

UNIT-V

PART-A

SPECTROSCOPIC TECHNIQUES

*Spectroscopy:- Spectroscopy involves the interaction between electromagnetic radiation and the substance under investigation.

Electromagnetic Spectrum:- The arrangement of all types of electromagnetic radiations in order of their increasing order of frequency and decreasing order of wavelength from Radio waves to Gamma rays is known as electromagnetic spectrum.

- * Radio waves - $> 0.1 \text{ m}$
- * Micro waves - $0.1 \text{ m} - 1 \text{ mm}$
- * Infra-Red - $1 \text{ mm} - 700 \text{ nm}$
- * Visible Light - $700 \text{ nm} - 400 \text{ nm}$
- * ultra Violet - $400 \text{ nm} - 1 \text{ nm}$
- * x-rays - $1 \text{ nm} - 10^{-3} \text{ nm}$
- * Gamma Rays - $< 10^{-3} \text{ nm}$

* Uses :-

- Radio waves are used radio and television signals
- Microwaves are used cooking and Radar telecommunication purpose.
- Infra-red rays are used to produce over heat to the body.
- Visible light produce Seven different colours to the object like visibility.
- Ultra violet rays are used in luminiscence lamps and light vision Spectacles.
- X-rays are used in medical purpose to Scan body parts like lungus.
- Gamma rays are used to control the density of Cancerous cells.

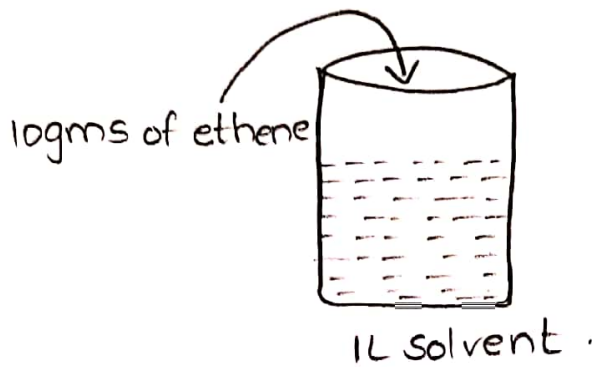
* UV SPECTROSCOPY :-

UV Spectroscopy is the measurement of the attenuation of a beam of light passing through a sample or after reflection from sample surface.

* ADSORPTION LAWS :-

- i) Beer's Law :- "When a beam of monochromatic light passed through a substance dissolved in a non-absorbing medium, The adsorption of light is directly proportional to the molar concentration of solution"

$$\log_{10} I_0/I \propto C.$$



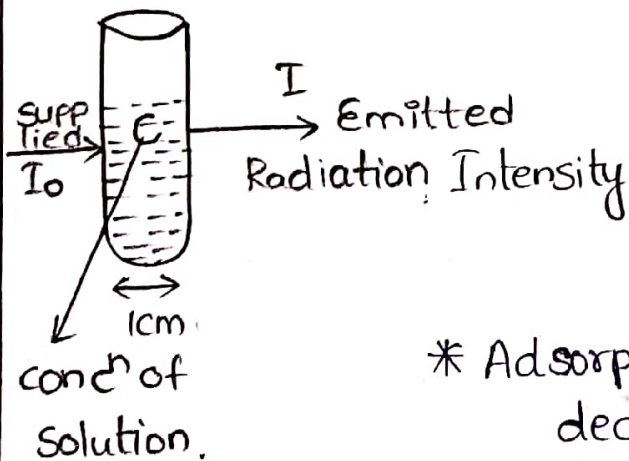
ii) Lambert's Law :- "when a beam of light is passed through a substance the absorption of light is proportional to the path length of the substance".

$$\log_{10} I_0/I \propto l$$

From Beer's and Lambert's law,

$$\log_{10} I_0/I \propto cl.$$

$$\log_{10} I_0/I = Ecl.$$



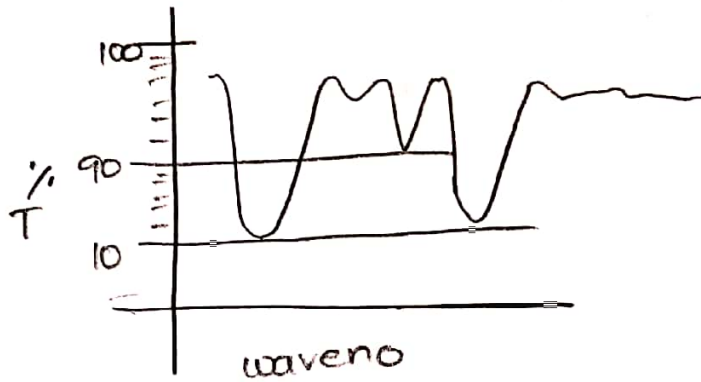
$$(I_0 - I)$$

$$(\log I_0 - \log I)$$

$$\log I_0/I$$

* Absorption increases transmission decreases

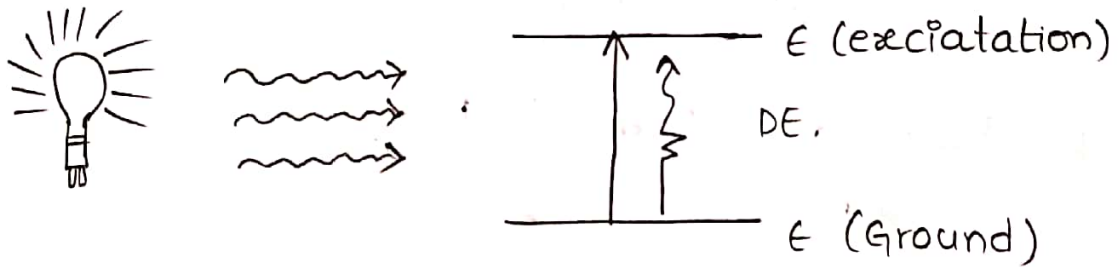
$$\uparrow A \propto \frac{1}{T} \downarrow$$



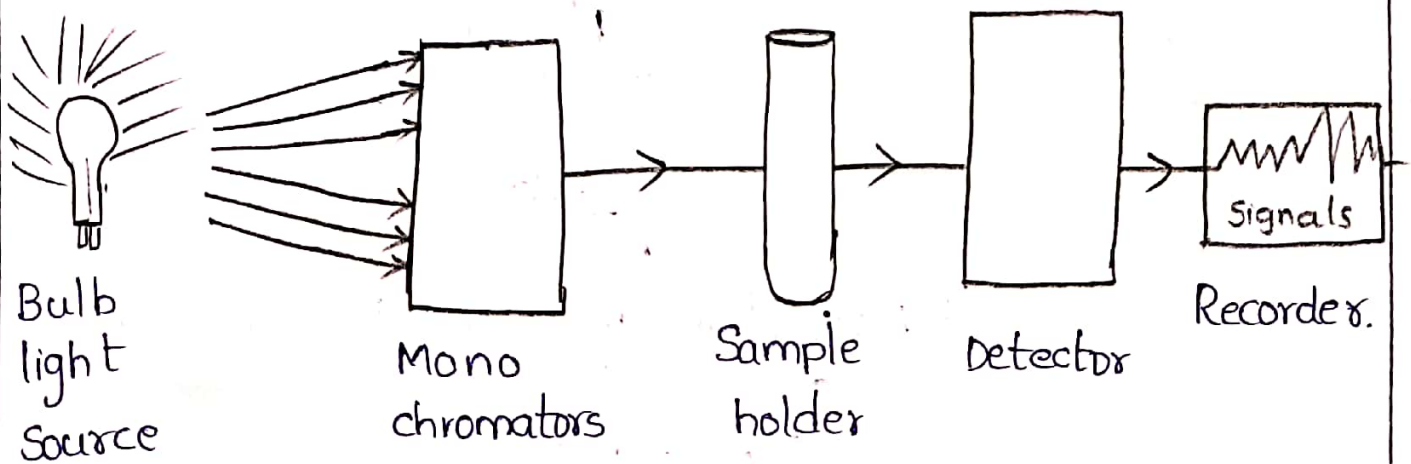
* Nature of Solvent:-

- Solvent should not absorb any kind of Radiation
- It should not be ~~Solvents~~ polar Solvents.

* Principle of UV-spectroscopy:-



* Instrumentation of UV spectroscopy:-
Components.



1) Light Source:-

(a) Deuterium lamp - UV region (200-400 nm)

(b) Tungsten halogen lamp - Visible region (400-750 nm)

2) Monochromator:- Monochromator is device use to resolve wide band of polychromatic light radiation into narrow band of monochromatic radiation.

Eg:- Filters, prisms, Gratings.

3) Sample holder:- Cuvette is used as sample holder made up of Quartz.

4) Detectors:- It will convert light energy into electrical signal that are displayed on readout devices

* Barrier layer cell

* photo tube.

* photo multiplier tube (most using)

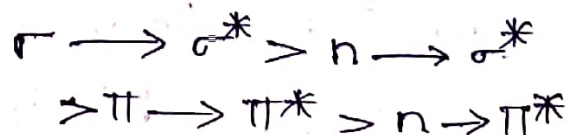
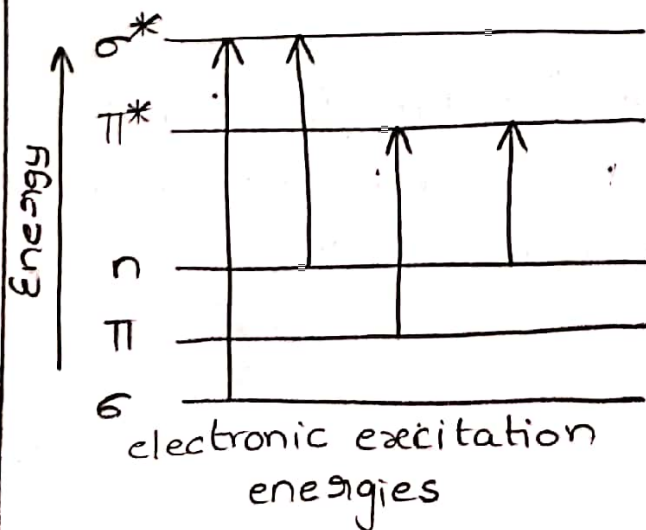
* Thermo couple.

* Balometer.

5) Amplifier & Recorder:- Amplifier Amplifies signal coming from detector and recorder records them which is displayed on readout device.

* Theory of electronic Spectroscopy

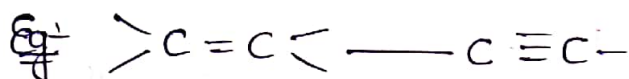
- when the molecule absorbs UV (or) Visible light, its electrons get promoted from ground state to the higher energy state.
- In the ground state, the spins of electrons in each molecular orbital are essentially paired.
- In the higher energy state, if the spins of electrons are paired is called excited singlet state.
- On the other hand spins of the electrons excited state are parallel is called excited Triplet state.
- Excited triplet state is more stable than excited single state.
- Excited Singlet state converts to triplet state emission of energy of light.
- The highly probable transition due to absorption of quantised energy involves the promotion of one electron from the highest occupied molecular orbital to the lowest available unfilled molecular orbital.



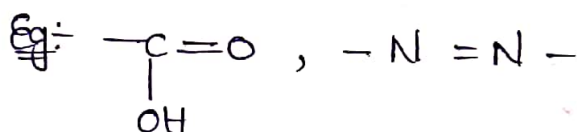
* CHROMOPHORES:- chromophores are covalently bonded moieties with any compound and responsible for absorption of UV-visible radiations.

Eg:- Aldehyde, ethylene, carbonyl etc....

① chromophores with $\pi-\pi^*$

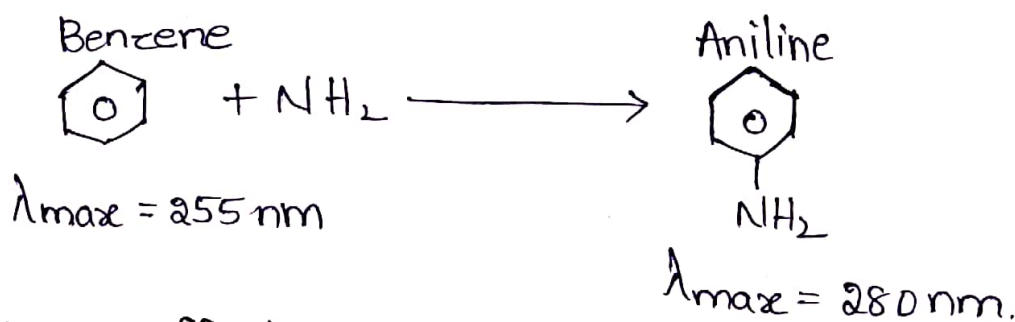


② chromophores with $n-\pi^*$



* AUXOCHROMES:- Any moiety which does not show any specific colour (or) absorption. when separated but when combined with any chromophores it increases the absorption wavelength towards longer wavelength towards by formation of a new chromophore.

Eg:- OH, NH₂, OR, NHR, -SH etc....



* Factors effecting absorption:-

1) Absorbing compounds
chromophores, Auxochromes.

2) Solvent effect

Benzene	255 nm	} Avoid these Solvents.
CCl ₄	265 nm	
chloroform	240 nm	

3) Temperature.

→ low temp is suitable for UV-spectroscopy.

4) Inorganic Moieties

→ Increases the absorption.

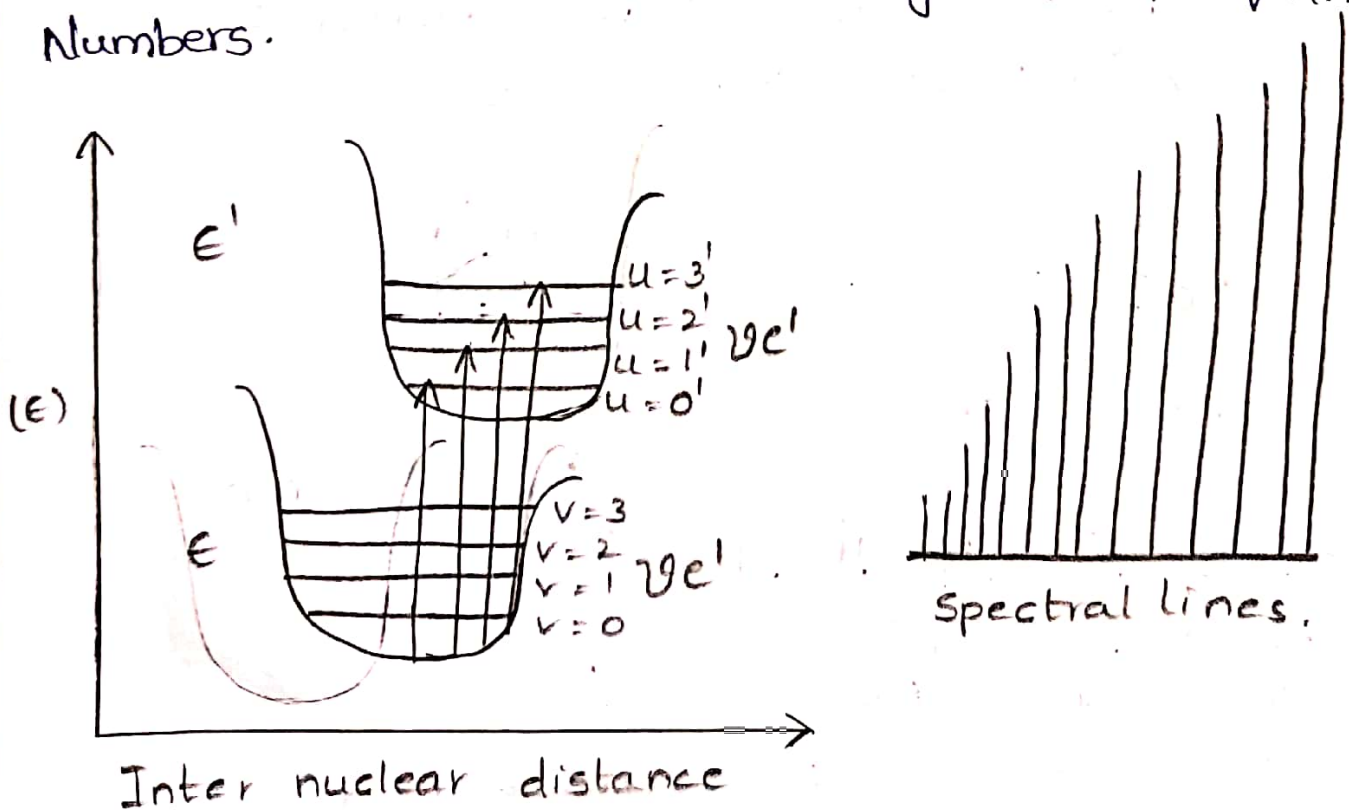
→ Complex inorganic Moieties → $Cr_2O_4^{2-}$, MnO_4^-

→ Single inorganic Moieties → Ag, Au etc ...

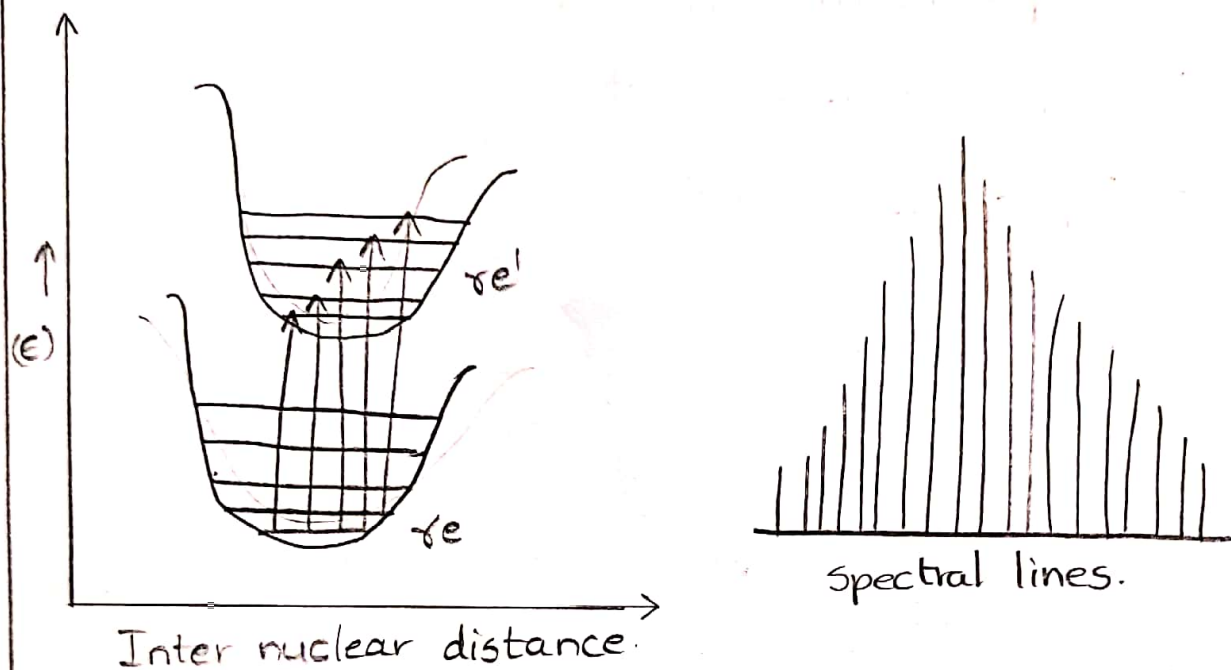
* Franck Condon Principle:-

"An electronic transition takes place so rapidly that a vibrating molecule does not change its inter-molecular distance during the transition"

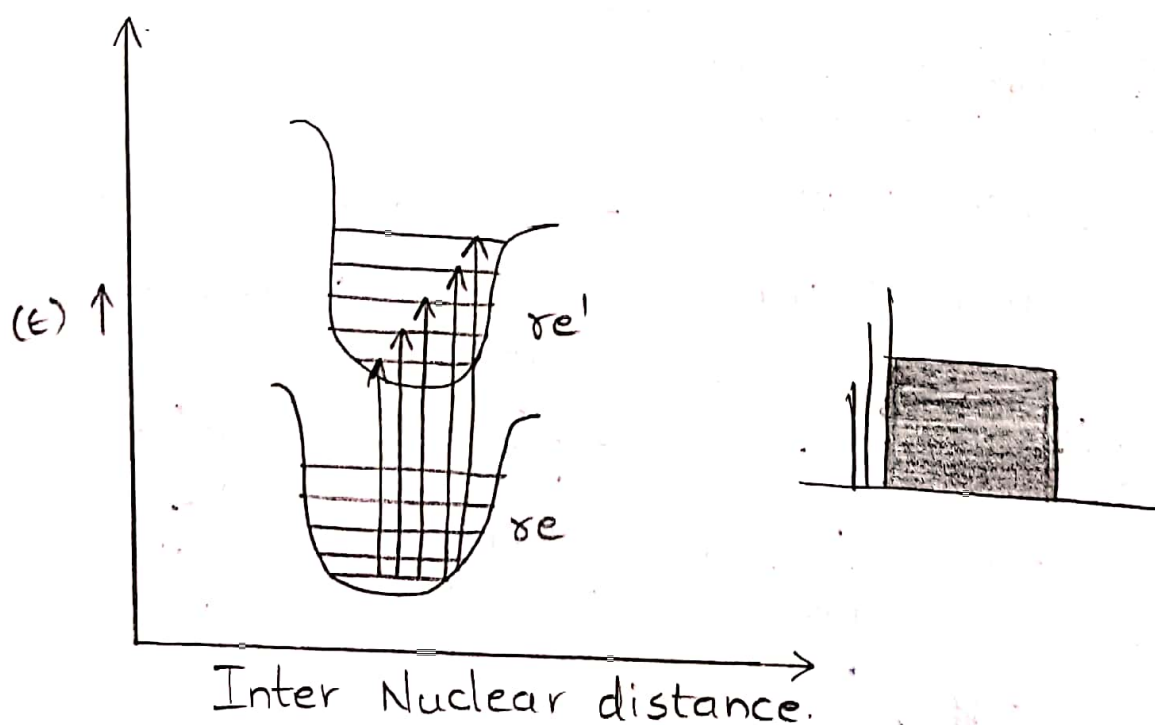
Case i:- when $x_e = x_{e'}$ the intensity of the spectral lines increases with increasing vibrational quantum numbers.



Case - ii:- When $r_{e'} > r_e$. The intensity of the spectral lines for intermediate vibrational levels is very high compared to the lower and higher vibrational levels.

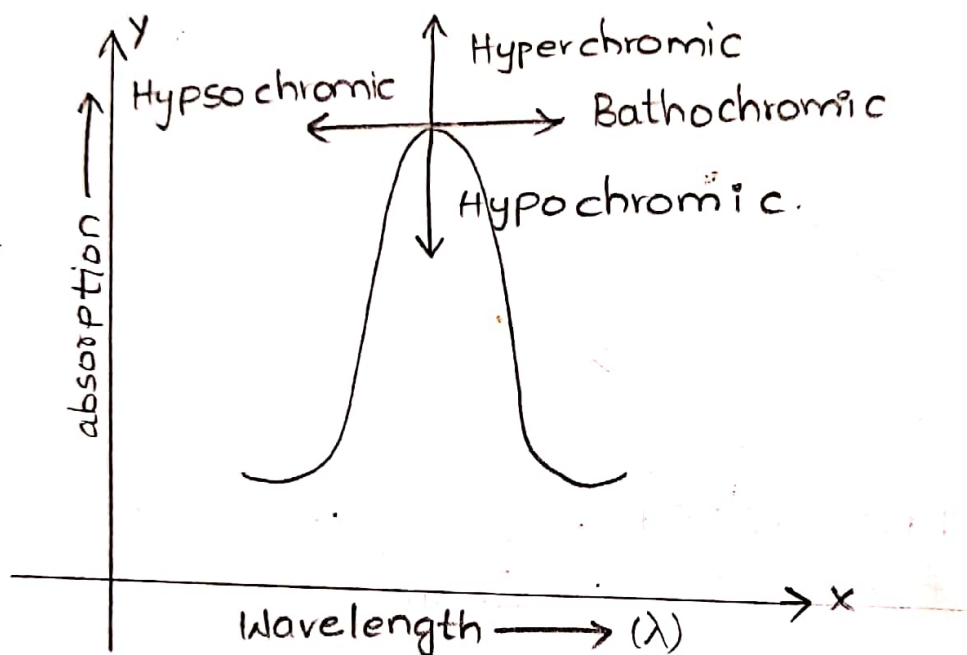


Case - iii:- When $r_{e'} \gg r_e$. we can observe only one (or) two lines followed by continuum.

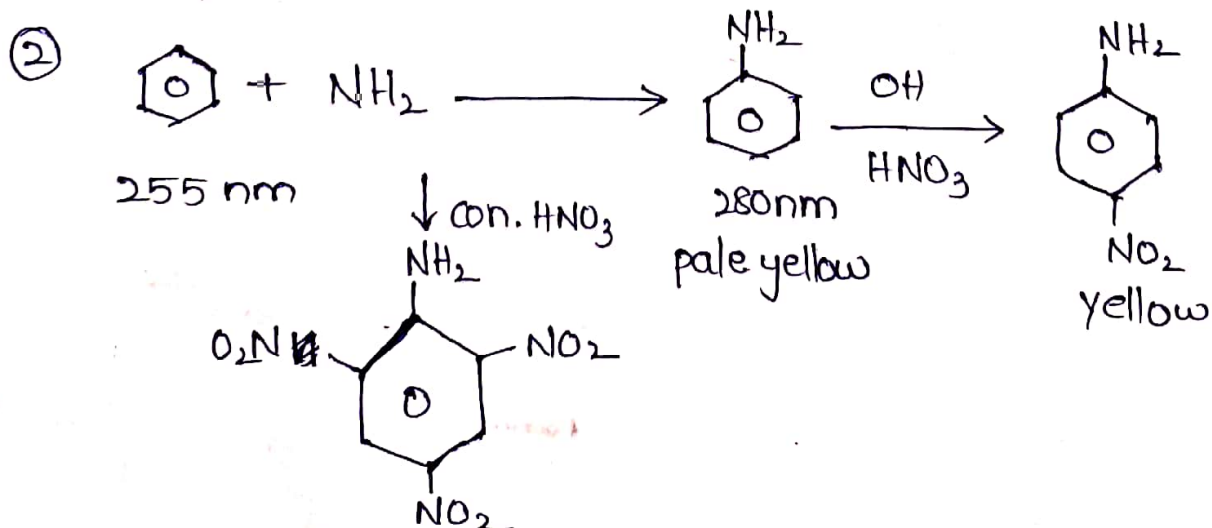
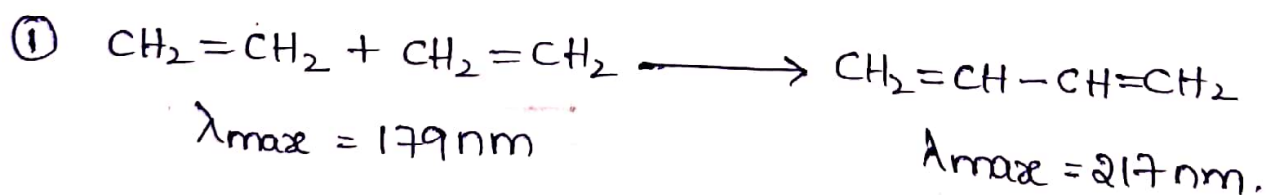


* INTENSITY SHIFTS :-

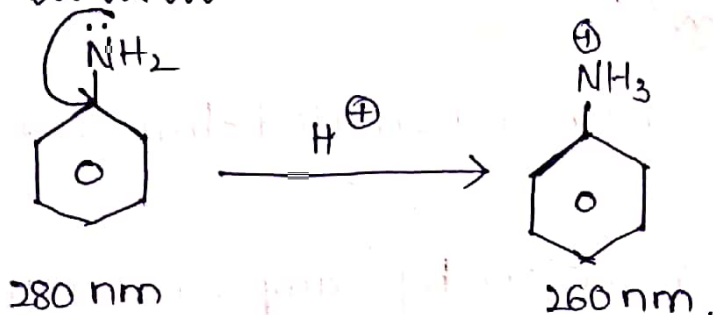
- * Bathochromic effect (or) Red shift.
- * Hypsochromic effect (or) Blue shift.
- * Hyperchromic effect.
- * Hypochromic effect.



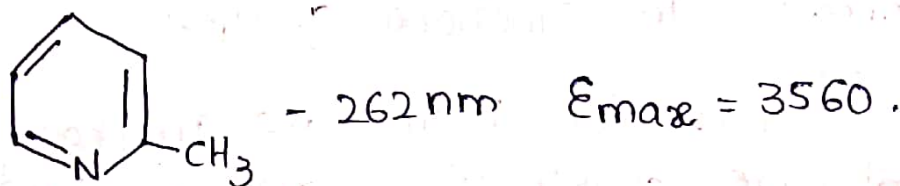
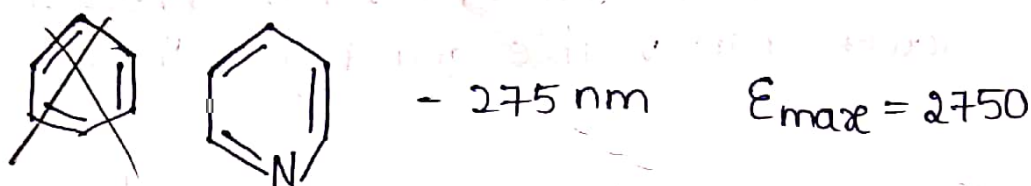
* Bathochromic shift :-



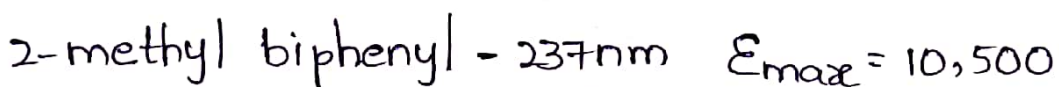
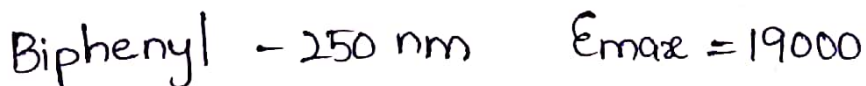
*Hypsochromic:-



*Hyperchromic Effect:- (Increasing Intensity)



*Hypochromic effect:- (Decreasing Intensity)



* Applications of Uv Spectroscopy:-

- 1) Determination of Molecular weight of a molecule.
- 2) Determination of impurities present in the sample.
- 3) Unknown concentration of a solution can be determined by this spectroscopy.
- 4) characterisation of aromatic compounds and in detect -ion of ~~is~~ Conjugation.

* FT-IR SPECTROSCOPY :-

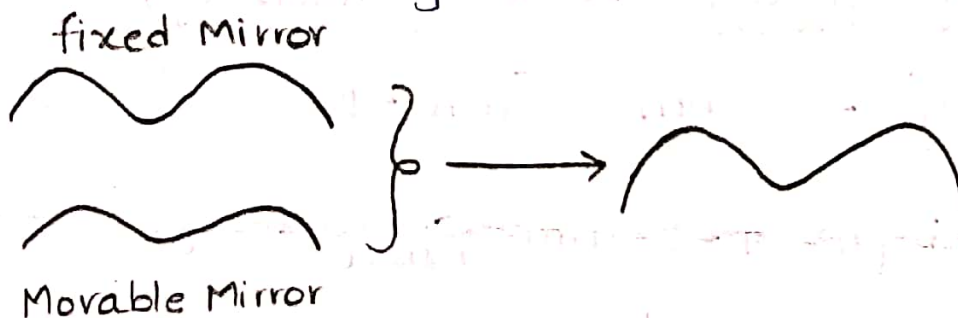
→ FT-IR means Fourier transmitted - Infra red Spectroscopy.

Absorption of IR radiation by Sample result in vibration transition.

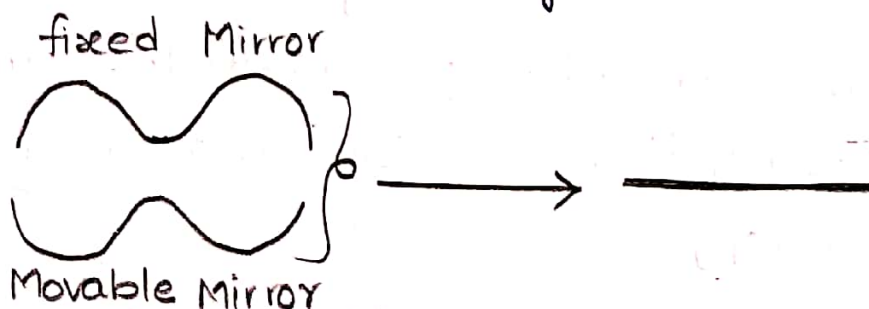
→ Infrared waves have wavelengths longer than visible and shorter than micro waves, and have frequencies which are lower than visible and higher than micro-waves.

→ IR spectra are mainly used in structure elucidation to determine the functional groups.

→ If the Radiation beams are in phase the beams will interfere constructively and resultant amplitude will be twice as high.



→ If the radiation beams are out of phase the beams will interfere destructively and cancelling out each other



* Instrumentation of FT-IR Spectrometer Components:-

① Source

② An optical system which uses interferometer.

(a) Beam splitter.

(b) stationary Mirror.

(c) Moving Mirror.

③ Sample

④ Detector.

1) Source:- Nerust glower, Global source, Tungsten lamps, Mercury arc.

2) Beam Splitter:- It is made of material which has 50% refractive index.

a) For Far IR:- Ny lar film sand wiced between halide plate of low refractive index solid used.

b) For Middle IR:- Thin film of Ge (or) Si deposited on CSI (or) CSBR (or) KCL (or) NaCl.

c) Near IR:- Thin film or ferric oxide deposited on calcium chloride.

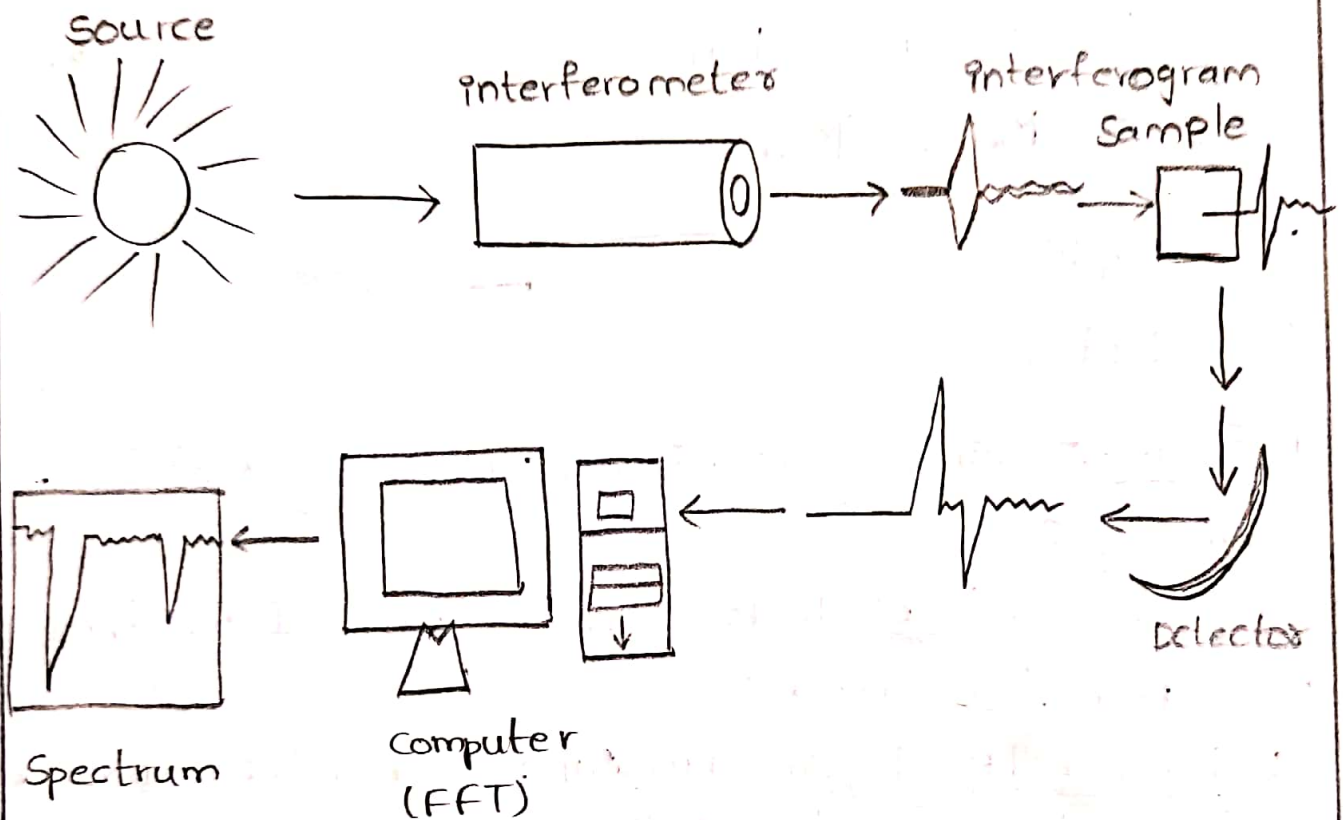
3) Detector:- pyro electric detector used

It consists of two perpendicular mirrors. One is stationary other is movable.

→ Movable Mirror is controlled by 'HeNe laser (632.8nm)

→ Between these mirrors set a beam splitter at 45° from the initial position of the movable mirror.

→ A parallel beam of radiation from the IR Source is passed on for the mirror through the beam splitter.

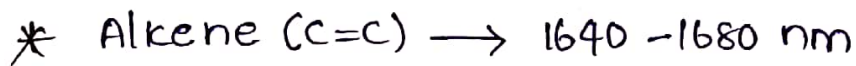
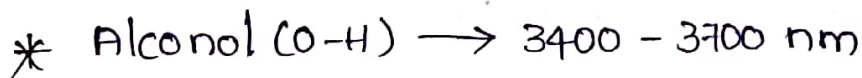
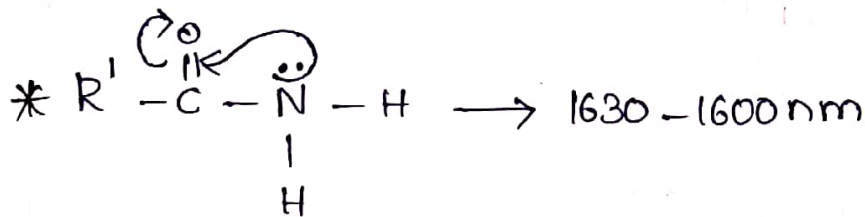
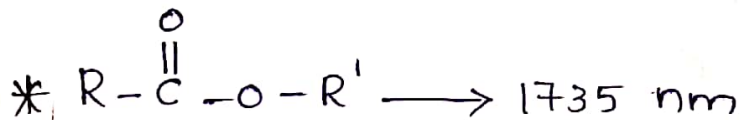
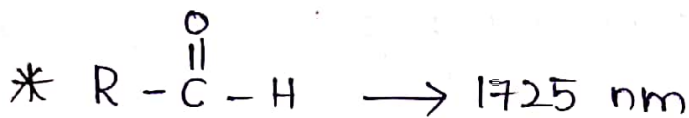
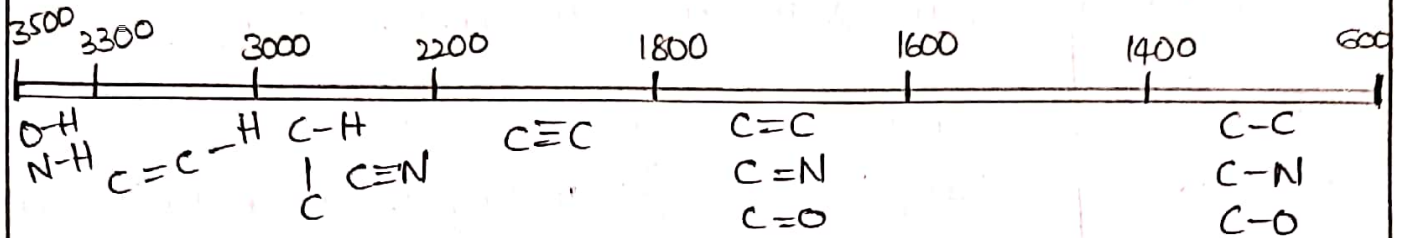


*Advantages:-

- 1) Better Sensitivity and brightness
- 2) Allows Simultaneous measurement over the entire wave number range.
- 3) Requires no slit device.
- 4) We can determine even small quantity of analyte.
- 5) Structural studies of cells & Bacterial.
- 6) Identify chemicals from paints, polymers, coatings, drugs, and contaminants.

→ Identify types of chemical bonds in functional groups.

* IR of Organic Compounds:-

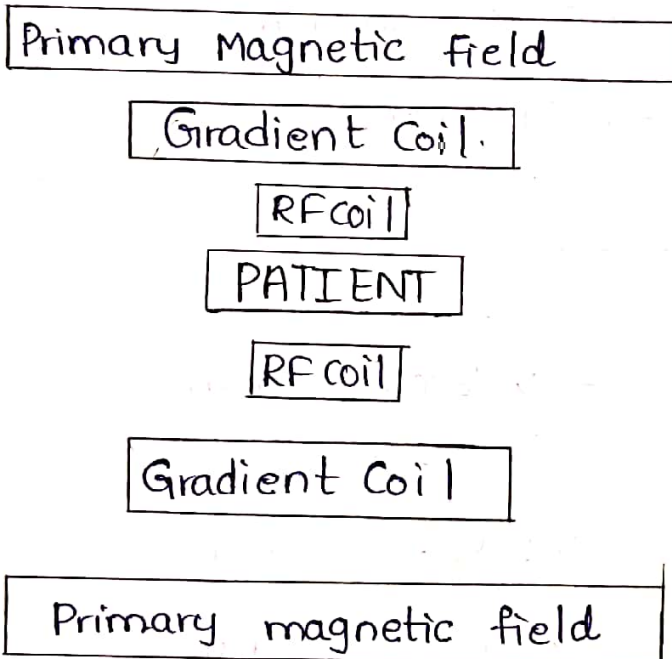


* MAGNETIC RESONANCE IMAGING:-

* felix bloch & Edward purcell - 1946.

* Raumann Damadian used in medical purpose.

MRI:- "MRI is ideal for diagnosis of conditions in tissues or ligaments. Any type of soft injury in the brain including Tumor and in the spine would be better spotted using an MRI"



* MRI Components:-

Super Conducting Magnet:-

They are large magnets that takes most of the space in the MRI machine. It creates a powerful magnetic field, strength of Super conducting magnetic field is 5000 - 20,000 gauss.

Gradient Magnets:- Variant Magnetic field which allows different parts of the body to be scanned the way from 180 Gauss to 270 gauss.

Coils:- Coils that transmit radiofrequency waves into the patient's body these are different for different body parts.

*Teeth - Bone \rightarrow H_2O poor tissue because of these are prepared by calcium.

* Procedure:-

- 1) patient reclines on the table and is moved into MRI machine.
- 2) patient is moved into active magnetic field.
- 3) Hydrogen atom with in patient's body align in response to magnetic field.
- 4) Radio frequency pulse is directed through coils into body part being scanned.
- 5) Radio frequency causes protons in certain hydrogen atoms to spin at a specific frequency.
- 6) Gradient magnets after the magnetic field following the machine to scan very precise sections of the body
- 7) Radiofrequency pulse is turned off. causing hydrogen protons to release absorbed energy.
- 8) Coils detect the energy released and Sends the data to the Computer which Generates MRI Images.

* Advantages:-

- 1) Sectional Images in any plane heart vessels, chambers and valves.
- 2) Sensitive to grey & white matter.
- 3) No use of Ionising radiation.

Disadvantages:-

- 1) Expensive Machine.
- 2) No Image for Bones & Teeth.
- 3) No Suitable for cardiac pacemakers implants.

* COMPUTED TOMOGRAPHY (CT):-

CT scan is ideal for any type of skeletal injuries, if there are bone injuries in the head, spine (or) chest then CT scan is the best way to identify problem.

⇒ X-ray Images are taken from different angles.

* Procedure:-

- 1) The patient will need to lie down on a motorized examination table that slides into a doughnut shaped CT scanner machine.
- 2) In most cases the patient will lie on their back, facing up, but, sometimes they may need to lie facedown (or) side ways.
- 3) After One x-ray picture the couch will move slightly and then machine will take another image and so on. The patient needs to lie very still for the best Result.

4) During the scan, everybody except for the patient will leave the room. An intercom will enable two-way communication between the radiographer and the patient.

5) If the patient is child, a parent (or) adult might be allowed to stand (or) sit near by but they will have wear a lead apron to prevent radiation exposure.

* Uses :-

- 1) Soft tissues.
- 2) The pelvis.
- 3) Blood vessels
- 4) lungs.
- 5) Brain
- 6) abdomen.
- 7) Bones.

* Disadvantages :-

- 1) There is a chance to develop cancer less than 1 in 2000.
- 2) Pregnant, breast feeding women avoided
- 3) claustrophobia patients avoided.

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UNIT-5
PART-B

①

NON CONVENTIONAL ENERGY SOURCES AND STORAGE DEVICES

Non conventional energy sources:-

Non conventional energy sources are those energy sources which are renewable and ecologically safe such as solar energy, wind energy, biomass energy, ocean energy, geothermal energy etc. The importance of increasing the use of non-conventional (or) renewable power was recognized in India in the early 1970.

* Solar energy:- solar energy in India is utilized through photovoltaic route and thermal route

* Biomass:- power generating systems based on biomass combustion as well as biomass gasification were launched in different places in central India.

* Wind energy:- Wind energy is used for power generation. Wind generator is used to generate power.

* Geothermal energy:- Geothermal energy generated from hot springs. It is generated in H.P and Jammu & Kashmir.

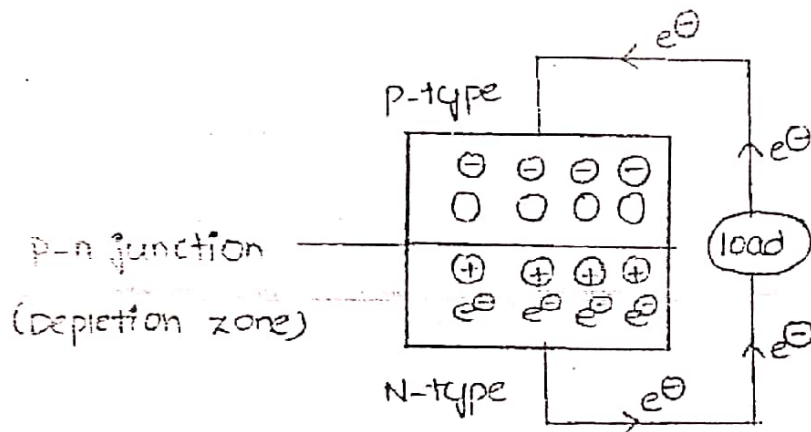
* Energy from urban & industrial waste:- power is generated from urban waste, which is an practice in Timarpur, Delhi and Tamilnadu.

→ Solar cell / photo voltaic cell:-

A device which converts from sun rays into electricity is known as solar cells.

* solar cells are prepared from semiconductor material like silicon.

* silicon is doped with 15th and group 13th elements to produce p-type and n-type semiconductor materials



N-type semiconductor materials results in an excess of electrons and p-type semiconductor materials results in an excess of holes.

Electrons diffuse across the p-n junction from the n-type material creating positive charges in the n-type material.

Holes diffuse across the p-n junction from the p-type material creating negative charge in the p-type material.

Depletion of ozone:-

The area near the p-n junction is called depletion zone because there are no charge carriers present.

The separated positive and negative charges create an electric field across the depletion zone.

→ When light is absorbed by the semiconductors extra free electrons and holes are created in the electric field makes the electron flow to the n-type material and holes flow to the p-type material.

* The separation of charges creates a potential difference across the p-n junction electrons flow through an external wire to the p-type material to unite with the holes producing an electric current.

$$I = I_l - I_D - I_{sh}$$

where I = output current in amperes

I_l = light produced current in amperes

I_D = Diode junction produced current in amperes

I_{sh} = short current released in amperes

Materials used in the preparation of solar cells:

1. crystalline silicons [like - poly silicons, ribbon silicon, mono crystalline silicon]
2. cadmium tellurides
3. copper, Indium, Gallium, selenides [CuInGaSe] ie [CIGS]
4. cadmium, Arsenide multifunction material
5. dye sensitized cells → Ru (Ruthenium), Arsenic
6. organic polymers like poly vinylene, poly propylene, carbon fullerenes

Applications of solar cells:-

1. To generate electricity

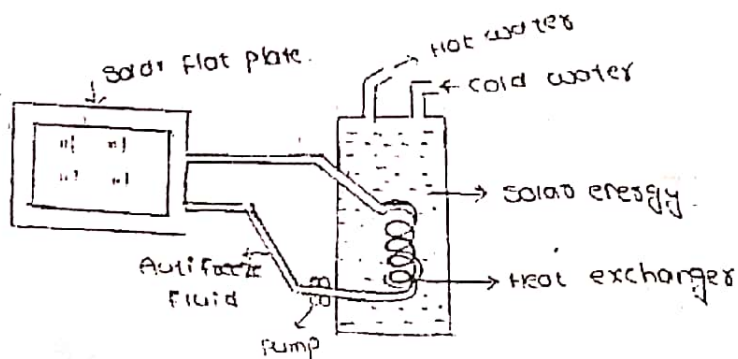
2. To prevent carbon foot print
3. These are used in agriculture sector to supply water from wells.
4. These are used as a water heaters
5. These are also used as a cooling of the water by using evaporation and condensation techniques
6. These are ecologically friendly resources.

Solar Heaters:

Solar water heaters consists of a storage tank placed above the cylinder at a certain height. the cylinder is connected to copper pipes, which are able to absorb the solar radiations resulting in the heating of the water passing through the copper pipes

Working:

Water from the storage tank fills into the cylinder and reaches into the copper pipes, which are heated by solar radiations and there will be the formation of hot water. The hot water from the pipes enters the lower portion of the cylinder and reaches to the different sites.

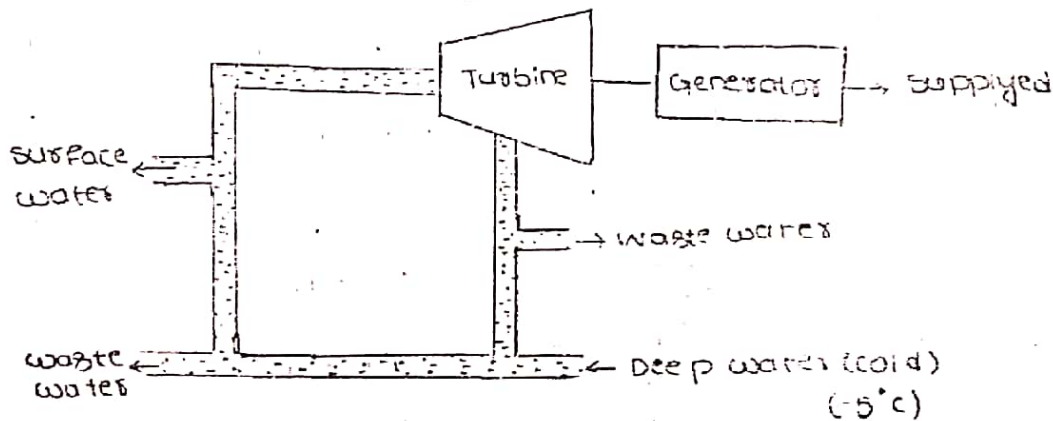


Ocean Thermal Energy conversion (OTEC):

It is a process that can produce electricity by using the temperature difference between cold ocean water and warm tropical surface water. OTEC plant pumps large quantities of deep cold sea water and surface sea water to run a power cycle and produce electricity. This theory was developed in 1880 and constructed in 1926.

An amount of large quantity of cold water is a by-product, that can be used for air conditioning and refrigeration. There are three types of OTEC systems

- 1) closed cycle
- 2) open cycle
- 3) Hybrid.



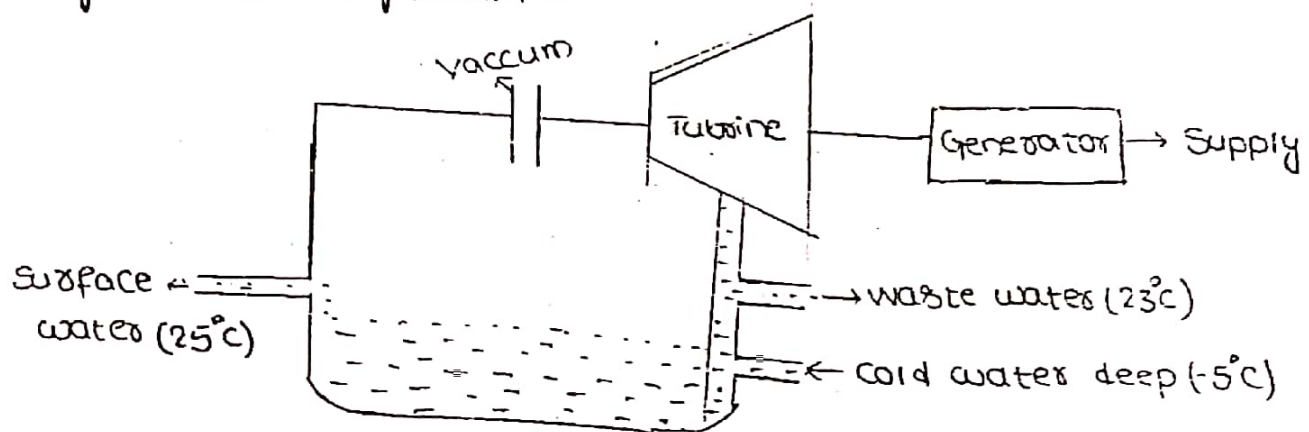
Here in the closed cycle, working fluid is ammonia used to power a turbine to generate electricity.

Warm sea water is pumped to heat exchanger, here the ammonia is vapourised and vapours of ammonia rotates the turbine and generates the electricity. The vapours with ammonia is converted into liquid in the bottom heat exchanger by passing deep cold water and the liquid

ammonia again enters into the top heat exchanger and the finally we will get cold water as byproduct coming from the bottom heat exchanger.

Open cycle OTEC:

Open cycle OTEC uses warm surface water directly to make electricity. The warm sea water is first pumped into a low pressure container which causes it to boil. In some processes, the expanding steam drives low pressure turbine attached to an electrical generator. The steam leaves its salt and contaminants in the low pressure container to give pure fresh water. It is condensed to a liquid by exposure to cold temperatures from deep-ocean water. This method produces desalinated fresh water suitable for drinking, irrigation and agriculture.



Hybrid OTEC:-

A hybrid cycle combines the features of closed and open cycle systems. In a hybrid warm sea water enters a vacuum chamber & flash evaporated similar to open

cycle evaporation process. The steam vaporizes the ammonia working fluid of closed cycle loop on the other side of an ammonia vaporizer. The vaporized fluid then drives a turbine to produce electricity. The steam condenses within the heat exchanger and provides desalinated water.

* Tidal And wave power:-

Tidal power is also called tidal energy is a form of hydro power that converts the energy obtained from tides into useful forms of power mainly electricity. The world's first large scale power plant is the Rance tidal power plant in France.

The ocean tides on the earth are ultimately due to gravitational interactions with the moon and sun and the earth's rotation. Tidal power is practically inexhaustible. Movement of tides causes a loss of mechanical energy in the earth moon system due to the pumping of water through natural restriction around coastlines and consequent viscous dissipation at the seabed and turbulence.

This loss of energy has caused the rotation of the earth to slow in the 4.5 billion years since its formation. During the last 620 million years. The period of rotation of the earth is slower than the rotation of earth since its formation.

Tidal power is taken from earth's oceanic tides.

The tidal forces are periodic variations in gravitational

attraction exerted by celestial bodies. Due to strong attraction to the oceans, a bulge in the water level is created, causing temporary increase in sea level when sea level is raised, water from the middle of the oceans is forced to move towards the shorelines creating a tide in an unending manner, due to consistent pattern of the moon's orbit around the earth.

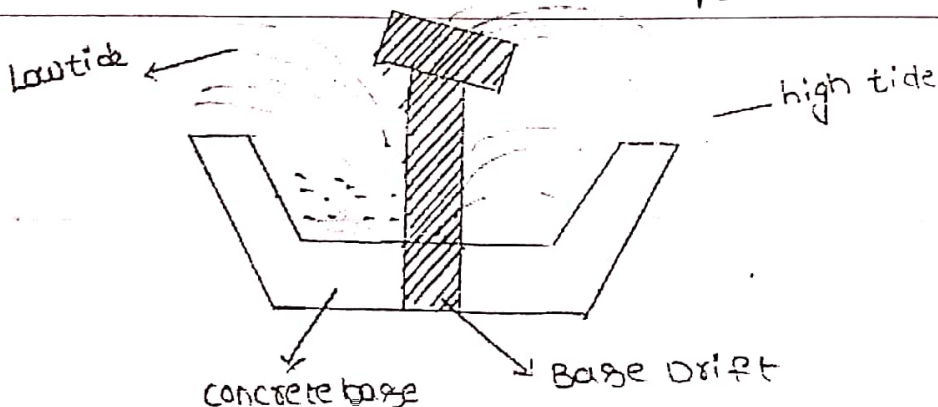
Tidal steam generator (TSG):-

This method make use of the kinetic energy of moving water to power turbines. These may be horizontal, vertical, open etc. placed near the bottom of the water column.

Tidal barrage method:-

Tidal barrage is a dam like structure used to capture the energy from masses of water moving in and out of a river due to tidal forces. The temporary increase in the level of the tide is channeled into a large base behind the dam & the potential energy of the tide is converted into mechanical energy to produce electric power through the use of generators.

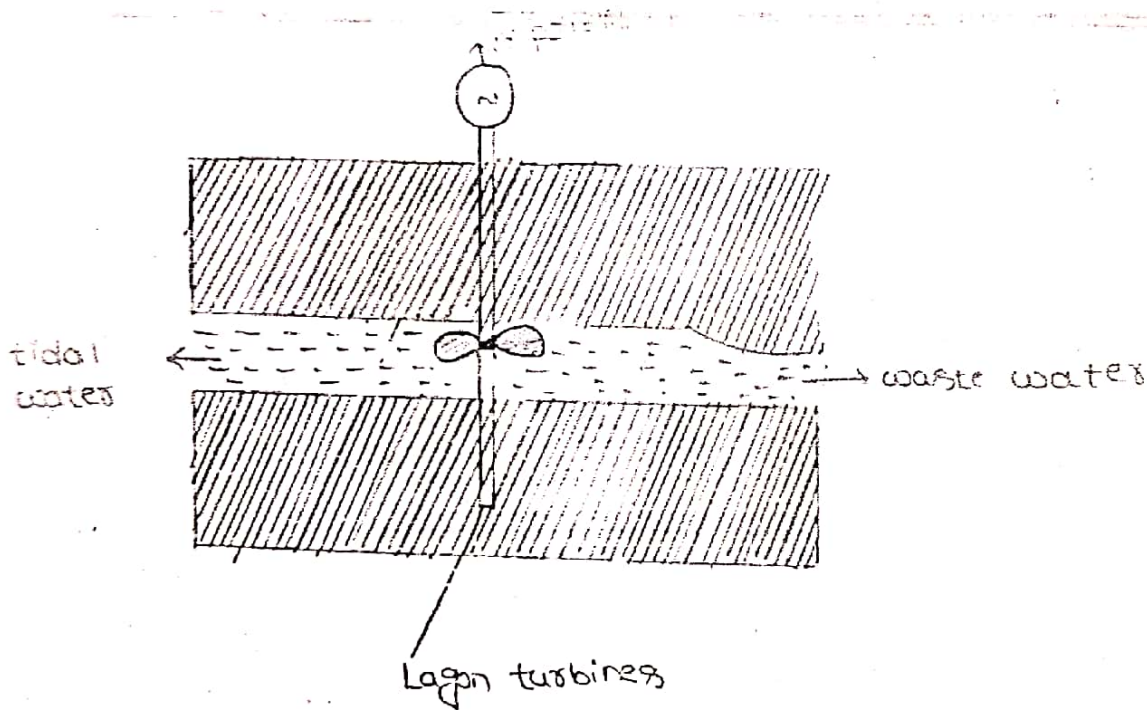
Dynamic tidal power method:- (DTP)



The interaction between potential and kinetic energies in tidal flows. Long dams are built into the ocean without enclosing an area, leading to a significant water level difference producing low and high tides from which power is generated.

Tidal lagoon method [TL]:

The reservoirs similar to tidal barrages are created called lagoon which can be in double format without



Hydro Power:-

Flowing water creates energy, that can be captured and turned into electricity. The power available in a river (or) stream depends on the rate at which the water is flowing and the height which it falls down. The hydro schemes are classified into four groups but the basic principle of operation are the same for all.

- * Large scale :- Where power output is about 2 Mw and above
- * Mini scale :- Where the power output is about 100 Kw - 2 Kw
- * Micro scale :- The power output is 5 Kw - 100 Kw
- * Pico scale :- Where the power output is less than 5 Kw.

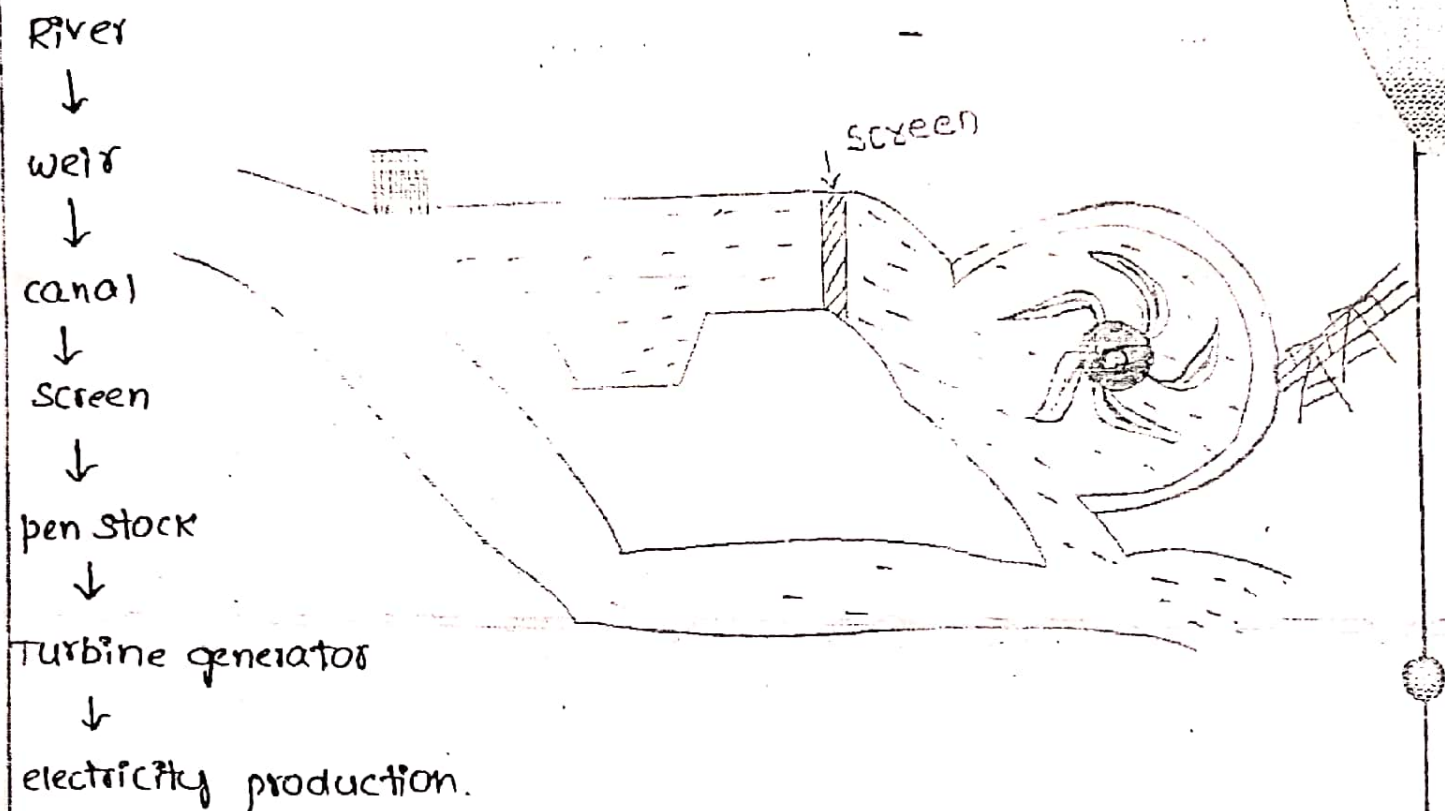
The core of a hydro scheme is the turbine, which is rotated by the moving water. Different types of turbines are used depending on the head and flow at the site.

pelton turbines - for low flow of flowwater.

Francis turbines - high flow & cross-flow

propeller turbines - large flow of water

River current turbines are like a wind turbines immersed in water and used to extract power from a large flow of water in river.



A small dam in the river bed directs the water to a settling tank (weir), which allows the silt to settle out of water and the clean water flow into a canal (or) a pipe to a settling tank called forebay which is sited above the power house. The canal can be long. The outlet from the forebay has a screen to trap silt and floating debris. Water flows out p into a pipe called penstock, which is made as steep as possible to transfer water to the turbine. Water leaving the turbine is led into the stream through the outlet pipe.

Geothermal Energy:-

It is the heat from the earth. It is clean and sustainable. Resources of geothermal energy range from shallow groups to hot water and hot rock found few miles beneath the earth's surface and deeper extremely high temperature molten rock called magma. The first geothermal electricity was produced in Italy in 1904.

To produce geothermal generated electricity wells of 1.6 kms deep (or) more are drilled into the underground reservoirs to tap steam and very hot water that drive turbine which inturn drive electricity generators.

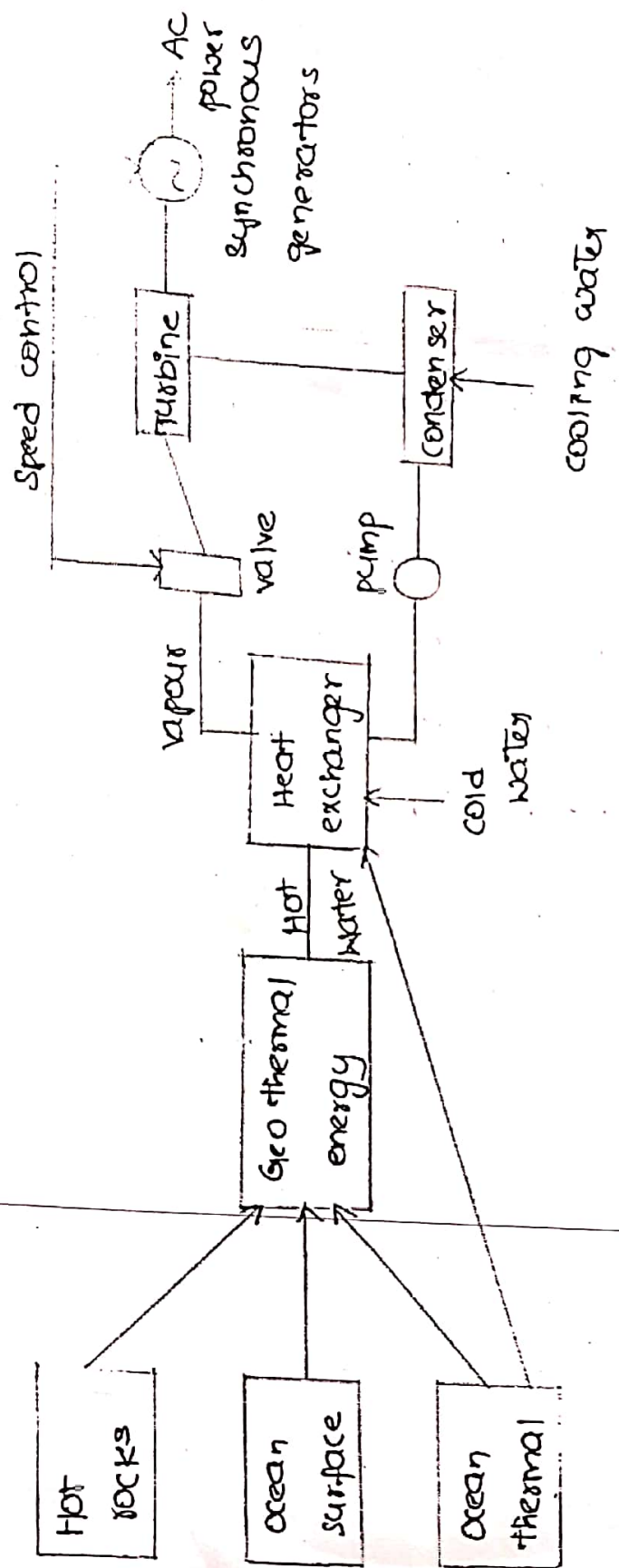
There are 3 types of geothermal power plants

* Dry steam:- Dry steam geothermal generator takes steam out of fractures in the ground and uses it directly to drive turbines.

* Flash geothermal plants:- It pulls deep, high pressure hot water into cooler. low pressure water. The steam that is produced is used to drive the turbine.

* Binary geothermal plant:- The hot water is passed by a secondary fluid with much lower boiling point than water, producing vapors of the secondary fluid, which can drive a turbine.

Geothermal plants have advantages over other thermal plants that no fossil fuel is burned no emission of CO_2 and other gases etc



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