Nanomaterials

Nanotechnology is the study of materials on the range of 1-100 nm. The physical properties of a material on nanoscale is different from properties of the same bulk material.

Consider a metal sample of dimensions L_x, L_y, L_z.

If $L_x < 100\ nm$ and $L_y, L_z \gg 100\ nm$, then electrons in the metal behave like a free particles along Y and Z axis but the motion of electrons is restricted along X axis.

The restriction of motion of a particle by physical dimensions of a system is called as quantum confinement.

Due to confinement, energies of electron become discrete along X axis but energies are continuous along Y and Z axis. Such structure is 2-D structure and is called as quantum well.

For a quantum wire, $L_x, L_y < 100\ nm$ and $L_z \gg 100\ nm$. This is 1-D structure. The quantum confinement is along X and Y axis. This is called as quantum wire.

For a quantum dot, $L_x, L_y, L_z < 100\ nm$. This is 0-D structure. The quantum confinement is along X, Y and Z axis. This is called as quantum dot.

Density of states- Density of states is useful to understand various spectroscopic and transport properties of materials. Density of states is defined as the number of states per unit energy range.

For a particle in an infinite potential well, the density of states is calculates as follows

The eigenenergy of the particle in the nth state is $E = \frac{n^2h^2}{8mL^2}$

Hence, $\frac{dE}{dn} = \frac{2nh^2}{8mL^2}$. So,

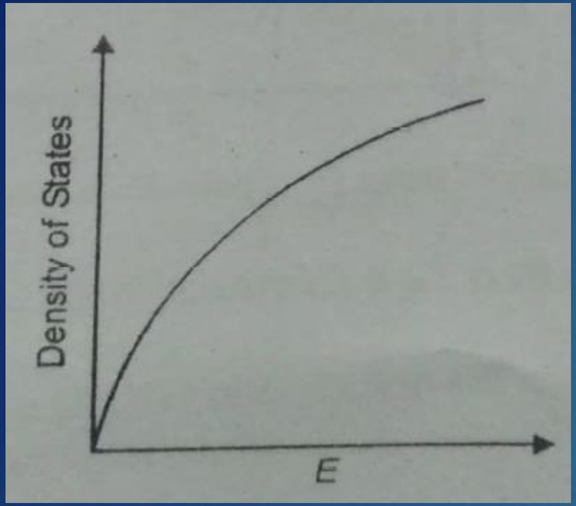
$$\frac{dn}{dE} = \frac{\sqrt{8m}\,L}{nh} \quad \frac{L}{2h}\sqrt{8m}$$

$$\frac{dn}{dE} = \frac{L}{2h}\sqrt{\frac{8m}{E}}$$

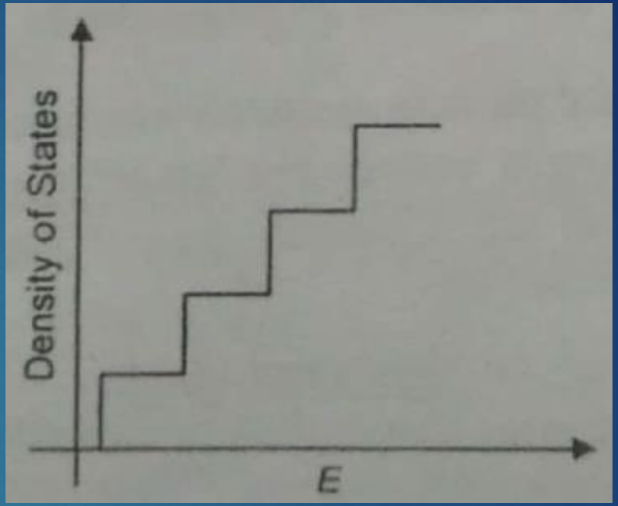
$$\frac{dn}{dE} = \frac{L}{h}\sqrt{\frac{2m}{E}}$$

as $\frac{\sqrt{8m}\,L}{nh} = \frac{1}{\sqrt{E}}$. Hence, $\frac{dn}{dE} \propto E^{-\frac{1}{2}}$.

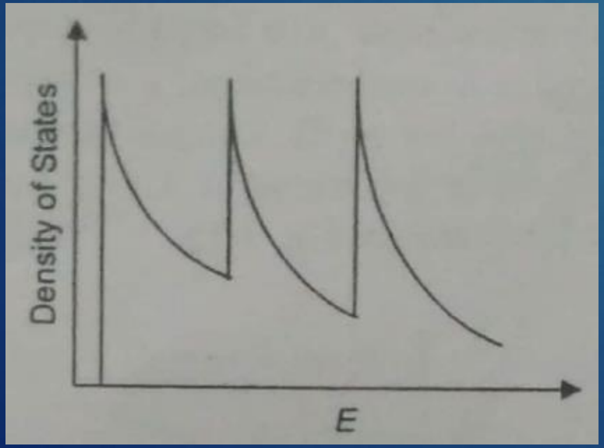
3-D $D(E) \propto E^{\frac{1}{2}}$



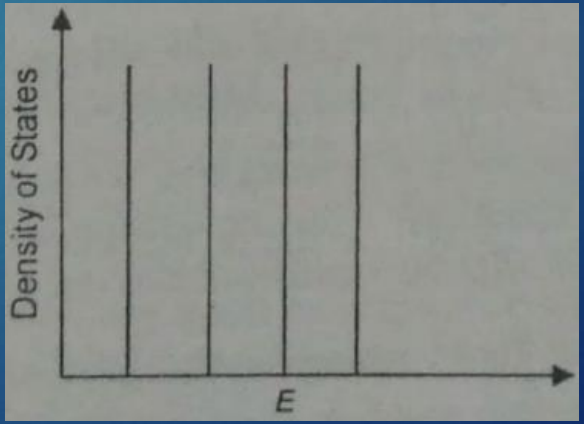
2-D $D(E) = \sum_{\varepsilon_i < E} 1$



1-D $D(E) \propto \sum_{\varepsilon_i < E} \delta(E - \epsilon_i)^{-\frac{1}{2}}$



0-D $D(E) \propto \sum_{\varepsilon_i} \delta(E - \epsilon_i)$



For bulk material, i.e., 3-D structure, density of states varies as $D(E) \propto E^{\frac{1}{2}}$ which indicates continuous distribution of energy levels in the material.

For 2-D structure density of state varies as $\sum_{\varepsilon_i < E} 1$, which shows that over a range of energies, the density of state is constant and thus it has a staircase structure.

For a 1-D structure, density of state varies as $\sum_{\varepsilon_i < E} \delta(E - \epsilon_i)^{-\frac{1}{2}}$

For 0-D structure, the energy levels are discreet and hence the density of state varies as $D(E) \propto \sum_{\varepsilon_i} \delta(E - \epsilon_i)$.

Two main techniques to produce nano-structures are

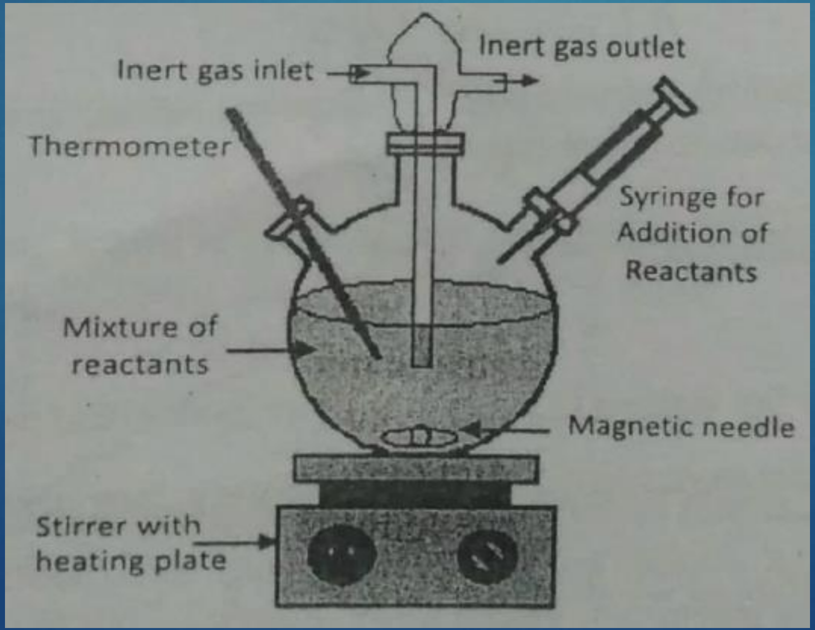
(1) Bottom up approach- In this approach, individual atoms or molecules are arranged together to form desired nano-structure. Usually it involves chemical reactions that are controlled by catalysts.

(2) Top down approach – In this approach, bulk structure is reduced to nano-structure, i.e., dimensions of the object are reduced to nanoscale gradually.

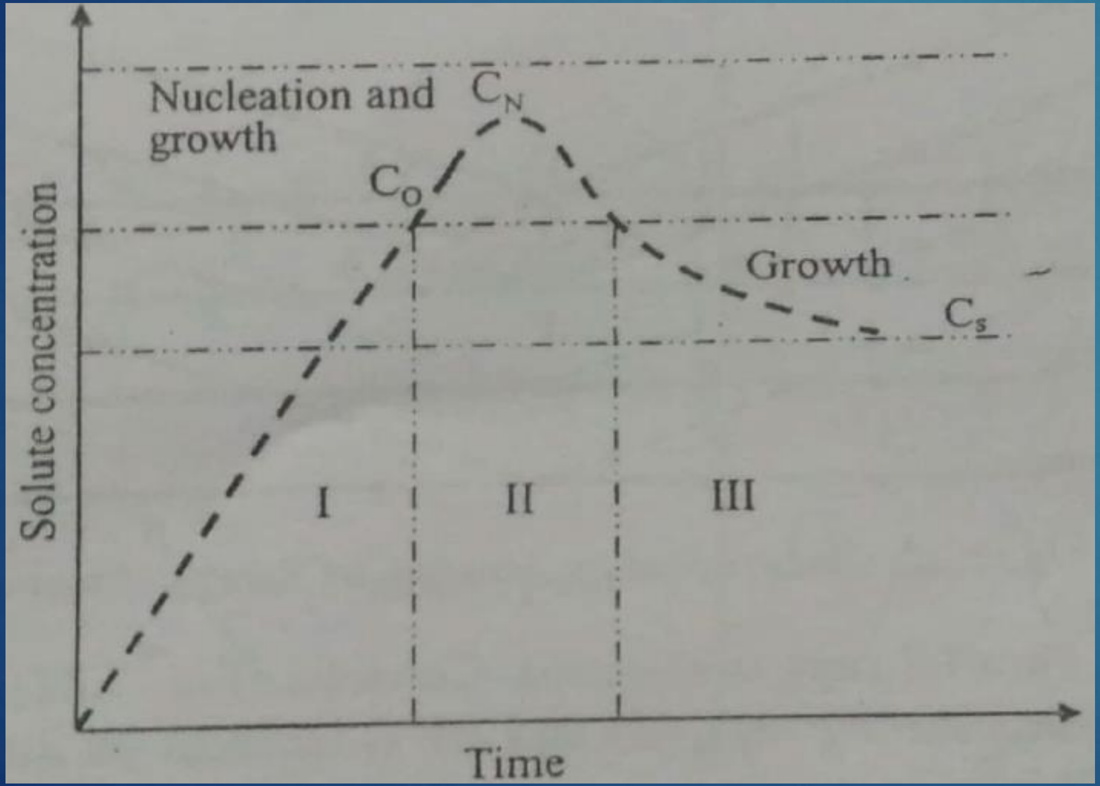
Colloidal technique

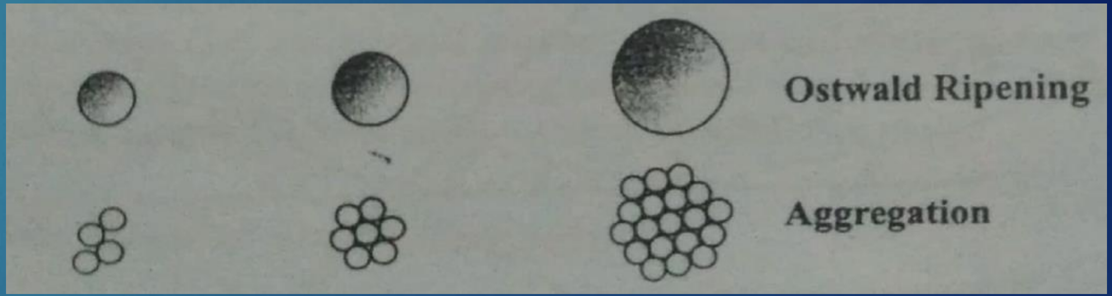
Colloidal is a class of materials in which 2 or more phases of same or different materials co-exists with one phase of dimension less that a 10^{-6}m.

Colloids are particles with large surface to volume ratio. Chemical reactions for colloidal particles are carried out in glass reactor of suitable size. The reactor has provision to introduce pre-cursor, gases, and to measure temperature. The reactions are carried out under inert atmosphere like argon or nitrogen. The reactants can be stirred during reaction using a magnetic needle. In this method, it is possible to control different steps in the reaction to achieve nano-particles of the same size.



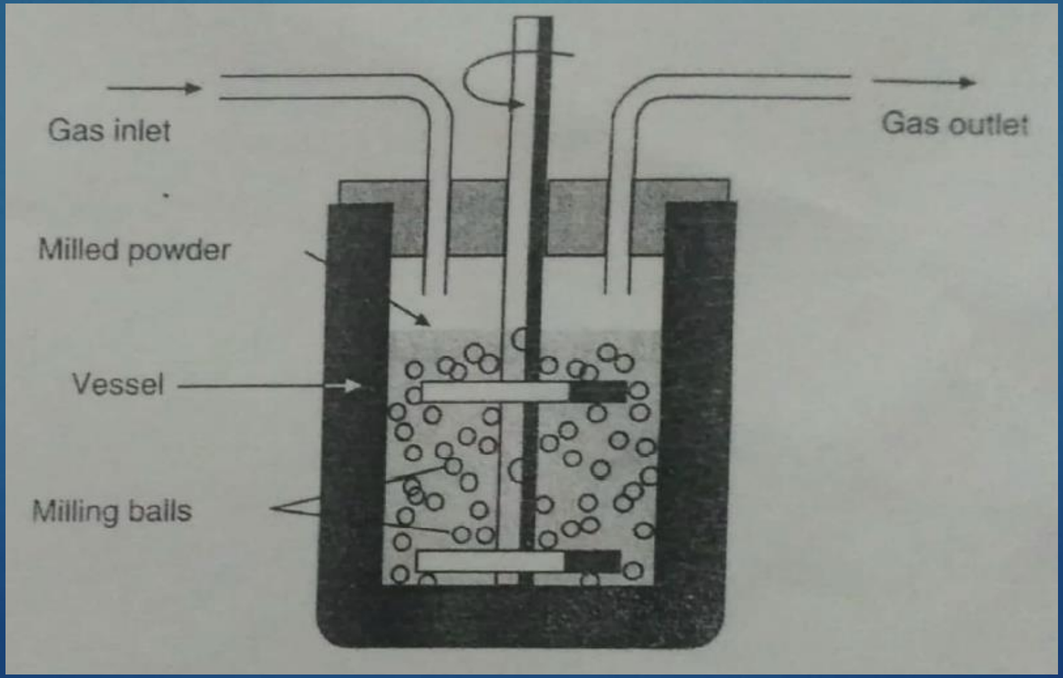
The concentration of reactants increases up to C_0 where formation of nuclei begins. Further increase in concentration leads to growth of nano-particles. The maximum rate of nucleation is observed at concentration C_N. As the nuclei formation reduces, the concentration reaches C_0. Once the concentration reaches C_N, the concentration of solute and diffusion is adjusted so that no new nuclei are formed. When the concentration reaches saturation, the growth can be due to either increase in size of nano-particles or by aggregation.



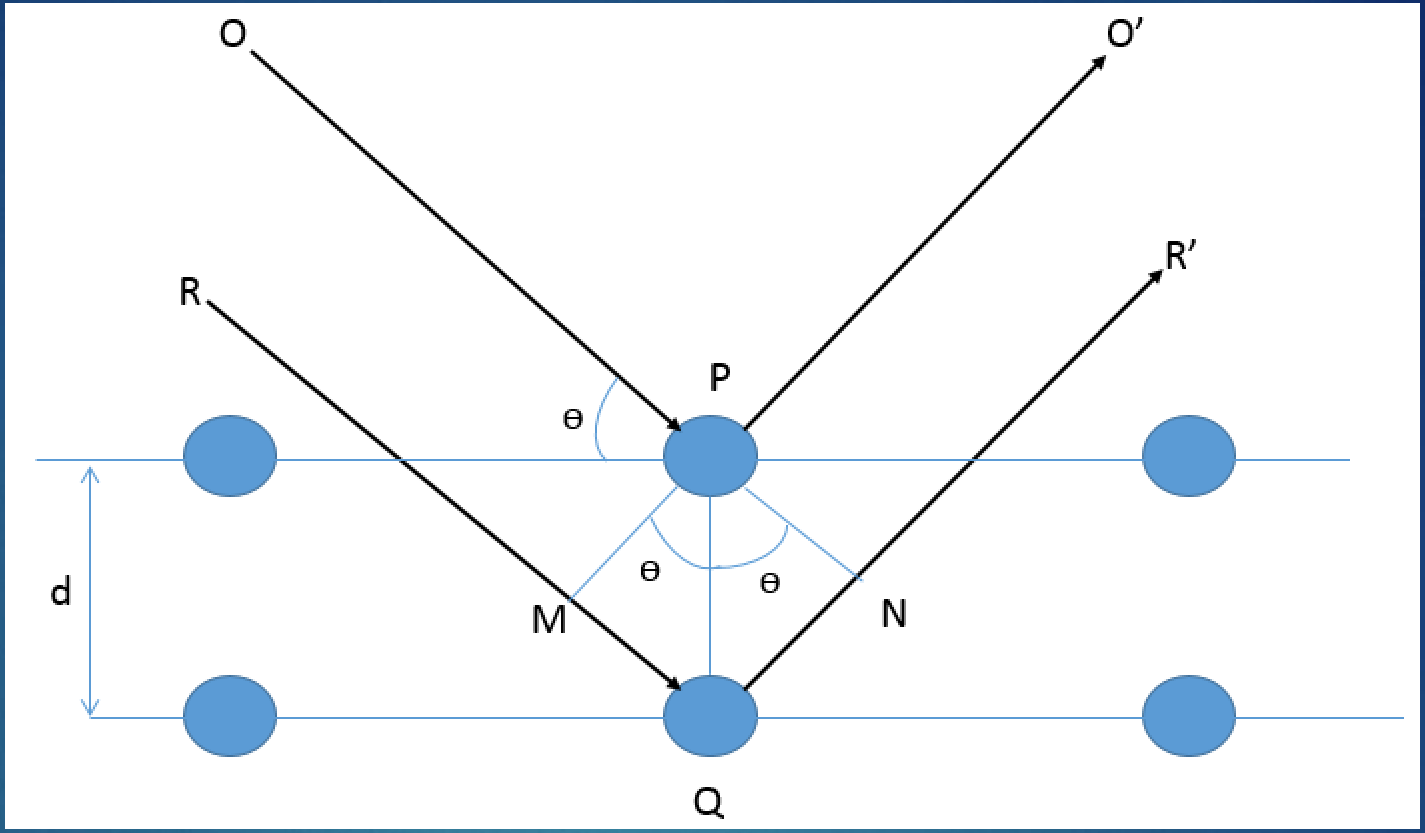


High energy ball milling – This technique is used to make nano-particles of some metals or alloys in the form of a powder. Hard steel or tungsten carbide balls are put in a container with powder of material. The grains are of a size of 50 microns in the powder. 2:1 ratio of balls to material is usually used.

The efficiency reduces if the container is more than half filled. Larger balls produce smaller grain size in milling but have larger defects. The container is rotated at about few hundred rpm. The container may also rotate around some central axis. The speed of rotation around this axis and the speed of rotation of container are controlled to obtain nano-particles of uniform size. Inert atmosphere or high vacuum is used to reduce impurity due to atmosphere.



X ray diffraction-



Consider two atomic planes that are separated by distance 'd' in a crystal. The X ray OP and RQ get scattered by atoms at P and Q. The path difference between ray OO' and RR' is Δ= $MQ + QN$

In ΔPNQ, $\sin\theta = \frac{NQ}{d} \Rightarrow NQ = d\sin\theta$.

In ΔPMQ, $\sin\theta = \frac{MQ}{d} \Rightarrow MQ = d\sin\theta$

Thus, $\Delta = MQ + QN = 2d\sin\theta$

For constructive interference, $\delta = 2n\pi --- (1)$

But $\delta = \frac{2\pi}{\lambda}\Delta = \frac{2\pi}{\lambda}(2d\sin\theta) --- (2)$

Thus, from equation (1) and (2), for constructive interference of X rays,

$$2d\sin\theta = n\lambda$$

which is also known as Bragg's diffraction condition.

Problem- The first order X ray diffraction at 1.5 A^0, is observed at glancing angle of 14.5^0, What is the spacing between neighbouring planes?

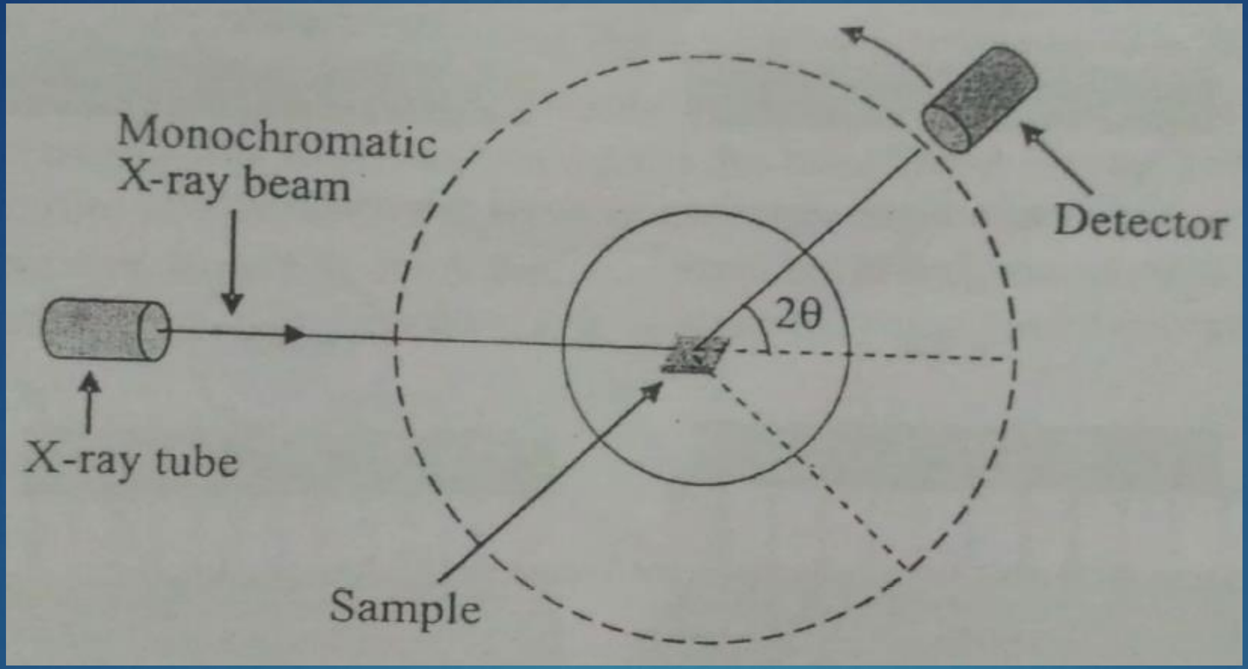
As

$$2d\sin\theta = n\lambda\ ,$$

$$d = \frac{n\lambda}{2\sin\theta} = 1 \times 1.5 \times 10^{-10}/(2 \times \sin 14.5)$$

$$d = 2.9A^0$$

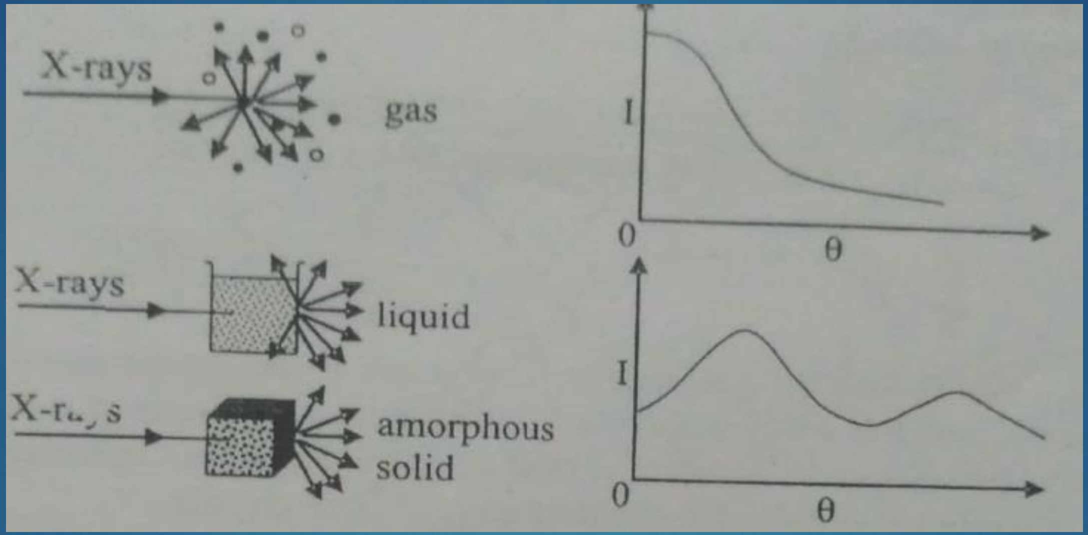
X ray diffractometer (Powder /Debye Scherrer diffractometer)



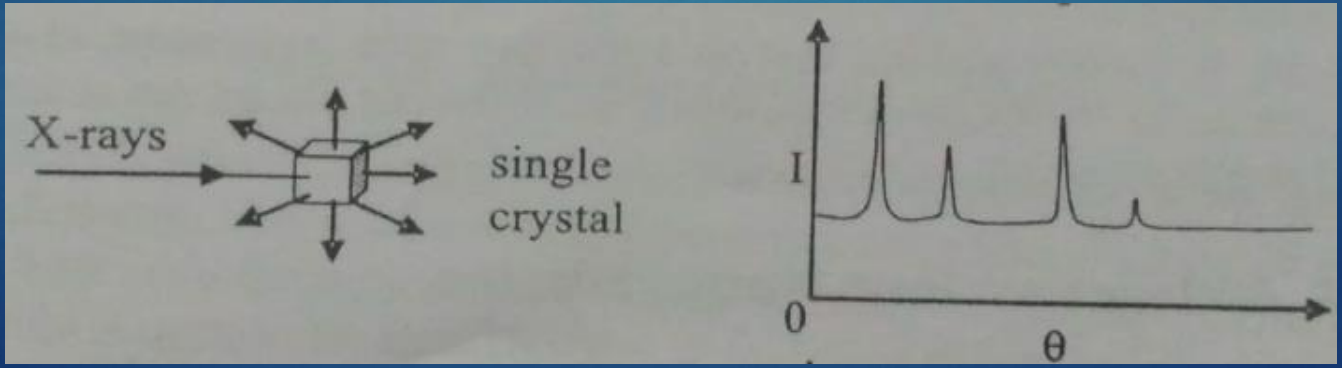
X-ray tube/source produces monochromatic X-rays usually of wavelength 1.54 A0. The sample and the detector can move around an axis passing through the centre of the sample. The diffracted ray makes and angle of 2ɵ at the detector with respect to incident beam and the plot of intensity vs. 2ɵ angle is used for further analysis. To record intensity, suitable photon counting detector is used.

Diffraction from different types of samples-

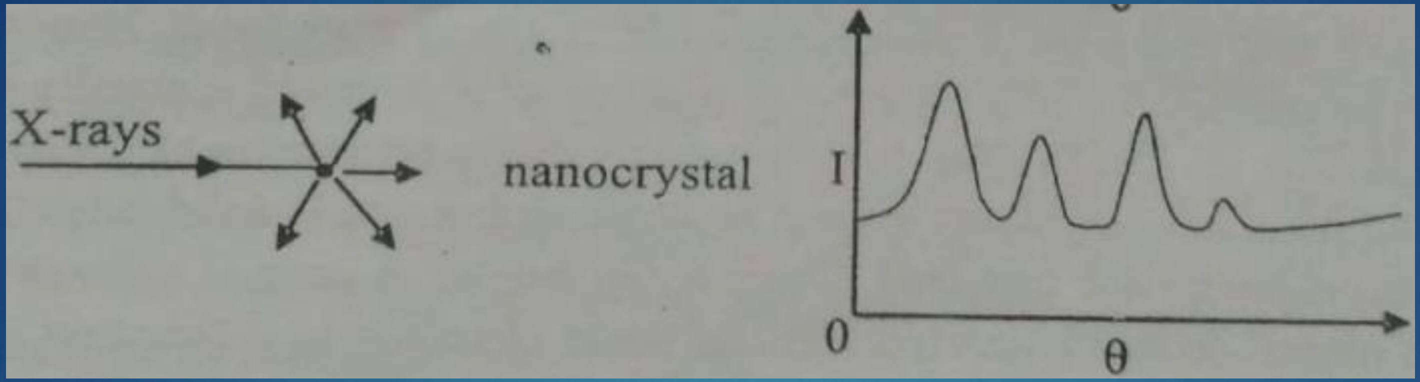
For gases, no diffraction peaks are observed. For liquids or amorphous solids, one or two peaks are observed due to short range order.



For a single crystal, sharp diffraction peaks are observed at various angles. The intensity of peak depends on crystal structure and atomic scattering factor.



For nanocrystal, diffraction peaks are broadened due to small number of atoms and planes in the crystal.



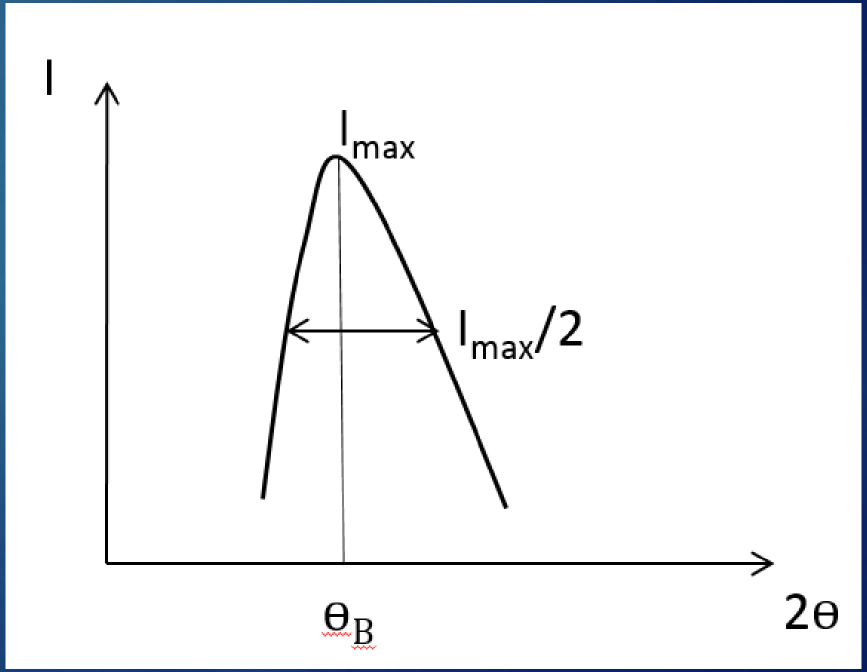
The size of nano-particles can be estimated by

Scherrer equation $T = \frac{0.9\lambda}{\beta \cos \theta_B}$, where

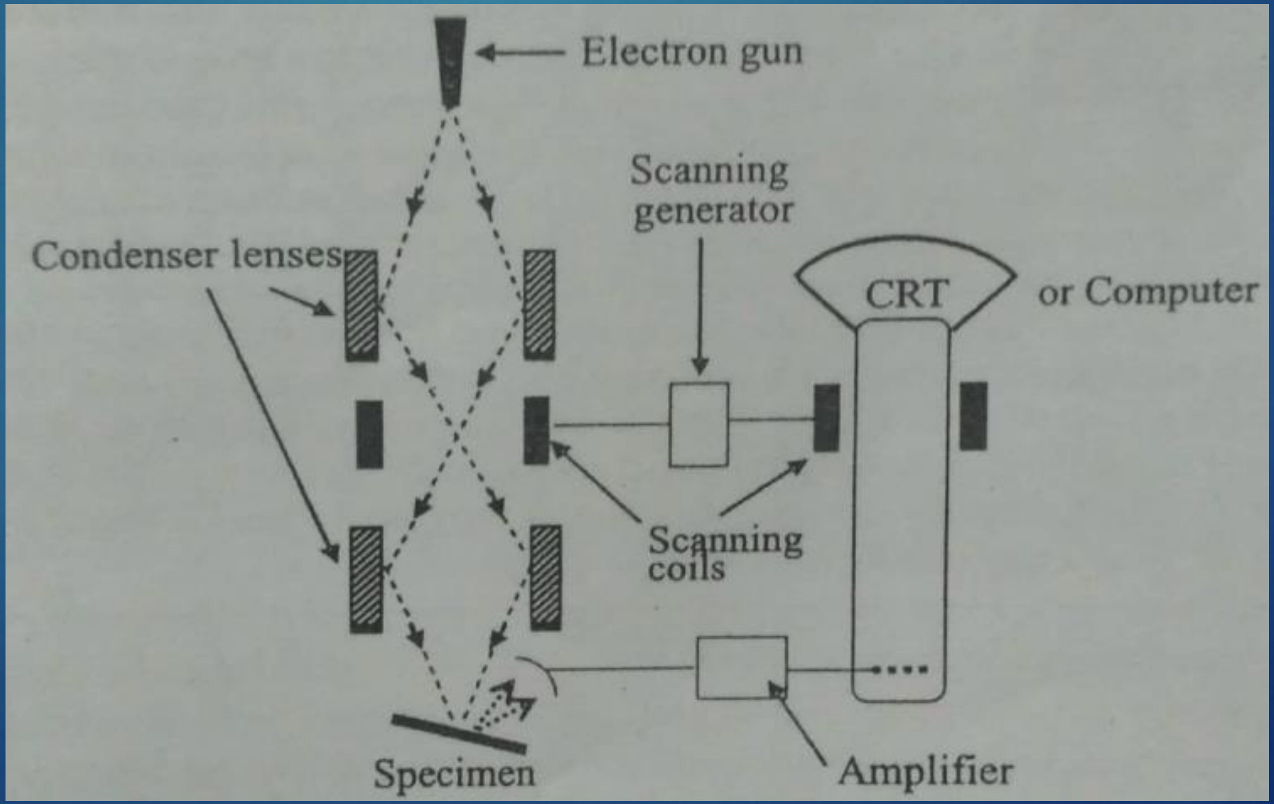
λ is the wavelength of X rays,

β is full width at half maxima

θ_B is the angle at which the peak is observed.



Scanning electron microscope (SEM)-The electron gun emits electrons either by heated filament (as in SEM) or by cold cathode under very high electric field (as in FE-SEM). In SEM, electron beam can be focused to a very small sized spot using electrostatic or magnetic lenses. The scanning generator scans the electron beam that is incident on the surface of the sample. The scattered electrons are collected by appropriate detector. The signal from scanning generator and amplified signal from detector are used to build the image of the sample surface. To avoid contamination and oxidation of filament, the sample and filament are housed in vacuum chamber.



Applications of nano-particles- In medicine, due to size, nanoparticles can be injected and moved to specific part of human body.

Early detection of cancer is currently based on nano-technology.

Nano-phosphorous can be used to image certain body parts

Drug delivery using encapsulated drugs in a nano-capsule can be done and it can be controlled to avoid damage of healthy cells.

For a quick, reliable and field detection of viruses or proteins or anti-bodies, nano-technology based techniques can be implemented.

Aerogels are low density nano-porous materials and have wide space and defence applications.

Nano-particle based solar cells can have higher efficiency.

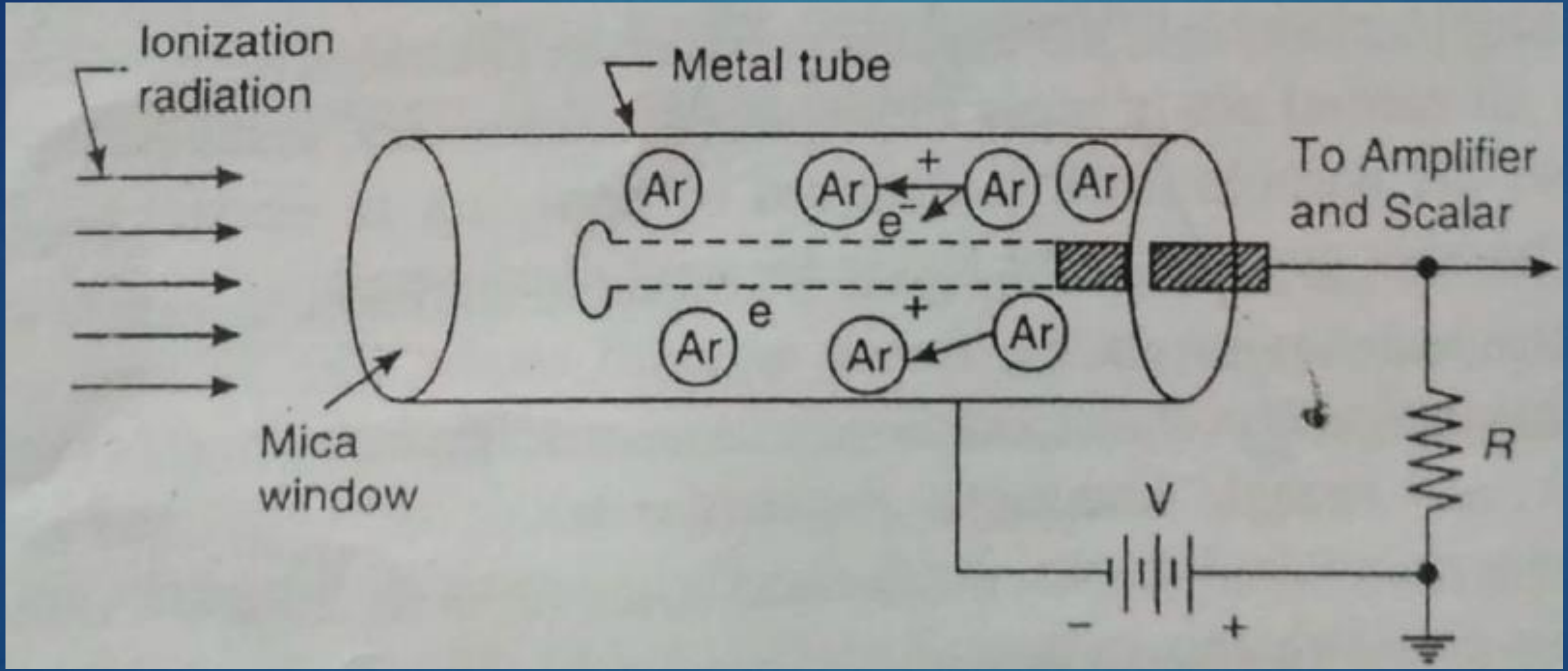
Nano-particle based composites perform better than micro-particle based composites when used in satellites for protection from radiation.

For aircrafts, fatigue resistant materials are required and nano-materials have promising longer life.

Nuclear physics

G. M. Counter (Geiger Muller counter)- G. M. counter consists of metal core enclosed in a glass tube. The metal case acts as cathode and tungsten wire is fixed at the centre of the metal case works as anode.

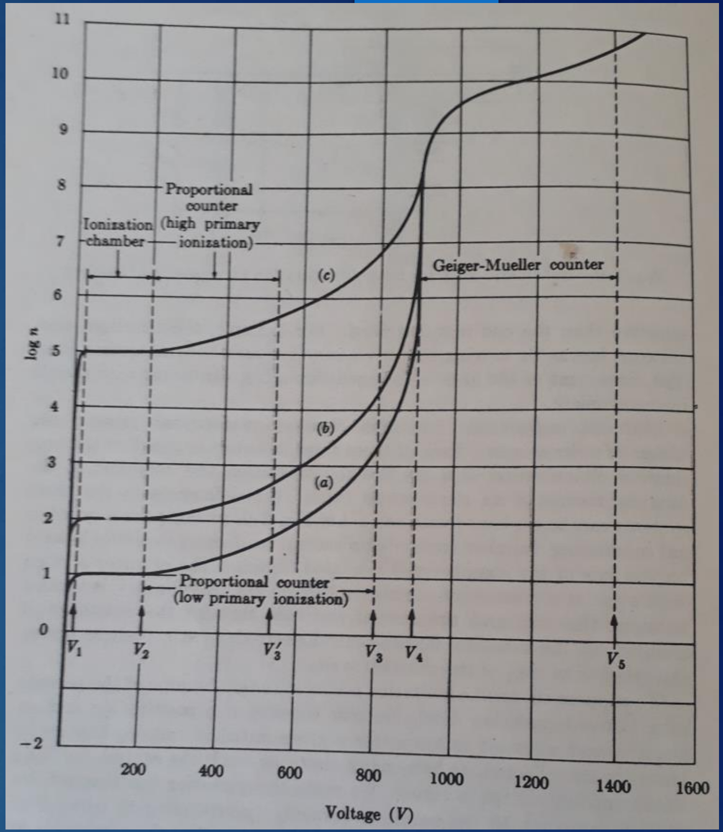
The tube is filled with 90% Argon or Helium gas and 10% ethyl alcohol. The ionisation radiation entering the metal case ionises the gas.



Free electrons and ions move to anode and cathode respectively because of high voltage applied (800 V to 2000 V) applied between them.

The electrons and the ions produce more electrons and ions as they move through the gas. This leads to multiplication of electrons and ions.

Between voltage V_1 and V_2, the number of ions and electrons collected is independent of voltage as the region is flat. In between V_2 and V_3, each electron contributes to multiplication effect individually. AboveV_3, multiplication effect is rapid. In the region between V_4 and V_5, the curve is independent of ionisation initiating it. This is region of operation of G.M. counter. The discharge through the tube generates a pulse which is independent of initial ionisation. The minimum voltage of such pulse is about 10 μV , which can be amplified up to 5-50 V. The measurement pulse is carried out to give a count. The count depends on



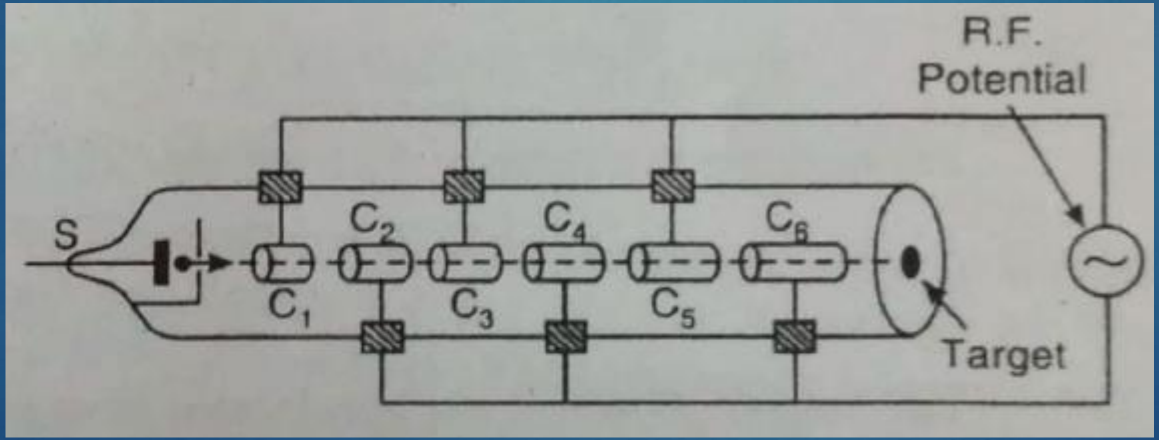
1. Dead time- Time taken by counter to recover between counts.
2. Recovery time- Time taken by counter to gain its original working condition.

Problem- A G. M. counter collects 10^8 electrons per discharge. What is average current if counting rate is 500 counts /min?

The current is $I = \frac{Q}{t} = \frac{10^8 \times 1.6 \times 10^{-19} \times 500}{60} = 0.133\ nA$

Particle accelerators- Electric and magnetic fields are used to accelerate particles to very high energy. Most of the particle accelerators work on the principle of increasing acceleration of particles in small steps.

1. Linear accelerators- In LINAC, charged particles are accelerated by an oscillating electric field applied to a series of electrodes with an applied frequency which is in resonance with the motion of particles.



Alternate cylinders enclosed in a glass vacuum are connected together. The odd number of cylinders are joined to one terminal of power supply and even number of cylinders are joined to other terminal of supply.

Charged particles from a discharge tube at one end move along axis of the tubes. The particles are accelerated on crossing the gaps between the tubes but move with constant speed inside the tube.

Let positively charged particle be accelerated and passed through tube 1. At that instant, tube 1 is negative and tube 2 is positive.

As the particles arrive at the right end of tube 1, the voltage is reversed and tube 1 is positive and tube 2 is negative. Thus, positive charged particles gets accelerated within the gap.

The particles are kept in phase with reversal of potential by making successive tubes longer for increased speed of particles. If N is the no. of tubes and V is the maximum voltage, then for particle of charge q,

$$\frac{1}{2}m\mathrm{v}_N^2 = NqV \Longrightarrow \mathrm{v}_N = \sqrt{\frac{2NqV}{m}}$$

If ν is the frequency of (r.f.) voltage, then time required to travel through tube is $t = \frac{1}{2\nu}$. If l_N is the length of N^{th} tube, then $t_N = l_N/\mathrm{v_N}$

$$l_N = \frac{\mathrm{v}_N}{2\nu}$$

$$l_N = \frac{1}{2\nu}\sqrt{\frac{2NqV}{m}}$$

$$l_N = \sqrt{\frac{NqV}{2m\nu^2}}$$

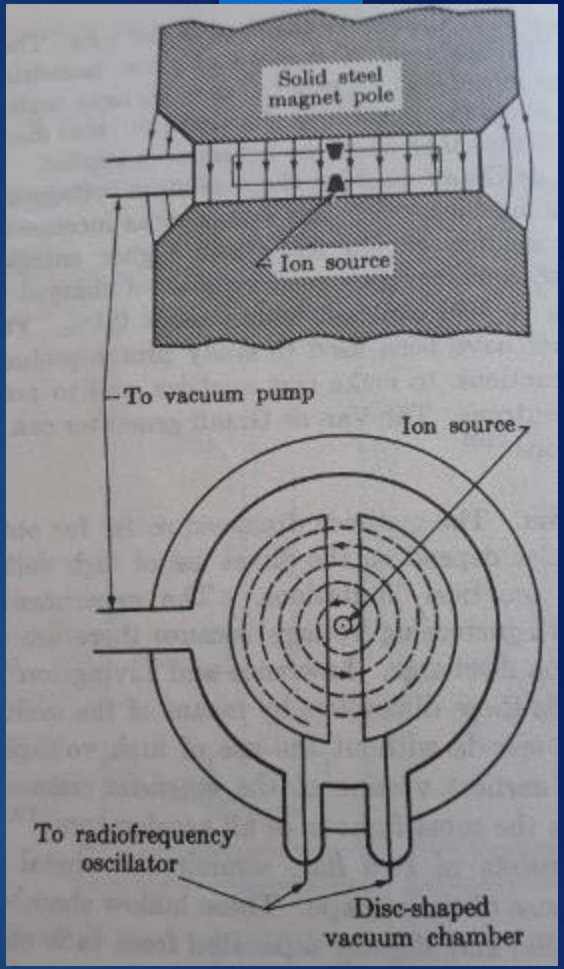
Problem – In LINAC, potential of 40 kV accelerates protons through 3rd tube. Calculate speed of protons if the length of 3rd tube is 28 cm. Calculate frequency of r.f. voltage.

The speed of protons, $\mathrm{v}_N = \sqrt{\frac{2NqV}{m}} = \sqrt{\frac{2\times3\times1.6\times10^{-19}\times40\times10^{3}}{1.67\times10^{-27}}} = 4.79\times10^{6}\ m/s$

The length of tube is $l_N = \frac{\mathrm{v}_N}{2\nu}$ gives

$$\nu = \frac{\mathrm{v_N}}{2l_N} = \frac{4.79\times10^{6}}{2\times0.28} = 8.5\ MHz$$

Cyclotron – In cyclotron, charged particles are accelerated using electric and magnetic field. The cyclotron consists of 2 semi-circular metal boxes called ‘D’s (or dees) that are slightly separated from each other. The source of ions is located at the mid point of the gap. D’s are connected to radio frequency oscillator to vary the potential between D’s rapidly. The region within D’s does not have electric field because of shielding effect. The D’s are placed between poles of electromagnet that provides magnetic field perpendicular to the plane of D’s. The charged particles or ions are injected by ion source. The electric field between the gap of D’s accelerate these particles. Due to magnetic field, particles move along circular path.



As centripetal force is equal to Lorentz force, $\frac{mv^2}{r} = evB$. Thus, $r = \frac{mv}{qB}$

Inside the D's the speed of the particles is constant. As the particles reach the gap between D's, direction of electric field is reversed. This results in acceleration of particles. Thus, the particles enter the second D with higher speed and move inside the second D with larger radius. When the particles complete a semi-circle, the direction of electric field is reversed and the particles are accelerated again.

The radio frequency of electric field is $\nu = \frac{1}{T}$, where T is period of revolution.

For particles moving with velocity 'v' in circle of radius R,

$$T = \frac{2\pi r}{\mathrm{v}} = \frac{2\pi}{\mathrm{v}}\left(\frac{m\mathrm{v}}{Bq}\right) = \frac{2\pi m}{Bq}$$

Thus, $\nu = Bq/2\pi m$ which is known as condition for resonance.

The particle is pulled out of circular path through a narrow aperture. The energy acquired by particles after N revolutions is $E = (2qV)N$ as each revolution contributes energy of $2qV$.

Why particle cannot be accelerated to high energies in cyclotron?

For the maximum radius of particles, the maximum velocity of particles is

$$\mathrm{v}_m = \frac{RBq}{m}$$

The maximum energy of the particle is $E_m = \frac{1}{2} m v_m^2 = \frac{1}{2} m \left(\frac{RBq}{m}\right)^2 = \frac{B^2 q^2 R^2}{2m}$

Thus, the maximum energy of the particle is independent of voltage.

As the speed of particles approaches 'c' , the relativistic mass of the particle is given as $m = \frac{m_0}{\sqrt{1-\frac{v^2}{c^2}}}$, where m_0 is the rest mass of the particle.

If the particle is moving at a non-relativistic speed,$v \ll c$, then time taken for one revolution is $T_0 = \frac{2\pi m_0}{Bq}$.

If the speed of the particle is relativistic, then time for revolution is

$$\mathrm{T} = \frac{2\pi m}{Bq} = \frac{2\pi m_0}{Bq\sqrt{1-v^2/c^2}} = \frac{T_0}{\sqrt{1-\frac{v^2}{c^2}}} = T_0\left(\frac{m}{m_0}\right) = T_0\left(\frac{mc^2}{m_0 c^2}\right) = T_0\left(\frac{E}{E_0}\right) = \frac{T_0(K+E_0)}{E_0}$$

Thus, $T > T_0$. It implies that the period of revolution is larger when the speed of particles approach the speed of light. So, the particles do not reach the gap when the voltage is reversed. Hence, the particles are de-accelerated instead of getting accelerated. Due to this, particles cannot be accelerated to high energies in cyclotron.

Problem – The radius of D's and magnetic field of a cyclotron is 2m and 0.75 Wb/m^2 respectively. What is the maximum energy of protons and deuterons that can be achieved in cyclotron?

For protons, $E_m = \frac{B^2q^2R^2}{2m} = \frac{0.75^2 \times (1.6\times10^{-19})^2 \times 2^2}{2\times1.67\times10^{-27}} = 1.72 \times 10^{-11} J$

For deuteron, $E_m = \frac{B^2q^2R^2}{2m} = \frac{0.75^2 \times (1.6\times10^{-19})^2 \times 2^2}{2\times3.34\times10^{-27}} = 8.62 \times 10^{-12} J$

Problem – In a cyclotron, magnetic field is 1.3 Wb/m^2 and D's of radius 0.5 m. (a) what is r.f. frequency? (b) What is the maximum energy of protons? (c)If total transit time is 3.3 μs, how much energy is imported to protons in each passage from one D to another D?

a) $\nu = \frac{Bq}{2\pi m} = \frac{1.3\times1.6\times10^{-19}}{2\pi\times1.67\times10^{-27}} = 19.8\ MHz$

b) $E_m = \frac{B^2q^2R^2}{2m} = \frac{1.3^2 \times (1.6\times10^{-19})^2 \times 0.5^2}{2\times1.67\times10^{-27}} = 3.23 \times 10^{-12} J = \frac{3.23\times10^{-12} J}{1.6\times10^{-19}\ \frac{J}{eV}} = 20.1\ MeV$

c) $N = 2\nu T = 2 \times 19.8 \times 10^6 \times 3.3 \times 10^{-6} = 131$

Thus, energy in each passage is

$$E = \frac{E_m}{N} = \frac{20.1\ MeV}{131} = 0.153\ MeV$$

Problem – If magnetic field strength in a cyclotron is 0.9Wb/m2 for Hydrogen ions, then a) what is r.f. frequency? b) If particles gain 60 keV for passing through a gap of D's and emerge with 6 MeV from cyclotron, what is transit time and radius of largest orbit?

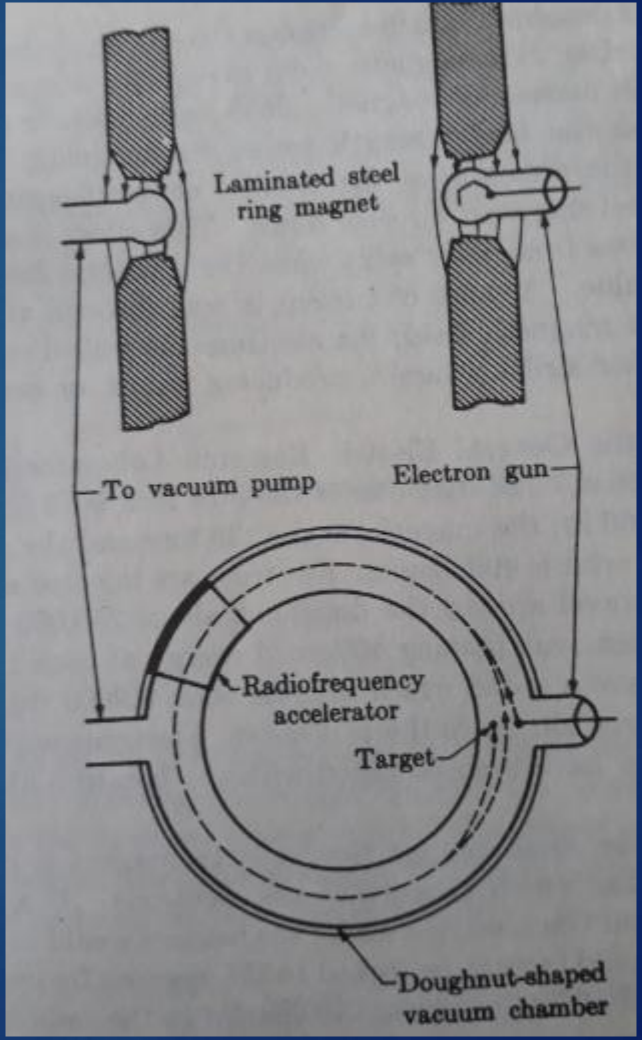
a) $\nu = \frac{Bq}{2\pi m} = \frac{0.9\times1.6\times10^{-19}}{2\pi\times1.67\times10^{-27}} = 13.72\ MHz$

b) $T = \frac{N}{2\nu} = \frac{E_m/E}{2\nu} = \frac{6MeV/0.06MeV}{2\times13.72\times10^6} = 3.64\mu s$

as $E_m = \frac{B^2q^2R^2}{2m}$, $R = \frac{\sqrt{2mE_m}}{Bq} = \frac{\sqrt{2\times1.67\times10^{-27}\times6\times10^6\times1.6\times10^{-19}}}{0.9\times1.6\times10^{-19}} = 0.39\ m$

Electron synchrotron –

The working principle of electron synchrotron is based on betatron and cyclotron. The working principle of betatron is same as that of the transformer in which AC current in primary coil induces a similar current in secondary coil. The current in primary coil induces an oscillating magnetic field which in turn induces oscillating potential in the secondary coil.

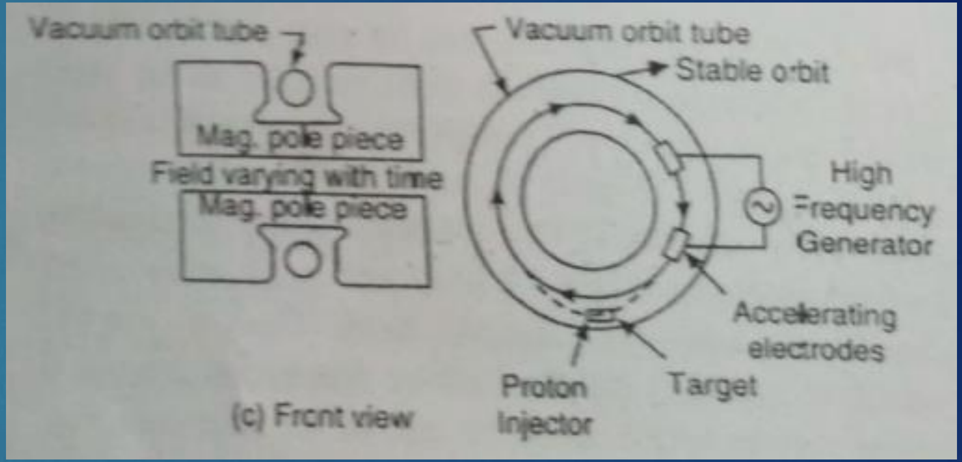


In betatron, secondary coil is replaced by electrons inside doughnut shaped chamber. In betatron, a large magnet is used to supply variable flux to accelerated electrons.

In electron synchrotron, these large magnets are replaced by R.F. accelerator and small magnets. The electrons are accelerated up to 2 MeV and a speed of 0.98 c. Beyond this speed, the speed of electrons doesn't change much.

As the angular velocity of electrons is $\omega = \frac{Be}{m}$, at relativistic velocity, magnetic field is increase such that it can balance relativistic mass to achieve constant angular velocity.

Proton synchrotron –



A proton synchrotron has same working principle as electron synchrotron. The proton are injected by injector and move in circular orbit in magnetic field. The R.F. accelerator accelerates protons. The The variation in magnetic field can also be used to accelerate protons. The variation in frequency in R.F. voltage and magnetic field is used to achieve circular orbits of protons. At the highest energy, the proton orbits are made unstable to strike the target.

Nuclear reactor- Nuclear reactors work on nuclear fission reactions. The energy released in these reaction is used to generate electricity. In nuclear reactor

self sustained, controlled nuclear fission reaction is executed.

The main components of reactor are

1. Nuclear fuel – Most of the reactors use uranium enrich in U-235 as fuel.

2. Moderators- Moderators are used to slow down neutrons. The high energy neutrons emitted in fission reaction cannot further cause fission reaction to initiate chain reaction. The slow neutrons have high probability of inducing chain reaction. Thus, light nuclei, known as moderators are used to for this purpose. Examples, heavy water, graphite.

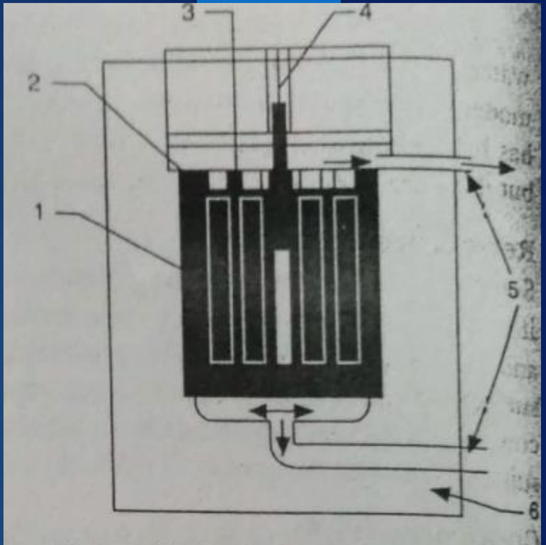


Fig. 21.16: Nuclear Reactor—1. Nuclear Fuel 2. Nuclear Reflector 3. Moderator 4. Control Rod 5. Coolant 6. Shield.

3. Reflectors- They are used to curb leaking of neutrons through reactor. They are made up of nickel, thorium

4. Coolant- It removes heat from the reactor and is further used for power generation.

5. Control rods- The number of neutrons in the core of reactor is maintained by rods of neutron absorbing materials such as cadmium. These rods are used to control the rate of nuclear fission reaction.

The reactor is said to be critical when number of neutrons is equal to the number required per reaction.

6. Shielding- The shielding minimizes the leaking of harmful radiation and neutrons to the surrounding.

The core, i.e., central part of the reactor has moderator block with fuel channels.

Types of reactors

1. Boiling water reactor- Water runs through the core of these reactors and tunes into steam. The steam is used to run the turbine. The disadvantage is that water can be radioactive and rupture of pipes can lead to spread of radioactive material.
2. Pressurized water reactor- Water under high pressure runs through the core of the reactor and does not turn into steam. This hot water is then used to heat secondary water system to turn water into steam. This steam is then used to run the turbines.
3. Research reactors- The neutrons emitted from these reactors are used for research purpose.

Medical application-

Radioactive isotope that can have affinity for certain organ can be introduced in human body. A sensitive detector can observe radiation from isotope and describe its activity. The image built on the activity can indicate any abnormality in the organ.

Positron emission can be used to build image. The positron emitted in decay combine with two electrons to produce two gamma photons that move in opposite direction. Using a detector, the location of decay can be identified. Large number of such events are used to produce an image that shows distribution of isotope in human body.

Radiation therapy uses radiation to destroy unwanted tissue in the body such as cancer cells. The radiation ionizes atoms in the tissue. The ionization leads to change in biological function and possibly destruction of cell.

Radiation in environment and its effects- The radioisotopes can disperse through environment and the study of movement of isotope is called as radio ecology. Some of the isotopes can move through food chain. The radiation from isotopes can produce genetic and psychological damage and even death.