### Chapter 5

### **Atomic Structure**



### **Discovery of Electron (Cathode Rays)**

Cathode rays are produced in a gas discharge tube.

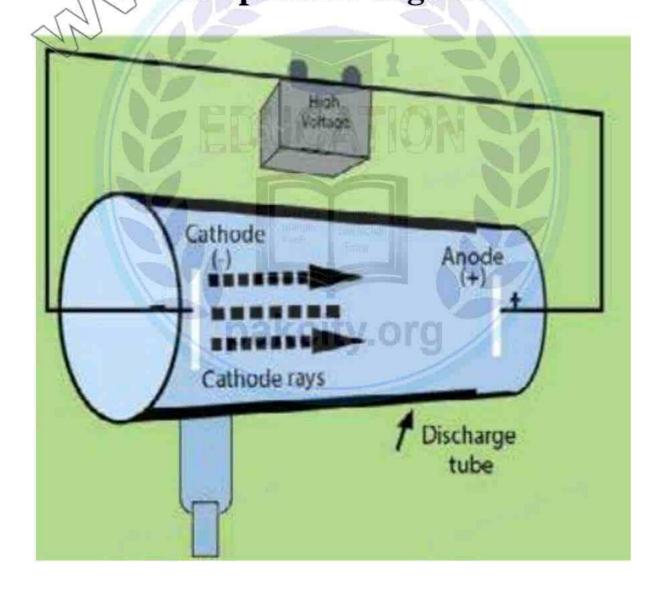
#### **Assembly**

- 1. A gas discharge tube fitted with two metallic electrodes acting as cathode and anode.
- 2. The tube is filled with a gas, air or vapours of a substance at any desired pressure.
- 3. The electrodes are connected to a source of high voltage.
- 4. The exact voltage required depends upon the length of the tube and the pressure inside the tube.
- 5. The tube is attached to a vacuum pump by means of a small side tube so that the conduction of electricity may be studied at any value of low pressure.

### Value of voltage for production of cathode rays

- 1. Current does not flow through the gas at ordinary pressure even at high voltage of 5000 volts.
- 2. When the pressure inside the tube is reduced and a high voltage of 5000-10000 volts is applied, then an electric discharge takes place through the gas producing a uniform glow inside the tube.
- 3. When the pressure is reduced further to about 0.01 torr, the original glow disappears.
- 4. Some rays are produced which create fluorescence on the glass wall opposite to the cathode. These rays are called cathode rays.

The colour of the glow or the fluorescence produced on the walls of the glass tube depends upon the composition of glass.



### **Properties of Cathode Rays**

Following are the properties of cathode rays:

1. Cathode rays are negatively charged

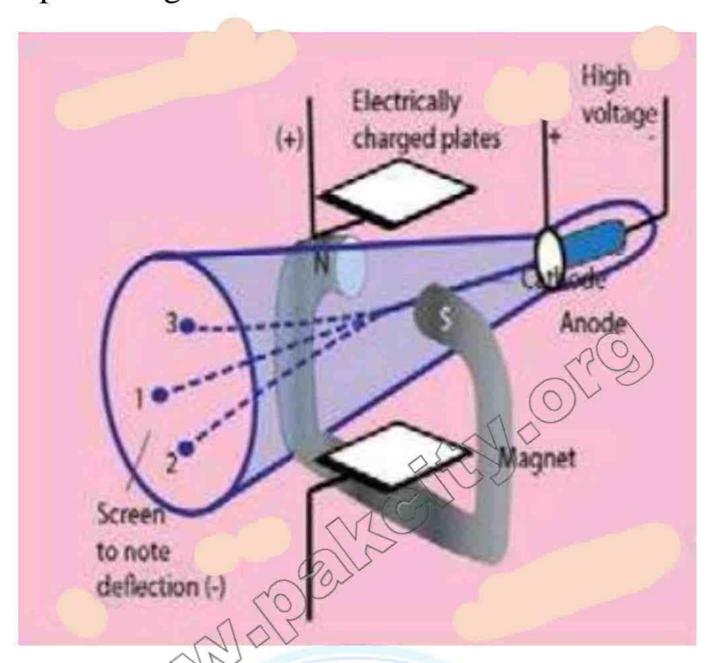
Cathode rays are negatively charged.

#### Work of J.Perrin

In 1895, J Perrin showed that when the cathode rays passed between the poles of the magnet, the path of the negatively charged particles was curved downward to point 2 by the magnetic field.

#### Work of J. Thomson

In 1897, J. Thomson established their electric charge by the application of electric field, the cathode ray particles were deflected upwards (towards the positive plate) to point 3. Thomson found that by carefully controlling the charge on the plates when the plates and the magnet were both around the tube, he could make the cathode rays strike the tube at point 1 again.

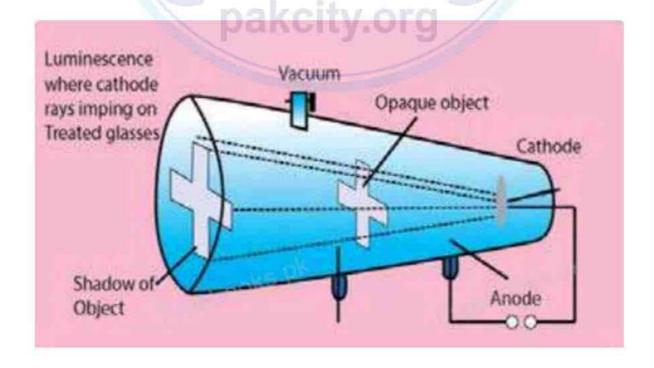


#### 2. Production of fluorescence

They produce a greenish fluorescence on striking the walls of the glass tube. These rays also produce fluorescence in rare earths and minerals. When placed in the path of these rays, alumina glows red and tin stone yellow.

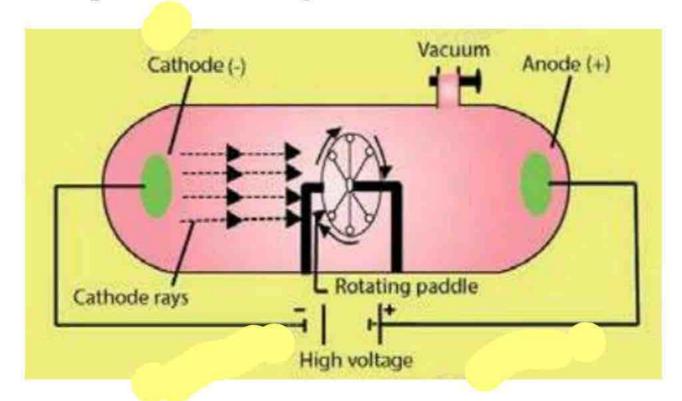
### 3. Shadow casting

Cathode rays cast a shadow when an opaque object is placed in their path. This proves that they travel in straight line perpendicular to the surface of cathode.



#### 4. Cathode rays possess momentum

These rays can drive a small paddle wheel placed in their path. This shows that these rays possess momentum. Cathode rays are not rays but material particles having a definite mass and velocity.



### 5. X-ray production

Cathode rays can produce X-rays when they strike an anode particularly with large atomic mass.

#### 6. Heat production

Cathode rays can produce heat when they fall on matter e.g. when cathode rays from a concave cathode are focussed on a platinum foil, it begins to glow.

### 7. Ionization of gases

Cathode rays can ionize gases.

### 8. Reducing effect

They can cause a chemical change, because they have a reducing effect.

### 9. Passage through metal foil

Cathode rays can pass through a thin metal foil like aluminum or gold foil.

# 10. e/m ratio equal to electrons

The e/m value of cathode rays shows that they are simply electrons.

#### Work of J.J. Thomson

He concluded from his experiments that cathode rays consist of streams of negatively charged particles. Thomson also determined the charge to mass ratio (e/m) of electrons. He found that the e/m value remained the same no matter which gas was used in the discharge tube. He concluded that all atoms contained electrons.

### Work of Stoney

He named these particles as electrons.

#### **Discovery of Proton (Positive Rays)**

#### **Historical Background**

In 1886, German physicist, E. Goldstein carried out the experiment for the discovery of proton.

#### **Experimental Work**

1. A discharge tube with a cathode having extremely fine holes in it was used.

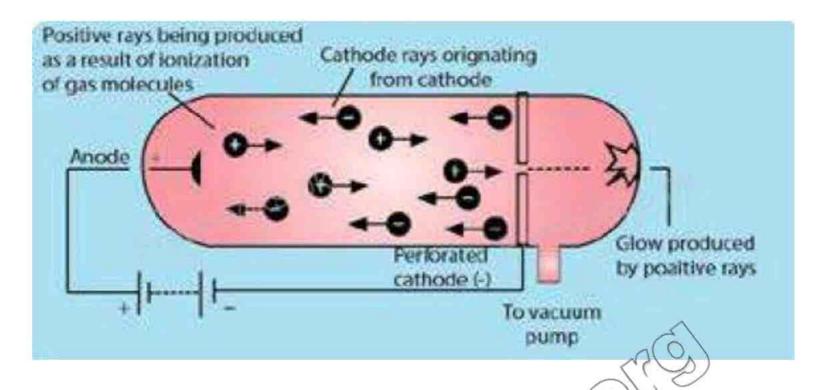
2. A large potential difference is applied between electrodes

#### **Observation**

- 1. There are rays, other than cathode rays, produced in opposite direction.
- 2. These rays after passing through the perforated cathode produce a glow on the wall opposite to the anode.
- 3. These rays pass through the canals or the holes of cathode, they are called canal rays.

### Origin of name

These rays are named as positive rays owing to the fact that they carry positive charge.



### **Reason for the Production of Positive Rays**

The high speed cathode rays (electrons) strike the molecules of a gas enclosed in the discharge tube. They knock out electrons from the gas molecules and positive ions are produced.

$$M + e^{-}$$
  $M^+ + 2e^{-}$ 

# **Properties of Positive Rays**

# 1. Effect of Electric and Magnetic Field

They are deflected by an electric as well as a magnetic field showing that these are positively charged.

# 2. Travel in straight lines

These rays travel in a straight line in a direction opposite to the cathode rays.

#### 3. Produce Flashes

They produce flashes on ZnS plate.

# 4. The charge/mass ratio

The e/m value for the positive rays is always smaller than that of electrons and depends upon the nature of the gas used in the discharge tube. Heavier the gas, smaller is the e/m value.

# Highest e/m ratio

The e/m value is found to be the maximum for hydrogen because the value of 'm' is the lowest for the hydrogen gas. The positive particle obtained from hydrogen gas is the lightest.

#### 5. Name of the Positive Particle

This particle is called proton, a name suggested by Rutherford.

#### 6. Mass of Proton

The mass of a proton is 1836 times more than that of an electron.

### **Discovery of Neutron**

# **Historical Background**

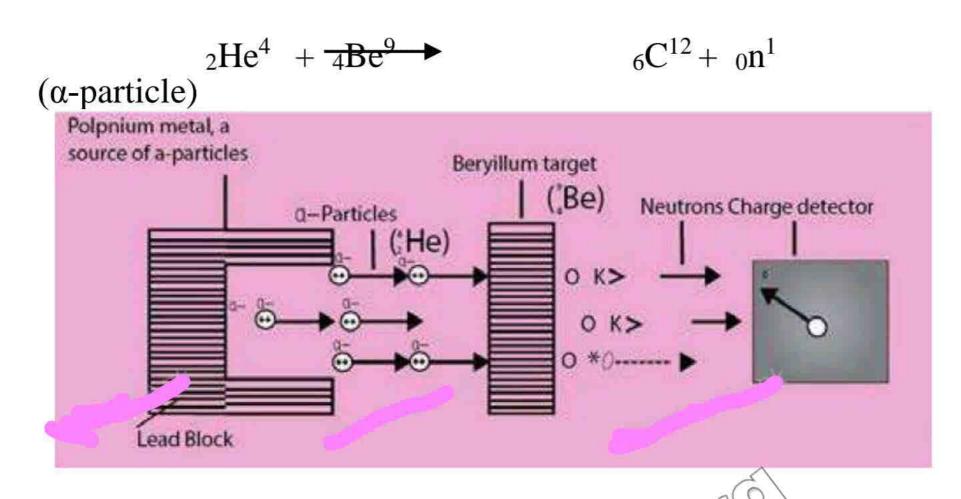
Proton and electron were discovered in 1886 and their properties were completely determined till 1895. Up to 1932 it was thought that an atom was composed of only electrons and protons. Rutherford predicted in 1920

that some kind of neutral particle having mass equal to that of proton must be present in an atom as atomic masses of atoms could not be explained otherwise.

### **Experimental Work**

Chadwick discovered neutron in 1932 and was awarded Nobel Prize in Physics in 1935. A stream of  $\alpha$ -particles produced from a polonium source was directed at beryllium ( $_4Be^9$ ) target. It was noticed that some penetrating radiations were produced. These radiations were called neutrons because the charge detector showed them to be neutral.

#### **Reaction involved**



# **Properties of Neutron**

### 1. Decay of a Neutron

Free neutron decays into a proton with the emission of an electron and a neutrino.

$${}_{0}^{1}n \rightarrow {}_{+1}^{1}P + {}_{-1}^{0}e + {}_{0}^{0}n$$

#### 2. Gas ionization

Neutrons cannot ionize gases.

### 3. Penetrating Particles

Neutrons are highly penetrating particles.

### 4. Expelling Protons

They can expel high speed protons from paraffin, water, paper and cellulose.

#### 5. Fast and Slow Neutrons

When neutrons travel with energy of 1.2 Mev they are called fast neutrons but with energy below 1ev are called slow neutrons. Slow neutrons are usually more effective than fast ones for the fission purposes.

#### 6. Neutrons as Projectiles

When neutrons are used as projectiles they can carry out the nuclear reactions. A fast neutron ejects an  $\alpha$ -particle from the nucleus of nitrogen atom and boron is produced along with  $\alpha$ -particles.

$${}_{7}^{14}N + {}_{0}^{1}n \rightarrow {}_{5}^{11}B + {}_{2}^{4}He$$

#### 7. Radioactivity

When slow moving neutrons hit the Cu metal then  $\gamma$  gamma radiations are emitted. The radioactive  $_{29}\text{Cu}^{66}$  is converted into  $_{30}\text{Zn}^{66}$ .

$$^{65}_{29}Cu + ^{1}_{0}n \rightarrow ^{66}_{29}Cu + hv(\gamma - raditions)$$

$$_{29}^{66}Cu \rightarrow _{30}^{66}Zn + _{-1}^{0}e$$
 (electron)

The radioactive copper emits an electron ( $\beta$ -particle) and its atomic number increases by one unit.

### **Application**

Because of their intense biological effects they are being used in the treatment of cancer.

### **Rutherford's Model of Atom**

In 1911, Lord Rutherford performed a classic experiment.

### **Experiment**

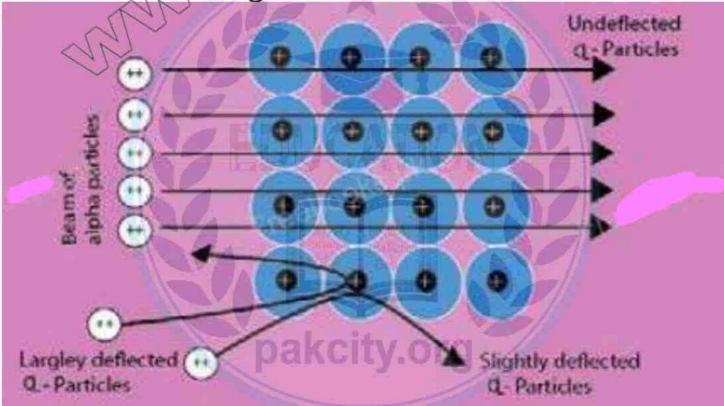
He studied the scattering of high speed  $\alpha$ -particles which were emitted from a radioactive metal (radium or polonium).

### **Setting**

- A beam of α-particles was directed onto a gold foil of 0.00004 cm thickness as target through a pin-hole in lead plate.
- A photographic plate or a screen coated with zinc sulphide was used as a detector.
- Whenever, an α-particle struck the screen, flash of light was produced at that point. It was observed that most of the particles went through the foil undeflected. Some were deflected at fairly large angles and a few were deflected backward.

### **Proposals**

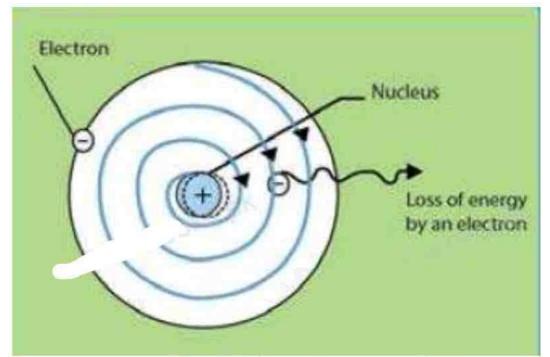
- Rutherford proposed that the rebounding particles must have collided with the central heavy portion of the atom which he called as nucleus.
- On the basis of these experimental observations, Rutherford proposed the planetary model (similar to the solar system) for an atom in which a tiny nucleus is surrounded by an appropriate number of electrons.
- Atom as a whole being neutral, therefore, the nucleus must be having the same number of protons as there are number of electrons surrounding it.



In Rutherford's model for the structure of an atom, the outer electrons could not be stationary as they could be attracted by the nucleus and ultimately fall into it. To have a stable atomic structure the electrons were supposed to be moving around the nucleus in closed orbits.

#### **Defects**

- Rutherford's planet-like picture was Electron defective and unsatisfactory because the moving electron must be accelerated towards the nucleus.
- The radius of the orbiting electron should become smaller and smaller and the electron should fall into the nucleus. An atomic structure proposed by Rutherford would collapse.



Measurement of e/m Value of Electron

In 1897, J.J Thomson devised an instrument to measure the e/m value of electron.

### **Apparatus**

The apparatus consists of a discharge tube.

### Working

### Passage of cathode rays through electric and magnetic fields

1. The cathode rays are allowed to pass through electric and magnetic fields.

#### When both fields are off

- 2. When both the fields are off then a beam of cathode rays consisting of electrons, produces bright luminous spot at **P1** on the fluorescent screen.
- 3. The north and south poles of magnetic field are perpendicular to the plane of paper in the diagram.

4. The electrical field is in the plane of paper.

### When only magnetic field is applied

5. When only magnetic field is applied, the cathode rays are deflected in a circular path and fall at the point **P3**.

### When only electric field is applied

6. When only electric field is applied, the cathode rays produce a spot at **P2**.

### When both fields are applied simultaneously

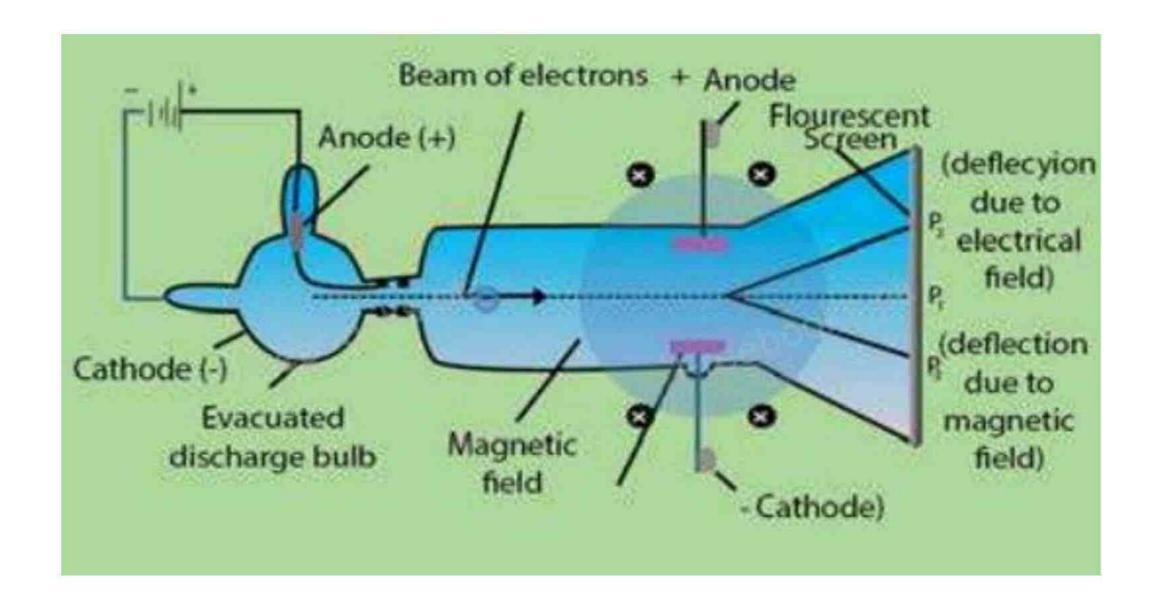
7. Both electric and magnetic fields are then applied simultaneously and their strengths adjusted in such a way that cathode rays again hit the point **P1**.

#### Determination of e/m value of electrons

8. In this way by comparing the strengths of the two fields one can determine the e/m value of electrons. It comes out to be  $1.7588 \times 10^{11}$  coulombs kg<sup>-1</sup>.

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This means that 1 kg of electrons have  $1.7588 \times 10^{11}$  coulombs of charge.



### Measurement of Charge on Electron-Millikan's Oil Drop Method

In 1909, Millikan determined the charge on electron by a simple arrangement.

### **Apparatus**

#### **Metallic Chamber**

1. The apparatus consists of a metallic chamber.

2. It has two parts.

3. The chamber is filled with air, the pressure of which can be adjusted by a vacuum pump.

#### **Electrodes**

1. There are two electrodes A and A

2. These electrodes are used to generate an electrical field in the space between the electrodes.

3. The upper electrode has a hole in it.

### Working

#### 1. Atomizer

A fine spray of oil droplets is created by an atomizer.

#### 2. Microscope

A few droplets pass through the hole in the top plate and into the region between the charged plates, where one of them is observed though a microscope.

### 3. Illumination

This droplet, when illuminated perpendicularly to the direction of view, appears in the microscope as bright speck against a dark background.

### 4. Force of gravity

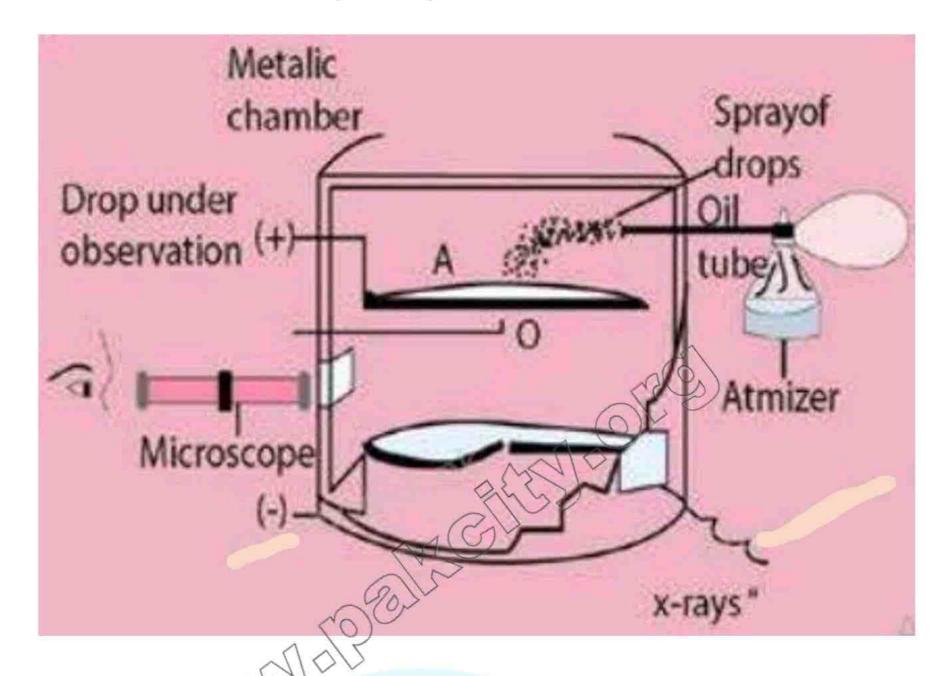
- 1. The droplet falls under the force of gravity without applying the electric field.
- 2. The velocity of the droplet is determined.
- 3. The velocity of the droplet  $(V_1)$  depends upon its weight, mg.

$$v_1 \alpha mg$$
 .....(1)

Where m=mass of the droplet g= acceleration due to gravity

### 5. Ionization of air

The air between the electrodes is ionized by X-rays.



# 6. Taking up of electron by droplet

The droplet under observation takes up an electron and gets charged.

### 7. Battery connection

Now, connect A and A' to a battery which generates an electric field having a strength, E.

# 8. Movement against the action of gravity

The droplet moves upwards against the action of gravity with a velocity (v<sub>2</sub>).

Where

e=charge on the electron

Ee=upward driving force on the droplet due to applied electrical field of strength E

Dividing eq (1) by (2)

$$\frac{\mathbf{v}_1}{\mathbf{v}_2} = \frac{\mathbf{mg}}{\mathbf{Ee-mg}} \qquad (3)$$

The values of  $v_1$  and  $v_2$  are recorded with the help of microscope.

The factors like g and E are also known.

Mass of the droplet can be determined by varying the electric field in such a way that the droplet is suspended in the chamber.

Hence 'e' can be calculated.

### Calculation of charge on each droplet

- 1. By changing the strength of electrical field, Millikan found that the charge on each droplet was different.
- 2. The smallest charge which he found was  $1.59 \times 10^{-19}$  coulomb which is very close to the recent value of  $1.6022 \times 10^{-19}$  coulombs.
- 3. This smallest charge on any droplet is the charge of one electron.
- 4. The other drops having more than one electron on them have double or triple the amount of this charge.
- 5. The charge present on an electron is the smallest charge of electricity that has been measured so far.

### Calculation of mass of electron

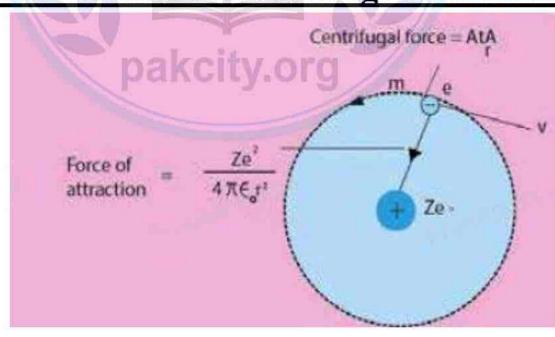
The value of charge on electron is 1.602 x 10<sup>-19</sup> coulombs, while e/m of electron is 1.7588 x 10<sup>11</sup> coulombs kg<sup>-1</sup>. So,

$$\frac{e}{m} = \frac{1.6022 \times 10^{-19} \text{coulombs}}{\text{Mass of electrons}} = 1.7588 \times 10^{11} \text{ coulombs kg}^{-1}$$

Mass of electron= 
$$1.6022 \times 10^{-19}$$
 coulombs  $1.7588 \times 10^{11}$  coulombs kg<sup>-1</sup>

Rearranging

### Derivation of Radius of Revolving Electron in nth Orbit



For a general atom, consider an electron of charge 'e' revolving around the nucleus having charge Ze+.

Z =proton number

e+ =charge on the proton

m = mass of electron

r = radius of the orbit

v =velocity of the revolving electron.

### Coulomb's law

According to Coulombs law, the electrostatic force of attraction between the electron and the nucleus will be given by the following formula.

$$\frac{Ze^*.e^*}{4\pi \in_0 r^2} = \frac{Ze^2}{4\pi \in_0 r^2}$$

 $\in$ ° is the vacuum permittivity and its value is 8.84 x 10<sup>-12</sup>C<sup>2</sup>J<sup>-1</sup>m<sup>-1</sup>. Balanced by mv<sup>2</sup>/r



$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi \in r^2}$$

$$mv^2 = \frac{Ze^2}{4\pi \in_0 r}$$

Rearrangement

$$r = \frac{Ze^2}{4\pi \in mv^2}$$

The radius of a moving electron is inversely proportional to the square of its velocity. Electron should move faster nearer to the nucleus in an orbit of smaller radius. If hydrogen atom has many possible orbits, then the promotion of electron to higher orbits makes it move with less velocity.

### **Angular momentum**

The angular momentum of the electron is given by:

$$v = \frac{\frac{\text{nh}}{2\pi}}{\frac{\text{nh}}{2\pi \text{mr}}}$$
eq (3)

Taking square root

$$v^2 = \frac{n^2 h^2}{4\pi^2 m^2 r^2}$$
 eq (4)

v<sup>2</sup> value substitution

$$r = \frac{Ze^2 \times 4\pi^2 m^2 r^2}{4\pi\varepsilon_0 mn^2 h^2}$$

Rearrangement

$$\mathbf{r} = \frac{\varepsilon_0 \mathbf{n}^2 \mathbf{h}^2}{\pi \mathbf{m} \mathbf{Z} \mathbf{e}^2}$$
 eq (5)

For Z=1

$$r = \frac{\varepsilon_0 n^2 h^2}{\pi m e^2} = \left(\frac{\varepsilon_0 h^2}{\pi m e^2}\right) n^2$$
eq (6)

The radius of hydrogen atom is directly proportional to the square of number of orbit (n). Higher orbits have more radii and vice versa.

$$\left(\frac{\varepsilon_0 h^2}{\pi me^2}\right)$$

Constant factor

Value=  $0.529 \times 10^{-10} \text{ m or } 0.529 \text{ A}^{\circ} (10^{-10} \text{ m} = 1 \text{ A}^{\circ})$ 

$$r=0.529 \text{ Å (n}^2)$$
 eq (7)

### Calculation of radii

By putting the values of n = 1,2.3,4... the radii of orbits of hydrogen atom are:

n=1 
$$r_1=0.529 \text{ Å}$$
 n=4  $r_2=8.4 \text{ Å}$  n=5  $r_3=4.75 \text{ Å}$  n=3  $r_3=4.75 \text{ Å}$ 

Orbits not equally spaced

$$r_2 - r_1 < r_3 - r_2 < r_4 - r_3 < \dots$$

The second orbit is four times away from the nucleus than first orbit, third orbit is nine times away and similarly fourth orbit is sixteen times away.

### **Energy of Revolving Electron**

Total energy of an electron= Kinetic energy + Potential energy

**Electrostatic force of attraction** 

$$\frac{Ze^2}{4\pi \in_0 r^2}$$

#### Work done

If the electron moves through a small distance dr, then the work done for moving electron is given by:

$$\frac{\mathrm{Ze}^2}{4\pi\varepsilon_* \mathrm{r}^2} \mathrm{dr}$$
 because work=(force x distance)

### Calculation of potential energy

Calculation of the potential energy of the electron at a distance r from the nucleus.

We calculate the total work done for bringing the electron from infinity to a point at a distance r from the nucleus. This can be obtained by integrating the above expression between the limits of infinity and r.

$$\int_{-\infty}^{r} \frac{Ze^2 dr}{4\pi \in_0} r^2 = \frac{Ze^2}{4\pi \in_0} \int_{-\infty}^{r} \frac{dr}{r^2} = \frac{Ze^2}{4\pi \in_0} \left[ \frac{-1}{r} \right]_{-\infty}^{r} - \frac{Ze^2}{4\pi \in_0} \left[ \frac{-1}{r} \right] = -\frac{Ze^2}{4\pi \in_0} r$$

$$\text{Work done} = \quad E_{\text{potential}} = -\frac{Ze^2}{4\pi \varepsilon_0 r}$$

The minus sign indicates that the potential energy of electron decreases, when it is brought from infinity to a point at a distance 'r' from the nucleus.

$$E = E_{\text{kinetic}} + E_{\text{potential}}$$

$$= \frac{1}{2} \text{ mv}^2 - \frac{Ze^2}{4\pi\varepsilon_o r}$$
eq (2)

We know

$$mv^{2} = \frac{Ze^{2}}{4\pi \in_{0} r}$$

$$E = \frac{Ze^{2}}{8\pi \in_{0} r} - \frac{Ze^{2}}{4\pi \in_{0} r}$$

$$E = \frac{Ze^2}{8\pi \in_0 r}$$

eq (3)

 $8\pi$ 

 $\frac{\in n^2h^2}{mZe}$   $= \frac{-mZ^2e^4}{8 \in_0^2 n^2h^2}$  eq.(4)

Where En is the energy of n<sup>th</sup> orbit.

For hydrogen atom, the number of protons in nucleus is one, so (Z = 1).

$$\mathbf{E}_{\mathbf{n}} = -\frac{\mathbf{me}^{4}}{8 \in_{0}^{2} \mathbf{h}^{2}} \left[ \frac{1}{\mathbf{n}^{2}} \right]$$

$$eq (5)$$

When the values of these constants are substituted along with their units, then it comes out to be  $2.178 \times 10^{-18} \text{ J}$ .

$$E_n = -2.178 \times 10^{-18} \left[ \frac{1}{n^2} \right] J$$
 eq (6)

As

Gives the energy associated with electron in the nth orbit of hydrogen atom. Its negative value shows that electron is bound by the nucleus i.e. electron is under the force of attraction of the nucleus.

The value of energy obtained for the electron is in joules/atom. If, this quantity is multiplied by Avogadro's number and divided by 1000, the value of En will become

$$E_{n} = \frac{6.02 \times 10^{23} \times 2.18 \times 10^{-18}}{1000} \left[ \frac{1}{n^{2}} \right] \text{kJmol}^{-1}$$

$$E_{n} = -\frac{1313.315}{n^{2}} \text{kJmol}^{-1} \qquad \text{eq (7)}$$

Substituting, the values of n as 1,2,3,4,5, etc. in equation 7

$$E_1 = -\frac{1313.31}{1^2} = -1313.31 \text{ kJmol}^{-1}$$

$$E_2 = -\frac{1313.31}{2^2} = -328.32 \text{ kJmol}^{-1}$$

$$E_3 = -\frac{1313.31}{3^2} = -145.92 \text{ kJmol}^{-1}$$

$$E = -\frac{1313.31}{100} = -82.08 \text{ kJmol}^{-1}$$

$$E_5 = -\frac{1313.31}{5^2} = -52.53 \text{ kJmol}^{-1}$$

$$E = -\frac{1313.31}{5^2} = -82.08 \text{ kJmol}^{-1}$$

$$E_s = -\frac{1313.31}{5^2} = -52.53 \text{ kJmol}^{-1}$$

$$E_{\infty} = -\frac{1313.31}{\infty^2} = 0 \text{ kJmol}^{-1} \text{ (electron is free from the nucleus)}$$

# Calculation of energy differences

$$E_2-E_1 = (-328.32)-(-1313.31) = 984.99 \text{ kJmol}^{-1}$$
  
 $E_3-E_2 = (-145.92)-(-328.32) = 182.40 \text{ kJmol}^{-1}$   
 $E_4-E_3 = (-82.08)-(-145.92) = 63.84 \text{ kJmol}^{-1}$ 

$$E_2-E_1>E_3-E_2>E_4-E_3>.....$$

These values show that the energy differences between adjacent orbits of Bohr's model of hydrogen atom go on decreasing sharply.

### Calculation of ionization energy of hydrogen

$$E_{\text{m}} - E_{1} = 0 - (-1313.31) = 1313.31$$
  
k|mol<sup>-1</sup>

1313.31 kJmol<sup>-1</sup> is the ionization energy of hydrogen. This value is the same as determined experimentally.

### **Defects of Bohr's Atomic Model**

### 1. Applicable to single electron system

Bohr's theory can successfully explain the origin of the spectrum of H-atom and ions like He<sup>+1</sup>, Li<sup>+2</sup> and Be<sup>+3</sup>, etc. These are all one electron systems. But this theory is not able to explain the origin of the spectrum of multi-electrons or poly-electrons system like He, Li and Be, etc.

#### 2. Fine structure

When the spectrum of hydrogen gas is observed by means of a high resolving power spectrometer, the individual spectral lines are replaced by several very fine lines, i.e. original lines are seen divided into other lines. The H $\alpha$ - line in the Balmer series consists of five -component lines. This is called fine structure or multiple structure. The appearance of several lines in a single line suggests that only one quantum number is not sufficient to explain the origin of various spectral lines.

### 3. Three dimensional space

Bohr suggested circular orbits of electrons around the nucleus of hydrogen atom, but researches have shown that the motion of electron is not in a single plane, but takes place in three dimensional space. The atomic model is not flat.

### 4. Zeeman effect and Stark effect

When the excited atoms of hydrogen (which give an emission line spectrum) are placed in a magnetic field, its spectral lines are further split up into closely spaced lines. This type of splitting of spectral lines is called Zeeman effect. When the excited hydrogen atoms are placed in an electrical field, then similar splitting of spectral lines takes place which is called Stark effect.

Bohr's theory does not explain either Zeeman or Stark effect.

### **Quantum numbers**

#### **Definition**

Quantum numbers are the sets of numerical values which give the acceptable solutions to Schrodinger wave equation for hydrogen atom. An electron in an atom is completely described by its four quantum numbers. Quantum numbers serve as identification numbers or labels, which completely describe an electron. These quantum numbers specify position of electron in an atom.

### (1) Principal quantum number (n)

The different energy levels in Bohr's atom are represented by 'n'. This is called principal quantum number by Schrodinger.

#### **Values**

Its values are non-zero, positive integers up to infinity.

$$n = 1, 2, 3, 4, 5, \dots$$

#### Advantages

- 1. The value of n represents the shell or energy level.
- 2. Letter notations K, L, M, N, etc are also used to denote the various shells.

For example, when n = 1, it is called K shell, for n = 2, it is L shell and so on.

- 3. The values of n also determine the location of electron in an atom, i.e the distance of electron from the nucleus.
- 4. Greater the value of 'n' greater will be the distance of electron from the nucleus.
- 5. It is a quantitative measure of the size of an electronic shell, 'n' also provides us the energy of electron in a shell.

#### (2) Azimuthal quantum number (l)

A spectrometer of high resolving power shows that an individual line in the spectrum is further divided into several very fine lines. Each shell is divided into subshells. Azimuthal quantum number represents the subshells.

#### **Values**

The values of azimuthal quantum number (1) are:

$$1=0, 1, 2, 3, \dots (n-1)$$

Its value depends upon n. The values of azimuthal quantum number always start from zero.

#### **Advantages**

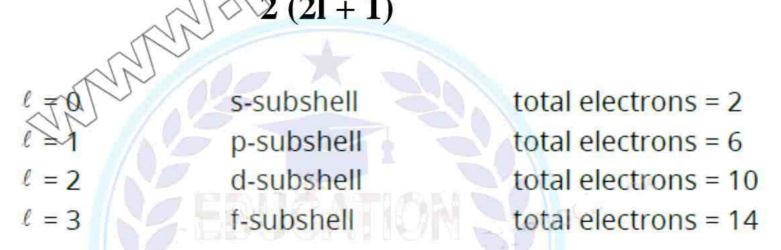
- 1. These values represent different sub-shells, which are designated by small letters, s, p, d, f. They stand for sharp, principal, diffused and fundamental, respectively.
- 2. A subshell may have different shapes depending upon the value of (l). It may be spherical, dumb-bell, or some other complicated shapes.
- 3. The value of '1' is related to the shape of the sub-shell as follows:

| $\ell = 0$ | s-subshell | spherical           |
|------------|------------|---------------------|
| € = 1      | p-subshell | dumb-bell           |
| $\ell = 2$ | d-subshell | (complicated shape) |

### Relationship between principal and azimuthal quantum number

| n = 1 | K-shell | $\{\ell=0$   | {s-subshell                      | should be called as        | 1s |
|-------|---------|--|----------------------------------|----------------------------|----|
| n = 2 | L-shell | $\begin{cases} \ell = 0 \\ \ell = 1 \end{cases}$                         | s-subshell<br>p-subshell         | 2s<br>2p                   |    |
| n = 3 | M-shell | $\begin{cases} \ell = 0 \\ \ell = 1 \\ \ell = 2 \end{cases}$             | s-subshell p-subshell d-subshell | 3s<br>3p<br>3d             |    |
| n = 4 | N-shell | $\begin{cases} \ell = 0 \\ \ell = 1 \\ \ell = 2 \\ \ell = 3 \end{cases}$ | s-subshell d-subshell f-subshell | 4s<br>4p<br>4d<br>4d<br>4f |    |
| -11-4 |         |  |                                  |                            |    |

# Formula for calculating electrons



### (3) Magnetic quantum number (m)

Strong magnetic field splits the spectral lines further. In order to explain this splitting, a third quantum number called the magnetic quantum number (m) has been proposed. It is also called orientation quantum number.

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#### **Values**

Its values are

$$m = 0, \pm 1, \pm 2, \pm 3,...$$

The value of 'm' depends upon values of 'l'

| $\ell = 0$ | s-subshell | m=0  |
|------------|------------|--|
| $\ell = 1$ | p-subshell | m=0, ±1(p-subshell has three degenerate orbitals)        |
| $\ell = 2$ | d-subshell | m=0,±1, ±2(d-subshell has five degenerate orbitals)      |
| $\ell = 3$ | f-subshell | m=0.±1, ±2, ±3(f-subshell has seven degenerate orbitals) |

For a given value of '1' the total values of 'm' values are (21+1).

#### **Advantages**

1. It tells about degeneracy of orbitals in space.

2. It tells us the number of different ways in which a given s, p, d or f-subshell can be arranged along x, y and z-axes in the presence of a magnetic field.

#### For s-subshell

- In case of s-subshell l = 0, so, m = 0.
- s-subshell of any energy level has only one space orientation and can be arranged in space only in one way along x, y and z-axes.
- s-subshell is not sub-divided into any other orbital.
- The shape of 's' orbital is such that the probability of finding the electron in all the directions from the nucleus is the same.
- It is a spherical and symmetrical orbital.

### For p-subshell

- For p-subshell, l = 1 and  $m = 0, \pm 1$ .
- These values of 'm' imply that p-subshell of any energy level has three space orientations and can be arranged in space along x, y, and z axes.
- These three orbitals are perpendicular to each other and named as px, py, and pz.
- They have egg shaped lobes which touch each other at the origin.
- In the absence of the magnetic field, all the three p-orbitals have the same energy and are called degenerate orbitals.
- These orbitals are said to be 3-fold degenerate or triply degenerate.

#### For d-subshell

- For d-subshell 1 = 2 so  $m = 0, \pm 1, \pm 2$ .
- It implies that it has five space orientations and are designated as dxy (m = -2), dyz (m = -1), dzx (m = +1),  $dx^2-y^2$ (m = +2) and  $dz^2$ (m 0)
- All these five d-orbitals are not identical in shape.
- In the absence of a magnetic field, all five d-orbitals have the same energy and they are said to be five-fold degenerate orbitals.

#### For f-subshell

- For f-subshell, 1 = 3 and  $m = 0, \pm 1, \pm 2, \pm 3$
- They have complicated shapes.

#### (4) Spin quantum number (s)

In 1925, Goudsmit and Uhlenbech suggested that an electron while moving in an orbital around the nucleus also rotates about its own axis either in a clockwise or anti-clockwise direction. This is also called self-rotation. Opposite magnetic fields are generated by the clockwise and anti-clockwise spins of electrons.

### **Background**

Alkali metals have one electron in their outermost shell. Their emission spectra are observed by means of high resolving power spectrometer and each line in the spectrum is found to consist of pair of lines. This is called doublet line structure. Lines of doublet line structure are widely separated from each other. This spin motion is responsible for doublet line structure in the spectrum.

### Important long questions from past papers

- 1. Write any four properties of cathode rays.
- 2. How did Rutherford discover the nucleus of atom?
- 3. Give properties of neutron in detail.
- 4. Write down the experiment how neutron was discovered.
- 5. Describe J.J Thomson's experiment for determining e/m value of electron.

- 6. Describe Millikan's oil drop method for the measurement of charge on electron.
- 7. Write four defects of Bohr's atomic model.
- 8. Derive the formula for calculating the energy of an electron in n<sup>th</sup> orbit using Bohr's model.
- 9. Derive an expression to determine the radius of an orbit using Bohr Model.
- 10. Define Quantum numbers. Discuss briefly Azimuthal quantum number/principal quantum number/magnetic quantum number and spin quantum number.

