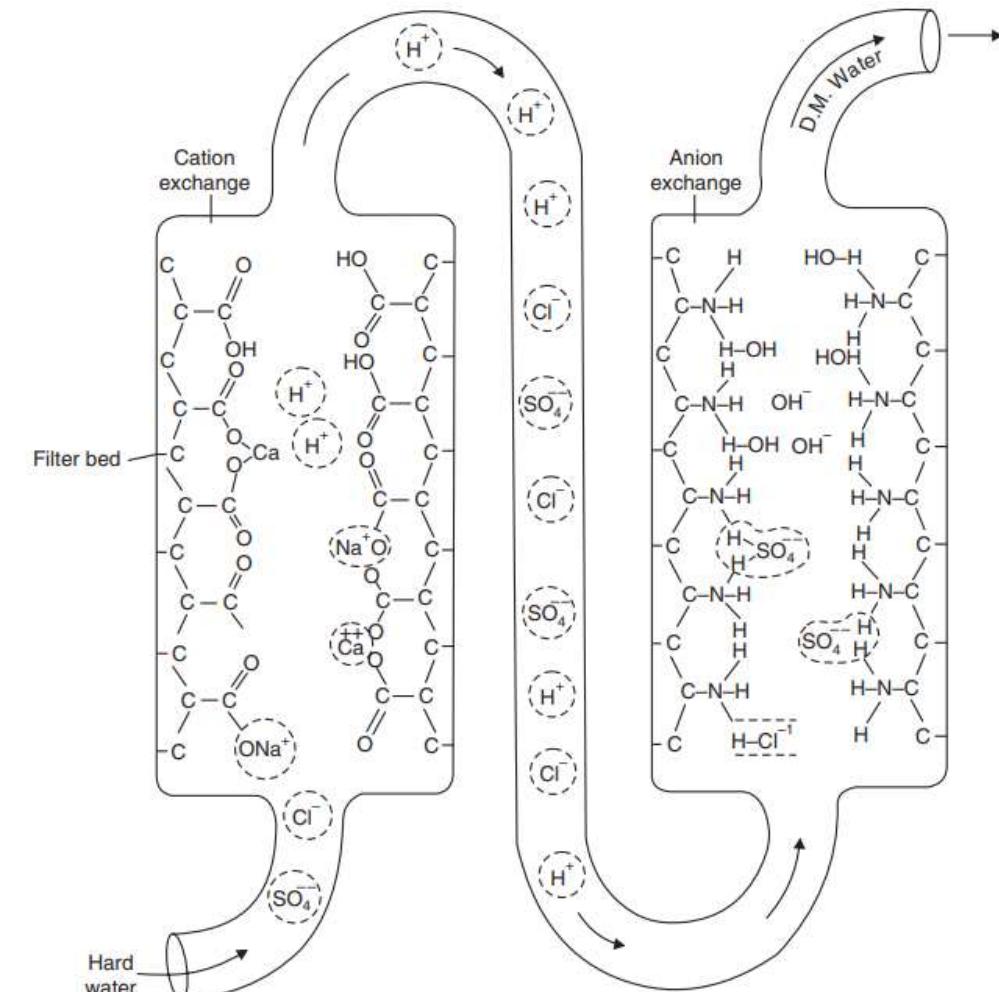
- $\text{H}^+$  and  $\text{OH}^-$  ions (released from cation exchange and anion exchange columns respectively) get combined to produce water molecule  $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$

- Thus, the water coming out from the exchanger is free from cations as well as anions. Ion-free water, is known as deionized or demineralised water.





Demineralization of water



Demineralization of water showing ions exchange



- **Regeneration:** When capacities of cation and anion exchangers to exchange H<sup>+</sup> and OH<sup>-</sup> ions respectively are lost, they are then said to be exhausted. The exhausted cation exchange column is regenerated by passing a solution of dil. HCl or dil. H<sub>2</sub>SO<sub>4</sub>.



- The exhausted anion exchange column is regenerated by passing a solution of dil. NaOH.



- The column is washed with deionised water and washing (which contains Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and Cl<sup>-</sup> or SO<sub>4</sub><sup>2-</sup> ions) are discarded.
- The regenerated ion exchange resins are then used again.

- **Advantages:**

- (i) Easy regeneration
- (ii) The process can be used to soften highly acidic or alkaline waters
- (iii) It produces water of very low hardness (around 2 ppm). So it is very good for treating water for use in high-pressure boilers

- **Disadvantage of ion-exchange process:**

- (i) The equipment is costly and more expensive chemicals are needed.
- (ii) If water contains turbidity, then the output of the process is reduced. The turbidity must be below 10 ppm. If it is more, it has to be removed first by coagulation and then by filtration.



- **BOILER FEED WATER:** One of the chief uses of water in industry is the generation of steam by boilers. In order to generate steam on a constant basis, boiler should be continuously supplied with water, called as feed water.
- **Feed water:** water that undergoes purification or preheating and is then supplied to boilers for hot water and steam production. It is typically found in thermal power plants where it is stored and conditioned in tanks, known as boiler feed water.
- The different impurities in the feed water can be due to dissolved gases, dissolved solids and suspended solids. Each of these impurities affects the boiler system in a different way, and therefore it is must to treat the feed water.
- **Requirements of boiler feed water:**
  - It should have zero hardness
  - It must be free from any dissolved gases like O<sub>2</sub> and CO<sub>2</sub>
  - It should be free from suspended impurities
  - It should be free from dissolved salts and alkalinity
  - It should be free from turbidity and oil
  - It should be free from hardness causing and scale forming constituents like Ca and Mg salts



Boilers

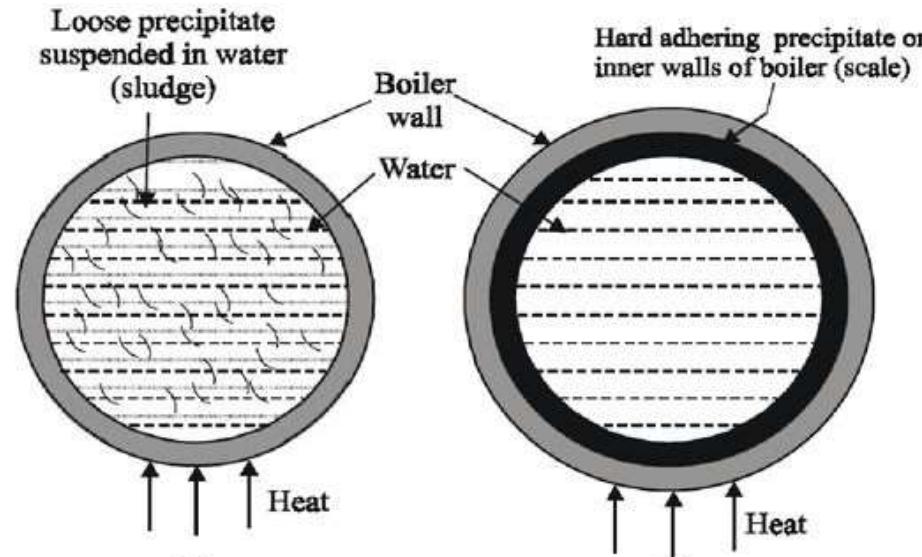


- **Disadvantages of using hard water in boilers:**

- i. Sludge and scale formation
- ii. Caustic embrittlement
- iii. Corrosion
- iv. Priming and foaming

i. **Sludge and scale formation:** On continuous evaporation of water in boilers, the concentration of soluble matter increases progressively leading to the deposition of salts

- If the precipitation takes place in the form of loose and slimy precipitate, it is called **sludge**.
- if the precipitated matter forms a hard, adhering crust/coating on the inner walls of the boiler, it is called **scale**.



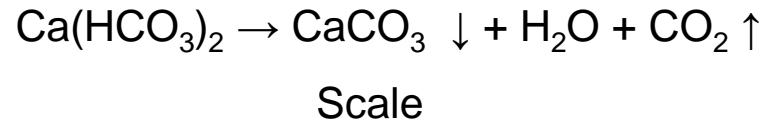


- **Sludge** is a soft, loose and slimy precipitate formed within the comparatively colder portions of the boiler and collects in areas of the system, where the flow rate is slow or at bends. It can be easily removed by scrapping with brush.
- Sludge is formed by substances which have greater solubility in hot water than in cold water, e.g.,  $MgCO_3$ ,  $MgCl_2$ ,  $CaCl_2$ ,  $MgSO_4$ , etc.
- **Disadvantages of sludge formation:**
  - It is poor conductor of heat, so they tend to waste a portion of heat generated.
  - If sludge is formed along with scales, then former gets entrapped in the latter and both get deposited as scales.
  - 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 well softened water
  - ii. By frequently performing 'blow-down operation', i.e., removing the concentrated salty water from time to time so that deposition of sludge is prevented





- **Scale** are hard deposits, which stick very firmly to the inner surfaces of the boiler.
- Scales are difficult to remove, even with the help of hammer and chisel, and therefore are the main source of troubles.
- Scale is formed by substances  $\text{Ca}(\text{HCO}_3)_2$ ,  $\text{CaSO}_4$  and  $\text{Mg}(\text{OH})_2$
- 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.



- ii. The solubility of **calcium sulphate** in water decreases with rise of temperature: solubility of  $\text{CaSO}_4$  is 3,200 ppm at 15 °C and reduces to 55 ppm at 230 °C and 27 ppm at 320 °C. In other words,  $\text{CaSO}_4$  is soluble in cold water, but almost completely insoluble in super-heated water. Consequently,  $\text{CaSO}_4$  gets precipitated as hard scale on the heated portions of the boiler, and is the main cause of scales 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 undergo hydrolysis (at prevailing high temperature inside the boilers) forming magnesium hydroxide precipitate, which forms a soft type of scale e.g.,



iv. Presence of **silica ( $\text{SiO}_2$ )**, even present in small quantities, deposits as calcium silicate ( $\text{CaSiO}_3$ ) and/ or magnesium silicate ( $\text{MgSiO}_3$ ). These deposits stick 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:**

1. **Wastage of fuel:** Scales have a low thermal conductivity, so the rate of heat transfer from boiler to inside water is greatly decreased. In order to provide a steady supply of heat to water, excessive or over heating is carried out and this causes increase in fuel consumption. The wastage depends upon 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%

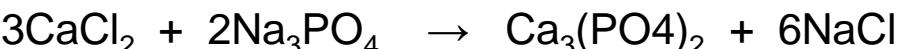
2. **Lowering of boiler safety:** Due to scale formation, over-heating of boiler is to be done in order to maintain a constant supply of steam. The over-heating of the boiler tube makes the boiler material softer and weaker and this causes distortion of boiler tube and makes the boiler unsafe to bear the pressure of the steam, especially in high-pressure boilers.



3. **Decrease in efficiency:** Scales may sometimes deposit in the valves and condensers of the boiler and choke them partially.
  4. **Danger of explosion:** When thick scales crack, due to uneven expansion, the water comes suddenly in contact with over-heated iron plates. This causes formation of a large amount of steam suddenly. So sudden high-pressure is developed, which may even cause explosion of the boiler.
- **Removal of scales:**
    - i. With the help of scraper or piece of wood or wire brush, if they are loosely adhering.
    - ii. By giving thermal shocks (i.e., heating the boiler and then suddenly cooling with cold water), if they are brittle
    - iii. By dissolving them by adding them chemicals, if they are adherent and hard. Thus, calcium carbonate scales can be dissolved by using 5-10% HCl. Calcium sulphate scales can be dissolved by adding EDTA (ethylene diamine tetra acetic acid), with which they form soluble complexes.
    - iv. By frequent blow-down operation, if the scales are loosely adhering. The operation actually involves the removal of very hard water from a tap at the bottom of the boiler and replenishing the water with softened water called 'make-up water'

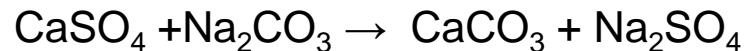


- **Prevention of scale formation:**
  1. **External treatment** includes efficient 'softening of water' (i.e. removing hardness producing constituents of water).
  2. **Internal treatment:** In this process (also called sequestration), an ion is prohibited to exhibit its original character by 'complexing' or converting it into other more soluble salt by adding appropriate reagent. An internal treatment is accomplished by adding a proper chemical to boiler water either : (a) to precipitate the scale forming impurities in the form of sludges, which can be removed by blow-down operation, or (b) to convert them into compounds, which will stay in dissolved form in water and thus do not cause any harm.
- Important internal conditioning/treatment methods are:
  - i. **Colloidal conditioning:** In low-pressure boilers, scale formation can be avoided by adding organic substances like kerosene, tannin, agar-agar (a gel), etc., which get coated over the forming precipitates, thereby yielding non-sticky and loose deposits, which can easily be removed by pre-determined blow-down operations.
  - ii. **Phosphate conditioning:** In high-pressure boilers, scale formation can be avoided by adding sodium phosphate, which reacts with hardness of water forming non-adherent and easily removable, soft sludge of calcium and magnesium phosphates, which can be removed by blow - down operation. Main phosphates used are : (a)  $\text{NaH}_2\text{PO}_4$ , sodium dihydrogen phosphate (acidic); (b)  $\text{Na}_2\text{HPO}_4$ , disodium hydrogen phosphate (weakly alkaline); (c)  $\text{Na}_3\text{PO}_4$ , trisodium phosphate (alkaline).





**iii. Carbonate conditioning :** In low-pressure boilers, scale-formation can be avoided by adding sodium carbonate to boiler water, where  $\text{CaSO}_4$  is converted into calcium carbonate in equilibrium.

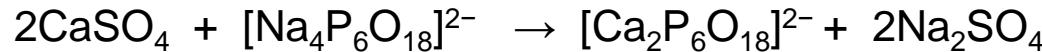


Consequently, deposition of  $\text{CaSO}_4$  as scale does not take place and calcium is precipitated as loose sludge of  $\text{CaCO}_3$ , which can be removed by blow-down operation.

**iv. Calgon conditioning** involves addition of calgon [sodium hexameta phosphate ( $\text{NaPO}_3)_6$ ] to boiler water. It prevents the scale and sludge formation by forming soluble complex compound with  $\text{CaSO}_4$ .

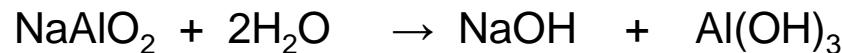


Calgon



Soluble complex ion

**v. Treatment with sodium aluminates ( $\text{NaAlO}_2$ ) :** Sodium aluminates gets hydrolyzed yielding  $\text{NaOH}$  and a gelatinous precipitate of aluminium hydroxide.

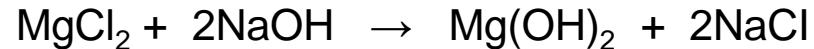


Sodium meta-aluminate

Gelatinous precipitation



The sodium hydroxide, so-formed, precipitates some of the magnesium as Mg(OH)<sub>2</sub>,



The flocculent precipitate of Mg(OH)<sub>2</sub> and Al(OH)<sub>3</sub>, produced inside the boiler, entraps finely suspended and colloidal impurities, including oil drops and silica. The loose precipitate can be removed by pre-determined blow-down operation.

vi. **Electrical conditioning:** Sealed glass bulbs, containing mercury connected to a battery, are set rotating in the boiler. When water boils, mercury bulbs emit electrical discharges, which prevents scale forming particles to adhere /stick together to form scale.

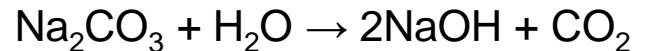
vii. **Radioactive conditioning:** Tablets containing radioactive salts are placed inside the boiler water at a few points. The energy radiations emitted by these salts prevent scale formation.

viii. Complexometric method involves addition of 1.5 % alkaline (pH = 8.5) solution of EDTA to feed-water. The EDTA binds to the scale-forming cations to form stable and soluble complex. As a result, the sludge and scale formation in boiler is prevented. Moreover, this treatment : (1) prevents the deposition of iron oxides in the boiler, (2) reduces the carryover of oxides with steam, and (3) protects the boiler units from corrosion by wet steam (steam containing liquid water).

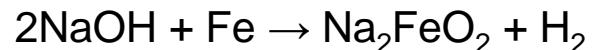


ii. **Caustic embrittlement:** type of boiler corrosion (electrochemical), caused by using highly alkaline water in the boiler i.e., when the concentration of NaOH is above 100 ppm

- **Embrittlement:** Boiler failure due to development of certain types of cracks resulting from excessive stress and chemical attack.
- During softening by lime-soda process, free  $\text{Na}_2\text{CO}_3$  is usually present in small proportion in the softened water, which decomposes to give sodium hydroxide and carbon dioxide at elevated temperatures in high pressure boilers thereby making water basic (caustic)



- The NaOH containing water flows into the minute hair-cracks, always present in the inner side of boiler, by capillary action, where water evaporates and the dissolved caustic soda concentration increases progressively. This caustic soda attacks the surrounding area, thereby dissolving iron of boiler as sodium ferroate ( $\text{Na}_2\text{FeO}_2$ ), which causes embrittlement of boiler parts, particularly stressed parts (like bends, joints, rivets, etc.), causing even failure of the boiler.



Caustic cracking



- **Prevention of caustic embrittlement:**

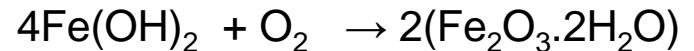
- i. by using sodium phosphate as softening agent, instead of sodium carbonate
- ii. by adding tannin or lignin to boiler water, since these blocks the hair-cracks, thereby preventing infiltration of caustic soda solution in these
- iii. by adding sodium sulphate to boiler water to ensure a weight ratio of  $\text{Na}_2\text{SO}_4 / \text{NaOH} > 2.5$ , whereby the deposition of  $\text{Na}_2\text{SO}_4$  prevents the penetration of NaOH into the cracks and stops caustic embrittlement in high pressure boilers
- iv. use of crack-resisting steel: certain steel containing Al added during manufacture appear to be resistant against caustic cracking
- v. By adjusting the pH of the feed water carefully between 8 and 9



**iii. Corrosion:** Boiler corrosion is decay of boiler material by a chemical or electro-chemical attack by its environment.

- **Main reasons** for boiler corrosion are:

**(1) Dissolved oxygen:** Water usually contains about 8 mL/L of dissolved oxygen at room temperature. Dissolved oxygen in water, in presence of prevailing high temperature, attacks boiler material:



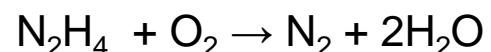
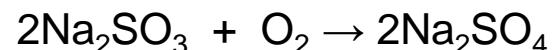
Ferrous hydroxide              Rust



- **Removal of dissolved oxygen :**

Boiler corrosion

- a) By adding calculated quantity of sodium sulphite or hydrazine or sodium sulphide.



Hydrazine





- b) By **mechanical de-aeration**, i.e., water spraying in a perforated plate-fitted tower, heated from sides and connected to vacuum pump. High temperature, low pressure and large exposed surface (provided by perforated plates) reduces the dissolved oxygen in water.

**(2) Dissolved carbon dioxide:** CO<sub>2</sub> is carbonic acid, which has a slow corrosive effect on the boiler material

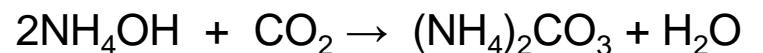


Carbon dioxide is also released inside the boiler, if water used for steam generation it contains bicarbonate, e.g.,

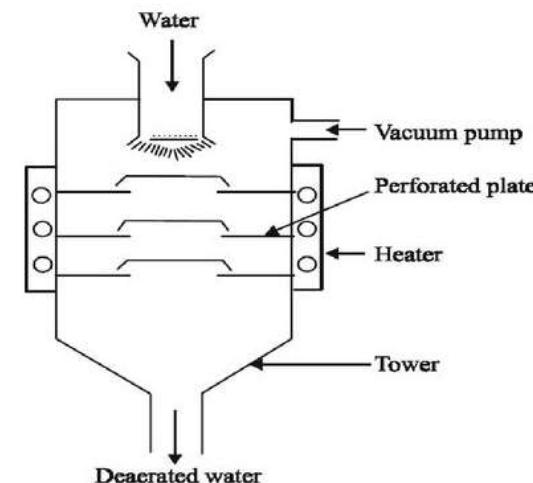
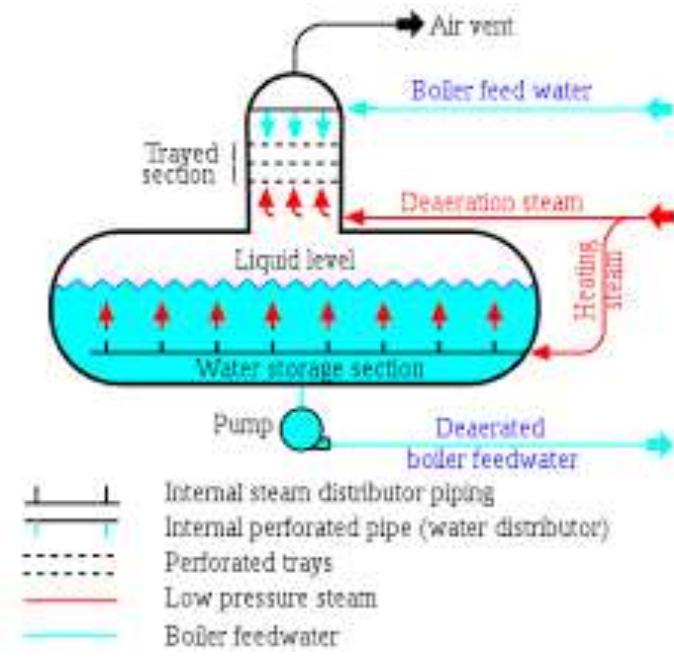


**• Removal of CO<sub>2</sub>:**

- a) By adding calculated quantity of ammonia



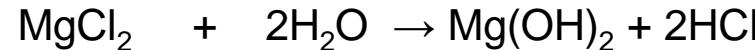
- b) By mechanical de-aeration process  
c) By heating



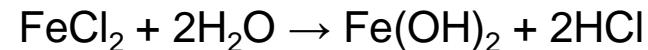
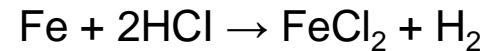
Mechanical de-aeration



**(3) Acids from dissolved salts:** Water containing dissolved magnesium salts liberate acids on hydrolysis, e.g.,



The liberated acid reacts with iron (of the boiler) in chain like reactions producing HCl again and again. Thus

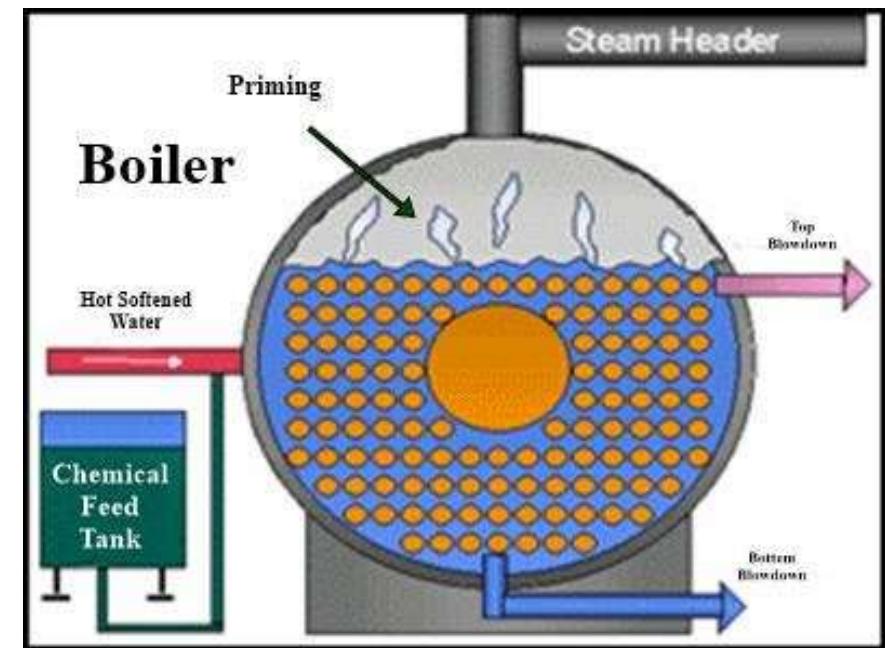


Consequently, presence of even a small amount of  $\text{MgCl}_2$  will cause corrosion of iron to a large extent.



#### iv. Priming and Foaming:

- When a boiler is steaming (i.e., producing steam) rapidly, some particles of the liquid water are carried along-with the steam. This process of 'wet steam' formation is called **priming**.
- **Reasons for priming:**
  - i. the presence of a large amount of dissolved solids
  - ii. high steam velocities
  - iii. sudden boiling
  - iv. improper boiler design
  - v. sudden increase in steam-production rate
- **Priming can be prevented by:**
  - i. fitting mechanical steam purifiers
  - ii. avoiding rapid changing steaming rate
  - iii. maintaining low water levels in boilers
  - iv. efficient softening and filtration of the boiler-feed water.
- Priming can be minimized by placing a series of baffle plates or spiral baffles near the steam outlet to facilitate the condensation of water droplets carried over by the steam.



Priming



- **Foaming** is the production of persistent foam or bubbles in boilers, which do not break easily.
- Foaming is due to presence of substances like oils, grease, organic matter or finely divided solids (which greatly reduce the surface tension of water).
- **Foaming can be prevented by:**
  - i. adding anti-foaming chemicals like castor oil
  - ii. removing oil from boiler water by adding compounds like sodium aluminates.
- Priming and foaming, usually, occur together.
- **They are objectionable because:**
  - (i) dissolved salts in boiler water are carried by the wet steam to super-heater and turbine blades, where they get deposited as water evaporates. This deposit reduces their efficiency.
  - (ii) dissolved salts may enter the parts of other machinery, where steam is being used, thereby decreasing the life of the machinery
  - (iii) actual height of the water column cannot be judged properly, thereby making the maintenance of the boiler pressure becomes difficult.



**Foaming**



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Engineering Chemistry-II (BS-104)

# Fuels

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- **Fuel:** It is a combustible substance, containing carbon as a main constituent, which on proper burning gives large amount of heat, which can be used economically for domestic and industrial purpose.
- Examples: Wood, charcoal, coal, kerosene, petrol, diesel, producer gas, oil gas etc.
- During the process of combustion, carbon, hydrogen, etc., combine with oxygen with a liberation of large amount of heat energy.
- The combustion reaction can be explained as



- In nutshell,



- The calorific value of a fuel depends mainly on the amount of Carbon and Hydrogen
- **Fossil fuels:** Non-renewable energy resources, which are derived from the fossil remains of dead plants and animals e.g., coal, crude oil and natural gas
- **Renewable source of energy:** one which is inexhaustible. Example: Solar energy.
- **Non-renewable source of energy:** one which is exhaustible. Example: Fossil Fuels.





- **Characteristics of good/ ideal fuel:**

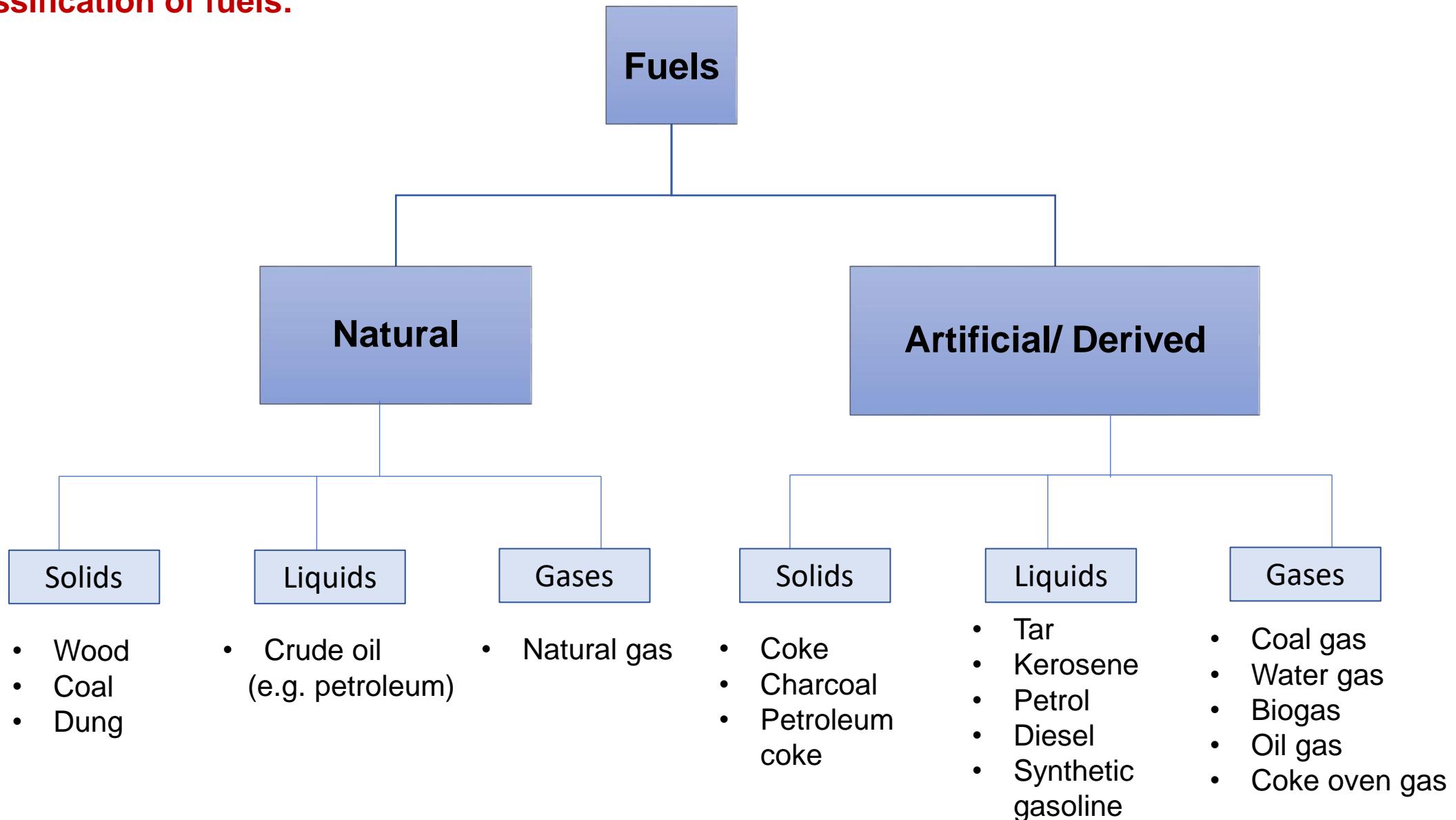
- i. Fuel should have high calorific value
- ii. Must have moderate ignition temperature
- iii. Fuel should have low moisture content
- iv. Should have low contents of non-combustible matter
- v. Available in bulk at low cost
- vi. Should not burn spontaneously
- vii. Must be free from objectionable and harmful gases like CO, SO<sub>x</sub>, H<sub>2</sub>S
- viii. Fuel should burn efficiently, without releasing hazardous pollutants
- ix. Handling, storage and transportation should be easy

- **Units of heat:**

- i. **Calorie:** it is the amount of heat required to raise the temperature of 1 g of water through one degree centigrade.
- ii. **British Thermal Unit (BTU):** it is the amount of heat required to raise the temperature of 1 pound of water to one degree Fahrenheit. 1 B.T.U. = 252 cal = 0.252 kcal; 1 kcal = 3.968 B.T.U.
- iii. **Centigrade Heat Unit (CHU):** it is defined as the amount of heat required to raise the temperature of 1 pound of water to one degree centigrade. 1 kcal = 3.968 B.T.U. = 2.2 C.H.U.



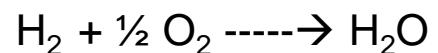
- Classification of fuels:





## Calorific Values

- **Calorific value** of fuel can be defined as the amount of heat evolved when one unit mass or volume of the fuel undergoes completely combustion in presence of oxygen. It is the most important characteristic property of any fuel.
- Different expressions for calorific value:
  - i. **Gross or High Calorific Value (GCV or HCV)**: The total heat generated when a unit quantity of fuel is completely burnt and the products of combustion are cooled to room temperature (25 °C or 77 °F).
  - ii. **Net or Low Calorific Value (NCV or LCV)**: The net heat produced when a unit quantity of fuel is completely burnt and the products of combustion are allowed to escape.
    - ⇒ Therefore net calorific value is always lower than gross calorific value by the amount corresponding to the heat of condensation of water vapors, i.e., 587 kcal/kg
    - ⇒  $LCV = HCV - \text{latent heat of water vapour}$
    - ⇒  $LCV = HCV - \text{mass of hydrogen} \times 9 \times \text{latent heat of steam (587 kcal/kg)}$
    - ⇒ 1 part by weight of  $H_2$  produces 9 parts by weight of  $H_2O$  as follows:



2g	16g	18g
1	8	9



Thus,

$$LCV = HCV - H/100 \times 9 \times 587 \text{ kcal/kg}$$

$$LCV = HCV - 0.09 H \times 587 \text{ kcal/kg}$$

where , H = % of  $H_2$  in the fuel.

- **Units of calorific value:**
- The calorific value is either expressed in either calorie/gram (cal/g) or kilocalorie/kg (kcal/kg) or British thermal unit/lb (B.T.U./lb) in the case of a solid or a liquid fuel
- In case of gaseous fuels, the units are kcal/m<sup>3</sup> or B.T.U./ft<sup>3</sup>



- **Theoretical Calculation of Calorific Value:**

➤ **Dulong's formula:** based on the percentage of the constituents (C, H, O and S) present in the fuel

$$\text{GCV (or) HCV} = \frac{1}{100} (8080C + 34500 [H - O/8] + 2240S) \text{ kcal/kg}$$

where, C, H, O & S represent the % of the corresponding elements in the fuel

- It is based on the assumption that the calorific values of C, H & S are found to be 8080, 34500 and 2240 kcal, when 1 kg of the fuel is burnt completely.
- However, all the oxygen in the fuel is assumed to be present in combination with hydrogen as water (fixed hydrogen) in the ratio H : O as 1 : 8 by weight. So the surplus hydrogen available for combustion is H – O/8.

⇒ Fixed hydrogen = *Mass of oxygen in the fuel / 8*

⇒ Then the amount of hydrogen available for combustion

⇒ = total mass of hydrogen in fuel – fixed hydrogen

⇒ = [H – O/8]

⇒ And **LCV = HCV – H/100 × 9 × 587 kcal/kg**

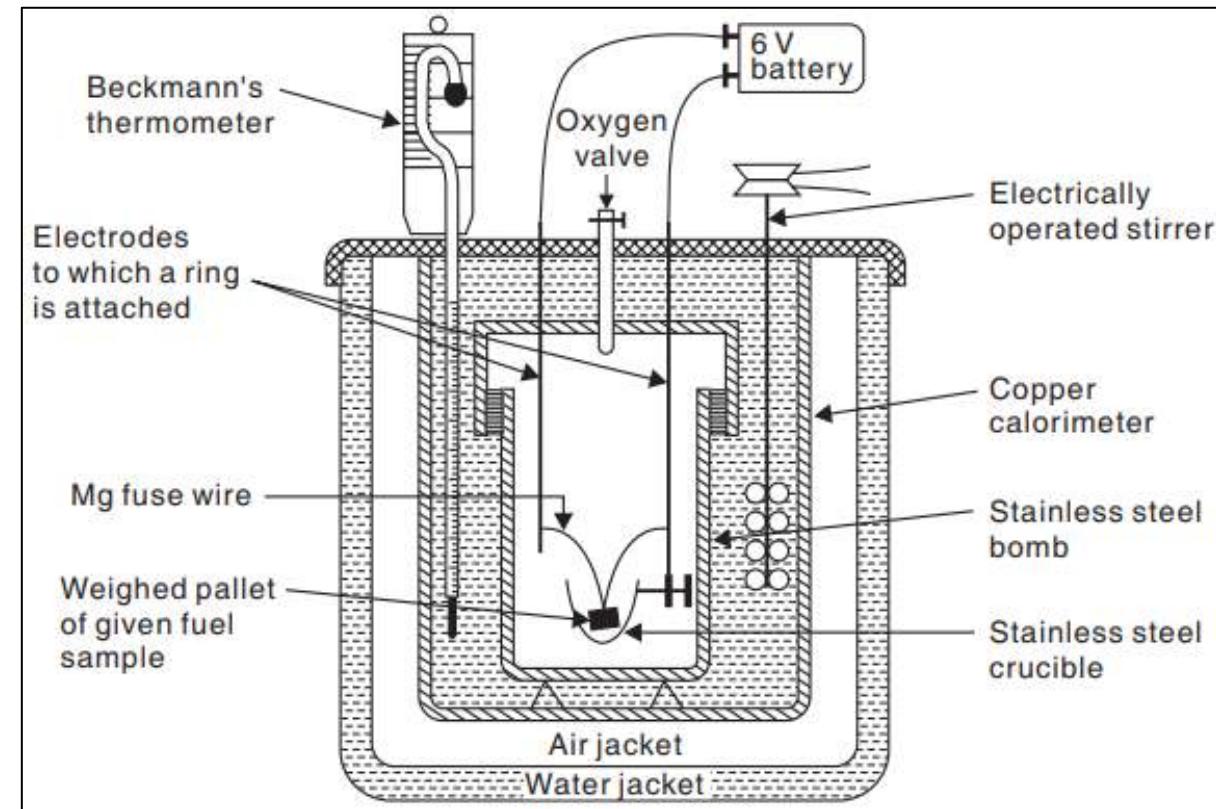


## Determination of calorific value:

I. **Bomb Calorimeter:** The apparatus used to determine the calorific value of solid and liquid fuels.

### Description of the apparatus:

- A bomb calorimeter contains a cylindrical bomb made by stainless steel inside which combustion of the fuel takes place.
- The lid is screwed to the bomb to make it air tight. The lid contains two stainless steel electrodes and an oxygen inlet valve through which oxygen is supplied for combustion. The electrode is attached with a small ring which supports nickel or stainless steel made crucible, where the sample is placed.
- The bomb is taken in a copper calorimeter containing a known weight of water. The copper calorimeter is also surrounded by air and water jacket in order to prevent the heat loss by radiation.
- The copper calorimeter also contains electrically operated stirrer and Beckmann's thermometer (take reading with temperature difference up to  $0.01^{\circ}\text{C}$ ).



**Bomb Calorimeter**



- **Working of the Bomb Calorimeter:**

- In a crucible, a known amount of the fuel is placed in the nickel or stainless steel crucible which is supported by a ring.
- A fine magnesium wire touches the fuel sample, which is already connected to the electrodes.
- The bomb lid lightly screwed and filled with oxygen at about 25 atm pressure, is placed in copper calorimeter containing a known amount of water.
- The electrically operated stirrer is driven and the initial temperature of water ( $T_1$ ) is recorded.
- After that both the electrodes are connected to a 6V battery to complete the circuit. The fuel sample is burnt and heat is liberated, which raises the temperature of water in the calorimeter.
- To maintain the uniform temperature, water is continuously stirred and the final temperature ( $T_2$ ) of water is noted.



- The calorific value of the fuel can now be calculated as follows:

⇒ Mass of fuel (solid or liquid) =  $x$  g

⇒ Mass of water taken in the calorimeter =  $W$  g

⇒ Water equivalent of calorimeter =  $w$  g

⇒ Initial temperature of water in calorimeter =  $T_1$  K

⇒ Final temperature of water in calorimeter =  $T_2$  K

⇒ High or gross calorific value =  $L$

⇒ Heat absorbed by water =  $W(T_2-T_1)$  cal

⇒ Heat absorbed by calorimeter =  $w(T_2-T_1)$  cal

⇒ Heat absorbed by water and calorimeter =  $W(T_2-T_1) + w(T_2-T_1) = (W+w)(T_2-T_1)$  cal

⇒ Heat liberated by fuel =  $x \times L$

⇒ Therefore, heat liberated by fuel = heat absorbed by water and calorimeter

$$\Rightarrow x \times L = (W+w)(T_2-T_1) \text{ cal}$$

$$\Rightarrow L (\text{HCV}) = (W+w)(T_2-T_1) / x \text{ cal/g}$$

The water equivalent of calorimeter can be determined by burning a fuel of known calorific value and using the above equation, e.g. benzoic acid (HCV = 6325 kcal/kg) and naphthalene (HCV = 9688 kcal/kg)



- **Correction factors** used to get more accurate results:
  - i. **Fuse wire correction:** Heat liberated during sparking should be subtracted from the heat liberated
  - ii. **Acid correction:** During ignition S and N present in the fuel get oxidized to the corresponding acids:
$$S + 2H + 2O_2 \longrightarrow H_2SO_4 + \text{Heat}$$
$$2N + H + 3O_2 \longrightarrow 2HNO_3 + \text{Heat}$$
Formation of these acids is exothermic process and hence, should be subtracted from the heat liberated
  - iii. **Cooling correction:** When bomb calorimeter is allowed to cool from maximum temperature to room temperature, some amount of heat is radiated. From the rate of cooling and actual time of cooling, cooling correction is made and is added to the temperature difference.

Therefore,

$$L (\text{HCV}) = (W + w) (T_2 - T_1 + \text{cooling correction}) - (\text{Acid} + \text{fuse correction}) / x \text{ cal/g}$$



## II. Boy's Gas Calorimeter:

The apparatus used to determine the calorific value of gaseous and liquid fuels.

- Known volume of gas is burnt by a uniform rate by a burner.
- Around the burners there is a chimney containing coils, wherein water at a constant rate is passed.
- Separate thermometers measure the incoming and outgoing temperatures of water ( $t_1$  and  $t_2$ ).

Let  $V$  = volume of gas burning.

$W$  = mass of cooling water used in time  $t$ .

$t_1$  and  $t_2$  = Incoming and outgoing water temperatures

$m$  = mass of steam condensed in time  $t$ .

$L$  = HCV.

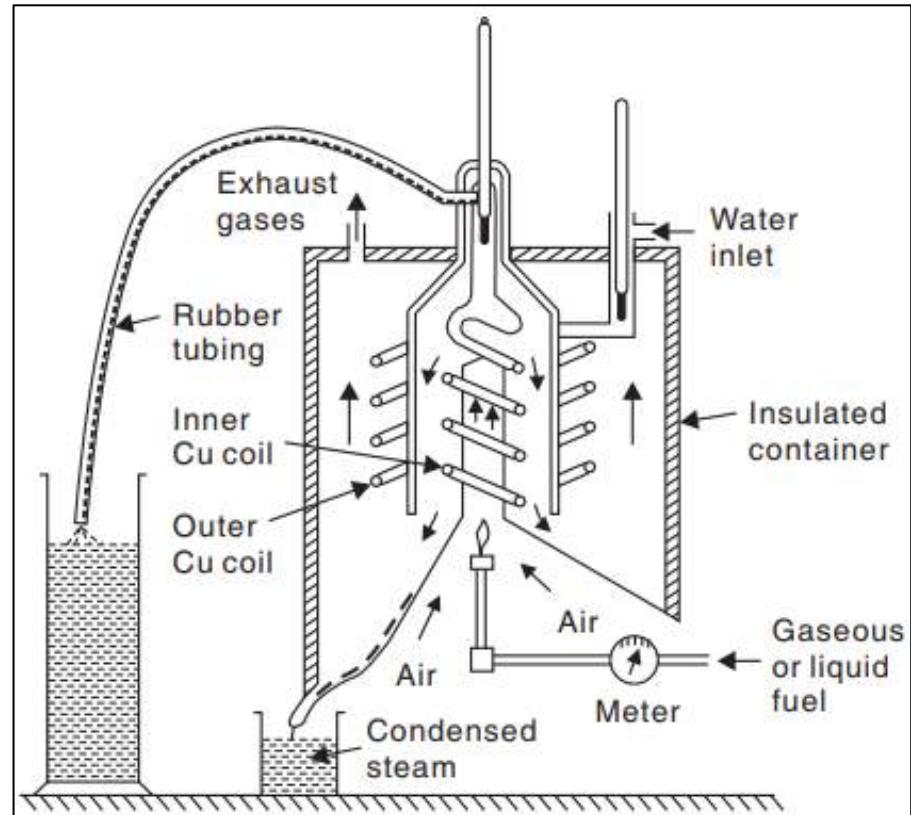
$$\text{We get } L = \frac{W(t_2 - t_1)}{V}$$

Mass of  $H_2O$  condensed per  $m^3$  of gas =  $m/V$  kg

Latent heat of steam per  $m^3$  of gas

$$= \frac{m \times 587}{V} \text{ kcal}$$

$$\therefore NCV = \left[ L - \frac{m \times 587}{V} \right] \text{ kcal/m}^3.$$



Boy's Gas Calorimeter



- **SOLID FUELS:**

- **Examples:** wood, coal, charcoal, coke

- **Advantages of Solid fuels**

1. Handling and transportation of solid fuels is easy
2. Solid fuels are cheap and easily available
3. They have a moderate ignition temperature
4. This type of fuel can be stored conveniently without any risk

- **Disadvantages of solid fuels:**

1. During burning, solid fuels produce a large amount of ash and disposal of ash is a big problem
2. The calorific value of solid fuel is comparatively low
3. Since a lot of air is required for complete combustion, its thermal efficiency is not so high
4. Combustion is a slow process and it cannot be easily controlled
5. A large space is required for storage

Wood



Dung cakes



Coal



Charcoal



## I. WOOD

- Wood is derived from trunks and branches of trees
- It contains lignocellulose- wood pulp mainly consists of  $\alpha$ -cellulose and a very small amount of  $\beta$ -cellulose, resins and proteins
- It contains about 15% moisture after air-drying
- Average composition on moisture free basis: C = 50%, H = 6%, O = 43% and ash = 1%
- Calorific value : 4000-6400 BTU/lb
- Mainly used as domestic fuel

## II. COAL

- Important primary solid fuel, derived from prehistoric plants
- Highly carbonaceous and composed of C, H, N, O and non-combustible inorganic matter
- It is formed as a result of alteration of vegetable matter under some favorable conditions through a continuous process extended over millions of years
- Vegetable matter, under the action of pressure, heat and anaerobic conditions, gets converted into different stages of coal:  
Wood → peat → lignite → sub-bituminous coal → bituminous coal --> anthracite
- The process of conversion of lignite to anthracite is called **coalification (or) metamorphism of coal**.



- Coal is classified on the basis of its rank. The rank of coal denotes its degree of maturity.
- With the progress of coal forming reaction, moisture content and oxygen content reduces and % of carbon increases. Also calorific value increases from peat to bituminous. (see Table)
- Peat is the most immature coal, hence it is lowest in rank whereas anthracite is the most matured coal, and hence it is highest in rank.
- Peat deposits are found in Nilgiri hills, lignites occur in Assam, Kashmir, Rajasthan and Tamil Nadu. Bituminous coal are found in Bihar, Bengal, M.P., Chhattisgarh and Orissa, while anthracites are found in Kashmir and eastern Himalayas.

Fuel	Nature	Calorific value k.cals/kg	Composition %	Uses
Peat	Highly fibrous light brown in colour	4000 - 5400	C = 57 H = 06 O = 35	Domestic fuel, power generation
Lignite	Fibrous, brown coloured coal	6500 - 7100	C = 67 H = 05 O = 26	Manufacture of producer gas & steam
Sub-bituminous coal	Black coloured, homogenous smooth mass,	7000 - 7500	C = 77 H = 05 O = 16	Manufacture of gaseous fuels
Bituminous coal	Black, brittle, burns with yellow smoky flame	8000 - 8500	C = 83 H = 05 O = 10	Power generation, coke making, domestic fuel
Anthracite	Hard & most matured coal, burns without smoke	8500 - 8700	C = 93 H = 03 O = 03	Boiler heating, metallurgical furnace



- **Classification of coal:**

**a) Peat**

1. Peat is the first stage in the formation of coal.
2. Its calorific value is about 4000-5400 kcal/kg.
3. It is an uneconomical fuel due to its high proportion of (80 - 90%) moisture and lower calorific value.
4. It is a brown fibrous mass.

**b) Lignite**

1. Lignite is an intermediate stage in the process of coal formation.
2. Its calorific value is about 6500-7100 kcal/kg.
3. Due to the presence of high volatile content, it burns with long smoky flame.

**c) Bituminous coal**

- Bituminous coal is further sub-classified on the basis of its carbon content into three types as:
  - i) Sub-bituminous coal
  - ii) Bituminous coal
  - iii) semi-bituminous coal

**d) Anthracite**

1. Anthracite is the superior grade of coal.
2. Its volatile, moisture and ash contents are very less.
3. Its calorific value is about 8650 kcal/kg.



- **Analysis of coal:** The quality of coal can be assessed by two analysis:
  - i. Proximate analysis
  - ii. Ultimate analysis

**i. Proximate analysis:**

- It determines the weight percentage of volatile carbonaceous matter, fixed carbon, ash and moisture of the air-dried coal
- This analysis gives the approximate composition of the main constituents of coal
- It is useful in deciding its utilization for a particular industrial use

- a) **Determination of moisture content in coal:** About 1 g of powdered, air dried coal sample is heated in silica crucible placed inside an electric hot air-oven at 105 to 110 °C for one hour. The crucible is then taken out, cooled in desiccators and weighed. Percentage of moisture can be calculated from the loss in weight of the coal sample as:

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

- Lesser the amount of moisture content, better the quality of fuel.



**b) Determination of volatile material in coal:** The moisture free coal sample is taken in a crucible, covered with a lid and placed in muffle furnace (electric furnace) at  $950 \pm 20$  °C for 7 minutes and then the crucible is removed from the oven and cooled first in air, then cooled in a desiccator and weighed again. Percentage of volatile matter can be calculated from the loss in weight of the coal sample as:

$$\% \text{ of volatile matter in coal} = \frac{\text{Loss in weight of moisture free coal}}{\text{Weight of coal initially taken}} \times 100$$

➤ Low quantity of volatile matter, better the quality of a coal.

**c) Determination of ash in coal:** The residual coal sample taken in a crucible and then heated without lid in a muffle furnace at  $700 \pm 50$  °C for an hour or two. The crucible is then taken out, cooled first in air, then in desiccators and weighed again. The process of heating, cooling and weighing are repeated until a constant weight is not obtained. The residue is reported as ash on percentage-basis. Percentage of ash content can be calculated from the loss in weight of the coal sample as:

$$\% \text{ of ash in coal} = \frac{\text{Weight of ash formed}}{\text{Weight of coal taken}} \times 100$$

➤ Ash is non-combustible substance which reduces the calorific value of a coal. Therefore, low quantity of ash contents, better the quality of a coal.



c) **Determination of fixed carbon:** It is determined by subtracting the sum of total moisture, volatile and ash contents from 100.

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

➤ Greater the calorific value, higher the % of fixed carbon.

• **Significance of proximate analysis:**

• **Moisture:** High moisture content in coal is undesirable because it,

i) Reduces Calorific Value of coal

ii) Increases the consumption of coal for heating purpose

iii) Lengthens the time of heating.

➤ Hence, lesser the moisture content, better is the quality of coal.

• **Volatile Matter:** During burning of coal, certain gases like CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, hydrocarbons etc. that come out are called volatile matter of the coal. The coal with higher volatile content,

i) Ignites easily (i.e : it has lower ignition temperature)

ii) Burns with long yellow smoky flame

iii) Has lower Calorific Value

iv) Will give more quantity of coal gas when it is heated in absence of air.



- **Ash:** Ash is the combustion product of mineral matters present in the coal. It consists mainly of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  with varying amounts of other oxides such as  $\text{Na}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{MgO}$  etc.
- Ash containing oxides of Na, Ca and Mg melt early (Low melting ash). During coke manufacture, the low melting ash forms a fused lumpy - expanded mass which block the interspaces of the 'grate' and thereby obstructing the supply of air leading to irregular burning of coal and loss of fuel.
- High ash content in coal is undesirable because it
  - i) increases transporting, handling, storage costs
  - ii) is harder and stronger
  - iii) has lower calorific value.
- **Fixed carbon:** It is the pure carbon present in coal. Higher the fixed carbon content of the coal, higher will be its calorific value.

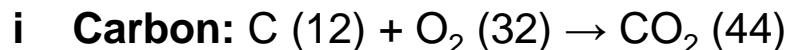


## ii. Ultimate analysis:

- It means finding out the weight percentage of carbon, hydrogen, nitrogen, oxygen and sulphur of the pure coal free from moisture and inorganic constituents.
- This analysis gives the elementary constituents of coal.
- It is useful to the designer of coal burning equipments and auxiliaries.

**a) Determination of carbon and hydrogen in coal:** A known amount (1 – 2 g) of coal is burnt in presence of oxygen thereby converting carbon and hydrogen of coal into  $\text{CO}_2$  ( $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ ) and  $\text{H}_2\text{O}$  ( $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$ ) respectively. The products of combustion ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) are made to pass over weighed tubes of anhydrous  $\text{CaCl}_2$  and KOH, which absorb  $\text{H}_2\text{O}$  and  $\text{CO}_2$  respectively. The increase in the weight of  $\text{CaCl}_2$  tube represents the weight of water formed while increase in the weight of KOH tube represents the weight of  $\text{CO}_2$  formed. % of carbon and hydrogen in coal can be calculated as follows.

Let X - the weight of coal sample taken; Y - the increase in the weight of KOH tube; Z - the increase in the weight of  $\text{CaCl}_2$  tube

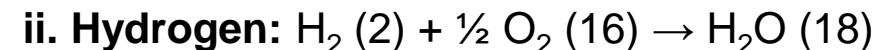


$\Rightarrow 44 \text{ g of CO}_2$  contain 12 g of carbon

$\Rightarrow 1 \text{ g of CO}_2$  contains  $12/44 \text{ g of carbon}$

$\Rightarrow Y \text{ g of CO}_2$  contains  $= (12 \times Y)/44 \text{ g of carbon}$

$\Rightarrow \% \text{ of C in coal} = \{(12 \times Y)/ (44 \times X)\} \times 100$



$\Rightarrow 18 \text{ g of water contain 2 g of hydrogen}$

$\Rightarrow 1 \text{ g of water contain } 2/18 \text{ g of hydrogen}$

$\Rightarrow Z \text{ g of water contains } = (2 \times Z)/18 \text{ g of hydrogen}$

$\Rightarrow \% \text{ of H in coal} = \{(2 \times Z)/ (18 \times X)\} \times 100$



**b) Determination of nitrogen in coal:** Nitrogen estimation is done by [Kjeldahl's method](#). A known amount of powdered coal is heated with conc.  $\text{H}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  in a long necked flask (called Kjeldahl's flask), there by converting nitrogen of coal to ammonium sulphate. When the clear solution is obtained (i.e. the whole nitrogen is converted into ammonium sulphate), it is heated with 50% NaOH solution.



The ammonia thus formed is distilled over and is absorbed in a known quantity of standard 0.1N HCl solution. The volume of unused 0.1N HCl is then determined by titrating against standard NaOH solution. Thus, the amount of acid neutralized by liberated ammonia from coal is determined.

Let, Volume of 0.1N HCl = A mL; Volume of unused HCl = B mL ; Acid neutralised by ammonia = (A - B ) mL

We know that 1000 mL of 1N HCl = 1 mole of HCl = 1 mole of  $\text{NH}_3$  = 14 g of  $\text{N}_2$

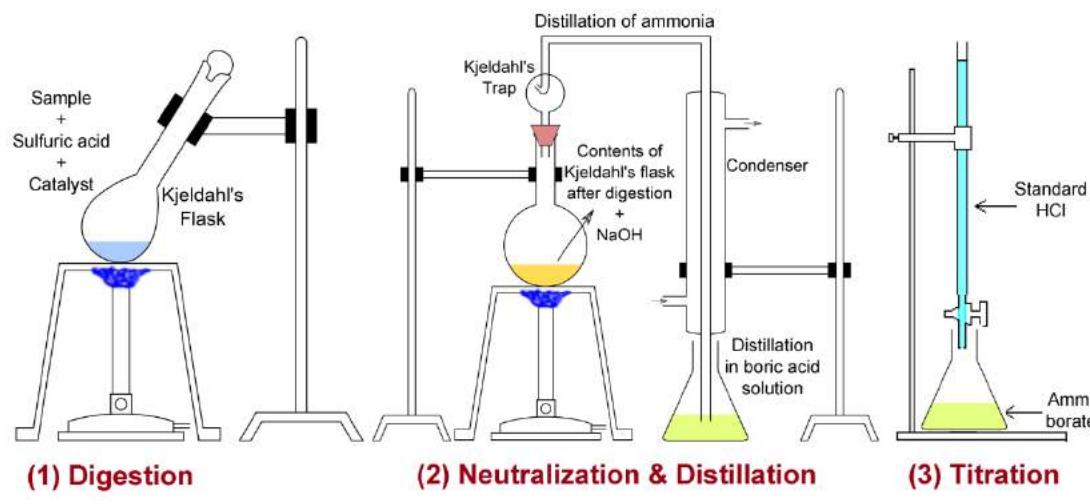
Therefore, (A - B) mL of 0.1N HCl =  $[14 \times (A-B) \times 0.1] / 1000 \times 1 \text{ g of N}_2$

$\Rightarrow X \text{ g of coal sample contains} = [14 \times (A-B) \times 0.1] / 1000 \times 1 \text{ g of N}_2$

% of Nitrogen

$$= \frac{14 \times \text{Volume of Acid consumed} \times \text{Normality}}{1000 \times \text{Weight of coal sample}(X)} \times 100\%$$

$$= \frac{1.4 \times \text{Volume of Acid consumed} \times \text{Normality}}{\text{Weight of coal sample}(X)} \%$$





c) **Determination of sulphur in coal:** A known amount of coal is burnt completely in bomb calorimeter in presence of oxygen. Ash thus obtained contains sulphur of coal as sulphate, which is extracted with dil HCl. The acid extract is then treated with  $\text{BaCl}_2$  solution to precipitate sulphate as  $\text{BaSO}_4$ . The precipitate is filtered, washed, dried, and weighed, from which the sulphur in coal can be computed as follows:

Let,       $X$  = weight of coal sample taken;       $M$  = weight of  $\text{BaSO}_4$  precipitate formed.



$\Rightarrow$  233 g of  $\text{BaSO}_4$  contains 32 g of sulphur

$\Rightarrow$  1 g of  $\text{BaSO}_4$  contains  $32 / 233$  g of sulphur

$\Rightarrow$   $\therefore M$  g of  $\text{BaSO}_4$  contains  $(32 / 233) \times M$  g of sulphur

$$\% \text{ of sulphur in coal} = \frac{32}{233} \times \frac{M}{X} \times 100$$

d) **Determination of ash content in coal:** Percentage of ash calculated by method given in proximate analysis.

e) **Determination of oxygen in coal:** It is calculated by subtracting the sum of total % of carbon, hydrogen, nitrogen, sulphur and ash from 100.

$$\% \text{ of oxygen} = 100 - [\% \text{ carbon} + \% \text{ hydrogen} + \% \text{ nitrogen} + \% \text{ sulphur} + \% \text{ ash}]$$



- **Significance of ultimate analysis:**

- **Carbon and Hydrogen:**

- i. Higher the % of carbon and hydrogen, better the quality of coal and higher is its calorific value.
- ii. The % of carbon is helpful in the classification of coal.
- iii. Higher % of carbon in coal reduces the size of combustion chamber required.

- **Nitrogen:**

- i. Nitrogen does not have any calorific value, and its presence in coal is undesirable.
- ii. Good quality coal should have very little nitrogen content.

- **Sulphur:** Though sulphur increases the calorific value, its presence in coal is undesirable because:

- i. The combustion products of sulphur, i.e.,  $\text{SO}_2$  and  $\text{SO}_3$  are harmful and have corrosion effects on equipments.
- ii. The coal containing sulphur is not suitable for the preparation of metallurgical coke as it affects the properties of the metal.

- **Oxygen:**

- i. Lower the % of oxygen higher is its calorific value.
- ii. As the oxygen content increases, its moisture holding capacity increases and the calorific value of the fuel is reduced.



- **LIQUID FUELS:**

- **Examples:** petrol, diesel, kerosene, gasoline

- **Advantages of liquid fuels**

1. Liquid fuels do not yield any ash after burning.
2. They require comparatively less storage space
3. Calorific value of liquid fuel is higher than that of solid fuels.
4. Their combustion is uniform and easily controllable

- **Disadvantages of liquid fuels:**

1. Liquid fuels are comparatively costlier than the solid fuels.
2. They give unpleasant odour during incomplete combustion.
3. Some amount of liquid fuels will escape due to evaporation during storage.
4. Special type of burners are for effective combustion.



Petrol.  
Diesel.  
Kerosene.  
Methanol.  
Ethanol.  
Butanol.



- **GASEOUS FUELS:**

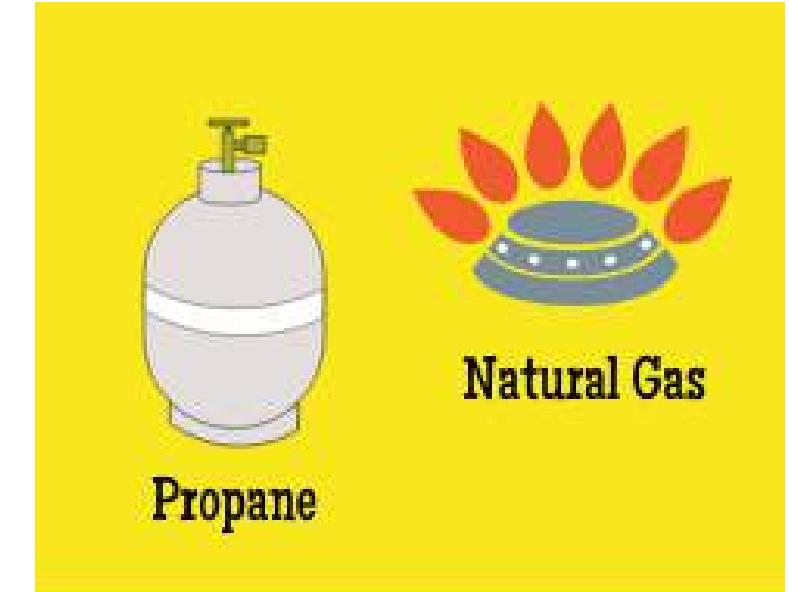
- **Examples:** natural gas, LPG, water gas, producer gas

- **Advantages of gaseous fuels**

1. Gaseous fuels can be easily transported through the pipes.
2. They do not produce any ash or smoke during burning.
3. They have high calorific value than the solid fuels.
4. They have high thermal efficiency.

- **Disadvantages of gaseous fuels:**

1. They are highly inflammable and hence the chances for fire hazards are high.
2. Since gases occupy a large volume, they require large storage tanks.





**I. NATURAL GAS:** It is always found above the oil in the oil wells. It is also called **Marsh gas**.

- Its calorific value varies from 12,000 to 14,000 kcal/m<sup>3</sup>.
- It consists of methane and other saturated paraffinic hydrocarbons. The average composition of natural gas is as follows :
  - Methane (88.5 %)
  - Ethane (5.5 %)
  - Propane (4 %)
  - Butane (1.5 %)
  - Pentane (0.5 %)
- If natural gas contains lower hydrocarbons like methane and ethane it is called **lean or dry gas**. If the natural gas contains higher hydrocarbons like propane, butane along with methane it is called **rich or wet gas**.
- **Uses:**
  1. It is used as a domestic and industrial fuel.
  2. It is used as a raw material for the manufacture of carbon black and hydrogen.
  3. It is also used for the generation of electricity by using it in fuel cells.
  4. It is used in the synthetic preparation of methane.



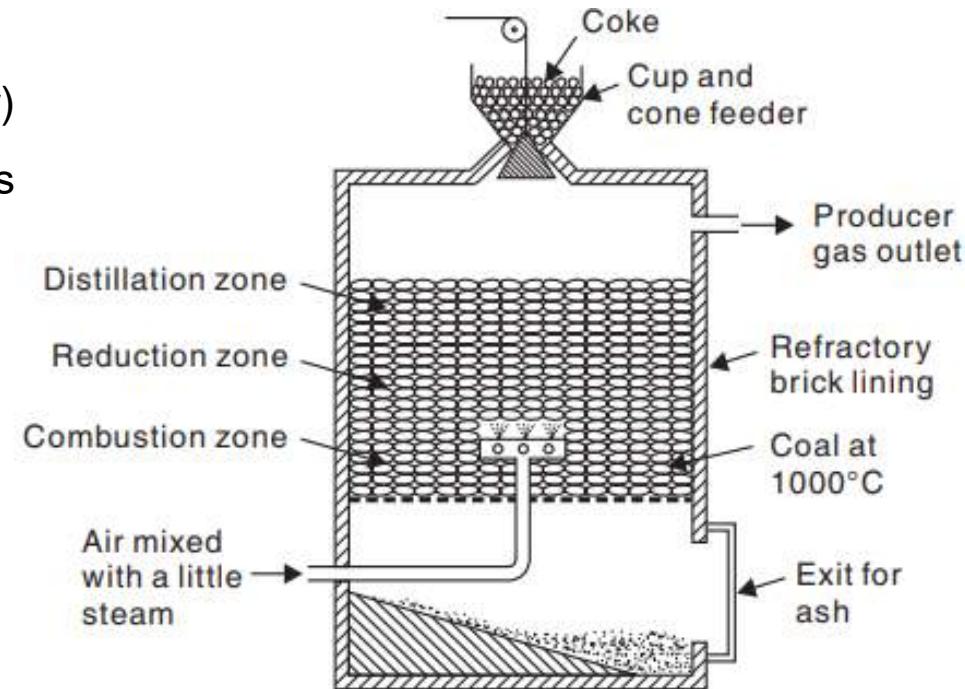
**II. PRODUCER GAS:** It is mixture of combustible gases such as CO (22-30%) and H<sub>2</sub> (8-12%) and large amount of non-combustible gases like N<sub>2</sub> (52-55%), CO<sub>2</sub> (3%) etc.

- It is prepared by passing air mixed with a little steam over a red hot coal (or) a coke bed maintained at above 1100 °C in a special reactor called “Gas Producer”.
- Its calorific value is low and varies from 1300 to 1800 kcal/m<sup>3</sup>.

**Properties:**

- It is a poisonous gas
- It is insoluble in water
- It is heavier than air

- **Synthesis:** The furnace used for the manufacture of producer gas is known as producer. It consists of large airtight steel cylindrical tower (4 m), lined inside with refractory bricks. At the bottom, there is an inlet for air and steam and an outlet for removing ash. Coal is added through a cone feeder at the top and producer gas comes out from the side outlet at the top.



**Gas Producer**



- **Reaction zones in a Gas Producer:**

- Ash zone:** The fuel bed in a normal producer is on metallic grate. The air-steam blast is pre-heated by the ash zone which also protects the grate from intense heat.
- Combustion or oxidation zone:** The oxygen is consumed within 75 to 100 mm of the bed, which constitutes the zone. When a mixture of air and steam is passed through a bed of red hot coal, carbon (of the coal) combines with oxygen (of the air) in the lower part of the furnace to form  $\text{CO}_2$ . The temperature of this zone is 1100 °C.



- Reduction zone:**  $\text{CO}_2$  so formed rises up through the red-hot coal and gets reduced to CO during its passage (**Bondonard reaction**). Its equilibrium constant greatly increases with rise in temperature.  $\text{N}_2$  of air remains unaffected throughout the process. Thus a mixture of CO and  $\text{N}_2$  with traces of  $\text{CO}_2$  and hydrocarbons comes out through the exit at the upper end of the producer. The temperature is around 1000 °C.





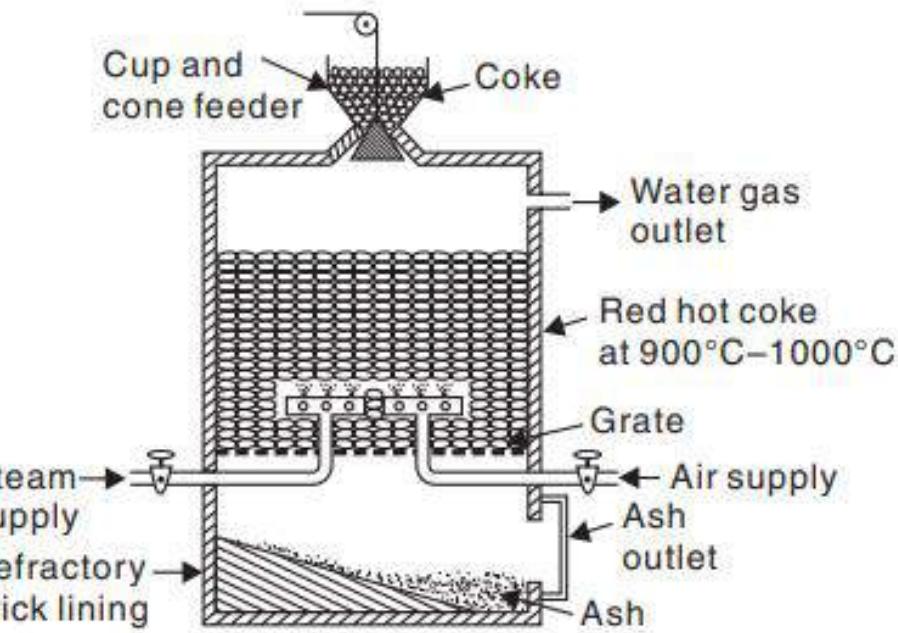
d) **Drying and carbonization zone:** The water vapor and the volatile matter are added to the escaping gas which results in the production of enriched gases. The temperature of this zone is 400 - 800 °C

- **Advantage of using air with steam:**
  - i. It raises the content of combustible components (CO) thereby increasing calorific value
  - ii. The endothermic reaction of steam and C prevents overheating of a fuel bed and leads to diminished clinker formation
- **Uses:**
  - i. It is used as fuel for heating open - hearth furnaces (used in steel and glass manufacture), muffle furnaces (used in coal gas and coke manufacture).
  - ii. It provides reducing atmosphere in certain metallurgical operations.



**III. WATER GAS (or BLUE GAS):** It is essentially a mixture of combustible gases like CO (41%), H<sub>2</sub> (51%) with a little non combustible gases like CH<sub>4</sub>, CO<sub>2</sub> (4%) and N<sub>2</sub> (4%)

- It is generated by gasifying solid incandescent source of carbon in superheated steam
- It is of medium calorific value: 2800 kcal/m<sup>3</sup>
- **Properties:**
  - It burns with blue flame owing to high content of CO and hence is known as blue water gas.
  - Its flame is short but very hot.
- **Synthesis:** A Water gas generator is a steel cylindrical vessel. At the top, it is provided with a hopper for adding coke. Water gas outlet is provided near the top. At the bottom, it is provided with an arrangement of taking out ash formed.



Water gas production



- **Working:** It is obtained by the action of steam on a bed of coke heated to 1000 - 1400 °C.



Since the above reaction is endothermic, the coal cools down after a few minutes and the reaction proceeds in a different way to form  $CO_2$  and  $H_2$  instead of water gas ( $CO + H_2$ ).



In order to avoid the above undesirable reaction, the blow of air replaces the blow of steam. The following reaction now occurs.



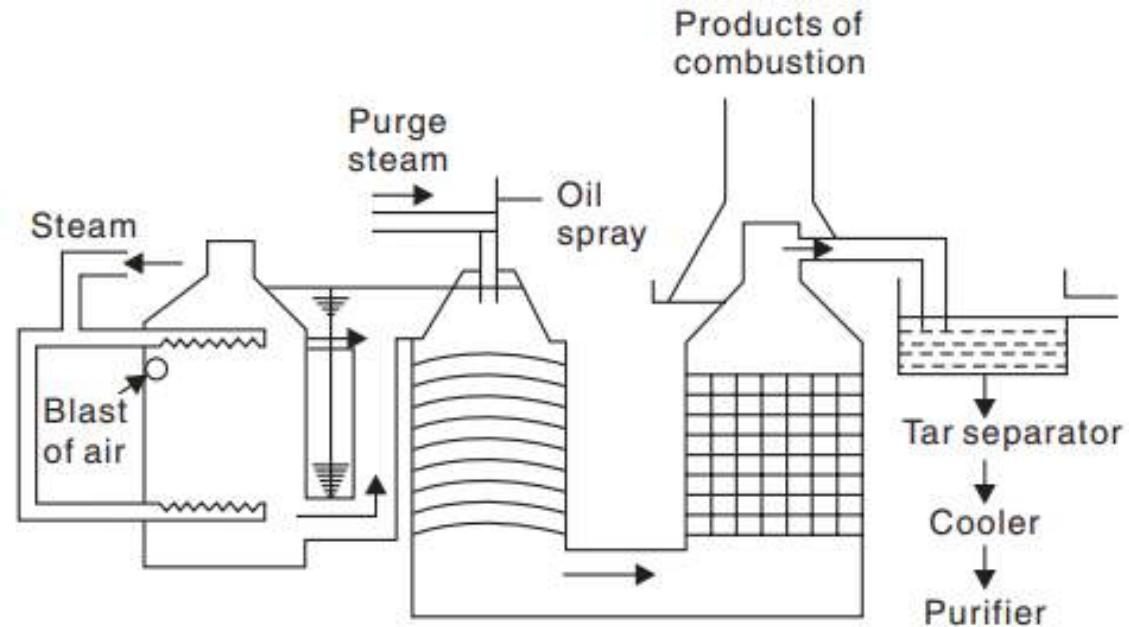
Due to exothermic reactions, the temperature of the bed rises and when the temperature increases to 1000 °C, air entry is stopped and steam is again passed. Thus steam and air are blown alternatively. Therefore, the manufacture of water gas is intermittent.

- **Uses:**

- i. It is used for the manufacture of ammonia by Haber's process.
- ii. Used as a source of hydrogen, as a fuel gas.
- iii. Carbureted water gas is used for lighting and heating.
- iv. Water gas is also used for welding purposes.
- v. Used for the manufacture of methyl alcohol and synthetic petrol.



- The calorific value of water gas can be enhanced by adding gaseous hydrocarbons to get carbureted water gas (calorific value: 4500 kcal/m<sup>3</sup>)
- Composition of carbureted water gas:
  - H<sub>2</sub>: 35%
  - CO: 25%
  - Saturated and unsaturated hydrocarbons: 35%
  - N<sub>2</sub> + CO<sub>2</sub>: 5%

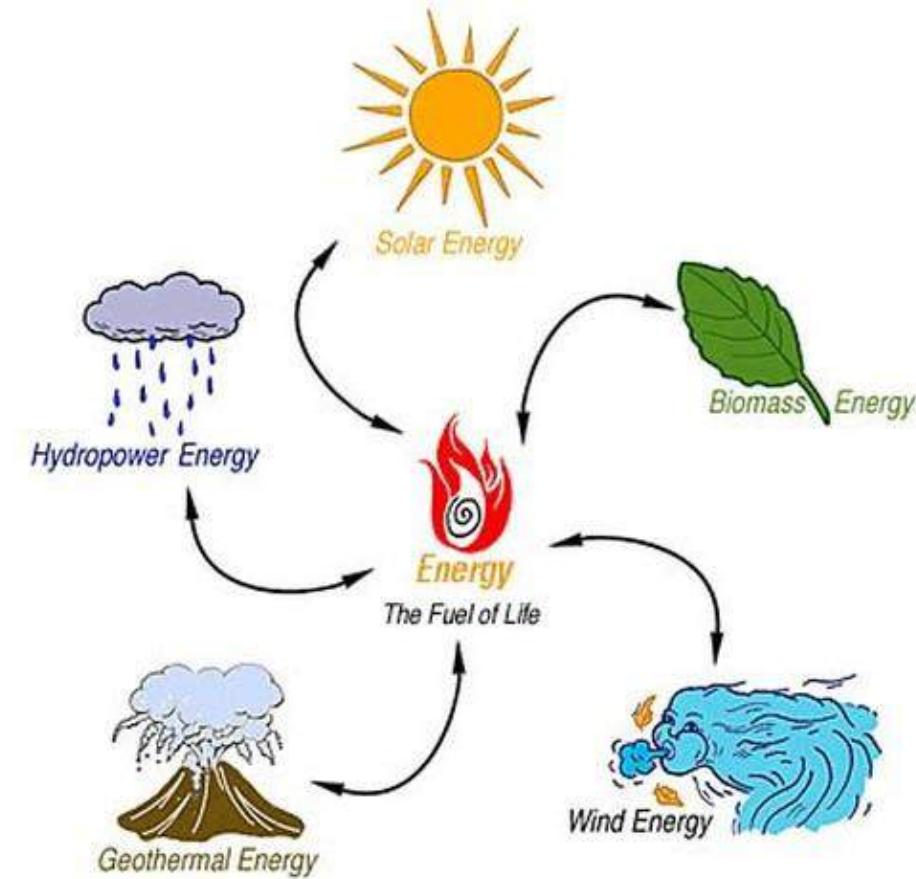


Carbureted water gas production



## ■ NON-CONVENTIONAL SOURCES OF ENERGY

- The sources of energy which are being produced continuously in nature and are inexhaustible are called renewable or non-conventional sources of energy
- Some of these sources are:
  - Solar energy
  - Wind energy
  - Tidal energy
  - Bio-mass
- A renewable energy system transforms energy from the sun, wind, falling water, sea waves, geothermal heat, or biomass into heat or electricity that humans can utilize
- With rising energy use, the population is becoming increasingly reliant on fossil fuels such as coal, oil, and gas. These fuels are costly and therefore in order to guarantee future energy supplies, we must employ more and more renewable energy sources





- **Advantages:**
  - i. They are renewable in nature.
  - ii. They produce little or no pollution as compared to traditional energy sources.
  - iii. They require little maintenance.
  - iv. They are a long-term cost-effective choice.
- **Disadvantages:**
  - i. The initial setup cost is greater.
  - ii. Energy cannot be taken 24/7 year-round, because certain days will be windier than others, and the sun will shine stronger on other days.
  - iii. Energy must be stored. Geographical locations might be difficult to navigate.



## I. SOLAR ENERGY

- It is the energy received from sun
- It is the most readily available source of energy
- Earth surface receives 182 peta-watts (PW) of energy from sun
- The energy supplied by the sun in one hour is almost equal to the amount of energy required by the human population in one year
- Solar thermal devices are utilized in residential and industrial solar water heaters, air warmers, solar cookers, and solar dryers

- **Advantages:**

- i. It is renewable
- ii. Non-polluting and eco-friendly
- iii. Free except for capital expenses
- iv. Low maintenance- solar panels require very little upkeep
- v. Longevity- solar panels can last upto 30 years

- **Disadvantages:**

- i. The major disadvantage is the cost of photovoltaic panels
- ii. Only areas of the world with lots of sunlight are suitable for solar power generation

- **Applications of solar energy:**

- i. Solar electric generation
- ii. Solar cars
- iii. Solar heaters
- iv. Solar cookers
- v. Solar lighting





## II. WIND ENERGY

- Wind energy is the process of harnessing wind power to generate electricity. The wind's kinetic energy is transformed into electrical energy.
- Windmills convert wind power to electrical power.
- **Applications of wind energy:**
  - i. Utility interconnected wind turbines generate power which is synchronous with the grid and are used to reduce utility bills
  - ii. Wind turbines generate DC current for battery charging
  - iii. Wind turbines for remote water pumping generate 3 phase AC current suitable for driving an electrical submersible pump directly





### III. OCEAN AND TIDAL ENERGY

#### a) Tidal energy:

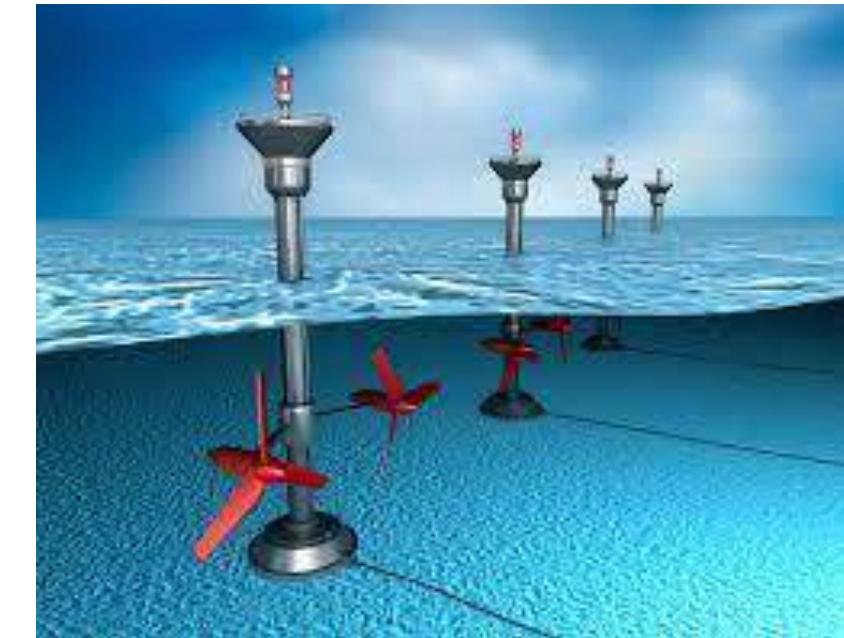
- The building of a barrage across an estuary to prevent the incoming and outgoing tides is required for tidal power generation. As with hydroelectric dams, the head of water is utilized to drive turbines that create energy from the raised water in the basin.
- Barrages can be built to generate power on the ebb, flood, or both sides of the river.
- The tidal range can range from 4.5 to 12.4 meters depending on the location. For cost-effective operation and adequate head of water for the turbines, a tidal range of at least 7 m is necessary.

#### b) Ocean energy:

- Oceans encompass more than 70% of the earth's surface, making them the biggest solar collectors on the planet.
- Ocean energy is derived from water waves, tides, and thermal energy (heat) stored in the ocean. The sun warms the top-water far more than the deep ocean water, storing thermal energy in the process.

#### c) Applications of tidal energy:

- i. Tidal electricity
- ii. Grain mills
- iii. Energy storage
- iv. Provide protection to coast in high storms





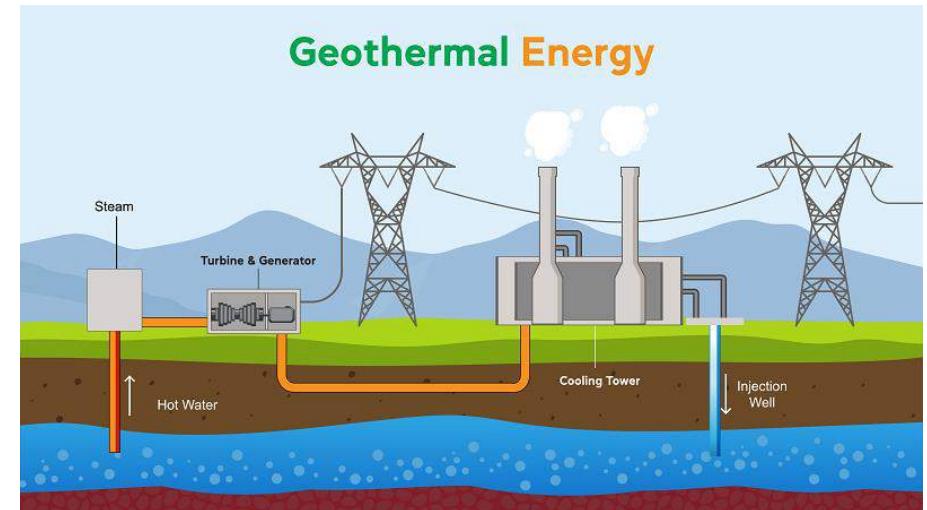
#### IV. HYDROPOWER

- The commencement of the industrial revolution was driven by the potential energy of falling water, which was collected and transformed to mechanical energy by waterwheels.
- Rivers and streams were dammed and mills were erected wherever there was enough head or change in elevation. A turbine spins because water under pressure flows through it. The Turbine is linked to a generator, which generates power.



#### V. GEOTHERMAL ENERGY

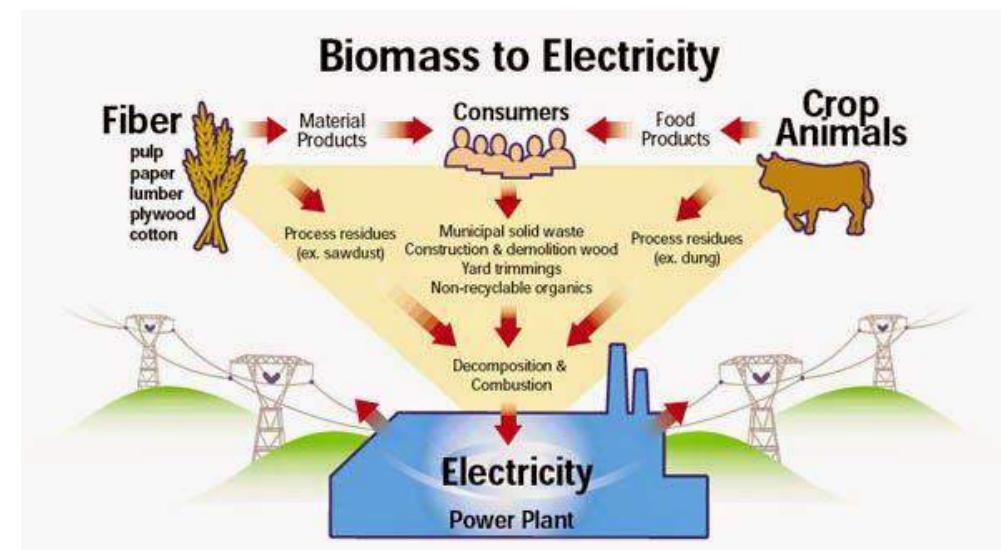
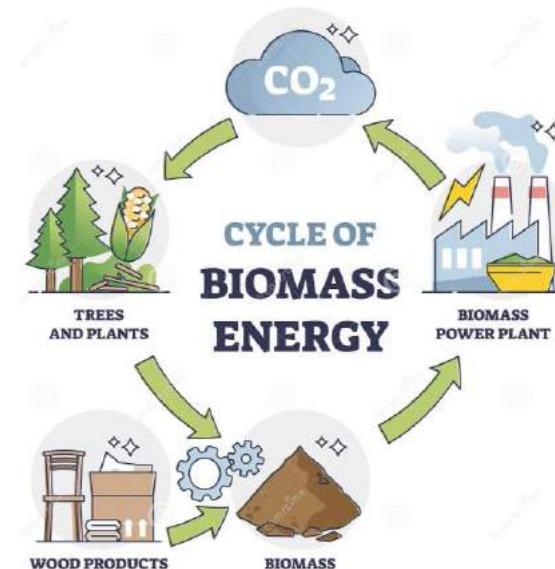
- It is a type of energy that comes from the earth. It is trapped in the earth's crust at a depth of 10 km in the form of hot springs, geysers, and other natural phenomena.
- About 250 hot springs with temperatures ranging from 90 to 130 °C have been discovered in areas like Puga Valley in Ladakh, Manikaran in Himachal Pradesh, and Tattapani in Chhattisgarh, indicating that India's geothermal potential is largely found along the Himalayas.
- The National Aerospace Laboratory in Bangalore has established a pilot project near Manikaran for research and development as well as data collection in order to construct larger geothermal power plants.





## VI. BIOMASS

- Biomass is a renewable energy source made up of carbon-based waste from human and natural activity.
- It comes from a variety of places, including wood industry by-products, agricultural crops, forest raw material, domestic trash, and so on.
- Biomass does not emit carbon dioxide into the atmosphere since it absorbs the same amount of carbon throughout its growth as it emits when burned.
- It has the benefit of being able to generate energy using the same equipment that is now used to burn fossil fuels.
- Biomass is a significant source of energy and, after coal, oil, and natural gas, the most important fuel on the planet. Bio-energy, in the form of biogas, has a better energy efficiency than direct burning and is anticipated to become one of the most important energy sources for worldwide sustainable development.
- Biogas is a clean and efficient fuel made from cow dung, human waste or any other biological substance that has been fermented anaerobically.
- The biogas contains 55-60% methane and the remainder is mostly carbon dioxide.
- Biogas is a non-toxic fuel that may be used for cooking and lighting. The by-product can be used as high-quality manure.





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Engineering Chemistry-II (BS-104)

# Spectroscopic Techniques-1

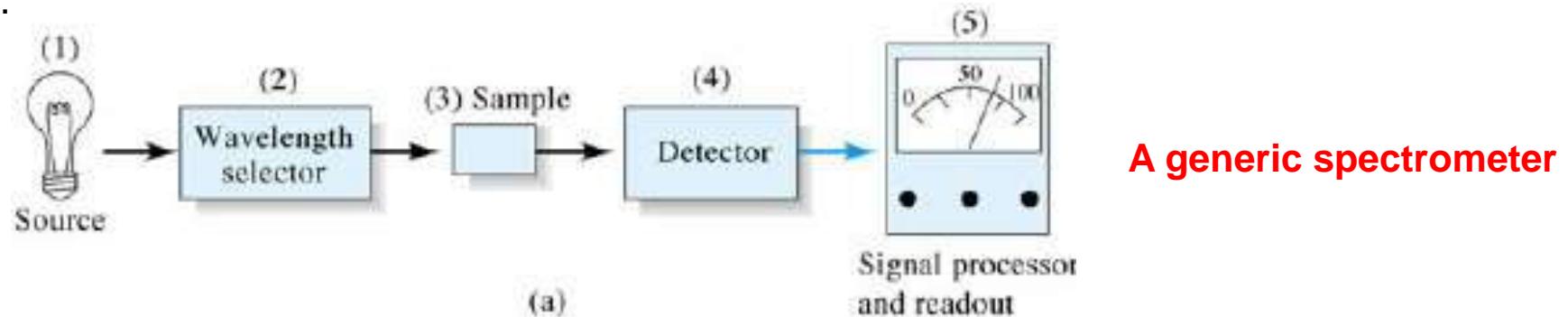
**Dr. Shruti Khanna Ahuja**

Assistant Professor

USAR, GGSIPU



- Study of interaction of electromagnetic radiation with matter defines the science of **spectroscopy**.
- **Spectroscopy** is that science which attempts to determine what specific energies and amounts of incident light are absorbed by specific substances, and what specific energies and amounts are later re-emitted.
- It includes different analytical techniques used for both quantitative and qualitative analyses of inorganic, organic and biological compounds.
- **Spectrometers** are optical instruments that reveal the light energies absorbed and emitted in terms of specific wavelengths or frequencies.
- **Spectra** are the records that provide us with important information pertaining to the atomic and molecular structure of the substances on which the electromagnetic energy is focused.
- These spectra provide us with “fingerprints” that are characteristic of—and therefore uniquely connected to—different elements and compounds.





- **Electromagnetic radiation** is a type of energy that is transmitted through space at enormous velocities. It is found to have dual nature - the particle nature (photons) and wave nature.
- It is a propagating wave of electrical energy with an orthogonal magnetic component oscillating with exactly the same frequency.
- Molecules absorb electromagnetic radiation in discrete packets of energy called “quanta”, which are measurable by spectroscopy.
- The many different types of EM waves are categorized according to their origins and their frequency/wavelength values.

$$c = \lambda v$$

c = speed of light =  $3 \times 10^8$  m/s

$\lambda$  = wavelength of radiation

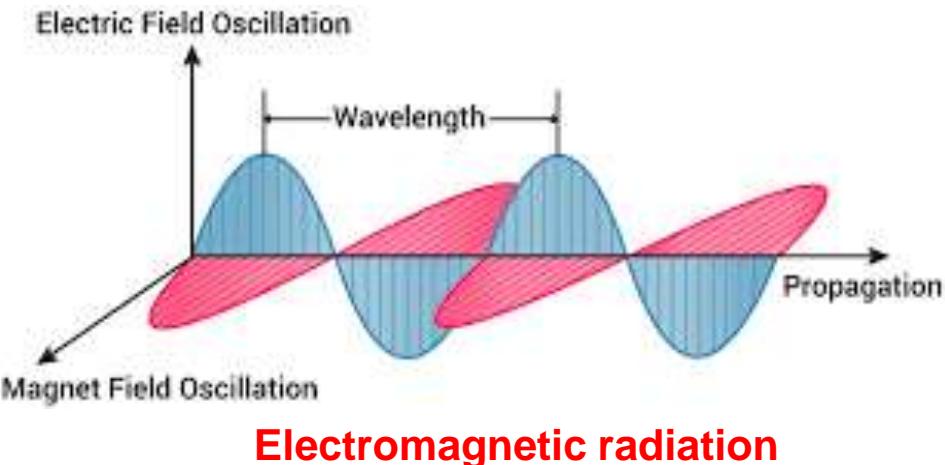
v = frequency of electromagnetic radiation

$$E = hv = hc/\lambda$$

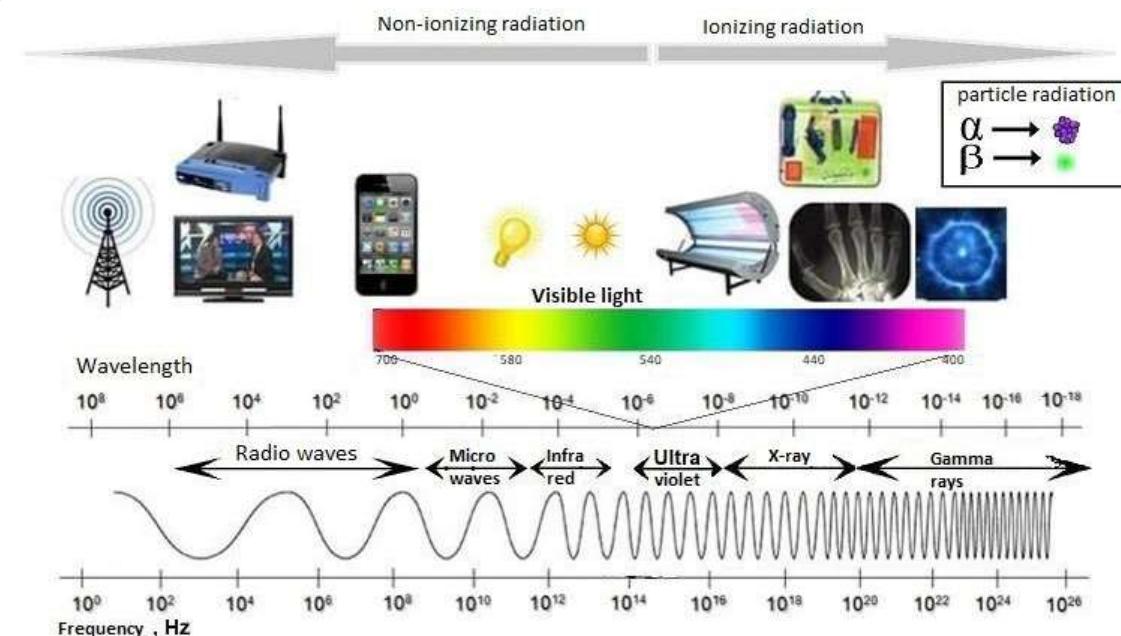
E = energy of electromagnetic radiation

$h$  = Planck's constant =  $6.62 \times 10^{-34}$  Js

As the energy increases, wavelength decreases

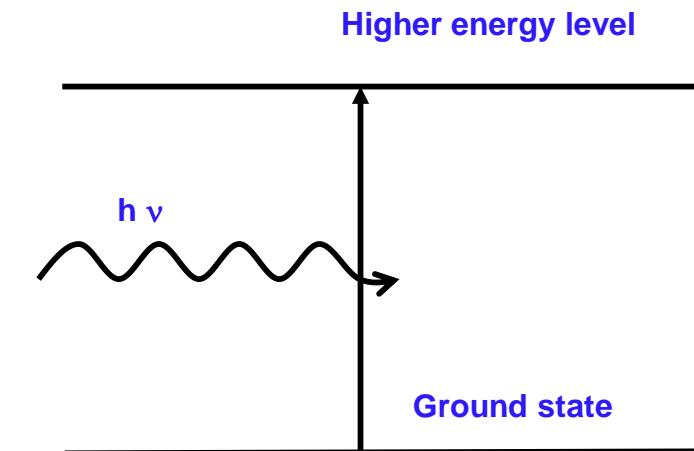


## Electromagnetic spectrum





- The field of spectroscopy is divided into two main classes:
  - i. Absorption      ii. Emission
- i. **Absorption spectra** are produced when white light is directed onto a particular substance and certain wavelengths in the spectrum of the white light are absorbed via internal energy excitations.
- The wavelength absorbed characterizes some specific functional group of the compound or the compound itself.
- The regions of electromagnetic radiation of greatest interest to organic chemists are 200-400 nm (UV), 400-800 nm (visible) and 800 nm-1 mm (infra-red)
- The mechanisms of absorption of energies is different in the ultra-violet, infra-red and nuclear magnetic resonance (NMR) regions, though the fundamental phenomenon is the absorption of certain amount of energy.
- Absorption in UV-vis is due to electronic transitions, in infra-red region, it is due to molecular vibrations, whereas in NMR, nuclear spin transitions take place.

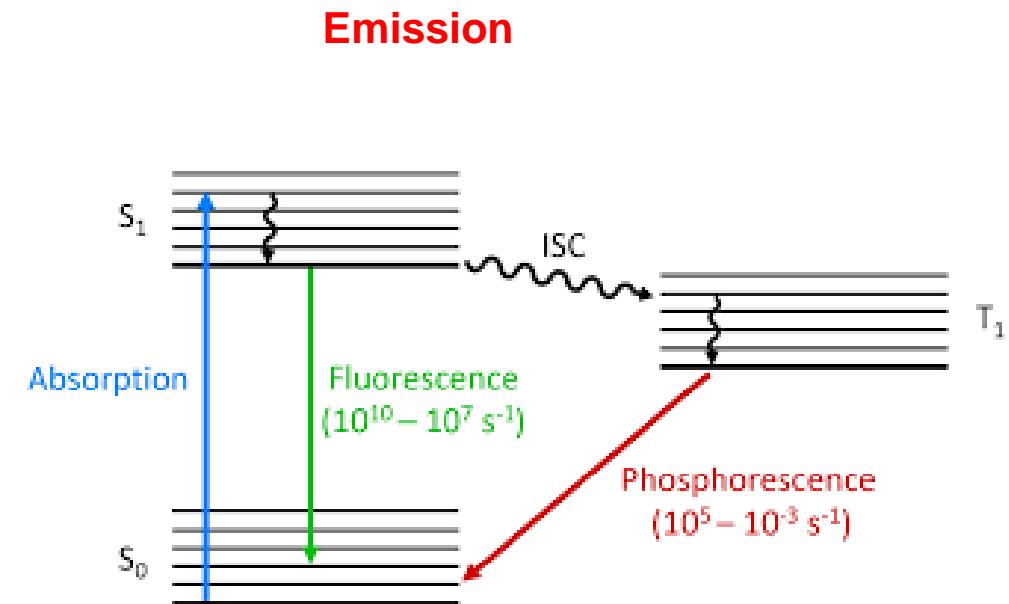
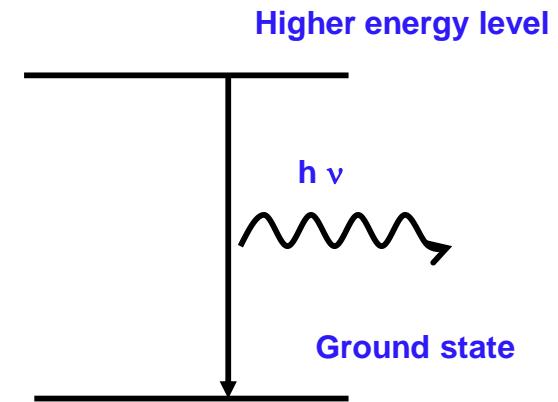


**Absorption**



ii. **Emission spectra** for a substance occurs when the substance receives energy from an external source, absorbs the energy to raise its electrons to higher energy metastable states (electrons having short life time here), then emits characteristic energy amounts as the excited electrons return to their previous energy levels.

- Fluorescent lights and colors obtained by heating salts of certain elements in the flame are very common examples of emission spectra
- Fluorescence:** The electron in the excited level return to its ground state either directly or in steps with the emission of certain amount of energy. When this emission of light is instantaneous the phenomenon is known as fluorescence
- Phosphorescence:** When the electron in the excited level return to it's ground state with the emission of light after some time lag, it is known as phosphorescence.



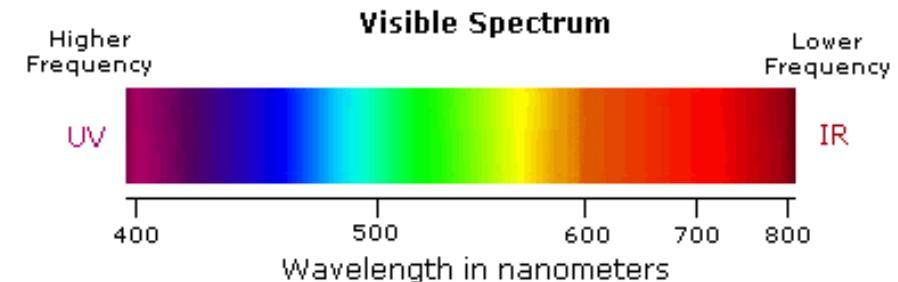


## 1. UV-VISIBLE SPECTROSCOPY

- A region of electromagnetic radiation whose interaction with a molecule gives rise to electronic transition exists at 200-800 nm
- It requires electromagnetic radiations of higher energy
- It is primarily used to measure the multiple bonds or aromatic conjugation within the molecules.
- When monochromatic light is passed through a medium containing particles, they interact with ions and molecules and electronic transitions occur by the excitation of electrons from the ground state to the excited state.
- Molecules that absorb in UV-vis region transfer the corresponding energy from that photon to one or several of its outermost electrons.
- This transfer of energy results in a change on the total mechanical energy associated with the molecule. The total energy will be equal to:

$$E_{\text{tot}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}},$$

where,  $E_{\text{elec}} > E_{\text{vib}} > E_{\text{rot}}$



**Violet:** 400 - 420 nm

**Indigo:** 420 - 440 nm

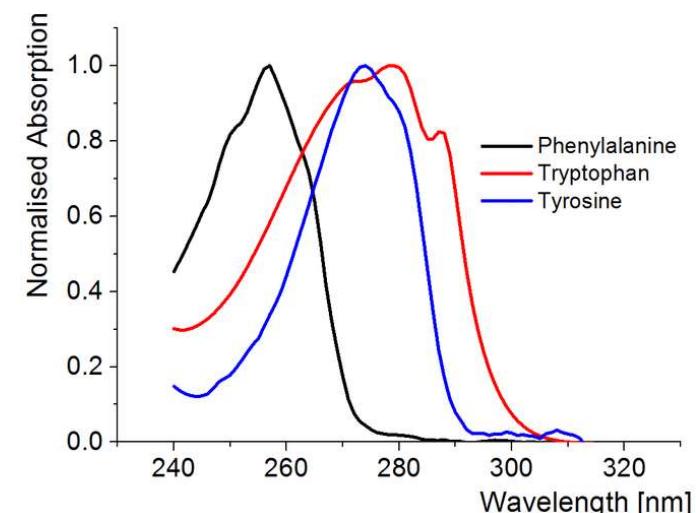
**Blue:** 440 - 490 nm

**Green:** 490 - 570 nm

**Yellow:** 570 - 585 nm

**Orange:** 585 - 620 nm

**Red:** 620 - 780 nm



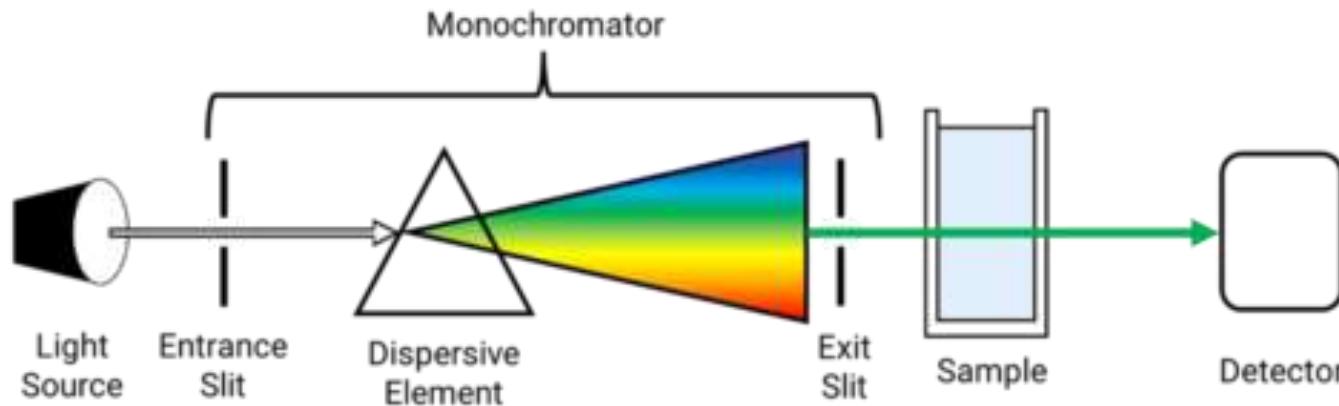


- **Instrumentation:**

1. **Light Source:** Tungsten filament lamps and Hydrogen-Deuterium lamps are the most widely used and suitable light sources 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.
2. **Monochromator:** Monochromators generally are composed of prisms and slits. 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 wavelengths to pass through the slits for recording purposes. The beam selected by the slit is monochromatic and further divided into two beams with the help of another prism.
3. **Sample and reference cells:** One of the two divided beams is passed through the sample solution and the second beam is passed through the reference solution. Both sample and reference solution is 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.**



4. **Detector:** Generally, two photocells serve the purpose of the detector in UV spectroscopy. One of the photocells receives the beam from the sample cell and the second detector receives the beam from the reference. The intensity of the radiation from the reference cell is stronger than the beam of the sample cell. This results in the generation of pulsating or alternating currents in the photocells.
5. **Amplifier:** The alternating current generated in the photocells is transferred to the amplifier. Generally, the current generated in the photocells is of very low intensity, the main purpose of the amplifier is to amplify the signals many times so we can get clear and recordable signals.
6. **Recording devices:** Most of the time amplifier is coupled to a pen recorder which is connected to the computer. The computer stores all the data generated and produces the spectrum of the desired compound.



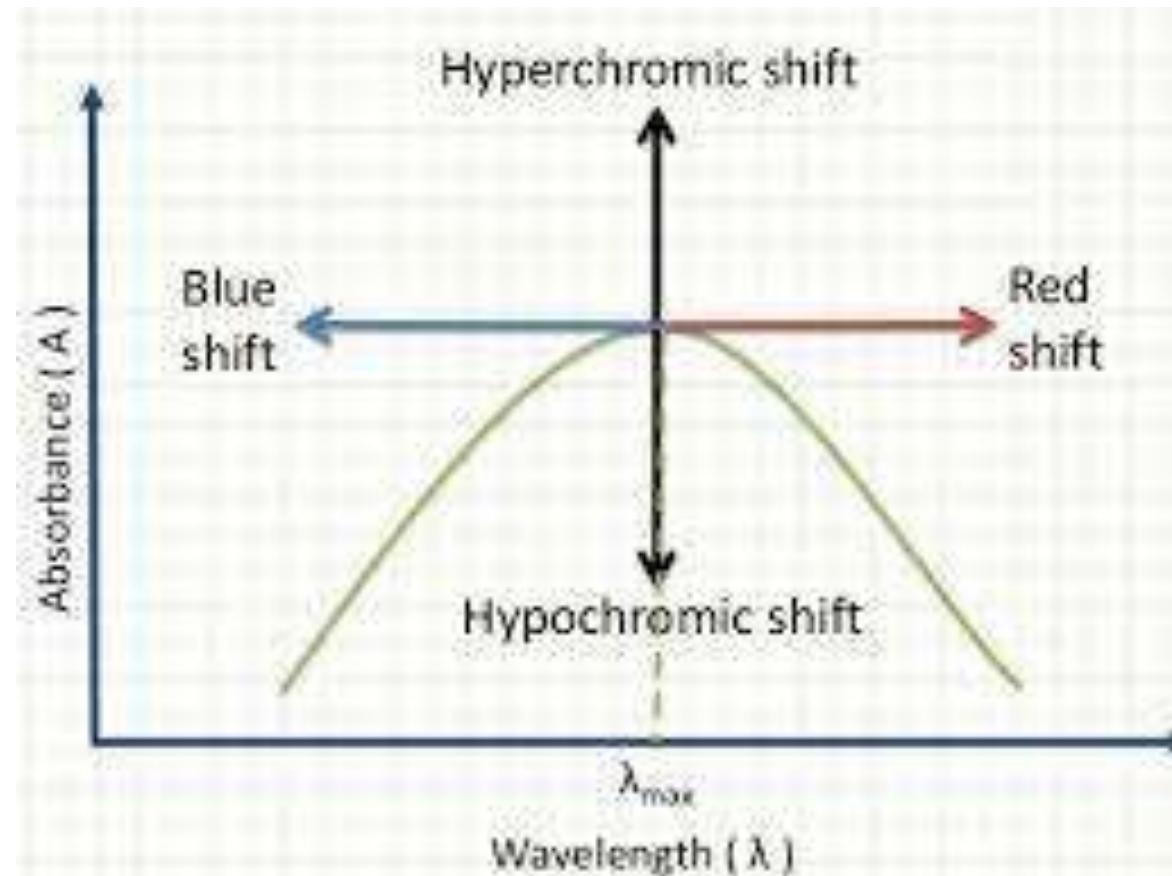
Schematic Representation



UV-Vis spectrophotometer



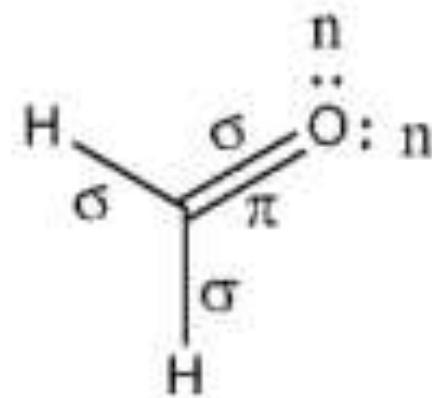
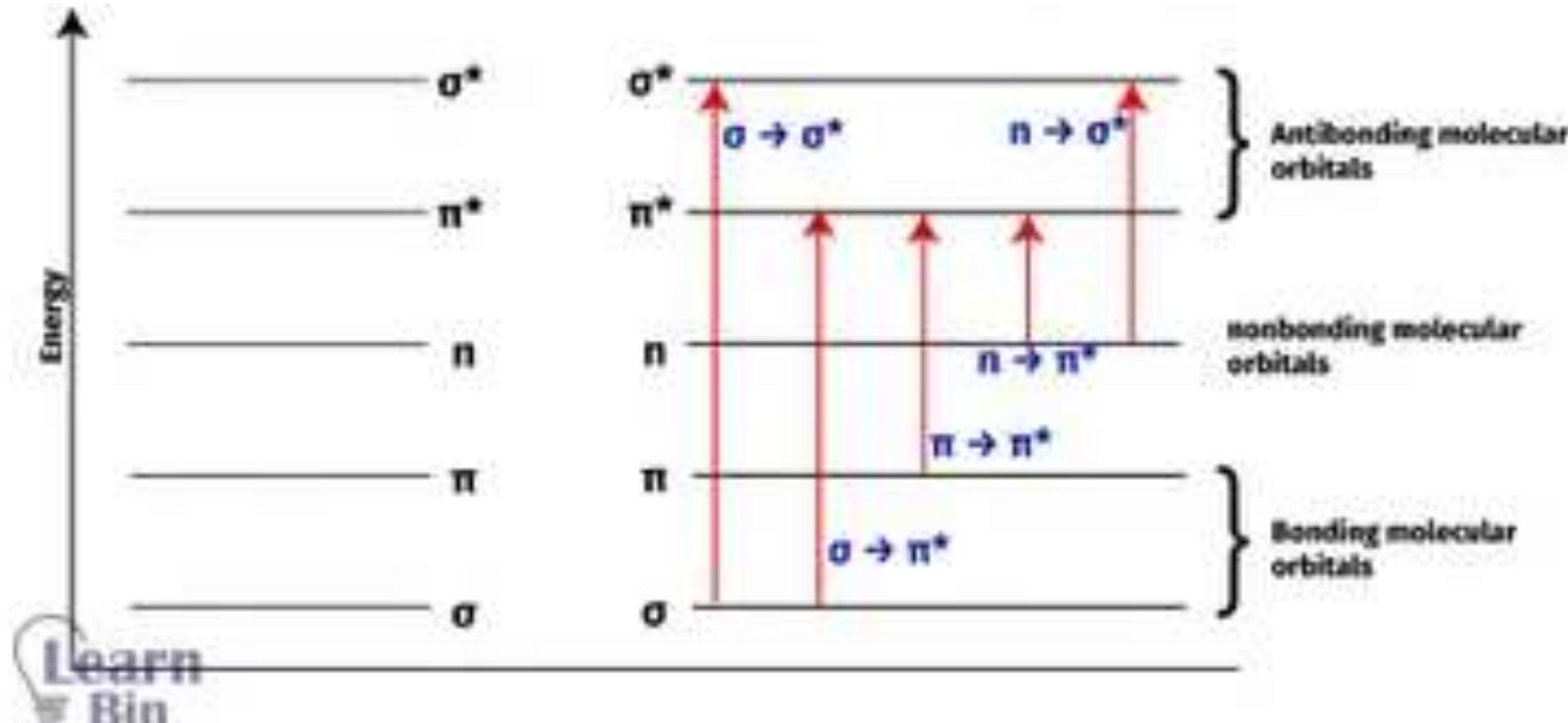
- **Chromophores:** It is a group of molecules, which is responsible for certain absorption of radiation. It is a minimum structural requirement for the absorption of radiation in the UV region, e.g. molecules having  $\pi$  electrons such as C=C, C=O, N=N
- **Auxochromes:** It is a saturated group containing unshared electrons which when attached to the chromophore changes both intensity as well wavelength of the absorption maxima, e.g. OH, NH<sub>2</sub>, Cl
- $\lambda_{\text{max}}$  : It is a wavelength at which there is a maximum absorption. It is a physical constant and characteristic of a molecular structure and is very useful for identification of compounds. It is independent of concentration.
- **Bathochromic shift:** It is the shifting of the absorption peak to the higher wavelength due to the effect of a substituent group or solvent. It is also known as **red shift**. E.g.,  $\lambda_{\text{max}}$  of ascorbic acid is 243 nm, while that in alkali medium is 299 nm
- **Hypsochromic shift:** It is the shifting of the absorption peak to the lower wavelength. It is also known as **blue shift**. E.g.,  $\lambda_{\text{max}}$  of phenol in basic media is 297 nm, while that in acidic media is 277 nm
- **Hyperchroism:** Increase in absorption intensity due to substituent, solvent, pH or some other factors
- **Hypochoism:** Decrease in absorption intensity due to substituent, solvent, pH or some other factors



Shifts in absorption position and intensity



- Electronic energy levels and transitions:

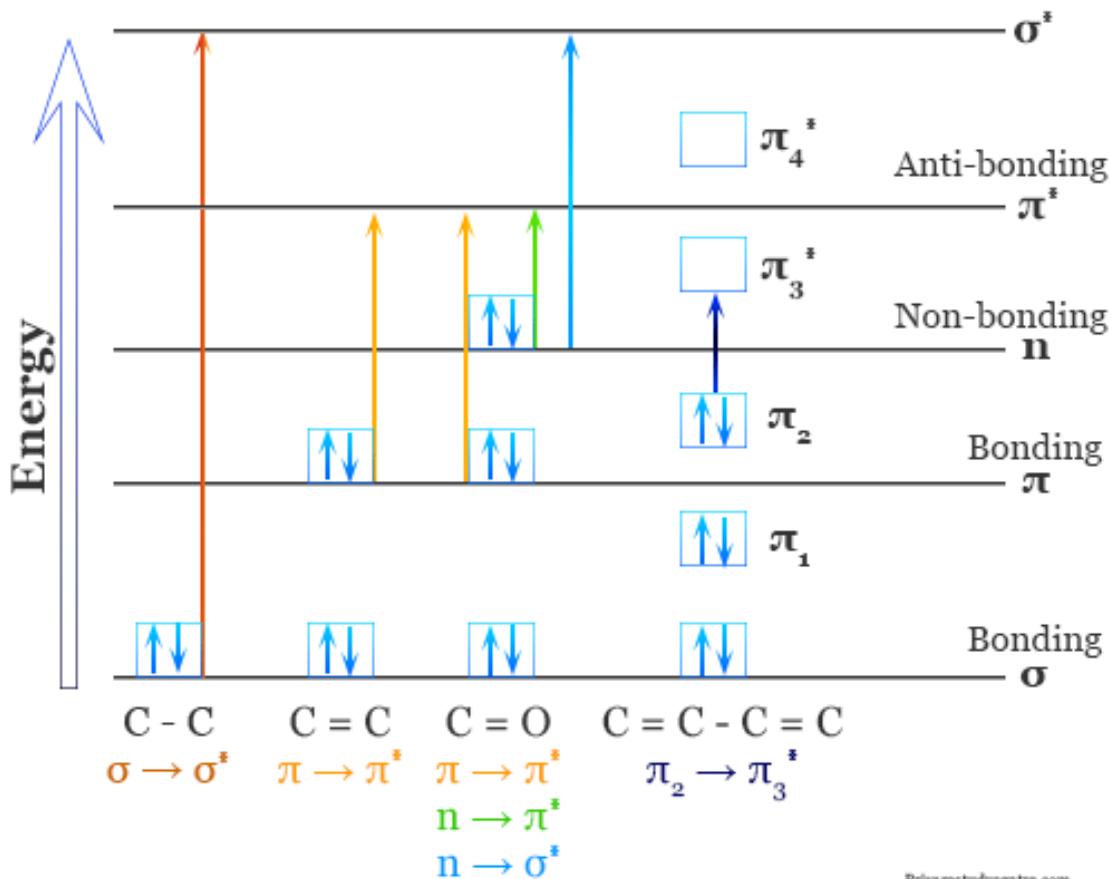
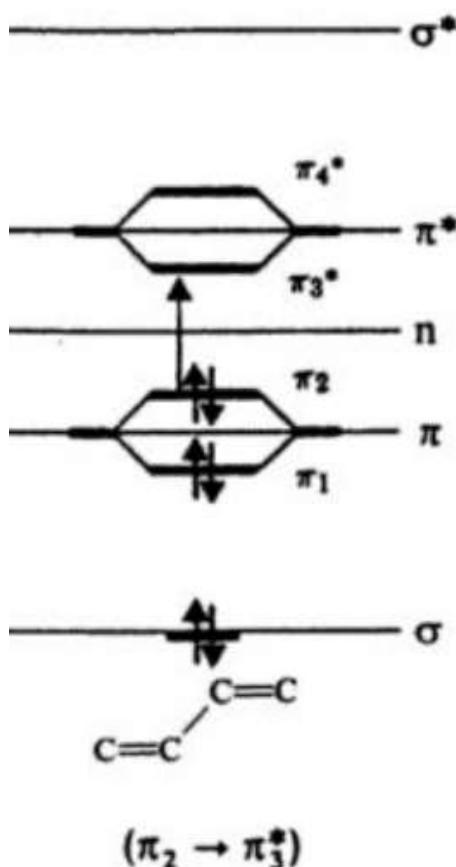




- **Types of electronic transitions:**
  - i.  **$\sigma-\sigma^*$  transition:** An electron is excited from bonding  $\sigma$  orbital to higher energy anti-bonding  $\sigma^*$  orbital. Sigma bonds, in general, are very strong and therefore the energy required for this transition is large and the band appear at short wavelengths <150 nm. It is observed with saturated compounds such as alkanes e.g.  $\lambda_{\max}$  for methane is 122 nm. This regions is usually less informative.
  - ii.  **$n-\sigma^*$  transition:** This transition involves saturated compounds with one heteroatom having unshared pair of electrons (n electrons) e.g. saturated alkyl halides, alcohols, ethers, aldehydes, ketones and amines etc. These transitions require comparatively lesser energy than  $\sigma-\sigma^*$  transitions. In saturated alkyl halides the energy required for this transition decreases with increase in size of the halogen atom (less electronegativity => loosely bound outermost electron => less energy) e.g.  $\lambda_{\max}$  for methyl chloride of 173 nm and that of methyl iodide is 258 nm. This transition is sensitive to H-bonding with the solvent molecules as in alcohols, amines thereby shifting the absorption peaks to shorter wavelength.
  - iii.  **$\pi-\pi^*$  transition:** It occurs in the compounds with unsaturated centers such as simple alkene, aromatics, carbonyl compounds. This transition is lesser in energy than  $n-\sigma^*$  transition. Unconjugated alkenes generally absorb in 170-205 nm.
  - iv.  **$n-\pi^*$  transition:** An electron form non-bonding orbital of a heteroatom is promoted to anti-bonding  $\pi^*$  orbital. It requires least energy out of all transitions and the absorption band appear at higher wavelengths.



**v. Conjugated systems:** In conjugated dienes, the  $\pi$  orbitals of the separate alkene groups combine to give new orbitals, i.e., the new bonding orbitals designated as  $\pi_1$  and  $\pi_2$  and two anti-bonding orbitals,  $\pi_3^*$  and  $\pi_4^*$ . The relative energy of  $\pi_2 \rightarrow \pi_3^*$  of a conjugated diene is of very low energy than  $\pi \rightarrow \pi^*$  transition in an unconjugated alkene. e.g.  $\lambda_{\text{max}}$  for ethene is 171 nm while the peak is shifted bathochromically in butadiene with  $\lambda_{\text{max}}$  at 217 nm.



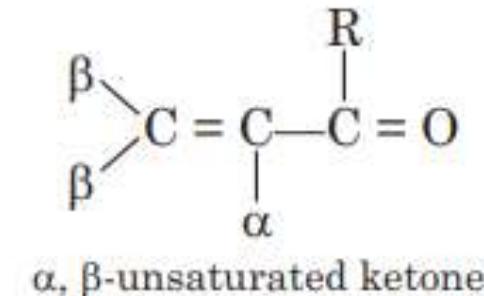
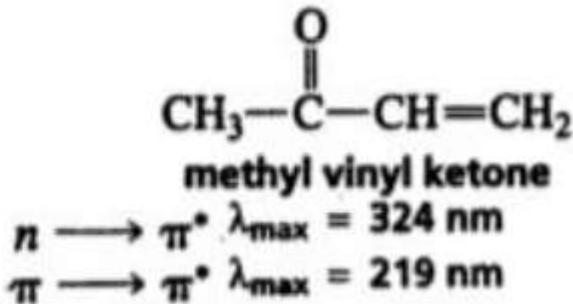
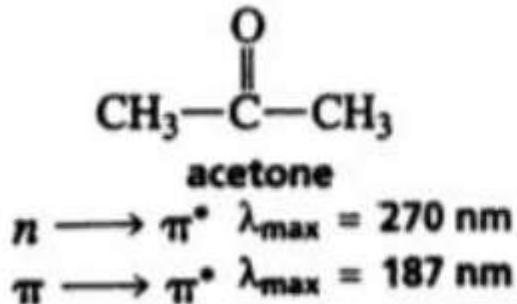


- **Types of absorption bands:** They occur due to electronic transition of a molecule.
- i. **R-bands:** These are observed in compounds containing **double bonds with heteroatoms** such as carbonyls (C=O), nitro (-NO<sub>2</sub>) etc. An electron from non-bonding orbital is promoted to anti-bonding π\* i.e. they undergo n-π\* transition. This transition require minimum energy of out of all transitions and shows absorption band at longer wavelength around 300 nm e.g. in acetone absorption band appear at 279 nm. Saturated aldehyde show both type of transitions: lower energy n-π\* and higher energy π-π\* thereby exhibiting absorption peaks at 290 and 180 nm, respectively. The ε<sub>max</sub> value is less than 100.
- ii. **K-bands:** These arise from π-π\* transitions in **π-π conjugated systems** like alkenes, alkynes, carbonyls, nitriles and aromatic compounds. The show ε<sub>max</sub> greater than 10,000. e.g. 1,3,5-hexatriene exhibits λ<sub>max</sub> at 258 nm
- iii. **B-bands:** These are due to **aromatic and hetero-aromatic systems**. The λ<sub>max</sub> values are between 230-270 nm and ε<sub>max</sub> less than 2000. These bands are called benzenoid bands. In the presence of K-bands the position of the B-band is shifted to larger wavelengths. The UV spectrum of benzaldehydye contains K, R and B bands.
- iv. **E-bands:** These are also known as **ethylenic bands** and are characteristic of the aromatic systems as are the B-bands. They are classified as E<sub>1</sub> and E<sub>2</sub> bands wherein E<sub>1</sub> bands appear at smaller wavelengths and are usually more intense, while E<sub>2</sub> bands for the same compound appear at longer wavelengths e.g. in naphthalene E<sub>1</sub> band is at 221 nm and E<sub>2</sub> band at 286 nm. The ε<sub>max</sub> values of these bands vary from 2000- 14000. The presence of auxochromic group shifts an E-band to a higher wavelength.



- Woodward-Fieser's rules for calculation of  $\lambda_{\max}$  values in conjugated systems:

- For  $\alpha, \beta$ -unsaturated aldehydes and ketones: Compounds in which C=O is conjugated with a C=C (enones) exhibit absorption band at longer wavelengths due to low energy n- $\pi^*$  (R-band) and  $\pi-\pi^*$  transitions (K-band). e.g.

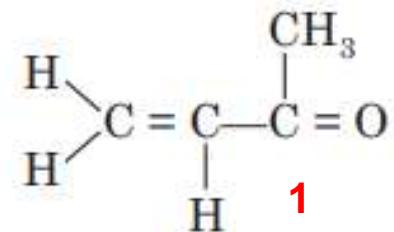


- Rules:
  - The base value of the chromophore (C=C and C=O) in an acyclic and a 6-membered ring system is assigned as 215 nm
  - For each  $\alpha$ -substituent (methyl) 10 nm is added to the base value
  - For each  $\beta$ -substituent (methyl) 12 nm is added to the base value
  - For each ring system (5 or 6 membered) to which the C=C is exocyclic (double bond outside ring), 5 nm is added to the base value
  - If the C=C and the C=O are in 5-membered ring i.e. cyclopentenone, the base value is 202 nm
- When cross conjugation i.e.  $\alpha, \beta$  –unsaturation on both sides,  $\lambda_{\max}$  is calculated by considering most highly substituted conjugated system.

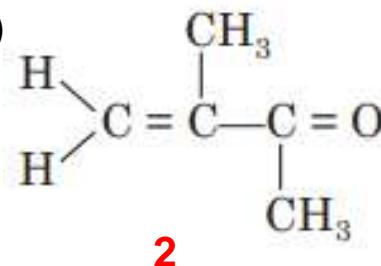


- **Examples:**

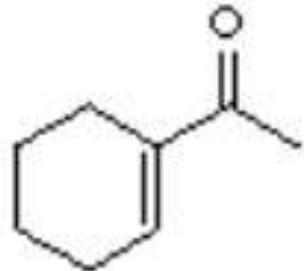
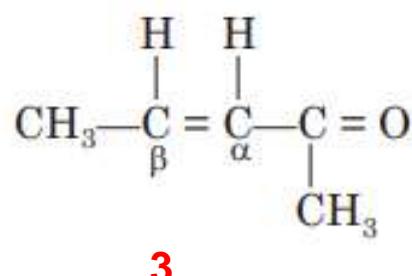
1. Methyl vinyl ketone: No  $\alpha$  and  $\beta$  substituents present, Cal  $\lambda_{\max}$ : 215 nm (Obs. : 213 nm)



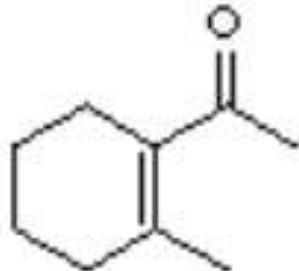
2. 2-Methyl-1-butene 3-one: one methyl at  $\alpha$ -position, Cal.  $\lambda_{\max}$ : 225 nm (Obs. : 220 nm)



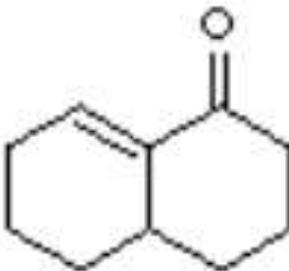
3. 3-pentene-2-one: one methyl at  $\beta$ -position, Cal.  $\lambda_{\max}$ : 227 nm (Obs. : 224 nm)



233 (13,000)  
calc: 237



245 (6,500)  
calc: 249



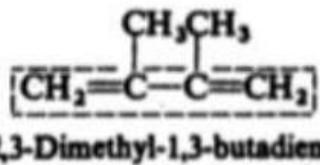
245 (5,500)  
calc: 242



## 2) Conjugated dienes (acyclic): Conjugation shifts the absorption band to higher wavelength.

e.g.  $\lambda_{\text{max}}$  for ethene, 1,3-butadiene and 1,3,5-hexatriene is 171, 217 and 258 nm, respectively

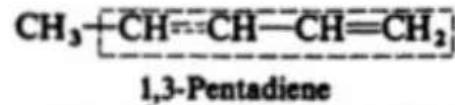
- **Rules:**
  - i. The base value for acyclic conjugated dienes and cyclic conjugated dienes containing a non-fused 6-membered ring system is 217 nm
  - ii. For each acyclic alkyl substituent 5 nm is added to the base value
  - iii. If C=C is exocyclic (double bond outside ring), 5 nm is added to the base value
  - iv. Trans-isomer absorbs at a longer wavelength due to steric effects. For effective overlap of  $\pi$ -orbitals and low  $\pi-\pi^*$  transition energy, the molecule should be coplanar. Cis-isomer adopts a non-planar conformation due to steric effects



2,3-Dimethyl-1,3-butadiene

$\lambda_{\text{max}}^{\text{calc}}$   
217 (base value, 1,3-butadiene  
+ 5 x 2 [two alkyl substituents])  
227 nm

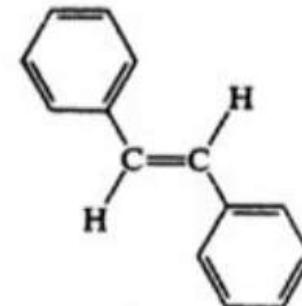
$\lambda_{\text{max}}^{\text{obs}} = 226 \text{ nm}$



1,3-Pentadiene

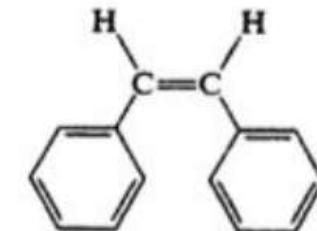
$\lambda_{\text{max}}^{\text{calc}}$   
217 (base value, 1,3-butadiene  
+ 5 (1 alkyl substituent)).  
222 nm

$\lambda_{\text{max}}^{\text{obs}} = 223 \text{ nm}$



trans-stilbene

$\lambda_{\text{max}} = 295 \text{ nm}, \epsilon = 27,000$



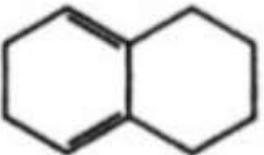
cis-stilbene

$\lambda_{\text{max}} = 280 \text{ nm}, \epsilon = 13,500$



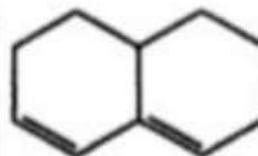
### 3) Conjugated dienes (cyclic):

- Rules:
  - i. The base value for heteroannular conjugated dienes (transoid) is 214 nm
  - ii. The base value for homoannular conjugated dienes (cisoid) is 253 nm
  - iii. For each acyclic alkyl substituent 5 nm is added to the base value
  - iv. If C=C is exocyclic (double bond outside ring), 5 nm is added to the base value



Homoannular diene  
(*cisoid* or *s-cis*)  
Less intense,  
 $\epsilon = 5,000-15,000$   
 $\lambda_{max} = 273\text{nm}$

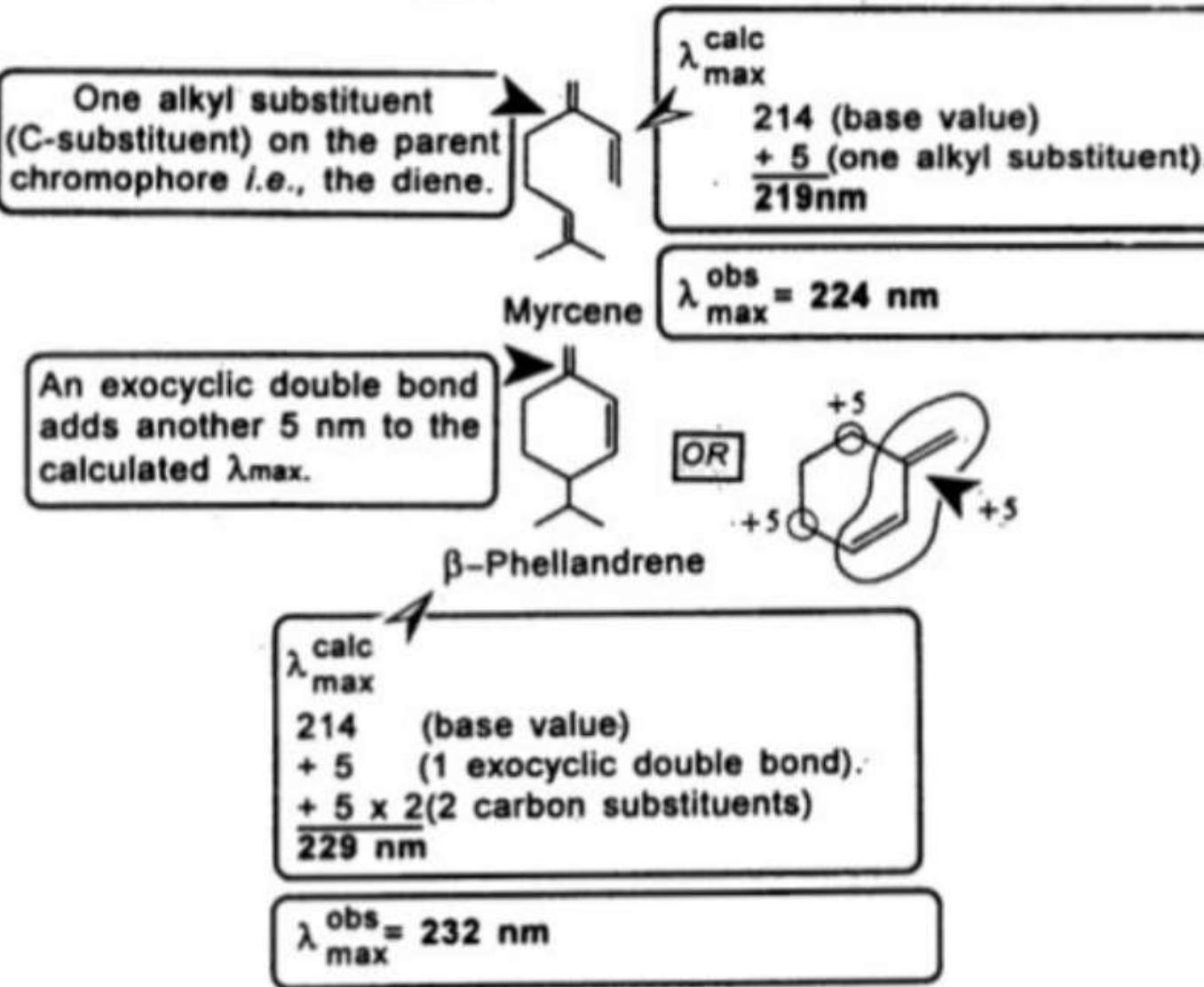
Homoannular diene is bathochromically shifted by 39nm compared to heteroannular diene.



Heteroannular diene  
(*transoid* or *s-trans*)  
More intense,  
 $\epsilon = 12,000-28,000$   
 $\lambda_{max} = 234\text{nm}$

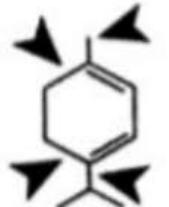


- Examples:





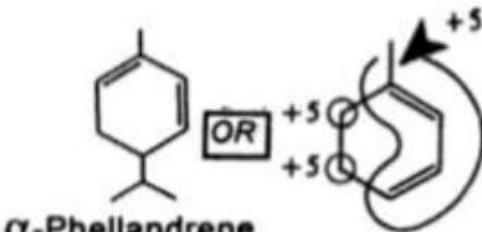
- Examples:



$\alpha$ -Terpinene

$\lambda_{\text{max}}^{\text{calc}}$   
 253 (base value)  
 homoannular diene  
 $+ 5 \times 4$  (4 alkyl substituents)  
 273 nm

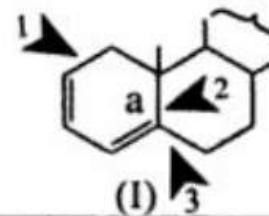
$\lambda_{\text{max}}^{\text{obs}} = 265 \text{ nm}$



$\alpha$ -Phellandrene

$\lambda_{\text{max}}^{\text{calc}}$   
 253 (base value)  
 homoannular diene  
 $+ 5 \times 3$  (3 alkyl substituents)  
 268 nm

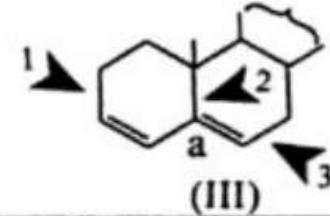
$\lambda_{\text{max}}^{\text{obs}} = 263 \text{ nm}$



(I)

$\lambda_{\text{max}}^{\text{calc}}$   
 253 (base value)  
 homoannular diene  
 $+ 15$  (3 ring residues, 1,2,3,  
*i.e.*, alkyl substituents).  
 $+ 5$  (1 exocyclic double bond, a)  
 273 nm

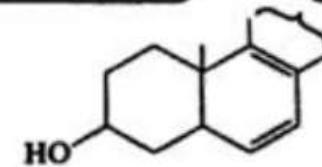
$\lambda_{\text{max}}^{\text{obs}} = 275 \text{ nm}$



(III)

$\lambda_{\text{max}}^{\text{calc}}$   
 214 (base value)  
 heteroannular diene  
 $+ 15$  (3 ring residues, 1,2,3,  
*i.e.*, alkyl substituents).  
 $+ 5$  (1 exocyclic double bond, a)  
 234 nm

$\lambda_{\text{max}}^{\text{obs}} = 235 \text{ nm}$



(II)

No exocyclic double bond  
 (the diene has four alkyl substituents.  
 $\lambda_{\text{max}}^{\text{calc}} = 273 \text{ nm}$ ;  $\lambda_{\text{max}}^{\text{obs}} = 275 \text{ nm}$ ;



- **Applications of UV-Vis spectroscopy in analytical chemistry:**
- **Qualitative analysis:**
  - Detection of functional groups
  - Extent of conjugation
  - Identification of unknown compound
  - Detection of impurities
- **Quantitative analysis:** Determination of unknown concentration of a given sample using Beer-Lambert's Law



- **Beer-Lambert's Law:**

➤ When the monochromatic radiation passes through a sample containing an absorbing species, the radiant power of a beam is progressively decreased as more energy is absorbed by the particles of that species. The decrease in power is expressed by

- 1) Lambert's law
- 2) Beer's law (or) Beer - Lambert's law

➤  $I_{\text{absorbed}} = I_0 - I_t$

where,  $I_0$  = intensity of incident light

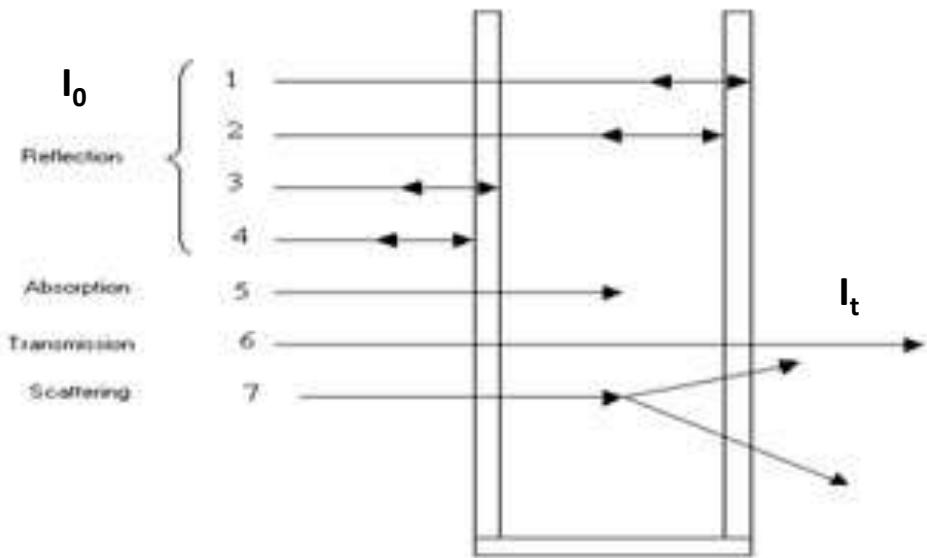
$I_t$  = intensity of transmitted light

The transmittance (T) is given :

$$T = I_t / I_0$$

$$\text{and } \%T = 100 I_t / I_0$$

➤ Transmittance is defined as the amount of light that "successfully" passes through the substance and comes out from the other side



**Reduction of the intensity of light by reflection, absorption, scattering**



• **Lambert's Law:**

- It states that “when a beam of monochromatic radiation is passed through a homogeneous absorbing medium, the rate of decrease of intensity of the radiation ‘ $dl$ ’ with thickness or path length of absorbing medium ‘ $dl$ ’ is proportional to the intensity of the incident radiation ‘ $I$ ’ ”.

$$-dl/dl = kl \quad \dots\dots\dots (1)$$

On integrating the equation (1), between the limits  $I = I_0$  at  $l = 0$  and  $I = I_t$  at  $l = l$ , we get

$$\int_0^l \frac{dI}{I} = - \int_0^l k dl \quad \dots\dots\dots (2)$$

where,  $k$  = absorption coefficient

i.e.,

$$\ln \frac{I}{I_0} = -k l$$

or,  $\log \frac{I_0}{I_t} = \frac{k_1 l}{2.303} \quad \dots\dots\dots (3)$  This is called Lambert's law

where  $\log \frac{I_0}{I_t}$  is called **Absorbance or optical density**

- Absorbance is reciprocal of transmittance

$$A = \log_{10} \frac{I_0}{I_t} = \log_{10} \left( \frac{1}{T} \right) = -\log_{10} T = 2 - \log (\% T).$$



- **Beer's Law:**

It states that “when the monochromatic radiation passes through a sample containing an absorbing species, the decrease in the radiant power of a beam is directly proportional to the concentration (C) of the sample”.

$$\frac{\log \frac{I_0}{I_t}}{2.303} = k_1 C \quad \dots \dots \dots (4)$$

This is called Beer's law

- **Beer- Lambert's Law:** When a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation ‘dl’ with thickness or path length of the absorbing solution ‘dl’ is proportional to the intensity of the incident radiation ‘l’ as well as the concentration of the solution ‘C’.

On combining equations (3) and (4)

$$\frac{A = \log \frac{I_0}{I_t}}{2.303} = k C l$$

or,  $A = \epsilon C l$  .....(5) This is called Beer-Lambert's law

where  $\epsilon = k / 2.303$  is known as molar absorptivity coefficient

- The larger the molar absorptivity, the more probable the electronic transition. In uv spectroscopy, the concentration of the sample solution is measured in mol L<sup>-1</sup> and the length of the light path in cm. Thus, given that absorbance is unitless, the units of molar absorptivity are L mol<sup>-1</sup> cm<sup>-1</sup>



- **Applications of Beer- Lambert's Law:** It can be used to determine the unknown concentration of a solution.
- A standard solution of known concentration  $C_s$  is first taken and it's absorbance  $A_s$  is measured. Then according to Beer-Lambert's law:

$$\frac{A_s}{C_s} = \epsilon x \quad \dots\dots\dots(1)$$

Let  $C_u$  be the unknown concentration of the solution which is to be determined. The absorbance  $A_u$  of the given solution is measured.

$$\frac{A_u}{C_u} = \epsilon x \quad \dots\dots\dots(2)$$

From equation (1) and (2), we get

$$\begin{aligned} \frac{A_s}{C_s} &= \frac{A_u}{C_u} \\ \Rightarrow C_u &= \frac{A_u}{A_s} \times C_s \quad \dots\dots\dots(3) \end{aligned}$$

We already know the concentration of standard solution  $C_s$  and the absorbance  $A_u$  and  $A_s$  were experimentally measured and hence the unknown concentration  $C_u$  can be calculated from the equation (3).



- **Limitations of Beer- Lambert's Law:**
- This law can be used only for
  - i. dilute solution.
  - ii. monochromatic radiation.
  - iii. the system maintained at constant temperature.
- **Specific Absorbance:** When absorbance is measured for 1% (w/v) solution in a 1 cm cell, then the equation takes the form:

$$A = A^{1\%}_{1\text{cm}} \cdot C \cdot l$$

where,  $A^{1\%}_{1\text{cm}}$  is known as specific absorbance

- **Colorimetric analysis:** It is also based on Beer-Lambert's law. Here, the visible light is used to analyze colored samples



- **Solved Examples:**

**Question 1:** The solution of concentration of  $2.5 \times 10^{-4}$  M has the percentage transmittance of 25% in a 1 cm cell.

Determine            i) the absorbance (A) and ii) the molar absorption coefficient ( $\epsilon$ ).

**Solution :** Given : % T = 25% (or) 0.25, C =  $2.5 \times 10^{-4}$  M ; l = 1 cm

i) Absorbance :  $A = -\log T = -\log 0.25 = 0.6021$

ii) The molar absorption coefficient,  $\epsilon = A / C l$

$$\begin{aligned} &= 0.6021 / 2.5 \times 10^{-4} \\ &= 2408 \end{aligned}$$

**Question 2:** A solution of thickness 2 cm transmits 40% incident light. Calculate the concentration of the solution given that  $\epsilon = 6000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ .

**Solution :** Given : % T = 40% (or) 0.40,  $\epsilon = 6000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ; l = 2 cm

i) Absorbance :  $A = -\log T = -\log 0.40 = 0.3980$

ii) The molar absorption coefficient,  $C = A / \epsilon l$

$$\begin{aligned} &= 0.3980 / 6000 \times 2 \\ &= 3.316 \times 10^{-5} \text{ mol dm}^{-3} \end{aligned}$$



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Engineering Chemistry-II (BS-104)

# Spectroscopic Techniques-II

**Dr. Shruti Khanna Ahuja**

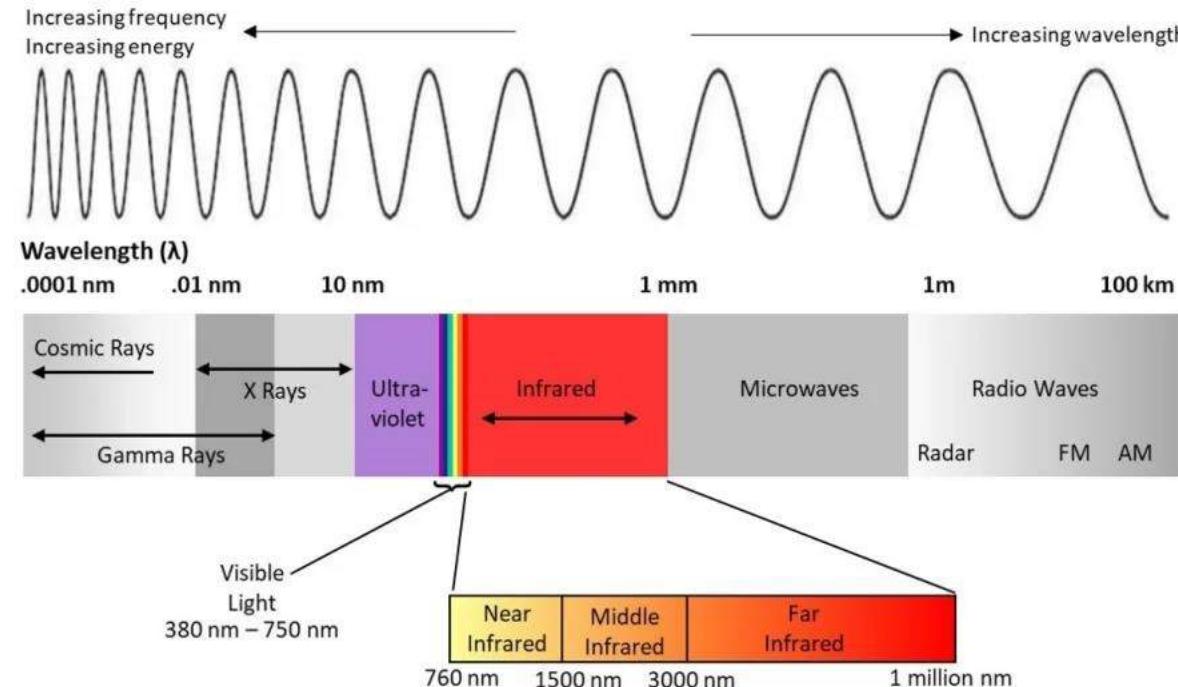
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## 2. INFRA-RED (IR) SPECTROSCOPY

- IR spectroscopy deals with the infrared region of the electromagnetic spectrum, i.e. light having a longer wavelength and a lower frequency than visible light.
- It generally refers to the analysis of the interaction of a molecule with infrared light (low energy).
- IR Spectroscopy detects frequencies of infrared light that are absorbed by a molecule. Molecules tend to absorb these specific frequencies of light since they correspond to the frequency of the vibration of bonds in the molecule.
- The absorption peaks within this region are usually sharper when compared with absorption peaks from the ultraviolet and visible regions. It is therefore one of the most widely used and sensitive tools for the detection of functional groups within a sample since different functional group absorbs different particular frequency of IR radiation.
- IR radiations does not have sufficient energy to cause the excitation of electrons, however, it causes atoms and group of atoms of organic compounds to vibrate faster about the covalent bonds which connect them.

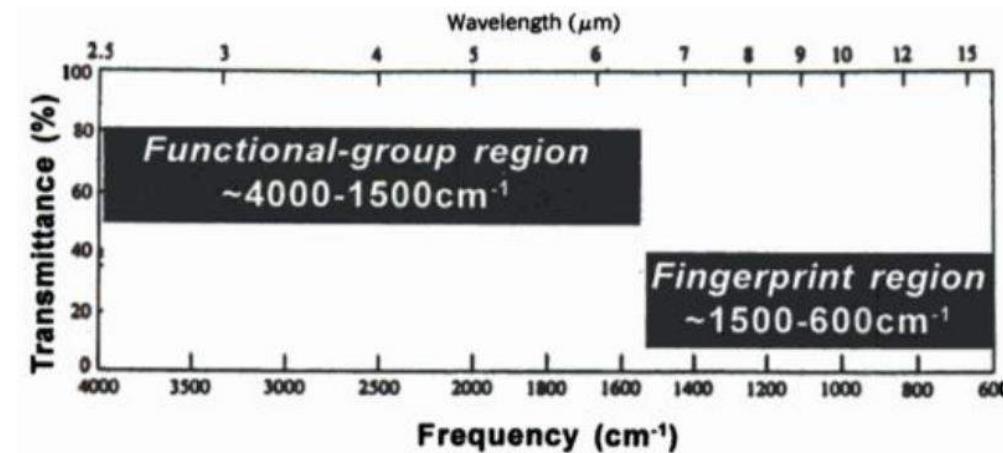
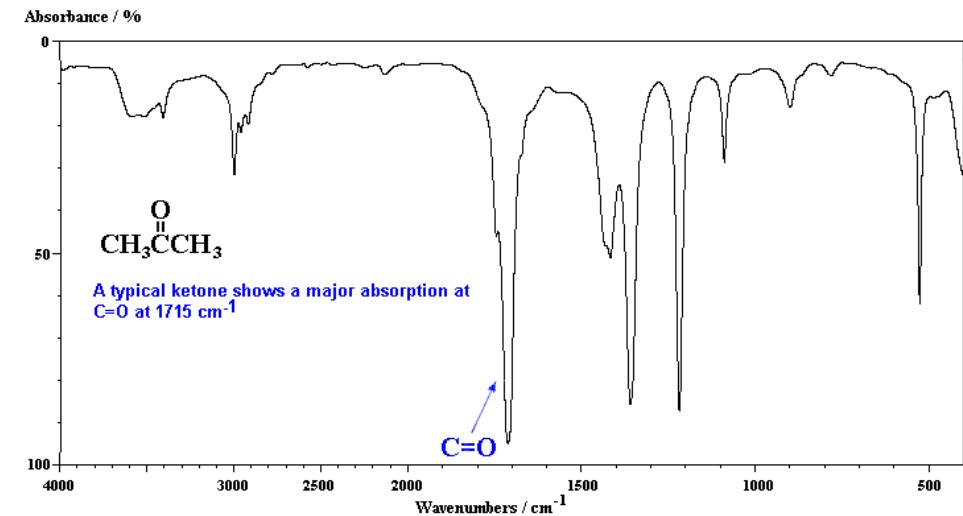




- The position of IR band is specified in frequency units by its wavenumber ( $\bar{\nu}$ ) measured as reciprocal of centimeter ( $\text{cm}^{-1}$ ).

$$\bar{\nu} = 1/\lambda \quad (\bar{\nu} = v/c, \text{ where } c = \text{velocity of light and } v = \text{freq. in Hz})$$

- In an infra-red spectrophotometer, IR radiations of successively increasing wavelength is passed through the sample and percentage transmittance is measured. IR spectrum shows percent transmittance vs frequency expressed as wavenumber. Each dip in a spectrum is called a band or a peak representing absorption of IR radiation by the sample at that frequency. A 100% transmittance means no absorption and if all the radiation is absorbed, the transmittance is 0%
- Most of the bands that indicate what functional group is present are found in the region from  $4000 \text{ cm}^{-1}$  to  $1300 \text{ cm}^{-1}$ . Their bands can be identified and used to determine the functional group of an unknown compound.
- Bands that are unique to each molecule, similar to a fingerprint, are found in the fingerprint region, from  $1300 \text{ cm}^{-1}$  to  $400 \text{ cm}^{-1}$ . These bands are only used to compare the spectra of one compound to another.

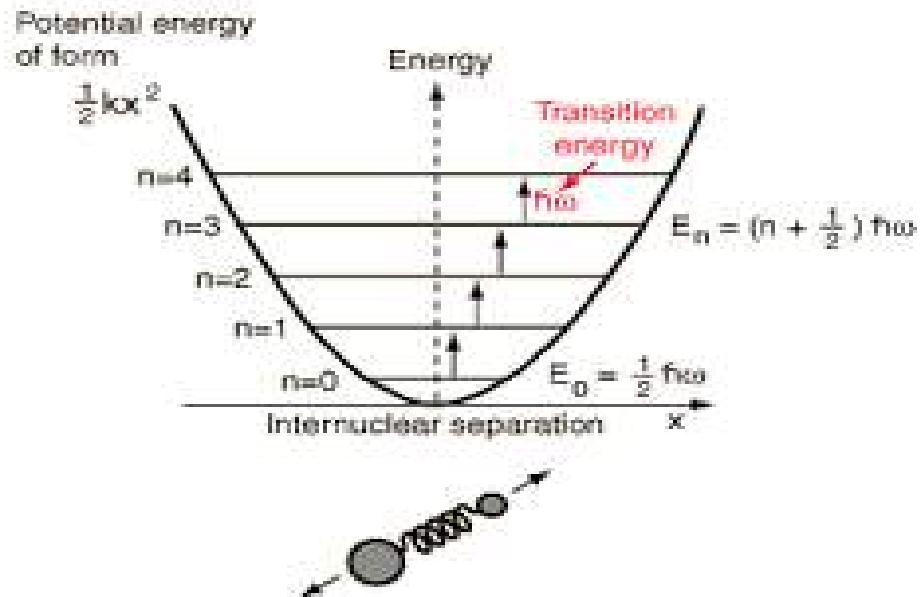
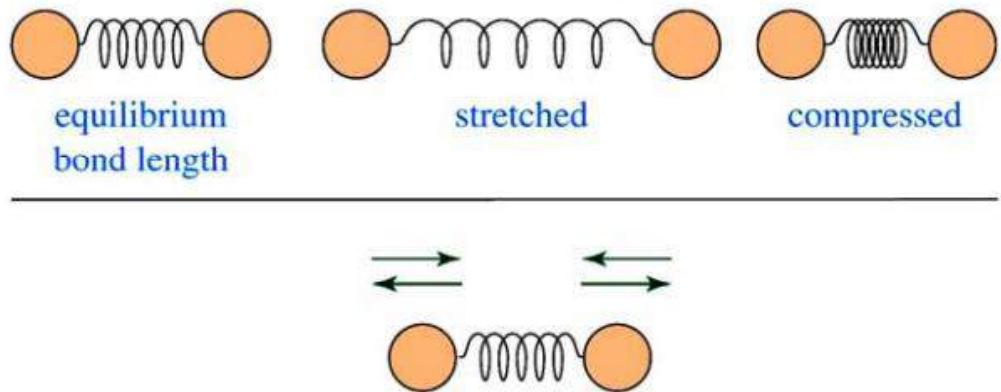




### • MOLECULAR VIBRATIONS:

- Atoms in a molecule do not remain at fixed positions w.r.t each other, but actually vibrate back and forth about an average value of interatomic distance. This vibrational motion is quantized.
- Infrared radiation is largely thermal energy. It induces stronger molecular vibrations in covalent bonds, which can be viewed as springs holding together two masses, or atoms.

Specific bonds respond to (absorb) specific frequencies

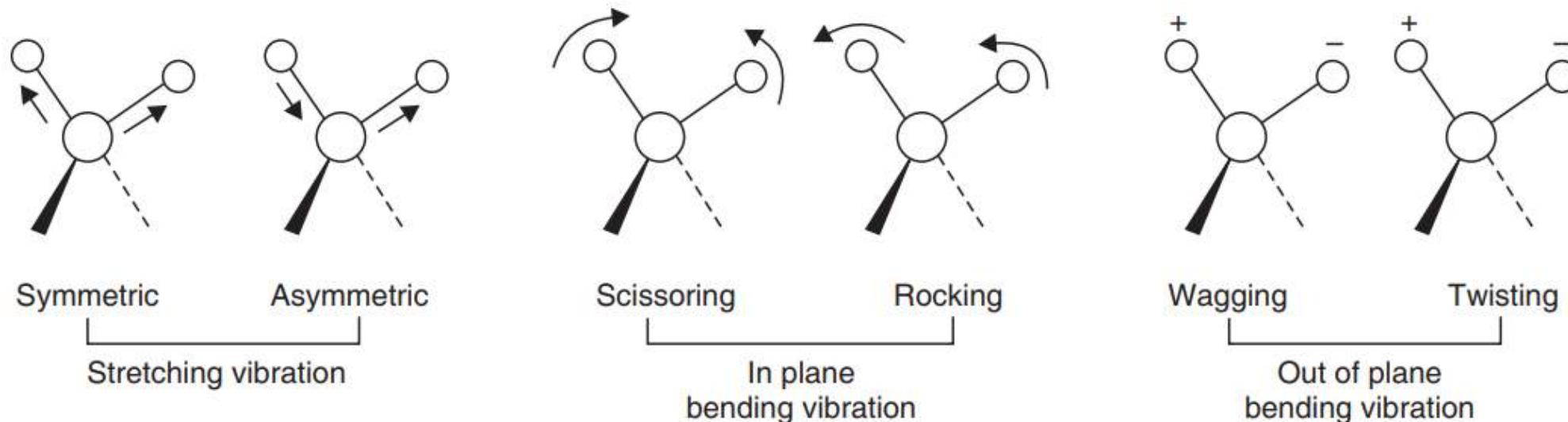


Vibrational levels for a vibrating bond

- More energy is required to stretch the spring than bending it. Thus, stretching energy is greater than the bending energy and stretching absorptions of a bond appear at higher frequencies in the IR spectrum than the bending absorption of the same bond



- **Vibrational modes:**
- The bond of a molecule experiences various types of vibrations and rotations. This causes the atom not to be stationary and to fluctuate continuously. Vibrational motions are defined by stretching and bending modes. These movements are easily defined for diatomic or triatomic molecules. This is not the case for large molecules due to several vibrational motions and interactions that will be experienced.
- When there is a continuous change in the interatomic distance along the axis of the bond between two atoms, this process is known as a **stretching vibration**. A change in the angle occurring between two bonds is known as a **bending vibration**. Four bending vibrations exist namely, wagging, twisting, rocking and scissoring.



Modes of vibration of the atoms in a molecule



- **Calculation of vibrational frequencies: using Hooke's law**

- It states that:

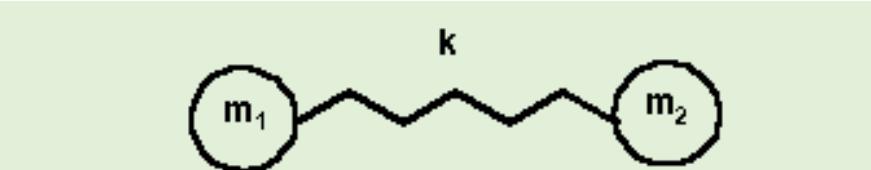
- the vibrational frequency is proportional to the strength of the spring; the stronger the spring, the higher the frequency.
- the vibrational frequency is inversely proportional to the masses at the ends of the spring; the lighter the weights, the higher the frequency.

- It implies that:

- stronger bonds absorb at higher frequencies.
- weaker bonds absorb at lower frequencies.
- bonds between lighter atoms absorb at higher frequencies.
- bonds between heavier atoms absorb at lower frequencies.

- Examples:

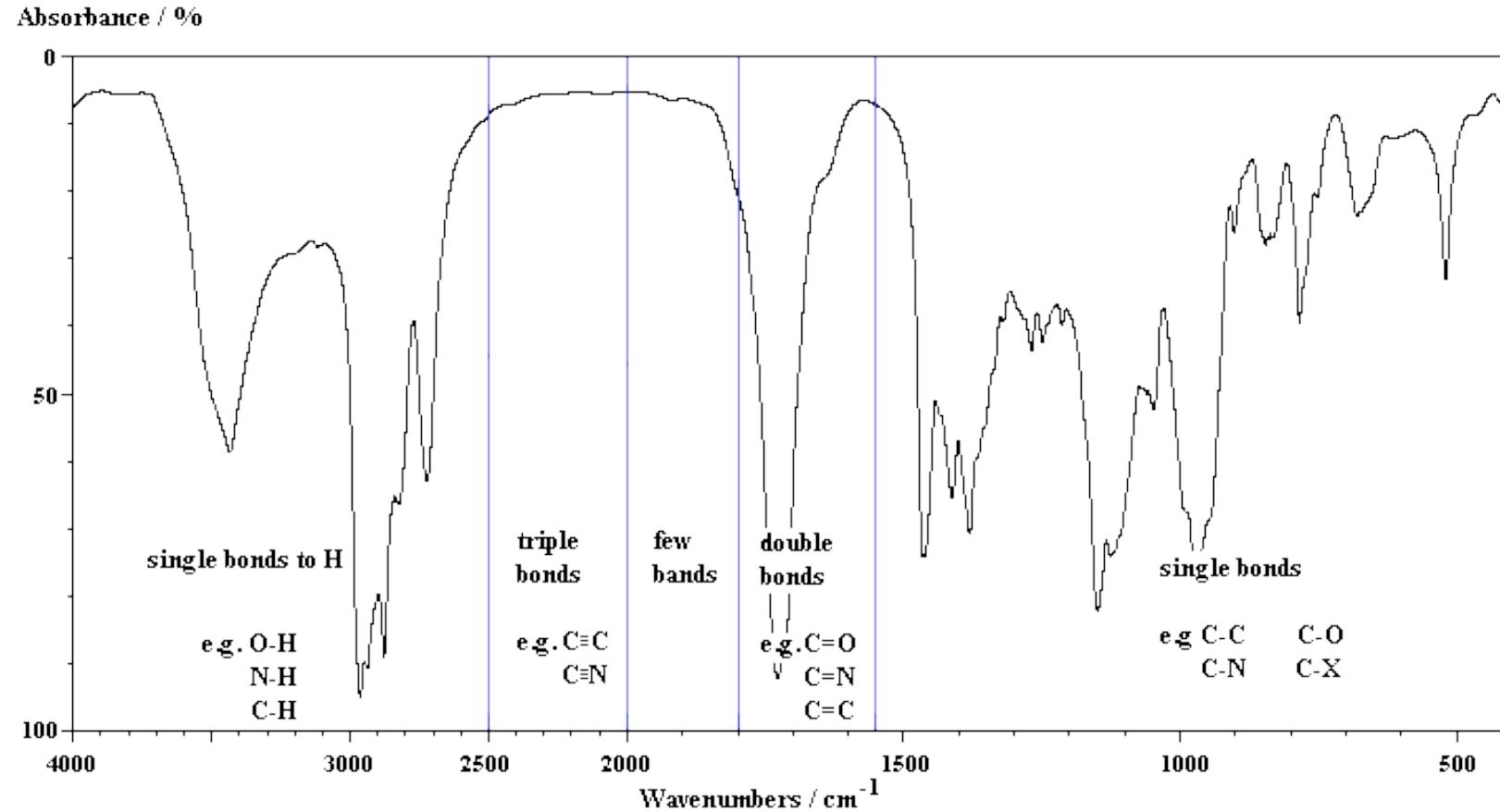
- in order of increasing bond strength, **CC bonds**: C-C ( $1000\text{ cm}^{-1}$ ), C=C ( $1600\text{ cm}^{-1}$ ) and C≡C ( $2200\text{ cm}^{-1}$ )  
**CH bonds**: C-C-H ( $2900\text{ cm}^{-1}$ ), C=C-H ( $3100\text{ cm}^{-1}$ ) and C≡C-H ( $3300\text{ cm}^{-1}$ )
- in order of increasing reduced mass, C-H ( $3000\text{ cm}^{-1}$ ), C-C ( $1000\text{ cm}^{-1}$ ), C-Cl ( $800\text{ cm}^{-1}$ ), C-Br ( $550\text{ cm}^{-1}$ ), C-I ( $\sim 500\text{ cm}^{-1}$ )


$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$
$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$\bar{v}$  = wavenumber ( $\text{cm}^{-1}$ ) corresponding to vibrational frequency of the bond  
 $c$  = velocity of light  
 $K$  = force constant of the bond (related to strength of the spring)  
 $\mu$  = reduced mass  
 $m_1$  and  $m_2$  = masses of two atoms



- The following diagram reflects some of the trends that can be accounted for using Hooke's Law. It also gives an approximate outline of where specific types of bond stretches may be found.



- The reasons explaining why C-H bending vibrations are at lower frequency than C-H stretching vibrations are also related to Hooke's Law:

- A H-C-H bending vibration involves three atoms, not just two, so the mass involved is greater than in a C-H stretch. That means lower frequency.
- Also, it turns out that the "stiffness" of a bond angle (analogous to the strength of a spring) is less than the "stiffness" of a bond length. Both factors lead to a lower bending frequency.

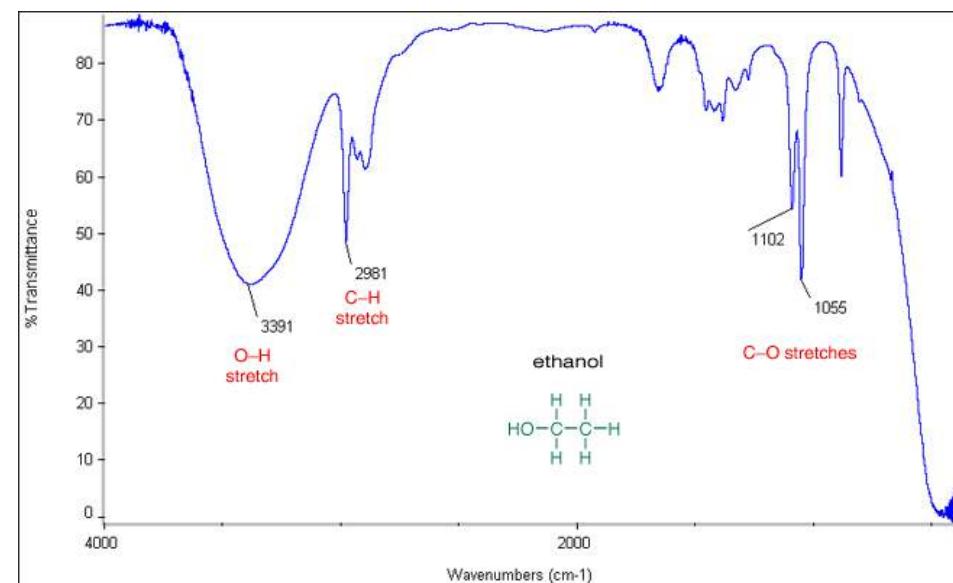
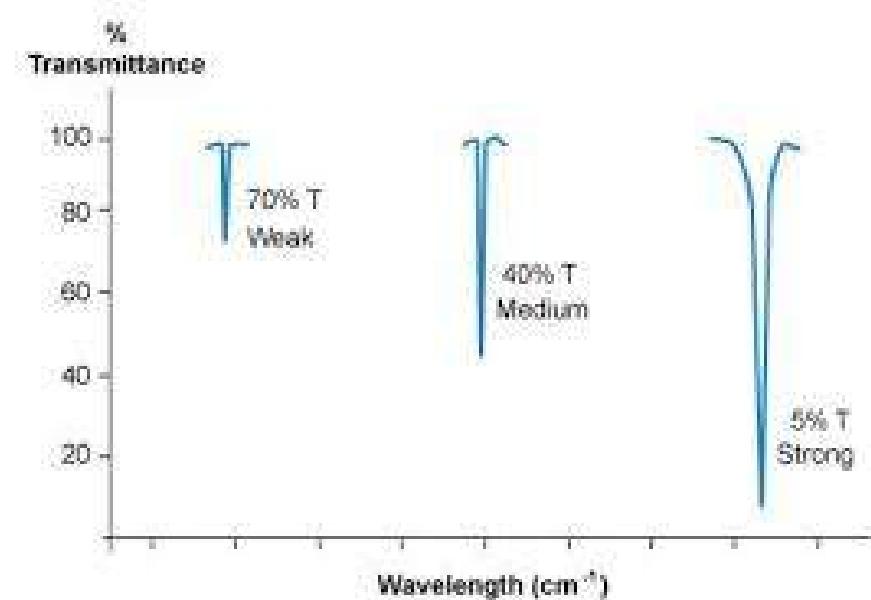


- **Classification of IR Bands:**

- IR bands can be classified as **strong (s), medium (m), or weak (w)**, depending on their relative intensities in the infrared spectrum. A strong band covers most of the y-axis. A medium band falls to about half of the y-axis, and a weak band falls to about one third or less of the y-axis.

- **Infrared Band Shapes:**

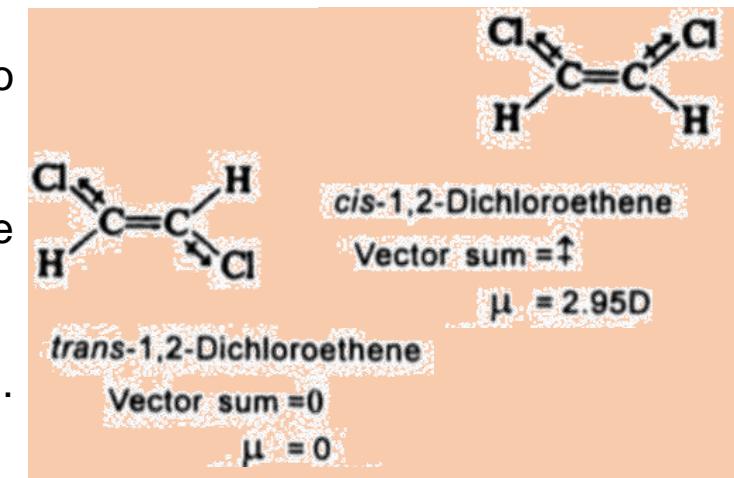
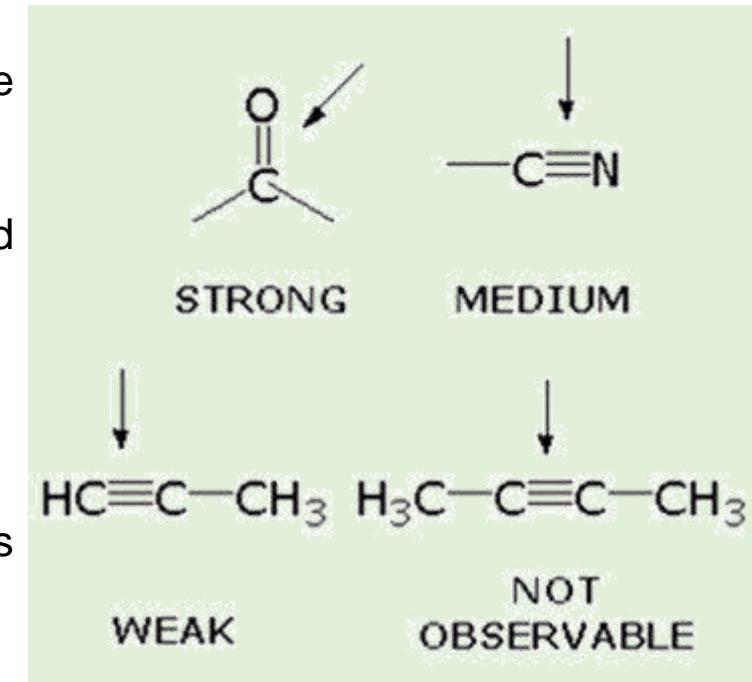
- Infrared band shapes come in various forms. Two of the most common are **narrow and broad**. Narrow bands are thin and pointed, like a dagger. Broad bands are wide and smoother.
- A typical example of a broad band is that displayed by O-H bonds, such as those found in alcohols and carboxylic acids. The broad shape of the absorption band results from the hydrogen bonding of the OH groups between molecules. The OH bond of alcohol group usually has absorption in the range of 3200-3600 cm<sup>-1</sup>, while the OH bond of carboxylic acid group occurs at about 2500-3300 cm<sup>-1</sup>.





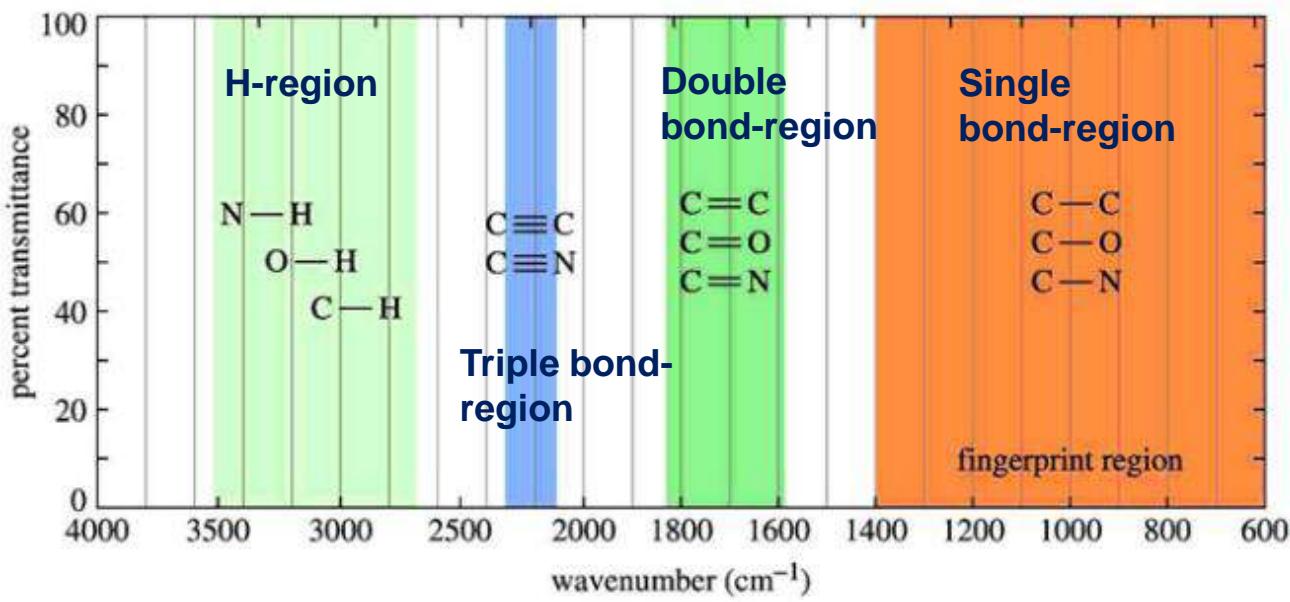
- **IR active bonds:**

- Not all covalent bonds display bands in the IR spectrum. Only polar bonds do so. These are referred to as IR active.
- The intensity of the bands depends on the magnitude of the dipole moment associated with the bond in question:
  - Strongly polar bonds such as carbonyl groups ( $\text{C}=\text{O}$ ) produce strong bands.
  - Medium polarity bonds and asymmetric bonds produce medium bands.
  - Weakly polar bond and symmetric bonds such as  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$  molecules produce weak or non observable bands.
- C-C bonds are usually nonpolar and usually do not show up as peaks in the IR spectrum.
- C-H bonds are not very polar and do not give rise to strong peaks in the IR spectrum.
- A whole lot of small C-H peaks can add up together to look like one big peak owing to many C-H bonds in a molecule.
- In general, molecular vibrations which will lead to change in dipole moment of the molecule will give rise to absorption bands in the IR spectrum.
- trans-dichloroethylene shows no  $\text{C}=\text{C}$  stretching, whereas cis-isomer shows this band. However, both the isomers will show bands for C-H and C-Cl stretchings.

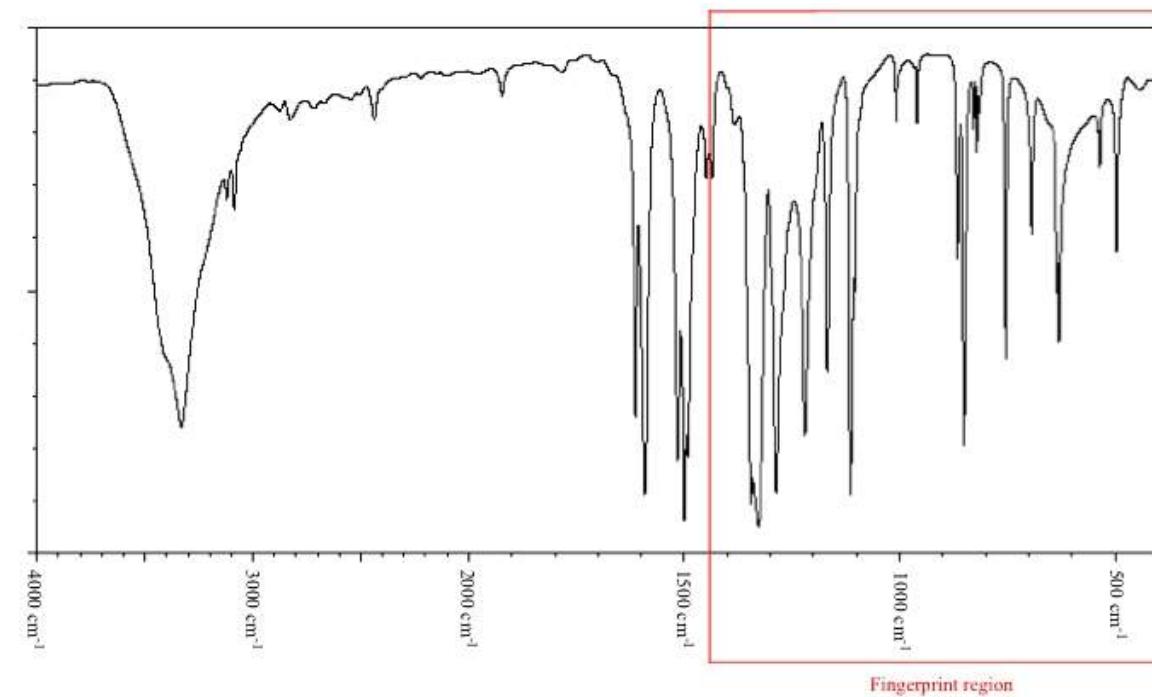




- **IR absorption range:**
- The typical IR absorption range for covalent bonds is 600-4000 cm<sup>-1</sup>. The graph shows the regions of the spectrum where the following types of bonds normally absorb. For example, a sharp band around 2200-2400 cm<sup>-1</sup> would indicate the possible presence of a C-N or a C-C triple bond.



- **The Fingerprint region:**
- Although the entire IR spectrum can be used as a fingerprint for the purposes of comparing molecules, the 600 - 1400 cm<sup>-1</sup> range is called the fingerprint region.
- This is normally a complex area showing many bands, frequently overlapping each other.





- Characteristic IR Frequencies of Stretching Vibrations:

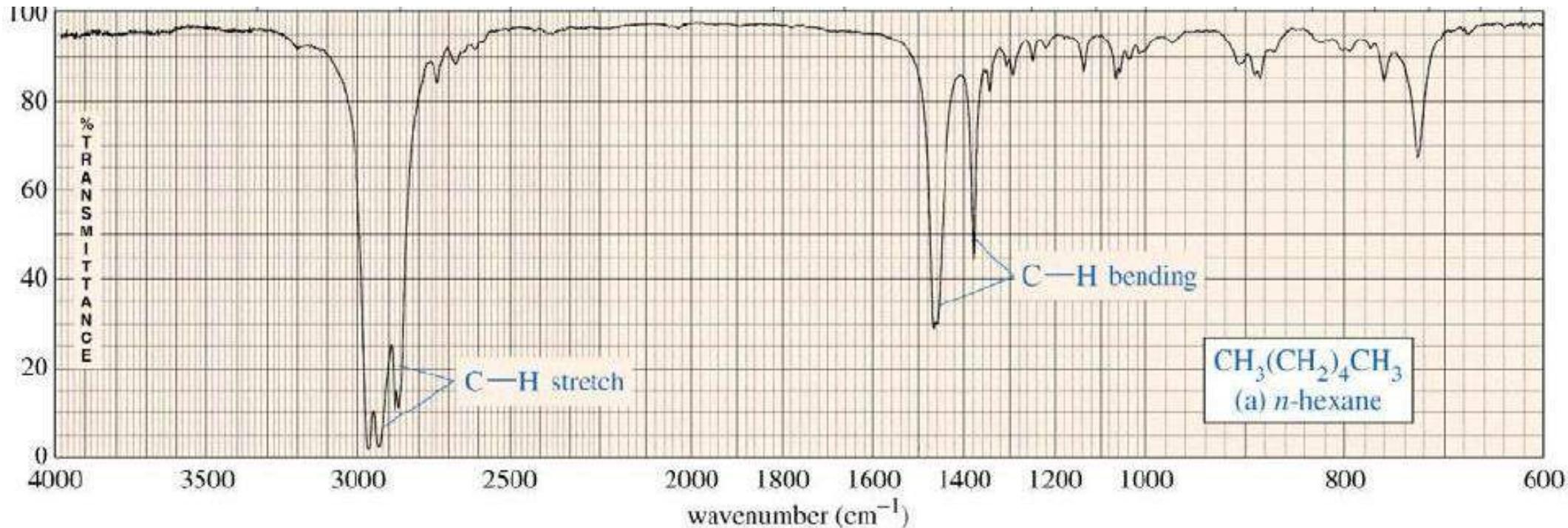
Formula	Bond	Characteristic IR Frequency range ( $\text{cm}^{-1}$ )
alcohol	O-H stretching	3200 – 3600 (broad)
carbonyl	C=O stretching	1650 – 1750 (strong)
aldehyde	C-H stretching	~ 2800 and ~ 2700 (medium)
carboxylic acid	C=O stretching	1700 – 1725 (strong)
	O-H stretching	2500 – 3300 (broad)
alkene	C=C stretching	1620 – 1680 (weak)
	vinyl =C-H stretching	3020 – 3080
benzene	C=C stretching	~ 1600 and 1500 – 1430 (strong to weak)
alkyne	C≡C stretching	2100 – 2250 (weak)
	terminal ≡C-H stretching	3250 – 3350
alkane	C-H stretching	2850-2950
amine	N-H stretching	3300-3500 (medium)

- The **C-H bond** stretching of all hydrocarbons occur in the range of **2800-3300  $\text{cm}^{-1}$** , and the exact location can be used to distinguish between alkane, alkene and alkyne. Specifically:
  - **≡C-H (sp C-H)** bond of terminal alkyne give absorption at about **3300  $\text{cm}^{-1}$**
  - **=C-H (sp<sup>2</sup> C-H)** bond of alkene give absorption at about **3000-3100  $\text{cm}^{-1}$**
  - **-C-H (sp<sup>3</sup> C-H)** bond of alkane give absorption at about **~2900  $\text{cm}^{-1}$**



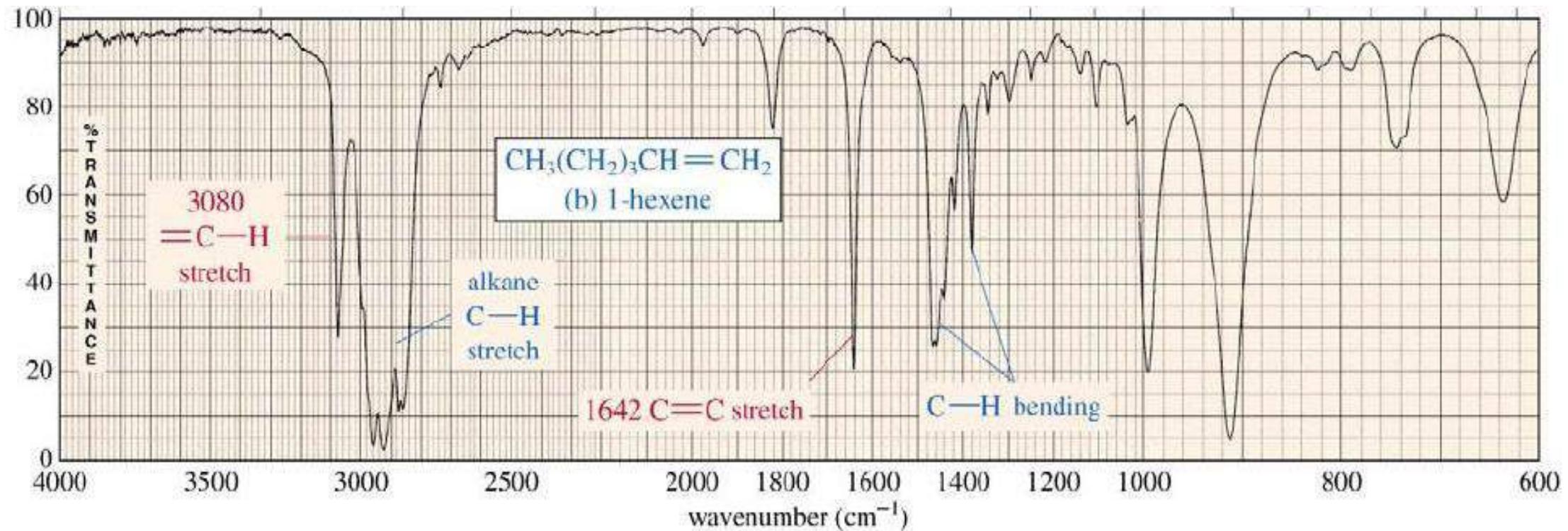
- **IR spectrum of alkanes:**

- Alkanes have no functional groups. Their IR spectrum displays **only C-C and C-H bond vibrations**. Of these the most useful are the **C-H stretching absorption bands** (present in both  $\text{CH}_3$  and  $\text{CH}_2$  groups), which appear around  $2925 \text{ cm}^{-1}$ .



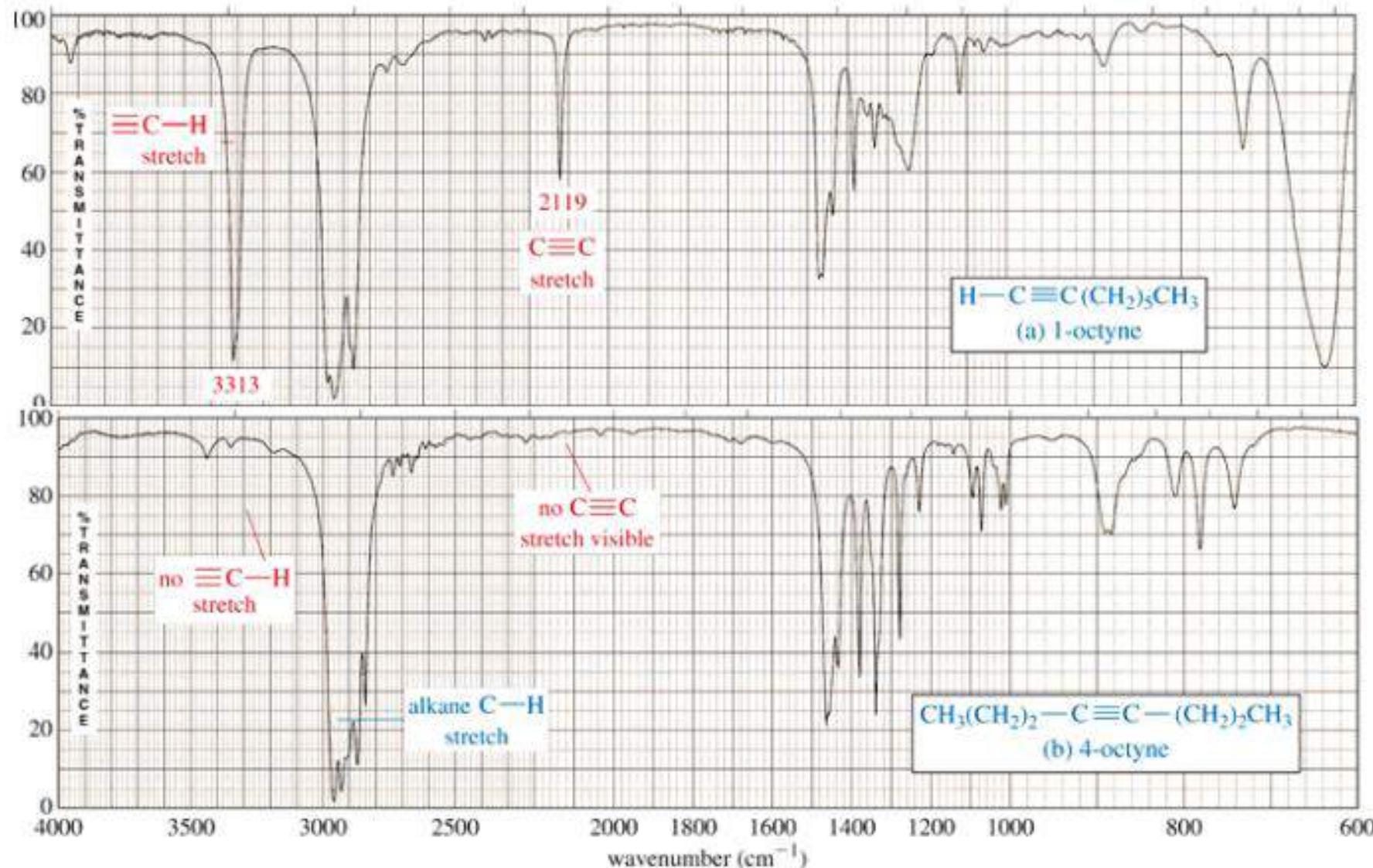


- **IR spectrum of alkenes:**
- Besides the presence of C-H bonds, **alkenes also show sharp, medium bands corresponding to the C=C bond stretching vibration at about 1600-1700 cm<sup>-1</sup>.** They also show a band for the **=C-H bond stretch**, appearing around **3080 cm<sup>-1</sup>**.



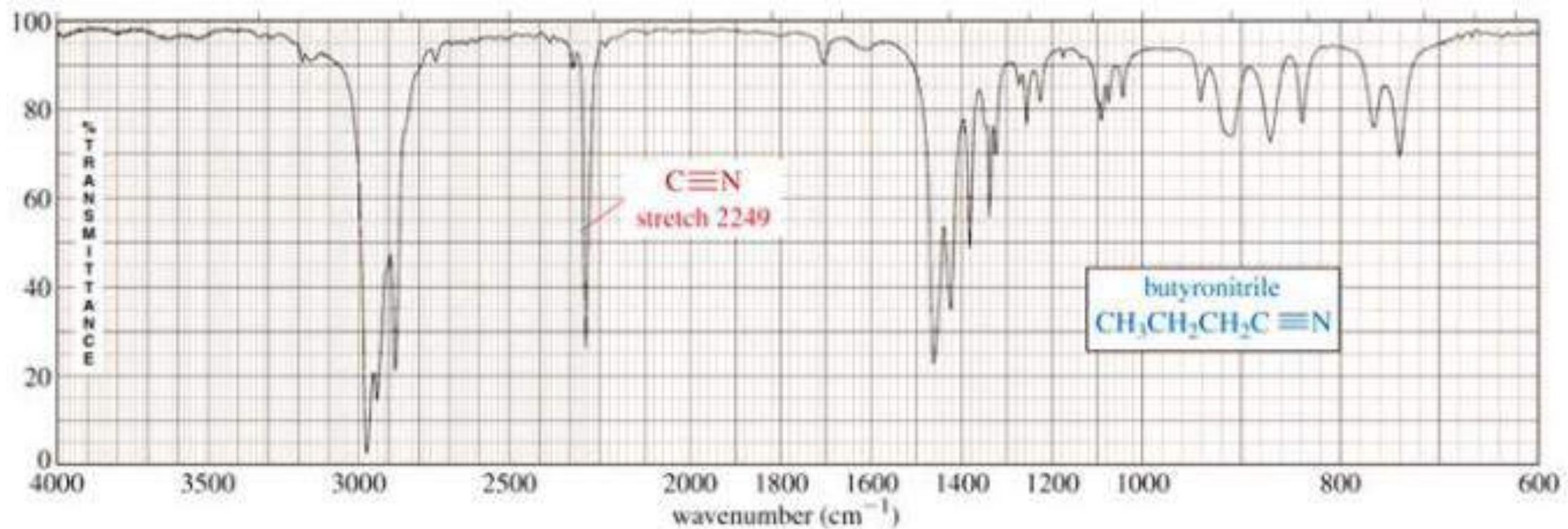


- **IR spectrum of alkynes:**
- The most prominent band in alkynes corresponds to the **carbon-carbon triple bond**. It shows as a **sharp, weak band at about  $2100\text{ cm}^{-1}$** . The reason it's weak is because the triple bond is not very polar. In some cases, such as in highly symmetrical alkynes, it may not show at all due to the low polarity of the triple bond associated with those alkynes.
- **Terminal alkynes**, that is to say those where the triple bond is at the end of a carbon chain, have C-H bonds involving the sp carbon (the carbon that forms part of the triple bond). Therefore they may also show a sharp, weak band at about  **$3300\text{ cm}^{-1}$**  corresponding to the **C-H stretch**.
- **Internal alkynes**, that is those where the triple bond is in the middle of a carbon chain, do not have C-H bonds to the sp carbon and therefore lack the aforementioned band.
- For example, a comparison between an unsymmetrical terminal alkyne (1-octyne) and a symmetrical internal alkyne (4-octyne).



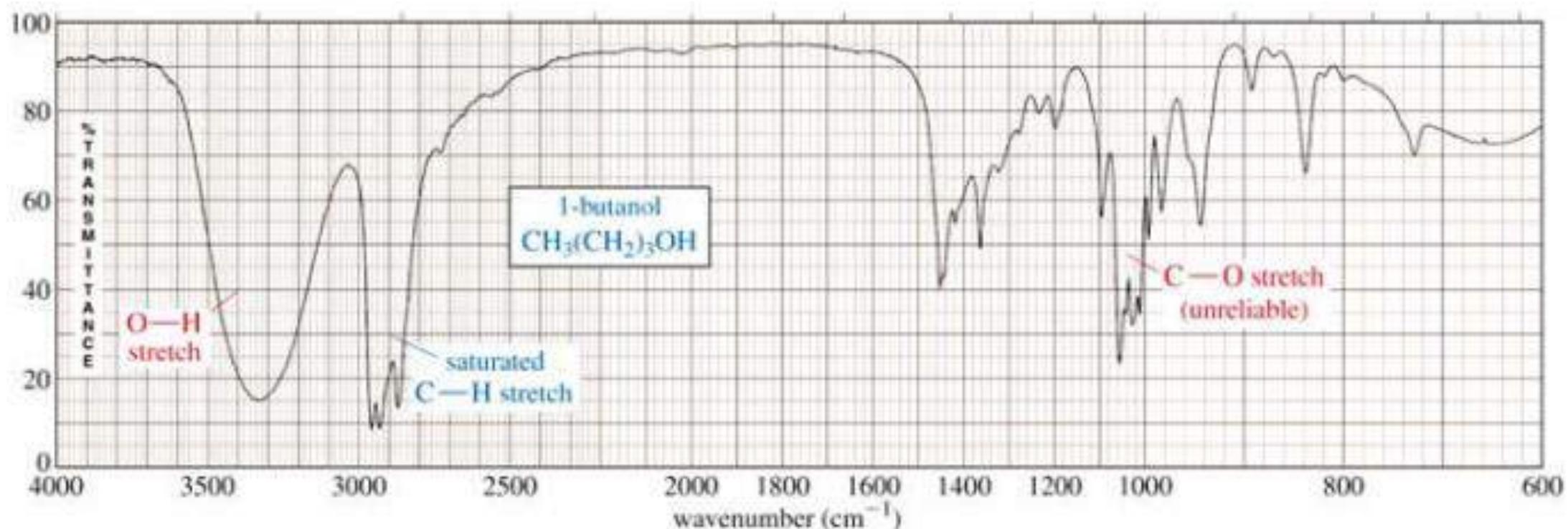


- **IR spectrum of nitriles:**
- Similar to alkynes, nitriles show a **prominent band around  $2250\text{ cm}^{-1}$**  caused by the **CN triple bond**. This band has a sharp, pointed shape just like the alkyne C-C triple bond, **but because the CN triple bond is more polar, this band is stronger than in alkynes.**



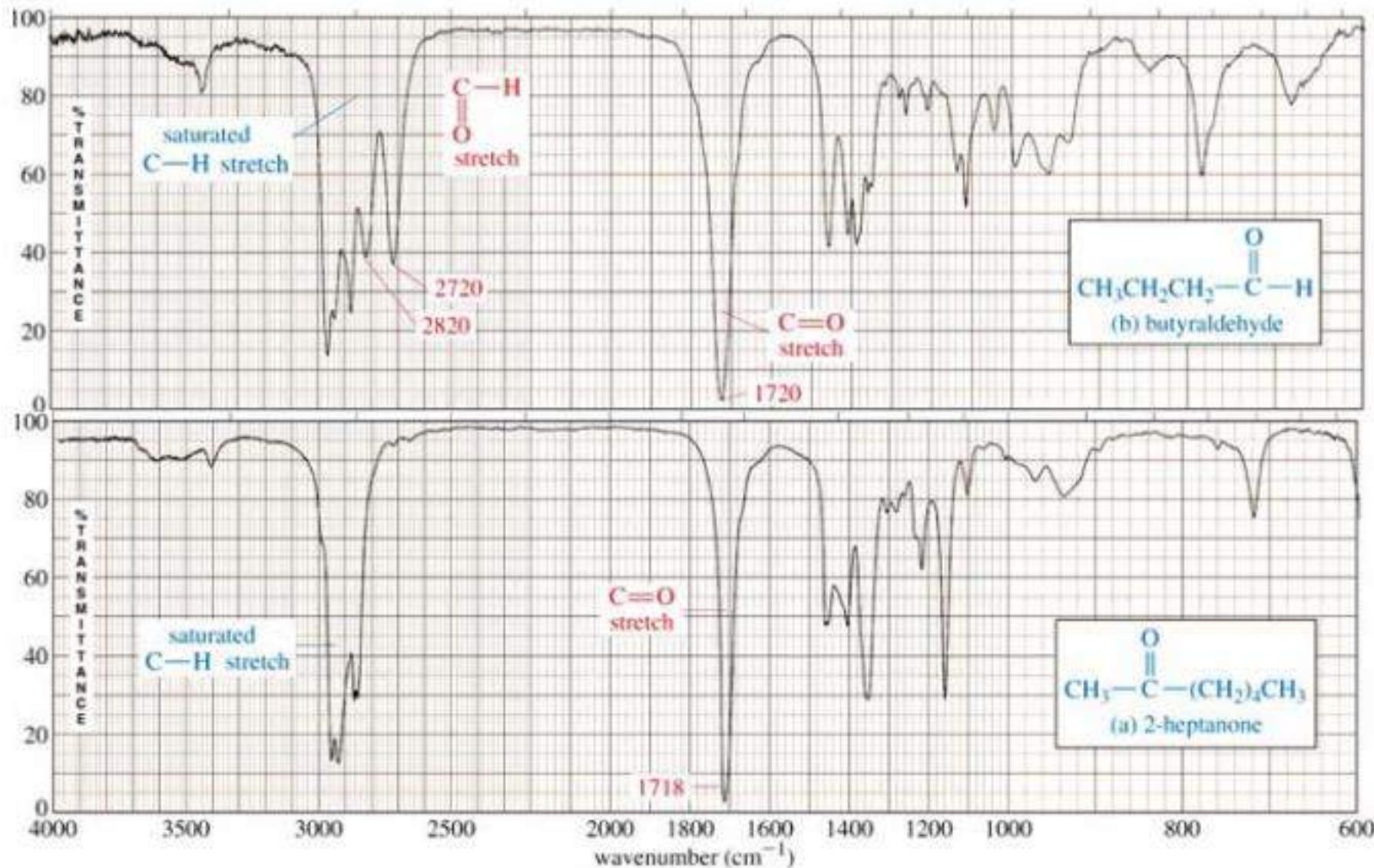


- **IR spectrum of alcohols:**
- The most **prominent band** in alcohols is due to the O-H bond, and it appears as a **strong, broad band** covering the range of **about 3000-3700 cm<sup>-1</sup>**, which is hard to miss.



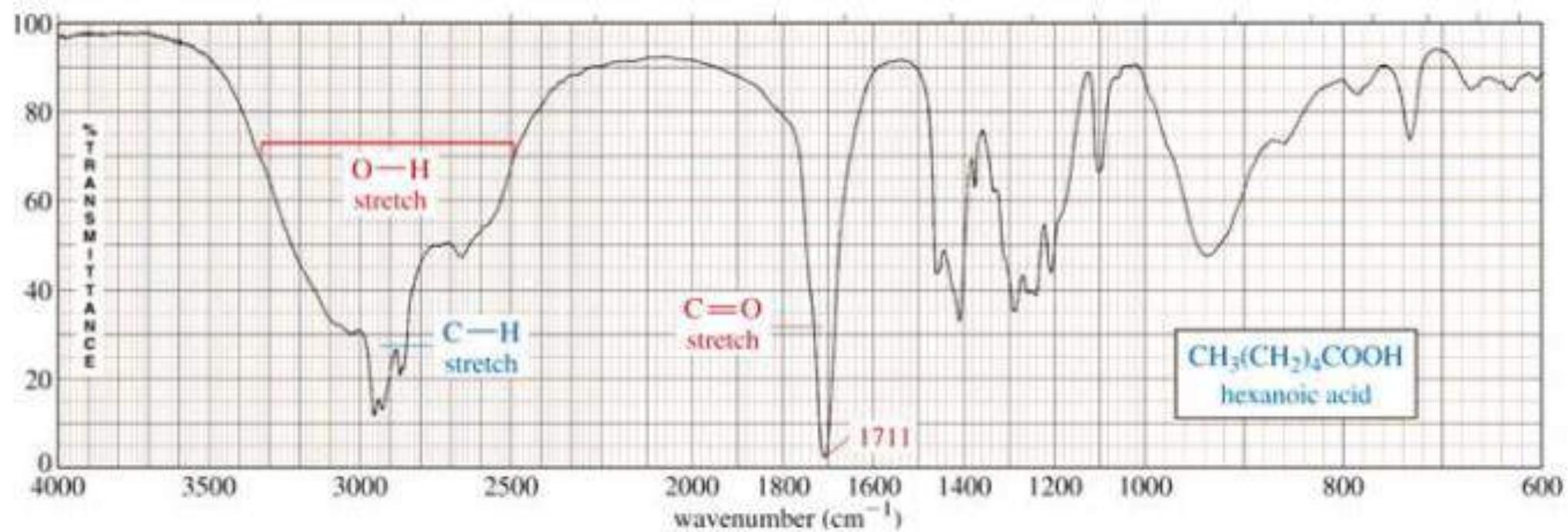


- **IR spectrum of aldehydes and ketones:**
- Carbonyl compounds are those that contain the C=O functional group. In aldehydes, this group is at the end of a carbon chain ( $\text{RCHO}$ ), whereas in ketones it's in the middle of the chain ( $\text{RCOR}'$ ). As a result, the carbon in the C=O bond of aldehydes is also bonded to another carbon and a hydrogen, whereas the same carbon in a ketone is bonded to two other carbons.
- Aldehydes and ketones show a **strong, prominent, stake-shaped band around  $1710 - 1720 \text{ cm}^{-1}$**  (right in the middle of the spectrum). This band is due to the **highly polar C=O bond**.
- Because **aldehydes also contain a C-H bond to the  $\text{sp}^2$  carbon of the C=O bond**, they also show **a pair of medium strength bands positioned about  $2700$  and  $2800 \text{ cm}^{-1}$** . These bands are missing in the spectrum of a ketone because the  $\text{sp}^2$  carbon of the ketone lacks the C-H bond.



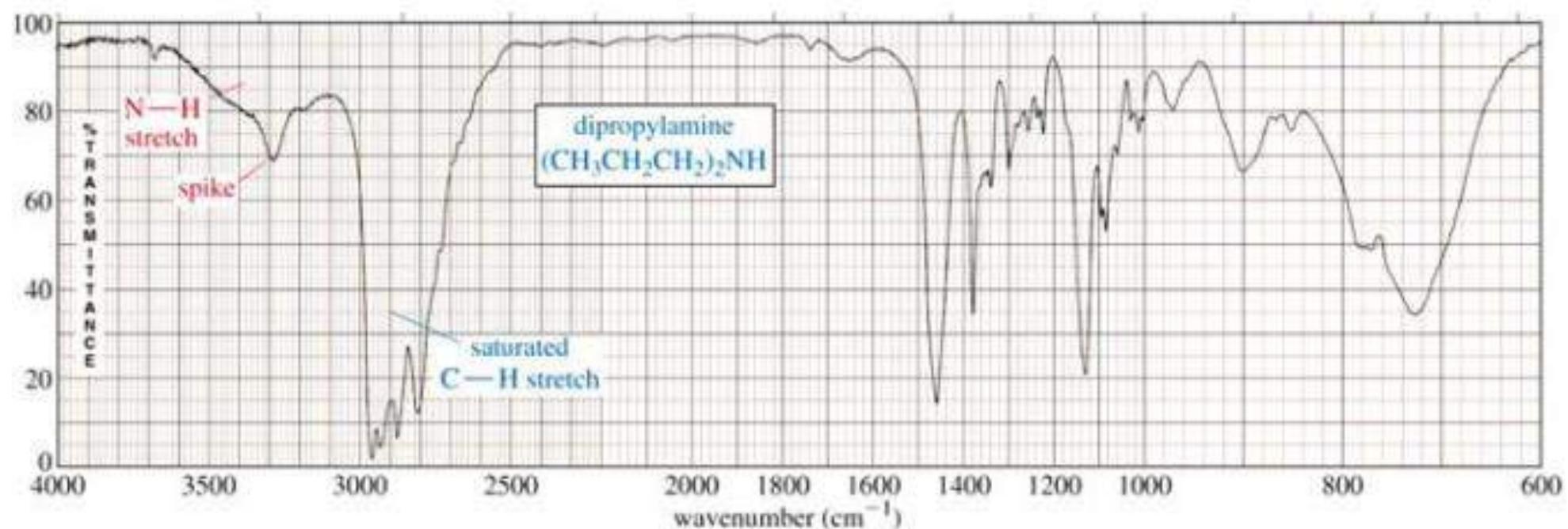


- **IR spectrum of carboxylic acids:**
- A carboxylic acid functional group **combines the features of alcohols and ketones** because it has both the O-H bond and the C=O bond. Therefore carboxylic acids show a very **strong and broad band** covering a wide range between **2800 and 3500 cm<sup>-1</sup>** for the O-H stretch. At the same time they also show the **stake-shaped band** in the middle of the spectrum around **1710 cm<sup>-1</sup>** corresponding to the C=O stretch.





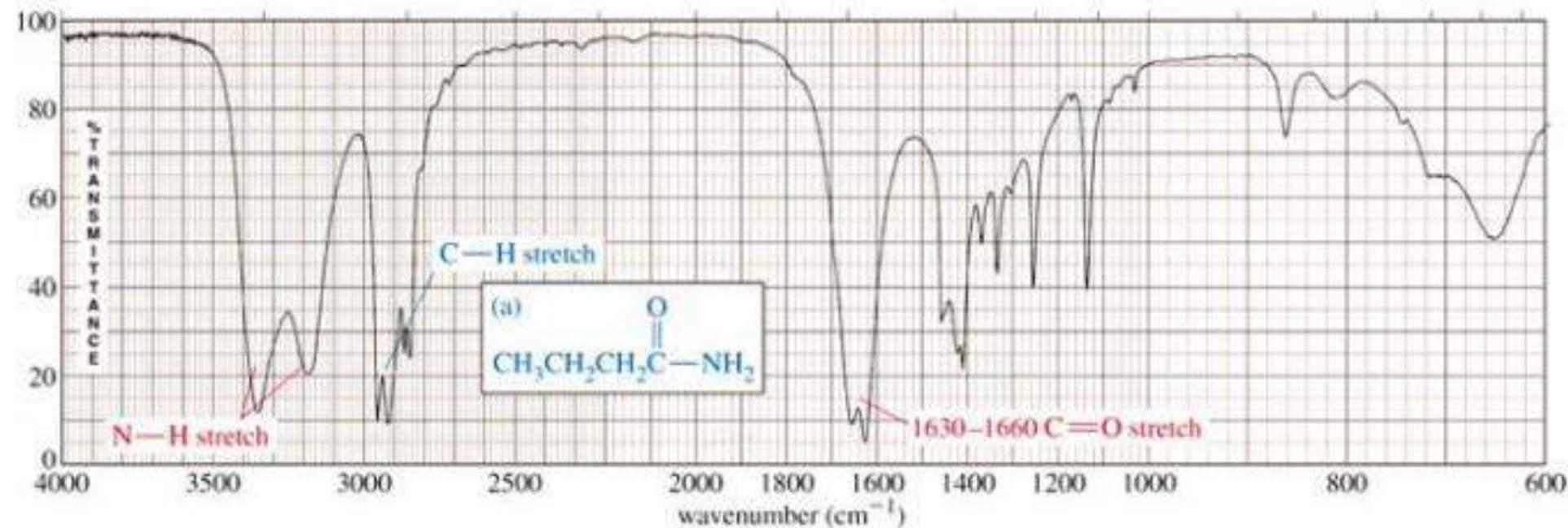
- **IR spectrum of amines:**
- The most characteristic band in amines is due to the **N-H bond stretch**, and it appears as a **weak to medium**, somewhat broad band (but not as broad as the O-H band of alcohols) in the range of about **3200-3600 cm<sup>-1</sup>**.
- **Primary amines have two N-H bonds**, therefore they typically show two spikes that make this band resemble a molar tooth. **Secondary amines have only one N-H bond**, which makes them show only one spike, resembling a canine tooth. Finally, **tertiary amines have no N-H bonds**, and therefore this band is absent from the IR spectrum altogether.





- **IR spectrum of amides:**

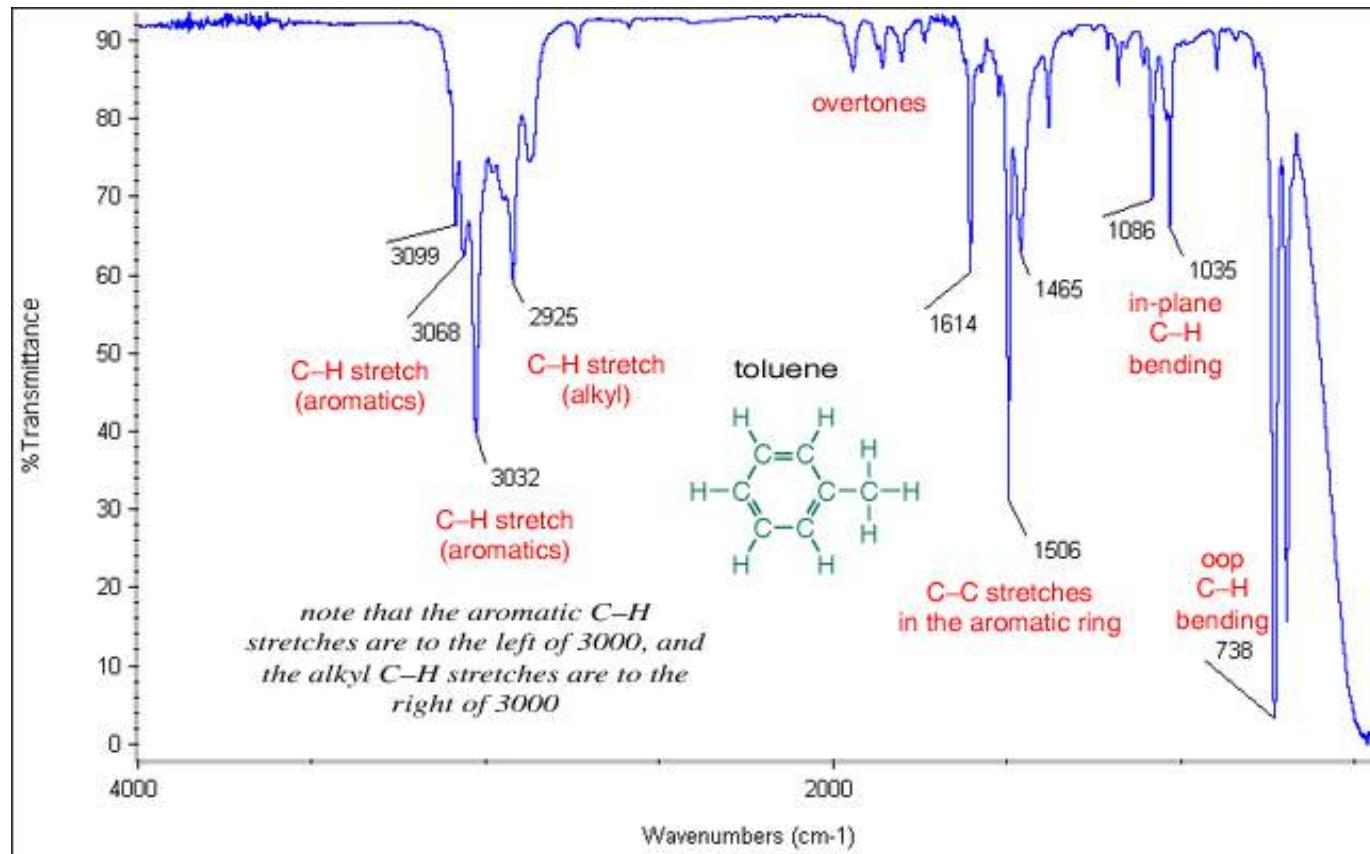
- The amide functional group **combines the features of amines and ketones** because it has both the N-H bond and the C=O bond. Therefore amides show a **very strong, somewhat broad band** in the range between **3100 and 3500 cm<sup>-1</sup>** for the **N-H stretch**. At the same time they also show the **stake-shaped band in the middle of the spectrum around 1710 cm<sup>-1</sup>** for the **C=O stretch**.
- As with amines, primary amides show two spikes, whereas secondary amides show only one spike.





- **IR spectrum of aromatic compounds:**

- Arenes possess a **characteristic absorption** at about  $3030\text{-}3100\text{ cm}^{-1}$  as a result of the **aromatic C-H stretch**. It is somewhat higher than the alkyl C-H stretch ( $2850\text{--}2960\text{ cm}^{-1}$ ), but falls in the same region as olefinic compounds.
- Two bands ( $1500$  and  $1660\text{ cm}^{-1}$ ) caused by C=C in plane vibrations are the most useful for characterization as they are intense and are likely observed.





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Engineering Chemistry-II (BS-104)

# Spectroscopic Techniques-III

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### 3. NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

- NMR technique involves the absorption of electromagnetic radiations in the radio-frequency (rf) region (4-900 MHz) (long wavelength, low energy and low frequency) by the nucleus of the atom.
- It is considered one of the most powerful methods to detect the number of protons ( $^1\text{H}$ ) and carbon atoms in the compound.
- It involves the change of the spin state of a nuclear magnetic moment when the nucleus absorbs electromagnetic radiations in a strong magnetic field.
- The theory of NMR spectroscopy is based on the **nuclear spin quantum number (I)**. The nuclear spin quantum number is related to the mass number (number of protons and neutrons) and the atomic number (number of protons) of the atom.

I	Atomic Mass	Atomic Number	Examples
Half-integer	Odd	Odd	$^1\text{H}$ (1/2)
Half-integer	Odd	Even	$^{13}\text{C}$ (1/2)
Integer	Even	Odd	$^2\text{H}$ (1)
Zero	Even	Even	$^{12}\text{C}$ (0)

NMR active      Not NMR active

- Only magnetic nuclei that contain **odd mass numbers** such as  $^1\text{H}_1$ ,  $^{13}\text{C}_6$ ,  $^{19}\text{F}_9$ ,  $^{31}\text{P}_{15}$  or **odd atomic numbers** such as  $^2\text{H}_1$  and  $^{14}\text{N}_7$  give rise to NMR signals
- The nuclei that contain **even atomic number and even atomic mass** are NMR inactive such as  $^{12}\text{C}_6$  and  $^{16}\text{O}_8$



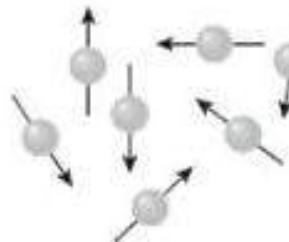
- **Principle of NMR:**

- It is based on the spinning of the nucleus on its axis that can generate the magnetic field. Thus, the nucleus can be considered as a tiny bar magnet.
- When there is no external magnetic field, the spins of the nucleus are arranged in a random manner; however, when an external magnetic field say  $B_0$  is applied to the sample, the spin present in the nucleus gets aligned in either with or against the direction of the applied magnetic field. Most nuclei generally align with the direction of the applied magnetic field because it is lower in energy.

A spinning proton creates a magnetic field.

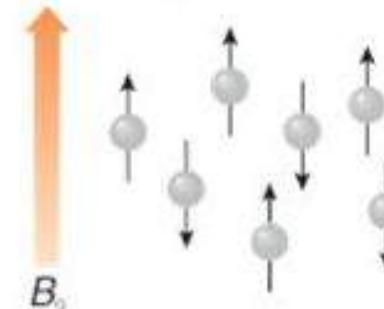


With no external magnetic field...



The nuclear magnets are randomly oriented.

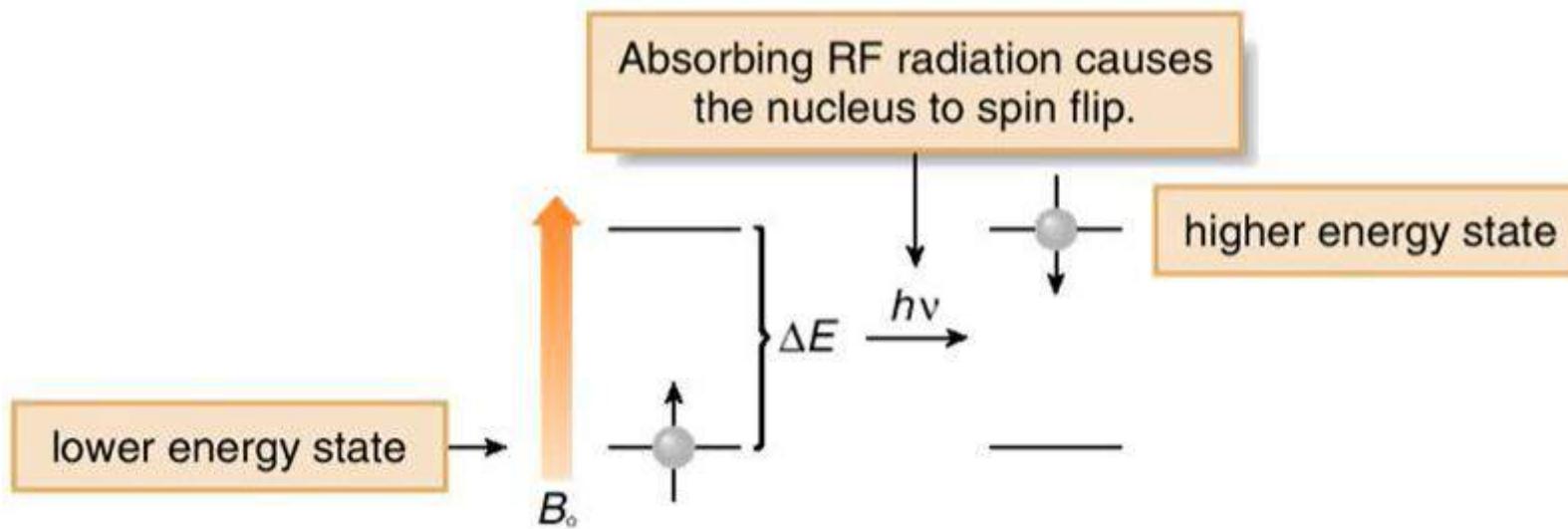
In a magnetic field...



The nuclear magnets are oriented with or against  $B_0$ .



- In a magnetic field, there are now two energy states for a proton: a lower energy state ( $\alpha$ -spin state) where the nucleus is aligned in the same direction as  $B_0$ , and a higher energy state ( $\beta$ -spin state) in which the nucleus is aligned against  $B_0$ .
- The application of the external magnetic field results in the generation of energy differences ( $\Delta E$ ) between the excited state and the ground state. This causes the nucleus to undergo “spin flip” corresponding to the energy absorption at the wavelength which is equivalent to the radio frequency.
- When the spin comes back to the initial ground state it emits the absorbed radiofrequency, and this emitted radiofrequency gives the NMR signal of the corresponding nucleus. The emitted radiofrequency is proportional to the magnitude of the applied magnetic field.



- A nucleus is in resonance when it absorbs rf radiation and “spin flips” to a higher energy state



## NMR Spectrophotometer



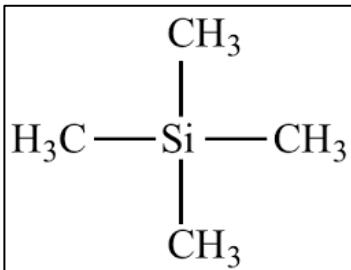
**NMR sample  
tube**

An **NMR spectrometer**. The sample is dissolved in a solvent, usually  $\text{CDCl}_3$  (deuterochloroform), and placed in a magnetic field. A radiofrequency generator then irradiates the sample with a short pulse of radiation, causing resonance. When the nuclei fall back to their lower energy state, the detector measures the energy released, and a spectrum is recorded.



- **Chemical Shift:**

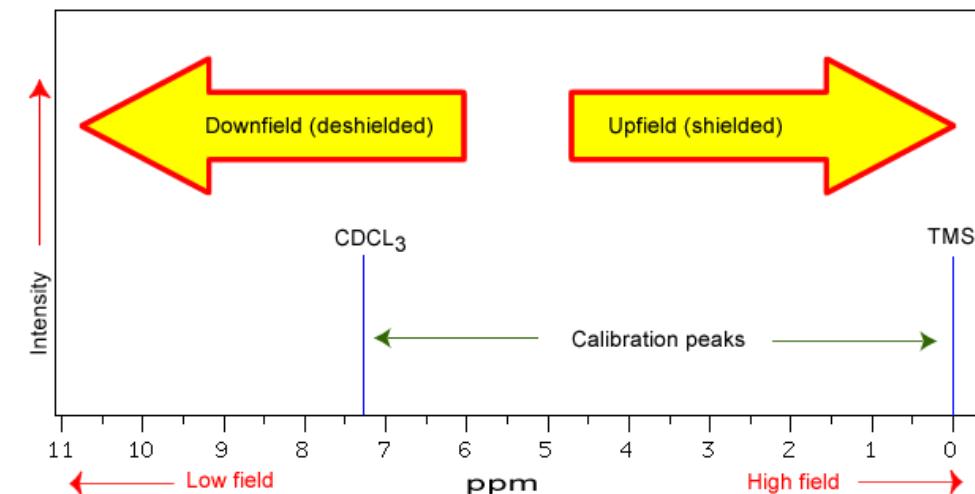
- The position on the plot at which the nuclei absorbs is called the **chemical shift**. It is the difference between the resonance frequency of the observed proton or hydrogen and the hydrogens of the **tetramethylsilane (TMS)**. It is represented **in ppm or in  $\delta$  units**. The usual scale of  $^1\text{H-NMR}$  is from 0-12 ppm or  $\delta$
- In NMR spectroscopy, TMS (at  $\delta = 0$  ppm) is considered as the reference compound and is used to define the zero position on the  $\delta$  scale.
- The terms “**upfield**” and “**downfield**” describe the relative locations of the peaks. The signal appearing at high magnetic field strengths are termed **upfield (towards the right)** and have **low  $\delta$  values**, while those occurring at lower field strengths are termed **downfield (towards the left)** have **large  $\delta$  values**.



TMS

$$\delta = \frac{\text{frequency of signal} - \text{frequency of standard}}{\text{spectrometer frequency}} \times 10^6$$

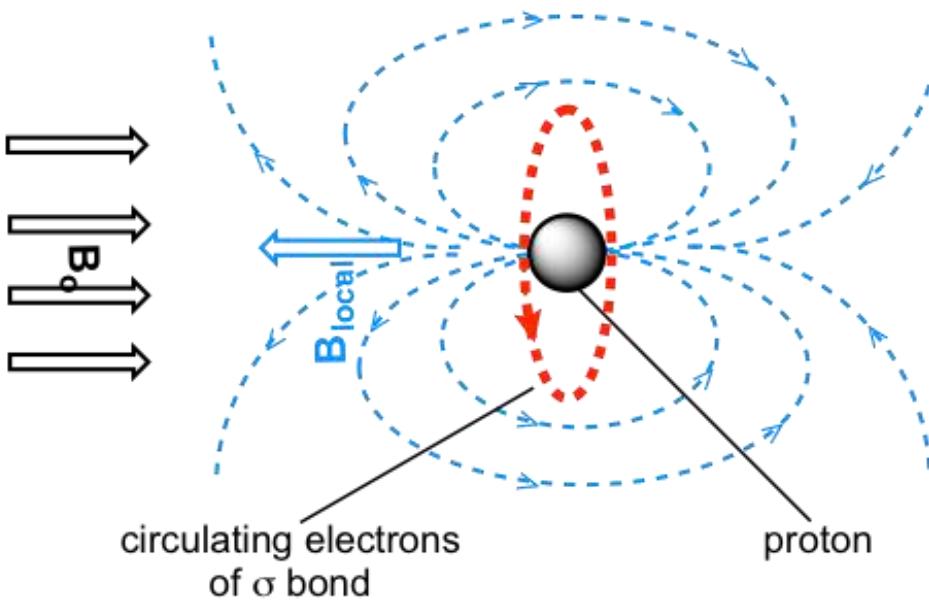
unit of frequency: Hz  
Spectrometer freq.: MHz  
 $1 \text{ MHz} = 10^6 \text{ Hz}$





- **Shielding and Deshielding effects:**

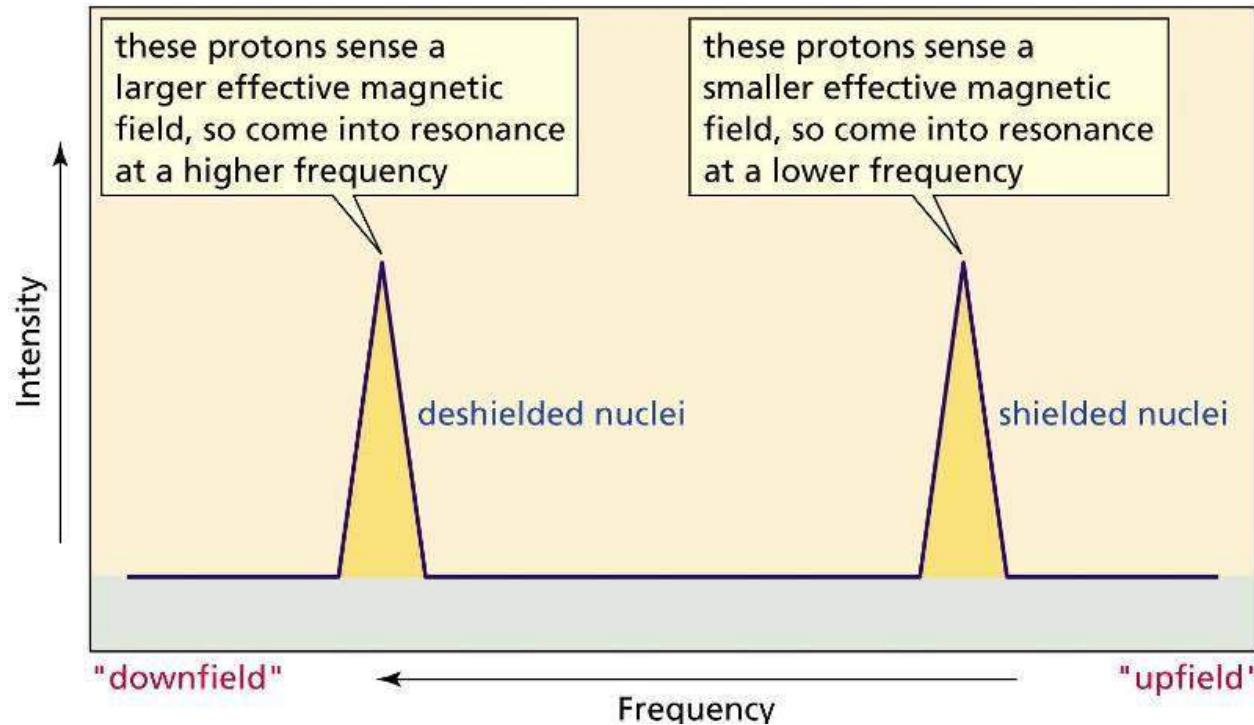
- The nucleus is also surrounded by an electron cloud which will also be circulating in the magnetic field, about the nucleus. The circulating electrons generate magnetic fields of their own, which act in opposition to the applied external field and will influence the resultant field at the nucleus. The nucleus is said to be shielded to some extent from the applied field.



**Shielding effect:**  $B_{\text{local}}$  generated by the circulation electrons of  $\sigma$  bond shield the proton from the external magnetic field  $B_0$ .



- **Shielding and Deshielding effects:**
- **Shielding of protons:** If the density of the electron around the nucleus is high, the opposition of the external magnetic field by the electrons will also be high, hence the greater will be the shielding of the protons as protons will experience the less external magnetic field. As a result, a lower frequency will be needed to achieve the resonance and the NMR signals are upfield (towards the right) in the spectrum.
- **Deshielding of protons:** If the density of the electrons around the nucleus is low, the opposition to the external magnetic field becomes less, hence the protons will experience more magnetic field, and the protons are said to be de-shielded. As the protons are experiencing a high magnetic field, hence high frequency will be needed to achieve the resonance, and the downfield shift (towards the left) in the chemical shift is observed.





- Factors affecting chemical shift:

**1. Electronegativity:** When an electronegative group such as bromine, iodine, and chlorine is attached to the carbon-hydrogen bonding system, they pulled the electron density towards themselves, which reduces the density of electrons around the protons, and de-shielding is observed, which results in an increase in the chemical shift.

Dependence of the Chemical Shift of  $\text{CH}_3\text{X}$  on the Element X

Compound $\text{CH}_3\text{X}$	$\text{CH}_3\text{F}$	$\text{CH}_3\text{OH}$	$\text{CH}_3\text{Cl}$	$\text{CH}_3\text{Br}$	$\text{CH}_3\text{I}$	$\text{CH}_4$	$(\text{CH}_3)_4\text{Si}$
Element X	F	O	Cl	Br	I	H	Si
Electronegativity of X	4.0	3.5	3.1	2.8	2.5	2.1	1.8
Chemical shift $\delta$	4.26	3.40	3.05	2.68	2.16	0.23	0

most  
deshielded

← TMS

deshielding increases with the  
electronegativity of atom X

**O-CH<sub>3</sub>, N-CH<sub>3</sub>, C-CH<sub>3</sub>**  
 $\delta$  3.4       $\delta$  2.2       $\delta$  0.9

most  
deshielded

Cumulative Effect

$\text{CHCl}_3$	$\text{CH}_2\text{Cl}_2$	$\text{CH}_3\text{Cl}$	ppm
7.27	5.30	3.05	ppm

The effect increases with greater numbers of electronegative atoms.

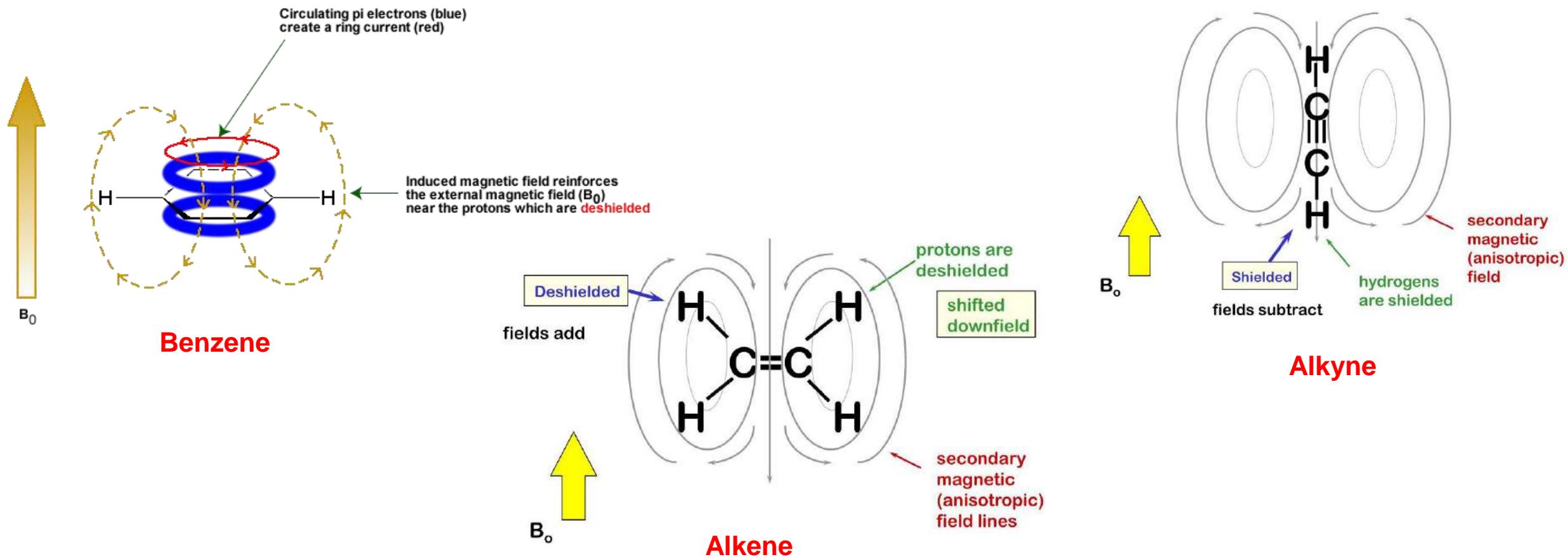
most  
deshielded

$-\text{CH}_2\text{-Br}$	$-\text{CH}_2\text{-CH}_2\text{-Br}$	$\times-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-Br}$	ppm
3.30	1.69	1.25	ppm

The effect decreases with increasing distance from the electronegative atom.  
 The effect completely vanished at the fourth bond from the electronegative atom.



**2. Magnetic anisotropy of  $\pi$ -systems:** The term anisotropy means non-uniform, the magnetic anisotropy implies the non-uniform magnetic field. When the magnetic field is applied to the  $\pi$ -electron systems such as alkenes, alkynes, carbonyl, aromatics, the  $\pi$  system induces its own magnetic field, which results in the magnetic anisotropy, i.e., the shielding and deshielding of the protons. Benzene is the simplest organic chemical compound that shows this effect.



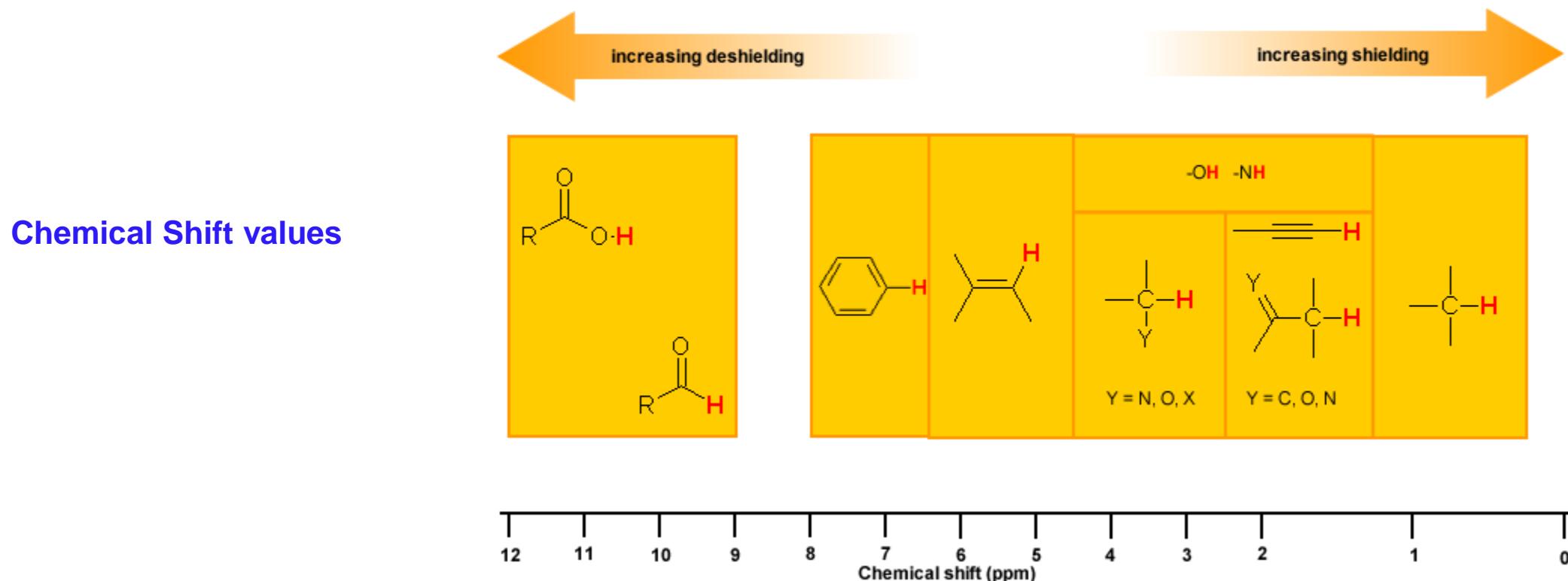


Proton Type	Effect	Chemical shift (ppm)
$C_6H_5-H$	highly deshielded	6.5 - 8
$C=C-H$	deshielded	4.5 - 6
$C\equiv C-H$	shielded*	~2.5
$O=C-H$	very highly deshielded	9 - 10

\* the acetylene H is shielded due to its location relative to the  $\pi$  system



**3. Hydrogen bonding:** Protons that are involved in hydrogen bonding (i.e. **-OH or -NH**) are usually observed over a wide range of chemical shifts. These are known as **labile protons**. This is due to the deshielding that occurs in the hydrogen bond. Since hydrogen bonds are dynamic, constantly forming, breaking and forming again, there will be a wide range of hydrogen bonds strengths and consequently a wide range of deshielding. This as well as solvation effects, acidity, concentration and temperature make it very difficult to predict the chemical shifts for these atoms.





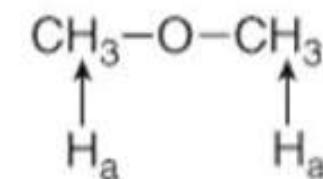
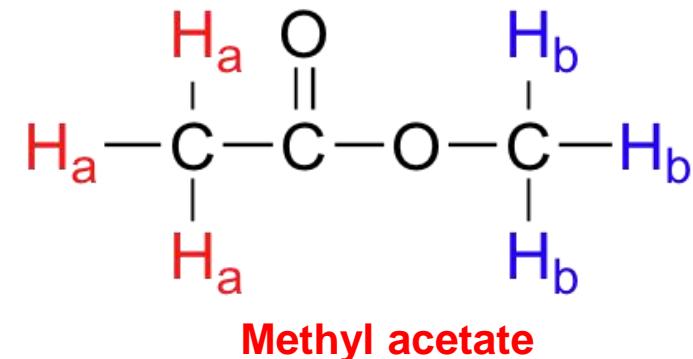
## Chemical Shift values

Type of proton	Chemical shift (ppm)	Type of proton	Chemical shift (ppm)
 sp <sup>3</sup>	0.9-2	 sp <sup>2</sup>	4.5-6
<ul style="list-style-type: none"><li>• RCH<sub>3</sub></li><li>• R<sub>2</sub>CH<sub>2</sub></li><li>• R<sub>3</sub>CH</li></ul>	<ul style="list-style-type: none"><li>~0.9</li><li>~1.3</li><li>~1.7</li></ul>	 C <sub>6</sub> H <sub>5</sub> -	6.5-8
 Z = C, O, N	1.5-2.5	 R-C(=O)-H	9-10
 -C≡C-H	~2.5	 R-C(=O)-OH	10-12
 Z = N, O, X	2.5-4	RO-H or R-N(H)-	1-5

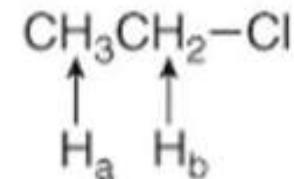


- **Chemical equivalence of protons:**

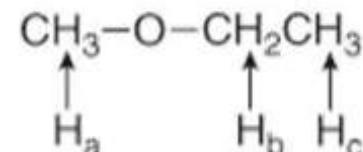
- In an external magnetic field of a given strength, protons in different locations in a molecule have different resonance frequencies, because they are in non-identical electronic environments.
- The number of NMR signals equals to the number of different types of protons in a compound.
- Protons in different chemical environments give different NMR signals.
- Equivalent protons give the same NMR signal.
- For example, the three methyl acetate protons labeled  $H_a$  have a different resonance frequency compared to the three  $H_b$  protons, because the two sets of protons are in non-identical electronic environments: the  $H_a$  protons are on a carbon next to a carbonyl carbon, while the  $H_b$  protons are on a carbon next to the oxygen. In the terminology of NMR, all three  $H_a$  protons are chemically equivalent to each other, as are all three  $H_b$  protons. The  $H_a$  protons are, however, chemically nonequivalent to the  $H_b$  protons. As a consequence, the resonance frequency of the  $H_a$  protons is different from that of the  $H_b$  protons.



All equivalent H's  
1 NMR signal



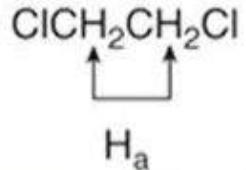
2 types of H's  
2 NMR signals



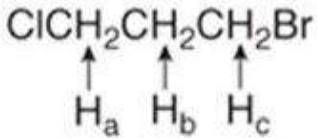
3 types of H's  
3 NMR signals



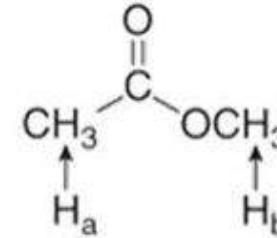
- Chemical equivalence of protons:



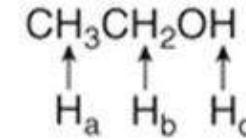
1 type of H  
1 NMR signal



3 types of H's  
3 NMR signals

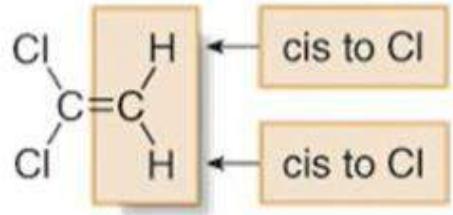


2 types of H's  
2 NMR signals



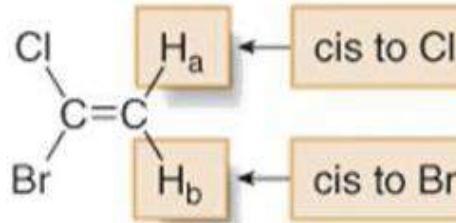
3 types of H's  
3 NMR signals

- In comparing two H atoms on a double bond, two protons are equivalent only if they are cis (or trans) to the same groups



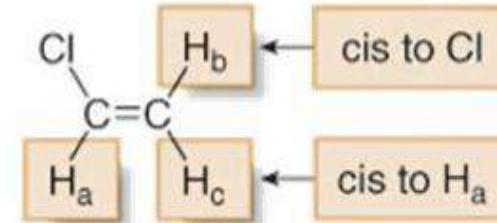
1,1-dichloroethylene

1 type of H  
1 NMR signal



1-bromo-1-chloroethylene

2 types of H's  
2 NMR signals

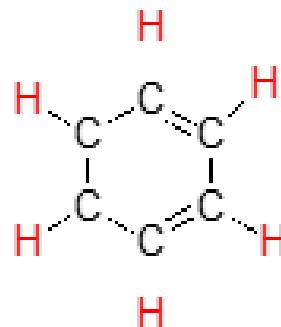


chloroethylene

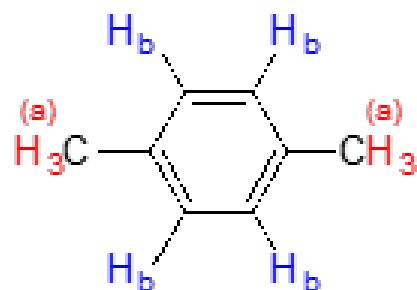
3 types of H's  
3 NMR signals



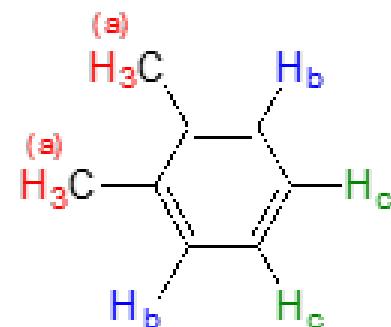
- **Chemical equivalence of protons:**
- All six protons on benzene are equivalent to each other and have the same resonance frequency in an NMR experiment.
- All four aromatic protons in 1,4-dimethylbenzene are chemically equivalent
- The constitutional isomer 1,2 dimethylbenzene has two sets of aromatic protons in addition to the six methyl ( $H_a$ ) protons.
- The 1,3-substituted isomer, on the other hand, has three sets of aromatic protons.



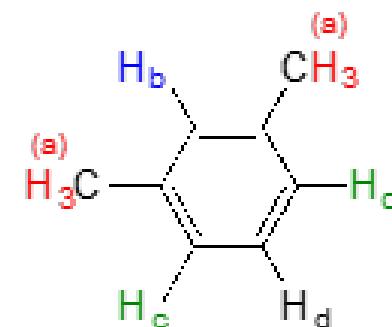
benzene



1,4-dimethylbenzene



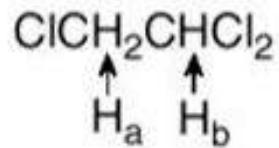
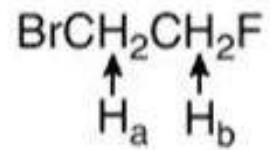
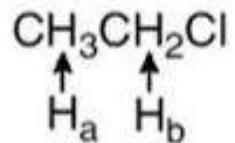
1,2-dimethylbenzene



1,3-dimethylbenzene



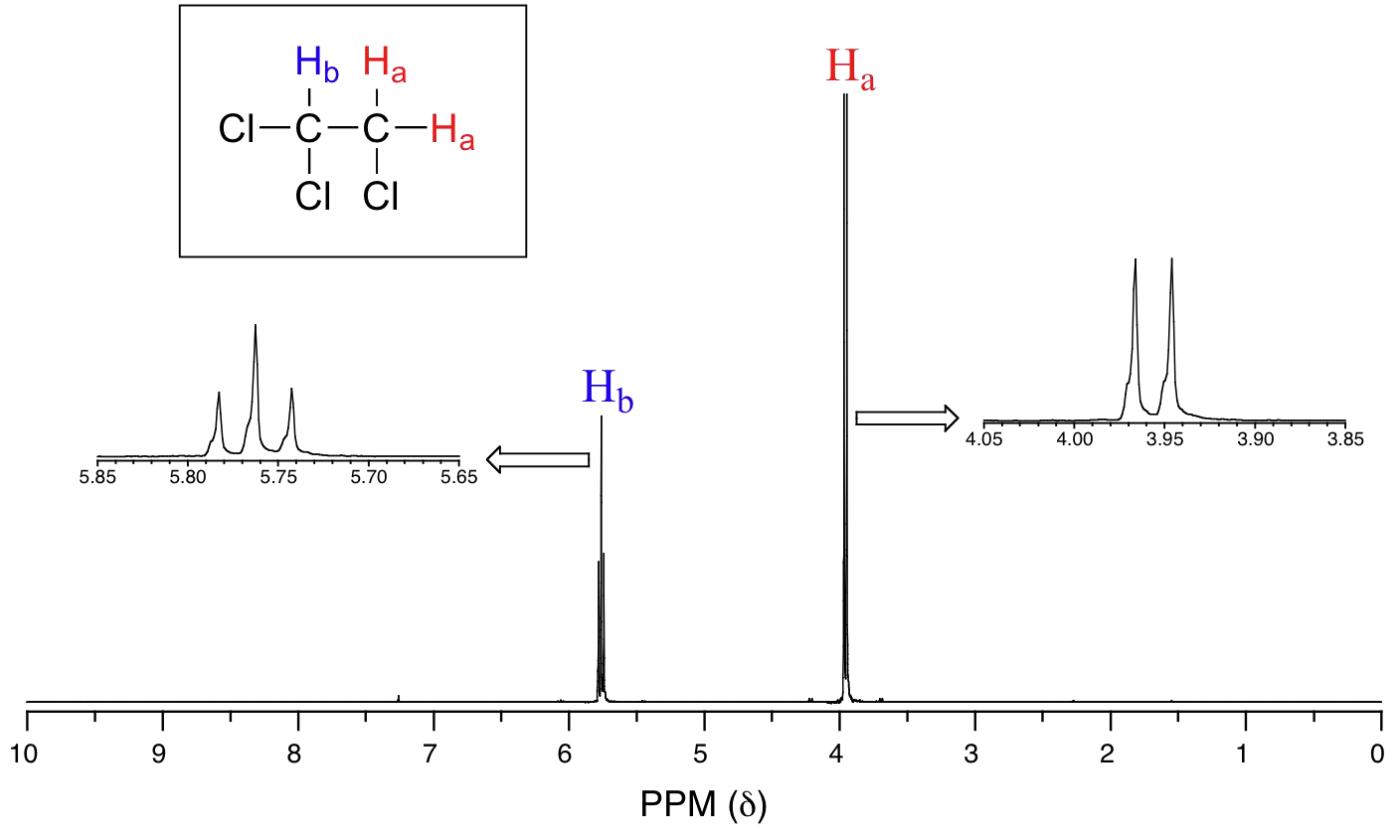
- **$^1\text{H}$  NMR- position of signals:**



- The  $\text{H}_b$  protons are **deshielded** because they are closer to the electronegative Cl atom, so they absorb **downfield** from  $\text{H}_a$ .
- Because F is more electronegative than Br, the  $\text{H}_b$  protons are more **deshielded** than the  $\text{H}_a$  protons and absorb farther **downfield**.
- The larger number of electronegative Cl atoms (two versus one) **deshields**  $\text{H}_b$  more than  $\text{H}_a$ , so it absorbs **downfield** from  $\text{H}_a$ .

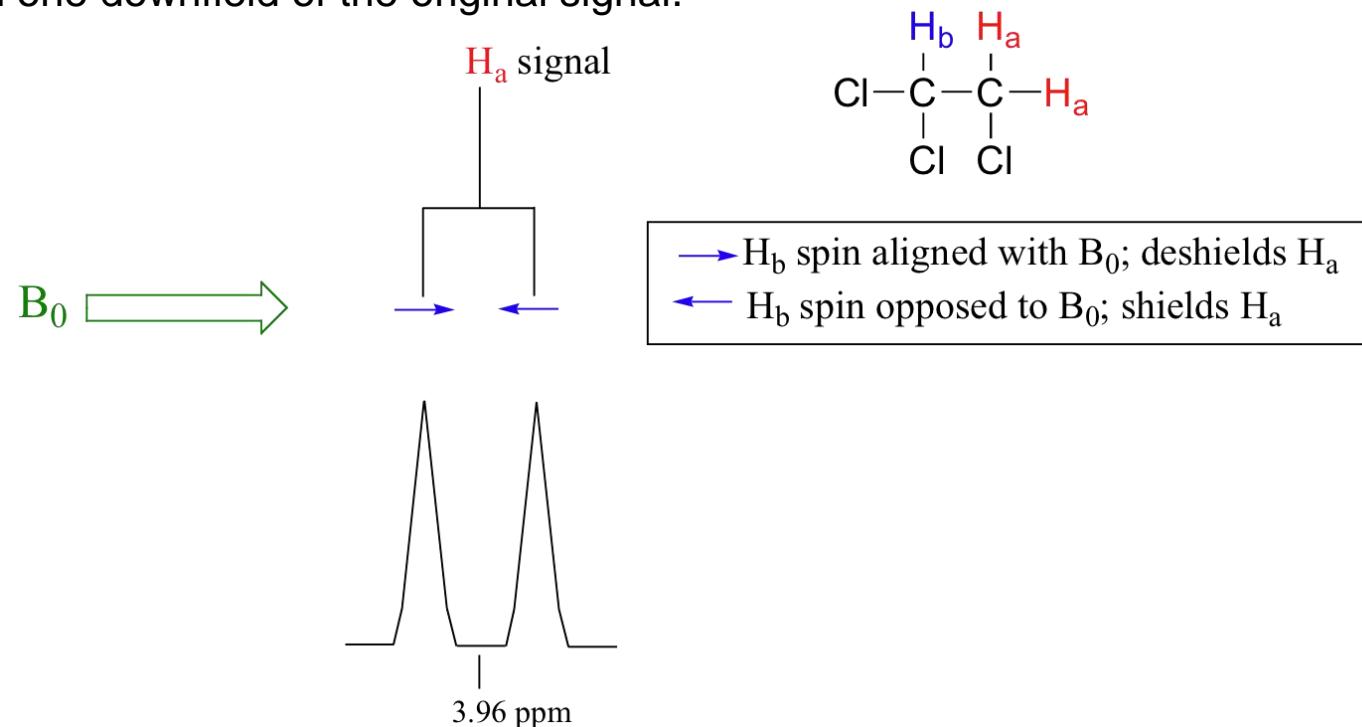


- **Spin-Spin Splitting:**
- In  $^1\text{H}$  NMR spectra, the signal due to a particular proton may not be a singlet (single sharp peak) but instead appears as a collection of peaks. The signal may be split into two peaks (a doublet), three peaks (a triplet) , four peaks (a quartet), and so on.
- **Splitting occurs only between nuclei with different chemical shifts. i.e., between chemically non-equivalent protons.**
- The number of peaks into which a proton signal is split equals one more than the number of equivalent neighboring protons  $n$ , following a **(n+1) rule**. That means a doublet (d) results from one adjacent proton, a triplet (t) results from two adjacent protons, a quartet (q) results from three adjacent protons, and so on.



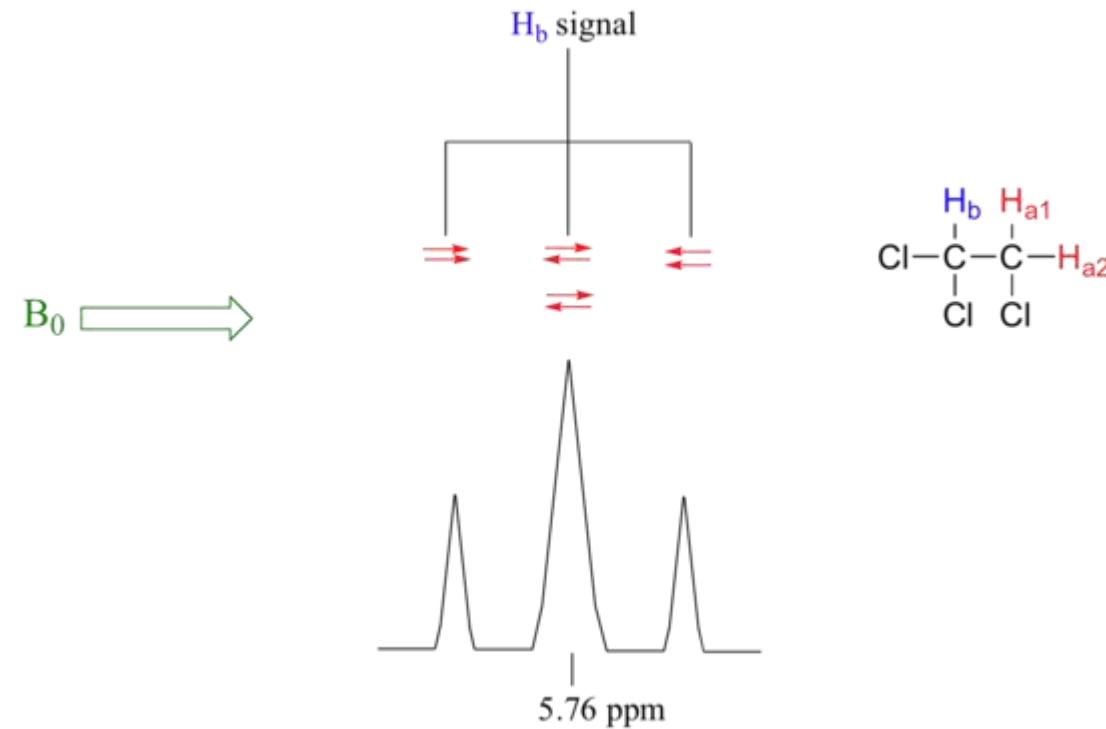


- In 1,1,2 trichloroethane, the  $H_a$  and  $H_b$  protons are spin-coupled to each other. **The  $H_a$  signal:** in addition to being shielded by nearby valence electrons, each of the  $H_a$  protons is also influenced by the small magnetic field generated by  $H_b$ . The magnetic moment of  $H_b$  will be aligned *with*  $B_0$  in half of the molecules in the sample, while in the remaining half of the molecules it will be opposed to  $B_0$ . The  $B_{\text{eff}}$  'felt' by  $H_a$  is a slightly weaker if  $H_b$  is aligned against  $B_0$ , or slightly stronger if  $H_b$  is aligned with  $B_0$ . In other words, in half of the molecules  $H_a$  is *shielded* by  $H_b$  (thus the NMR signal is shifted slightly upfield) and in the other half  $H_a$  is *deshielded* by  $H_b$  (and the NMR signal shifted slightly downfield). Thus  $H_a$  peak has been split into two sub-peaks (a doublet), one upfield and one downfield of the original signal.





- **The  $H_b$  signal:** The magnetic environment experienced by  $H_b$  is influenced by the fields of both neighboring  $H_a$  protons, which we will call  $H_{a1}$  and  $H_{a2}$ . There are four possibilities here, each of which is equally probable. First, the magnetic fields of both  $H_{a1}$  and  $H_{a2}$  could be aligned with  $B_0$ , which would deshield  $H_b$ , shifting its NMR signal slightly downfield. Second, both the  $H_{a1}$  and  $H_{a2}$  magnetic fields could be aligned opposed to  $B_0$ , which would shield  $H_b$ , shifting its resonance signal slightly upfield. Third and fourth,  $H_{a1}$  could be with  $B_0$  and  $H_{a2}$  opposed, or  $H_{a1}$  opposed to  $B_0$  and  $H_{a2}$  with  $B_0$ . In each of the last two cases, the shielding effect of one  $H_a$  proton would cancel the deshielding effect of the other, and the chemical shift of  $H_b$  would be unchanged.



The signal for  $H_b$  is a **triplet**, with the middle peak twice as large as the two outer peaks



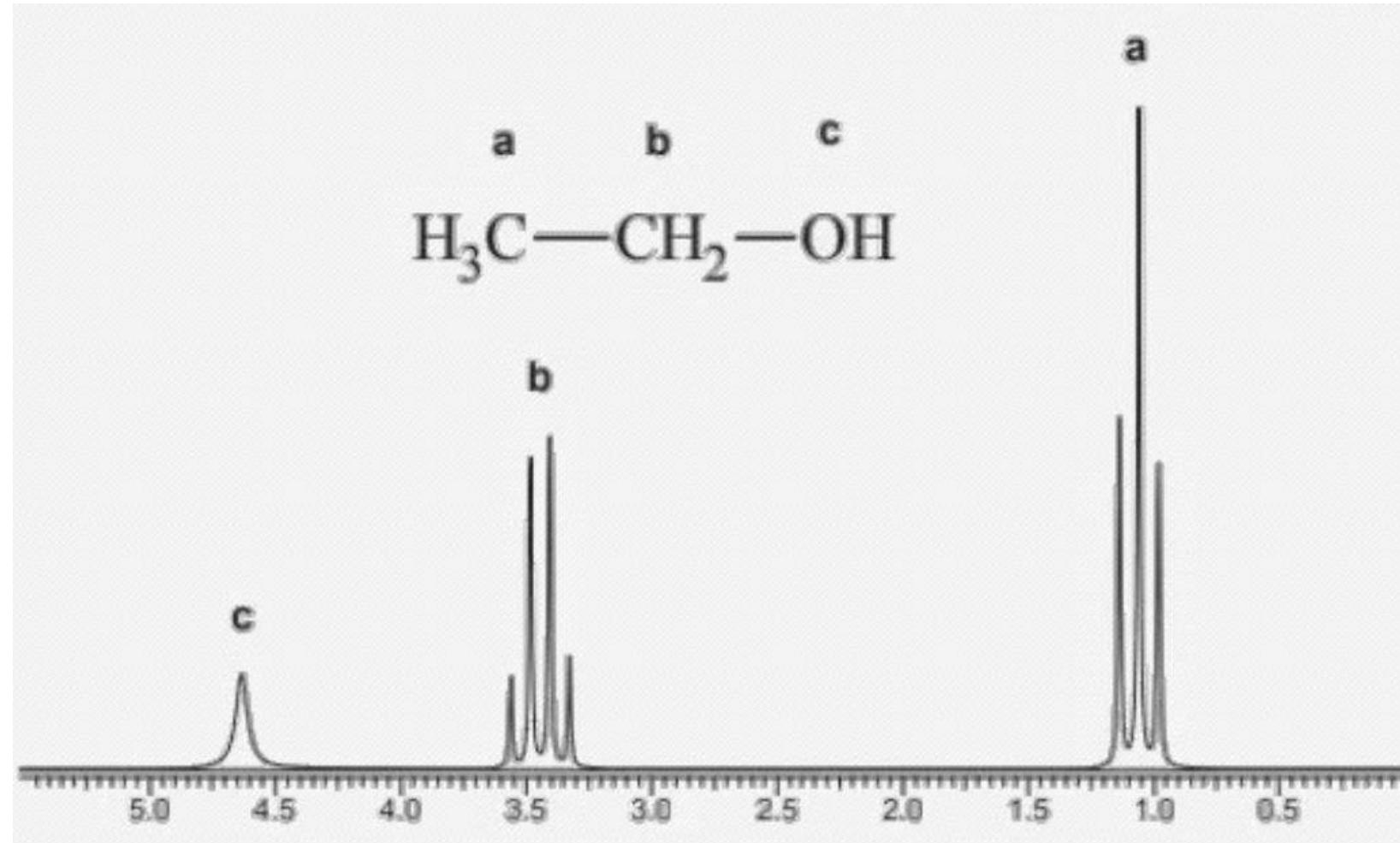
- **Spin-Spin Splitting:**
- The relative intensities of the split peaks produced are in proportion of a binomial distribution given by Pascal's Triangle.

no. of neighbors	relative intensities	pattern	example
0	1	singlet (s)	
1	1 1	doublet (d)	
2	1 2 1	triplet (t)	
3	1 3 3 1	quartet (q)	
4	1 4 6 4 1	pentet	$\text{RCH}_2\text{-}\text{CHR}'\text{-}\text{CH}_2\text{R}$
5	1 5 10 10 5 1	sextet	$\text{CH}_3\text{-}\text{CH}_2\text{-}\text{CH}_2\text{R}'$ (equal J's)
6	1 6 15 20 15 6 1	septet	$\text{CH}_3\text{-}\text{CHR}-\text{CH}_3$



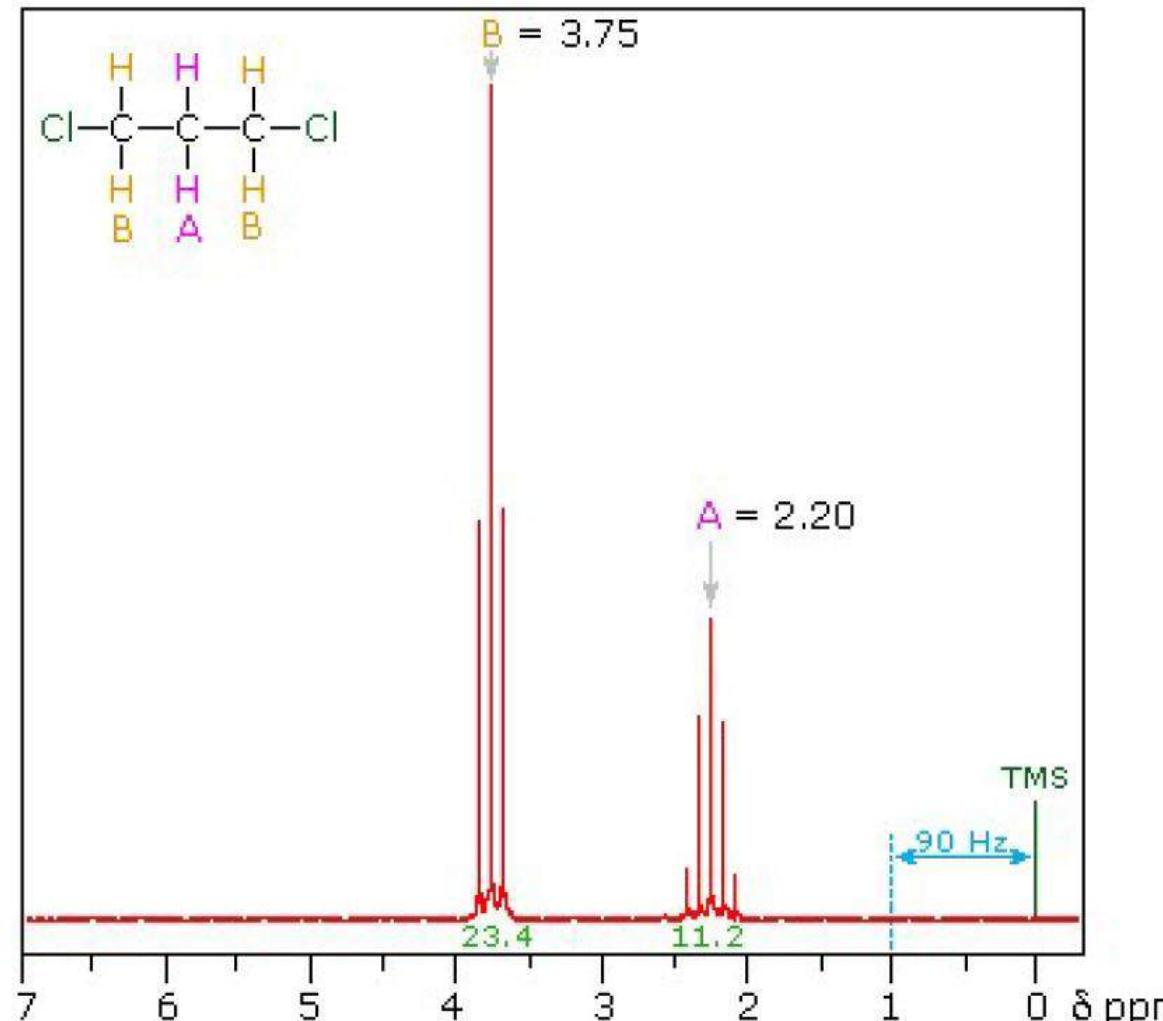
- Some Examples:

**<sup>1</sup>H NMR spectrum of ethanol**





### **<sup>1</sup>H NMR spectrum of 1,3-dichloropropane**





### **<sup>1</sup>H NMR spectrum of 1,1,2-trichloroethaneane**

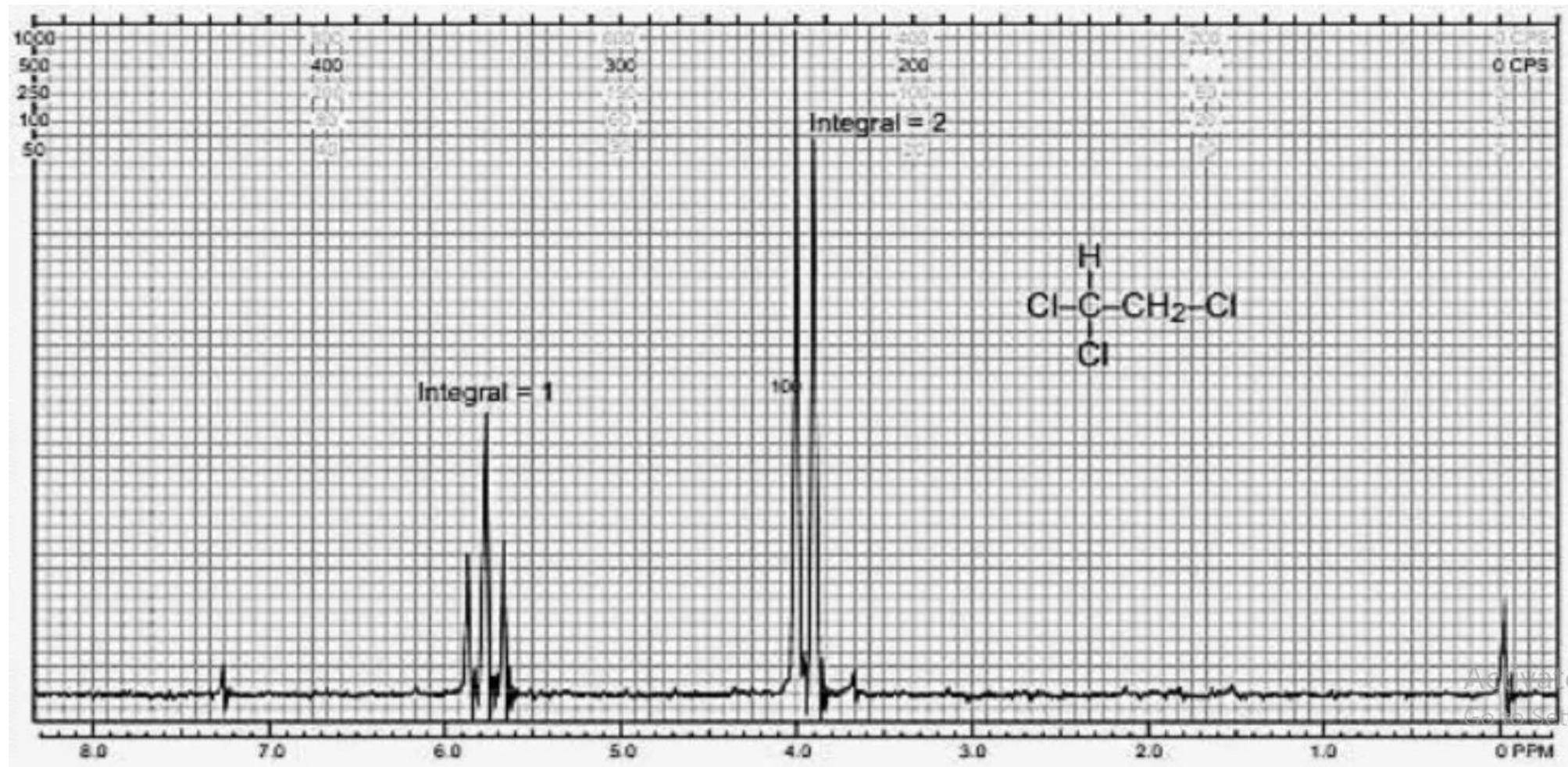




Image adapted from  
<https://sdbs.db.aist.go.jp>

spectra adaptations  
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### $^1\text{H}$ NMR spectrum of 2-bromopropane

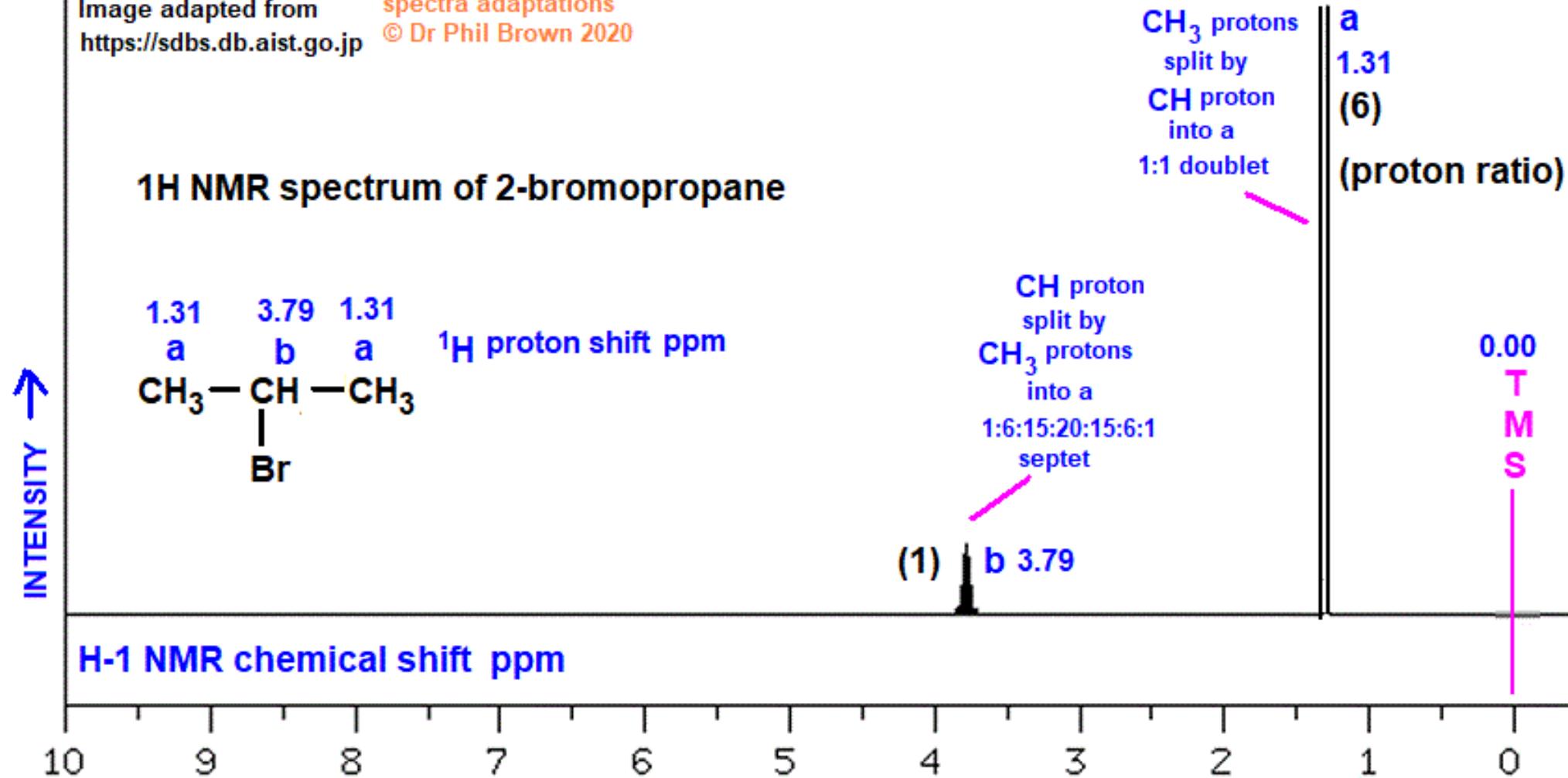
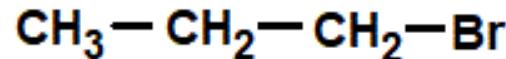




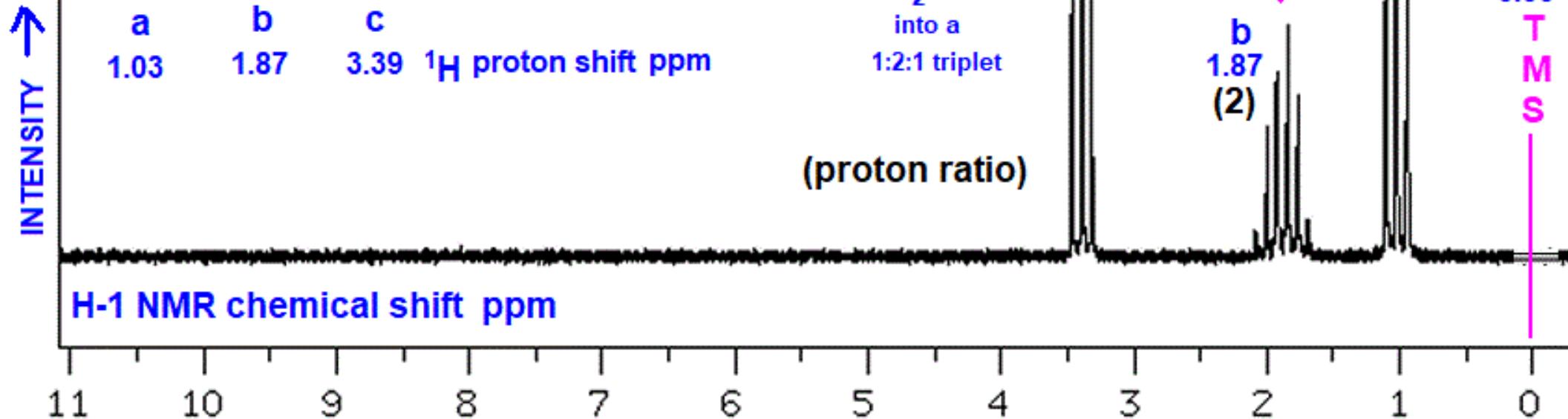
Image adapted from  
<https://sdbs.db.aist.go.jp>

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### 1H NMR spectrum of 1-bromopropane



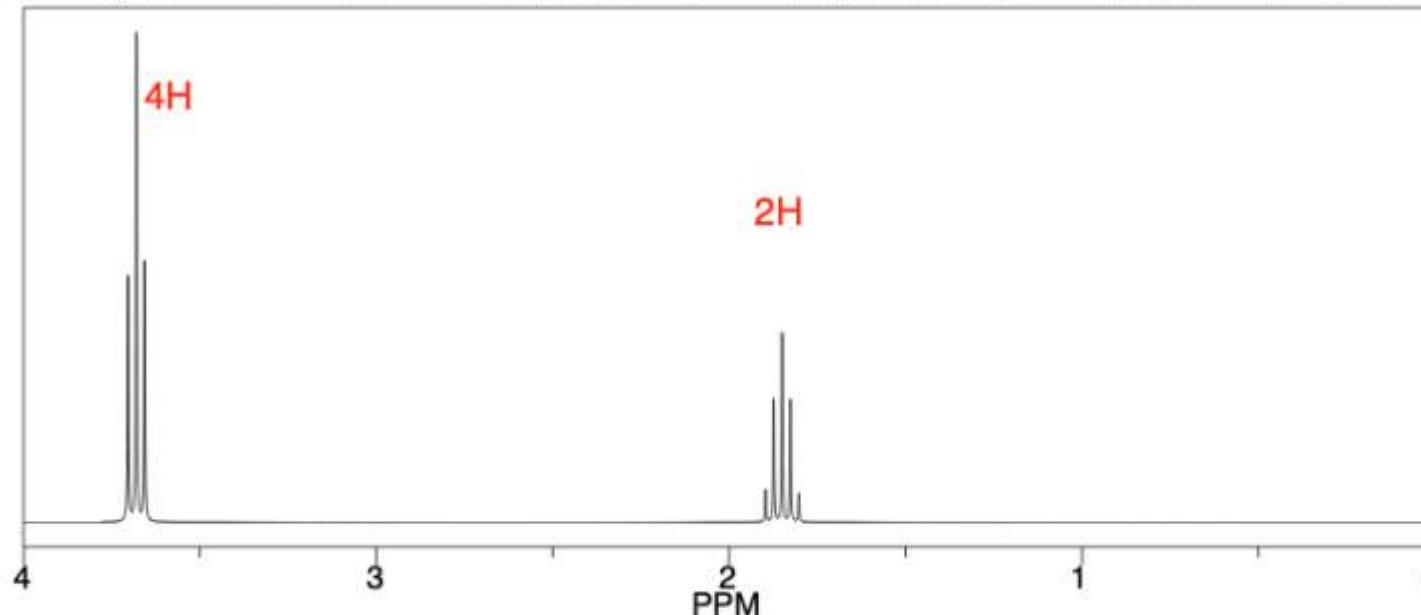
a      b      c  
1.03    1.87    3.39     $^1\text{H}$  proton shift ppm





• **Problem Question:**

Radical chlorination of propane gives a very small yield of a dichlorinated product whose full  $^1\text{H}$  NMR spectrum is shown below. Drawing out the possibilities, and considering the possible splitting patterns, determine which of the four possible dichloropropane isomers this spectrum represents.



- 1,3-dichloropropane
- 2,2-dichloropropane
- 1,2-dichloropropane
- 1,1-dichloropropane



- **Applications of NMR Spectroscopy:**

- The most basic application of NMR spectroscopy is molecular structure analysis.
- NMR spectroscopy is used to check the presence of impurities in the given sample.
- As NMR spectroscopy can provide real-time data analysis of the chemical processes, so it is used by the researchers to examine the photosynthesis process in the algae and the plants to understand the survival rate of the particular crop in the different climatic conditions.
- It is used in the pharmaceutical sector for drug analysis and quality control.
- It is used in the analysis of nucleic acids, cells and biofluids.
- The applications of NMR spectroscopy is also seen in the development of the batteries. NMR bench-top spectrometer is used to get the molecular details of the potential of the battery for storing the energy.
- The NMR spectroscopy is used in the MRI techniques.
- It's not only used to determine the structure of the molecule but also to compare the obtained NMR spectra of the unknown compound with the spectral libraries.
- NMR spectroscopy is considered one of the best methods for analysing the structure of organic compounds. It is used in the food sectors to determine the amino acid profile, lipid fractions, structure of the protein, and organic acids.



- **Advantages of NMR Spectroscopy:**
  - It is a non-destructive method, and the examined sample can be obtained back into its original form after distillation or other processes, which can be used for further examination.
  - The NMR spectra reveal a large number of details about the structure of the molecule, such as chemical shift, spin-spin splitting, relative peak size, type of functional group attached, and other detailed information about the chemical environment of the molecule.
  - NMR spectroscopy can be used for the analysis of both the simple and the complex molecules as the size of the molecule is not a problem in the case of NMR spectroscopy.
  
- **Disadvantages of NMR Spectroscopy:**
  - The NMR spectroscopy requires comparatively a larger amount of sample to give the NMR signal than the other conventional methods.
  - The NMR spectroscopy of solids needs some special devices (magic-angle spinning machine) to give well-resolved NMR spectra.
  - NMR spectroscopy also gives the NMR spectra of a large number of unwanted impurities present in the nuclei sample.



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Engineering Chemistry-II (BS-104)

# Polymers

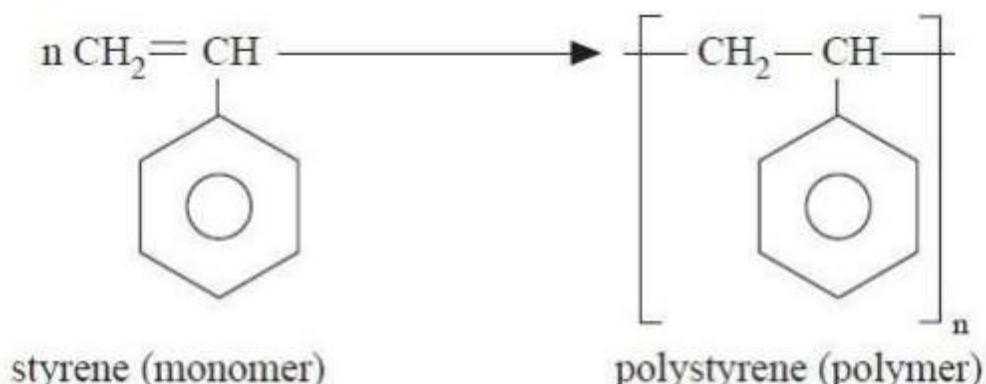
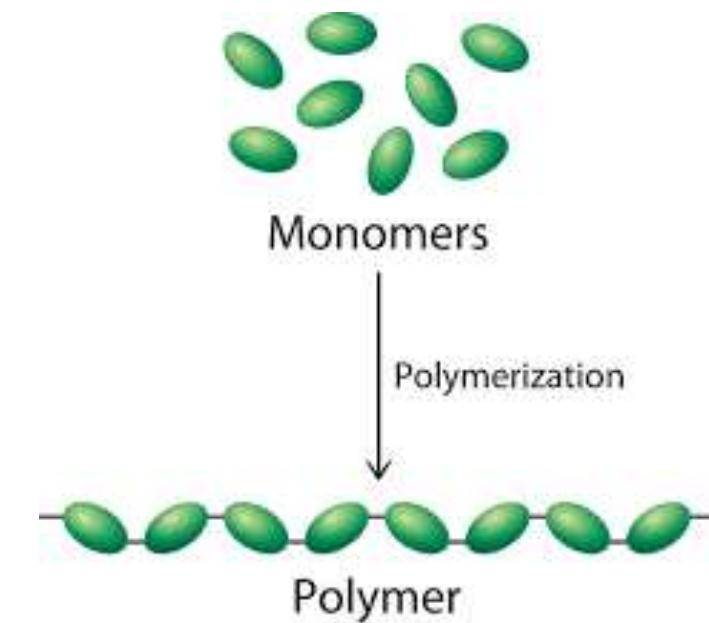
**Dr. Shruti Khanna Ahuja**

Assistant Professor

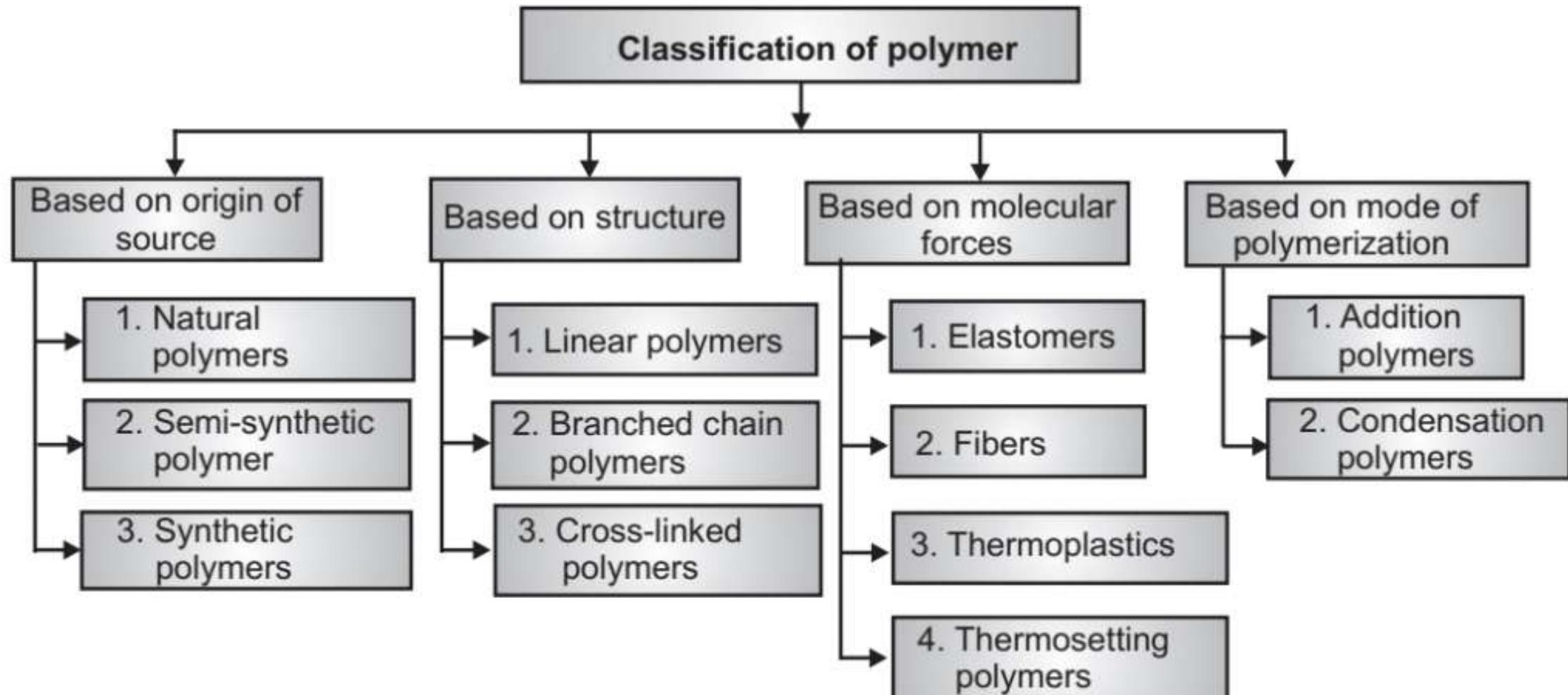
USAR, GGSIPU



- **Polymers** is a larger molecule or a macromolecule with very high molecular masses ( $10^3$  -  $10^7$  microns), each molecule of which consists of a very large number of simple repeating structural units joined together through covalent bonds.
- The simple and reactive molecules from which the repeating structural units are derived are called **monomers**.
- The process by which monomers are converted into polymers is called **polymerization**.
- Their consequently large molecular mass, relative to small monomers, produces unique physical properties such as toughness and viscoelasticity



The styrene molecule contains a double bond and is the monomeric unit. The resulting structure, enclosed in square brackets, is the polymer polystyrene (2). The unit in square brackets is called the repeating unit.



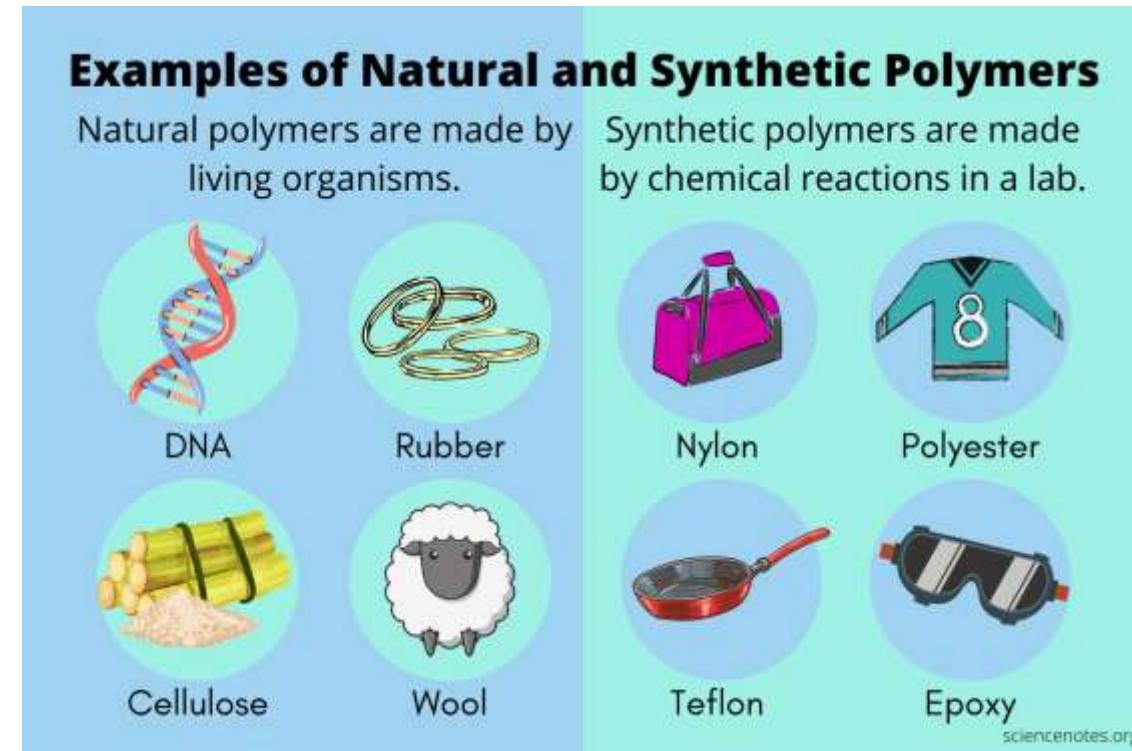


- **Based on origin of source:** Polymers are broadly divided into the following three classes:

(i). **Natural polymers:** They occur naturally and are found in plants and animals. Enzymes, nucleic acids, proteins, carbohydrates are polymers of natural origin. Their structures, are normally very complex. Starch, cellulose, and natural rubber, on the other hand, are examples of polymers of plant origin (natural) but have relatively simpler structures than those of enzymes or proteins.

(ii). **Semi-synthetic polymers:** They are derived from naturally occurring polymers and undergo further chemical modification. For example, cellulose nitrate, cellulose acetate.

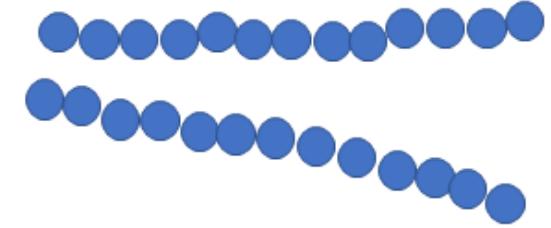
(iii). **Synthetic polymers:** These are man-made polymers, which are extensively used in daily life as well as in industry. These include fibers (nylon, polyester), plastics (polythene, polypropylene), rubbers (neoprene, polystyrene), etc.





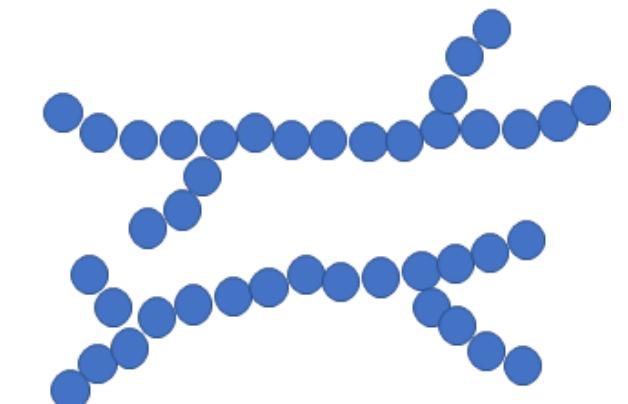
- **Based on structure of the monomer chain:**

(i). **Linear polymers:** Polymers in which monomer units are connected end-to-end along the whole length of the chain. The polymeric chains are stacked over one another, held together by van der Waals and H-bonding interactions. These type of polymers are often quite flexible and have high melting points, high densities and high tensile strength. E.g. polyvinyl chloride (PVC), high density polythene.



**Linear Polymers**

(ii). **Branched chain polymers:** In these, the monomer units not only combine to produce the linear main chain but also forms branches of different lengths. These polymer molecules because of branches do not pack well and have therefore lower melting points, densities and tensile strength. E.g. low density polythene.

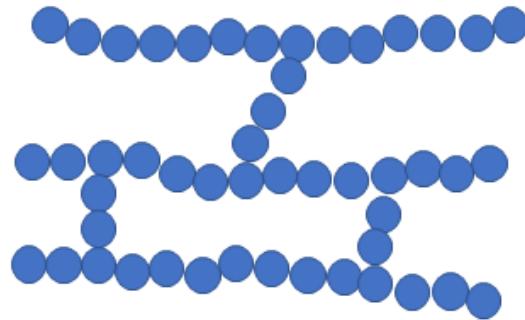


**Branched Polymers**

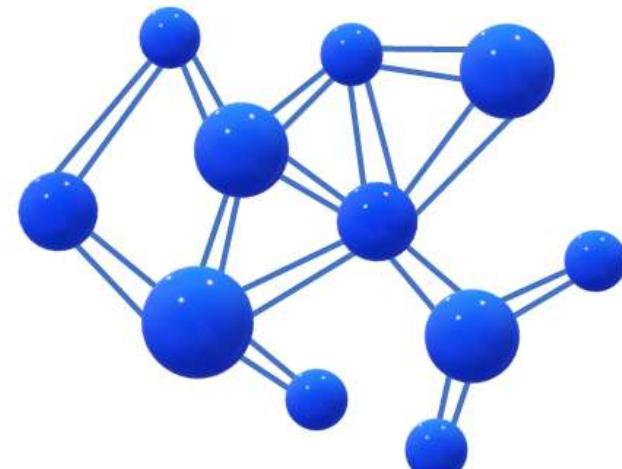


(iii). **Cross-linked polymers:** They are composed of bifunctional monomers. They have a stronger covalent bond in comparison to other linear polymers and are hard, rigid and brittle. Bakelite and melamine are examples.

(iv) **Network polymers:** They are trifunctional and have three points on the monomer that can react leading to three-dimensional network structure. They are highly cross-linked. In other words, a cross-linked polymer that includes numerous interconnections between the chains. E.g. phenol-formaldehyde resins, epoxy.



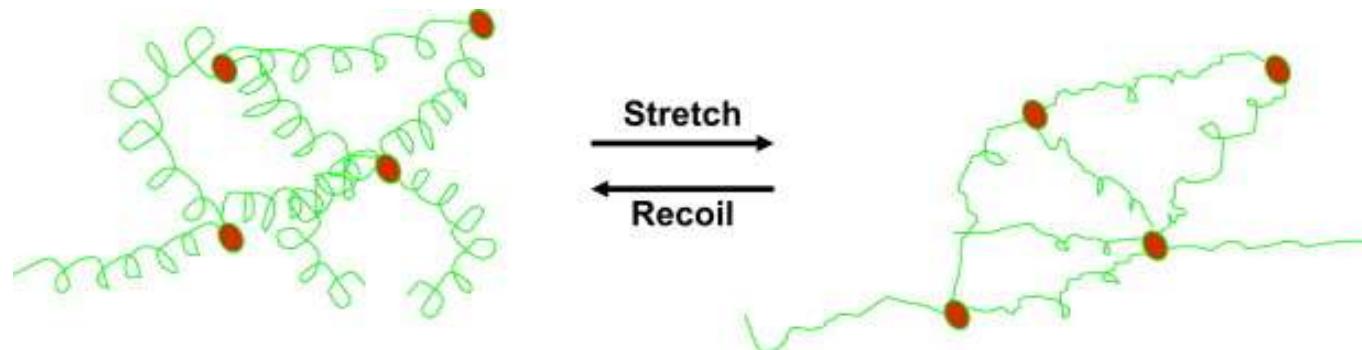
**Crosslinked Polymers**



**Networked Polymers**



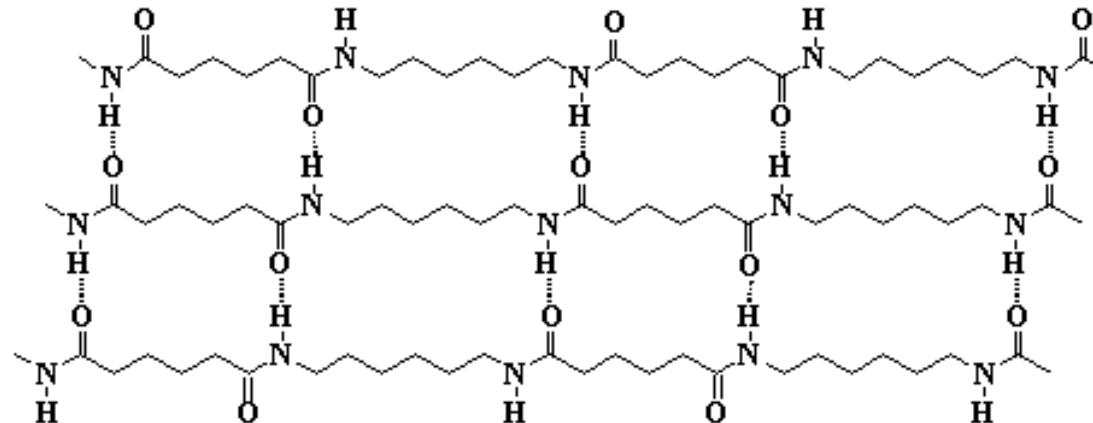
- **Based on molecular forces:** The application of polymers in the relevant are depends largely on its mechanical properties such as tensile strength, elasticity, toughness etc., which in turn depend on the intermolecular forces of attraction such as van der Waals forces, hydrogen bonds and dipole-dipole interactions between the adjacent polymeric chains. Greater the length of the polymeric chain, stronger are the intermolecular forces.
- Depending upon the magnitude of these intermolecular forces, polymers have been divided into four categories:
  - (i). **Elastomers:** Polymers with weakest intermolecular forces of attraction.
    - They are amorphous polymers and have high degree of elasticity i.e., they have ability to stretch out over 10 times their normal length and return to their original position when the force is withdrawn.
    - Whereas weak van der Waals forces of attraction permit the polymer chains to be stretched, the cross links enable the polymer to come back to the original position.
    - They consist of randomly coiled molecular chains of irregular shape having a few cross links. E.g. **natural rubber**, vulcanized rubber, Buna-S etc.





(ii). **Fibers:** Polymers with **strongest** intermolecular forces of attraction, which are due to H-bonding or dipole-dipole interactions.

- They have high modulus, high tensile strength and least elasticity.
- The molecules of these polymers are long, thin and thread-like and hence can be easily packed.
- This close packing results in their high melting points and low solubility.
- E.g. nylon (polyamides with H-bonding), polyesters and polyacrylonitrile (dipole-dipole interactions between the polar carbonyl groups and between carbonyl and cyano groups, respectively)

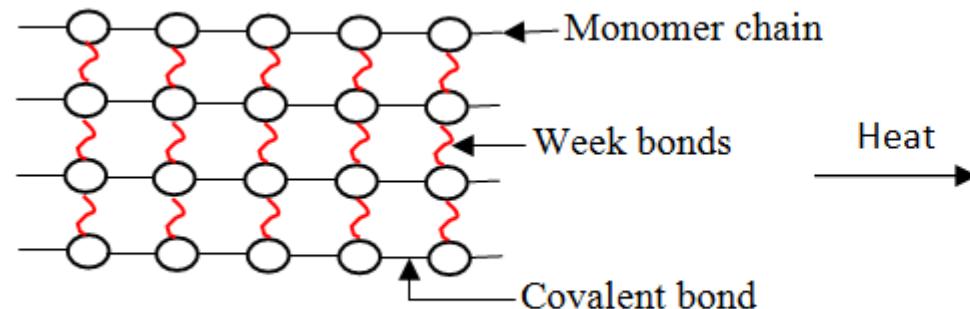


In nylon 6,6, the carbonyl oxygens and amide hydrogens can hydrogen bond with each other. This allows the chains to line up in an orderly fashion to form fibers.

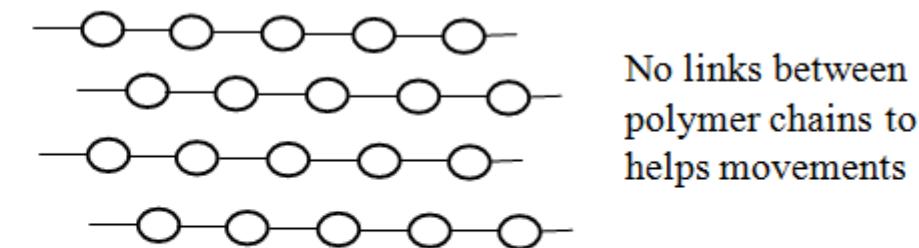


(iii). **Thermoplastics:** Polymers in which the intermolecular forces of attraction are in between those of elastomers and fibers.

- They are linear or slightly branched chain polymers which are hard at room temperature, become soft and viscous on heating and again rigid on cooling. They have little or no cross-links.
- As a result, these plastics can be easily moulded.
- E.g. polythene, polypropylene, polystyrene, PVS, nylon 6, nylon 6,6.
- **Plasticizers:** Those plastics which do not soften very much on heating can be made soft and readily working by addition of organic compounds known as plasticizers. E.g. dialkyl phthalates



**Figure 1.** Thermoplastic polymer

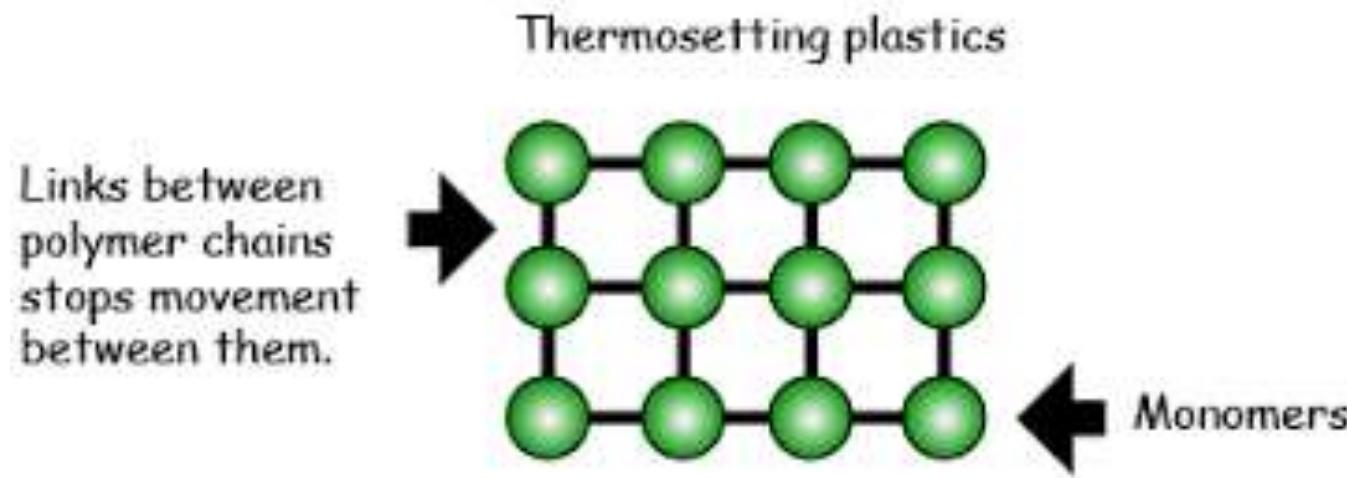


**Figure 2.** Thermoplastic softened state



(iv). **Thermosetting polymers:** These are semi-fluid substances with low molecular masses which when heated in a mould undergo a permanent change in chemical composition to give a hard and infusible mass.

- This hardening on heating is due to extensive cross-linking between different polymer chains to give a 3D-network solid.
- E.g. phenol-formaldehyde (Bakelite), urea-formaldehyde, melamine-formaldehyde.

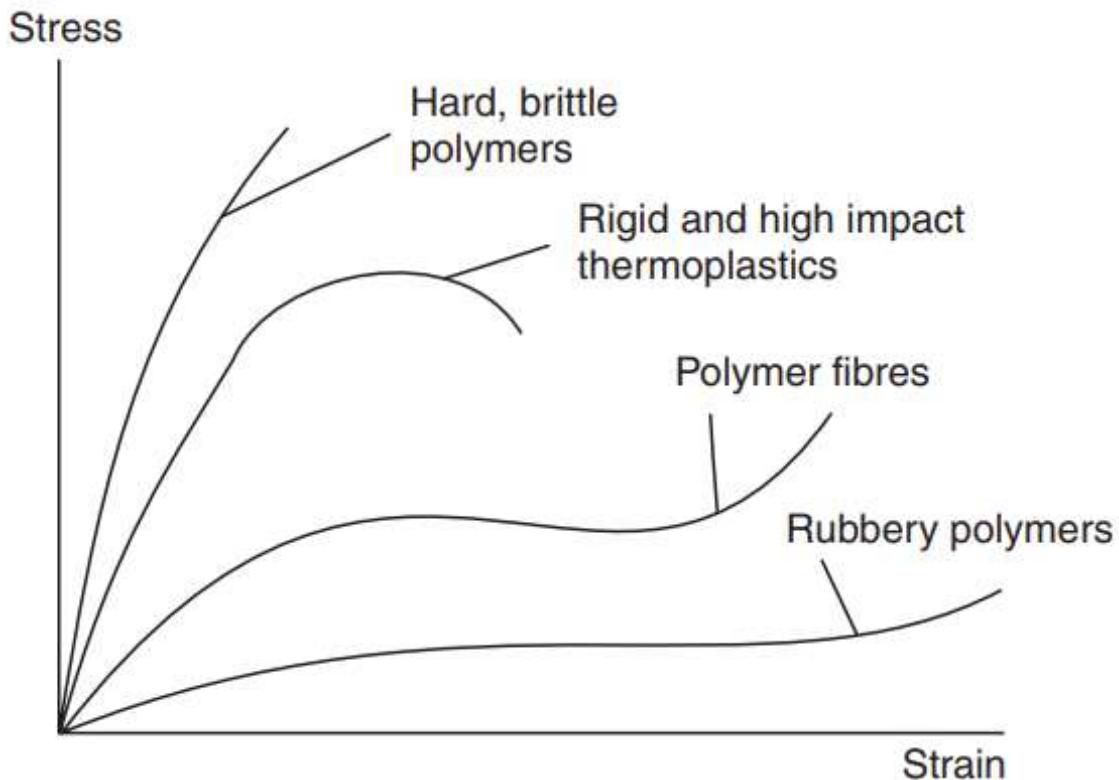




Thermoplastic	Thermosetting plastic
A) Maximum thermoplastic polymer are formed by addition polymerization in few cases condensation polymerization. B) The molecular forces are normally weak. C) Polymer backbone chains are connected together by Van der Wall's or dipole-dipole attraction or H-bonding. D) These polymers are normally soft and flexible. E) These polymers are normally linear or branch F) On application of heat these polymers become soft and again become hard on cooling. G) On continuous heating these polymer get melt. H) These polymers are recyclable. I) These polymers soluble in many organic solvent. J) Example of these hese polymers are PF resin(Bakelite), MF resin, UF resin Epoxy rein, Polyester resin etc.	A) Thermosetting plastic polymer are formed by only condensation polymerization. B) The molecular forces are tremendously strong. C) Polymer backbone chains are connected together by strong covalent bond. D) These polymers are normally hard and brittle. E) These polymers are normally cross linked polymer F) On application of heat the these polymers become more hard due to farther cross linking. G) On continuous heating these polymers get burnt. H) These polymers are not recyclable. I) These polymers insoluble in organic solvent. J) Example of these hese polymers are PVC,PE, PP



- **Mechanical properties of polymers:**



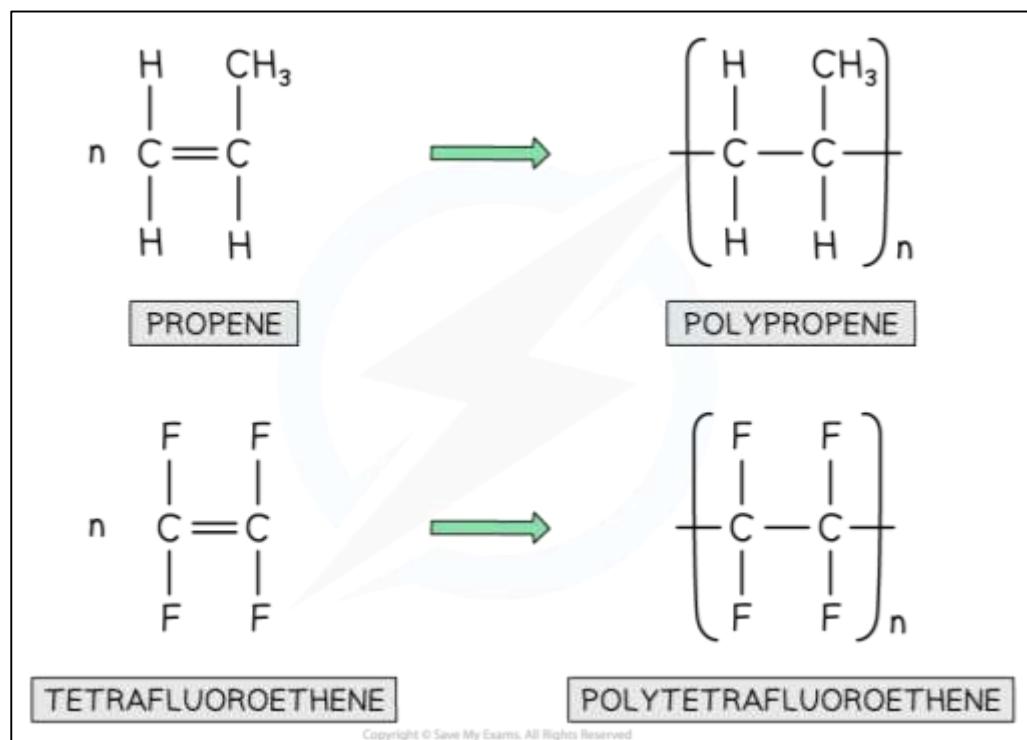
Four types of stress-strain curves illustrating how polymers of different types behave (the lines end where the sample breaks).



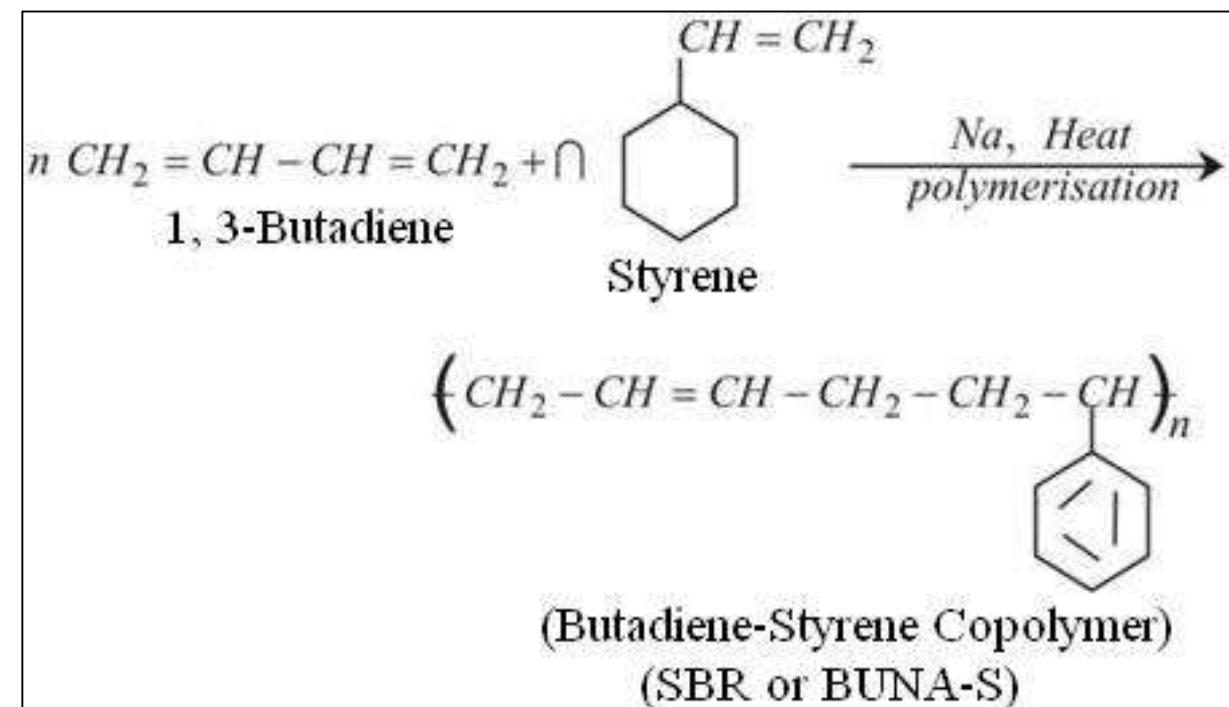
- **Based on mode of polymerization:**

(i). **Addition or chain growth polymers:** They are formed by repeated addition of a large number of same or different monomers possessing **double and triple bonds**.

- They can be either addition homopolymers or addition copolymers.



**Addition homopolymers**

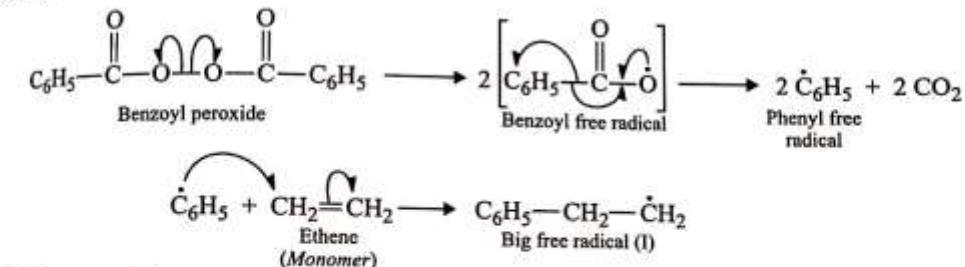


**Addition copolymers**

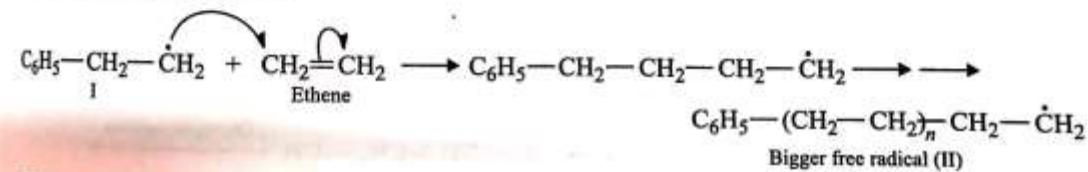


- Addition polymerization involves successive addition of monomer units to the growing chain carrying a reactive intermediate such as a free radical, a carbocation or a carbanion
- It is also known as chain growth polymerization as it takes place in stages leading to increase in chain length and each stage produces a reactive intermediate for use in next stage of growth of the chain.
- The manufacture of polyethylene employs a free-radical initiator that donates its unpaired electron to the monomer, making the latter highly reactive and able to form a bond with another monomer at this site.
- Common radical initiators are benzoyl peroxide, t-butyl peroxide, dioxygen

**Chain initiating steps :**

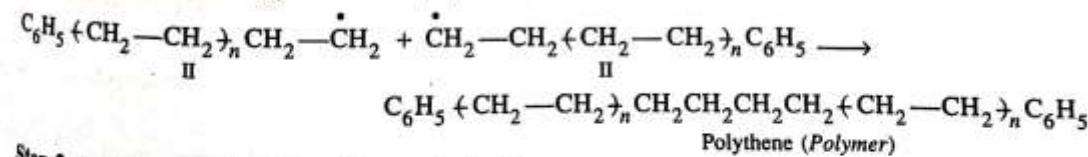


**Chain propagating steps :**

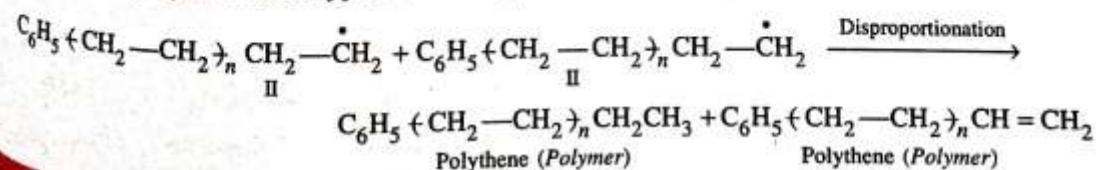


**Chain terminating steps :**

*Step 1. By combination of free radicals (II) :*



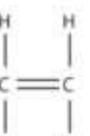
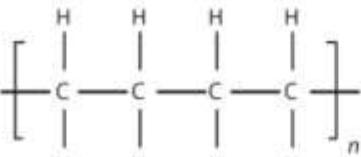
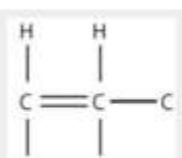
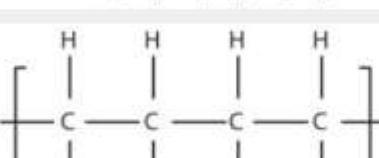
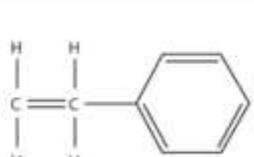
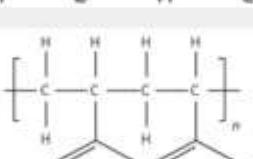
*Step 2. By disproportionation of free radicals (II) :*



**Free radical addition polymerization**



- Common examples of addition polymers:

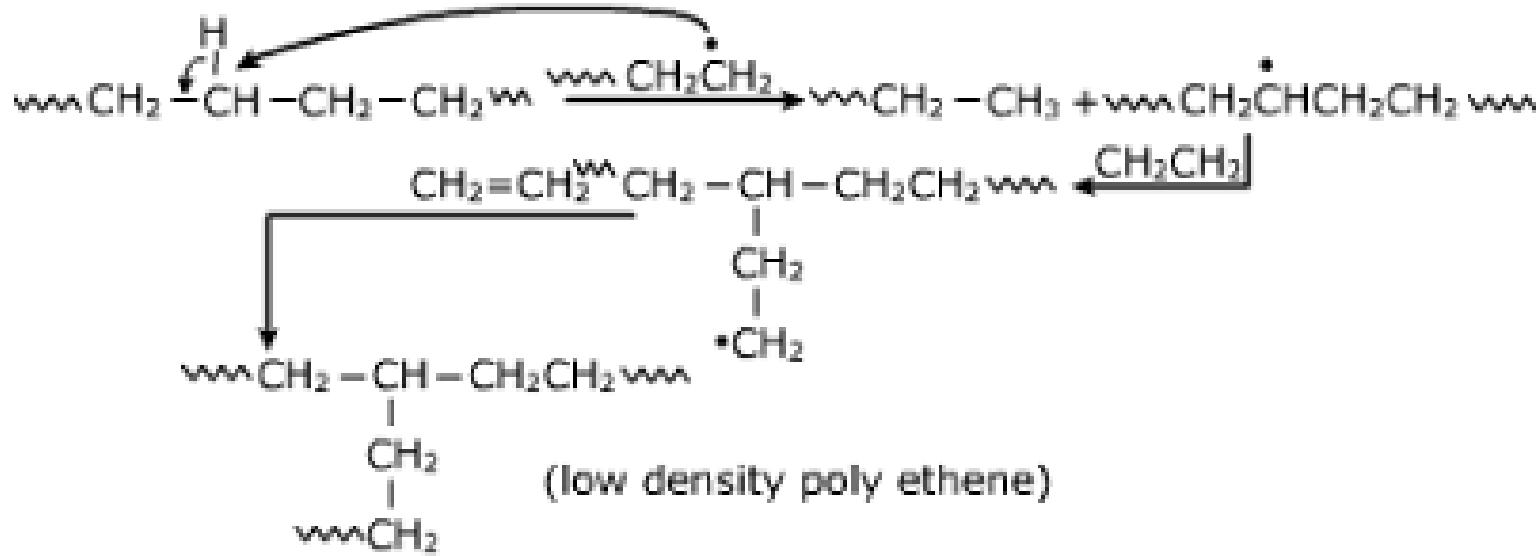
Monomer	Polymer	Polymer Name [Trade Name(s)]	Some Uses
 $\text{CH}_2=\text{CH}_2$	 $\sim\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\sim$	polyethylene	plastic bags, bottles, toys, electrical insulation
 $\text{CH}_2=\text{CHCH}_3$		polypropylene	carpeting, bottles, luggage, exercise clothing
 $\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$		polystyrene	"take-out trays", foam "packing peanuts", CD cases, foam-walled drink cups, and other thin-walled and moldable parts.
$\text{CH}_2=\text{CHCl}$	$\sim\text{CH}_2\text{CHCH}_2\text{CHCH}_2\text{CH}_2\sim$ 	polyvinyl chloride	bags for intravenous solutions, pipes, tubing, floor coverings
$\text{CF}_2=\text{CF}_2$	$\sim\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\sim$	polytetrafluoroethylene (Teflon)	Non-stick coating for cooking utensils, chemically resistant specialty plastic parts, Gore-Tex



- **Synthesis of some important addition polymers:**

**1. Polythene or polyethylene:** Prepared by free radical or high-temperature polymerization of ethane.

a. **Low Density Polyethylene (LDPE):** It is prepared by heating ethylene monomer at 250°C under high pressure (1000 - 4000 atm) in presence of oxygen or hydrogen peroxide (free radical generator). In this process huge branched chains are formed through out every long back bone chain. The presence of branches repel each other and the long chains are not well fitted to each other having some gap produce low density (0.91 to 0.925 gm/cc) and low melting point (384 K) polymer.



- **Uses:**

- a) As LDPE is a good insulator they normally used for the preparation of electrical wires and cables.
  - b) Pouch pack, squeeze bottles, delivery pipes are prepared from LDPE.
  - c) Toys, refill for ball pen and ball pen also prepared from LDPE.



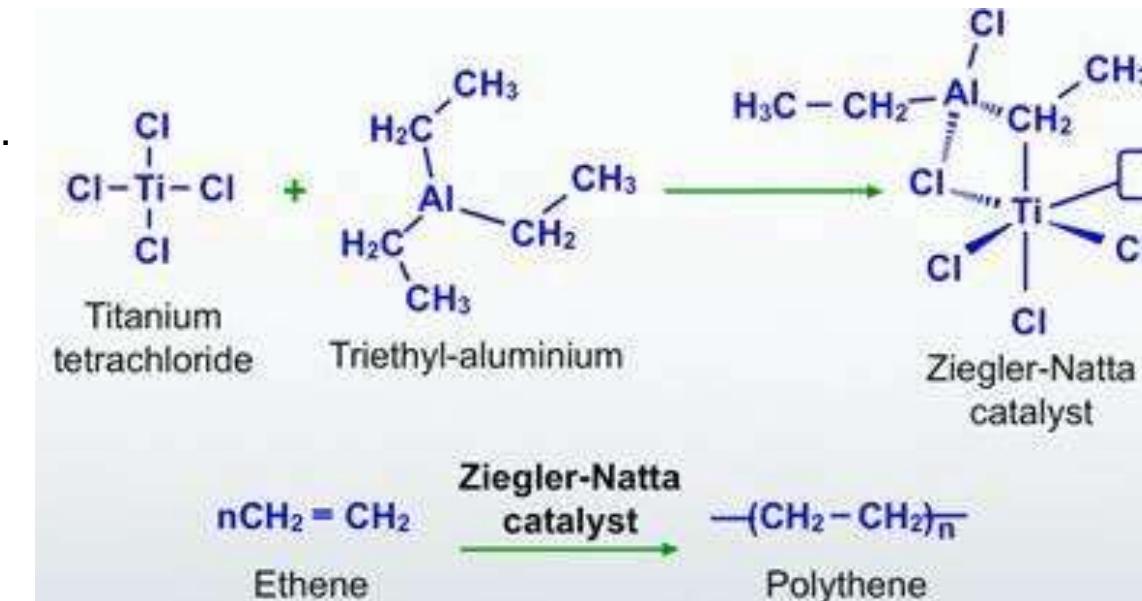
**b. High Density Polyethylene (HDPE):** polymerization of ethylene monomer at low pressure (5 - 7 atm) and temperature (60–700C) in presence of **Ziegler Natta catalyst** like triethyl aluminum and titanium tetrachloride. In this process of polymerization as there is absence of branch through out the long chain back bone, the chains are well fitted to each other which makes the polymer a high density (0.95 to 0.97 gm/cc) polymer.

- **Characteristics** of high density polythene:

- i. High density polyethylene have high density (0.95 to 0.97 gm/cc).
- ii. It is less branched.
- iii. Highly crystalline polymer having crystallinity 80-90 percent.
- iv. Chemically inert, nonpolar and having dielectric property zero.
- v. Highly tough but flexible.
- vi. Melting point 130 – 1350C.

- **Uses** of high density polythene:

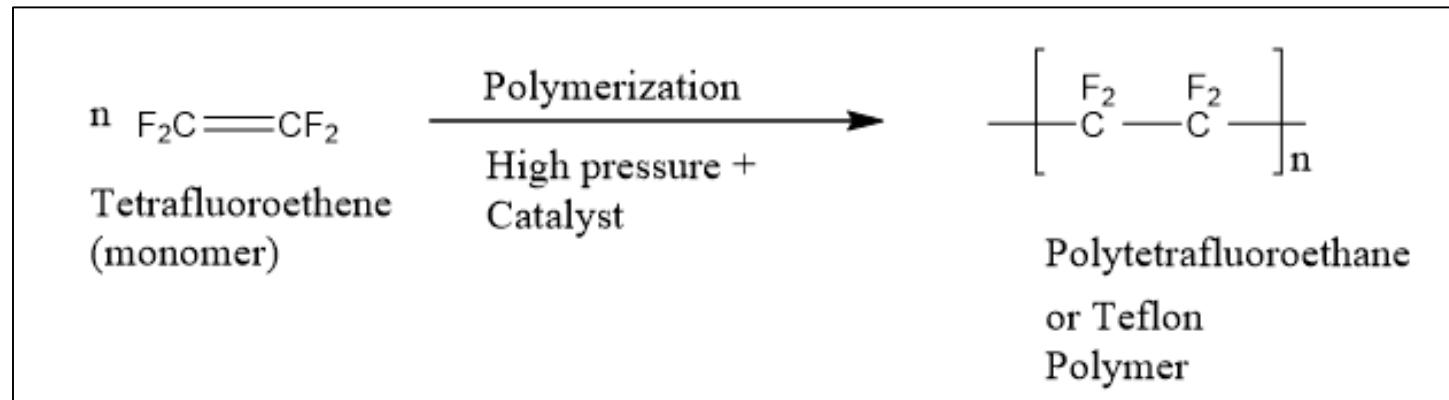
- i. As HDPE is a good insulator they normally used for the preparation of high performance electrical cables.
- ii. Bucket, cup, toys.
- iii. Due to inertness it is used for the storage of  $H_2SO_4$ , pipes for LPG gas and water reservoir also.





## 2. Polytetrafluoroethylene (PTFE) or Teflon:

- Catalyst used: peroxides or ammonium persulfate at high pressure.
- **Characteristics:**
  - i. Chemically inert and resistant to attack by corrosive reagents
  - ii. High thermal stability
- **Uses:**
  - i. Used for making non-stick utensils
  - ii. Used for making gaskets, pump-packings, valves, seals, etc.





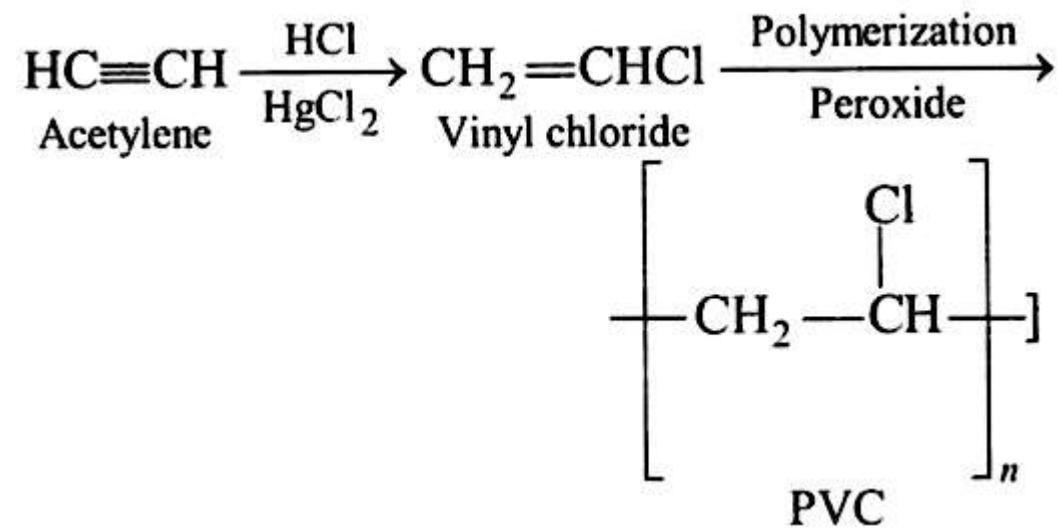
### **3. Polyvinyl chloride (PVC):**

- **Characteristics:**

- i. Colorless, odorless, non-inflammable, chemically-inert powder
  - ii. High rigidity but brittle
  - iii. Resistant to water, light, O<sub>2</sub>, inorganic acids and alkalis, oil, but soluble in hot chlorinated hydrocarbons.

- **Uses:**

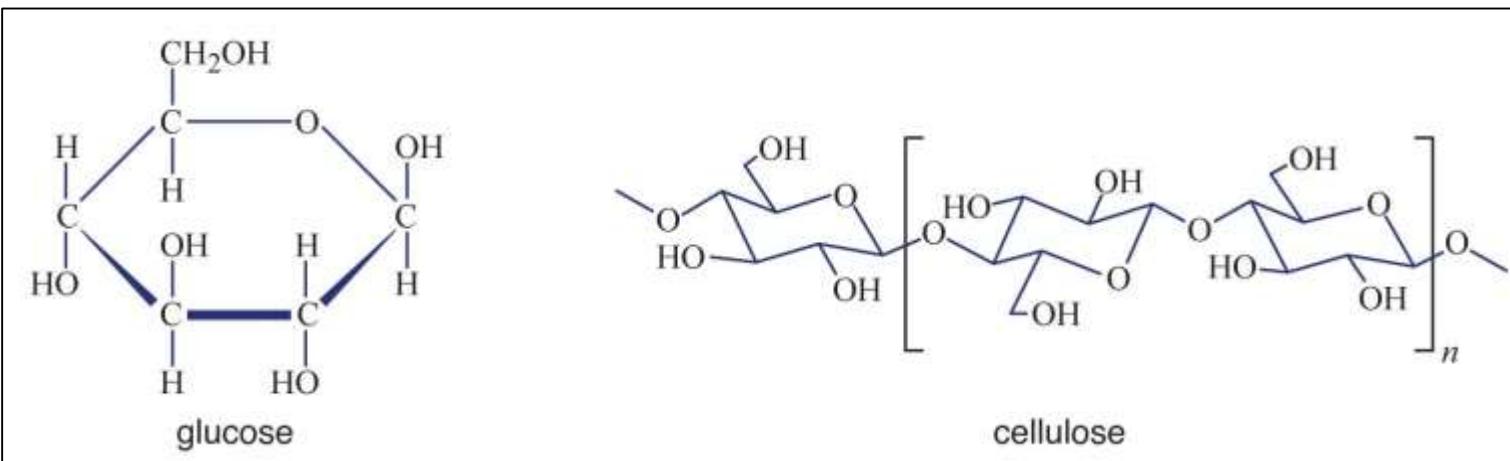
- i. Used for making cables, water hoses, pipes of petroleum industry, refrigerator components
  - ii. Used for making toys, raincoats, tyres, cycles etc.



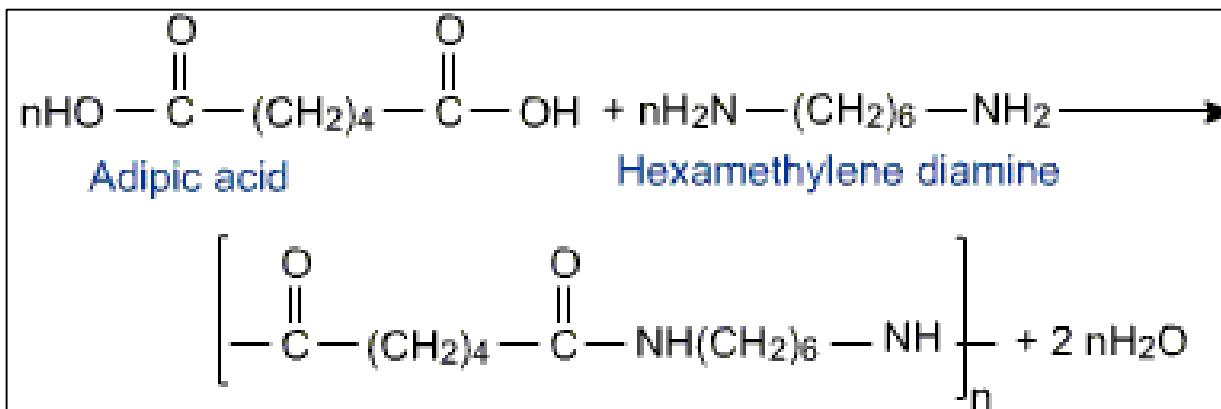


(ii). **Condensation or step growth polymers:** They are formed by repeated condensation reaction between two bifunctional and trifunctional monomer units usually with elimination of small molecules like water, alcohol, ammonia,  $\text{CO}_2$ ,  $\text{HCl}$  etc.

- They can be either condensation homopolymers or addition copolymers.



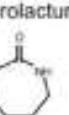
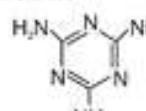
**Condensation homopolymers**



**Condensation copolymers**



• Common examples of condensation polymers:

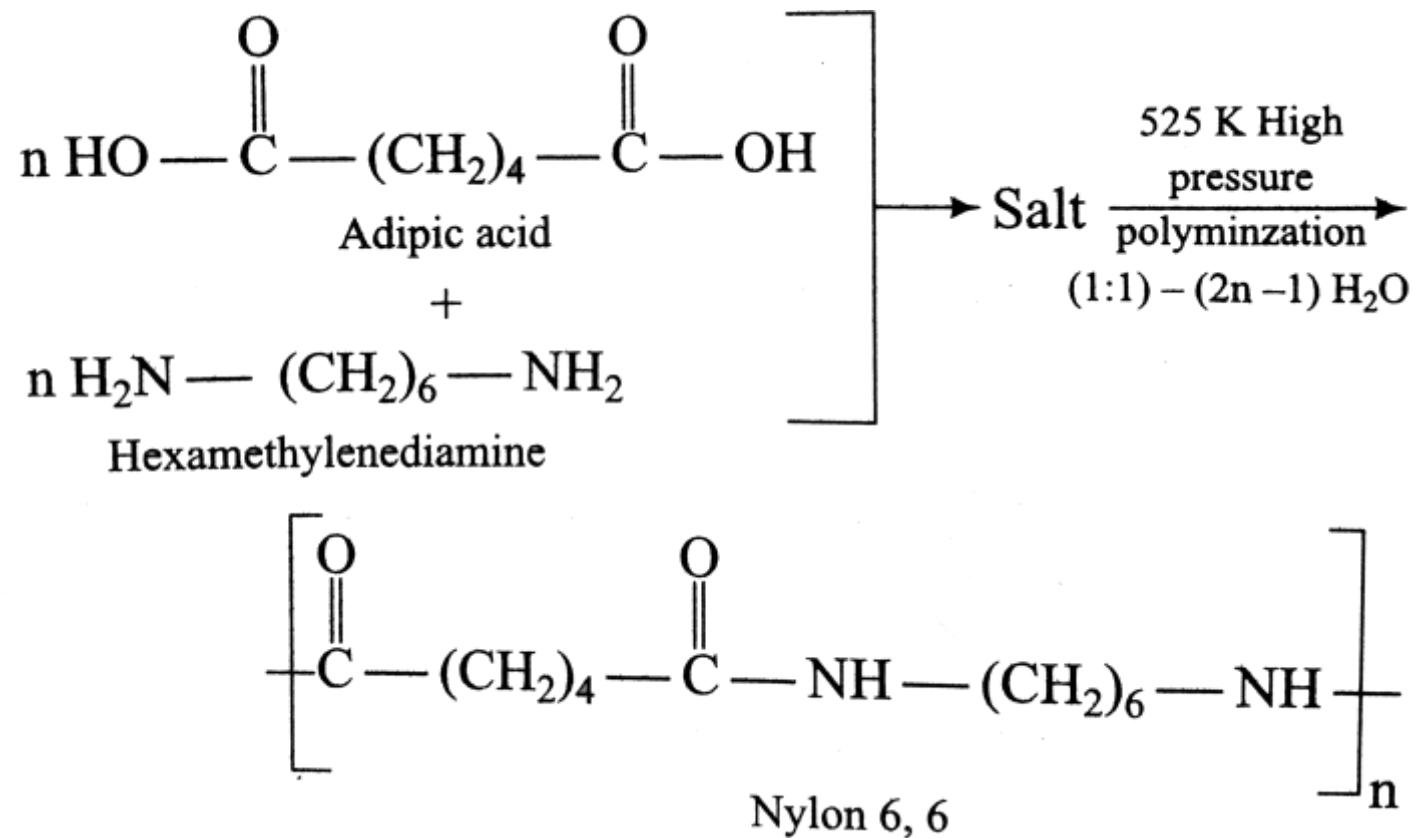
POLYMER	MONOMER	STRUCTURE	USES
1. Nylon 6, 6	a) Adipic acid $\text{HOOC-(CH}_2)_4\text{-COOH}$ b) Hexamethylene diamine $\text{NH}_2\text{-(CH}_2)_6\text{-NH}_2$	$\text{H} \quad \text{H} \quad \text{O} \\   \quad   \quad    \\ +\text{N-(CH}_2)_6\text{-N=C-(CH}_2)_4\text{-C+} \\    \quad   \\ \text{O} \quad \text{O}$	For making fabrics, for clothing, sports wear, combs, bristles of brushes.
2. Nylon 6	Caprolactum 	$\text{O} \quad \text{O} \quad \text{H} \quad \text{O} \\    \quad    \quad   \quad    \\ \text{NH-C-(CH}_2)_5\text{-NH=C-(CH}_2)_5\text{-N-C}$	Mainly used for making cords for types, ropes and fabrics.
3. Polyester	a) Ethyleneglycol $\text{CH}_2\text{OH}$ $\text{CH}_2\text{OH}$ b) Terephthalic acid $\text{HOOC-C}_6\text{H}_4\text{-COOH}$	$\text{O} \quad \text{O} \\    \quad    \\ \text{O-C-O-C-O-CH}_2\text{-CH}_2\text{-O+}$	Crease resistant fibres, safety helmets.
4. Phenol - formaldehyde Resin (Bakelite)	a) Phenol  b) Formaldehyde $\text{HCHO}$	$\left[ \begin{array}{c} \text{OH} & \text{OH} \\   &   \\ \text{O} & \text{C} \\   &   \\ \text{CH}_3 & \text{CH}_3 \end{array} \right]$	Manufacture of switches, plugs, cooker handles, iron handles and parts.
5. Melamine-Melamine - formaldehyde Polymer	a) Melamine  b) Formaldehyde $\text{CH}_2\text{O}$ or $\text{HCHO}$	$\left[ \begin{array}{c} \text{H} & \text{H} \\   &   \\ \text{N} & \text{N} \\   &   \\ \text{H} & \text{N-CH}_3 \\   &   \\ \text{N} & \text{N} \\   &   \\ \text{H} & \text{H} \end{array} \right]$	In the manufacture of unbreakable tableware, trays, clocks, knobs, utensil handles etc.



- **Synthesis of some important condensation polymers:**

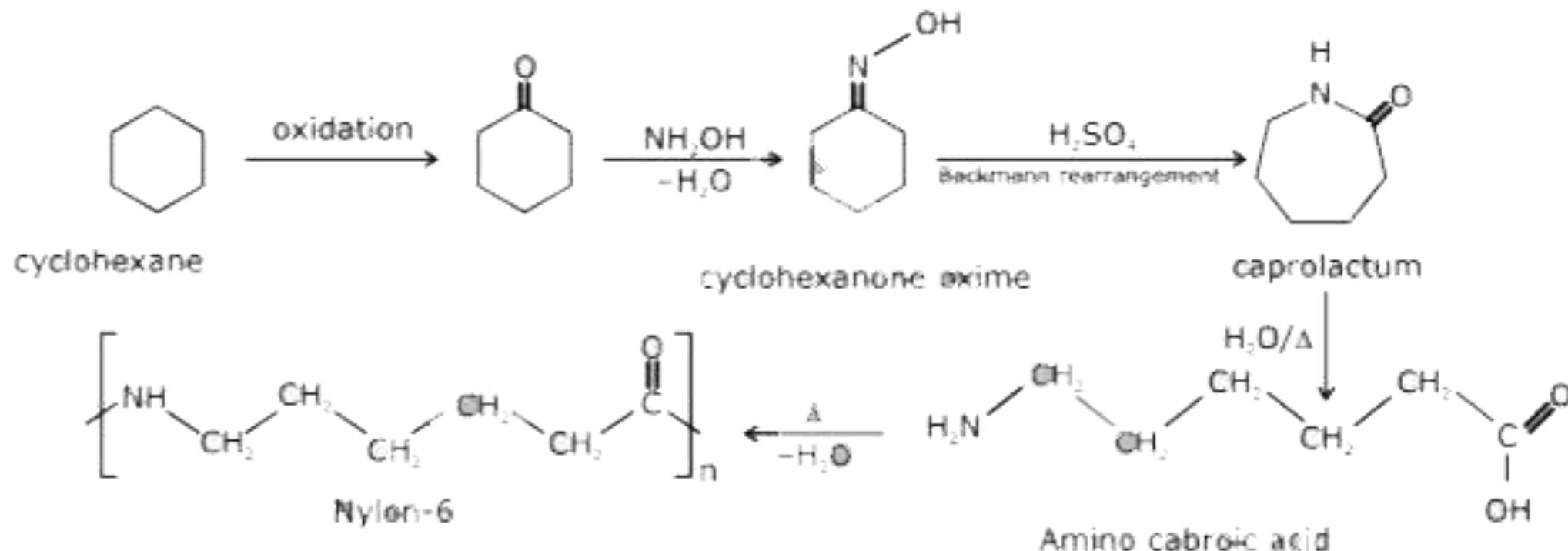
1. **Polyamides:** Polymers with amide linkages. E.g., nylon 6,6 and nylon 6

a. **Nylon-6,6:**





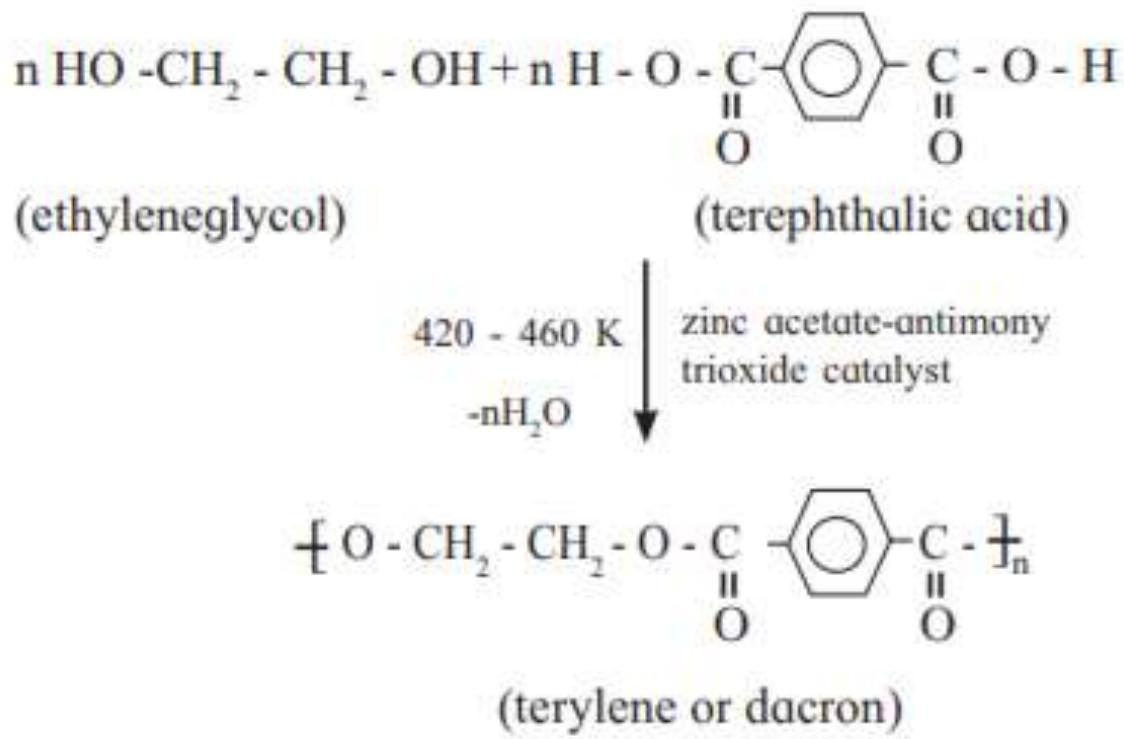
b. Nylon 6:





**2. Polyesters:** Polymers with ester linkages. E.g., terylene or Dacron

**a. Terylene:**





### 3. Phenol-formaldehyde polymers: E.g., bakelite

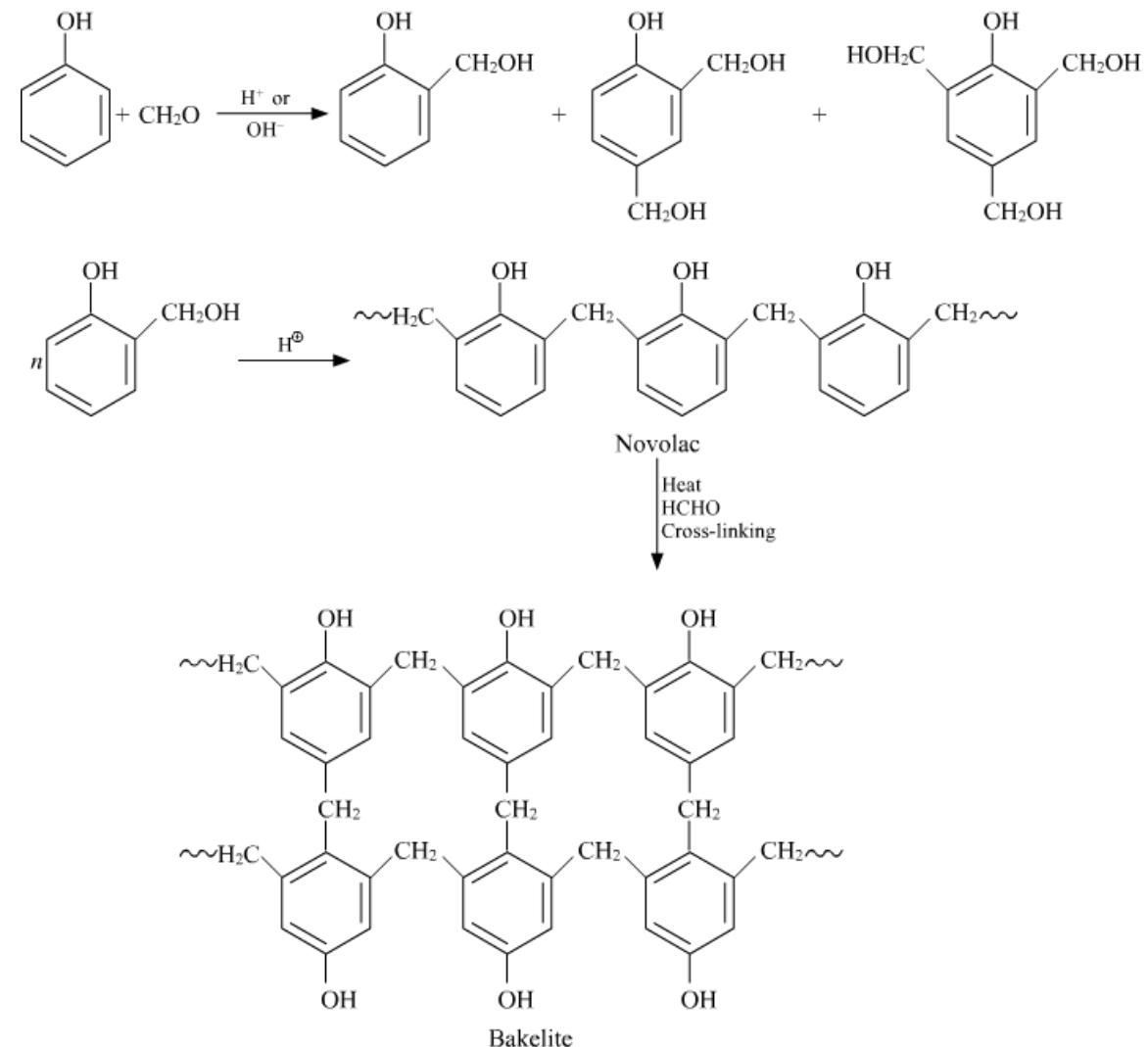
#### a. Bakelite:

##### Properties of bakelite:

- a) It is high thermal and electrical resistance.
- b) It is hard rigid and scratch proof.
- c) It is resistant to many inorganic and base.

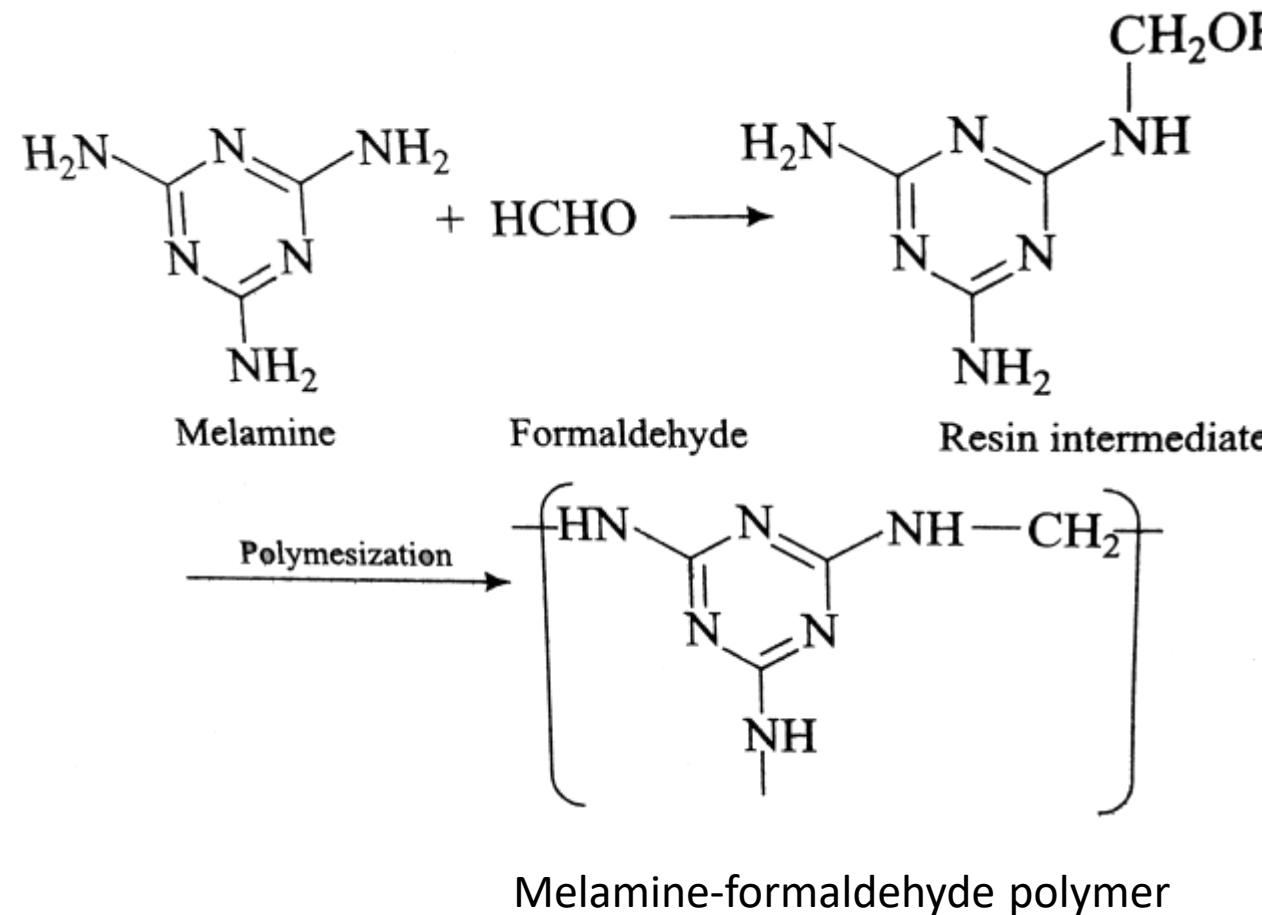
##### Use of bakelite:

- a) Novoloc is used for the preparation of laminates.
- b) Resol is used for preparation of comb, P.O. Box, marine grade, shutter grade, Boiling water proof ply board, block board, flush door etc.
- c) Resol is used for preparation of electrical board, switch etc.





#### 4. Melamine-formaldehyde polymers: E.g. Melmac





### 3. Phenol-formaldehyde polymers: E.g., bakelite

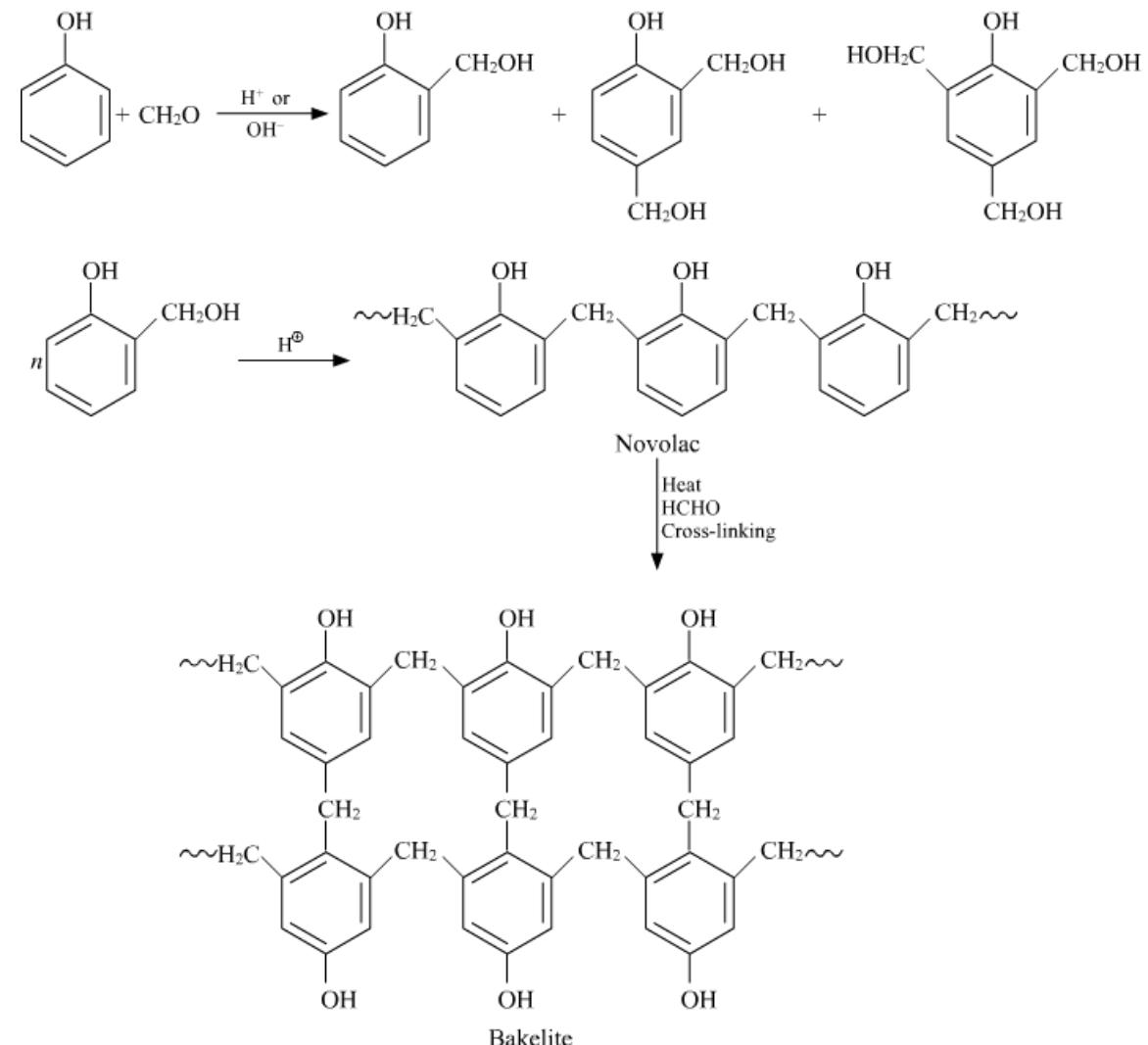
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- **Molecular weight of a polymer:**
- The properties of polymers depend largely upon their molecular size and structure.
- Since the polymers are made up of monomeric units with different molecular mass in different chain length, the polymer as a whole has an average molecular mass.
  - i. **Number average molecular mass ( $\bar{M}_n$ ):** It is the simple arithmetic mean and is defined as the total mass (w) of all the molecules of a polymer divided by the total number of molecules present. In other words, it gives the average of the molecular masses of the individual macromolecules. It is the **mole fraction of molecules** in a polymer sample.
- If  $N_1, N_2, N_3\dots$  are the number of macromolecular with molecular masses.  $M_1, M_2, M_3\dots$ , respectively then the number average molecular masses of the polymer is given by:

$$\bar{M}_n = \frac{w}{\Sigma N} = \frac{\Sigma N_i M_i}{\Sigma N_i}$$

where  $N_i$  is the number of molecules of mass  $M_i$ .  $\bar{M}_n$  can be determined by measuring the colligative properties like lowering of vapor pressure, depression of freezing point etc.



- **Molecular weight of a polymer:**

ii. **Weight average molecular mass ( $M_w$ ):** It is the **weight fraction of molecules** in a polymer sample. It is another way of determining the molecular mass of a polymer. It gives the average of the molecular masses of the individual macromolecules in the polymer sample.

- If  $w_i$  is the weight fraction of molecules having mass  $M_i$ , then the weight average molecular masses of the polymer is given by:

$$\overline{M}_w = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

- We can determine this parameter using static light scattering, small angle neutron scattering, X-ray scattering, and sedimentation velocity.
- The weight-average molecular weight is larger than or equal to the number-average molecular weight.
- The ratio of the weight-average and number-average molecular weights,  $M_w / M_n$  is a measure of the **polydispersity** of a polymer mixture - how widely distributed the range of molecular weights are in the mixture. A ratio that is around 1.0 indicates that the range of molecular weights in the mixture is narrow; a high ratio indicates that the range is wide. With rare exceptions, all synthetic polymers are polydisperse.



- **Molecular weight of a polymer:**

iii. **Viscosity average molecular mass ( $M_v^-$ ):** The molecular weight of the polymer is measured by using viscometer and the molecular weight obtained by this technique is called viscosity average molecular weight. The molecular weight of the polymer solution is very high so the viscosity of polymer solution is very high compared to that of pure solvent.

From the Mark-Houwink equation the relationship among the molecular weight and viscosity are given below:

$$[\eta] = KM^\alpha$$

Where  $[\eta]$  is the intrinsic viscosity, M is the Molecular weight, K and  $\alpha$  are constants for a particular polymer solvent system. If we know the K and  $\alpha$  values for a given polymer solution the intrinsic viscosity and molecular weight can be calculate using the above equation.



- **Degree of Polymerization (DP):**
- It is usually defined as the number of recurring monomeric units in a macromolecule or polymer or oligomer molecule.
- The chain length in a polymer generally varies from 100 to 200 or sometimes even 1000, hence we use the term average degree of polymerization ( $DP^-$ ).
- The degree of polymerization has a dramatic effect on the mechanical properties of a polymer. As chain length increases, mechanical properties such as ductility, tensile strength, and hardness rise sharply and eventually level off.
- For a homopolymer, there is only one type of monomeric unit and the number-average degree of polymerization is given by

$$DP_n \equiv X_n = M_n / M_0$$

where,  $M_n$  is the number-average molecular weight and  $M_0$  is the molecular weight of the monomer unit.

- **Ex:** calculate the degree of polymerization of a sample of polyethylene  $[(CH_2-CH_2)_n]$ , which has a molecular weight of 150,000 g/mol.
- The molecular weight of a repeating unit,  $M_0 = (12 \times 2 + 1 \times 4) \text{ g/mol} = 28 \text{ g/mol}$

$$DP = M/M_0 = 150,000 \text{ g/mol} / 28 \text{ g/mol}$$

$$= 5.35 \times 10^3$$

=> The particular molecule contains  $5.35 \times 10^3$  of repeat units.



University School of Automation and Robotics  
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Engineering Chemistry-II (BS-104)

# Nanotechnology

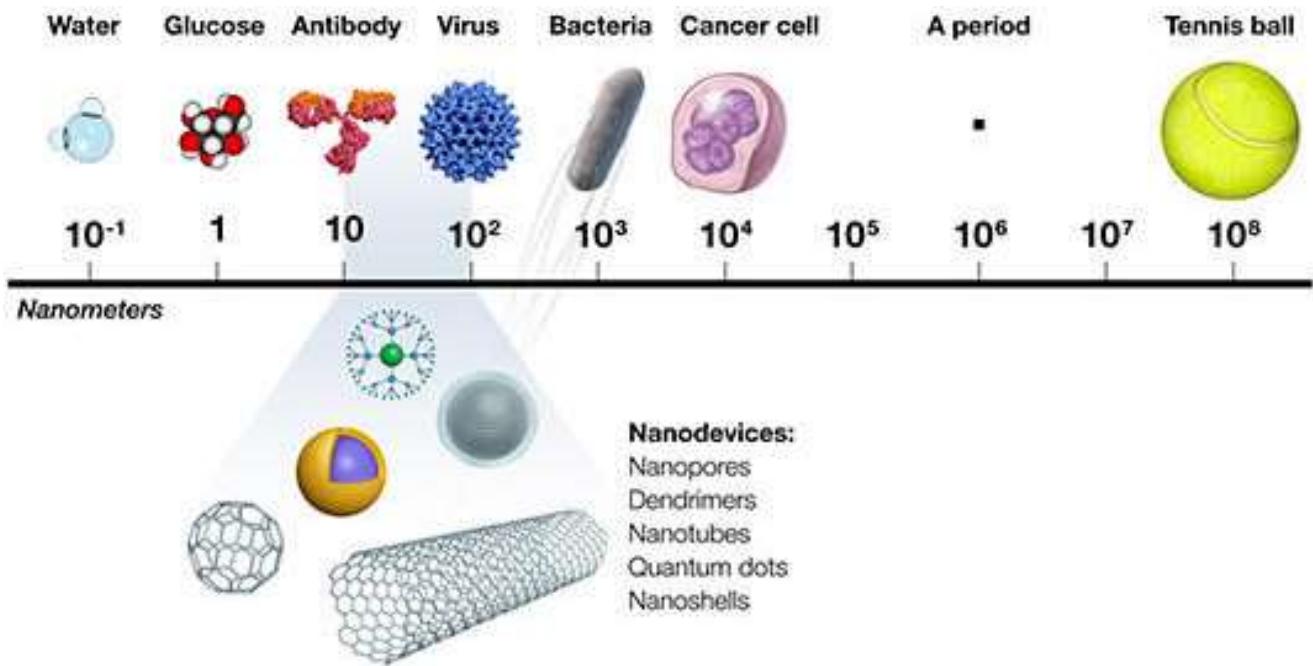
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Assistant Professor

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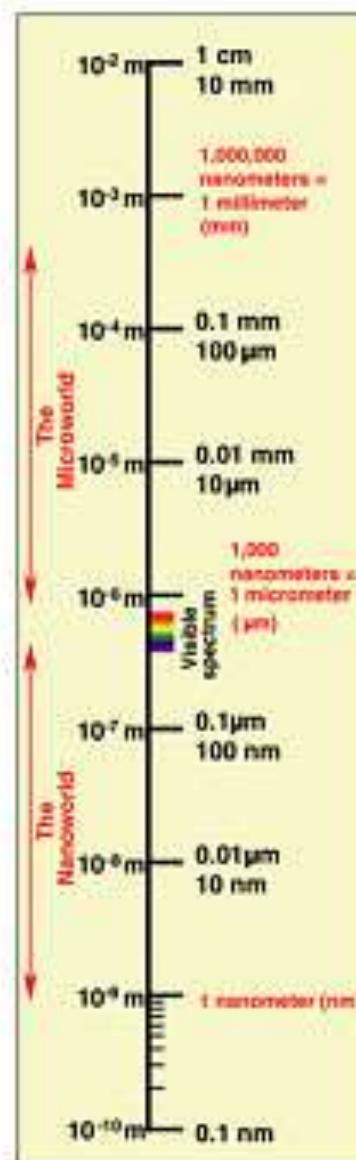
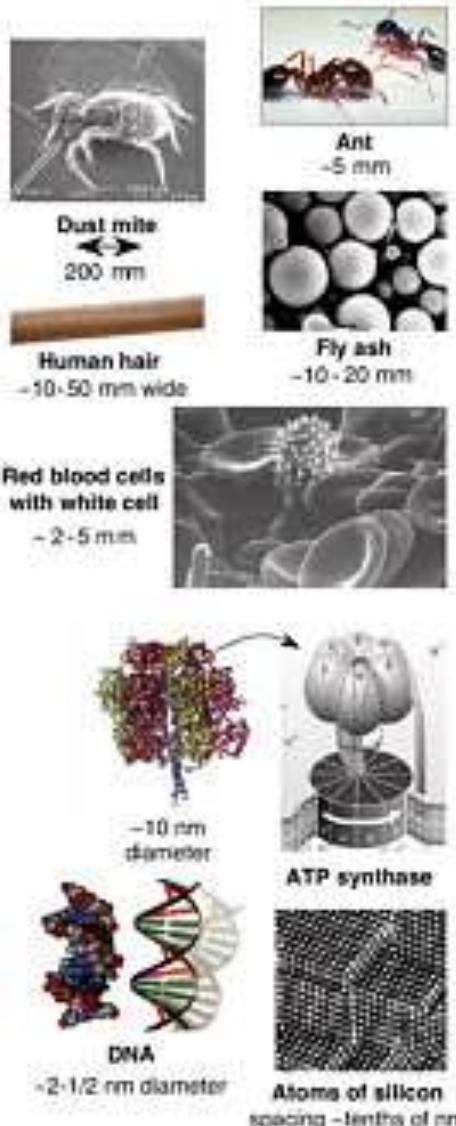


- **Nanotechnology** is defined as the design and fabrication of materials, devices and systems with control at nanometer dimensions.
- The essence of nanotechnology is therefore **size and control**.
- The nanometer,  $10^{-9}$  m, i.e. one millionth of a millimeter
- In 1959, the physicist Richard Feynman, Nobel Prize winner for Physics in 1965, came up with the brilliant concept of the nano when he said “**there is plenty of room at the bottom**” during a conference of the American Physical Society.
- The term nanotechnology was first used in 1974 by Norio Taniguchi (University of Tokyo)

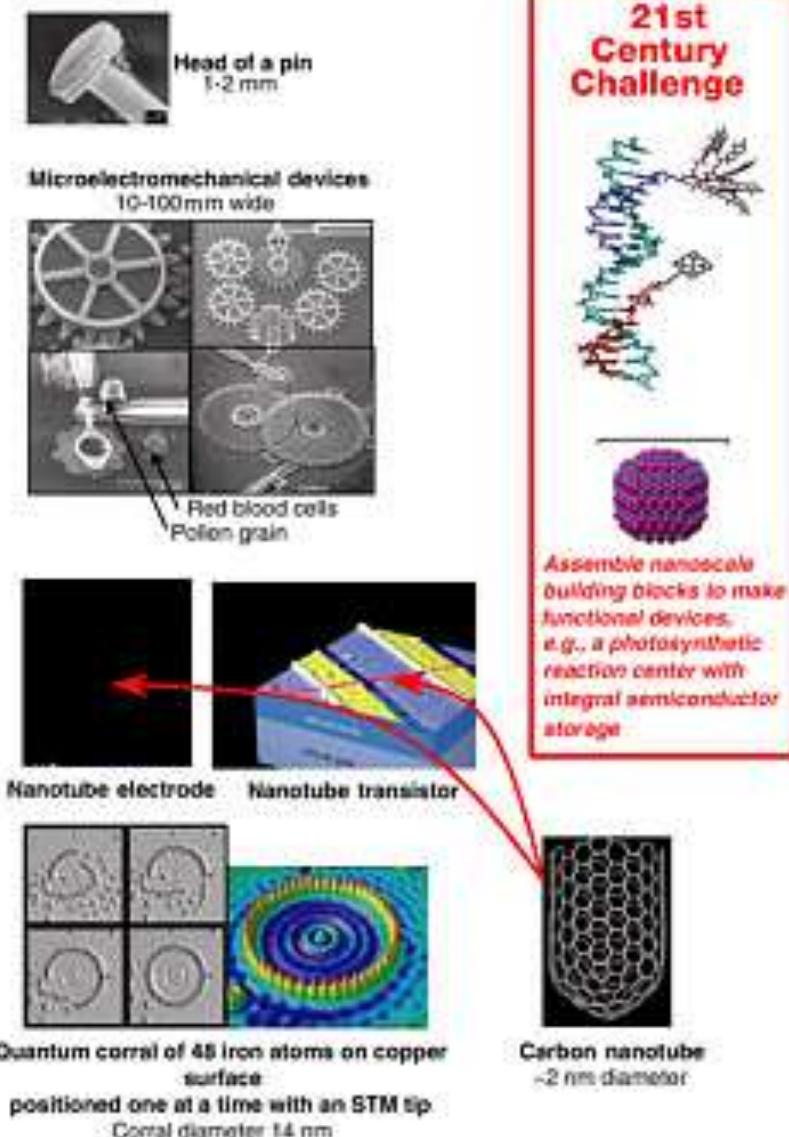




## Things Natural

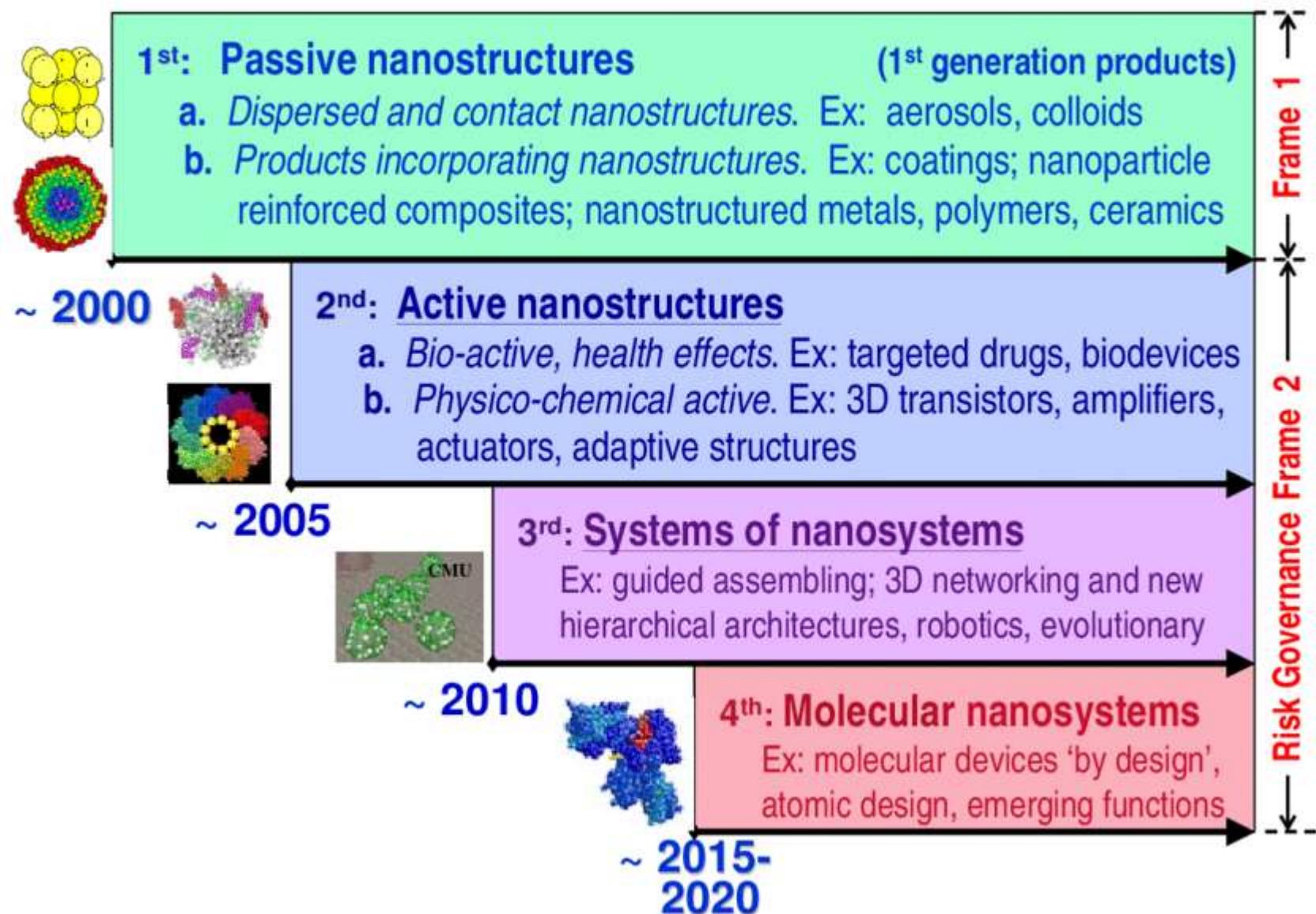


## Things Man-made





- Nanotechnology Timeline:

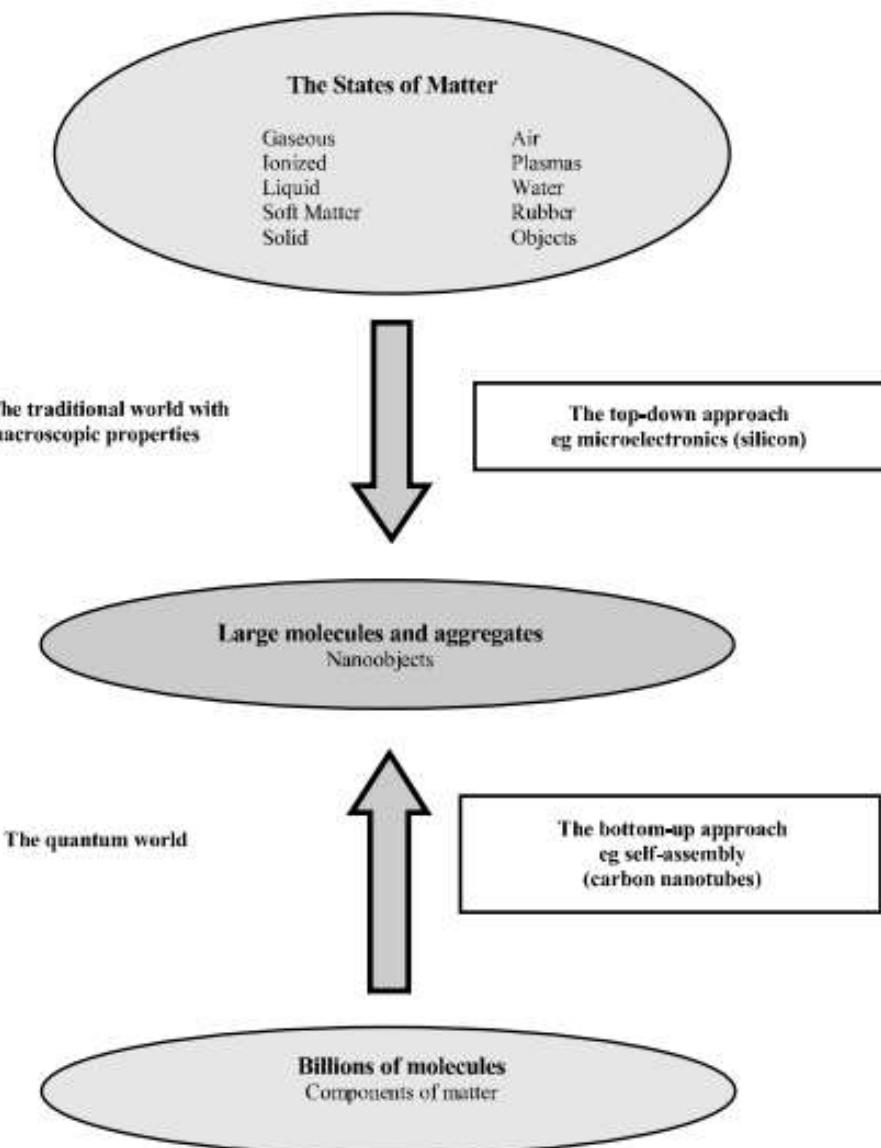




- Two technological approaches to the nanoworld:

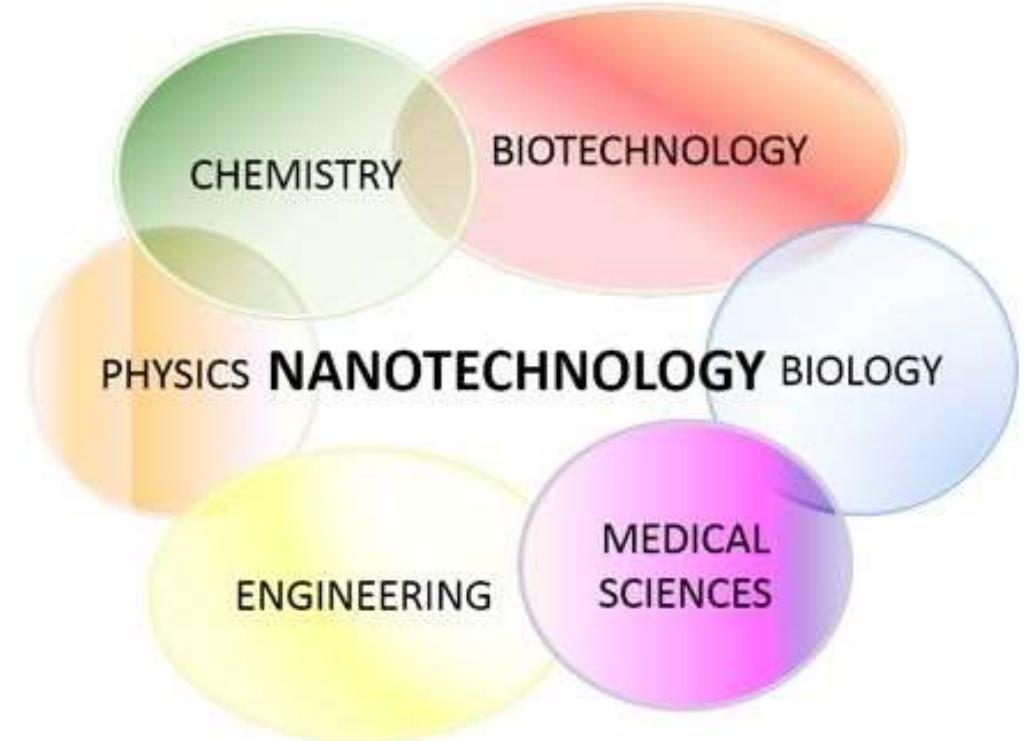
(i). **Top-down:** which enables us to control the manufacture of smaller, more complex objects, as illustrated by micro and nanoelectronics;

(ii) **Bottom-up:** which enables us to control the manufacture of atoms and molecules, as illustrated by supramolecular chemistry.



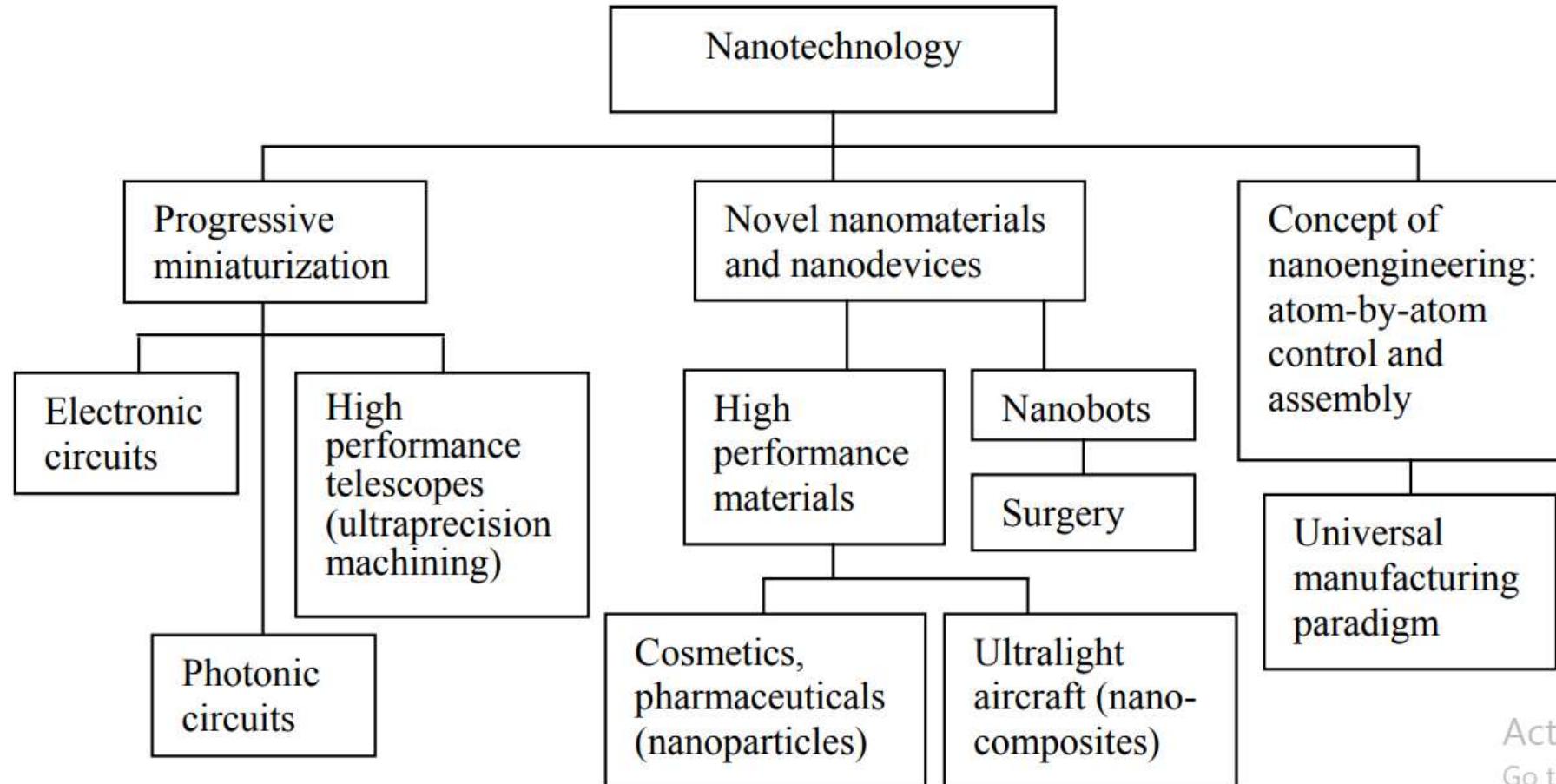


- **Nanotechnology: An Interdisciplinary field**
- Nanoscience and nanotechnology could be defined via the convergence of chemistry, biology, physics and engineering.
- Physics, chemistry and biology strongly overlap with nanoscience (defined as the study of matter at the molecular scale), but differ essentially from nanotechnology, which seeks to impose control over materials and devices at that scale.
- Quantum mechanics affects the performance of devices at the lower end of the size range of nano-objects.





- What can nanotechnology do for us?

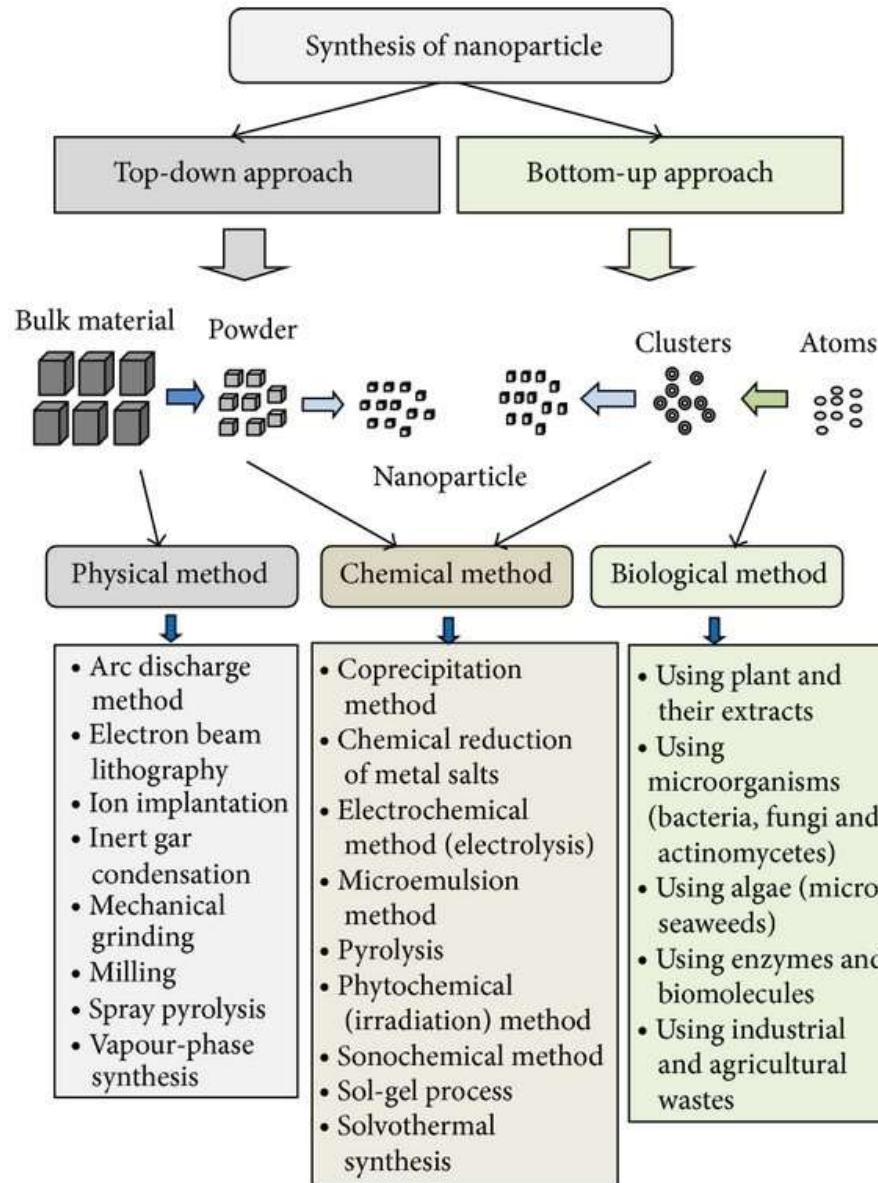




- **Nanoparticles (NPs):** are wide class of materials that include particulate substances, which have one dimension less than 100 nm at least.
- The different groups include fullerenes, metal NPs, ceramic NPs, and polymeric NPs.
- They can be classified into different classes based on their properties, shapes or sizes.
- NPs possess unique physical and chemical properties due to their high surface area and nanoscale size.
- Their optical properties are reported to be dependent on the size, which imparts different colors due to absorption in the visible region.
- Their reactivity, toughness and other properties are also dependent on their unique size, shape and structure.
- Due to these characteristics, they are suitable candidates for various commercial and domestic applications, which include catalysis, imaging, medical applications, energy-based research, and environmental applications.

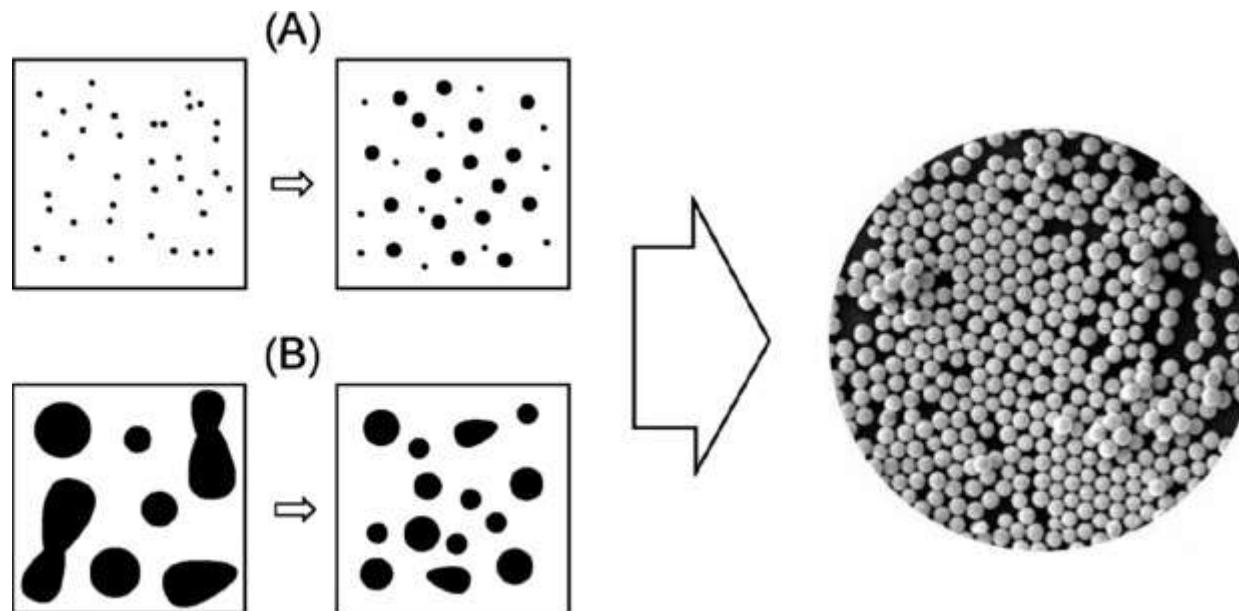


- **Synthesis of nanoparticles:** Synthesis methods play a very important role to control the size and surface area of nanomaterials. The techniques applied in synthesizing nanoparticles greatly influence their morphology, size, structure, and performance. The synthesis methods for nanoparticles are broadly divided into top-down and bottom-up approaches.





- 1) Top-down approach:** Top-down method is a destructive method that breaks down large molecules into smaller parts before converting into the relevant nanoparticles. This approach involves some decomposition strategies like chemical vapor deposition (CVD), milling process, and physical vapor deposition (PVD).
- 2) Bottom-up approach:** This approach involves the formation of nanoparticles from simple materials in a build-up manner. It is environmentally friendly, less poisonous, feasible, and of low cost. The materials used are usually Reduction and sedimentation processes like green synthesis, bio-chemical, spin coating, sol–gel etc. adopt this approach.



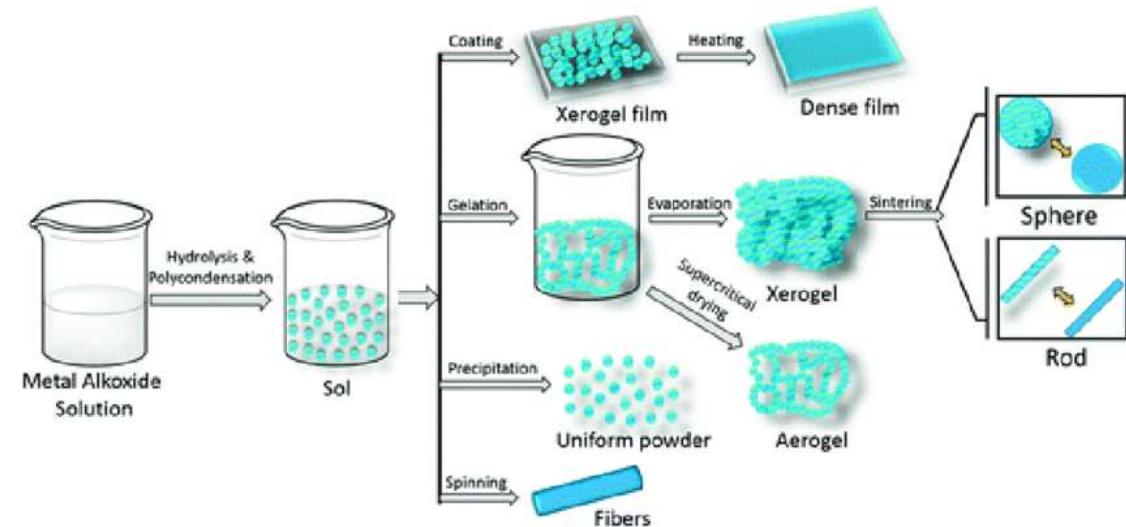
Scheme: (A) Bottom-up approach: A molecular precursor is disintegrated to simpler metal atoms that grow into colloids. (B) Top-down approach: Large drops of a metal broken into smaller drops



**1) Chemical methods:** Some chemical methods adopted in synthesizing nanoparticles include sol gel, precipitation, hydrothermal, thermal decomposition, solvothermal, vapor synthesis etc

➤ **Sol-gel method** is an easy means of producing nanostructures by homogenously mixing precursors in a solvent to form a gel material which is then heated to produce the required nanoparticle. E.g.  $\text{TiO}_2$  nanoparticles

➤ **Hydrothermal method** utilizes high pressure and temperature to power heterogeneous reactions under aqueous solvents like water. The kind of pressure, pH, and temperature applied affects the features of the synthesized nanoparticles. Such nanoparticles are suitable for biotechnological use because of their hydrophilic surface nature. E.g.  $\text{Fe}_2\text{O}_3$  nanoparticles



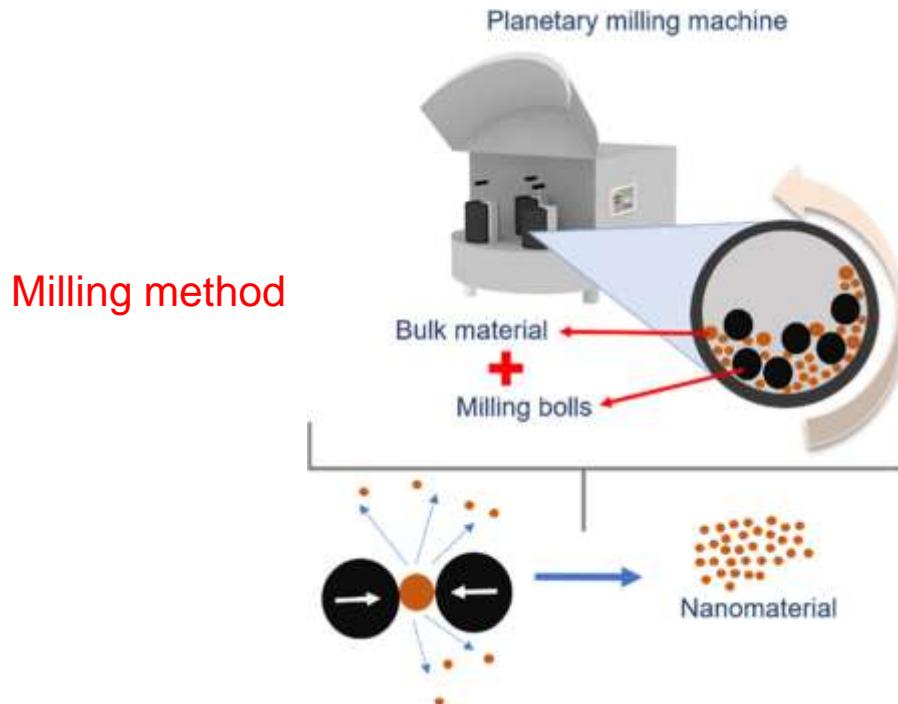
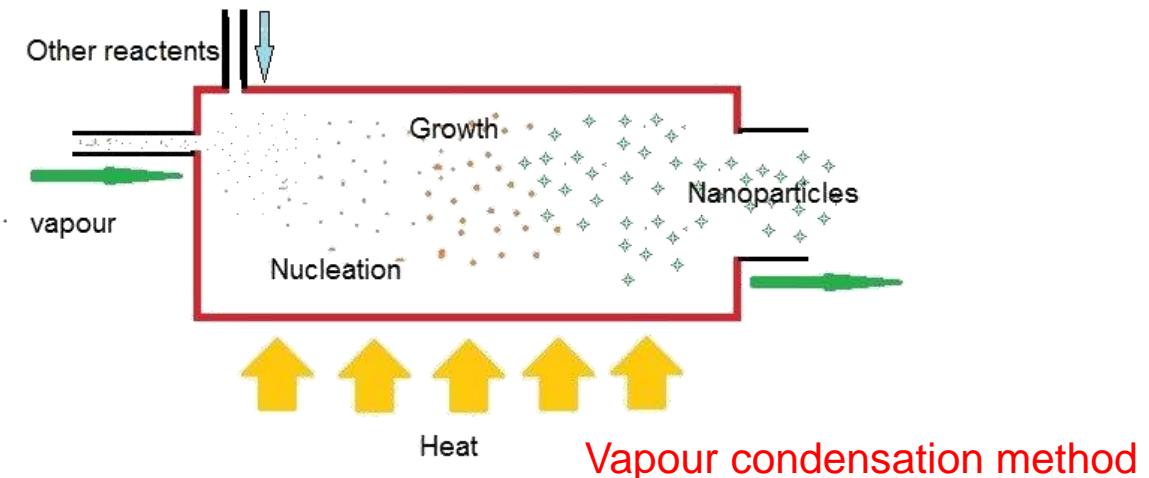
**Sol-gel synthesis method**



**Hydrothermal method**



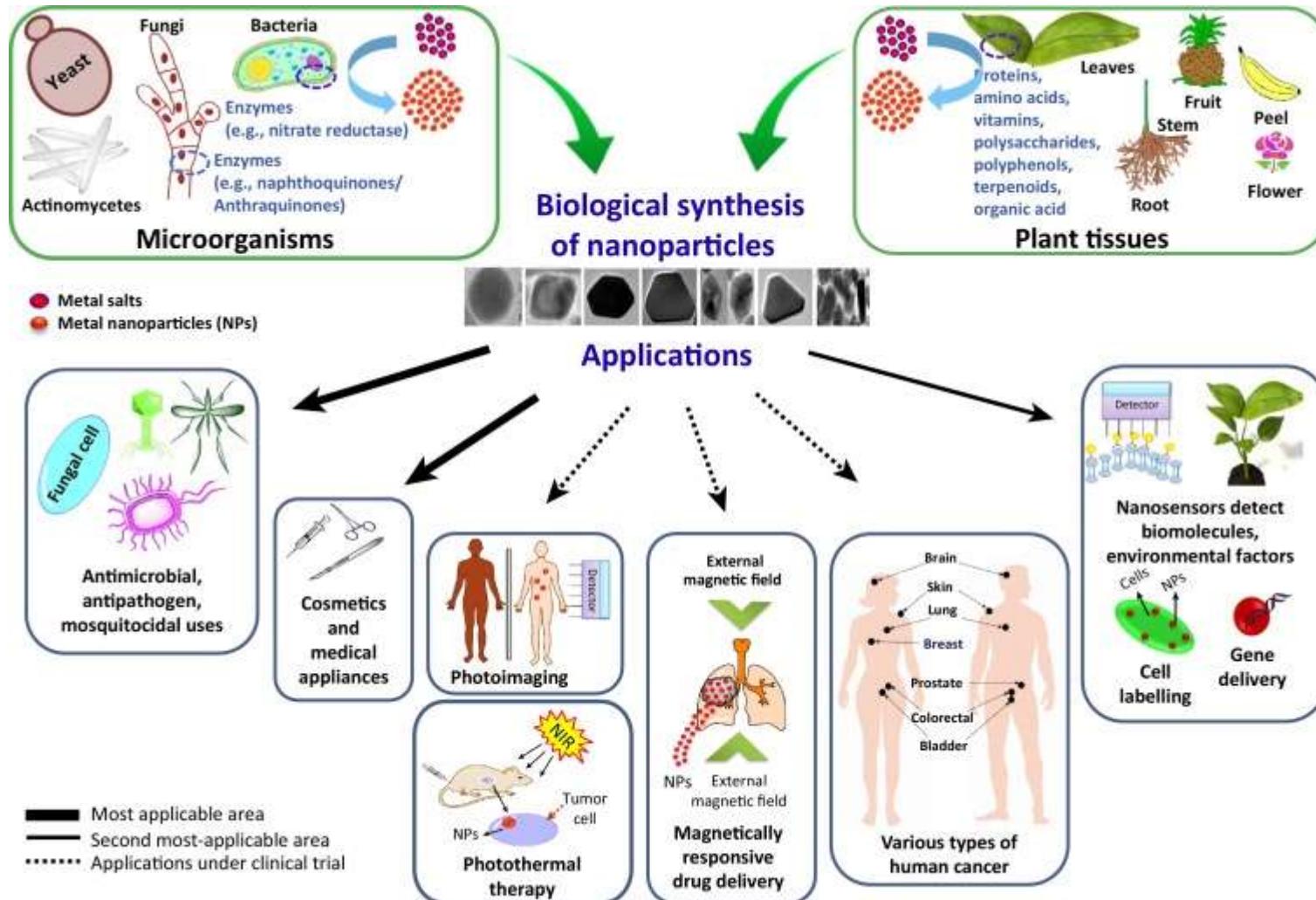
- In **vapor synthesis**, gaseous molecules chemically react to produce a phase which condenses and leads to particle growth. The higher the temperature, the faster the particles are formed.
- **Chemical reduction** method involves the reduction of metal salt precursor in presence of a reducing agents and a capping agent e.g. AgNPs, AuNPs

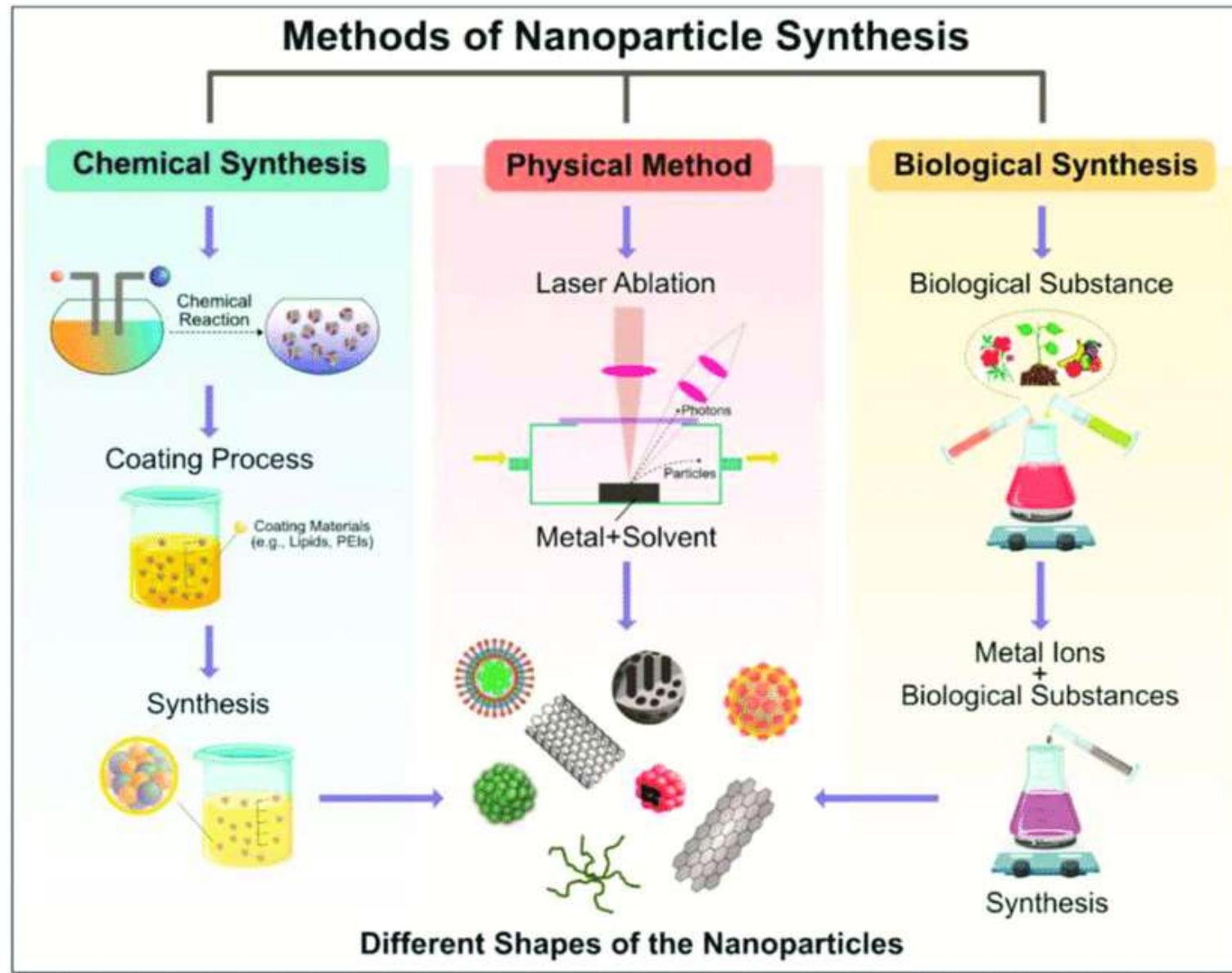


2. **Physical methods:** Nanoparticles can also be synthesized by mechanical methods like mechanical alloying, milling, and mechanochemical processes.
  - Milling method regenerates interfacial chemical operations at low temperatures. Mechanochemical technique involves continuous welding operations that adequately select milling materials and minimize agglomerations. Nanoparticles of oxides, iron, nickel, silver, cobalt can be synthesized using these methods.



**3). Biological methods:** Biological or biosynthesis of nanoparticles is an environmentally-friendly, green, and non-toxic method involving microorganisms. Nanoparticles of iron oxide, silver, nickel oxide, copper oxide, zinc ferrite have been synthesized using this method. Biogenic means of producing nanoparticles are green and cheap; with the involvement of fungi, waste materials, and bacteria. Phytonanotechnology is compatible with biological systems, available source materials, high stability, and entails synthesizing nanoparticles from plants.



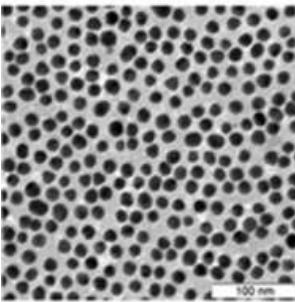




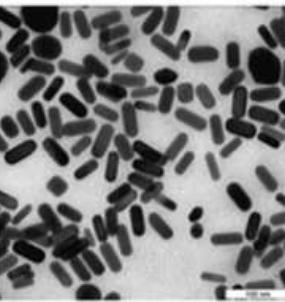
- **Characterization of nanoparticles:** Properties of nanoparticles like shape, size, surface morphology, crystalline nature, light absorption etc. need to be completely described using relevant characterization techniques.

**1) Morphological features:** The morphology of nanoparticles greatly influence the properties exhibited by nanoparticles. Microscopy methods applied on nanoparticles are usually electron microscopy or scanning probe microscopy. Scanning electron microscope (SEM) gives nanoscale and surface information of the dispersion and morphology of nanoparticles. Transmission electron microscopy (TEM) uses transmittance of electrons to provide bulk information at high and low magnifications.

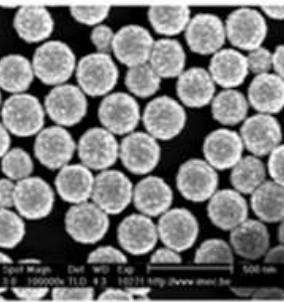
(a)



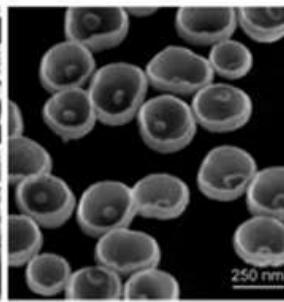
(b)



(c)

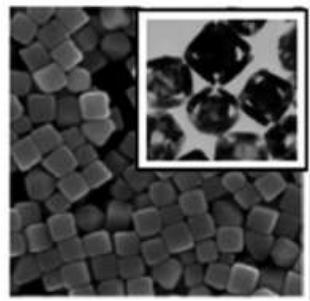


(d)

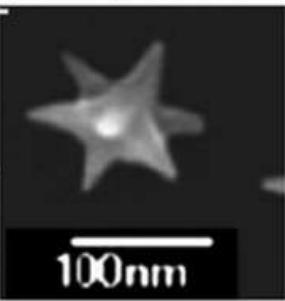


SEM images of ZnO

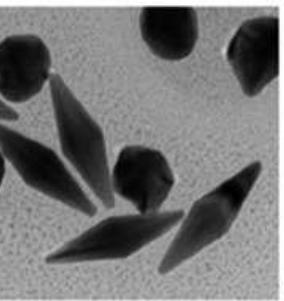
(e)



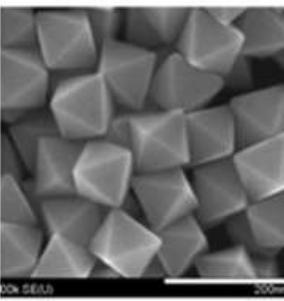
(f)



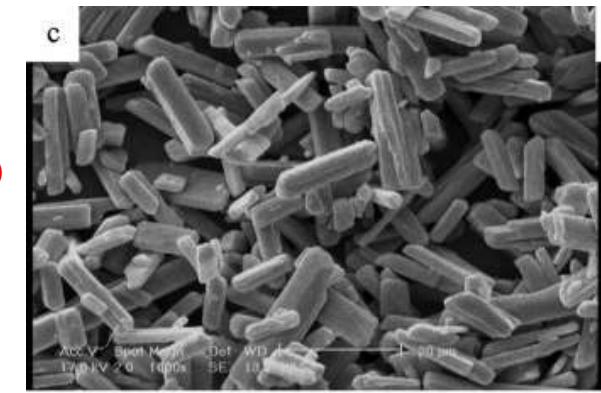
(g)



(h)



TEM images of different form of gold NPs, synthesized by different techniques





**2) Optical studies:** Optical methods reveal reflectance, transmittance, photochemical, and luminescence features of nanoparticles. Spectroscopy uses the interaction of particles with electromagnetic radiation to determine the shape, concentration, and size of nanoparticles. Spectroscopic techniques like infrared, ultraviolet-visible, photoluminescence (PL), UV/vis-diffuse reflectance spectrometer (DRS), and magnetic resonance methods are applied to nanoparticles. The sizes of nanoparticles affect their optical features and make it useful in bioimaging devices.

**3) Structural analysis:** The structure of nanoparticles gives details about the kind of bond existing between the atoms and the features of the bulk material. Some of the structural techniques used on nanoparticles include BET, X-ray diffractometry (XRD), IR etc. XRD describes the phase, particle size, type of NP, and crystal nature of the nanoparticles.

**4) Elemental analysis:** The elemental composition of nanoparticles can be determined using energy dispersive X-ray spectroscopy (EDX), XPS, Raman, FT-IR etc. EDX details the elemental components of bulk particles. XPS is a very sensitive spectroscopic method used to obtain the exact compositional ratio of the elements, their bonding nature, depth profile analysis. Raman and FTIR techniques use vibrational methods to show functionalized peaks and particle information.

**5) Size analysis:** Sizes of nanoparticles can be estimated using scanning electron microscope, transmission electron microscope, X-ray diffractometer, atomic force microscope etc. The sizes of the nanoparticles are obtained using size distribution profiles and give more precise results when used alongside digital models.



**6) Physicomechanical properties:** Mechanical properties, optical activity, surface area, and chemical reactions of nanoparticles are physiochemical characteristics obtainable from nanoparticles. Free surface electrons on nanoparticles are very mobile and are not scattered upon light illumination. The magnetic features of NPs are manifested at small nanoscales due to their uneven distribution, influenced by the synthesis technique adopted, and find vast application in biomedicine, resonance imaging, and catalytic devices. Mechanical characteristics of nanoparticles like stress, surface coatings, hardness, strain, friction, adhesiveness etc. aid an understanding of NPs and greatly affect the quality of the surface. Nanoparticles have great conduction to heat especially on the surface.

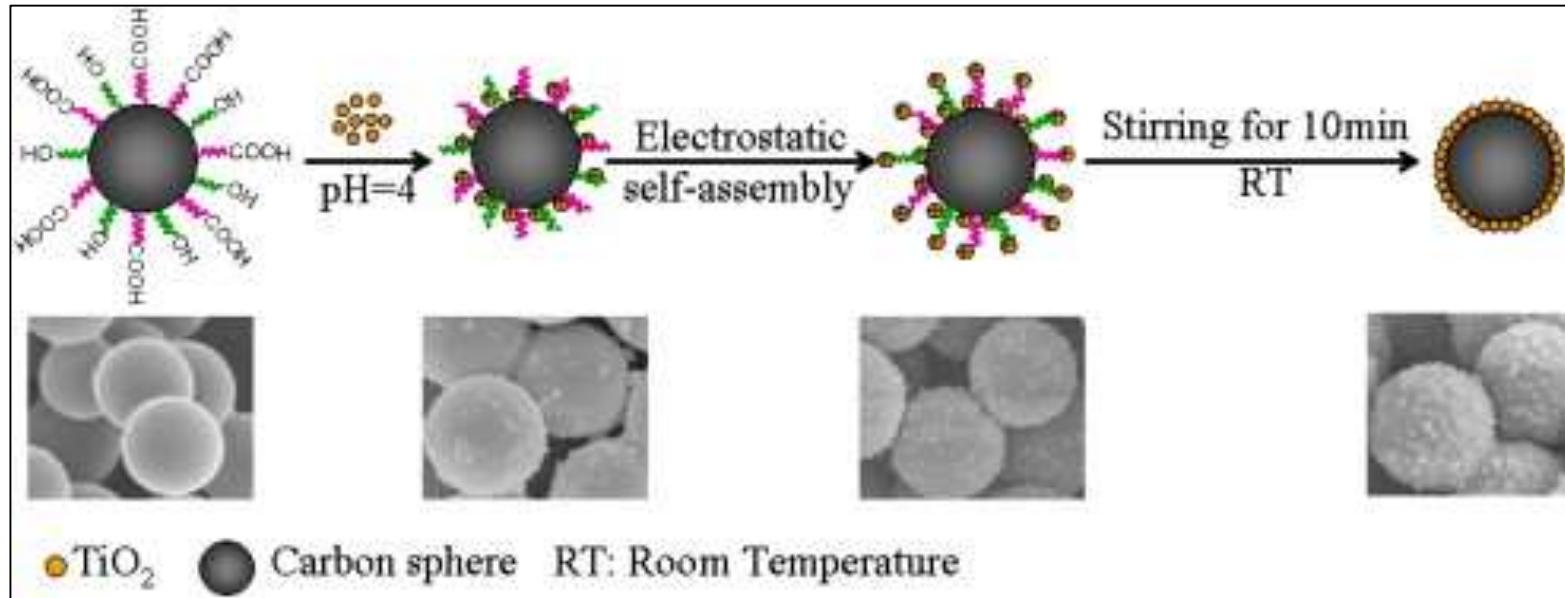


Table: Characterization methods and analysed properties

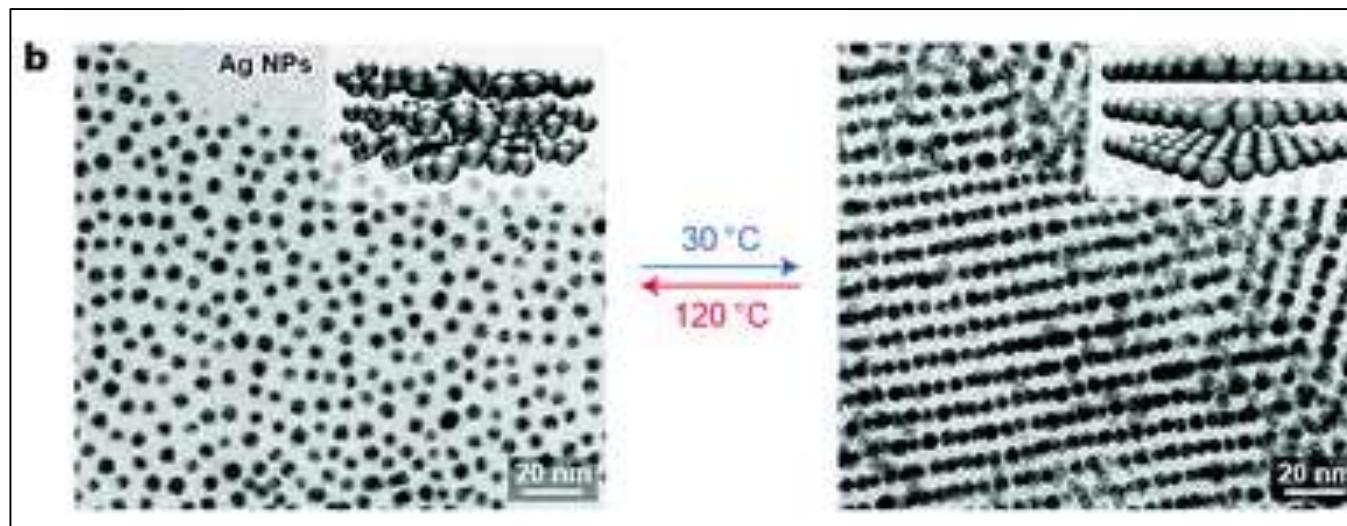
Characterization Method	Information obtained	Method	Properties to be Analyzed
Dynamic light scattering (DLS)	Size and size distribution of MNPs in solution	SEM/TEM	Particle shape, size and morphology.
UV-Vis spectrum	Formation of colloidal MNPs (Plasmon band)	XRD	Extent of Crystallization of the sample.
X-ray diffraction (XRD)	Crystal structure and size, chemical composition	BET	Accessible surface area
Nuclear magnetic resonance (NMR)	Molecular physics, crystals and non-crystalline materials	FT-IR	Vibrational stretch frequency of metal-oxygen bonds.
X-ray photoelectron spectroscopy (XPS)	Surface composition of supported MNPs	UV-VIS spectra	UV absorption of the amorphous gels and crystalline ceramic samples heated at different temperatures.
Transmission electron microscopy (TEM) Scanning electron microscopy (SEM)	Size and Morphology of MNPs	TG-DTA	Weight loss and thermal effect during the conversion of precursors to final method oxides in the heat-treatment process
Energy Dispersive X-Ray (EDX)	Element and distribution of MNPs	SLS	Particle size distribution.
Scanning tunneling microscope	Size and structure of MNPs	HRTEM	Crystallographic structure of a sample at an atomic scale.
		EELS	Loss of energy, change in momentum and ionization potential of a atom
		EDS/EDX	Chemical characterization, investigation of a sample through interactions between light and matter and analyzing X-rays in its particular case.



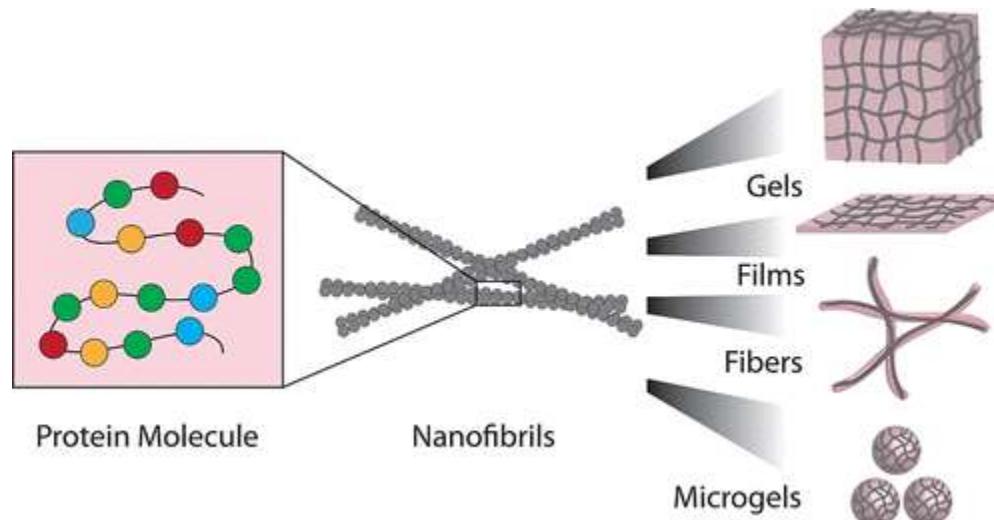
- **Self assembly of nanomaterials:**
- Molecular self-assembly is an autonomous process whereby disordered building blocks gradually form larger, well-organized patterns, driven by mutual interactions of the building blocks toward reducing the system free energy.
- It occurs under kinetic and thermodynamic conditions that allow local and specific molecular interactions such us electrostatic or hydrophobic interactions,  $\pi$ - $\pi$  interactions, hydrogen bonding, and Van der Waals forces to keep molecules at a stable state, achieving minimal energy in the system.
- The self-assembly of micro-/nanoparticles, among various kinds of building blocks, has generated intense interest because the self-assembled patterns commonly possess unique physical properties and find various applications in the fields of nanophotonics, solar cells, catalysts, data storage.
- Self-assembly of nanostructured materials holds promise as a low-cost, high-yield technique with a wide range of scientific and technological applications.



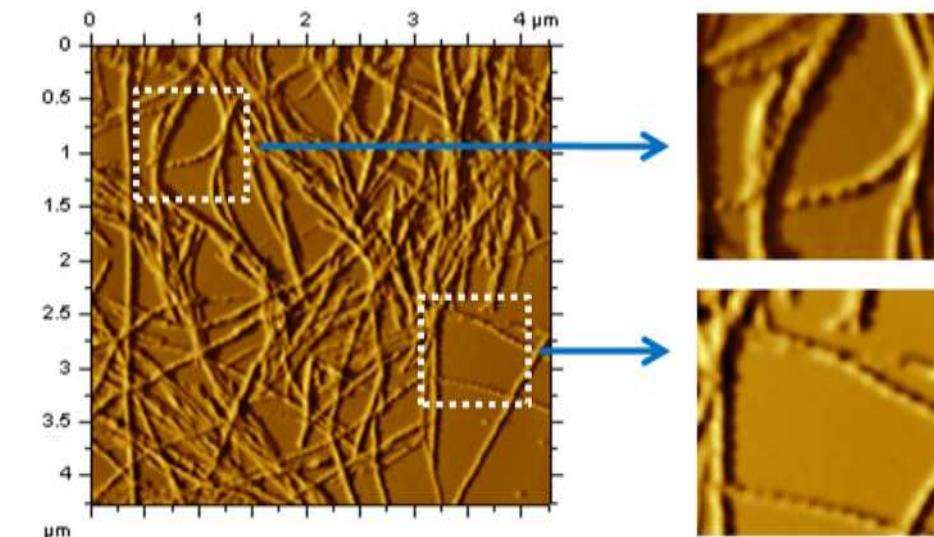
Electrostatic self-assembly of TiO<sub>2</sub> nanoparticles particles onto carbon spheres



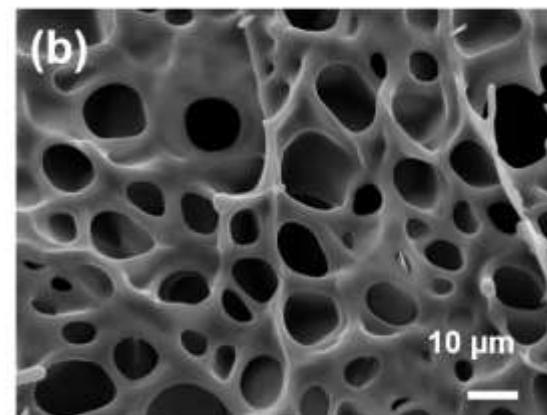
Temperature-induced transition between isotropic (left) and lamellar (right) phases of Ag NPs



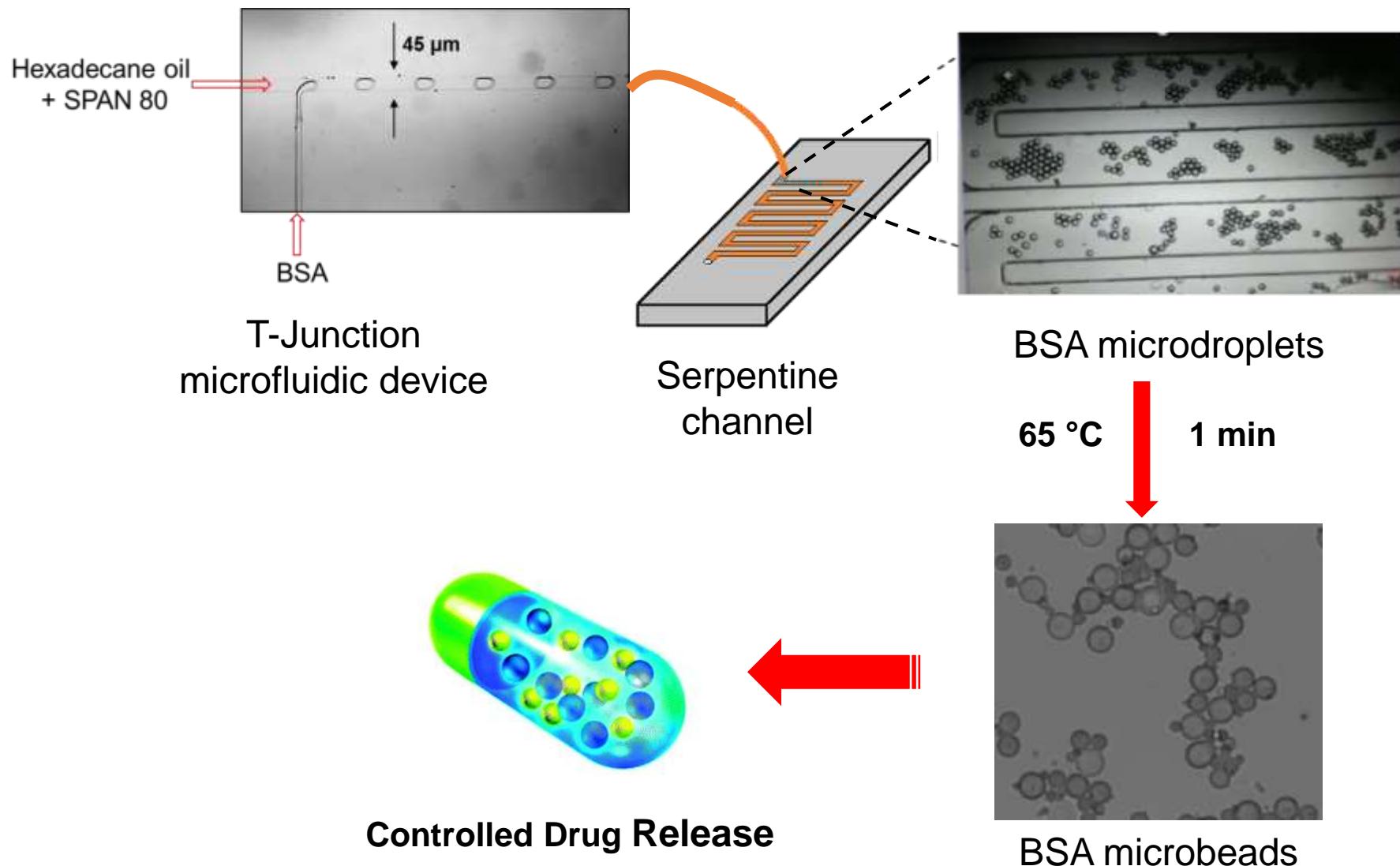
Different self-assemblies in proteins



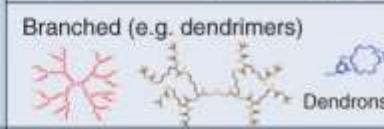
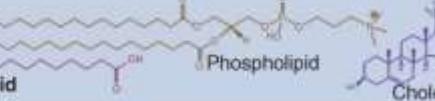
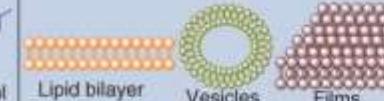
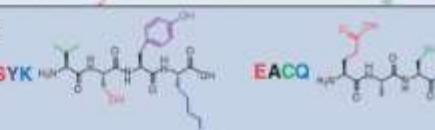
AFM image of aggregated Bovine Insulin fiber



(a) Hydrogels of Bovine serum albumin (BSA), (b) porous structure of BSA hydrogel

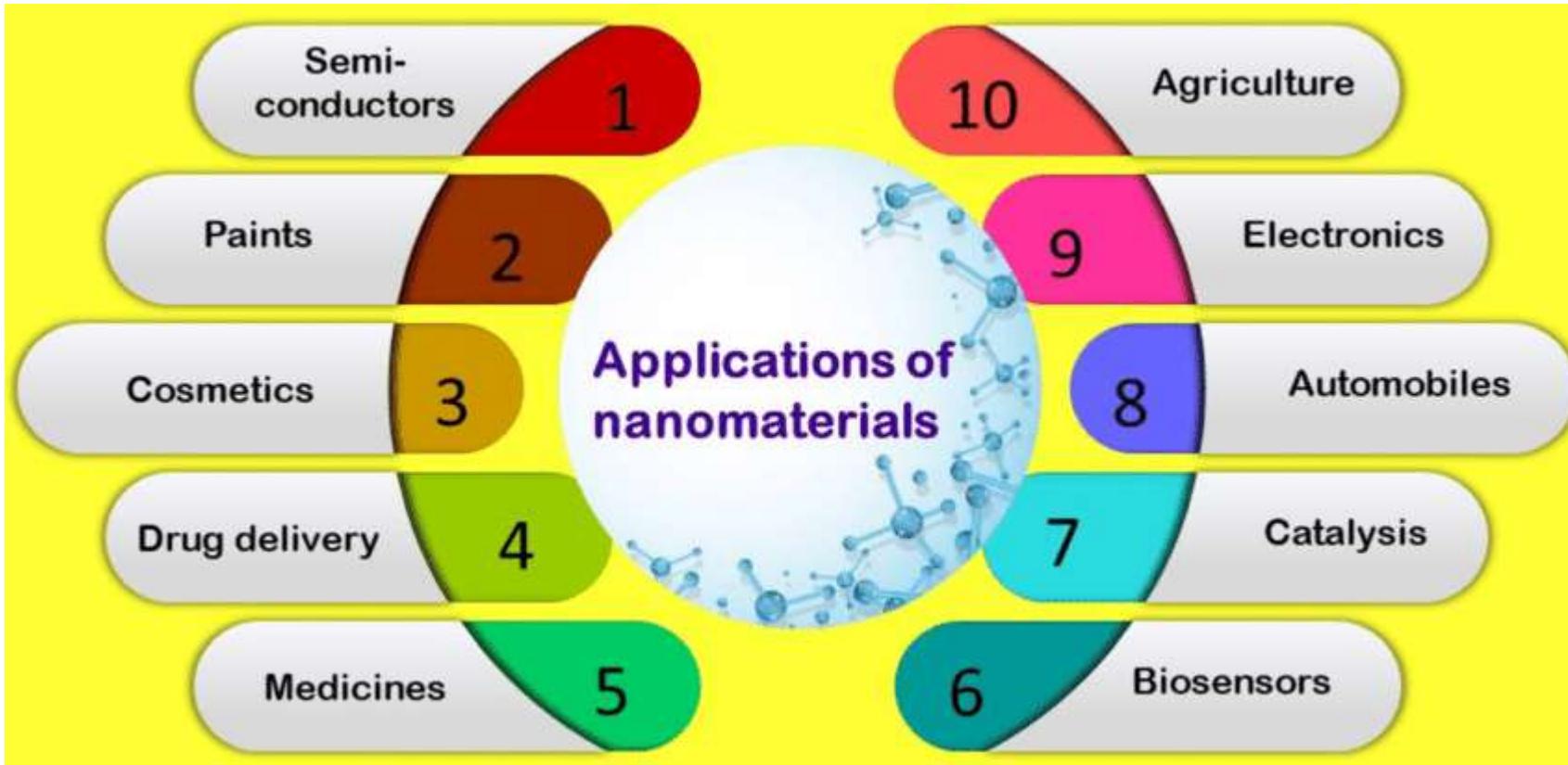




Building-Blocks			Supramolecular Assemblies	Applications
Synthetic	Polymers	Linear (e.g. block-co-polymers) 	Micelles Vesicles Tubes	Nanoreactors; artificial organelles; nanocarriers drug delivery <sup>21, 22</sup>
		Branched (e.g. dendrimers) 	Nanoparticles Nanofibers	Nanocarriers for drug and gene delivery <sup>23–25</sup>
	Surfactants	Anionic Neutral Cationic 	Micelles Vesicles	Drug and gene delivery systems; antimicrobial and antifungal activity <sup>26, 27</sup>
	Others	Graphene Porphyrin Rotaxane 	Nanotubes Toroids Carbon nanotubes 	Nanomedicine; drug delivery; hydrogels <sup>8, 28, 29</sup>
Biological	Viruses	CPMV λ phage hHPBV 	Aligned phage film Fibrils Particles 	Biomaterials; cell culture substrates <sup>30–33</sup>
	Nucleic acids	RNA DNA 	DNA origami 	Therapeutics (vehicles for drug delivery); diagnostics (biosensing) <sup>11, 34, 35</sup>
	Lipids	Fatty acid Phospholipid Cholesterol 	Lipid bilayer Vesicles Films 	Nanoreactors; artificial organelles; controlled drug delivery <sup>19, 36–37</sup>
	Saccharides	Amylose (helical) Cyclodextrin (cyclic) 	Double helix Nanotube Spherical micelle 	Drug delivery; biosensors <sup>38, 39</sup>
	Peptides	VSYK EACQ 	Random coil β-sheet α-helix Helix protein 	Hydrogel biomaterials; drug delivery; tissue engineering; 3D cell culture <sup>40–48</sup>



- Applications of nanoscale materials:



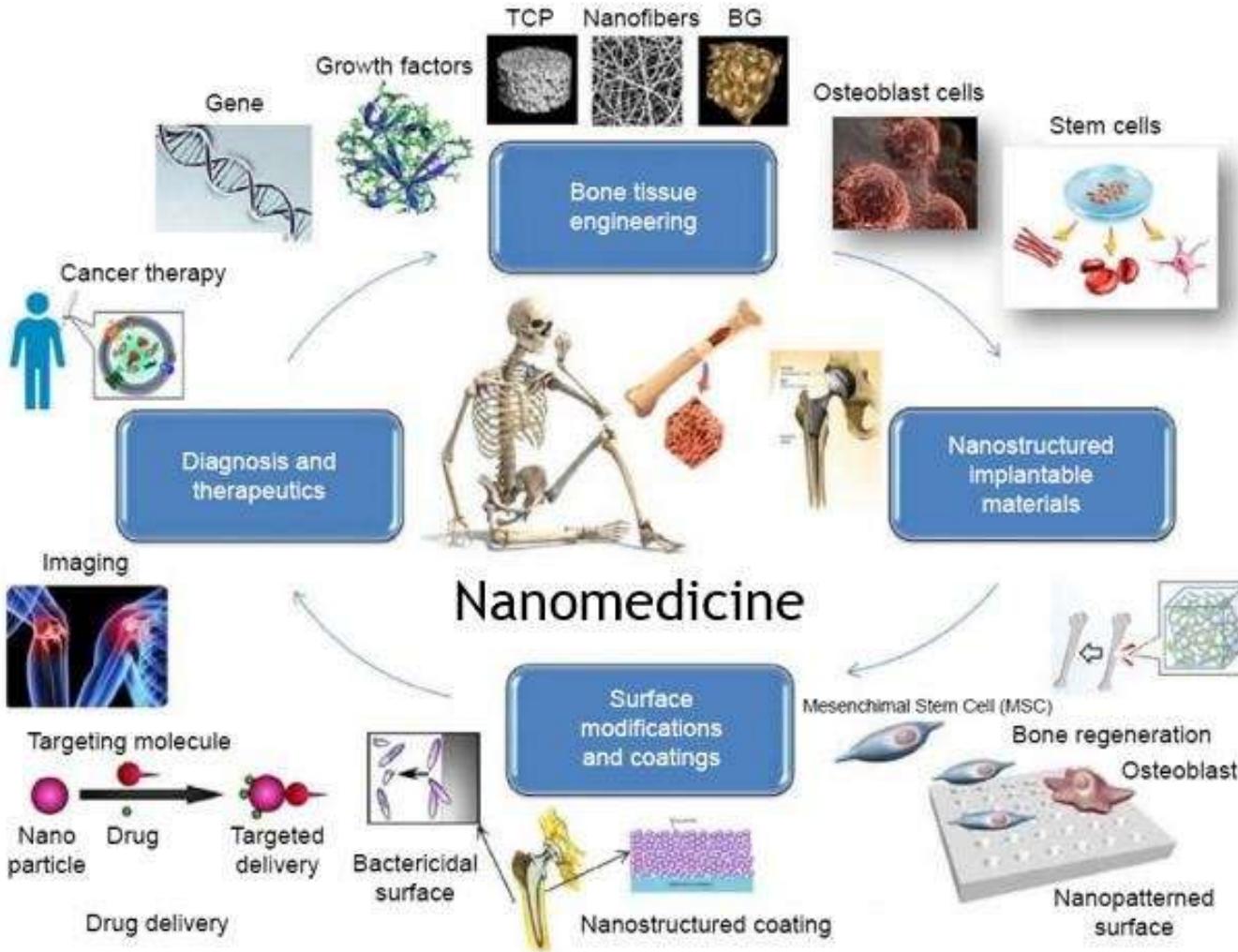


## I. Applications of nanomaterials in medicine:

- **Drug Delivery** - Nanotechnology uses nanoparticles for delivering drugs to body parts. Drug delivery means the drug is delivered to the required location of the body in specified quantities. The use of nanoparticles ensures that the drug reaches only the specified location and its side effects are reduced considerably.
- **Diagnostic Techniques** - Nanotechnology is making rapid progress in diagnosing diseases with the help of nanoparticles. Methods are developed/being developed for early detection of diseases like: Cancer, Parkinson's disease, Alzheimer's disease, Kidney Damage, Flu viruses, etc. Present methods of detecting diseases like cancer are uncomfortable for the patients and are time-consuming. These methods are invasive also. However, these issues can be removed with the help of nanosensors. These nanosensors use the application of nanotubes, cantilevers, nanowires or atomic force microscopy for early detection of diseases. The most important aspect of these nanosensors is that they improve sensitivity.
- **Medical Imaging** - Since nanoparticles have varied chemical composition, they are fast becoming drivers of developing newer imaging techniques. There is a need for fast and detailed imaging of tissue microstructures and lesion characterization. This kind of imaging requires non-toxic contrast agents which can circulate for a longer duration, and nanotechnology fulfills that requirement. It provides nanoparticles based contrast agents which can be used in most of the imaging methods.



## I. Applications of nanomaterials in medicine:



Structure type	Composition	Properties
Quantum dots	CdTe nanocrystal core, stabilizing ligand: 3-thiopropionic acid, bound ligand: lectin	High fluorescence efficiency, stable fluorescence, selective binding to cells
Mesoporous silica nanoparticles	Spherical porous nanoparticles (diameter approx. 100 nm), containing surfactant-dispersed doxorubicin)	pH-dependent release of drug substance, cancer cell penetration capacity
Silver nanoparticles	Ampicillin-modified surface area of silver nanoparticles	Synergic antibacterial activity of silver nanoparticles and the antibiotic
Graphene, graphene derivatives	Surface area of graphene and its derivatives modified with enzymes, antibodies and polymers	Formations (electrodes) sensitive to concentrations of various substrates
Dendrimers	Synthetic polyamidamine polymers with branched chains and common central core	Nucleic acid binding capacity
Iron-cobalt nanoparticles	Spherical FeCo nanoparticles, coated with graphite, functionalized with polyoxyethylene glycol and biocompatible phospholipide	Capacity to penetrate the cell and interact with the exterior magnetic field
Carbon nanotubes	Single-walled carbon nanotubes, functionalized with folic acid	Capacity to absorb near-infrared radiation (NIR)



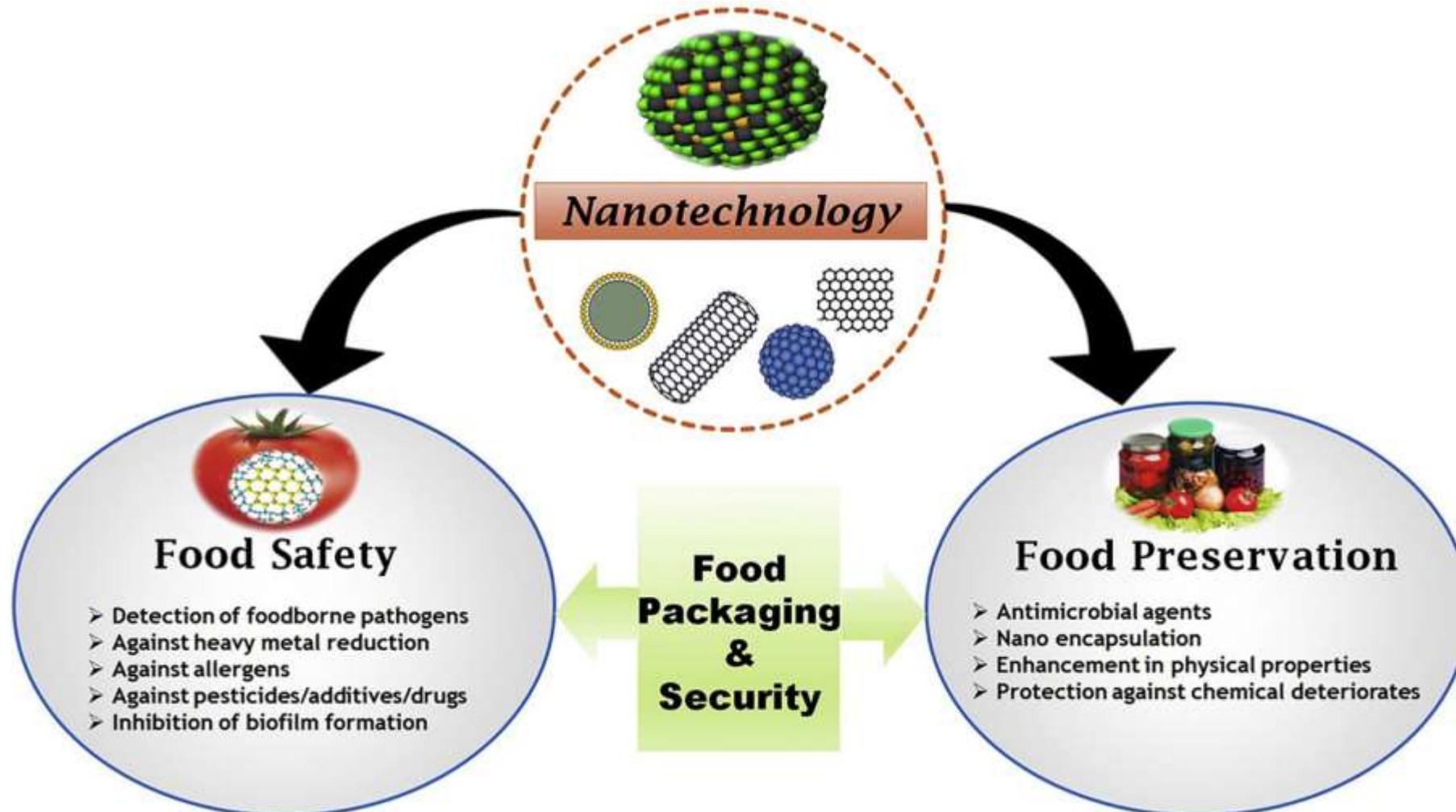
## II. Applications of nanomaterials in consumer products:

- **Cosmetics** - Nanotechnology is being used in the skincare products and the products protecting us from harmful sunlight. This keeps our skin youthful and glowing. The applications of nanoparticles in consumer products also include moisturizers and hair care products. Nanotechnology uses them as ultraviolet filters. They also act as delivery agents. The cosmetic industry uses Liposomes for this purpose.
- **Food** - Nanotechnology can be used in various aspects of food. These include production, processing, packaging and even safety of food. As the concerns about the quality of foods and their nutritional value and benefits grow, the need to find ways to enhance the quality of foods without disturbing their nutritional value is also growing. The food industry is also seeing a growth in the demand for nanomaterials in the food as they are found to be non-toxic. Apart from this, they are also stable at high temperatures. Thus, nanoparticles have a great role and use in all aspects of the food industry including manufacturing, processing, and packaging.
- **Glass** - Nanoparticles are being used to make glass photocatalytic and hydrophilic. In a photocatalytic glass, nanoparticles are energized when ultraviolet rays fall on it and start loosening the dirt particles on the glass. Similarly, hydrophilic glass has a property that makes water spread evenly on the surface, making it easy to clean. These glasses are being used to manufacture scratchproof eyeglasses. This system is also being used to manufacture self-cleaning windows.



II.

## Applications of nanomaterials in food industry:





### **III. Applications of nanomaterials in environment and energy:**

- Two of the gravest challenges being faced by the world today are the environmental pollution and shortage of energy. The evolution of nanotechnology has helped in the discovery and creation of newer nanomaterials. And these nanomaterials are acting as stimulators for various environmental applications thus improving upon environmental sustainability.
- Some examples are:
  - The process of manufacturing propylene oxide has many polluting byproducts. It has been established in research that if nanoclusters are used as catalysts, these polluting byproducts are considerably reduced. This propylene oxide is used to manufacture various plastics, paints, detergents, etc.
  - Nanoparticles are being used for treating groundwater. It is done when iron nanoparticles spread all through the water body and clean up the organic solvents present in the groundwater.
  - Nanoparticles can be used in cleaning oil spills. They are in a grid that provides more surface area for the reaction which is useful in cleaning the oil spills.



- Concerns regarding the shortage of energy are being addressed with the following developments:
  - Stronger and lower weight windmill blades are being manufactured with epoxy made with nanotubes. Windmills using these blades generate more electricity than others.
  - Nanotrapods with nanocarbon particles are being used to make low-cost electrodes for fuel cells.
  - Low-cost and high-efficiency solar cells are being developed using silver nanowires.

**Environmental Applications Nanotechnology**



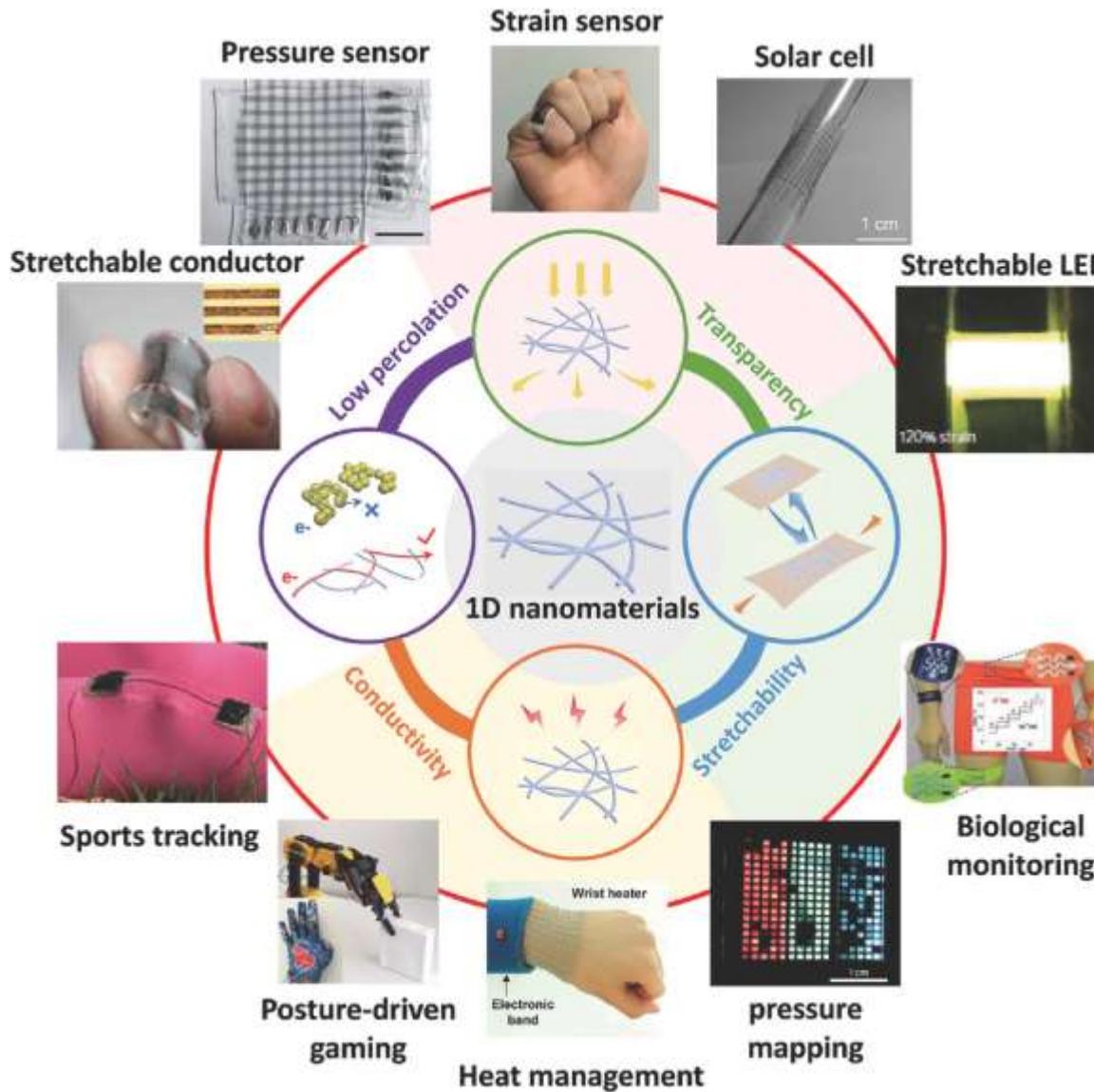
**Water and wastewater treatment**  
Nanoabsorbents  
Nanocatalysts  
Nanomembranes  
Remediation

**Energy**  
Solar cells  
Fuel cells  
Rechargeable batteries  
Supercapacitors  
LED lighting  
**Environmental Sensing**



IV.

## Applications of nanomaterials in electronics:





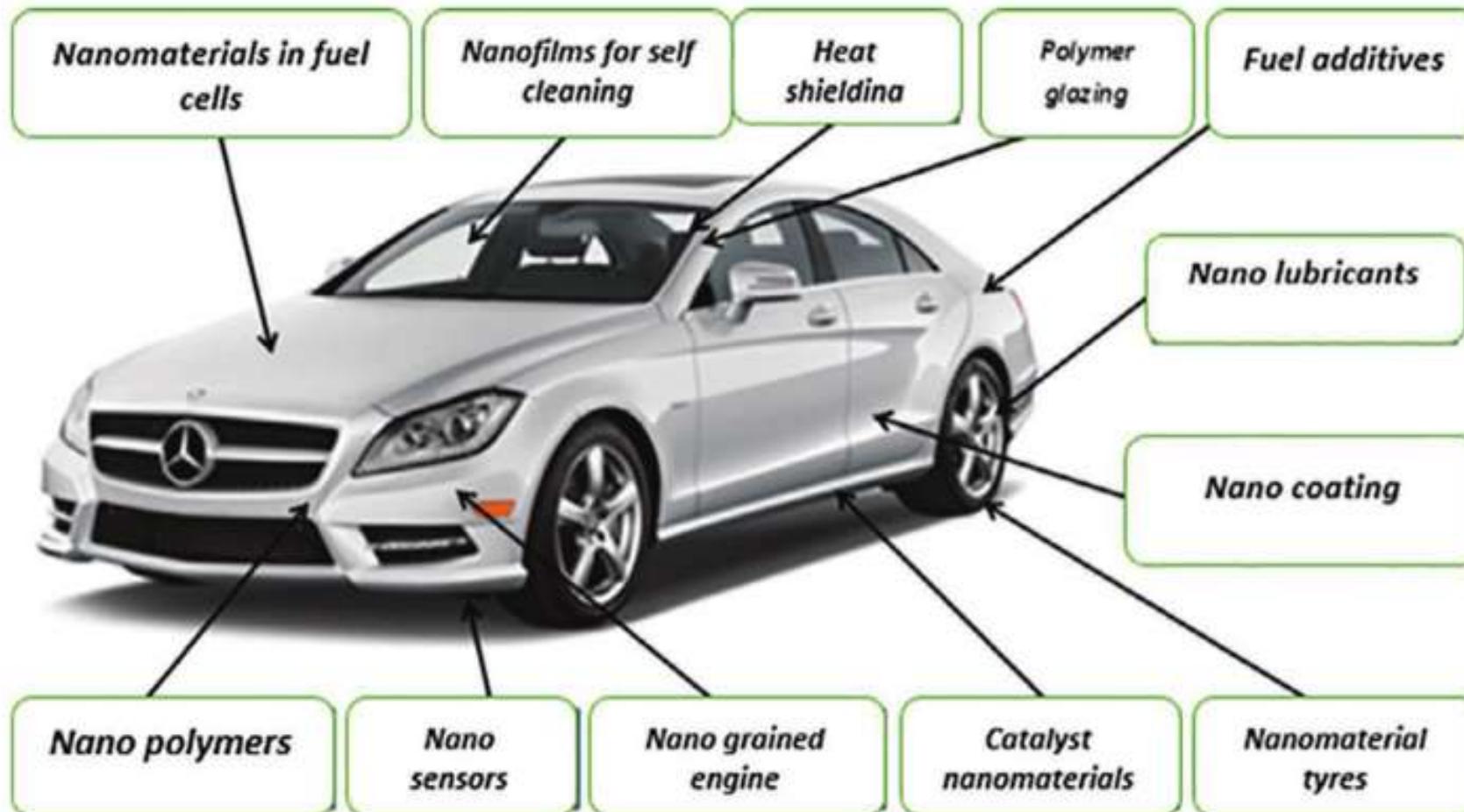
#### **IV. Applications of nanomaterials in electronics:**

- The use of nanotechnology is making a big difference in the manufacture of electronics. Some researches have shown how the capability of an electronic device can be increased while reducing its weight and power consumption at the same time.
  - A method to print prototype circuit boards on standard inkjet printers by using silver nanoparticle ink has been developed by the researchers. This ink forms the conductive lines needed to print circuit boards.
  - Nanomagnets have been used as switches, like transistors in electrical circuits. Using them results in electrical circuits consuming much less power than the transistor-based circuits.
  - Nanoparticles are being used in ultra HD displays of the television as well as in the memory chips.
  - The use of nanowires makes the flat panel display more flexible and thinner than the ones being manufactured currently.



V.

## Applications of nanomaterials in automobiles:





## V. Applications of nanomaterials in automobiles:

- Nanotechnology is set to play a major role and is going to be one of the core technologies in the automobile sector in the future. Key areas like fuel consumption, safety, environmental impact, driver information, and comfort are being addressed by the use of nanoparticles. The automobile sector can benefit from nanomaterials by way of lightweight, less wear, and corrosion, and advanced electronics and sensors as also advanced tire technology.
- In cars, nanotechnology offers the following advantages:
  - Lighter materials that are also strong and result in less fuel consumption and increased safety.
  - Hydrogen and fuel cell-powered cars have less effect on the environment.
  - Better electronics systems in smaller sizes.
  - For gasoline-powered cars, improvement in engine efficiency and fuel consumption.
  - Lower component failure resulting in longer life of the car.
- Some major applications of nanotechnology are as under:
  - Traditional metallic chassis parts are being replaced by nonengineered thermoplastic parts which help in a weight reduction of the vehicle up to 40%.
  - Paint adhesion and color durability improve when used on nanostructured surfaces. Along with this, scratch-resistant, dirt-repellant, and UV-repellant paints are being made available.



- A new nanomagnetic material Spintronics is bringing revolutionary changes in the car computing system of the vehicles. This is used in recuperating technologies like reusing the braking energy.
- With the increased insistence on the use of electric cars, makers are trying to find ways to reduce the costs of these cars. One of the major breakthroughs in this area has been the use of Lithium-ion batteries. Nanotechnology has a great scope of improving the life and performance of these batteries. It can also help in reducing the size and weight of batteries while improving their safety and stability at the same time. It will also shorten their recharge time.
- The automobile industry has been using Carbon black as a nanomaterial in tires as a pigment and reinforcing agent. This reinforcing agent provides properties such as better grip, resistance to wear and tear, and abrasion resistance. The addition of nanomaterials in the rubber used for tires improves the safety and durability of tires.
- Driving during the day and the night becomes difficult due to different types of lights. For safer and secure mirrors and windows, an ultra-thin layer of aluminum oxide (thickness less than 100 nm) is provided on the glass. This is done to reduce the impact of UV rays during the day and glare of the lights of the vehicles coming from the opposite side during the night. This nanolayer of aluminum oxide makes the glass dirt and water repellent.



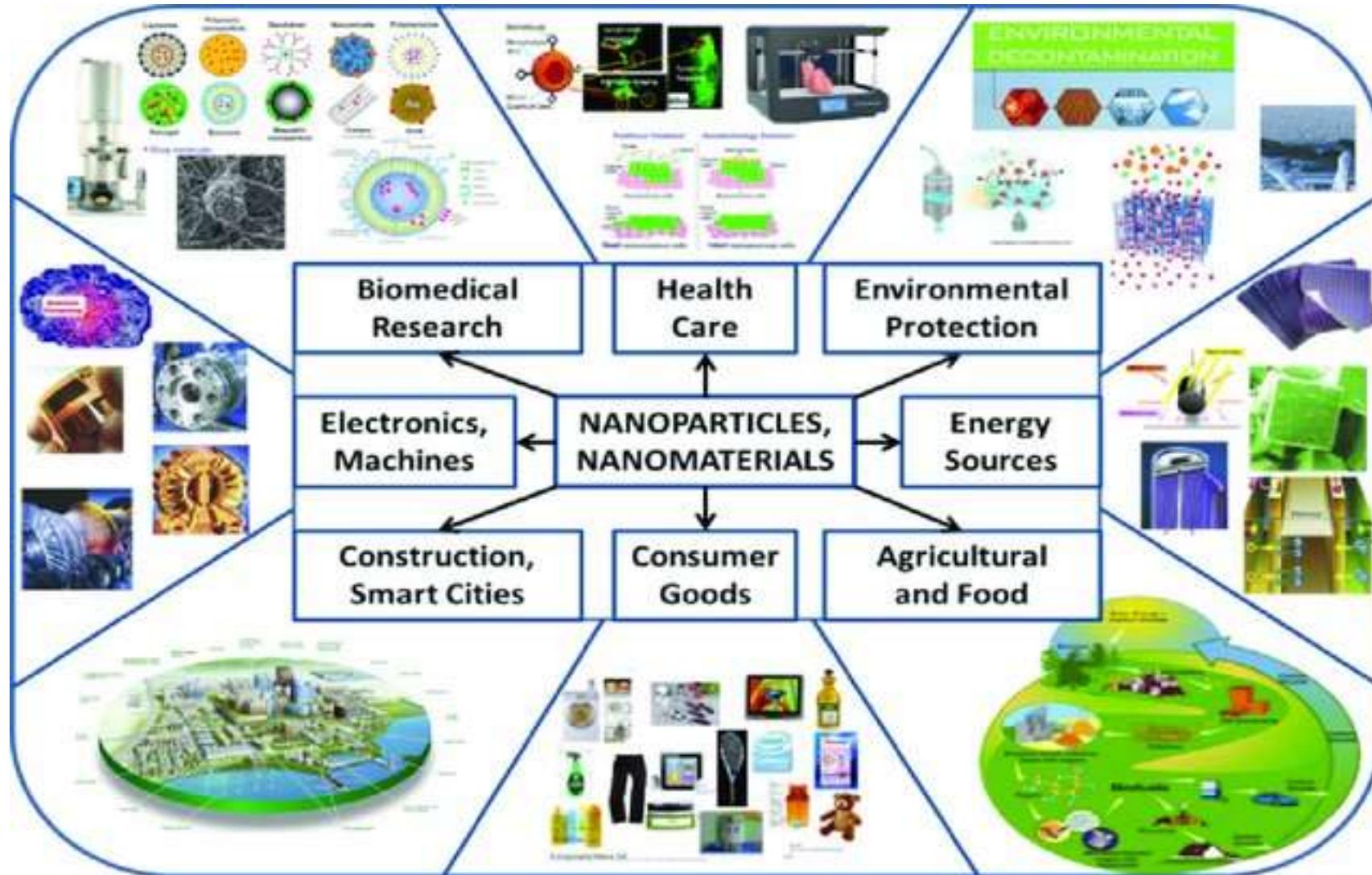
VI.

## Applications of nanomaterials in textile industry:





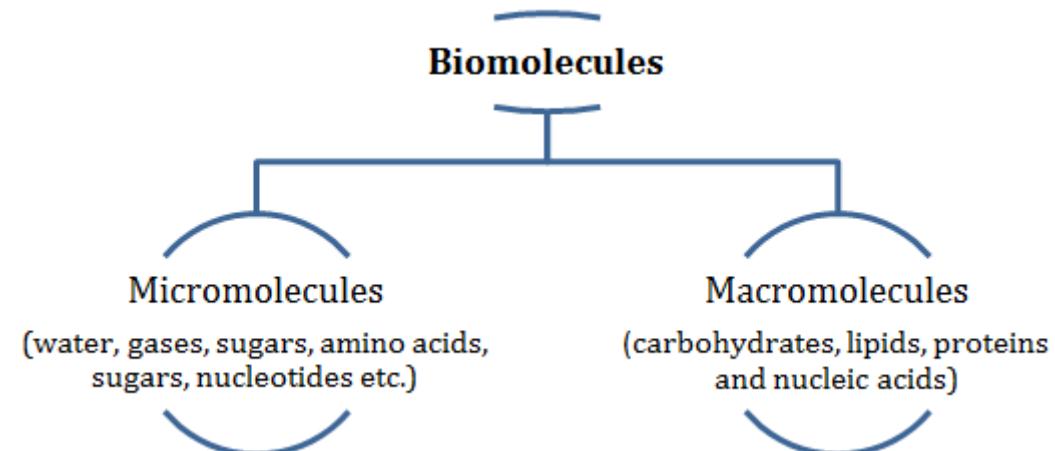
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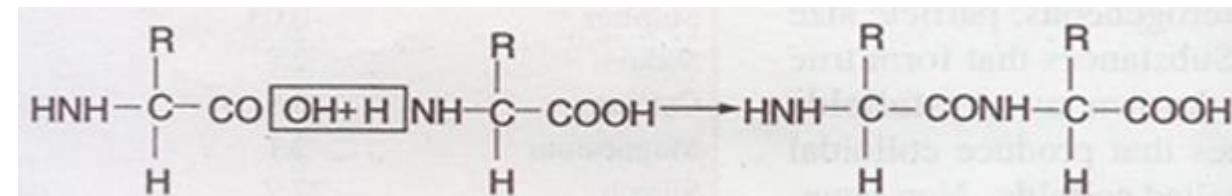
# Unit-4b

## Biomolecules

- Chemicals or molecules present in the living organism are known as biomolecules. Biomolecules are divided into two types- inorganic and organic.
- Inorganic biomolecules includes minerals, gases and water and organic biomolecules includes carbohydrates, fats, proteins, nucleic acids, vitamins, etc.
- Different biomolecules can be classified as aldehyde, ketones and aromatic compounds as chemical forms. The amino acids, nucleotides and fatty acids can be classified as biochemical forms.



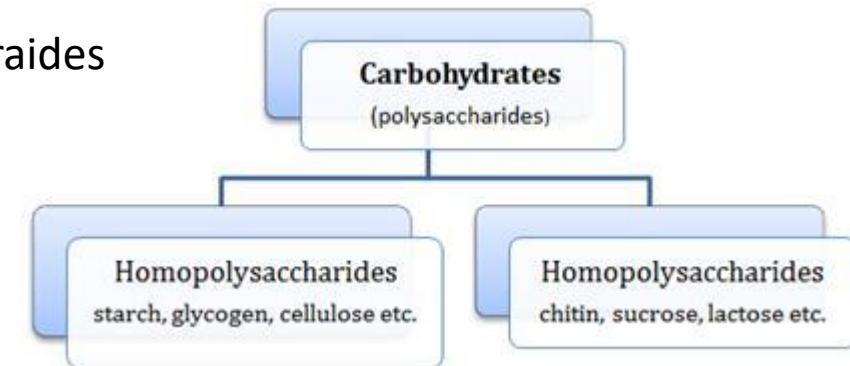
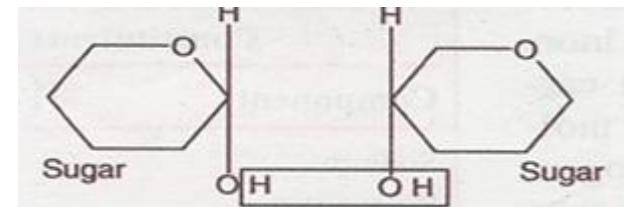
- Except lipids, macromolecules are formed by polymerization of sub-units called monomers.
- Proteins are polymers of amino acids. Amino acids are linked by **peptide bond** formed by dehydration between COOH group of one amino acids and NH<sub>3</sub> group of next with the removal of H<sub>2</sub>O.



- In nucleic acids, the phosphate molecules links 3' C of sugar of one nucleoside to the 5' C of sugar of next nucleosides releasing two water molecules to form 3'-5' **phosphodiester bond**.
- In polysaccharides, the mono-saccharides are linked by **glycosidic bonds** formed by dehydration between two carbon atoms of two adjacent monosaccharides.

## Carbohydrates (Polysaccharides)

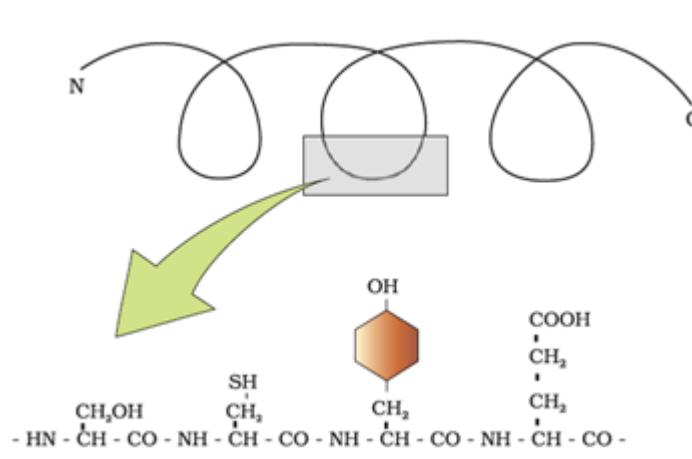
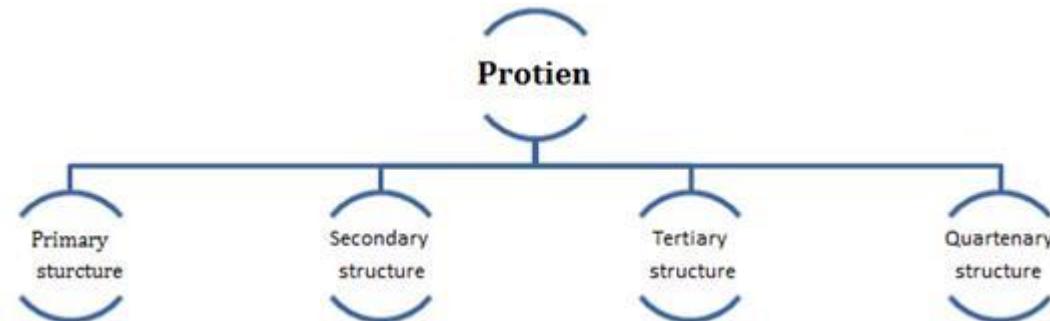
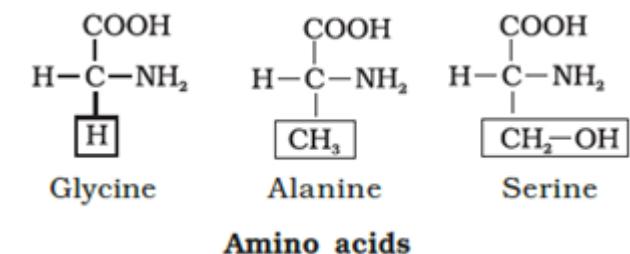
- Polysaccharides are long chain of sugar containing different monosaccharaides as a building block.
- Starch is present in plants as store house of energy. It forms helical secondary structure. It can hold the  $I_2$  molecules in the helical structure.
- Cellulose molecules contain glucose molecules joined together by 1-4  $\beta$  linkage. It is the most abundant organic molecules on earth.
- Glycogen is called animal starch as it is the reserve food materials for animals, bacteria and fungi. In this, glucose molecules are arranged in highly branched bush like chain having two types of linkage 1-4  $\alpha$  in straight chain and 1-6 linkage in branching.



**Proteins** are polypeptide chains made up of amino acids. There are 20 types of amino acids joined together by peptide bond between amino and carboxylic group. There are two kinds of amino acids-

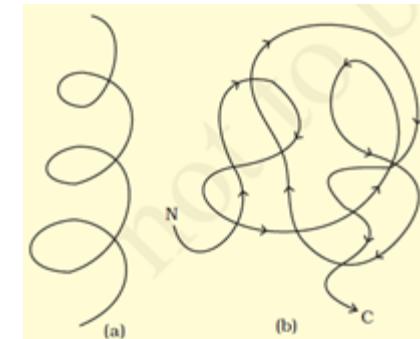
1. **Essential amino acids** are obtained by living organism along with food.
2. **Non-essential amino acids** can be prepared by our body from raw materials.

- The main functions of protein in living cell are
  1. Transport of nutrient across the membrane.
  2. Fight infectious organisms.
  3. Produce enzyme and proteins.
- Collagen is the most abundant protein in animal world.



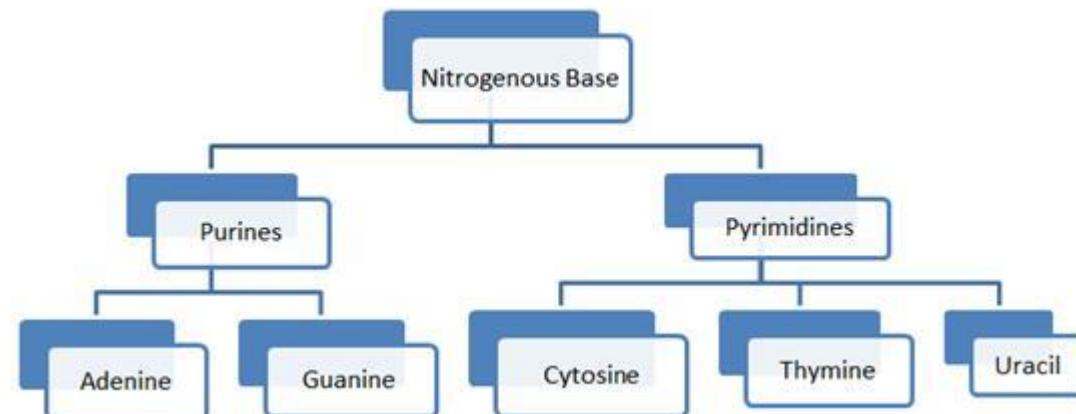
- **Primary structure of protein** is the basic structure of protein in which a number of polypeptides are involved having sequence of amino acids. The first amino acid of sequence is called N-terminal amino acid and last amino acid of peptide chain is called C-terminal amino acid.

- **Secondary structure protein** threads forms helix. There are three types of secondary structure-  $\alpha$  helix,  $\beta$  pleated and collagen. In  $\alpha$  helix, the polypeptide chain is coiled spirally in right handed manner.
- In  $\beta$  pleated secondary proteins, two or more polypeptide chains are interconnected by hydrogen bonds. In collagen there are three strands or polypeptides coiled around one another by hydrogen bonds.
- In **Tertiary structure** long protein chain is folded upon itself like a hollow woolen ball to give three dimensional view of protein.
- In **Quaternary structure** each polypeptide develops its own tertiary structure and function as subunit of protein. e.g. Hemoglobin. In adult human hemoglobin 4 sub-units are involved. The two subunits are of  $\alpha$  type and two subunits of  $\beta$  types.



(a) secondary structure  
(b) Tertiary structure

**Nucleic Acid:** Nucleic acids are polynucleotides. A nucleic acid has three chemically distinct components- heterocyclic compound (nitrogenous base), polysaccharides (ribose/ deoxy-ribose sugar) and phosphate or phosphoric acid.



- The sugar found in nucleic acid is either ribose or deoxyribose. Nucleic acid containing deoxyribose sugar is called DNA (Deoxyribonucleic Acid) and those containing ribose sugars are called RNA (Ribonucleic acid).
- Biomolecules are constantly being changed into some other biomolecules and also made from other biomolecules. This breaking and making is through chemical process called **metabolism**.
- In living organism, all the metabolic reactions are enzyme catalyzed. Catalysts are those substances that alter the rate of reaction. The protein with catalytic power is called enzyme.

### **Metabolic Basis for living organism**

- The metabolic pathways that lead to more complex structure from simpler structure are called biosynthetic or **anabolic pathways** and those pathways that lead to simpler structure from complex structure are called **catabolic pathways**.
- Photosynthesis and protein synthesis are example of anabolic pathway. Respiration and digestion are examples of catabolic pathway.
- ATP (adenosine triphosphate) is the most important form of energy currency in living world.
- All living organism exist in steady state characterized by concentration of each of the metabolites. The living state is a non-equilibrium steady state to be able to perform work.

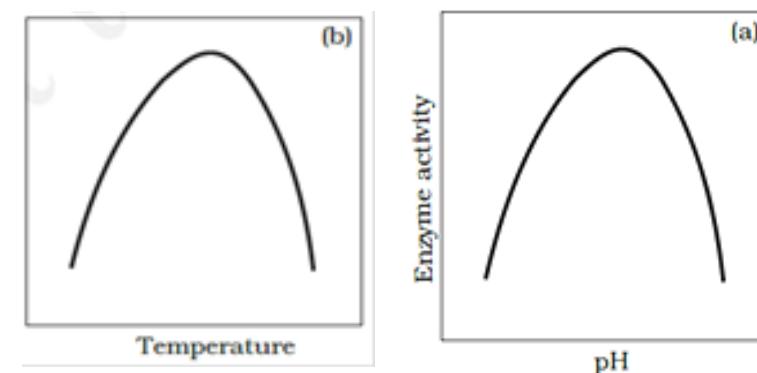
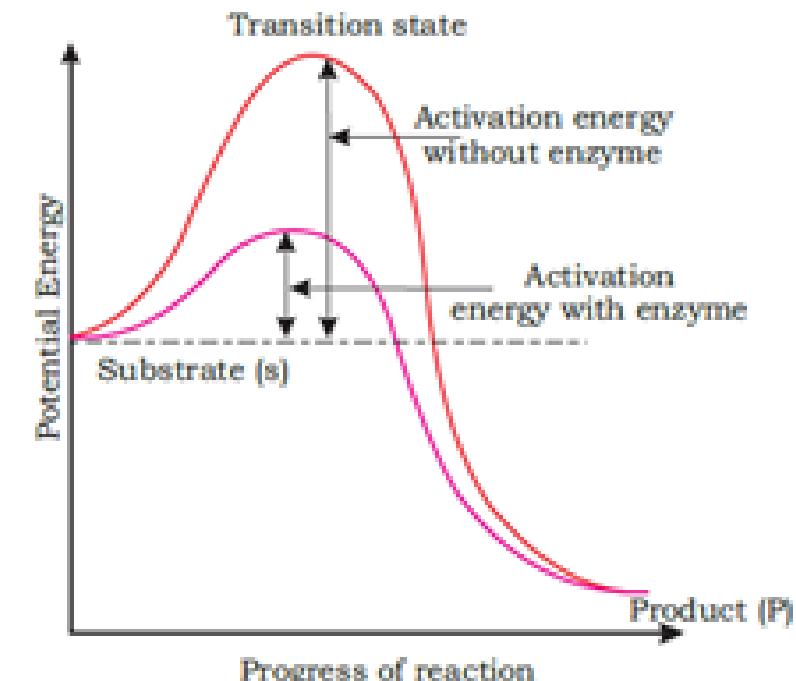
### **Enzymes**

- Enzymes are commonly proteinaceous substances which are capable of catalysing chemical reactions of biological origin without themselves undergoing any change. They are commonly called as **biocatalysts**.
- The nucleic acids that behave like enzymes are called ribozymes.

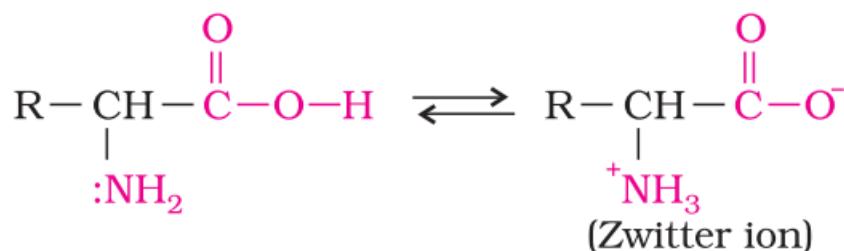
- The tertiary structure of protein/Enzyme has pockets or crevice into which substrate fit to form **ES complex**.
- The formation of the ES complex is essential for catalysis.  
 $E + S \rightarrow ES \rightarrow EP \rightarrow E + P$
- The structure of substrate gets transformed into the structure of product through formation of transient state structure.
- The major difference between inorganic and organic catalyst is inorganic catalyst works effectively at high temperature and pressure but enzyme get damaged at high temperature.
- The external energy required to start a chemical reaction is called activation energy.

### Factors influencing Enzyme Activity

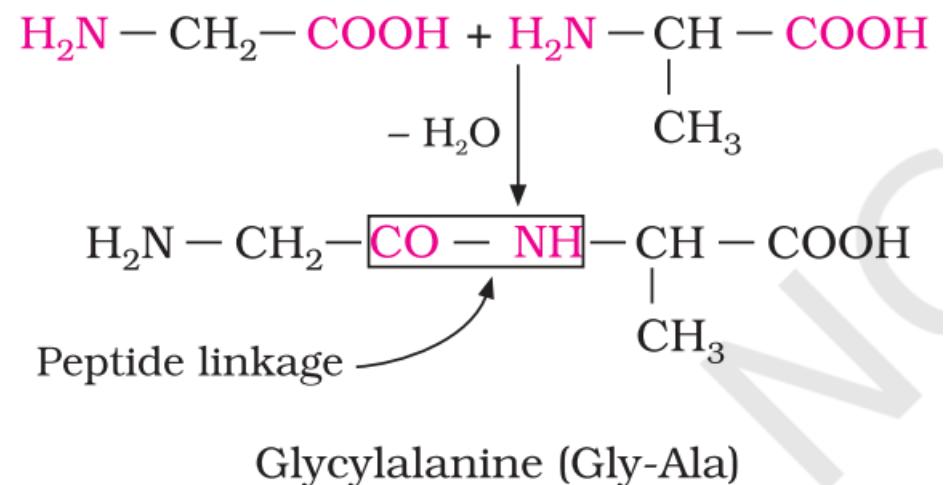
- Temperature**- An enzyme is active within a narrow range of temperature. Temperature ate which enzyme is most active is called **optimum temperature**. The enzyme activity decrease above and below this temperature.
- pH** – every enzymes has an optimum pH at which it is maximum active. Most of the intracellular enzymes work at neutral pH.
- Concentration of Substrate**– increase in substrate concentration increases the rate of reaction due to occupation of more active sites by substrate.



Amino acids are usually colourless, crystalline solids. These are water-soluble, high melting solids and behave like salts rather than simple amines or carboxylic acids. This behaviour is due to the presence of both acidic (carboxyl group) and basic (amino group) groups in the same molecule. In aqueous solution, the carboxyl group can lose a proton and amino group can accept a proton, giving rise to a dipolar ion known as *zwitter ion*. This is neutral but contains both positive and negative charges.



In zwitter ionic form, amino acids show amphoteric behaviour as they react both with acids and bases.



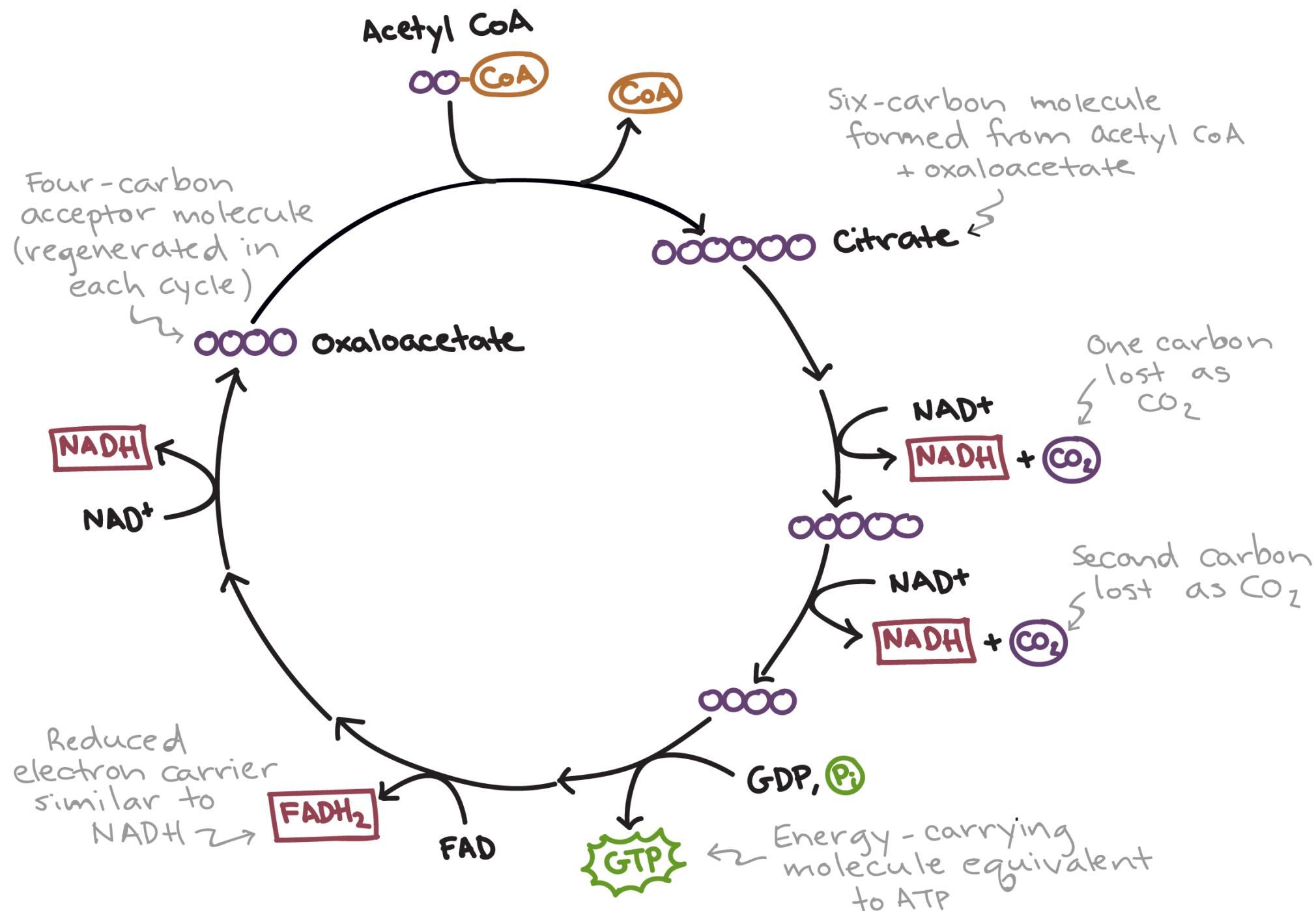
# The citric acid cycle

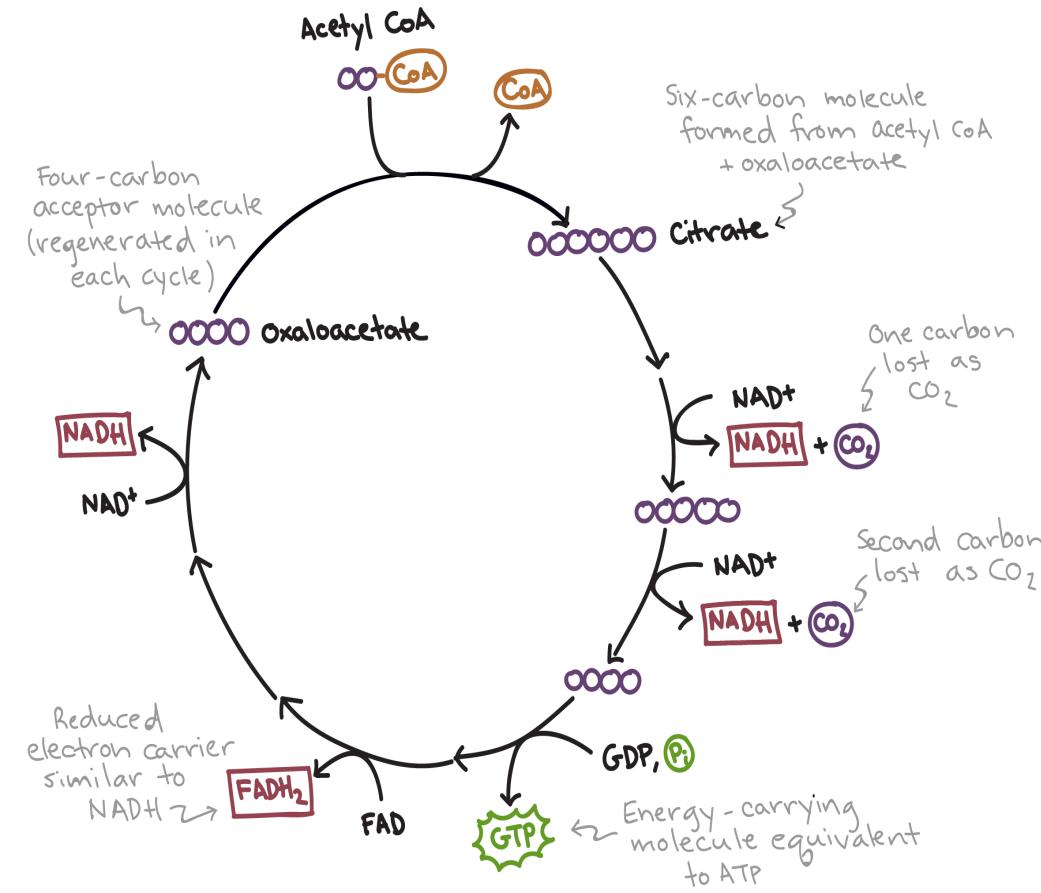
- Also known as the Krebs cycle or tricarboxylic acid (TCA) cycle.
- The name we'll primarily use here, the citric acid cycle, refers to the first molecule that forms during the cycle's reactions—citrate, or, in its protonated form, citric acid. However, you may also hear this series of reactions called the tricarboxylic acid (TCA) cycle, for the three carboxyl groups on its first two intermediates, or the Krebs cycle, after its discoverer, Hans Krebs.

## Overview of the citric acid cycle

In eukaryotes, the citric acid cycle takes place in the matrix of the mitochondria, just like the conversion of pyruvate to acetyl CoA. In prokaryotes, these steps both take place in the cytoplasm. The citric acid cycle is a closed loop; the last part of the pathway reforms the molecule used in the first step. The cycle includes eight major steps.

**Coenzyme A** (CoA, CoASH, or HSCoA) is a coenzyme, well known for its role in the synthesis and oxidation of fatty acids, and the oxidation of pyruvate in the citric acid cycle.





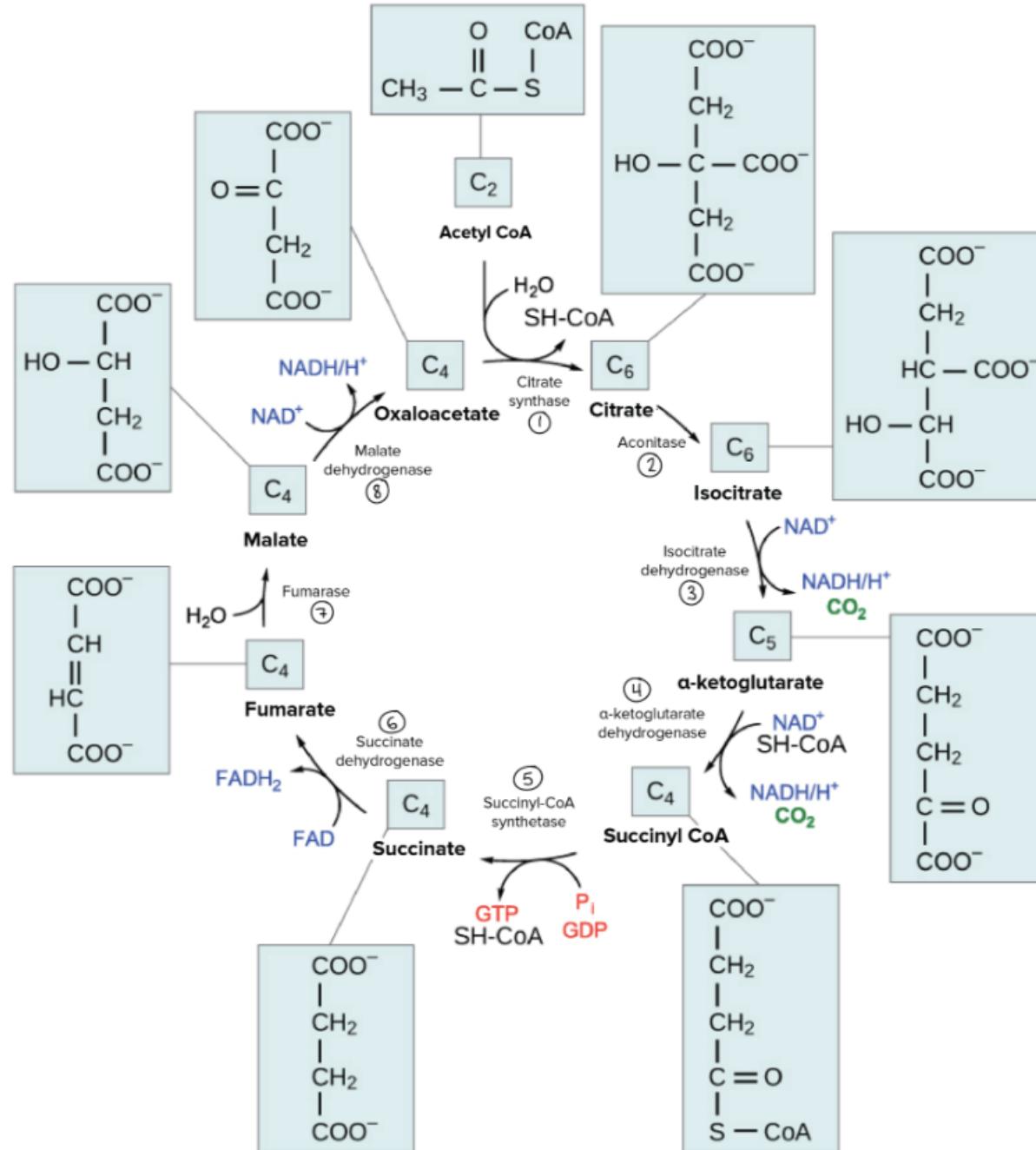
In the first step of the cycle, acetyl CoA combines with a four-carbon acceptor molecule, oxaloacetate, to form a six-carbon molecule called citrate. After a quick rearrangement, this six-carbon molecule releases two of its carbons as carbon dioxide molecules in a pair of similar reactions, producing a molecule of NADH each time. The enzymes that catalyze these reactions are key regulators of the citric acid cycle, speeding it up or slowing it down based on the cell's energy needs.

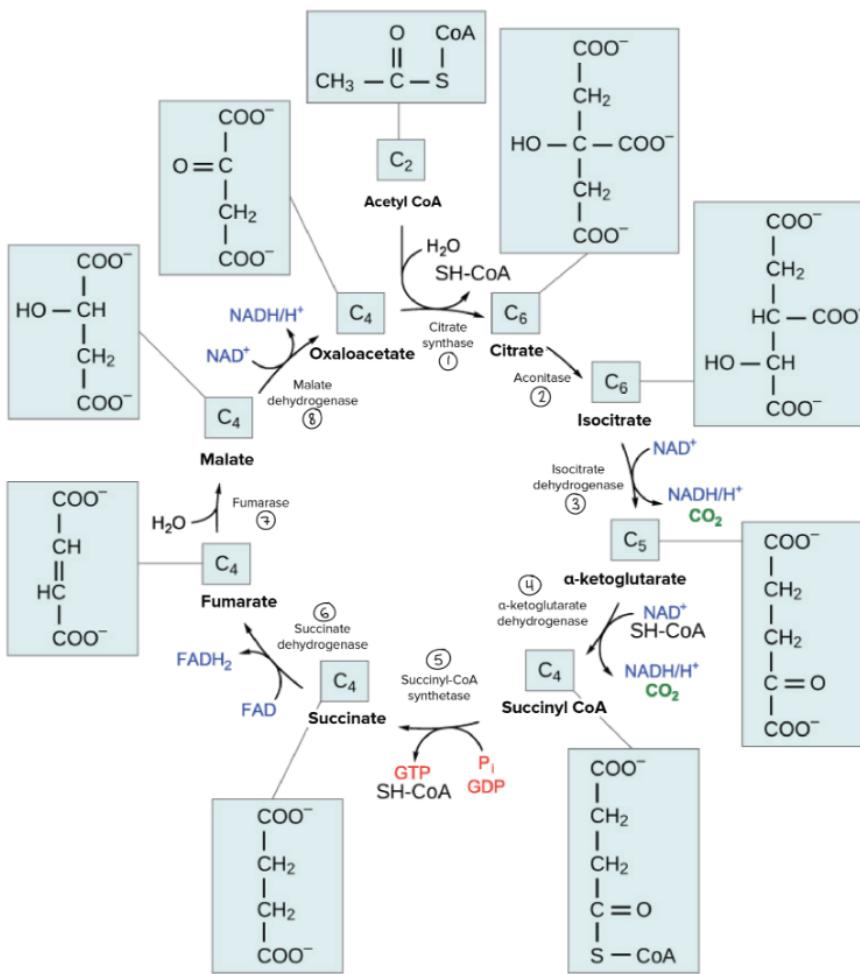
The remaining four-carbon molecule undergoes a series of additional reactions, first making an ATP molecule—or, in some cells, a similar molecule called GTP—then reducing the electron carrier FAD to FADH<sub>2</sub>, and finally generating another NADH. This set of reactions regenerates the starting molecule, oxaloacetate, so the cycle can repeat.

Overall, one turn of the citric acid cycle releases two carbon dioxide molecules and produces three NADH, one FADH<sub>2</sub>, and one ATP or GTP. The citric acid cycle goes around twice for each molecule of glucose that enters cellular respiration because there are two pyruvates—and thus, two acetyl CoAs—made per glucose.

NADH: nicotinamide adenine dinucleotide hydride

FADH: Flavin adenine dinucleotide



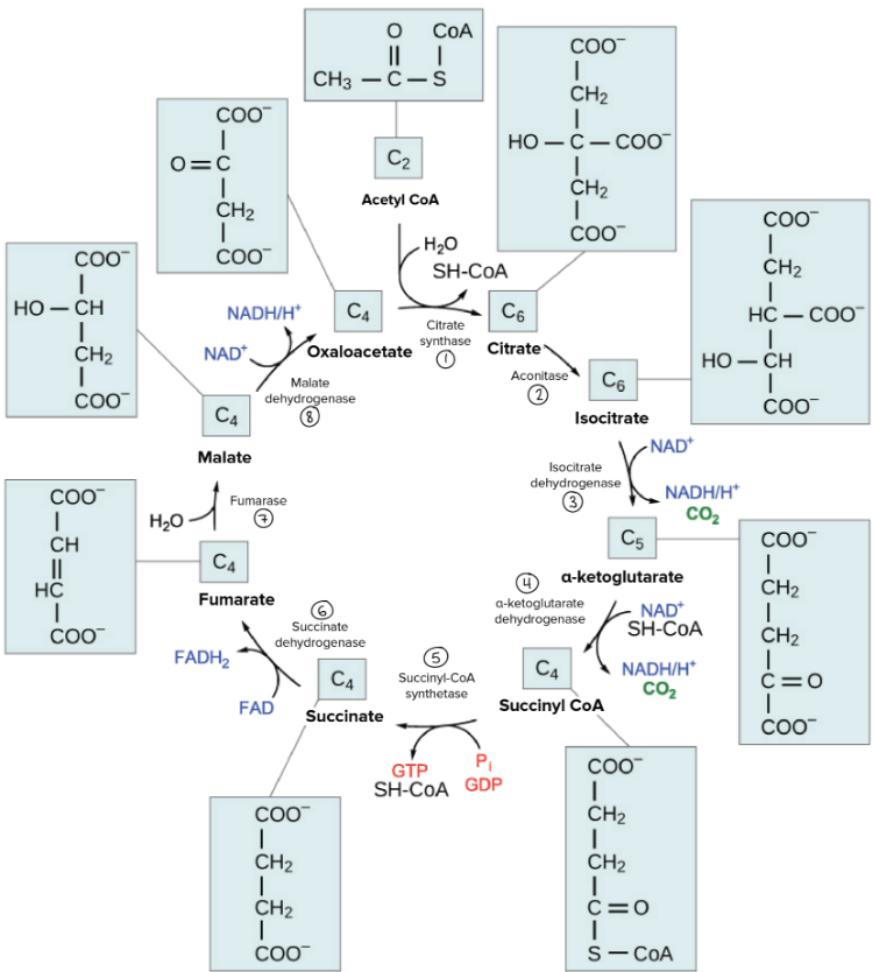


**Step 1.** In the first step of the citric acid cycle, acetyl CoA joins with a four-carbon molecule, oxaloacetate, releasing the CoA group and forming a six-carbon molecule called citrate.

**Step 2.** In the second step, citrate is converted into its isomer, isocitrate. This is actually a two-step process, involving first the removal and then the addition of a water molecule, which is why the citric acid cycle is sometimes described as having nine steps—rather than the eight listed here<sup>1</sup>.

**Step 3.** In the third step, isocitrate is oxidized and releases a molecule of carbon dioxide, leaving behind a five-carbon molecule— $\alpha$ -ketoglutarate. During this step, NAD<sup>+</sup> is reduced to form NADH. The enzyme catalyzing this step, **isocitrate dehydrogenase**, is important in regulating the speed of the citric acid cycle.

**Step 4.** The fourth step is similar to the third. In this case, it's  $\alpha$ -ketoglutarate that's oxidized, reducing NAD<sup>+</sup> to NADH and releasing a molecule of carbon dioxide in the process. The remaining four-carbon molecule picks up Coenzyme A, forming the unstable compound succinyl CoA. The enzyme catalyzing this step,  **$\alpha$ -ketoglutarate dehydrogenase**, is also important in regulation of the citric acid cycle.

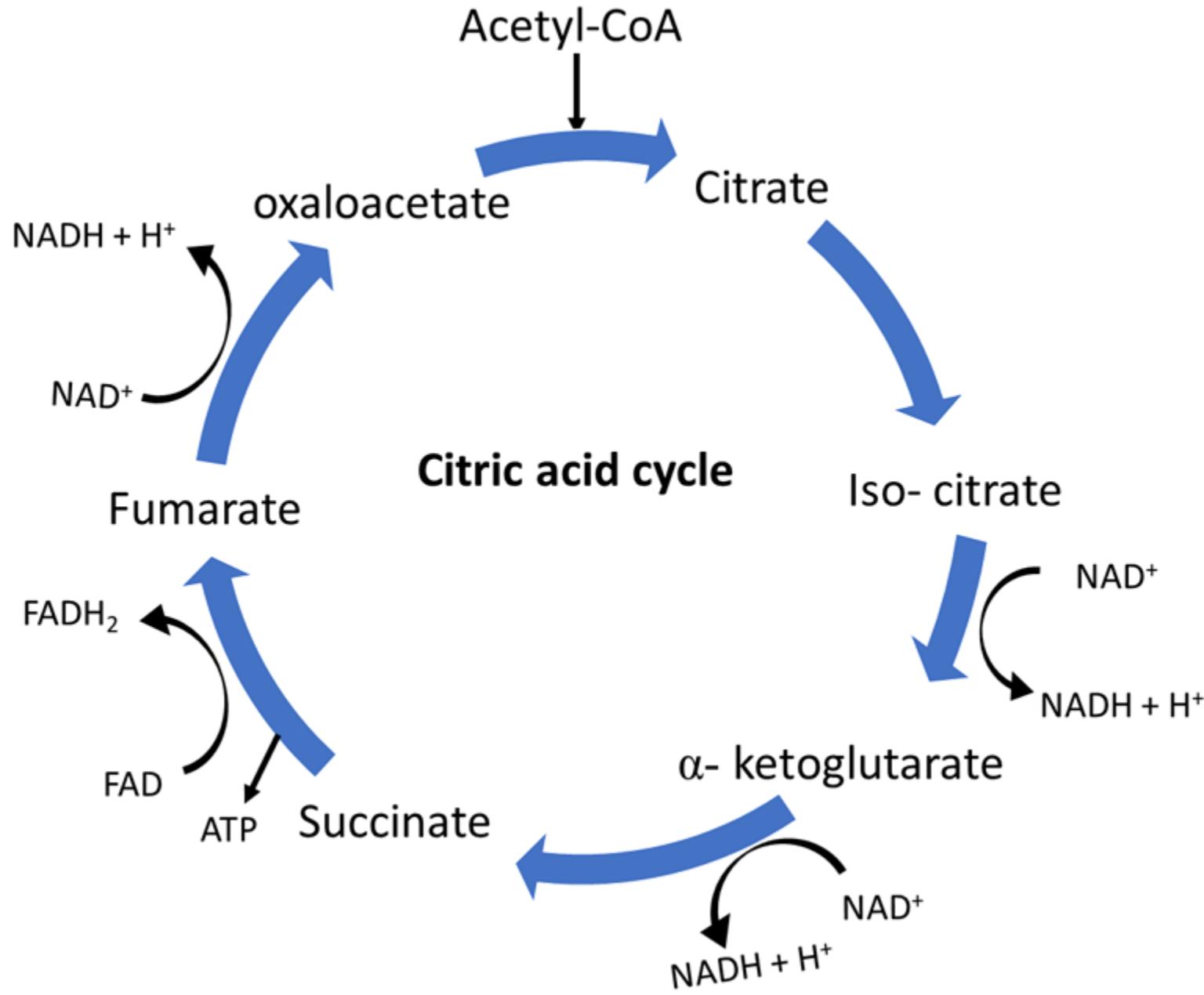


**Step 5.** In step five, the CoA of succinyl CoA is replaced by a phosphate group, which is then transferred to ADP to make ATP. In some cells, GDP—guanosine diphosphate—is used instead of ADP, forming GTP—guanosine triphosphate—as a product. The four-carbon molecule produced in this step is called succinate.

**Step 6.** In step six, succinate is oxidized, forming another four-carbon molecule called fumarate. In this reaction, two hydrogen atoms—with their electrons—are transferred to FAD, producing FADH<sub>2</sub>. The enzyme that carries out this step is embedded in the inner membrane of the mitochondrion, so FADH<sub>2</sub> can transfer its electrons directly into the electron transport chain.

**Step 7.** In step seven, water is added to the four-carbon molecule fumarate, converting it into another four-carbon molecule called malate.

**Step 8.** In the last step of the citric acid cycle, oxaloacetate—the starting four-carbon compound—is regenerated by oxidation of malate. Another molecule of NAD<sup>+</sup> is reduced to NADH in the process.



## Distinguish between glycolysis and citric acid cycle.

Both methods are involved in respiration with the aim of fulfilling the energy requirement of the body. Glycolysis is the initiative involved within the process of respiration and occurs within the cytoplasm of the cell. The citric acid cycle is the second process of respiration which occurs within the mitochondria of the cell.

Glycolysis	Citric acid cycle
Glycolysis is a linear pathway.	The citric acid cycle (Krebs cycle) is a cyclic pathway.
It occurs in the cytoplasm.	It occurs in the mitochondria.
It occurs in both aerobic and anaerobic respiration.	It occurs in aerobic respiration only.
No carbon dioxide evolved.	Carbon dioxide evolved.
Net gain of two molecules of ATP and two molecules of NADH gained for every molecule of glucose broken down.	Each turn of the Krebs cycle yields three molecules of NADH and two molecules of $FADH_2$ .
Also known as the EMP pathway or Cytoplasmic respiration.	Also known as the TCA cycle, Kreb's cycle, or Mitochondrial respiration.
It is not connected with oxidative phosphorylation.	It is connected with oxidative phosphorylation.

Both glycolysis and the Krebs cycle are enzyme-mediated and are under constant regulation based on the energy requirement of the cell/organism. The rates of these processes vary under various conditions such as the well-fed state, fasting state, exercised state, and starvation state.

## Why do we need oxygen?

You, like many other organisms, need oxygen to live. As you know if you've ever tried to hold your breath for too long, lack of oxygen can make you feel dizzy or even black out, and prolonged lack of oxygen can even cause death. But have you ever wondered why that's the case, or what exactly your body does with all that oxygen?

As it turns out, the reason you need oxygen is so your cells can use this molecule during oxidative phosphorylation, the final stage of cellular respiration. Oxidative phosphorylation is made up of two closely connected components: the electron transport chain and chemiosmosis. In the electron transport chain, electrons are passed from one molecule to another, and energy released in these electron transfers is used to form an electrochemical gradient. In chemiosmosis, the energy stored in the gradient is used to make ATP.

So, where does oxygen fit into this picture? Oxygen sits at the end of the electron transport chain, where it accepts electrons and picks up protons to form water. If oxygen isn't there to accept electrons (for instance, because a person is not breathing in enough oxygen), the electron transport chain will stop running, and ATP will no longer be produced by chemiosmosis. Without enough ATP, cells can't carry out the reactions they need to function, and, after a long enough period of time, may even die.

## **oxidative phosphorylation**

Oxidative phosphorylation is the final step in cellular respiration. It occurs in the mitochondria. It is linked to a process known as electron transport chain. The electron transport system is located in the inner mitochondrial membrane. The electrons are transferred from one member of the transport chain to another through a series of redox reactions.

## Oxidative Phosphorylation Steps

The major steps of oxidative phosphorylation in mitochondria include:

### Delivery of Electrons by NADH and FADH<sub>2</sub>

Reduced NADH and FADH<sub>2</sub> transfer their electrons to molecules near the beginning of the transport chain.

After transferring the electrons, they get oxidised to NAD<sup>+</sup> and FAD and are utilised in other steps of cellular respiration.

### Electron Transport and Proton Pumping

The electrons move from a higher energy level to a lower energy level, thereby releasing energy. Some of the energy is used to move the electrons from the matrix to the intermembrane space. Thus, an electrochemical gradient is established.

### Splitting of Oxygen to form Water

The electrons are then transferred to the oxygen molecule which splits into half and uptakes H<sup>+</sup> to form water.

### ATP Synthesis

The H<sup>+</sup> ions pass through an enzyme called ATP synthase while flowing back into the matrix. This controls the flow of protons to synthesize ATP.

## Chemiosmosis

Oxidative phosphorylation uses the chemical reactions that release energy to drive a chemical reaction that requires energy. These 2 sets of reactions are coupled and interrelated.

The electrons that flow through electron transport chain is an exergonic process and the synthesis of ATP is an endergonic process. These two processes are ingrained within a membrane. As a result, energy will be transmitted from the electron transport chain to ATP synthase by the movement of proteins. This process is termed as chemiosmosis.

Endergonic Process is a chemical reaction in which energy is absorbed. There will be a change in free energy and it is always positive. Exergonic Process is a chemical reaction in which there will be a positive flow of energy from the system to the surrounding environment. Chemical reactions are also considered exergonic when they are spontaneous.

## Electron Transport Chain

Most of the biochemical catabolic processes like the citric acid cycle, glycolysis, beta-oxidation, etc. produce the coenzyme NADH. It consists of electrons having high transfer potential.

These reactions release a huge amount of energy on oxidation. These reactions are also known to be the uncontrollable reactions since the energy within the cells is not released at once.

The electrons are separated from the NADH and then passed to the oxygen with a series of enzymes releasing a small amount of energy. All these series of enzymes having complexes is known as electron transport chain.

This chain can be seen in the inner layer or membrane of mitochondria. The salts of succinic acid are also oxidized by this electron chain transport system.

In the case of eukaryotes, the enzymes make use of energy that has been released in the electron transport system from the oxidation of NADH that pumps protons across the inner membrane of the mitochondria. This results in the generation of the electrochemical gradient across the membrane. This can be considered as one of the best examples to understand the concept of oxidative phosphorylation.

# oxidative phosphorylation

