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- (ii) Physical state of halogens changes does the group. Why?
- (iii)  $\text{H}_2\text{O}$  has higher boiling point than  $\text{HF}$  &  $\text{NH}_3$ . Why?
- (iv)  $\text{I}_2$  has higher heat of sublimation. Why?
- (v) Water boils at low temperature on Murree Hills. Why?
- (vi) Differentiate b/w Amorphous & crystalline solids.
- (vii) Ionic crystals are brittle. Why?
- (viii) Lattice energy increases with decrease in size of cation or anion. Why?
- (ix) Covalent crystals are dissolved in non-polar solvents. Why?
- (x) Define crystal lattice and lattice point.
- (xi) Metallic crystals are not brittle. Why?
- (xii) Bubbles continuously come out of a boiling liquid. Why?

**Q3. Answer any Eight parts from the followings.**

- (i) What type of forces are present in substances like He, Ne, Ar,  $\text{Cl}_2$ ,  $\text{CH}_4$ , etc.?
- (ii) How sea life survives under frozen sea?
- (iii) Boiling points of noble gases increase down the group. Why?
- (iv) Boiling point of  $\text{C}_2\text{H}_6$  (ethane) is  $-88.6^\circ\text{C}$  and that of  $\text{C}_6\text{H}_{14}$  is  $+68.7^\circ\text{C}$ . Why?
- (v)  $\text{HF}$  is a weaker acid than  $\text{HCl}$ . Why?
- (vi) Why  $\text{H}_2\text{O}$  is a liquid and  $\text{H}_2\text{S}$  is a gas at room temperature?
- (vii) Electronegativity of F is more than oxygen, but boiling point of water is higher than that of  $\text{HF}$ . Why?
- (viii) Ethyl alcohol is soluble in water, but hydrocarbons are insoluble in water. Why?
- (ix) Why the metals are malleable and ductile?
- (x) Why acetone is soluble in chloroform?
- (xi) Why the melting and boiling point of alkanes increase with increase in molar mass?
- (xii) What is transition temperature?

**Q4. Answer any Eight parts from the followings.**

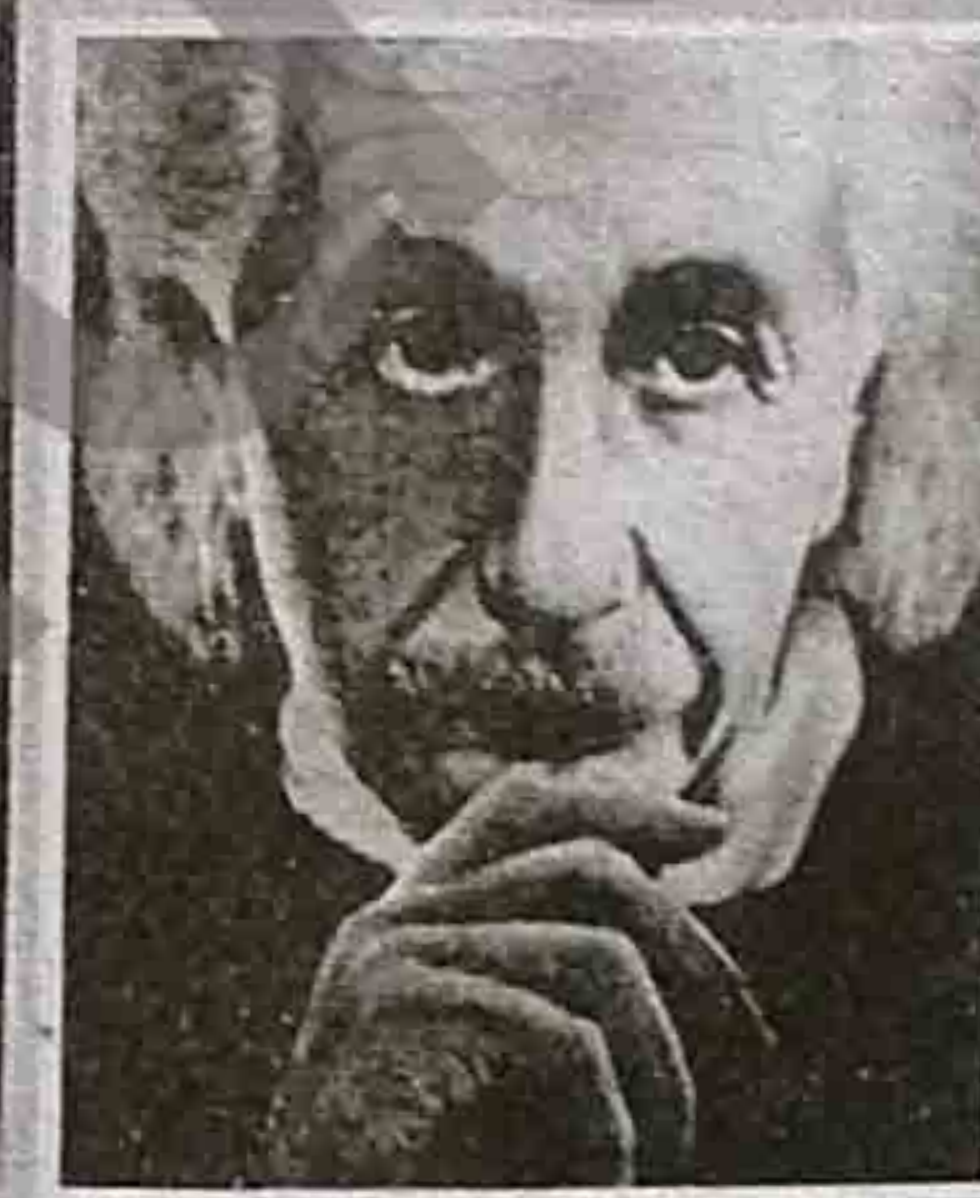
- (i) Metallic crystals are lustrous. Why?
- (ii)  $\text{NaCl}$  is an insulator but sodium is conductor of electrons. Explain with reason?
- (iii) Ice floats on water. Justify it.
- (iv) Why cleavage is an anisotropic behaviour?
- (v) Define crystal lattice and lattice point?
- (vi) What is the relationship between boiling point of a liquid and external pressure?
- (vii) What do you mean by symmetry? Give elements of symmetry?
- (viii) Ionic compounds do not have molecule. Why?
- (ix) Molecular crystals are soft. Why?

**Section - II (Attempt any three questions) (8x 3) = 24**

- Q5.** (a) What are covalent solids? Give their properties. (03)
- (b) Give five uses of liquid crystals. (03)
- (c) Differentiate b/w isomorphism & polymorphism. (02)
- Q6.** (a) What is polarizability? On What factors does it depend? (02)
- (b) What is the mechanism of generation of London forces? (03)
- (c) How does H-bonding saves the aquatic life? (03)
- Q7.** (a) Define Allotropy. Give examples. (02)
- (b) Define crystal system. Describe tetragonal, hexagonal and orthorhombic crystal systems. (04)
- (c) Ionic crystals do not conduct electricity in solid form. Why? (02)
- Q8.** (a) How does crystallography helps to determine Avogadro's number? (04)
- (b) Evaporation causes cooling. Explain (02)
- (c) Define habit of a crystal with example. (02)
- Q9.** (a) What is hydrogen bonding. Explain role of hydrogen bonding in food and biological materials (04)
- (b) Explain the structure of  $\text{NaCl}$ . Show that ratio of  $\text{Na}^+$  and  $\text{Cl}^-$  ions in its unit cell is 1:1 (04)

# Chapter 5

## ATOMIC STRUCTURE



Albert Einstein



Niels Bohr

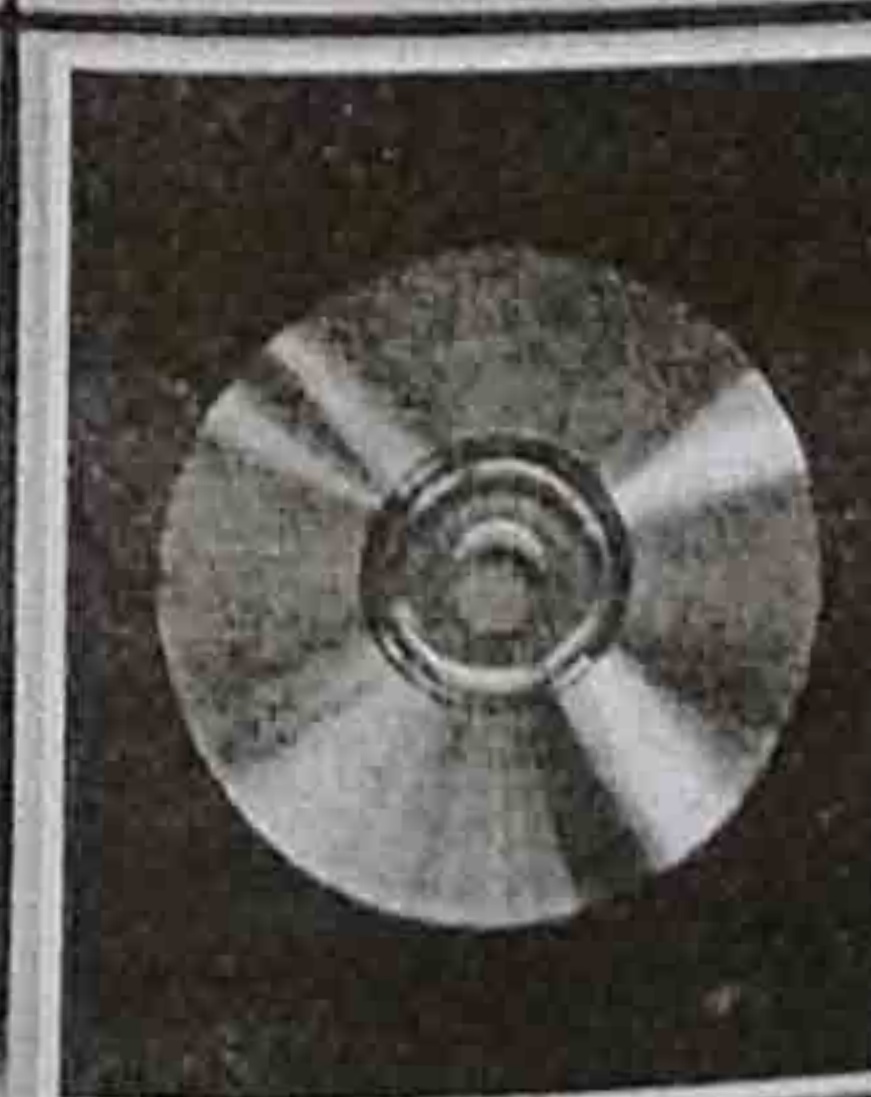
Continuous Spectrum



Line Emission Spectrum



Line Absorption Spectrum



Diffraction on Compact Disc (CD) Surface



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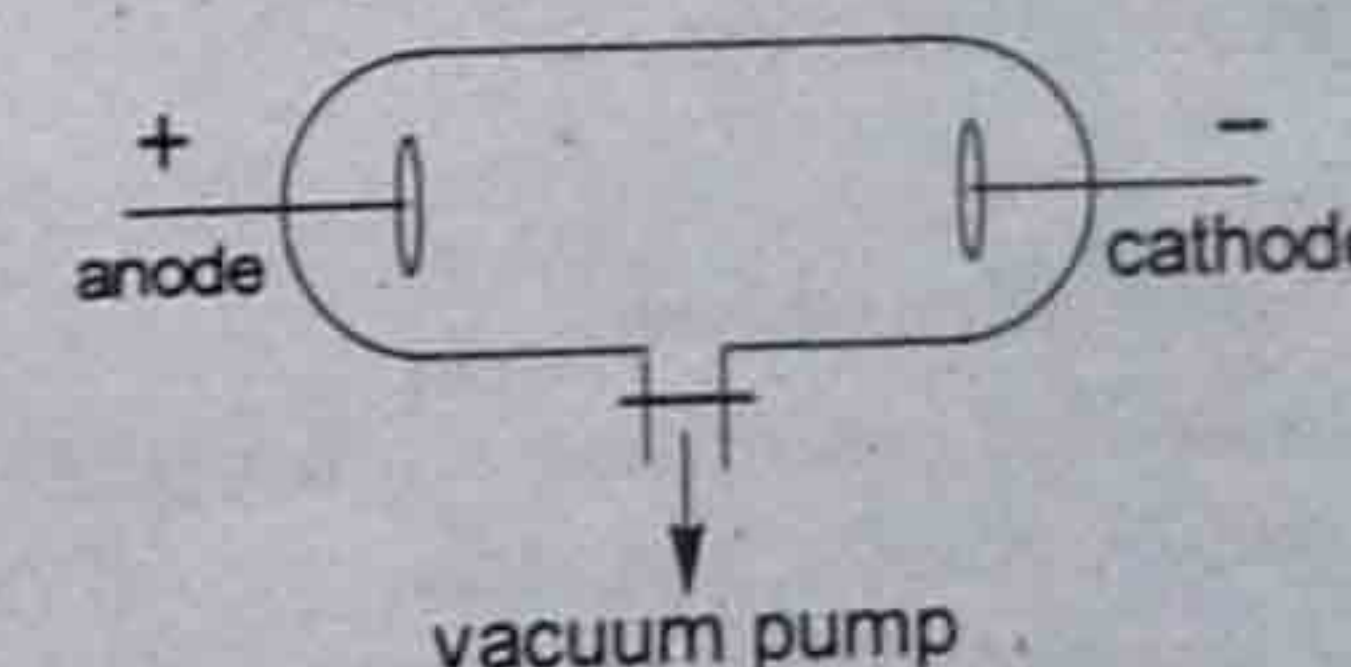
#### SUB-ATOMIC PARTICLES OF ATOM

- Matter is composed of very small particles called atom.
- According to Dalton's atomic theory, atom cannot be divided further.
- However, modern researches show that atom is divisible. Several sub-atomic particles like electron, proton and neutron have been discovered.

#### Discovery of Electron (Cathode Rays)

##### Gas Discharge Tube

- It is a glass tube having two metallic electrodes sealed into it.
- It may contain a gas, air or vapours of any substance at any pressure.
- It tube can be connected to a vacuum pump to maintain any low pressure.
- The electrodes are connected to a high voltage battery. The exact voltage required depends upon the length of the tube and the pressure inside it.
- A slit can be used in it to get a sharp beam of radiations.



Gas Discharge Tube

##### Example:

A 'neon sign' is also a discharge tube, which contain neon gas at a pressure of about 10 torr. Television and computer monitor screen are also gas discharge tubes called cathode ray tube (CRT)

#### Discovery of Electrons (or Cathode Rays)

##### William Crooks Experiment

In late 19<sup>th</sup> century, William Crooks studied the passage of electric current through gases. For this purpose, he used a gas discharge tube.

##### Results of William Crooks Experiment

- He obtained following results
- At normal pressure, gases do not conduct electricity even if the voltage is as high as 5000 volts.

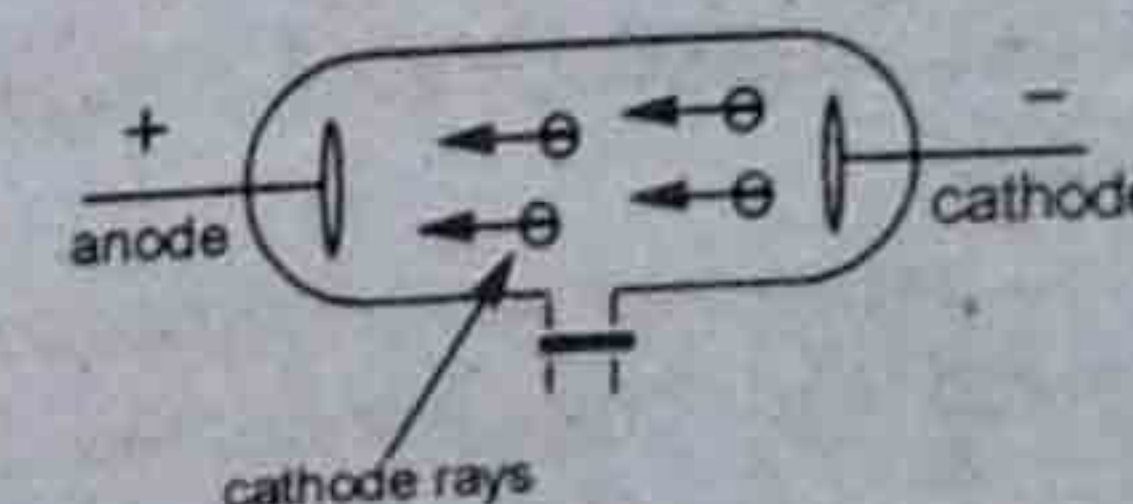


Figure: Production of cathode rays



- However, when the pressure inside the gas discharge tube is reduced and high voltage of 5000–10000 volts is applied, the gases begin to conduct electricity and a uniform glow appears inside the tube.
- When the pressure is further reduced to 0.01 torr, uniform glow disappears and fluorescence appears on the glass walls opposite to the cathode. This is actually due to the striking of some rays on the glass wall. These rays are called Cathode rays.
- The colour of the fluorescence depends upon the composition of glass.
- Different gases and vapours of different substances were used in the discharge tube. Also different metals were used as electrodes. But always same rays were produced.

### Properties of Cathode Rays

#### 1. Travel in a Straight Line

In 1869, Hittorf showed that Cathode rays travel in a straight line.

He found that cathode rays produce a sharp shadow of an opaque object placed in their path. It shows that these rays travel in a straight line, perpendicular to the surface of cathode.

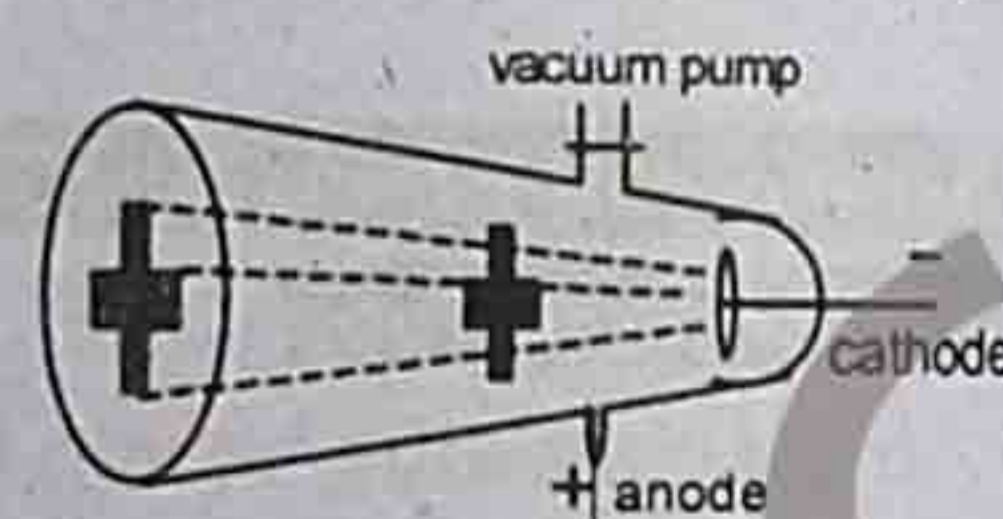


Figure: Cathode rays cast a shadow of an opaque object

#### 2. Possess Momentum.

These rays can drive a small paddle wheel placed in their path. Cathode rays strike against the paddles of the paddle wheel and make it move.

This shows that cathode rays are actually beam of particles which have momentum (i.e. mass and velocity).

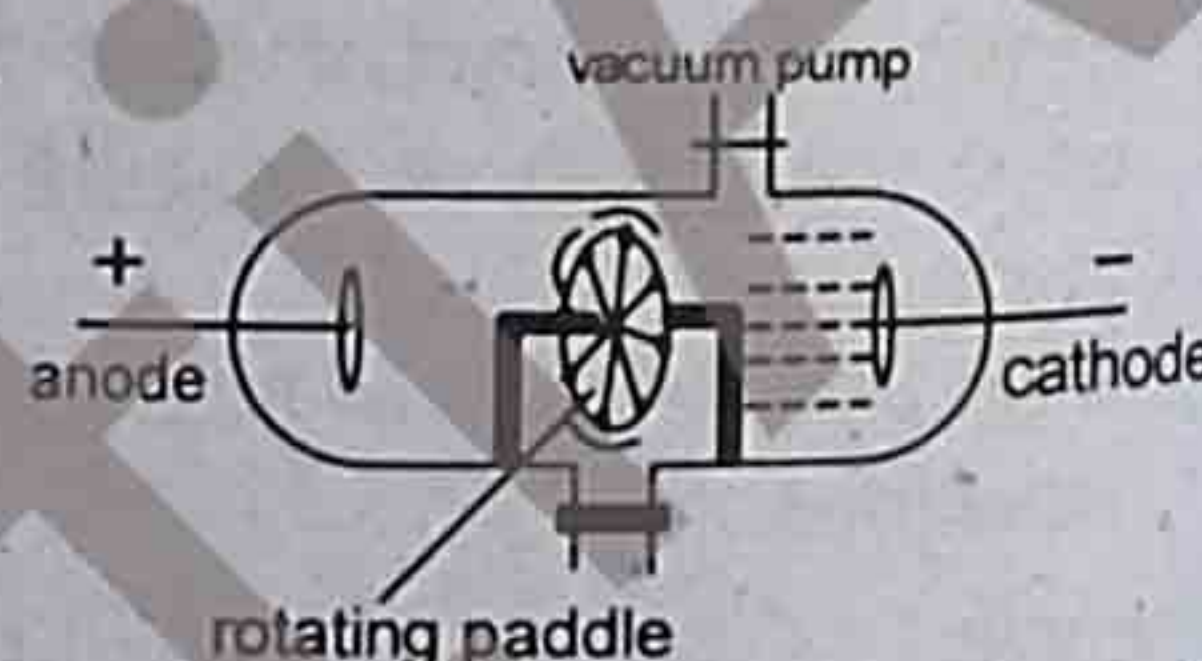


Figure: Cathode rays drive a small paddle wheel

#### Exercise Q4 (d):

The bending of the cathode rays in the electric and magnetic fields shows that they are negatively charged.

#### 3. Negatively Charged

In 1895, J Perrin showed that cathode rays are negatively charged.

He found that when cathode rays are passed through a magnetic field, these are curved downward by the magnetic field.

Moreover, in 1897, J.J. Thomson showed that when cathode rays are passed through an electric field, these are deflected towards positively charged plate.

These experiments show that cathode rays are negatively charged.

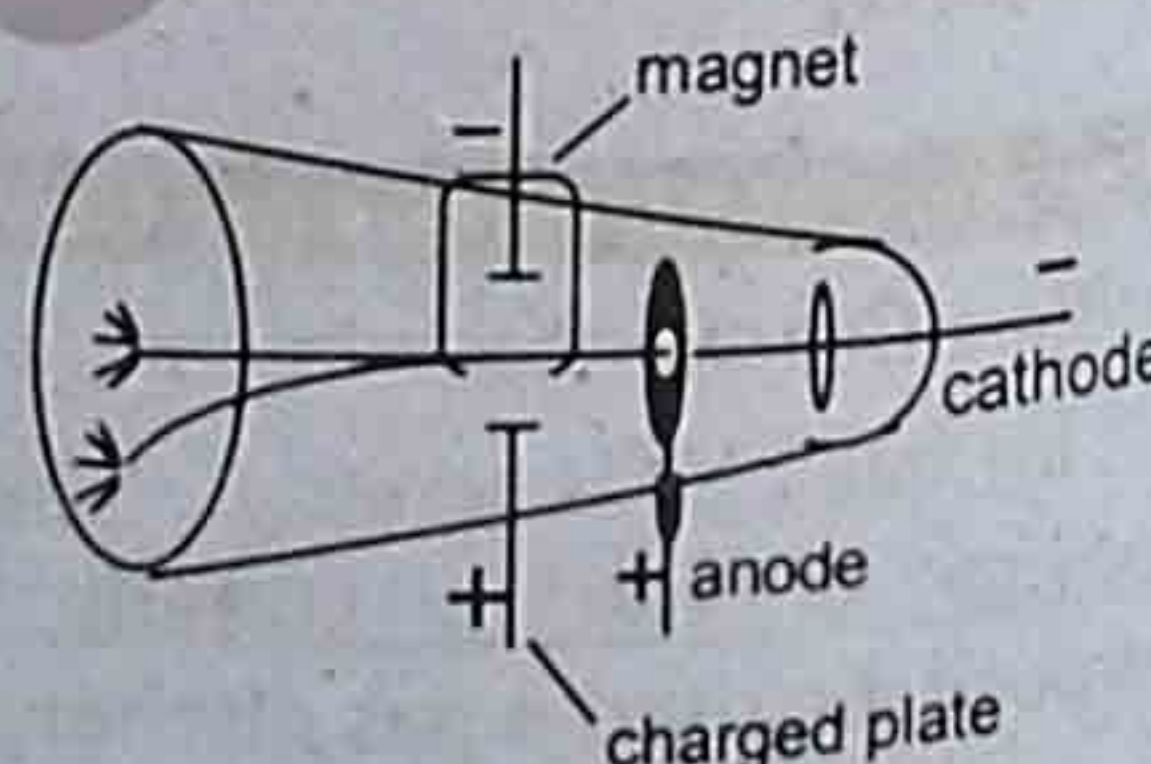


Figure: Deflection of cathode rays in electric and magnetic field

#### 4. Produce Fluorescence

They produce greenish fluorescence on striking the walls of the glass tube.

They also produce fluorescence in rare earths and minerals.

e.g. alumina glows red and tin stone glows yellow.

#### 5. Produce X-rays

Cathode rays can produce X-rays, when strike an anode particularly with high atomic mass.

#### 6. Possess Energy (Energetic Rays)

When cathode rays strike an object, it becomes heat up showing that cathode rays are energetic rays. When cathode rays from a concave cathode fall on a platinum foil, it begins to glow.

#### 7. Ionize Gases

These can ionize gases by removing electron from them. Thus, positive ions are produced.

#### 8. Cause Chemical Change

These are negatively charged. So, their addition cause reduction of a substance. Thus, these can cause a chemical change.

#### 9. Pass through thin foil

These can pass through a thin metal foil like aluminium or gold foil.

#### 10. Charge to mass (e/m) ratio

Their e/m ratio shows that they are simply electrons.

### Conclusions

- J.J. Thomson proved that cathode rays are actually a stream of negatively charged particles. He calculated their e/m ratio. He found that the e/m ratio remains same for every gas used in the discharge tube. He concluded that these are fundamental particles of atom.
- Stoney called these rays as 'electrons'.

### Discovery of Proton (Positive Rays)

In 1886, a German physicist, Eugen Goldstein discovered another type of rays called positive rays or canal rays, in the gas discharge tube.

#### Experiment

Eugen Goldstein used a perforate cathode in discharge tube. When a large voltage is applied, a glow appears on the glass wall opposite to anode. It is because some rays travel opposite to the cathode rays

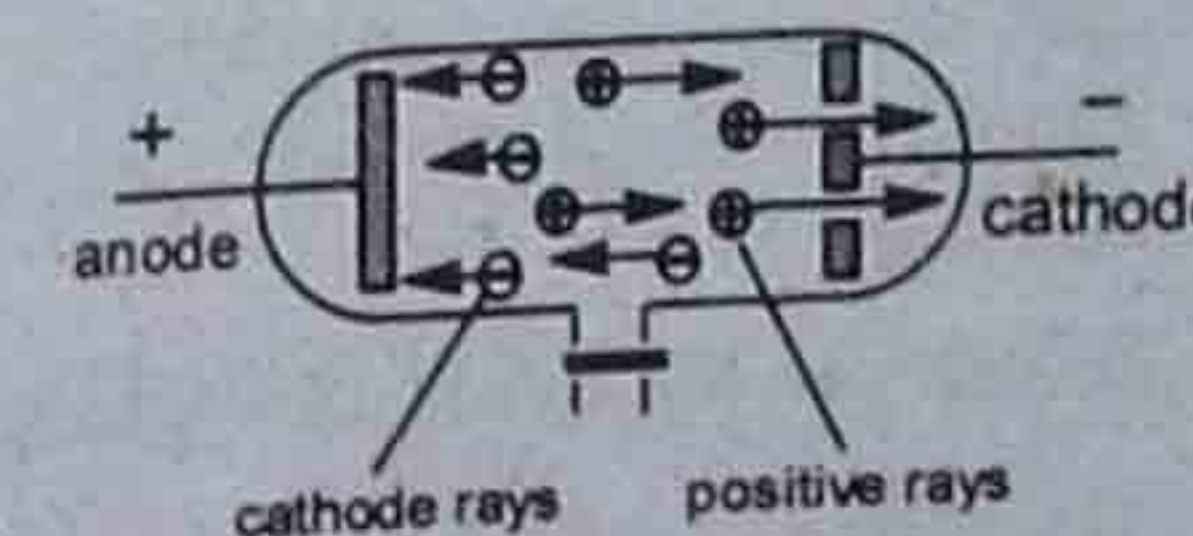


Figure: Production of positive rays

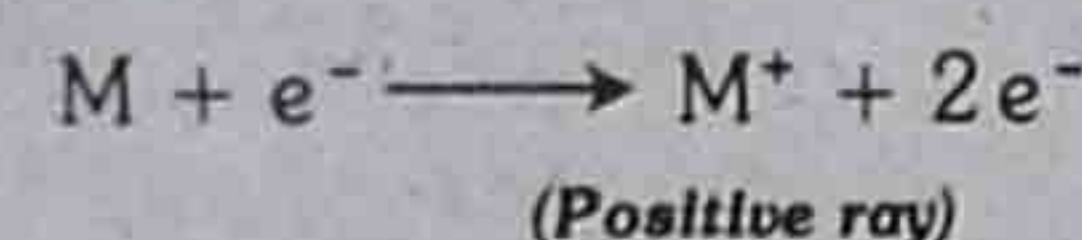


and after passing through perforated cathode, they produce glow on the wall.

- Since these rays pass through the holes (canals) in the cathode, therefore, these are called canal rays.
- These rays are called positive rays since they carry positive charge.

#### How Canal Rays are Produced? (Origin of Positive Rays)

These rays are produced when high-speed cathode rays (electrons) strike the gas molecules present inside the gas discharge tube. Cathode rays remove electrons from the gas molecules and convert them into positive ions. These ions then move towards the cathode as positive ray.



#### Properties of Positive Rays

##### 1. Travel in a straight line

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

##### 2. Produce Flashes (Fluorescence)

They produce flashes on striking ZnS plate.

##### 3. Positively Charged

These rays are deflected in an electric and magnetic field in a way that shows their positive charge.

##### 4. Charge to mass (e/m) ratio

- The charge to mass ratio (e/m) for these rays is always smaller than for electrons.
- The e/m ratio depends upon the nature of the gas used in the gas discharge tube. Heavier the gas, smaller is the e/m value.
- The e/m ratio is highest when hydrogen is present. It is because, the positive particle obtained from hydrogen have least 'm' value. Hence its e/m ratio is highest.

#### Conclusions

- Hydrogen produces the lightest positive particle. Rutherford called this positive particle as proton. It is also considered as the fundamental particle of an atom.
- From e/m ratio of proton, the mass of proton was calculated to be  $1.6726 \times 10^{-27}$  kg or 1.0073 amu.
- The mass of proton is 1836 times greater than that of electron.

Protons and Electrons were discovered until 1886 and their properties were completely understood until 1895.

#### Exercise Q6. (a):

Discuss Chadwick's experiment for the discovery of neutrons.



#### Discovery of Neutron

##### Rutherford Prediction

In 1920, Rutherford predicted the presence of a neutral particle (neutron) in the nucleus of an atom. It is because the atomic masses of atoms could not be explained on the basis of protons and electrons only.

##### Chadwick's Experiment

- Chadwick discovered neutron in 1932. He was awarded Nobel Prize in Physics in 1935.
- Chadwick bombarded the nucleus of beryllium with  $\alpha$ -particles (produced from polonium metal source) and found that it gave highly penetrating radiation. Charged detector showed these radiations as neutral. These radiations were called neutrons.

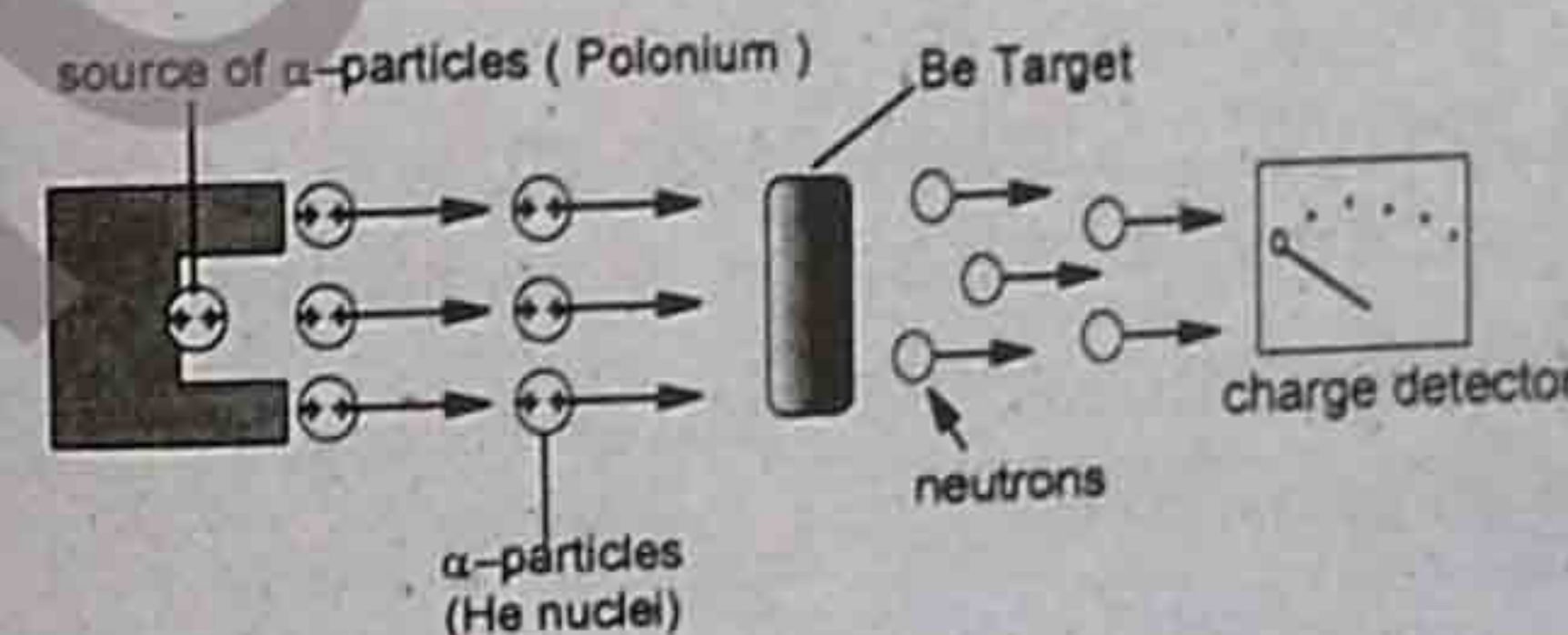
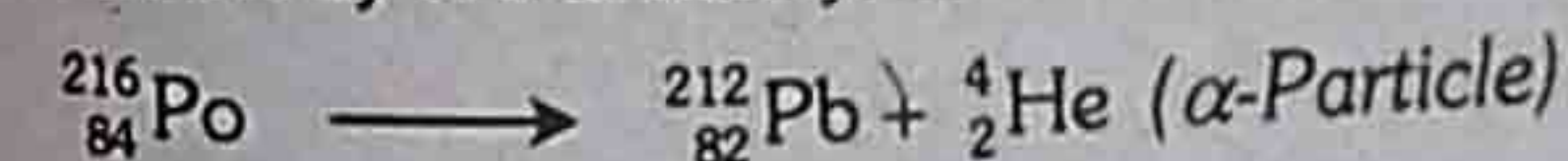
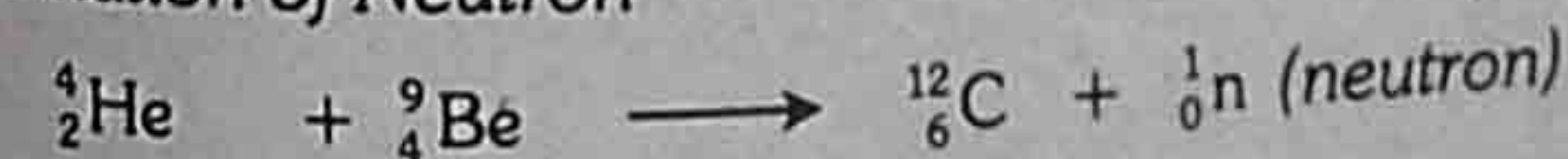


Figure: Bombardment of Be with  $\alpha$  particles and discovery of neutron

- Nuclear Reactions: This neutron was produced as Formation of  $\alpha$ -Particle from Polonium



##### Formation of Neutron



- Like electrons and protons, neutrons are also considered as a fundamental particle of atom.

#### Properties of Neutron

##### 1. Cannot ionize gases

Neutron can not ionize gases because it is a neutral particle

##### 2. Free Neutron Decays

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





### 3. High Penetrating Power

Neutrons have high penetrating power. They can knock out high-speed protons from paraffin, water, paper and cellulose.

### 4. Fast and Slow Neutrons

- Neutrons travelling with 1.2 MeV energy are called fast neutrons
- Neutrons travelling with energy less than 1 eV are called slow neutrons.
- Slow neutrons are more effective than fast ones for the nuclear fission process.

### 5. Carry out Nuclear reactions

They can carry out nuclear reactions when used as projectiles.

Examples:

(i) a neutron can eject an  $\alpha$ -particle from the nucleus of nitrogen and boron is produced.

$${}_0^1\text{n} + {}_7^{14}\text{N} \longrightarrow {}_{11}^{11}\text{B} + {}_2^4\text{He}$$

(ii) Slow moving neutrons produce  $\gamma$ -radiations on striking Cu metal. In this process radioactive  ${}_{29}^{66}\text{Cu}$  is converted into  ${}_{30}^{66}\text{Zn}$ . Neutron is captured by the nucleus of  ${}_{29}^{66}\text{Cu}$  and  ${}_{29}^{66}\text{Cu}$  is produced. This radioactive  ${}_{29}^{66}\text{Cu}$  emits an electron ( $\beta$ -particle) and its atomic number is increased by one unit.



### 6. Biological Activity:

These are used in the treatment of cancer due to their biological activity.

Particle	Charge (C)	Relative charge	Mass (kg)	Mass (amu)
Proton	$+1.6022 \times 10^{-19}$	+1	$1.6726 \times 10^{-27}$	1.0073
Neutron	0	0	$1.6750 \times 10^{-27}$	1.0087
Electron	$-1.6022 \times 10^{-19}$	-1	$9.1095 \times 10^{-31}$	$5.4858 \times 10^{-4}$

### Exercise Q5. (b):

What is J.J Thomson's experiment for determining e/m value of electron?

### Measurement of Charge to Mass Ratio (e/m) of Electron

J.J Thomson determined the e/m ratio of cathode (electrons) rays in 1897. But he could not determine the charge or mass of the electrons separately.

- He subjected a beam of cathode rays to the simultaneous effects of electric and magnetic fields as shown in the figure.
  - ✓ In the absence of electric & magnetic field, the electrons strike at  $P_1$ .
  - ✓ When only magnetic field is applied, the electrons strike at  $P_2$ .
  - ✓ When only electric field is applied, the electrons strike at  $P_3$ .
- The strength of electric and magnetic field is so adjusted that the electrons strike at  $P_1$ .
- Now from the comparison of the strengths of electric and magnetic fields e/m ratio is calculated.
- The calculated value of e/m is  $1.7588 \times 10^{11}$  Coulomb/kg.
- It means one kg of electron carries a charge of  $1.7588 \times 10^{11}$  Coulombs.

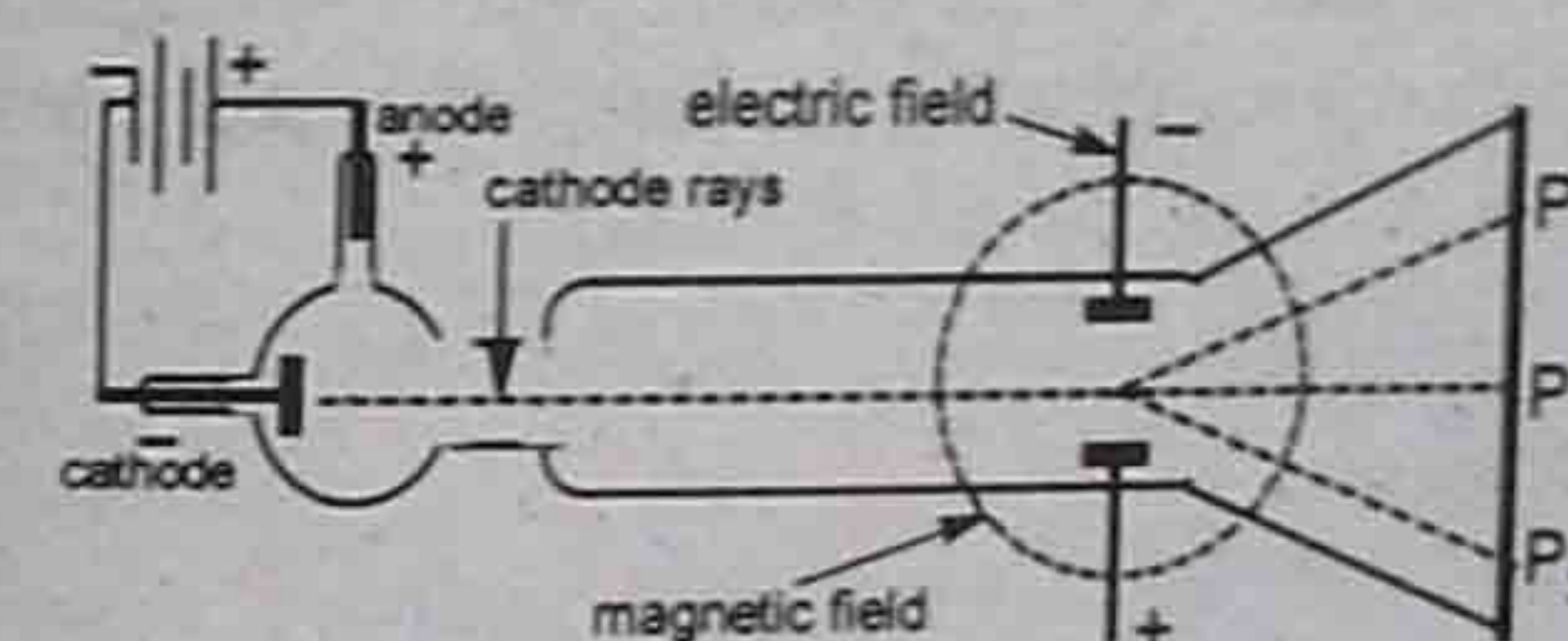


Figure: Measurement of e/m value of electron by J.J Thomson

### Exercise Q5. (a):

Explain Millikan's oil drop experiment to determine the charge of an electron?

### Measurement of Charge on Electron

#### (Millikan Oil Drop Experiment)

In 1909, R.A. Millikan determined the charge of an electron with the help of an apparatus as shown in the figure.

#### Construction

- It consists of a metallic chamber consisting of two parts.
- It also has two parallel electrodes in it.
- The upper electrode has a hole in it.
- The chamber is filled with air and its pressure can be

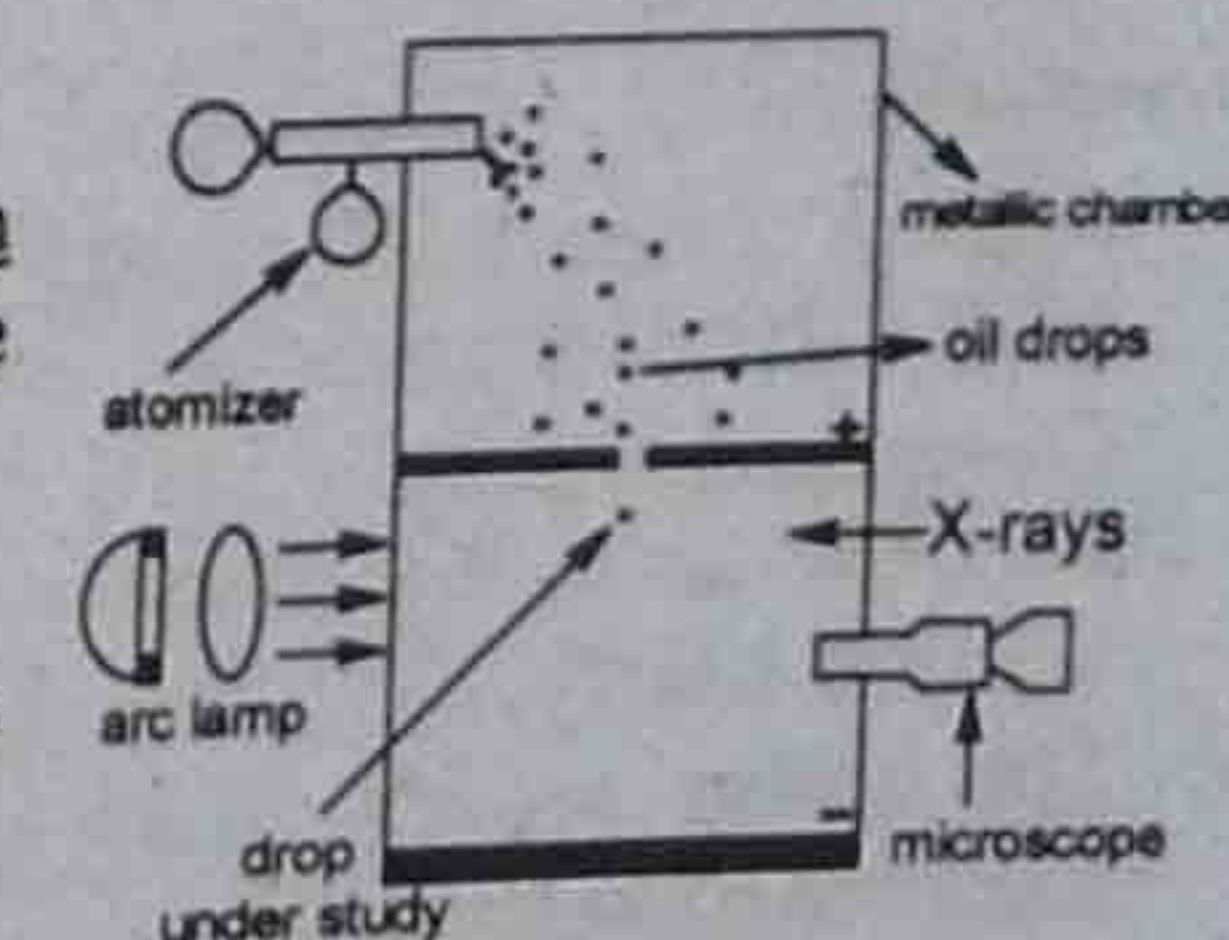


Figure: Millikan's oil drop method for determination of charge of electron



adjusted with a vacuum pump.

- The apparatus has an atomizer to introduce fine droplets into the chamber.
- It has a microscope and arc lamp to see the motion of droplets. The falling droplet is illuminated by the arc lamp perpendicular to the direction of view. Thus, it appears as bright speck (spot) against dark background.
- An X-ray generator is used to ionize the gas in the chamber.

### Working

- Tiny droplets of oil are introduced into the chamber by an atomizer. Some droplets enter into the hole.
- Droplets fall under the action of gravity.
- Falling velocity of the droplets is directly proportional to its weight.

$$\text{i.e. } v_1 \propto mg \quad (1)$$

where  $m$  = mass of droplet.  $g$  = acceleration due to gravity

- Now the air between the electrodes is ionised by X-rays. Oil droplets take electrons from the ionized air and become negatively charged.
- The electrodes are then connected to the an electric field of strength  $E$ . The oil droplets, being negatively charged, rises up towards the positively charged plates, against the force of gravity with velocity  $v_2$ .

$$\text{i.e. } v_2 \propto Ee - mg \quad (2)$$

where  $e$  = charge on the droplet.

- Divide eq (1) by (2)

$$\frac{v_1}{v_2} = \frac{mg}{Ee - mg} \quad (3)$$

- The strength of the electric field is so adjusted that the droplet becomes stand still. Under this condition, mass of the droplet ( $m$ ) can be determined.
- Thus if  $v_1$ ,  $v_2$ ,  $E$ ,  $g$  and  $m$  are known, charge on the droplet can be determined using equation (3)

### Conclusions

- Millikan determined charge on many oil droplets and found that it was always  $1.59 \times 10^{-19} \text{ C}$  or some multiple of it.
- The least charge  $1.59 \times 10^{-19} \text{ C}$  on oil droplet is because when it picks up one electron from the air in the chamber. This value is very close to the modern value of charge which is  $1.6022 \times 10^{-19} \text{ C}$ . Thus charge on one electron =  $1.6022 \times 10^{-19} \text{ C}$
- This charge present on an electron is the smallest charge of electricity that has been determined so far.

### Exercise Q5. (c):

Evaluate mass of electron from the above two experiments.

### Determination of Mass of Electron

From  $e/m$  ratio of electrons, mass of electron can be calculated as

Since

$$\frac{e}{m} = 1.7588 \times 10^{11} \text{ C/Kg}$$

$$m = \frac{e}{1.7588 \times 10^{11}}$$

$$m = \frac{1.6022 \times 10^{-19} \text{ C}}{1.7588 \times 10^{11} \text{ C kg}^{-1}}$$

$$m = 9.1096 \times 10^{-31} \text{ kg}$$

### Exercise Q6. (b):

Rutherford's atomic model is based on the scattering of  $\alpha$ -particles from a thin gold foil. Discuss it and explain the conclusions.

### RUTHERFORD'S MODEL OF ATOM (DISCOVERY OF NUCLEUS)

#### $\alpha$ -scattering experiment

- In 1911, Lord Rutherford bombarded a thin gold foil 0.00004 cm thickness with high-speed  $\alpha$ -particles, coming from a radioactive material (radium or polonium).
- A beam of  $\alpha$ -particles was obtained by using a pinhole in lead sheet. A photographic plate or a screen coated with ZnS was used as a detector. When  $\alpha$ -particles struck the screen, flashes of light were produced.
- Rutherford observed that most of the particles went straight through the foil.
- A few were deflected at various angles and some were deflected backward.

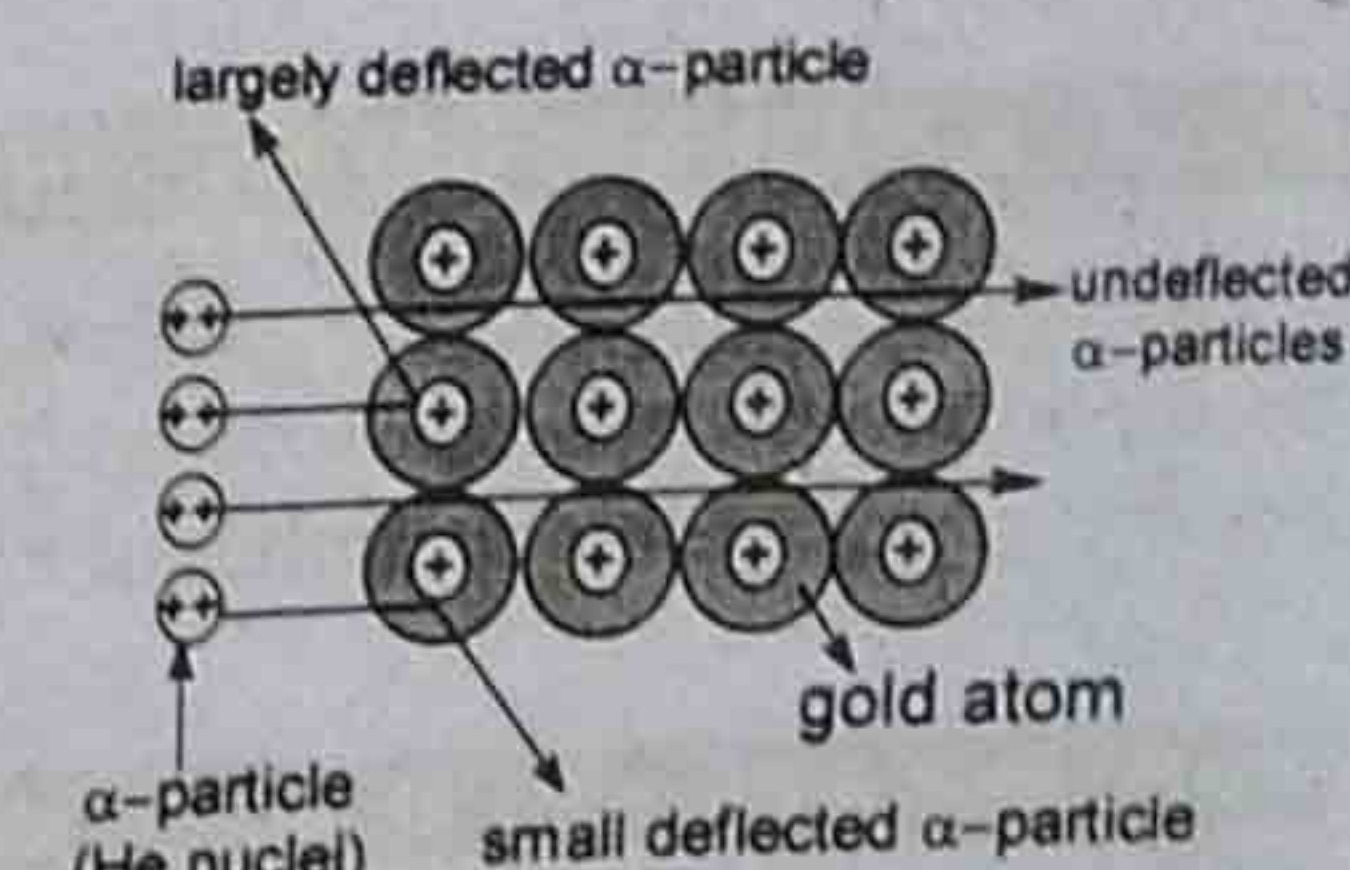


Figure: Rutherford's experiment for scattering of  $\alpha$ -particles

### Conclusions

1. Since most of the  $\alpha$ -particles went straight, therefore, most of the space in an atom is empty.
2. The central heavy region, which deflects the  $\alpha$ -particles, must have heavy positive charge. This part of the atom is called Nucleus.
3. Nucleus occupies very small volume of the atom. Remaining volume of the atom is occupied by extra nuclear moving electrons.



**Rutherford's Atomic Model**

Based on  $\alpha$ -scattering experiment, Rutherford proposed a planetary model of atom, in 1911. This model was similar to solar system.

**Postulates**

1. An atom consists of a nucleus containing positive charge and practically the whole of its mass.
2. The nucleus is surrounded by a number of electrons equal to the number of protons in the nucleus.
3. The electrons are in constant motion around the nucleus in closed orbit like that of planets around the sun. The centrifugal force is balanced by the electrostatic force of attraction between the electrons and nucleus. Thus, electrons revolve around the nucleus.

**Defects**

1. Rutherford's model is based upon laws of motion and gravitation. These laws can be easily applied to neutral bodies but not to the charged bodies such as electrons and protons.
2. A revolving electron must emit energy continuously. As a result, electron will move in a spiral path and will fall into the nucleus. Thus, whole atom would collapse. However, it never happens.
3. If electron emits energy continuously, then a continuous spectrum should be formed. Actually, atoms form line spectrum.



Figure: Expected spiral path of electron around the nucleus

**PLANCK'S QUANTUM THEORY**

In 1900, Max Planck proposed quantum theory of light to explain emission and absorption of radiations. According to his theory, energy travels in a discontinuous manner. It is composed of large number of tiny discrete (separate) units called quanta.

**Postulates of Planck's Quantum theory:**

1. Energy is not emitted or absorbed continuously. It is emitted or absorbed in a discontinuous manner in the form of wave packets called quanta. In case of light, the quantum of energy is often called photon.
2. Each wave packet or quantum has a definite amount of energy.
3. A body can emit or absorb energy only in terms of quanta.
4. The energy of the quantum is directly related to the frequency of radiation by the equation

$$E \propto \nu$$

$$\text{or } E = h\nu \quad (1)$$

where  $E$  = Energy of the quantum  $\nu$  = Frequency of radiation

$$h = \text{Planck's constant} = 6.625 \times 10^{-34} \text{ Js}$$

**Properties of Waves****Frequency**

It is the number of waves, which passes through a given point in one second.

It is denoted by  $\nu$ . Its units are cycles  $\text{s}^{-1}$  or  $\text{s}^{-1}$  or Hertz (Hz).

$$1 \text{ Hz} = 1 \text{ cycles s}^{-1}$$

It is related to wavelength as

$$c = \nu \lambda \quad \text{or} \quad \nu = c / \lambda \quad (2)$$

Where  $c$  = velocity of light =  $3 \times 10^8 \text{ ms}^{-1}$

$\lambda$  = wavelength of any light radiation

**Wave Length**

It is the distance between two adjacent crests or troughs in a beam of radiation.

It is denoted by  $\lambda$ .

Its units are meter, nanometre or angstrom etc.

$$1 \text{ \AA} = 10^{-10} \text{ m}, 1 \text{ nm} = 10^{-9} \text{ m}, 1 \text{ pm} = 10^{-12} \text{ m}$$

Put eq. 2 in eq. 1

$$E = hc / \lambda \quad (3)$$

$\lambda$  is related to the wave number i.e.,  $\bar{\nu}$  as

$$\lambda = 1 / \bar{\nu} \quad (4)$$

**Wave Number**

It is the number of waves per unit distance.

It is denoted by  $\bar{\nu}$ . Its units are  $\text{m}^{-1}$  or  $\text{cm}^{-1}$  etc.

Put eq. 4 in eq. 3

$$E = hc\bar{\nu} \quad (5)$$

- Equations 1, 3 and 5 shows that energy of light is directly proportional to its frequency and wave number but inversely proportional to its wavelength.
- Greater the wave number of photons, greater is the energy associated with them
- The relationships of energy, frequency, wavelength, wave number about the photon of light are accepted by scientists and used by Bohr in his atomic model.



## Exercise Q7. (a):

Give the postulates of Bohr's atomic model. Which postulate tells us that orbits are stationary and energy is quantized?

## THE BOHR ATOMIC MODEL

In 1913, Bohr proposed a model of atom which removed the defects of Rutherford's atomic model and explained the spectrum of hydrogen atom. Bohr used Planck's quantum theory and proposed that electrons are present in hydrogen atom in certain quantized energy levels.

## Postulates of Bohr's Atomic Model

1. Electron revolves outside the nucleus in circular orbits. Each orbit has fixed energy and a quantum number.
2. Electron does not radiate energy as long as it remains in a fixed orbit. Energy is emitted or absorbed only when an electron jumps from one orbit to another orbit.
3. The electron emits energy when it jumps from an outer to an inner orbit and absorbs energy when it jumps from an inner to an outer orbit.

When an electron jumps, the energy change  $\Delta E$  is given by

$$\Delta E = h\nu = E_2 - E_1$$

4. Electron can revolve only in those orbits, which have fixed value of angular momentum ( $mvr$ ). The angular momentum of an electron in any orbit is an integral multiple of  $h/2\pi$ .

$$\text{Angular momentum} = mvr = \frac{nh}{2\pi}$$

where  $n$  = principal quantum number and its value is 1, 2, 3, ...

$v$  = velocity of electron

$r$  = radius of the electronic orbit

$m$  = mass of electron

$h$  = Planck's constant =  $6.625 \times 10^{-34}$  Js.

Thus, the permitted values of angular momenta are  $\frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi}$  etc. Hence, electron is present only in any one of these orbits and not in between them. I.e., angular momentum is quantized.

Based on these assumptions, Bohr presented a model of hydrogen atom and ions like  $\text{He}^+$ ,  $\text{Li}^{2+}$  etc.

## Exercise Q7. (b):

Derive the equation for the radius of  $n$ th orbit of hydrogen atom using Bohr's model.

## Radius of Orbit

Consider an electron of mass ' $m$ ', and charge ' $e$ ', moving in a circular orbit of radius ' $r$ ', with velocity ' $v$ ' around the nucleus of charge ' $Ze$ '. The ' $Z$ ' is the proton number (atomic number) and

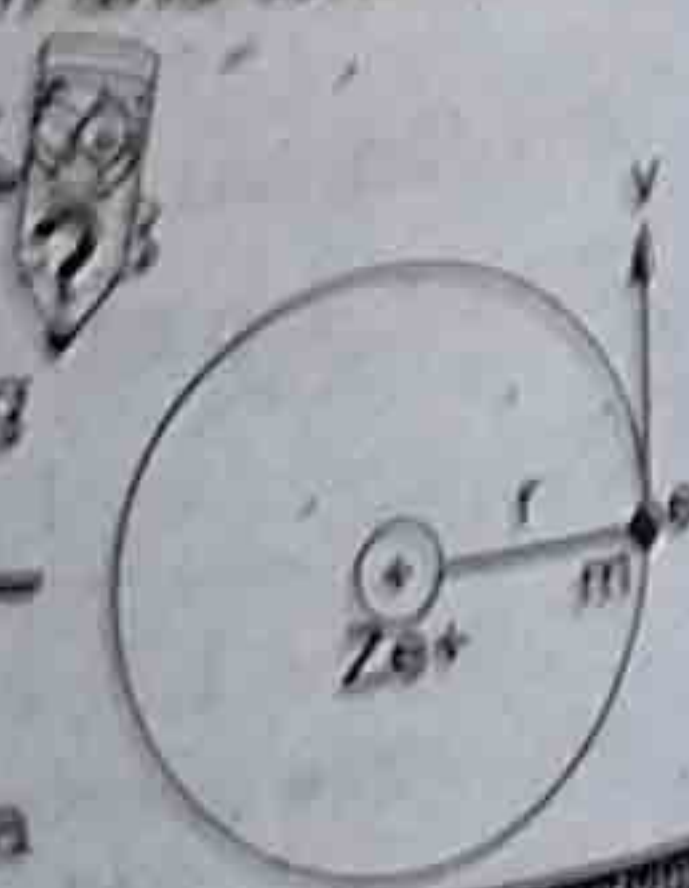


Figure: Electron revolving around the nucleus

' $e$ ' is the charge on proton.

According to Coulomb's law

The force of attraction between two charged bodies is directly proportional to the product of the magnitude of their charges, and inversely proportional to the square of distance between them.

Thus for two charges  $Q_1, Q_2$  separated by distance  $r$

$$F = \frac{Q_1 Q_2}{4\pi\epsilon_0 r^2}$$

→ The coulombic force of attraction between the nucleus and the electron provides the centripetal force for the motion of electron. It is given by

$$F = \frac{Zee}{4\pi\epsilon_0 r^2} = \frac{Ze^2}{4\pi\epsilon_0 r^2} \quad (1)$$

where  $1/4\pi\epsilon_0$  = Coulomb's law constant,

$\epsilon_0$  is the vacuum permittivity. Its value is  $8.84 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$

→ The centrifugal force acting on the electron is given by

$$F = \frac{mv^2}{r} \quad (2)$$

→ For uniform circular motion, the centripetal and the centrifugal forces balance each other. Thus

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\epsilon_0 r^2}$$

So, the equation for velocity of an electron in any orbit is

$$v^2 = \frac{Ze^2}{4\pi\epsilon_0 r m} \quad (3)$$

This eq shows that square of velocity of electron is inversely proportional to the radius of orbit. It means electrons revolve faster in an orbit of smaller radius nearer to the nucleus. As the electron moves to higher orbits of larger radius, its velocity decreases.

→ According to Bohr's postulate

$$mvr = n \frac{h}{2\pi}$$



$$v = \frac{nh}{2\pi mr}$$

Squaring on both sides

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

Comparing eq. 3 and eq. 4, we get

$$\frac{Ze^2}{4\pi\epsilon_0 r m} = \frac{n^2 h^2}{4\pi^2 m^2 r^2}$$

or

$$r = \frac{\epsilon_0 n^2 h^2}{\pi m Ze^2}$$

$$r = \frac{\epsilon_0 h^2}{\pi m e^2} \times \frac{n^2}{Z}$$

$$r = (a_0) \times \frac{n^2}{Z}$$

where

$$a_0 = \frac{\epsilon_0 h^2}{\pi m e^2} = \text{constant. Its value is } 5.29 \times 10^{-11} \text{ m or } 0.529 \text{ \AA}$$

→ For hydrogen,  $Z = 1$ , therefore

$$r = a_0 \times n^2$$

So, the equation for radius of orbits 'n' in an hydrogen atom is

$$r = 0.529 \times n^2$$

This eq. shows that radius of the orbit is directly proportional to the square of orbit number. Hence higher orbits have more radii and vice versa. It means that radius of orbits goes on increasing with increasing orbit numbers.

→ Examples:

$$\text{For } n = 1 \quad r = 0.529 \times 1^2 = 0.529 \text{ \AA}$$

$$\text{For } n = 2 \quad r = 0.529 \times 2^2 = 2.11 \text{ \AA}$$

$$\text{For } n = 3 \quad r = 0.529 \times 3^2 = 4.75 \text{ \AA}$$

$$\text{For } n = 4 \quad r = 0.529 \times 4^2 = 8.4 \text{ \AA}$$

$$\text{For } n = 5 \quad r = 0.529 \times 5^2 = 13.22 \text{ \AA}$$

Thus radius of orbits goes on increasing with increasing orbit numbers. The orbits are not equally spaced.

Hence, we have  $r_2 - r_1 < r_3 - r_2 < r_4 - r_3 < \dots$

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



### Exercise Q8:

Derive the formula for calculating the energy of an electron in nth orbit using Bohr's model. Keeping in view this formula explain the followings.

### Energy of the Revolving Electron

The total energy of an electron in an orbit is equal to the sum of its K.E. due to its motion and P.E. due to electrostatic interaction with the nucleus.

$$\text{i.e. } E = \text{K.E.} + \text{P.E.}$$

#### → Kinetic Energy

K.E. is given by

$$\text{K.E.} = \frac{1}{2} m v^2$$

$$\text{K.E.} = \frac{1}{2} m \frac{Ze^2}{4\pi\epsilon_0 r m}$$

$$\text{or K.E.} = \frac{Ze^2}{8\pi\epsilon_0 r}$$

$$\text{since } v^2 = \frac{Ze^2}{4\pi\epsilon_0 r m} \text{ from eq.(3)}$$

#### → Potential Energy

Work done is given by

$$\text{Work} = \text{Force} \times \text{distance}$$

The electrostatic force of attraction between the nucleus and the electrons is the coulombic force  $= \frac{Ze^2}{4\pi\epsilon_0 r^2}$ . If the electron moves through a small distance dr, the work done for moving electron is given by

$$\text{work} = \frac{Ze^2}{4\pi\epsilon_0 r^2} \times dr \quad (\text{work} = \text{force} \times \text{distance})$$

In order to calculate the total P.E. of electron at a distance 'r' from the nucleus, total work done is calculated in bringing electron from infinity to distance 'r'. Thus above eq. is integrated between the limits infinity and r

$$\text{Thus P.E.} = \int_{\infty}^r \frac{Ze^2}{4\pi\epsilon_0 r^2} dr$$

$$\text{P.E.} = -\frac{Ze^2}{4\pi\epsilon_0 r}$$



The minus sign indicates that the P.E. decreases when the electron is brought from infinity distance 'r'. At infinity, the electron is not attracted by any thing, thus P.E. is zero. At a point nearer to the nucleus, electron is attracted by nucleus, thus P.E. is less than zero.

→ Thus

$$\text{Total energy} = E = \text{K.E.} + \text{P.E.}$$

$$E = \frac{Ze^2}{8\pi\epsilon_0 r} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

$$E = \frac{Ze^2}{\pi\epsilon_0 r} \left( \frac{1}{8} - \frac{1}{4} \right)$$

$$E = -\frac{Ze^2}{8\pi\epsilon_0 r} \quad (6)$$

→ On substituting the value of 'r' from equation (5) in eq. (7) we get

$$E = -\frac{Ze^2}{8\pi\epsilon_0 \frac{\epsilon_0 n^2 h^2}{\pi m Z e^2}}$$

$$\text{Or } E_n = -\frac{m Z^2 e^4}{8\epsilon_0^2 n^2 h^2} \quad (7)$$

Where  $E_n$  is the energy of the electron in nth orbit.

→ Putting the values of  $m, e, \epsilon_0, h$

$$E = -2.18 \times 10^{-18} \times \frac{Z^2}{n^2} \text{ J}$$

For hydrogen atom  $Z=1$ . Thus

$$E = -2.18 \times 10^{-18} \times \frac{1}{n^2} \text{ J}$$

→ The value of energy associated with 1 mole of H (i.e. 1.008 g) will be

$$E_n = -2.18 \times 10^{-18} \times \frac{1}{n^2} \times \frac{6.02 \times 10^{23}}{1000}$$

$$\text{or } E_n = -\frac{1313.31}{n^2} \text{ kJ/mol}$$

Hence

$$\text{Since } r = \frac{\epsilon_0 n^2 h^2}{\pi m Z e^2} \text{ from eq. (5)}$$

$$\text{For } n=1 \quad E_1 = -\frac{1313.31}{1^2} = -1313.31 \text{ kJ/mol}$$

$$\text{For } n=2 \quad E_2 = -\frac{1313.31}{2^2} = -328.32 \text{ kJ/mol}$$

$$\text{For } n=3 \quad E_3 = -\frac{1313.31}{3^2} = -145.92 \text{ kJ/mol}$$

$$\text{For } n=4 \quad E_4 = -\frac{1313.31}{4^2} = -82.08 \text{ kJ/mol}$$

$$\text{For } n=5 \quad E_5 = -\frac{1313.31}{5^2} = -52.53 \text{ kJ/mol}$$

$$\text{For } n=\infty \quad E_\infty = -\frac{1313.31}{\infty^2} = 0 \text{ kJ/mol (i.e. electron is free from the nucleus)}$$

Thus, value of energy goes on increasing towards higher orbits.

→ The energy differences between adjacent orbits are

$$E_2 - E_1 = (-328.32) - (-1313.31) = 984.99 \text{ kJ/mol}$$

$$E_3 - E_2 = (-145.92) - (-328.32) = 182.40 \text{ kJ/mol}$$

$$E_4 - E_3 = (-82.08) - (-145.92) = 63.84 \text{ kJ/mol}$$

Thus, difference of energy between adjacent energy levels goes on decreasing.

$$\text{i.e. } E_2 - E_1 > E_3 - E_2 > E_4 - E_3 > \dots$$

→ The energy difference between first and infinite energy level is given as

$$E_\infty - E_1 = (0) - (-1313.31) = 1313.31 \text{ kJ/mol}$$

It is the ionization energy of the hydrogen. This value agrees well with the experimental value.

## SPECTRUM

A visual display or dispersion of the components of white light, when it is passed through a prism is called a spectrum.

Examples:

### Spectrum of White Light:

Light from sun and electric bulb consists of radiations of different wavelengths.

When this light is passed through a prism, it is separated into a band of different colours. It is because, the light of longer wavelengths bend to a smaller degree while

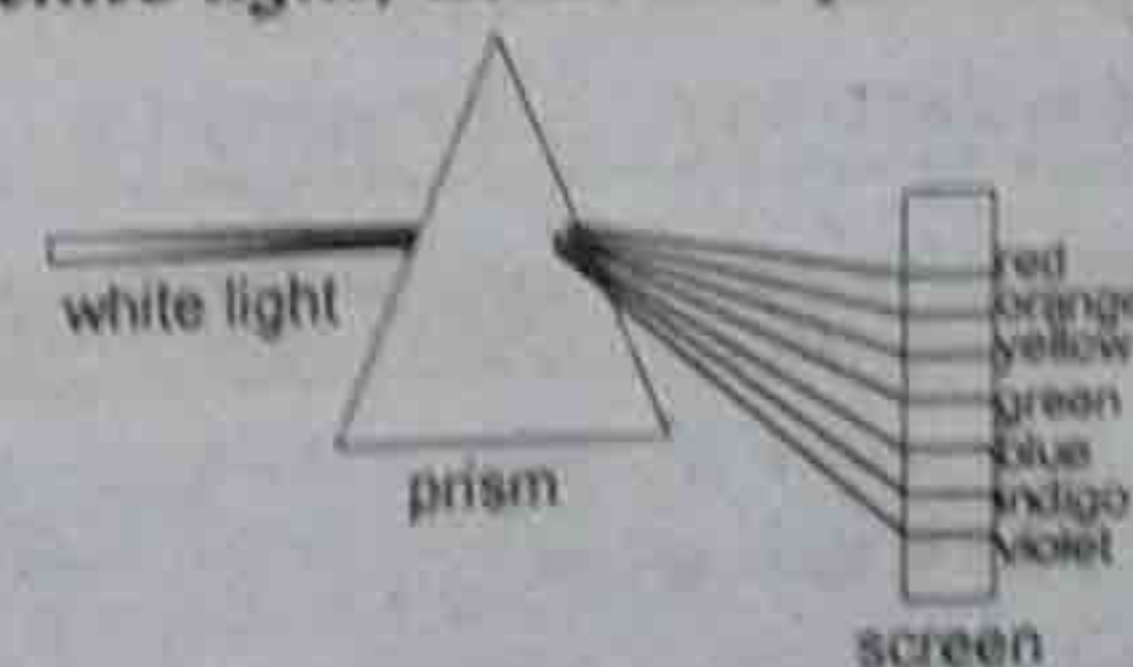
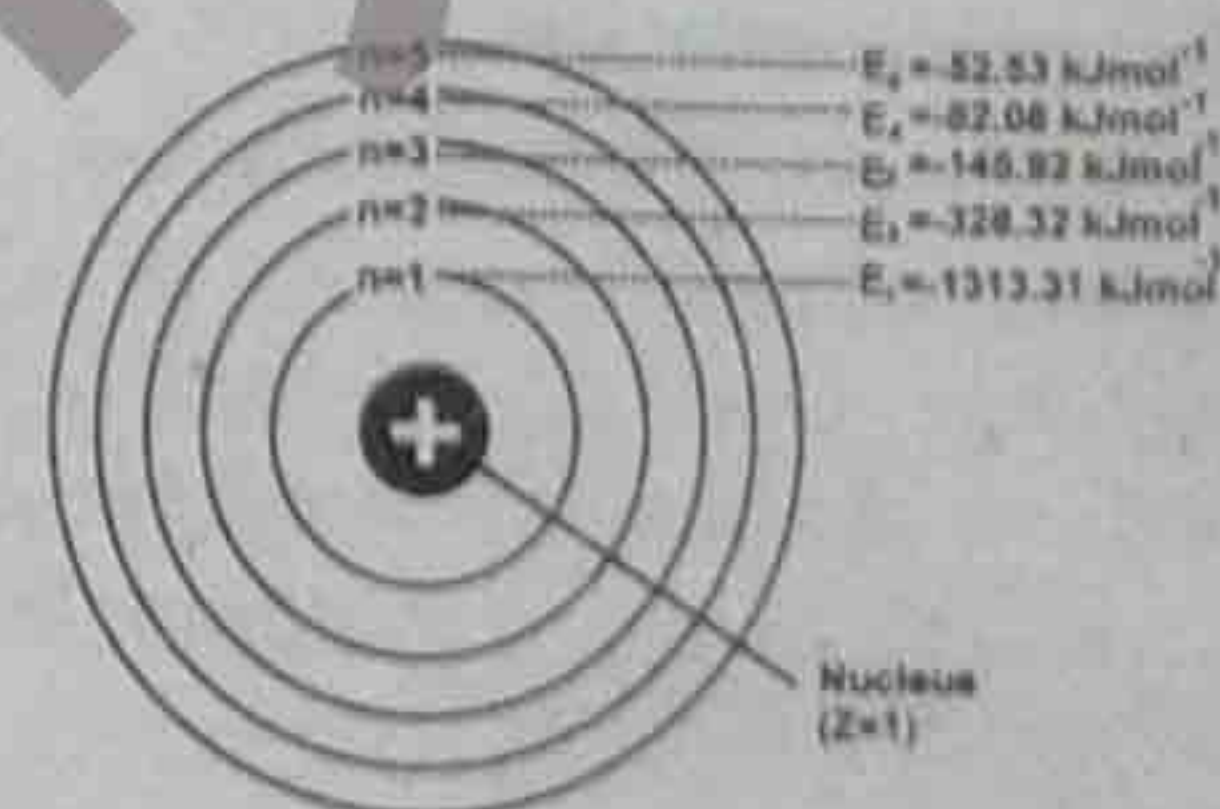


Figure: Visible Spectrum



the light of shorter wavelengths bend to a greater degree and thus different colours are obtained as shown in the figure.

### Electromagnetic Spectrum:

#### (Visible and Invisible Spectrum)

There are seven regions in electromagnetic spectrum. One is the visible region. The spectrum of white light is visible to the naked eye & is known as visible spectrum. Its range is from 400 nm to 800 nm.

Others are:

- The rays having wavelengths below violet are Ultraviolet, X-rays and  $\gamma$ -rays. These have photons with greater energy.
- Above red are infrared, microwaves and radio waves. All these are not visible to the naked eye.
- These rays form the invisible spectrum.

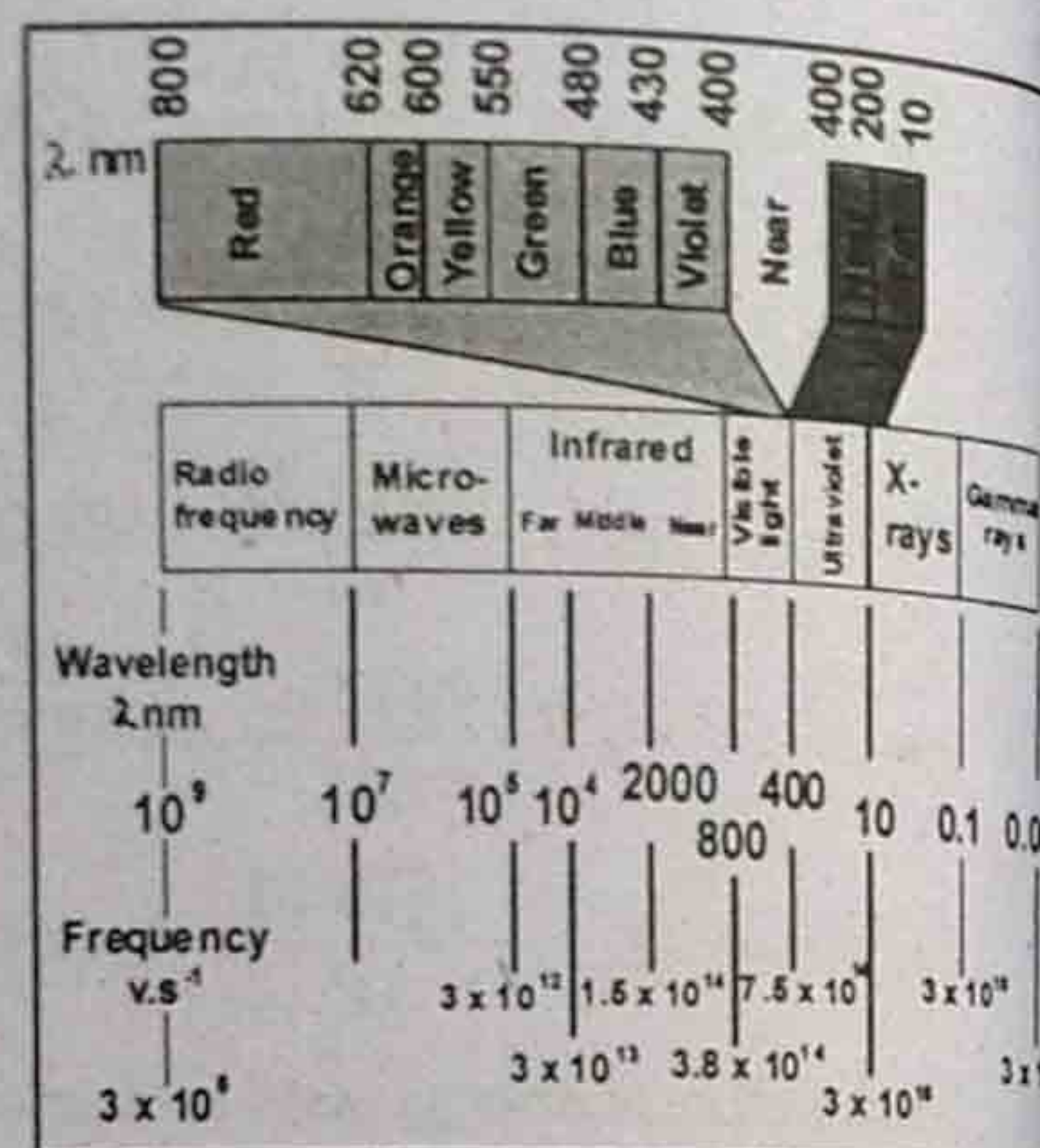


Figure: The visible and other regions of spectrum

### Types of Spectrum

There are two types of spectrum

- Continuous Spectrum e.g. Rainbow
- Line Spectrum e.g. Atomic Spectrum

#### (i) Continuous Spectrum

The spectrum in which rays of different wavelengths diffuse into one another and no definite boundary can be drawn between them is called continuous spectrum.

Example: Rainbow

It is obtained from the light emitted by the sun or incandescent (electric light) solids. It is the property of matter in bulk.



Exercise Q10. (c):

What is the origin of line spectrum?

#### (ii) Line Spectrum ( Or Atomic Spectrum )

The spectrum in which dark or bright lines are separated by bright or dark spaces called line spectrum.

#### Origin of Line Spectrum

Line spectrum is characteristic of an atom. When an element or its compound is volatilized on a flame, it emits light. When this light is seen through a spectrometer, distinct

lines are seen separated by dark spaces. The number of lines and distance between them depends upon the nature of element.

Examples:

- Line spectrum of Na consists of two yellow lines separated by a definite distance.
- Similarly, the spectrum of hydrogen consists of a number of lines of different colours separated by definite distances. In hydrogen atom spectrum, distance between lines decreases with decrease in wavelength and after certain wavelength, the spectrum becomes continuous.

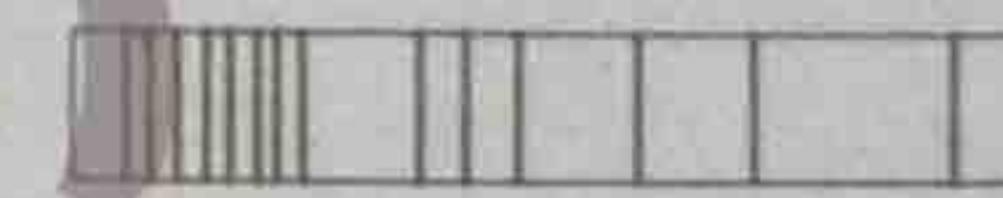


Figure: Atomic spectrum of hydrogen

### Types of Atomic or Line Spectrum

Atomic Spectrum can be of two types.

- Atomic absorption spectrum
- Atomic emission spectrum

#### Atomic Absorption Spectrum or Atomic Absorption Spectrum.

In this, dark lines are separated by bright bands.

Example: (Origin of Line [Atomic] Absorption Spectrum)

When white light is passed through a sample of a substance, it may absorb particular radiations. This light on passing through prism will form a spectrum in which dark lines will be present in place of absorbed radiations.

It has been shown in the fig.

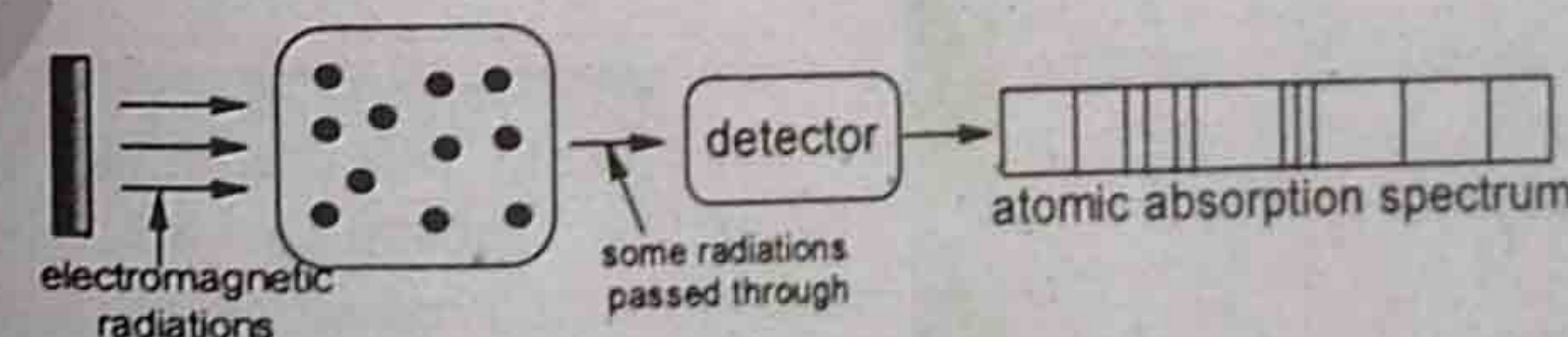


Figure: Atomic absorption spectrum

#### Atomic Emission Spectrum or Atomic Emission Spectrum.

In this, bright lines are separated by dark bands.

Example (Origin Of Atomic Emission Spectrum)

When a substance is heated or subjected to electric discharge, it emits radiations of definite wavelengths. These radiations will produce bright lines on a dark screen as shown in the figure.

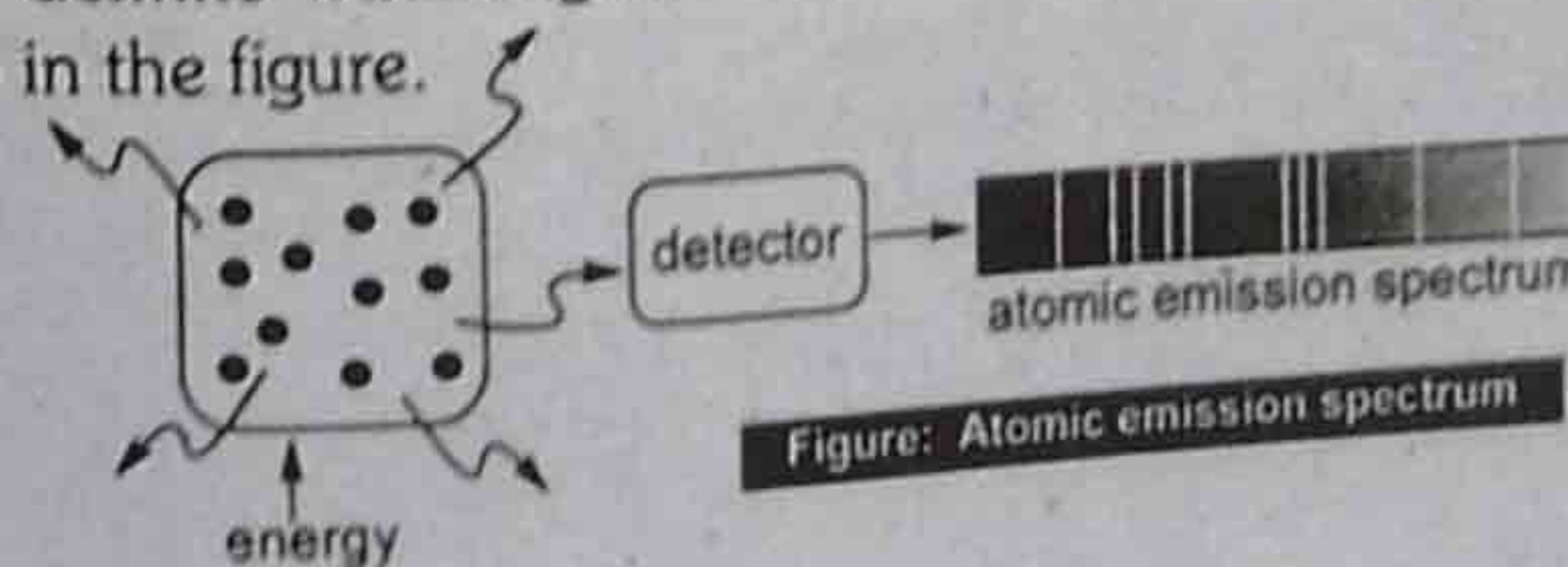


Figure: Atomic emission spectrum



**NOTE**

- The position or wavelength of lines in both emission and absorption spectrum of an element is same.
- In emission spectrum, the lines appear bright while in absorption spectrum these lines appear black.

**Exercise Q10. (a):**

What is spectrum. Differentiate between continuous spectrum and line spectrum.

Continuous Spectrum		Line Spectrum	
1	In this, coloured are diffused into each other and they are not separated.	1	It consists of dark or bright lines separated by bright or dark bands.
2	Each colour in the band has a range of frequencies.	2	Each line in the spectrum has its own characteristic colour and frequency.
3	There is not sharp boundary between the colours.	3	There is distance between the lines.
4	It is characteristic of the molecules.	4	It is characteristic of atoms.
5	It is obtained by passing polychromatic light through a triangular prism.	5	It is obtained by heating a substance or by passing polychromatic light through a substance and then passing emitted radiations through a prism.
6	It has only one type	6	It is of two types (i) line emission spectrum (ii) line absorption spectrum
7	Example Rainbow	7	Example Balmer series of hydrogen spectrum.

**Exercise Q10. (b):**

Compare line emission and line absorption spectra.



Line Emission Spectrum Or (Atomic Emission Spectrum)		Line Absorption Spectrum Or (Atomic Absorption Spectrum)	
1	In this bright lines are separated by dark bands.	1	In this dark lines are separated by bright bands.
2	It is formed when the substance is in excited state.	2	It is formed when the substance is in unexcited state.
3	It is formed when the substance is excited to vapour state	3	It is formed by transparent gases, transparent liquids and solids.
4	For its formation electron jumps from higher energy level to lower energy level and emit energy as light. The emitted radiations are indicated by coloured lines.	4	For its formation electron jumps from lower energy level to higher energy level by absorbing energy. The absorbed radiations are indicated by dark lines.
5	Emission spectrum of sodium has two yellow lines separated by dark bands.	5	Absorption spectrum of sodium has two dark lines separated by bright bands.

**Emission Spectrum of Hydrogen**

When hydrogen is filled in a discharge tube at a very low pressure, it emits bluish light. This light when seen with spectrometer shows many lines called spectral lines. These lines can be classified into five groups called spectral series.

- Lyman series (U.V. region)
- Balmer series (Visible region)
- Paschen series (I.R. region)
- Brackett series (I.R. region)
- Pfund series (I.R. region)

First four series were discovered before Bohr's atomic model. The wave number of spectral lines decreases from Lyman to Pfund series. The lines of Balmer series have been given specific names as  $H_\alpha$ ,  $H_\beta$  ... etc.



Table Wave numbers of various series of hydrogen spectrum

Lyman series (U.V. region)	Balmer series (Visible region)	Paschen series (I.R. region)	Bracket series (I.R. region)	Pfund series (I.R. region)
$82.20 \times 10^8$	$15.21 \times 10^8$ (H $\alpha$ line)	$5.30 \times 10^8$	$2.46 \times 10^8$	$1.34 \times 10^8$
$97.60 \times 10^8$	$20.60 \times 10^8$ (H $\beta$ line)	$7.80 \times 10^8$	$3.80 \times 10^8$	$2.14 \times 10^8$
$102.70 \times 10^8$	$23.50 \times 10^8$ (H $\gamma$ line)	$9.12 \times 10^8$	$4.61 \times 10^8$	
$105.20 \times 10^8$	$24.35 \times 10^8$ (H $\delta$ line)	$9.95 \times 10^8$		
$106.20 \times 10^8$	$25.18 \times 10^8$			
$107.10 \times 10^8$				

**Origin Of Hydrogen Spectrum On The Basis Of Bohr's Model**

According to Bohr's theory, when hydrogen atom is heated or subjected to electric discharge, its electron moves from lower orbit ' $n_1$ ' to higher orbit ' $n_2$ '. When this electron comes back, it emits same energy in the form of photon of light.

Five series of spectral lines are present in hydrogen atom spectrum.

Series Name	$n_1$	$n_2$	Region of Spectrum
Lyman series	1	2, 3, 4...	ultraviolet
Balmer series	2	3, 4, 5...	visible
Paschen series	3	4, 5, 6...	infrared
Brackett series	4	5, 6, 7...	infrared
Pfund series	5	6, 7, 8...	infrared

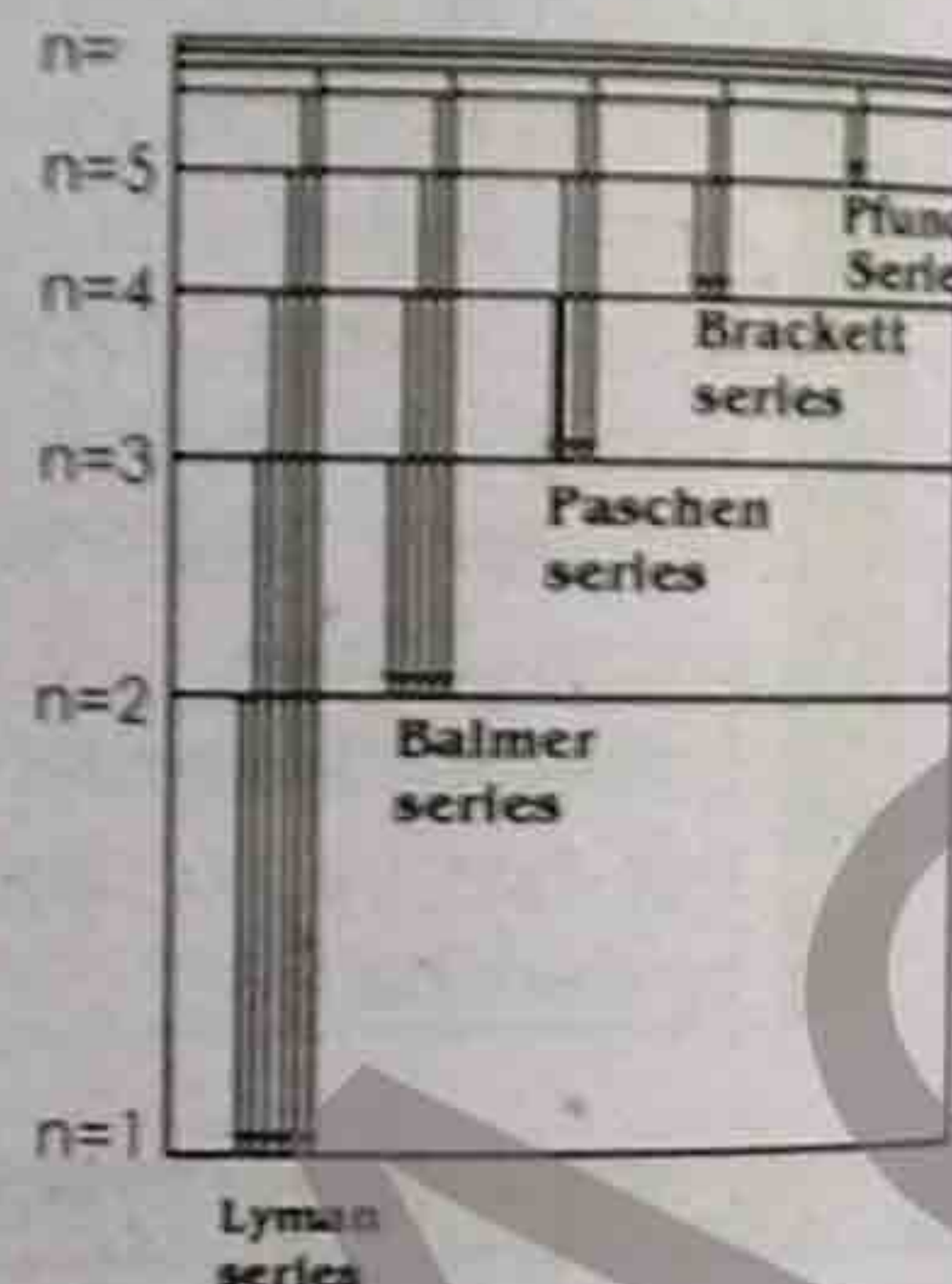


Figure: Series of spectral lines in H-atom spectrum

**Exercise Q9. (a):** Derive the following equations for hydrogen atom which are related to:



- Energy difference between two levels,  $n_1$  and  $n_2$ .
- Frequency of photon emitted which an electron jumps from  $n_2$  to  $n_1$ .
- Wave number of the photon when the electron jumps from  $n_2$  to  $n_1$ .

**Calculation of Wave Numbers of Photons of Various Spectral Series by Bohr's Theory****Energy of Photon**

→ According to Bohr's postulate, an electron emits energy in the form of photon when it jumps from higher energy orbit to lower energy orbit such that

$$\Delta E = h\nu = E_2 - E_1$$

→ Let energy of electron in higher energy orbit  $n_2$  is

$$E_2 = -\frac{mZ^2e^4}{8\epsilon_0^2n_2^2h^2}$$

and, energy of electron in lower energy orbit  $n_1$  is

$$E_1 = -\frac{mZ^2e^4}{8\epsilon_0^2n_1^2h^2}$$

So, 
$$\Delta E = E_2 - E_1 = -\frac{mZ^2e^4}{8\epsilon_0^2n_2^2h^2} - \left(-\frac{mZ^2e^4}{8\epsilon_0^2n_1^2h^2}\right) \text{ J}$$

So, 
$$\Delta E = -\frac{mZ^2e^4}{8\epsilon_0^2n_2^2h^2} + \frac{mZ^2e^4}{8\epsilon_0^2n_1^2h^2}$$

$$\Delta E = \frac{mZ^2e^4}{8\epsilon_0^2h^2} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

→ Since for hydrogen atom  $Z=1$ , therefore

$$\Delta E = 2.18 \times 10^{-18} \text{ J} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

**Frequency of Photon**

→ Since  $\Delta E = h\nu$

Therefore

$$h\nu = \frac{mZ^2e^4}{8\epsilon_0^2h^2} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\nu = \frac{mZ^2e^4}{8\epsilon_0^2h^3} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ Hz}$$

This eq shows that the frequency of photon emitted goes on decreasing between adjacent levels as we move towards higher orbits.

**Wave Number of Photon**

→ Since  $c = \nu\lambda$  or  $\nu = \frac{c}{\lambda}$  and  $\lambda = \frac{1}{\bar{\nu}}$ , therefore  $\nu = c\bar{\nu}$ , Hence

$$c\bar{\nu} = \frac{mZ^2e^4}{8\epsilon_0^2h^3} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$



→ For hydrogen atom  $Z=1$

$$\bar{\nu} = \frac{me^4}{8\epsilon_0^2 ch^3} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) m^{-1}$$

where  $R = \frac{me^4}{8\epsilon_0^2 ch^3} = 1.09678 \times 10^7 m^{-1} = \text{Rydberg constant}$



### Exercise Q9 (b):

Justify that Bohr's equation for the wave number can explain the spectral lines of Lyman, Balmer and Paschen series.

### Calculations of Wave numbers Of Various Lines Present In H-Atom Spectrum

Bohr's theory can be used to calculate the wavenumbers of spectral series of emission spectrum of hydrogen atom.

#### Lyman Series

First line  $n_1=1$  (lower orbit) &  $n_2=2$  (higher orbit)

$$\bar{\nu} = 1.09678 \times 10^7 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = 1.09678 \times 10^7 \left( \frac{1}{1^2} - \frac{1}{2^2} \right) = 82.26 \times 10^5 m^{-1}$$

Second line  $n_1=1$  &  $n_2=3$

$$\bar{\nu} = 1.09678 \times 10^7 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = 1.09678 \times 10^7 \left( \frac{1}{1^2} - \frac{1}{3^2} \right) = 97.49 \times 10^5 m^{-1}$$

Limiting line  $n_1=1$  &  $n_2=\infty$

$$\bar{\nu} = 1.09678 \times 10^7 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = 1.09678 \times 10^7 \left( \frac{1}{1^2} - \frac{1}{\infty^2} \right) = 109.678 \times 10^5 m^{-1}$$

The limiting line of Lyman series lies in UV region.

#### Balmer Series

First line  $n_1=2$  &  $n_2=3$

$$\bar{\nu} = 1.09678 \times 10^7 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = 1.09678 \times 10^7 \left( \frac{1}{2^2} - \frac{1}{3^2} \right) = 15.234 \times 10^5 m^{-1}$$

Second line  $n_1=2$  &  $n_2=4$

$$\bar{\nu} = 1.09678 \times 10^7 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = 1.09678 \times 10^7 \left( \frac{1}{2^2} - \frac{1}{4^2} \right) = 20.566 \times 10^5 m^{-1}$$

Third line  $n_1=2$  &  $n_2=5$

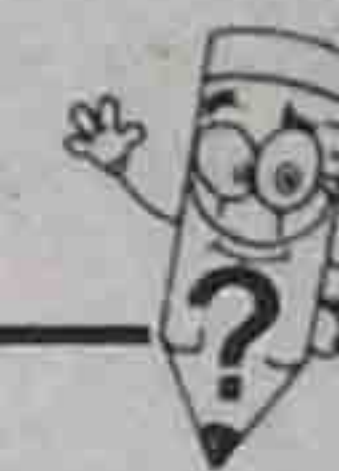
$$\bar{\nu} = 1.09678 \times 10^7 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = 1.09678 \times 10^7 \left( \frac{1}{2^2} - \frac{1}{5^2} \right) = 23.00 \times 10^5 m^{-1}$$

Limiting line  $n_1=2$  &  $n_2=\infty$

$$\bar{\nu} = 1.09678 \times 10^7 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = 1.09678 \times 10^7 \left( \frac{1}{2^2} - \frac{1}{\infty^2} \right) = 27.421 \times 10^5 m^{-1}$$

The limiting line of Balmer series lies in U.V. region, while other lines fall in visible region.

- Similarly wave numbers of other series of lines i.e. Paschen, Brackett and Pfund series can also be calculated.
- Thus, Bohr's theory explained the spectrum of hydrogen atom.



### Exercise Q13:

Point out the defects of Bohr's model. How these defects are partially covered by dual nature of electron and Heisenberg's uncertainty principle?

### Defects of Bohr's Atomic Model

Bohr's theory explains the stability of atom, ionization energy and the spectra of hydrogen and hydrogen like atoms containing one electron e.g.  $He^+$ ,  $Li^{2+}$ ,  $Be^{3+}$  etc.

It has following defects

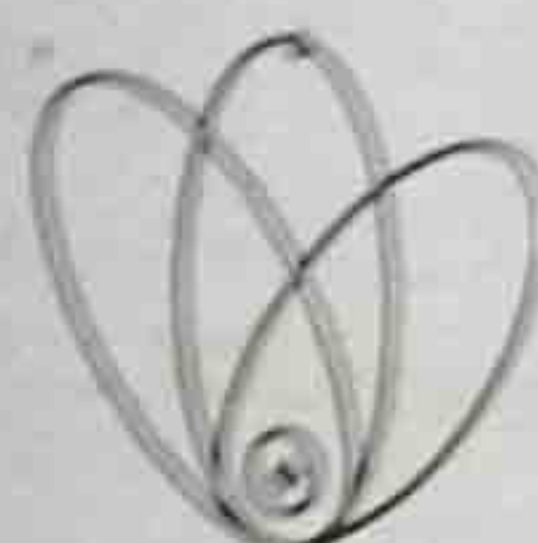
- It can not explain the spectrum of multi-electron systems like He, Li, Be etc
- High resolving spectrometer shows that individual lines in line spectrum of an atom actually consist of several lines. e.g.  $H_\alpha$ -line in Balmer series consists of five component lines. This is called fine structure or multiple lines. Bohr's theory cannot explain this fine structure. Splitting of lines shows that only principle quantum number is not sufficient. Azimuthal quantum explains the splitting of spectral lines.
- Bohr suggested circular orbits for electrons. However, researches have shown that the motion of electron around the nucleus takes place in three dimensional space. Thus atomic model is not flat
- When the spectrum of atom is taken in the magnetic field, some new lines are created. This is called Zeeman effect. e.g. when Na spectrum is taken in a weak magnetic field, its single line is split up into two component lines. Similarly, when emission spectrum of excited H-atom is taken in an electrical field, lines are split up into component lines. This is called Stark effect. Bohr's theory cannot explain Zeeman effect and Starks effect.



**Sommerfeld modification of Bohr Atomic model**

To explain Zeeman and Stark effect, Sommerfeld suggested in 1915 that electrons revolve in elliptical orbits rather than in circular orbit.

In this model, nucleus is present at one of the foci of the ellipse. The elliptical path of electron goes on changing in space and thus nucleus is covered by the electron cloud from all sides.

**Exercise Q12. (a):**

What are X-rays? What is their origin? How was the idea of atomic number derived from the discovery of X-rays?

**X-RAYS AND ATOMIC NUMBER**

When fast moving electrons strike a heavy metal anode surface in a discharge tube, some highly energetic rays are produced. These rays are called X-rays.

**Origin of X-rays**

In a gas discharge tube, electrons produced by heated tungsten filament are accelerated by high voltage. This gives them sufficient energy. Thus, when an electron suddenly stops on collision, energy is released in the form of electromagnetic waves called X-rays.

The wavelength of X-rays depends upon the nature of the target material. Every metal has its own characteristic X-rays.

**Analysis of X-rays**

When X-rays are generated, they emit in all directions. These are passed through a slit and then through aluminium window. These are then thrown on a crystal of  $K_4 [Fe(CN)_6]$ , which analyze the X-rays. The rays are diffracted from the crystal and a line spectrum of X-rays is obtained. This is taken on a photographic plate. This X-ray spectrum is characteristic of the target material. This spectrum has discrete spectral lines. These lines are grouped into K-series, L-series and M-series. Each series has various lines as  $K_\alpha$ ,  $K_\beta$ ,  $L_\alpha$ ,  $L_\beta$ ,  $M_\alpha$ ,  $M_\beta$  etc.

**Moseley's Law: Relationship of Atomic Number with X-rays**

It states,

The frequency of a spectral line in X-ray spectrum varies as the square of atomic number of the element emitting it.

$$\sqrt{\nu} = a(Z - b)$$

This linear equation is the Moseley's Law.

where  $\nu$  = frequency of emitted X-rays,

$a$  = proportionality constant

$Z$  = atomic number of element

$b$  = screening constant of the metals

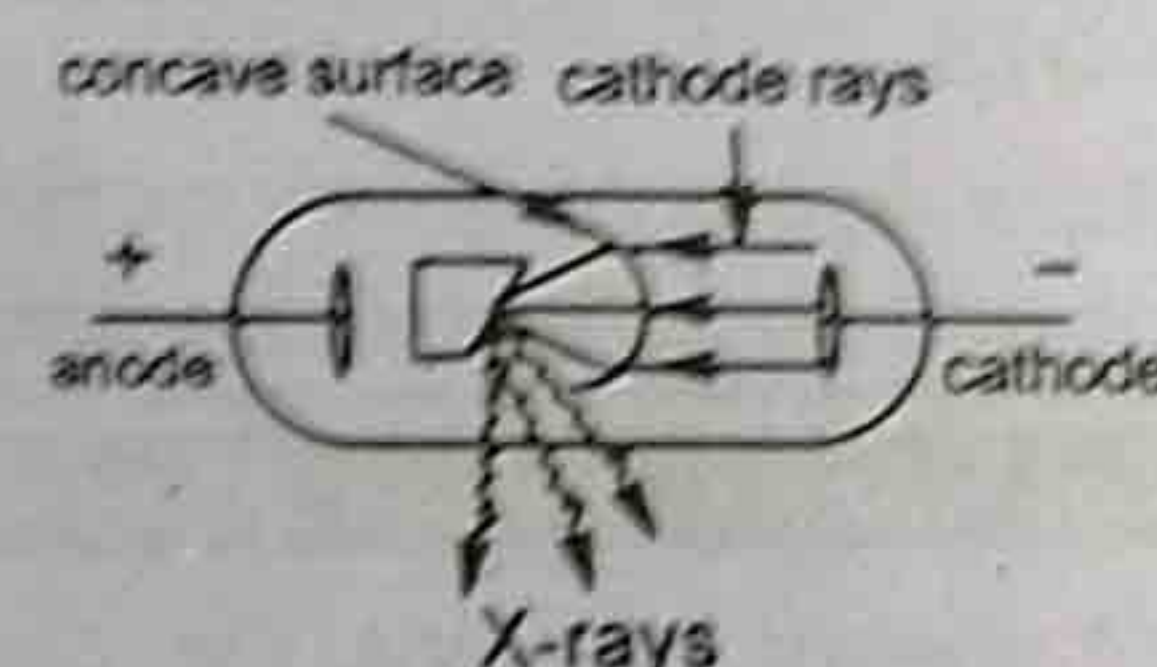


Figure: Production of X-rays

If  $\sqrt{\nu}$  for K-series is plotted against  $Z$ , a straight line is obtained.

This law shows that physical and chemical properties of an element depend upon atomic number and not on atomic mass. Hence, Modern periodic table is based upon atomic number.

**Moseley's Experiment**

In 1913 - 1914, an English Scientist, Mosley studied the X-rays emitted by various metals. He used 38 different elements from Aluminium to Gold as target and covered a wavelength range of  $0.04 - 8 \text{ \AA}$ . He obtained many useful results.

**Results of Mosley's Research**

- The emitted rays are classified into two groups
  - One with shorter wavelengths are called K-series, and
  - One with longer wavelengths are called L-series.
- Wavelength of emitted X-rays decreases with increase in atomic number of target material.
- The relationship between frequency ( $\nu$ ) of a particular line in X-rays and atomic number of the element is given by

**Importance of Moseley's Law**

- Moseley arranged K and Ar, Ni and Co in a proper way in Mendeleev periodic table.
- This law has led to the discovery of many elements e.g. Tc (43), Pm(61), Rh(45)
- The atomic number of rare earths have been determined by this law

**WAVE-PARTICLE NATURE OF MATTER (DUAL NATURE OF MATTER)****de-Broglie Hypothesis**

Einstein and Plank showed that light has both wave-like and particle-like properties.

In 1924, a French scientist, Louis de Broglie, said that all matter particles in motion also have wave-like properties. Thus, electron, proton, neutron, atoms and molecules all have both particle and wave like properties. This is called wave-particle duality.

He obtained a relationship between the wavelength and the momentum of the particle, by using Einstein & Planck equations.

Einstein eq.is

$$E = mc^2 \quad (1)$$

Plank's eq.is

$$E = h\nu \quad (2)$$



Comparing eq. (1) and (2)

$$mc^2 = hv$$

$$mc^2 = \frac{hc}{\lambda}, \quad \text{Since } v=c/\lambda$$

$$mc = \frac{h}{\lambda}$$

$$\lambda = \frac{h}{mc}$$

For a particle of mass (m) & velocity (v) the de Broglie equation will be

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

where  $p = mv$  = momentum of particle,  $h$  = Planck's constant =  $6.625 \times 10^{-34} \text{ J s}$

This equation shows that

- Particle has both wavelength ( $\lambda$ ) and momentum. i.e., it has both wave and particle properties. Thus, it has dual nature.
- The wavelength of particle is inversely proportional to its momentum.

#### Examples

- Consider an electron moving with velocity  $2.188 \times 10^6 \text{ m s}^{-1}$ . Its wavelength can be calculated as

$$\text{Mass of electron} = m = 9.108 \times 10^{-31} \text{ kg}$$

$$\text{Planck's constant} = h = 6.625 \times 10^{-34} \text{ J s}$$

$$\text{Velocity of electron} = v = 2.188 \times 10^6 \text{ m s}^{-1}$$

$$\text{Wavelength} = \lambda = ?$$

Hence

$$\lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34}}{9.108 \times 10^{-31} \times 2.188 \times 10^6}$$

$$\lambda = 0.33 \times 10^{-9} \text{ m}$$

$$\text{Or } \lambda = 0.33 \text{ nm}, \quad \text{Since } 1 \text{ nm} = 10^{-9} \text{ m}$$

- This wavelength of moving electron of first orbit of H-atom is similar to that of X-rays and can be measured.
- For a proton moving with the same velocity, wavelength would be 1836 times smaller than that of electron.

- Similarly, an  $\alpha$  - particle moving with same velocity would have wavelength, 7344 times smaller than that of electron.
- Now consider a mass of 0.001 kg (1 g) moving with a velocity of 10 m/s, its wavelength will be

$$\lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34}}{0.001 \times 10}$$

$$\lambda = 6.625 \times 10^{-32} \text{ m}$$

This wavelength is much shorter. It cannot be measured by any method.

Thus, heavier bodies also have wavelength but their wavelength can not be measured. Thus, it is said that heavier bodies do not have waves.

#### Experimental Verification of Dual Nature of Matter

##### Davisson and Germer Experiment

In 1927, two American scientists, Davisson and Germer gave experimental verification of the wave nature of electron.

They bombarded a thin Ni foil with fast moving electrons. Electrons are obtained from heated tungsten filament and accelerated by the potential difference through the charged plates. They observed that electron's diffraction was similar to the X - rays diffraction.

Moreover, they experimentally calculated the wavelength of electron, which was similar to that calculated theoretically using de-broglie eq.

Thus, Davisson and Germer verified de-broglie's eq. and dual nature of electron.

- Davisson and Germer got Nobel Prize for inventing apparatus to prove the matter waves.
- De-Broglie also got separate Noble prize for giving the equation of matter waves.

#### HEISENBERG'S UNCERTAINTY PRINCIPLE

It was given by Werner Heisenberg in 1927. It states

**It is impossible to determine simultaneously and precisely, both position and momentum of a small fast moving particle e.g. electron.**

##### Explanation

It means the more we certain about the position of a particle, the less will be the certainty about its momentum and vice versa.

Let uncertainty in position is  $\Delta x$  and uncertainty in momentum is  $\Delta p$ , then according to Heisenberg



$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

To satisfy this eq., it is clear that if uncertainty in position i.e.,  $\Delta x$  is small, uncertainty in momentum i.e.,  $\Delta p$  will be large, and vice versa.

Heisenberg uncertainty principle is negligible in case of large objects. (Macroscopic objects)

#### Explanation in terms of Compton Effect

This principal can be understood in terms of Compton Effect.

An electron is a very small particle. Therefore, to locate its position light having wavelength shorter than its size is used. (e.g. X-rays)

However, according to de-broglie equation,

$$\lambda = h / mv$$

i.e.; Photon with shorter wavelength will have high momentum. When such photon strikes an electron, it pushes the electron and disturbs its momentum. This is called Compton Effect. Thus, while determining the position of electron; we will become uncertain about the momentum of electron. If we use light of longer wavelength then determination of the position of electron becomes impossible.

Hence we cannot determine both position & momentum of electron simultaneously.

#### Comparison with Bohr's Theory

Bohr, in his theory, assumed that electrons are material particles and revolve around the nucleus in some definite orbits. Thus, their momentum and position can be determined with accuracy. But with the idea of wave nature of electron Heisenberg says that it can not be done.

#### Exercise Q14. (a):

Briefly discuss the wave mechanical model of atom. how has it given the idea of orbital. Compare orbit and orbital.  
(Rawalpindi Board, 2012)

#### Orbital

The volume of space in which chance of finding an electron is maximum (95%) is called orbital.

#### Explanation: Wave Mechanical Model of Atom

- Heisenberg uncertainty principle says that it is impossible to determine simultaneously and precisely, both position and momentum of a small fast moving particle e.g. electron.
- To overcome this problem, Schrödinger, Dirac and Heisenberg proposed wave mechanical model of atom. The best theory is that of Schrödinger.

- According to Schrödinger theory, electron is considered as a standing wave and it does not occupy a definite position in space. Schrödinger gave a wave equation, which gives probability of finding electrons in various regions in an atom. These regions are called orbitals.

Example: For H-atom, the maximum probability of finding electron is at a distance of 0.053 nm from the nucleus.

This is the same distance as calculated by Bohr for the 1<sup>st</sup> orbit of H-atom.

Hence, for a distance shorter or longer than 0.053 nm, probability of finding electron decreases sharply in a hydrogen atom.

The orbital is actually a spread of charge around the nucleus. It is often called electron cloud.

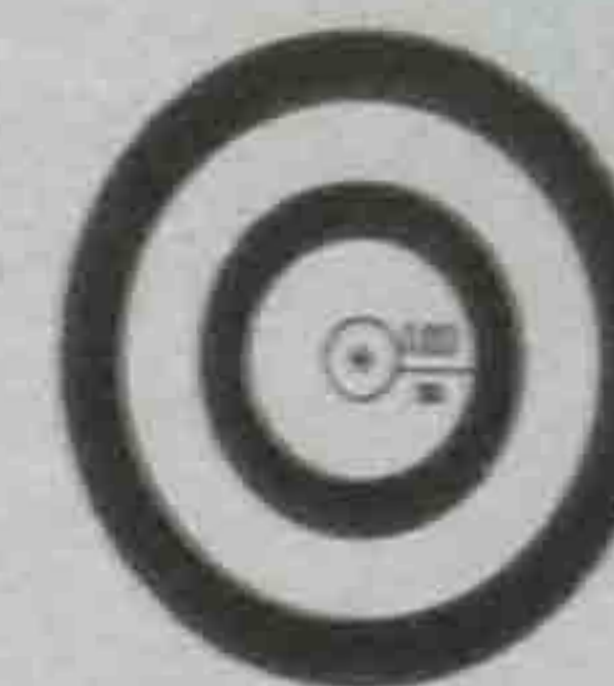


Figure: Probable electron density diagram for H-atom

Orbit	Orbital
1 It is the circular path on which electron revolves around the nucleus.	1 It is the region in space in which probability of finding electron is maximum (about 95%)
2 This term is used in the Bohr's theory of atomic structure.	2 This term is used in quantum mechanical model.
3 It is two dimensional	3 It is three dimensional
4 Number of electrons in an orbit is given by the formula, $2n^2$ . Where 'n' is the number of orbit.	4 Each orbital contains maximum two electrons.
5 In this exact position of electron is indicated.	5 Only probability of electron is given in an orbital.

#### Exercise Q14. (b):

What are quantum numbers? Discuss their significance.

#### QUANTUM NUMBERS

The behaviour of electrons in space around the nucleus is described by a set of four numbers called quantum numbers.

Quantum numbers are sets of numerical values which give acceptable solutions to Schrödinger equation for hydrogen atom.

Three quantum numbers are obtained by solving Schrödinger wave equation while spin quantum number is due to the two different orientations of electron in a magnetic field. i.e., clockwise & anticlockwise.

Four quantum numbers are



**(1) Principal Quantum Number (n)**

It gives information about Shells.

- It shows the approximate distance of electron from the nucleus of an atom.
- It is denoted by 'n'. Its value are:  $n=1, 2, 3, \dots$
- Value of 'n' tells about the energy and distance of electron from the nucleus.

Greater the value of n, greater will be the energy and distance of electron from the nucleus & vice versa. It is the measure of size of electronic shell.

- The value of n corresponds to a definite shell e.g.
- The electrons in a shell can be determined by the formula  $2n^2$

n	Shell	Capacity ( $2n^2$ )
1	K	$2 \times 1^2 = 2$
2	L	$2 \times 2^2 = 8$
3	M	$2 \times 3^2 = 18$
4	N	$2 \times 4^2 = 32$

**(2) Azimuthal Quantum Number (l)**

It gives information about Sub-shells

**Origin of Azimuthal Quantum Number**

- A spectrometer of high resolving power shows that an individual line in a line spectrum of an atom is actually further divided into several fine lines. It means that an individual shell is further divided into several sub-shells.

These sub-shells are explained in terms of azimuthal quantum number.

- Azimuthal quantum number is denoted by "l"
- It has value from  $0, 1, 2, 3, \dots (n-1)$ .
- The numbers  $0, 1, 2, 3, \dots$  corresponds for various subshells

Examples:

0 stands for s-subshell means 'sharp'

1 stands for p-subshell means 'principle'

2 stands for d-subshell means 'diffused'

3 stands for f-subshell means 'fundamental'

These terms are used to describe the series of lines in the spectrum.

**Number of Electrons in a Sub-Shell**

It describes the shape of a subshell in which the electron is present.

Maximum number of electrons in a subshell can be obtained by using the formula  $2(2l + 1)$

Thus for

$$l = 0 \quad \text{s-subshell } 2(2 \times 0 + 1) = 2 \text{ electrons}$$

$$l = 1 \quad \text{p-subshell } 2(2 \times 1 + 1) = 6 \text{ electrons}$$

$$l = 2 \quad \text{d-subshell } 2(2 \times 2 + 1) = 10 \text{ electrons}$$

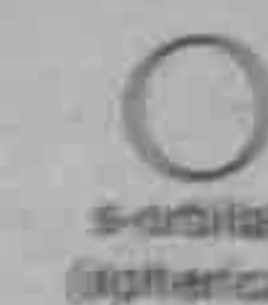
$$l = 3 \quad \text{f-subshell } 2(2 \times 3 + 1) = 14 \text{ electrons}$$

**Shape of Sub-Shells**

Value of "l" also tells about the shape of orbital

A brief summary is given below

"l"	Subshell	Shape	Maximum number of Electrons
0	s	spherical	2
1	p	dumbbell	6
2	d	sausage	10
3	f	complex	14



s-orbital (spherical)



p-orbital (dumbbell)



d-orbital (sausage)

**Relationship between Principal and Azimuthal Quantum No.**

The relationship is as follows

n	Shell	l	Subshell
1	K	0	s (1s)
2	L	0	s (2s)
		1	p (2p)
3	M	0	s (3s)
		1	p (3p)
		2	d (3d)
4	N	0	s (4s)
		1	p (4p)
		2	d (4d)
		3	f (4f) etc.
		4	

**(3) Magnetic Quantum Number (m)**

It gives information about the different orientation of orbitals in space.



**Origin of Magnetic Quantum Number**

- In the presence of magnetic field, lines in the line spectrum of an atom are further split up into various very fine lines. The appearance of these lines is explained by magnetic quantum number.
- It is represented by 'm'.
- It gives the orientation and degeneracy of the orbital in space. Hence, it is also called orbital orientation quantum number.
- It has value from  $m = -\ell \dots 0 \dots +\ell$  or  $m = 0, \pm\ell, \dots$
- The value of 'm' shows the different ways in which a particular orbital can be arranged in space. e.g.

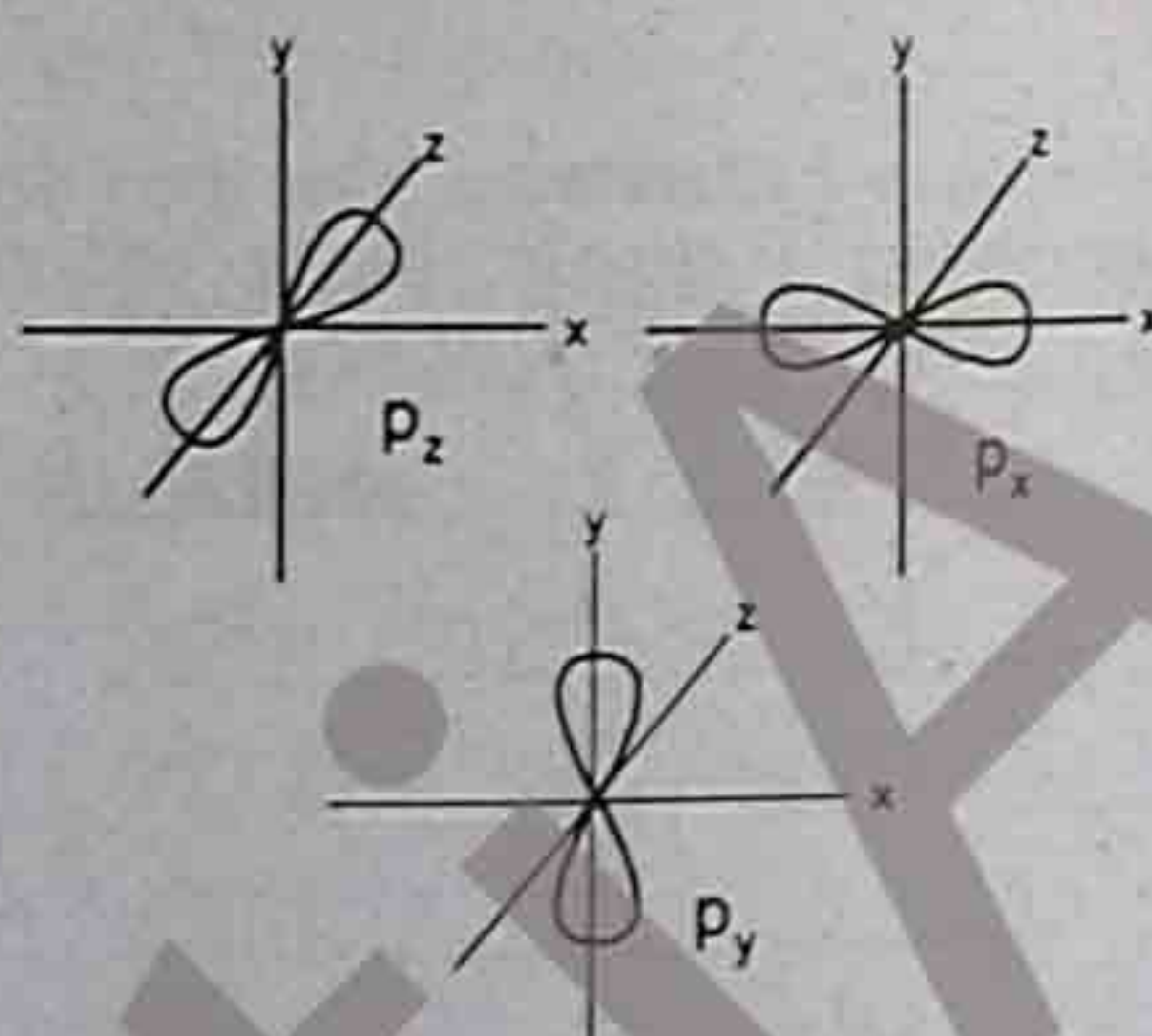
**Examples:**

(i) When  $\ell = 0$ , s-subshell,  $m = 0$

It shows that s-orbital can be arranged in space only in one way. Thus, it is not further sub-divided into other orbitals. It is a spherical and symmetrical orbital. In this probability of finding electron is same in all directions.

(ii) When  $\ell = 1$ , p-subshell,  $m = -1, 0, +1$

It means that p-orbital have three possible orientations in space. Thus, p-orbital is further sub-divided into three orbitals along X, Y and Z-axis. These are written as  $p_x, p_y, p_z$ . These three orbitals are present perpendicular to each other.



In the absence of magnetic field all the three p-orbitals have same energy. These are called 3-fold degenerate or triply degenerate orbitals.

(iii) When  $\ell = 2$ , d-subshell,  $m = -2, -1, 0, +1, +2$

Thus, d-subshell is 5-fold degenerate.

(iv) When  $\ell = 2$ , d-subshell,  $m = -3, -2, -1, 0, +1, +2, +3$

Thus, f-subshell is 7-fold degenerate etc.

**Formula for number of possible orientation of orbitals**

For a given value of ' $\ell$ ', the total values of 'm' are  $(2\ell + 1)$

Thus for $\ell = 0$	s-subshell	$(2 \times 0 + 1) = 1$ orientation
$\ell = 1$	p-subshell	$(2 \times 1 + 1) = 3$ orientation
$\ell = 2$	d-subshell	$(2 \times 2 + 1) = 5$ orientation
$\ell = 3$	f-subshell	$(2 \times 3 + 1) = 7$ orientation

**Relationship between Principal, Azimuthal and Magnetic Quantum Nos.**

The relationship is given below

n	$\ell$	m		
1	0	0	1s	
2	0	0	2s	
		1	-1 2p <sub>x</sub>	Three Possible Orientations of orbitals
		0	2p <sub>y</sub>	
		+1	2p <sub>z</sub>	
3	0	0	3s	
	1	-1	3p <sub>x</sub>	Three Possible Orientations of p-orbitals
		0	3p <sub>y</sub>	
		+1	3p <sub>z</sub>	
	2	-2	3d <sub>xy</sub>	Five Possible Orientations of d-orbitals
		-1	3d <sub>yz</sub>	
		0	3d <sub>z<sup>2</sup></sub>	
		+1	3d <sub>xz</sub>	
		+2	3d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	

**(4) Spin Quantum Number(s)**

It describes the spin of electron in an atom. It is denoted by s.

**Origin of Spin Quantum Number**

- Alkali metals have one electron in their valence shell. When this electron jumps from the excited state to the ground state, it emits light and forms a line spectrum. High resolving spectrometer shows that each line in the line emission spectrum consists of two lines. This is called doublet structure. This doublet structure is different from the fine line structure, which is explained by azimuthal quantum number.
- The lines explained by azimuthal quantum number are closely spaced, while in doublet structure two lines are widely spaced.
- In 1925, Goudsmit and Uhlenbeck suggested, that an electron also revolve about its axis. This is called self-rotation. It may be clockwise or anticlockwise. So an electron generates two opposite magnetic fields due to two opposite spins. This spin motion produces doublet line structure in the emission spectrum of an atom. It can be explained by spin quantum number.
- The spin quantum number of an electron may be  $+\frac{1}{2}$  or  $-\frac{1}{2}$

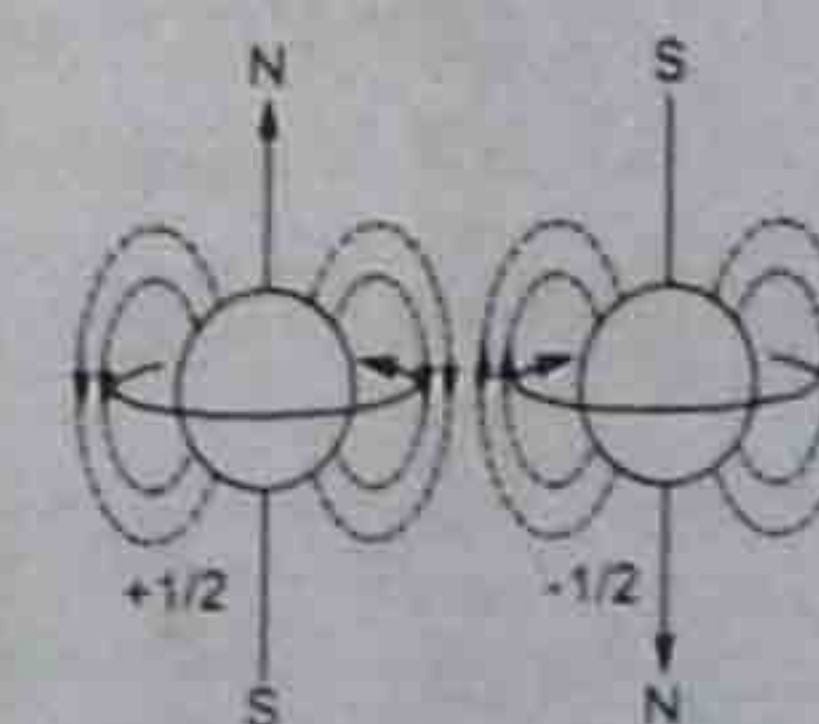




Table 5.3 Quantum numbers of electrons

		Azimuthal Quantum number 'l'	Magnetic Quantum number 'm'	Spin Quantum number 's'	Number of electrons accommodated
1	K	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2
2	L	0, 1	0, $+1, 0, -1$	$+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$	2 6
3	M	0, 1, 2	0, $+1, 0, -1$ $+2, +1, 0, -1, -2$	$+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$	2 6 10
4	N	0, 1, 2, 3	0, $+1, 0, -1$ $+2, +1, 0, -1, -2$ $+3, +2, +1, 0, -1, -2, -3$	$+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$	2 6 10 14

**Exercise Q16:** Draw the shapes of s, p and d-orbitals. Justify these by keeping in view the azimuthal and magnetic quantum numbers.

### SHAPES OF ORBITALS

The shapes of orbitals can be explained on the basis of azimuthal and magnetic quantum number.

Consider the shapes of s, p and d-orbitals

#### Shape of s-Orbital

There is only one value of magnetic quantum number for s-orbital. Thus it has only one orbital.

s-orbital is spherical in shape. It is represented by a circle as shown in figure.

Size of s-orbitals increase with increase in the value of principal quantum number (n). Thus 2s orbital is larger in size than 1s orbital and 3s orbital is larger in size than 2s orbital.

The probability of finding electron is zero between two orbitals. This region is called nodal plane or nodal surface.

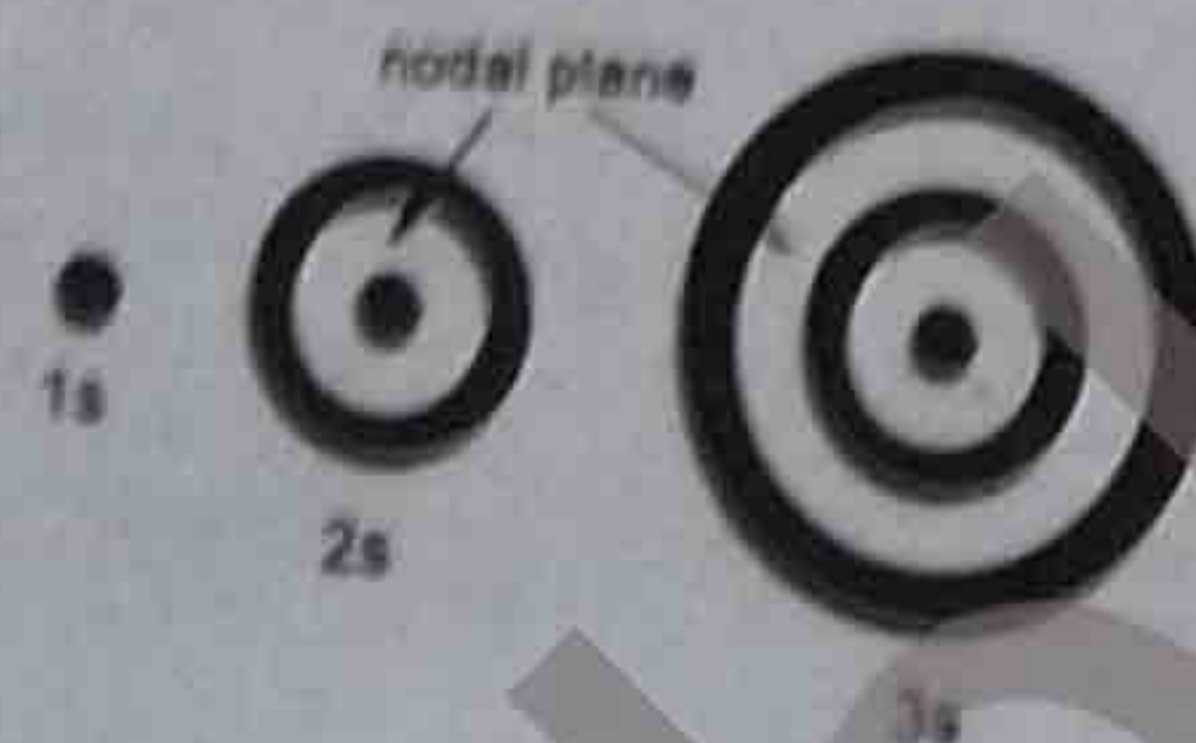


Figure: Shapes of s-orbitals

#### Shape of p-Orbital

There are three values of magnetic quantum number for p-subshell. Thus, it has three orientations in space along three axes X, Y and Z.

These three orbitals are written as  $p_x$ ,  $p_y$  and  $p_z$  as shown in figure. These three orbitals are present perpendicular to each other.

p-orbital has directional nature. Thus it gives definite shape to molecules.

All the p-orbitals have similar shapes.

But the size of p-orbital increases with increase in value of principal quantum number.

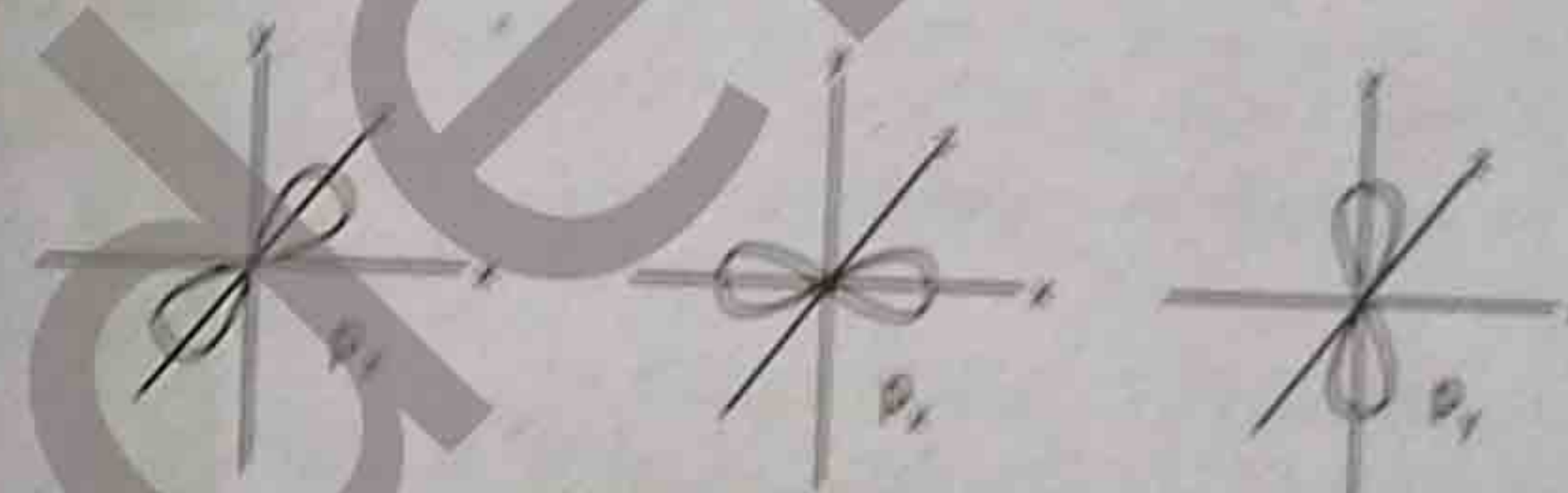


Figure: Shapes of p-orbital

#### Shapes of d-Orbitals

There are five values of magnetic quantum number for d-orbital. Thus it has five orientations in space.

These five orbitals are written as  $d_{xy}$ ,  $d_{xx}$ ,  $d_{yz}$ ,  $d_{z^2-y^2}$  and  $d_{z^2}$ .

All the five orbitals do not have same shape.  $d_{xy}$ ,  $d_{xx}$ ,  $d_{yz}$  and  $d_{z^2-y^2}$  have four lobes each, while  $d_{z^2}$  have only two lobes and a doughnut at the centre.

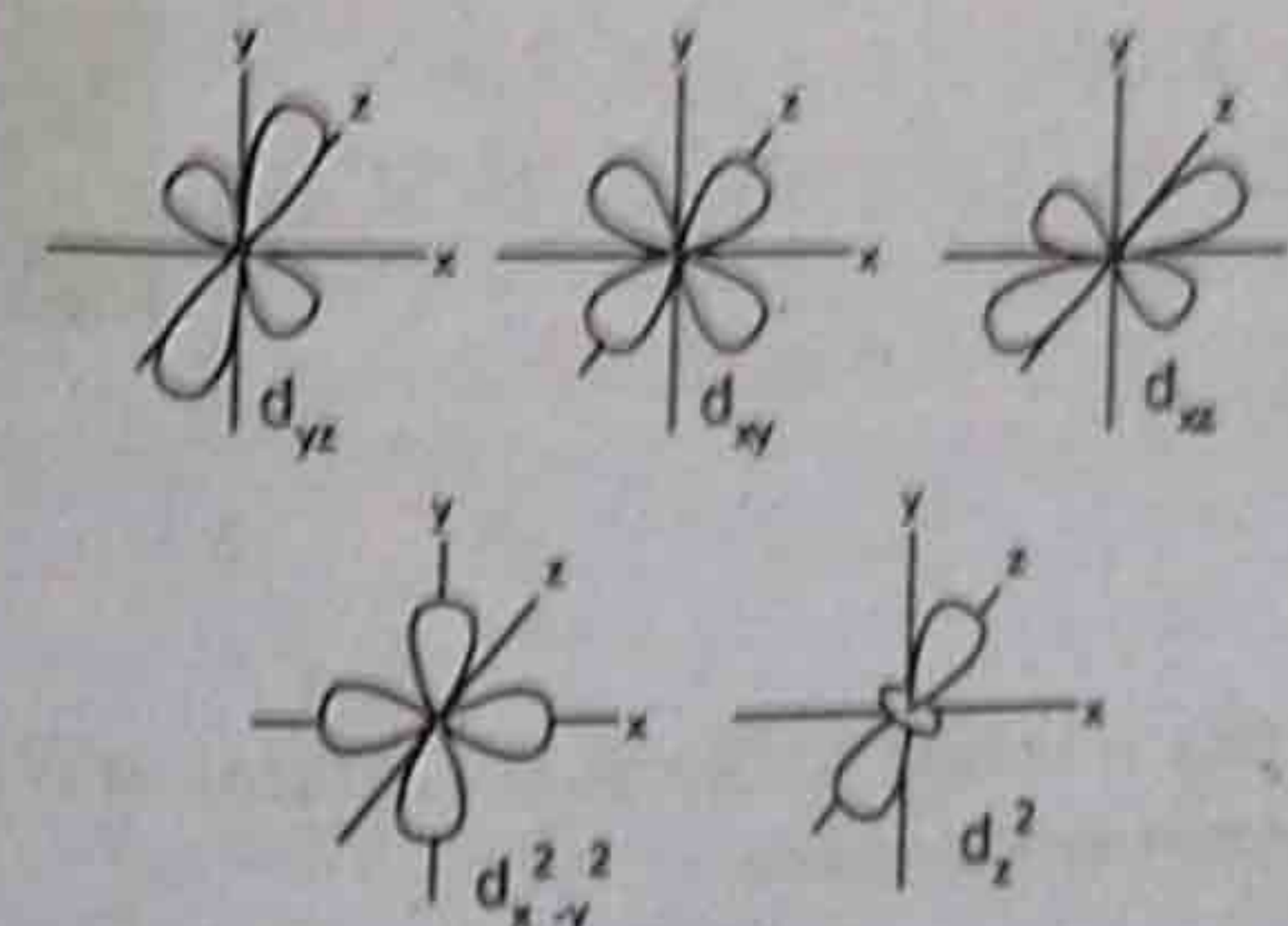


Figure: Shapes of d-orbitals

Shape of f-orbitals is very complicated



**Exercise Q15. (a):**

Discuss rules for the distribution of electrons in energy sub-levels and in orbitals.

**ELECTRONIC DISTRIBUTIONS**

1. An orbital like s, p<sub>x</sub>, p<sub>y</sub>, p<sub>z</sub> and d<sub>xy</sub> etc. can have maximum two electrons.
2. The maximum number of electrons in a shell is calculated by the formula  $2n^2$ , where 'n' is the orbit number.

There are some rules for the distribution of electrons in different sub-shells.

**(1) Aufbau Principle**

According to Aufbau (German word, Building up) principle

**Electrons are filled in subshells in order of increasing energy values.**

- The energy of orbital is determined from the  $(n+l)$  rule.
- Lower the  $(n+l)$  value lower will be the energy of orbital & vice versa.
- If two orbital have same  $(n+l)$  value then lower the value of n lower will be the energy of orbital & vice versa.

**Examples**

Orbital	$(n+l)$ value	n value	Remarks
4s	$4+0=4$	4	Thus, 4s is of
3d	$3+2=5$	3	lower energy
4p	$4+1=5$	4	Thus, 3d is of
3d	$3+2=5$	3	lower energy

Thus on the basis of this rule, order of filling of orbitals will be

1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f 6d 7p...

**(2) Pauli's Exclusion Principle**

According to this principle

**It is impossible for two electrons residing in the same orbital of a poly-electron atom to have the same values of four quantum numbers.**

or

**Two electrons in the same orbital should have opposite spin ( $\uparrow\downarrow$ )**

**Example**

Consider 1s orbital.

For a single electron in this orbital

Table 5.4 Arrangement of orbitals according to  $n+l$  rule

	n	l	n+l
1s	1	0	$1+0=1$
2s	2	0	$2+0=2$
2p	2	1	$2+1=3$
3s	3	0	$3+0=3$
3p	3	1	$3+1=4$
3d	3	2	$3+2=5$
4s	4	0	$4+0=4$
4p	4	1	$4+1=5$
4d	4	2	$4+2=6$
4f	4	3	$4+3=7$
5s	5	0	$5+0=5$
5p	5	1	$5+1=6$
5d	5	2	$5+2=7$
5f	5	3	$5+3=8$
6s	6	0	$6+0=6$
6p	6	1	$6+1=7$
6d	6	2	$6+2=8$
6f	6	3	$6+3=9$
7s	7	0	$7+0=7$

$$n=1 \quad l=0 \quad m=0 \quad \text{let } s = +1/2 \text{ indicated by } \uparrow$$

Another electron enters in this orbital only if it has opposite spin to that of first.

Thus for this second electron

$$n=1 \quad l=0 \quad m=0 \quad \text{let } s = -1/2 \text{ indicated by } \downarrow$$

Thus two electrons in an orbital will have opposite spin indicated by  $\uparrow\downarrow$  and their one quantum number i.e.; spin quantum number will be different.

The arrangements  $\uparrow\uparrow$  and  $\downarrow\downarrow$  are not possible.

Orbital containing two electrons with opposite spin is called completely filled orbital and electrons are said to be paired.

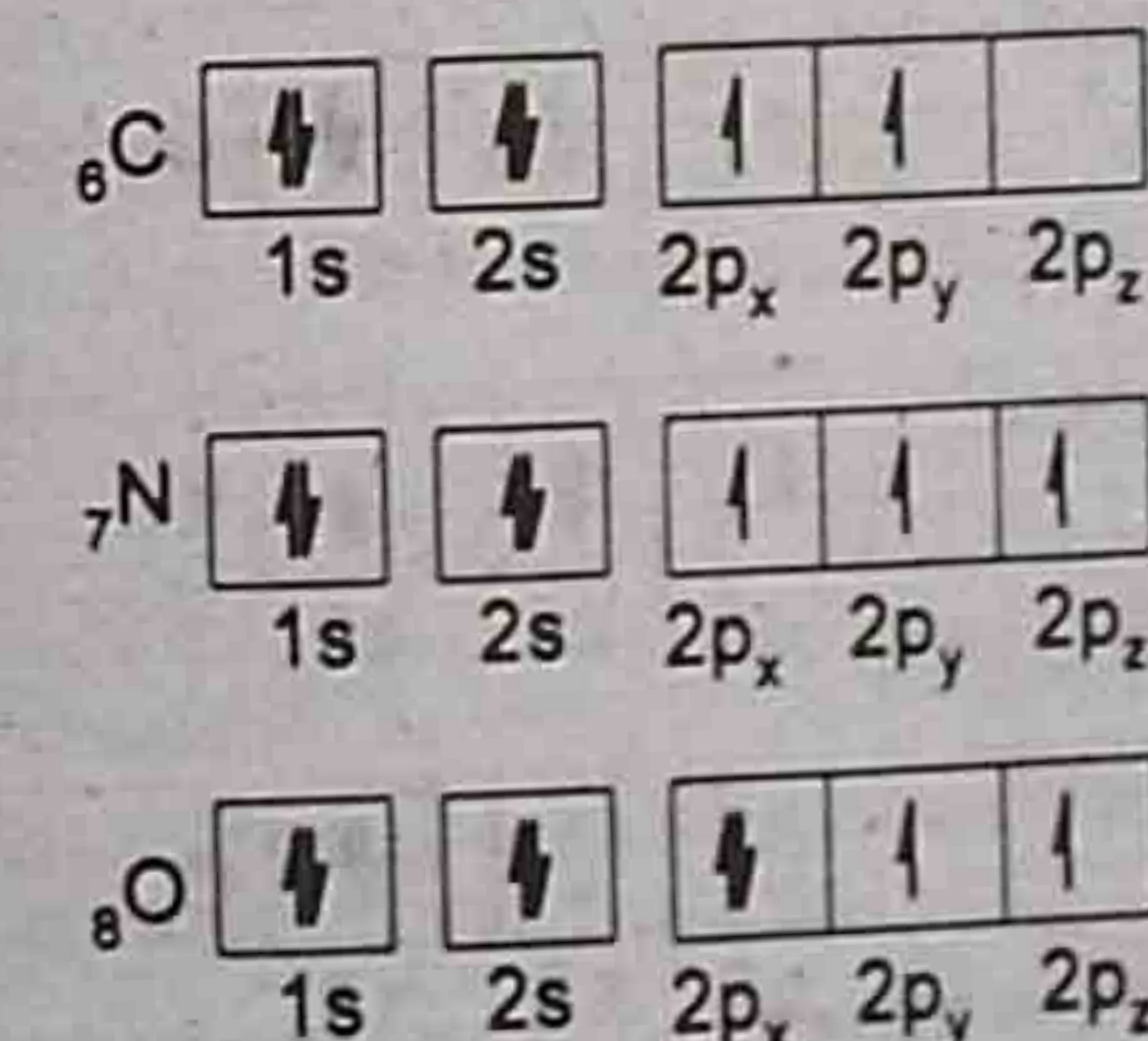
Orbital containing one electron is called half-filled orbital & electron is said to be unpaired.

**(3) Hund's Rule**

According to this rule

**If orbitals of same energy are available, then electrons will go in separate orbitals with same spin, rather than in same orbital with opposite spin.**

In other words, electrons are distributed in an atom in such a way to give maximum number of unpaired electrons.

**Examples:**



## Electronic Configuration of Elements

Table 5.5 Electronic configuration of elements

	Atomic number	Electron Configuration Notation
Hydrogen	1	1s <sup>1</sup>
Helium	2	1s <sup>2</sup>
Lithium	3	1s <sup>2</sup> 2s <sup>1</sup>
Beryllium	4	1s <sup>2</sup> 2s <sup>2</sup>
Boron	5	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>1</sup> <sub>x</sub> 2p <sup>0</sup> <sub>y</sub> 2p <sup>0</sup> <sub>z</sub>
Carbon	6	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>1</sup> <sub>x</sub> 2p <sup>1</sup> <sub>y</sub> 2p <sup>0</sup> <sub>z</sub>
Nitrogen	7	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>1</sup> <sub>x</sub> 2p <sup>1</sup> <sub>y</sub> 2p <sup>1</sup> <sub>z</sub>
Oxygen	8	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>2</sup> <sub>x</sub> 2p <sup>1</sup> <sub>y</sub> 2p <sup>1</sup> <sub>z</sub>
Fluorine	9	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>2</sup> <sub>x</sub> 2p <sup>2</sup> <sub>y</sub> 2p <sup>1</sup> <sub>z</sub>
Neon	10	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>2</sup> <sub>x</sub> 2p <sup>2</sup> <sub>y</sub> 2p <sup>2</sup> <sub>z</sub>
Sodium	11	[Ne] 3s <sup>1</sup>
magnesium	12	[Ne] 3s <sup>2</sup>
Aluminum	13	[Ne] 3s <sup>2</sup> 3p <sup>1</sup> <sub>x</sub> 3p <sup>0</sup> <sub>y</sub> 3p <sup>0</sup> <sub>z</sub>
Silicon	14	[Ne] 3s <sup>2</sup> 3p <sup>1</sup> <sub>x</sub> 3p <sup>1</sup> <sub>y</sub> 3p <sup>0</sup> <sub>z</sub>
Phosphorus	15	[Ne] 3s <sup>2</sup> 3p <sup>1</sup> <sub>x</sub> 3p <sup>1</sup> <sub>y</sub> 3p <sup>1</sup> <sub>z</sub>
Sulphur	16	[Ne] 3s <sup>2</sup> 3p <sup>2</sup> <sub>x</sub> 3p <sup>1</sup> <sub>y</sub> 3p <sup>1</sup> <sub>z</sub>
Chlorine	17	[Ne] 3s <sup>2</sup> 3p <sup>2</sup> <sub>x</sub> 3p <sup>2</sup> <sub>y</sub> 3p <sup>1</sup> <sub>z</sub>
Argon	18	[Ne] 3s <sup>2</sup> 3p <sup>2</sup> <sub>x</sub> 3p <sup>2</sup> <sub>y</sub> 3p <sup>2</sup> <sub>z</sub>
Potassium	19	[Ar] 4s <sup>1</sup>
Calcium	20	[Ar] 4s <sup>2</sup>
Scandium	21	[Ar] 4s <sup>2</sup> 3d <sup>1</sup> <sub>xy</sub> 3d <sup>0</sup> <sub>yz</sub> 3d <sup>0</sup> <sub>xz</sub> 3d <sup>0</sup> <sub>2-2</sub> 3d <sup>0</sup> <sub>z</sub>
Titanium	22	[Ar] 4s <sup>2</sup> 3d <sup>1</sup> <sub>xy</sub> 3d <sup>1</sup> <sub>yz</sub> 3d <sup>0</sup> <sub>xz</sub> 3d <sup>0</sup> <sub>2-2</sub> 3d <sup>0</sup> <sub>z</sub>
Vanadium	23	[Ar] 4s <sup>2</sup> 3d <sup>1</sup> <sub>xy</sub> 3d <sup>1</sup> <sub>yz</sub> 3d <sup>1</sup> <sub>xz</sub> 3d <sup>0</sup> <sub>2-2</sub> 3d <sup>0</sup> <sub>z</sub>
Chromium	24	[Ar] 4s <sup>1</sup> 3d <sup>1</sup> <sub>xy</sub> 3d <sup>1</sup> <sub>yz</sub> 3d <sup>1</sup> <sub>xz</sub> 3d <sup>1</sup> <sub>2-2</sub> 3d <sup>1</sup> <sub>z</sub>
Manganese	25	[Ar] 4s <sup>2</sup> 3d <sup>1</sup> <sub>xy</sub> 3d <sup>1</sup> <sub>yz</sub> 3d <sup>1</sup> <sub>xz</sub> 3d <sup>1</sup> <sub>2-2</sub> 3d <sup>1</sup> <sub>z</sub>
Iron	26	[Ar] 4s <sup>2</sup> 3d <sup>2</sup> <sub>xy</sub> 3d <sup>1</sup> <sub>yz</sub> 3d <sup>1</sup> <sub>xz</sub> 3d <sup>1</sup> <sub>2-2</sub> 3d <sup>1</sup> <sub>z</sub>
Cobalt	27	[Ar] 4s <sup>2</sup> 3d <sup>2</sup> <sub>xy</sub> 3d <sup>2</sup> <sub>yz</sub> 3d <sup>1</sup> <sub>xz</sub> 3d <sup>1</sup> <sub>2-2</sub> 3d <sup>1</sup> <sub>z</sub>
Nickel	28	[Ar] 4s <sup>2</sup> 3d <sup>2</sup> <sub>xy</sub> 3d <sup>2</sup> <sub>yz</sub> 3d <sup>2</sup> <sub>xz</sub> 3d <sup>1</sup> <sub>2-2</sub> 3d <sup>1</sup> <sub>z</sub>
Copper	29	[Ar] 4s <sup>1</sup> 3d <sup>2</sup> <sub>xy</sub> 3d <sup>2</sup> <sub>yz</sub> 3d <sup>2</sup> <sub>xz</sub> 3d <sup>2</sup> <sub>2-2</sub> 3d <sup>2</sup> <sub>z</sub>
Zinc	30	[Ar] 4s <sup>2</sup> 3d <sup>2</sup> <sub>xy</sub> 3d <sup>2</sup> <sub>yz</sub> 3d <sup>2</sup> <sub>xz</sub> 3d <sup>2</sup> <sub>2-2</sub> 3d <sup>2</sup> <sub>z</sub>
Gallium	31	[Ar] 4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>1</sup> <sub>x</sub> 4p <sup>0</sup> <sub>y</sub> 4p <sup>0</sup> <sub>z</sub>
Germanium	32	[Ar] 4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>1</sup> <sub>x</sub> 4p <sup>1</sup> <sub>y</sub> 4p <sup>0</sup> <sub>z</sub>
Arsenic	33	[Ar] 4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>1</sup> <sub>x</sub> 4p <sup>1</sup> <sub>y</sub> 4p <sup>1</sup> <sub>z</sub>
Selenium	34	[Ar] 4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>2</sup> <sub>x</sub> 4p <sup>1</sup> <sub>y</sub> 4p <sup>1</sup> <sub>z</sub>
Bromine	35	[Ar] 4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>2</sup> <sub>x</sub> 4p <sup>2</sup> <sub>y</sub> 4p <sup>1</sup> <sub>z</sub>
Krypton	36	[Ar] 4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>2</sup> <sub>x</sub> 4p <sup>2</sup> <sub>y</sub> 4p <sup>2</sup> <sub>z</sub>

## OBJECTIVE AND SHORT ANSWER, QUESTIONS (Exercise)

Q1. Select the most suitable answer for the given questions.

(i) The nature of positive rays depends on (Lahore board, 2013)

- (a) the nature of electrode
- (b) the nature of the discharge tube
- (c) the nature of the residual gas
- (d) all of the above

(ii) The velocity of photon is

- (a) Independent of its wavelength
- (b) Depends on its wavelength
- (c) Equal to square of its amplitude
- (d) Depends on its amplitude

(Faisalabad Board, 2009) (D.G. Khan Board, 2012) (Multan Board, 2011)

(iii) The wave number of the light emitted by a certain source is  $2 \times 10^6 \text{ m}^{-1}$ . The wavelength of this light will be

- (a) 500 nm
- (b) 500m
- (c) 200nm
- (d)  $5 \times 10^7 \text{ m}$

(D.G. Khan Board, 2009) (Rawalpindi board, 2011) (Gujranwala board, 2012)

(iv) Rutherford's model of atom failed because (Multan Board, 2012)

- (a) the atom did not have a nucleus and electron
- (b) it did not account for the attraction between proton and neutrons
- (c) it did not account for the stability of the atom
- (d) there is actually no space between the nucleus and the electrons

(v) Bohr's model of atom is contradicted by (Multan Board, 2008)

- (a) Planck quantum theory
- (b) Pauli's exclusion principle
- (c) Heisenberg's uncertainty principle
- (d) All of the above

(vi) Splitting of spectral lines when atoms are subjected to strong electric field is called.

- (a) Zeeman effect
- (b) Stark effect
- (c) Photoelectric effect
- (d) Compton effect

(Faisalabad Board, 2007) (Gujranwala Board, 2009) (Bahawalpur Board, 2010) (Rawalpindi board, 2011) (Gujranwala board, 2013) (Rawalpindi board, 2012) (Gujranwala board, 2010) 2012 (Sargodha Board, 2014)

(vii) In the ground state of an atom, the electron is present

- (a) in the nucleus
- (b) in the second shell
- (c) nearest to the nucleus
- (d) farthest from the nucleus

(Bahawalpur Board, 2009) (D.G. Khan Board, 2012) (Gujranwala board, 2013, 2014)

(viii) Quantum number values for 2p orbitals are

- (a)  $n = 2, l = 1$
- (b)  $n = 1, l = 2$
- (c)  $n = 1, l = 0$
- (d)  $n = 2, l = 0$

(Faisalabad Board, 2008) (Multan Board, 2010) 2013) (Sargodha Board, 2011, 2012) (Gujranwala board, 2010) (Lahore board, 2013)



- (ix) Orbitals having same energy are called  
 (a) hybrid orbitals (b) valence orbitals  
 (c) degenerate orbitals (d) d-orbitals

(Faisalabad Board, 2008) (Bahawalpur Board, 2009) (Sargodha Board, 2009, 2012) (Rawalpindi Board, 2009) (Multan Board, 2010) (Faisalabad Board, 2011) (D.G. Khan Board, 2012) (D.G. Khan Board, 2012)

- (x) When 6d orbital is complete, the entering electron goes into  
 (a) 7f (b) 7s (c) 7p (d) 7d

(Lahore Board, 2007) (Sargodha Board, 2009) (Rawalpindi Board, 2010, 2012) (Gujranwala board, 2012) (Multan Board, 2011) (Gujranwala board, 2014)

## ANSWERS TO MULTIPLE CHOICE QUESTIONS

## (i) Ans: (c)

Positive rays are produced due to ionization of gases present in the discharge tube.

e.g. consider the ionization of He and Ne  
 $\text{He} + e^- \rightarrow \text{He}^+ + 2e^-$

(positive ray)

$\text{Ne} + e^- \rightarrow \text{Ne}^+ + 2e^-$

(positive ray)

Since different gases have different nature of nuclei. Therefore, nature of positive rays is different for different gases.

## (iii) Ans: (a)

Wave length of light is given by

$$\lambda = \frac{c}{\nu}, \text{ since } \nu = 2 \times 10^6 \text{ m}^{-1}, \text{ therefore}$$

$$\lambda = \frac{1}{2 \times 10^6} = 0.5 \times 10^{-6} \text{ m} = 500 \times 10^{-9} \text{ m}$$

$$= 500 \text{ nm}$$

Since  $1 \text{ nm} = 10^{-9} \text{ m}$

## (ii) Ans: (a)

Light travels in the form of photons. Since velocity of light is a constant quantity, therefore, velocity of photon is also constant.

## (iv) Ans: (c)

According to Rutherford's atomic model, a revolving electron must emit energy continuously. As a result, electron will move in a spiral path and will fall into the nucleus. Therefore, whole atom would collapse. Hence, Rutherford's model does not account for the stability of atom.

## (v) Ans: (c)

Bohr's model indicates the exact position and momentum of electron. However, according to Heisenberg uncertainty principle, both position and momentum of electron cannot be determined simultaneously. Hence, these two are opposite (contradicted) to each other.

## (vi) Ans: (b)

When emission spectrum of excited H-atom is taken in an electrical field, lines are split up into component lines. This is called Stark effect

## (vii) Ans: (c)

In the ground state of an atom, the electron will be present at the lowest energy level. This lowest energy level will be nearest to the nucleus.

## (viii) Ans: (a)

For 2p orbital, 2 stands for principle quantum number. Hence, for 2p orbital,  $n=2$ . According to Azimuthal quantum number, when  $n=2$ ,  $l=0,1$ . Here '0' stands for 's-orbital' and '1' stands for 'p' orbital. Hence, for 2p orbital,  $l=1$ . Thus, for 2p orbital,  $n=2$ ,  $l=1$

## (ix) Ans: (c)

Orbitals having same energy are called degenerate orbitals.

## (x) Ans: (c)

According to  $(n+l)$  rule, orbitals are filled energy wise. Thus orbitals are filled in following order  
 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p...

Hence, when 6d orbital is complete, the entering electron will go into 7p orbital.

## Q2. Fill in the blanks with suitable words

- (i)  $\beta$ -particles are nothing but \_\_\_\_\_ moving with a very high speed.  
 (ii) The charge on one mole of electrons is \_\_\_\_\_ coulombs.  
 (iii) The mass of hydrogen atom is \_\_\_\_\_ grams.  
 (iv) The mass of one mole of electrons is \_\_\_\_\_ grams.  
 (v) Energy is \_\_\_\_\_ when electron jumps from higher to a lower orbit.  
 (vi) The ionization energy of hydrogen atom can be calculated from \_\_\_\_\_ model of atom.  
 (vii) For d sub-shell, the azimuthal quantum number has \_\_\_\_\_ value.  
 (viii) The number of electrons in a given subshell is given by formula \_\_\_\_\_.  
 (ix) The electronic configuration of  $\text{H}^+$  is \_\_\_\_\_.

## Answers:

- (i) electrons (ii) 96500 (iii)  $1.66 \times 10^{-24}$  (iv)  $5.48 \times 10^{-4}$   
 (v) released (vi) Bohr's (vii) two (viii)  $2(2l+1)$   
 (ix)  $1s^2$

## Q3. Indicate true or false as the case may be

- (i) A neutron is a slightly lighter particles than a proton.  
 (ii) A photon is the massless bundle of energy but has momentum.  
 (iii) The unit of Rydberg constant is the reciprocal of unit of length.  
 (iv) The actual isotopic mass is a whole number.  
 (v) Heisenberg's uncertainty principle is applicable to macroscopic bodies.  
 (vi) The nodal plane in an orbital is the plane of zero electron density.  
 (vii) The number of orbitals present in a sub-level is given by the formula  $(2l+1)$ .  
 (viii) The magnetic quantum number was introduced to explain Zeemann and Stark effects.  
 (ix) Spin quantum number tells us the direction of spin of electron around the nucleus.

## Answers:

- (i) False (ii) True (iii) True (iv) False (v) False (vi)  
 True (vii) True (viii) True (ix) False

## Q4. Keeping in mind the discharge tube experiment, answer the following questions.



(a) Why is it necessary to decrease the pressure in the discharge tube to get the cathode rays? (Faisalabad Board, 2007; Sargodha Board, 2010; Gujranwala Board, 2012)

OR Gases do not conduct electricity at normal pressure. Why? (D.G. Khan Board, 2007)

At high pressure, large amount of gas is present in the discharge tube. It will cause hindrance for the movement of electrons (cathode rays). Thus, conduction of electricity is difficult.

However, at low pressure amount of gas is less; therefore, electrons (cathode rays) can move and conduct electricity easily. Hence, it is necessary to decrease the pressure in discharge tube to get the cathode rays.

(b) Whichever gas is used in the discharge tube, the nature of the cathode rays remains the same. Why? (D.G. Khan Board, 2011; Gujranwala Board, 2013)

OR Cathode rays do not depend upon the nature of the gas. Discuss: (D.G. Khan Board, 2008, 2012)

OR Why cathode rays are independent of nature of gas used in the discharge tube? (D.G. Khan Board, 2009; Gujranwala Board, 2014)

OR Why  $e/m$  values of cathode rays is same for all gases: (Sargodha Board, 2007; Lahore Board, 2009, 2013)

The cathode rays are actually electrons. Since electrons are present in all atoms and their nature is same. Therefore, these are considered as fundamental particle of atom. Thus, nature of cathode rays remains same, no matter which gas is used in the discharge tube.

It was proved experimentally by J.J. Thomson. He calculated  $e/m$  ratio of cathode rays by taking different gases in the discharge tube. But he always found the same  $e/m$  ratio. It shows that cathode rays obtained by different gases have same nature.

(c) Why  $e/m$  value of the cathode rays is just equal to that of electron?

(Faisalabad Board, 2007; D.G. Khan Board, 2012; Bahawalpur Board, 2010; Sargodha Board, 2009; Bahawalpur Board, 2009; Gujranwala Board, 2012)

$e/m$  ratio of cathode rays is  $1.7588 \times 10^{11}$  C/Kg, which is equal to that of electron. It is because cathode rays are basically electrons.

(d) The bending of the cathode rays in the electric and magnetic fields shows that they are negatively charged.

Solved on Page 240

(e) Why positive rays are also called canal rays?

(Multan Board, 2007; Azad Kashmir Board, 2012; Gujranwala Board, 2010; Bahawalpur Board, 2008, 2010; Sargodha Board, 2010; D.G. Khan Board, 2008; Gujranwala Board, 2012)

Eugen Goldstein used a perforated cathode for the discovery of positive rays. The perforated cathode have small pores which act as small canals. Since positive rays pass through these canals, therefore, these are also called canal rays.

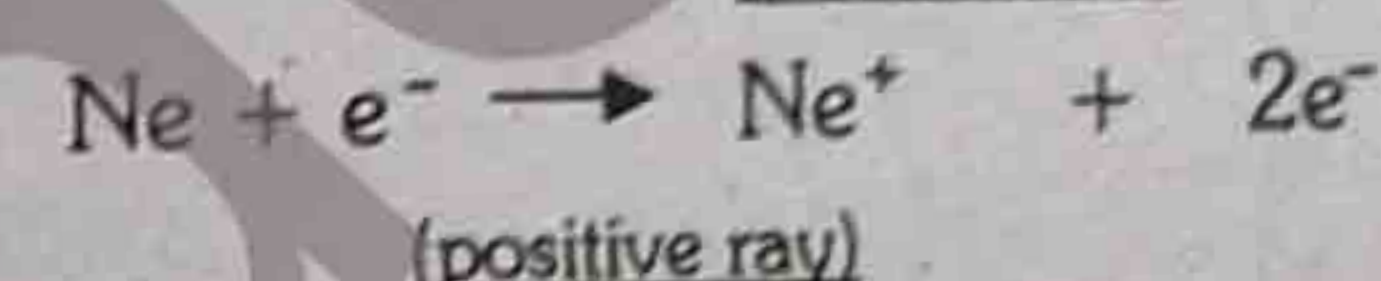
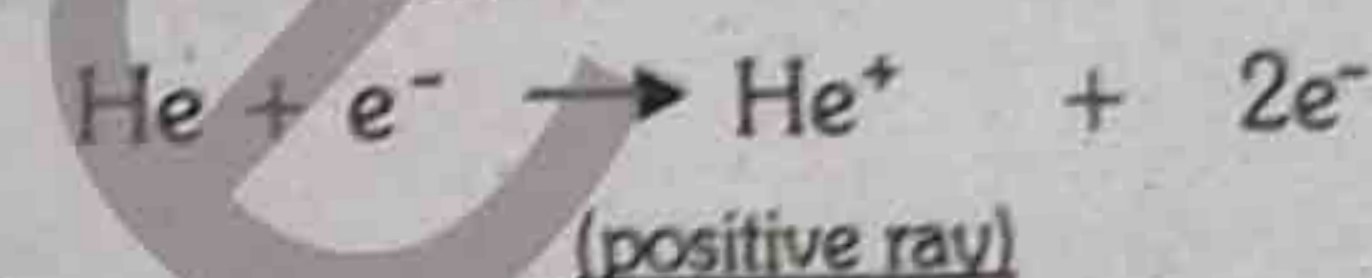
(f) The  $e/m$  value of positive rays for different gases are different but those for cathode rays the  $e/m$  values is the same. (Lahore Board, 2010; Rawalpindi Board, 2011)

OR Why the properties of positive rays depend upon the nature of the gas? (Rawalpindi Board, 2007)

Cathode rays are electrons. Moreover, nature of electrons is same in all atoms. Thus,  $e/m$  ratio is same for different gases.

Positive rays are produced due to ionization of gases present in the discharge tube.

e.g. consider the ionization of He and Ne



It shows that positive rays are nuclei of gases. Different gases have different nature of nuclei. Hence,  $e/m$  ratio for different positive rays is different.

(g) The  $e/m$  value for positive rays obtained from hydrogen gas is 1836 times less than that of cathode rays. (Lahore Board, 2007; Gujranwala Board, 2011)

Positive rays obtained from hydrogen gas in a discharge tube consists of protons and the cathode rays consists of electrons. A proton and an electron have equal magnitude of charge but mass of a proton is 1836 times greater than that of an electron. Hence,  $e/m$  value of positive ray obtained from hydrogen gas is 1836 times less than that of cathode rays.

Q5. (a) Explain Millikan's oil drop experiment to determine the charge of an electron?

Solved on Page 245

(b) What is J.J Thomson's experiment for determining  $e/m$  value of electron?

Solved on Page 245

(c) Evaluate mass of electron from the above two experiments.

Solved on Page 247

Q6. (a) Discuss Chadwick's experiment for the discovery of neutrons.

Solved on Page 243

(b) Rutherford's atomic model is based on the scattering of  $\alpha$ -particles from a thin gold foil. Discuss it and explain the conclusions.

Solved on Page 247



Q7. (a) Give the postulates of Bohr's atomic model. Which postulate tells us that orbits are stationary and energy is quantized?

Solved on Page 250

(b) Derive the equation for the radius of  $n^{\text{th}}$  orbit of hydrogen atom using Bohr's model.

Solved on Page 250

(c) How does the above equation tell you that

(i) Radius is directly proportional to the square of the number of orbit.

(ii) Radius is inversely proportional to the number of protons in the nucleus.

The equation for radius of  $n^{\text{th}}$  orbit of hydrogen atom is

$$r = \frac{\epsilon_0 n^2 h^2}{\pi m Z e^2}$$

$$\text{or } r = \frac{\epsilon_0 h^2}{\pi m e^2} \times \frac{n^2}{Z} \quad \text{or } r \propto \frac{n^2}{Z}$$

Hence, this equation shows that

(i) the radius is directly proportional to the square of the number of orbit ( $n$ ).

(ii) the radius is inversely proportional to the atomic number ( $Z$ ) which corresponds to the number of protons in the nucleus.

(d) How do you come to know that the velocities of electrons in higher orbits are less than those in lower orbits of hydrogen atom?

According to Bohr's theory, the equation for velocity of an electron in any orbit is

$$v^2 = \frac{Ze^2}{4\pi\epsilon_0 r m} \quad \text{or } v^2 \propto \frac{1}{r}$$

This equation shows that square of velocity of electron is inversely proportional to the radius of orbit ( $r$ ). It means electrons revolve faster in an orbit of smaller radius nearer to the nucleus. As the electron moves to higher orbits of larger radius, its velocity decreases.

(e) Justify that the distance gaps between different orbits go on increasing from the lower to the higher orbits.

According to Bohr's theory, the equation for radius of orbit is

$$r = 0.529 \times n^2$$

This equation shows that radius of the orbit is directly proportional to the square of orbit number ( $n$ ). Hence, higher orbits have more radii and vice versa. It means that radius of orbits goes on increasing with increasing orbit numbers.

Examples:

$$\text{For } n = 1 \quad r = 0.529 \times 1^2 = 0.529 \text{ \AA}$$

$$\text{For } n = 2 \quad r = 0.529 \times 2^2 = 2.11 \text{ \AA}$$

$$\text{For } n = 3 \quad r = 0.529 \times 3^2 = 4.75 \text{ \AA}$$

So, we have  $r_2 - r_1 < r_3 - r_2 \dots$

Thus, radius of orbits goes on increasing with increasing orbit numbers.

Q8. Drive the formula for calculating the energy of an electron in  $n^{\text{th}}$  orbit using Bohr's model. Keeping in view this formula explain the followings:

Solved on Page 253

(a) The potential energy of the bounded electron is negative.

According to Bohr's theory, Potential Energy = P.E. =  $-\frac{Ze^2}{4\pi\epsilon_0 r}$

The minus sign indicates that the P.E. decreases when the electron is brought from infinity to distance ' $r$ '. At infinity, the electron is not attracted by any thing, thus P.E. is zero. At a point nearer to the nucleus, electron is attracted by nucleus, thus P.E. is less than zero i.e. negative.

(b) Total energy of the bounded electron is also negative.

According to Bohr's theory, Total Energy =  $E_n = -\frac{mZ^2e^4}{8\epsilon_0^2 n^2 h^2}$

The minus sign indicates that the energy decreases when the electron is brought from infinity to distance ' $r$ '. At infinity, the electron is not attracted by any thing, thus energy is zero. At a point nearer to the nucleus, electron is attracted by nucleus, thus energy is less than zero i.e. negative.

(c) Energy of an electron is inversely proportional to  $n^2$ , but energy of higher orbits are always greater than those of the lower orbits.

According to Bohr's theory, the energy of electron in  $n^{\text{th}}$  orbit of hydrogen atom is given as

$$E_n = -\frac{1313.31}{n^2} \text{ kJ/mol}$$

Thus, it shows

(i) The energy of an electron is inversely proportional to  $n^2$ .

(ii) The negative sign indicates the attraction between electron and nucleus. As the electron moves to higher orbits, its attraction with nucleus decreases and hence its energy increases.



Examples:

$$\text{For } n=1 \quad E_1 = -\frac{1313.31}{1^2} = -1313.31 \text{ kJ/mol}$$

$$\text{For } n=2 \quad E_2 = -\frac{1313.31}{2^2} = -328.32 \text{ kJ/mol etc.}$$

Thus, the energy ' $E_2$ ' is greater than ' $E_1$ '

(d) The energy difference between adjacent levels goes on decreasing sharply.

$$\text{According to Bohr's theory, Total Energy} = E_n = -\frac{mZ^2e^4}{8\epsilon_0^2n^2h^2}$$

This equation shows that the energy of an electron is inversely proportional to  $n^2$ . Hence energy difference between adjacent levels goes on decreasing sharply.

The energy differences between adjacent orbits are

$$E_2 - E_1 = (-328.32) - (-1313.31) = 984.99 \text{ kJ/mol}$$

$$E_3 - E_2 = (-145.92) - (-328.32) = 182.40 \text{ kJ/mol}$$

$$E_4 - E_3 = (-82.08) - (-145.92) = 63.84 \text{ kJ/mol}$$

$$\text{Thus, } E_2 - E_1 > E_3 - E_2 > E_4 - E_3 > \dots$$

Q9. (a) Derive the following equations for hydrogen atom which are related to:

(i) Energy difference between two levels,  $n_1$  and  $n_2$ .

(ii) Frequency of photon emitted which an electron jumps from  $n_2$  to  $n_1$ .

(iii) Wave number of the photon when the electron jumps from  $n_2$  to  $n_1$ .

Solved on Page 260

(b) Justify that Bohr's equation for the wave number can explain the spectral lines of Lyman, Balmer and Paschen series.

Solved on Page 262

Q10. (a) What is spectrum. Differentiate between continuous spectrum and line spectrum.

Solved on Page 258

(b) Compare line emission and line absorption spectra.

Solved on Page 259

(c) What is the origin of line spectrum?

Solved on Page 256

Q11. (a) Hydrogen atom and  $\text{He}^+$  are monoelectronic system, but the size of  $\text{He}^+$  is much smaller than H. Why? (Multan Board, 2009)

Both hydrogen atom and  $\text{He}^+$  ion have one electron in their outermost shell. However, the nucleus of  $\text{He}^+$  has greater positive charge (due to two protons) than that of hydrogen atom (due to one proton). Therefore, nucleus of  $\text{He}^+$  attracts its electron more powerfully as compared to hydrogen. Hence, size of  $\text{He}^+$  becomes smaller than hydrogen.

(b) Do you think that the size of  $\text{Li}^{2+}$  is even smaller than  $\text{He}^+$ ? Justify with calculations.

Both  $\text{He}^+$  and  $\text{Li}^{2+}$  ions have one electron in their outermost shell. However, the nucleus of  $\text{Li}^{2+}$  has greater positive charge (due to three protons) than that of  $\text{He}^+$  ion (due to two protons). Therefore, nucleus of  $\text{Li}^{2+}$  attracts its electron more powerfully as compared to  $\text{He}^+$ . Hence, size of  $\text{Li}^{2+}$  becomes smaller than hydrogen.

Mathematical Calculations

For monoelectronic systems, Bohr's equation for radius of orbit is given by

$$r = \frac{n^2}{Z} \times a_0$$

Where

$n$  = number of orbit       $Z$  = Atomic number      &

$a_0$  = constant =  $0.529 \text{ \AA}$

Thus for  $1^{\text{st}}$  orbit of  $\text{Li}^{2+}$

$$n = 1 \quad Z = 3$$

$$r = \frac{1^2}{3} \times 0.529 = 0.176 \text{ \AA}$$

For  $1^{\text{st}}$  orbit of  $\text{He}^+$  ion

$$n = 1 \quad Z = 2$$

$$r = \frac{1^2}{2} \times 0.529 = 0.264 \text{ \AA}$$

It shows that size of  $\text{Li}^{2+}$  is smaller than  $\text{He}^+$

Q12. (a) What are X-rays? What is their origin? How was the idea of atomic number derived from the discovery of X-rays?

Solved on Page 264

(b) How does the Bohr's model justify the Moseley's equation?

According to Bohr's theory, the frequency of emitted photon is given as

$$\nu = \frac{mZ^2e^4}{8\epsilon_0^2h^3} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$



$$\text{or } \nu \propto Z^2$$

$$\text{or } \sqrt{\nu} \propto Z$$

Thus, when electron jumps from higher orbit ' $n_2$ ' to lower orbit ' $n_1$ ', the square root of frequency of photon emitted is directly proportional to the atomic number of the element which is the Moseley's law i.e.,

$$\sqrt{\nu} = a(Z - b)$$

$$\text{or } \sqrt{\nu} \propto Z$$

**Q13.** Point out the defects of Bohr's model. How these defects are partially covered by dual nature of electron and Heisenberg's uncertainty principle?

Solved on Page 263

**Q14. (a)** Briefly discuss the wave mechanical model of atom. how has it given the idea of orbital? Compare orbit and orbital.  
(Rawalpindi Board, 2012)

Solved on Page 268

**(b)** What are quantum numbers? Discuss their significance.

Solved on Page 269

**(c)** When azimuthal quantum number has a value 3, then there are seven values of magnetic quantum number. Give reasons.

**OR** Find the value of magnetic quantum number,  $m$ , when the azimuthal quantum number,  $\ell$ , is 3.  
(Sargodha Board, 2014)

The values of magnetic quantum number ( $m$ ) is related to azimuthal quantum number ( $\ell$ ) by the relation

$$m = -\ell \dots 0 \dots +\ell$$

Hence

When  $\ell = 3$  it is f-orbital. &  $m = -3, -2, -1, 0, +1, +2, +3$

Thus  $m$  has 7 values for  $\ell = 3$

These seven values show that f-orbital has seven different orientations in space.

**Q15. (a)** Discuss rules for the distribution of electrons in energy sub-levels and in orbitals.

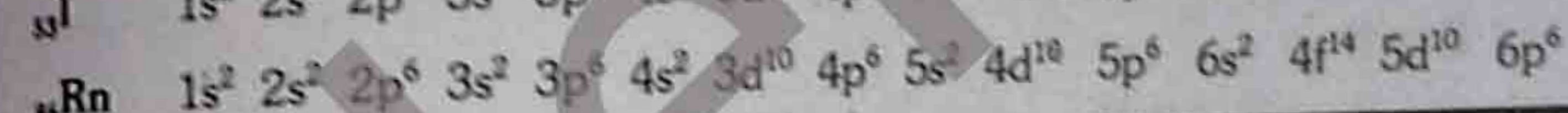
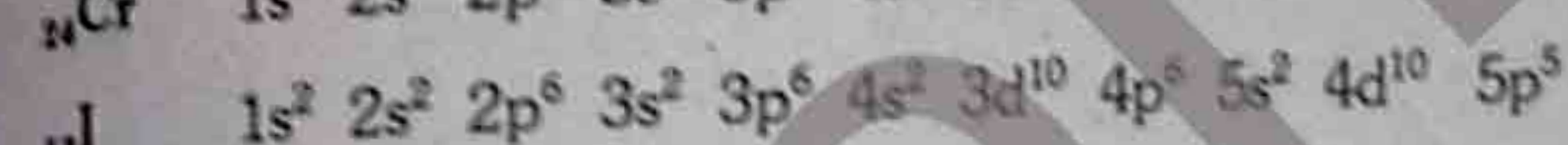
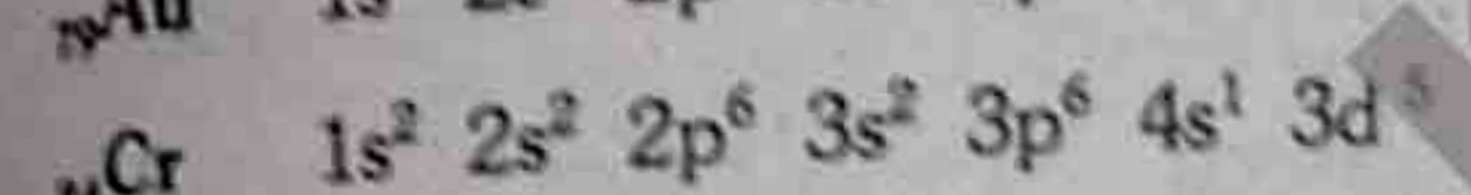
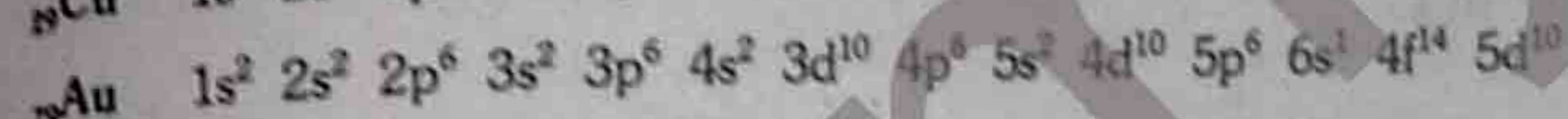
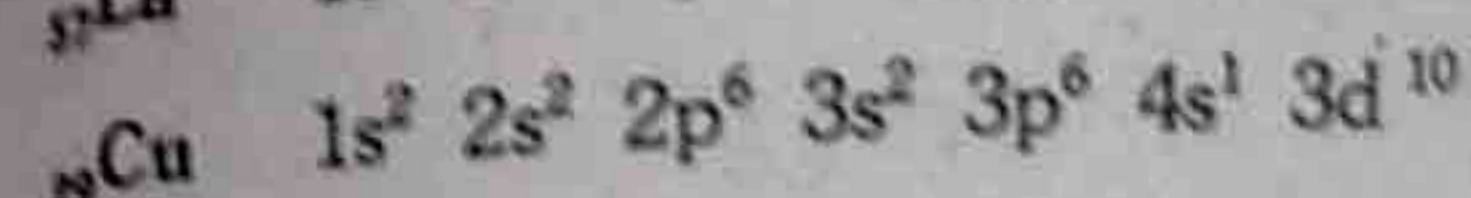
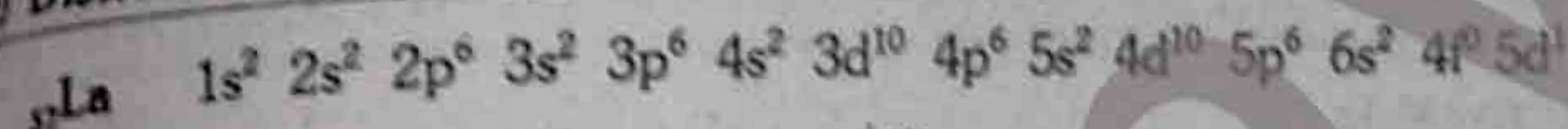
Solved on Page 276

**(b)** What is  $(n + \ell)$  rule. Arrange the orbitals according to this rule. Do you think that this rule is applicable to degenerate orbitals?

The orbitals of a subshell having same  $(n + \ell)$  value are called degenerate orbitals, because they have same energy. Hence,  $(n + \ell)$  rule cannot be applied to degenerate orbitals. However, degenerate orbitals have different values of magnetic quantum

number( $m$ ), therefore, they can be differentiated by ' $m$ ' values. e.g.  $2p_x$ ,  $2p_y$ ,  $2p_z$  are degenerate orbitals. Their  $(n + \ell)$  are same i.e.,  $(2 + 1) = 3$  but their  $m$  values are different.

**(c)** Distribute electrons in orbitals of  $_{57}\text{La}$ ,  $_{29}\text{Cu}$ ,  $_{79}\text{Au}$ ,  $_{24}\text{Cr}$ ,  $_{53}\text{I}$ ,  $_{86}\text{Rn}$



**Q16.** Draw the shapes of s, p and d-orbitals. Justify these by keeping in view the azimuthal and magnetic quantum numbers.

Solved on Page 274

### IMPORTANT FORMULAS

Energy ( $E$ ), frequency ( $\nu$ ), wavelength ( $\lambda$ ),

wavenumber ( $\bar{\nu}$ ) and mass interconversions:

$$E = h\nu \quad c = \nu\lambda \quad \lambda = 1/\bar{\nu} \quad E = mc^2$$

Bohr's equations:

$$\text{Angular momentum} = mvr = \frac{nh}{2\pi}$$

Radius of an orbit

$$r = \frac{\epsilon_0 h^2}{\pi m e^2} \times \frac{n^2}{Z} \quad \text{Or} \quad r = a_0 \times n^2$$

Energy of an electron

$$E_n = -\frac{m Z^2 e^4}{8 \epsilon_0^2 n^2 h^2} \quad \text{Or} \quad E = -2.18 \times 10^{-18} \times \frac{Z^2}{n^2}$$

$$\text{Or } E_n = -\frac{1313.31}{n^2}$$

Wavenumber of a photon

$$\bar{\nu} = \frac{m e^4}{8 \epsilon_0^2 c h^3} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\text{And } \text{P.E.} = -\frac{Z e^2}{4 \pi \epsilon_0 r}$$

$$\text{K.E.} = \frac{Z e^2}{8 \pi \epsilon_0 r}$$

Moseley's equation

$$\sqrt{\nu} = a(Z - b)$$

de-Broglie equation

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

Constants used in equations

Permittivity of vacuum

$$\epsilon_0 = 8.84 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$$

Planck's constant

$$h = 6.625 \times 10^{-34} \text{ Js}$$

Charge on an electron

$$e = 1.6022 \times 10^{-19} \text{ C}$$

Mass of an electron

$$m = 9.108 \times 10^{-31} \text{ kg}$$

Velocity of light

$$c = 3 \times 10^8 \text{ ms}^{-1}$$

Rydberg constant

$$R = \frac{m e^4}{8 \epsilon_0^2 c h^3} = 1.09678 \times 10^7 \text{ m}^{-1}$$

$$\text{and } a_0 = 0.529 \text{ \AA}$$



## NUMERICAL PROBLEMS (Exercise)

Q17. (a) A photon of light with energy  $10^{-19}$  J is emitted by a source of light. (a) Convert this energy into the wavelength, frequency and wave number of the photon in terms of meters, hertz and  $m^{-1}$  respectively.

Solution:

$$E = 10^{-19} \text{ J}$$

$$h = 6.625 \times 10^{-34} \text{ Js}$$

$$c = 3 \times 10^8 \text{ m/s}$$

$$\nu = ?$$

$$\lambda = ?$$

$$\bar{\nu} = ?$$

Since  $E = h\nu$

Or  $\nu = \frac{E}{h} = \frac{10^{-19}}{6.625 \times 10^{-34}} = 1.509 \times 10^{14} \text{ s}^{-1}$

Since  $\lambda = \frac{c}{\nu} = \frac{3 \times 10^8}{1.509 \times 10^{14}} = 1.988 \times 10^{-6} \text{ m}$

Since  $\bar{\nu} = \frac{1}{\lambda} = \frac{1}{1.988 \times 10^{-6}} = 5.030 \times 10^5 \text{ m}^{-1}$

(b) Convert this energy of the photon into ergs and calculate the wave length in cm, frequency in Hz and wave number in  $\text{cm}^{-1}$

$$h = 6.625 \times 10^{-34} \text{ Js} \quad c = 3 \times 10^8 \text{ m/s}$$

$$E = 10^{-19} \text{ J} = 10^{-19} \times 10^7 = 10^{-12} \text{ erg}$$

$$h = 6.625 \times 10^{-34} \text{ Js} = 6.625 \times 10^{-34} \times 10^7 \text{ erg s} = 6.625 \times 10^{-27} \text{ erg s}$$

$$c = 3 \times 10^8 \text{ m/s} = 3 \times 10^{10} \text{ cm/s}$$

$$\nu = ?$$

$$\lambda = ?$$

$$\bar{\nu} = ?$$

$$\nu = \frac{E}{h} = \frac{10^{-12}}{6.625 \times 10^{-27}} = 1.509 \times 10^{14} \text{ s}^{-1}$$

$$\lambda = \frac{c}{\nu} = \frac{3 \times 10^{10}}{1.509 \times 10^{14}} = 1.988 \times 10^{-4} \text{ cm}$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{1.988 \times 10^{-4}} = 5.030 \times 10^3 \text{ cm}^{-1}$$

1 J =  $10^7$  erg  
1 m = 100 cm  
erg is the unit  
of energy in  
c.g.s. system.

Q18. The formula for calculating the energy of an electron in hydrogen atom given by Bohr's model

$$E_n = -\frac{me^4}{8\epsilon_0^2 n^2 h^2}$$

Calculate the energy of electron in first orbit of hydrogen atom.

Solution:

$$\epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$$

$$h = 6.625 \times 10^{-34} \text{ Js}$$

$$m = 9.1 \times 10^{-31} \text{ kg}$$

$$e = 1.6022 \times 10^{-19} \text{ C}$$

$$E_1 = ?$$

$$n = 1$$

Energy in the first orbit is given by

$$E_1 = -\frac{me^4}{8\epsilon_0^2 n^2 h^2}$$

$$E_1 = -\frac{(9.1 \times 10^{-31})(1.602 \times 10^{-19})^4}{8 \times (8.85 \times 10^{-12})^2 \times 1^2 \times (6.625 \times 10^{-34})^2}$$

$$E_1 = -2.18 \times 10^{-18} \text{ J}$$

Q19. Bohr's equation for the radius of nth orbit of electron in hydrogen atom is

$$r_n = \frac{\epsilon_0 n^2 h^2}{\pi m e^2}$$

While doing calculations take care of units of energy parameter.

(a) When the electron moves from  $n = 1$  to  $n = 2$ , how much does the radius of the orbit increases.

Solution:

$$\epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$$

$$h = 6.625 \times 10^{-34} \text{ Js}$$

$$m = 9.1 \times 10^{-31} \text{ Kg}$$

$$e = 1.6022 \times 10^{-19} \text{ C}$$

Radius of nth orbit is given by

$$r_n = \frac{\epsilon_0 h^2}{\pi m e^2} \times n^2$$

$$r_n = \frac{(8.85 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1})(6.625 \times 10^{-34} \text{ Js})^2}{3.14 \times (9.1 \times 10^{-31} \text{ kg})(1.602 \times 10^{-19} \text{ C})^2} \times n^2$$



$$r_n = 0.529 \times 10^{-10} \text{ m} \times n^2 = 0.529 \text{ \AA} \times n^2$$

Thus for  $n=1$

$$r_1 = 0.529 \times 1^2 = 0.529 \text{ \AA}$$

Thus for  $n=2$

$$r_2 = 0.529 \times 2^2 = 2.11 \text{ \AA}$$

$$\text{Hence increase in radius} = r_2 - r_1 = 2.11 \text{ \AA} - 0.529 \text{ \AA} = \boxed{1.581 \text{ \AA}}$$

(b) What is the distance travelled by the electron when it goes from  $n=2$  to  $n=3$  and  $n=3$  to  $n=10$ ?

Solution:

$$\text{Since } r_n = 0.529 \times 10^{-10} \text{ m} \times n^2 = 0.529 \text{ \AA} \times n^2 \quad \boxed{10^{-10} \text{ m} = 1 \text{ \AA}}$$

Thus for  $n=2$

$$r_2 = 0.529 \times 2^2 = 2.11 \text{ \AA}$$

Thus for  $n=3$

$$r_3 = 0.529 \times 3^2 = 4.75 \text{ \AA}$$

$$\text{Hence distance travelled} = r_3 - r_2 = 4.75 \text{ \AA} - 2.11 \text{ \AA} = \boxed{2.65 \text{ \AA}}$$

Also for  $n=9$

$$r_9 = 0.529 \times 9^2 = 42.849 \text{ \AA}$$

And for  $n=10$

$$r_{10} = 0.529 \times 10^2 = 52.9 \text{ \AA}$$

$$\text{Hence distance travelled} = r_{10} - r_9 = 52.9 \text{ \AA} - 42.849 \text{ \AA} = \boxed{10.05 \text{ \AA}}$$

**Q20.** Answer the following questions, by performing the calculations.

(a) Calculate the energy of first five orbits of hydrogen atom and determine the energy difference between them.

Energy of electron in  $n$ th orbit is given by

$$E_n = -2.18 \times 10^{-18} \times \frac{Z^2}{n^2}$$

Where  $Z$  = atomic number  $n$  = number of orbit

For Hydrogen Atom  $Z = 1$

Therefore

$$E_n = -2.18 \times 10^{-18} \times \frac{1}{n^2}$$

Thus

$$\text{For } n=1 \quad E_1 = -2.18 \times 10^{-18} \times \frac{1}{1^2} = -2.18 \times 10^{-18} \text{ J}$$

$$\text{For } n=2 \quad E_2 = -2.18 \times 10^{-18} \times \frac{1}{2^2} = -5.45 \times 10^{-19} \text{ J} = -0.545 \times 10^{-18} \text{ J}$$

$$\text{For } n=3 \quad E_3 = -2.18 \times 10^{-18} \times \frac{1}{3^2} = -2.42 \times 10^{-19} \text{ J} = -0.242 \times 10^{-18} \text{ J}$$

$$\text{For } n=4 \quad E_4 = -2.18 \times 10^{-18} \times \frac{1}{4^2} = -1.36 \times 10^{-19} \text{ J} = -0.136 \times 10^{-18} \text{ J}$$

$$\text{For } n=5 \quad E_5 = -2.18 \times 10^{-18} \times \frac{1}{5^2} = -8.72 \times 10^{-20} \text{ J} = -0.0872 \times 10^{-18} \text{ J}$$

Energy differences will be

$$E_2 - E_1 = (-0.545 \times 10^{-18}) - (-2.18 \times 10^{-18}) = 1.635 \times 10^{-18} \text{ J}$$

$$E_3 - E_2 = (-0.242 \times 10^{-18}) - (-0.545 \times 10^{-18}) = 0.303 \times 10^{-18} \text{ J}$$

$$E_4 - E_3 = (-0.136 \times 10^{-18}) - (-0.242 \times 10^{-18}) = 0.106 \times 10^{-18} \text{ J}$$

$$E_5 - E_4 = (-0.0872 \times 10^{-18}) - (-0.136 \times 10^{-18}) = 0.0488 \times 10^{-18} \text{ J}$$

(b) Justify that energy difference between second and third orbits is approximately five times smaller than that between first and second orbits.

Energy difference between  $E_2 - E_1$  and  $E_3 - E_2$   
The ratio of the energy difference between  $E_2 - E_1$  and  $E_3 - E_2$  is given by

$$\frac{E_2 - E_1}{E_3 - E_2} = \frac{1.635 \times 10^{-18}}{0.303 \times 10^{-18}} \approx 5$$

$$\text{or } \frac{1}{5}(E_2 - E_1) \approx (E_3 - E_2)$$

Hence, energy difference between  $E_3 - E_2$  is approximately five times smaller than  $E_2 - E_1$ .



(c) Calculate the energy of electron in  $\text{He}^+$  in first five orbits and justify that the energy differences are different from those of hydrogen atom

For  $\text{He}^+$  ion  $Z = 2$

Therefore

$$E_n = -2.18 \times 10^{-18} \times \frac{Z^2}{n^2} = -2.18 \times 10^{-18} \times \frac{2^2}{n^2}$$

Thus

$$\text{For } n = 1 \quad E_1 = -2.18 \times 10^{-18} \times \frac{2^2}{1^2} = -8.72 \times 10^{-18} \text{ J}$$

$$\text{For } n = 2 \quad E_2 = -2.18 \times 10^{-18} \times \frac{2^2}{2^2} = -2.18 \times 10^{-18} \text{ J}$$

$$\text{For } n = 3 \quad E_3 = -2.18 \times 10^{-18} \times \frac{2^2}{3^2} = -9.68 \times 10^{-19} \text{ J} = -0.968 \times 10^{-18} \text{ J}$$

$$\text{For } n = 4 \quad E_4 = -2.18 \times 10^{-18} \times \frac{2^2}{4^2} = -5.45 \times 10^{-19} \text{ J} = -0.545 \times 10^{-18} \text{ J}$$

$$\text{For } n = 5 \quad E_5 = -2.18 \times 10^{-18} \times \frac{2^2}{5^2} = -3.488 \times 10^{-19} \text{ J} = -0.3488 \times 10^{-18} \text{ J}$$

Energy differences will be

$$E_2 - E_1 = (-2.18 \times 10^{-18}) - (-8.72 \times 10^{-18}) = 6.54 \times 10^{-18} \text{ J}$$

$$E_3 - E_2 = (-0.968 \times 10^{-18}) - (-2.18 \times 10^{-18}) = 1.21 \times 10^{-18} \text{ J}$$

$$E_4 - E_3 = (-0.545 \times 10^{-18}) - (-0.968 \times 10^{-18}) = 0.423 \times 10^{-18} \text{ J}$$

$$E_5 - E_4 = (-0.3488 \times 10^{-18}) - (-0.545 \times 10^{-18}) = 0.196 \times 10^{-18} \text{ J}$$

Hence, difference of energy between the energy levels of  $\text{He}^+$  is different from hydrogen.

(d) Do you think that groups of the spectral lines of  $\text{He}^+$  are at different places than those for hydrogen atom? Give reasons.

Since energy difference between energy levels in  $\text{He}^+$  ion is different from hydrogen, therefore spectral lines in  $\text{He}^+$  ions spectrum will be different from that of hydrogen spectrum.

Q21. Calculate the value of principal quantum number if an electron in hydrogen atom revolves in an orbit of energy  $-0.242 \times 10^{-18} \text{ J}$ .

Solution:

$$E = -0.242 \times 10^{-18} \text{ J}$$

$$Z = 1$$

$$n = ?$$

Energy of electron in  $n$ th orbit is given by

$$E_n = -2.18 \times 10^{-18} \times \frac{Z^2}{n^2}$$

$$\text{Hence } -0.242 \times 10^{-18} = -2.18 \times 10^{-18} \times \frac{1^2}{n^2}$$

$$\text{or } n^2 = \frac{-2.18 \times 10^{-18}}{-0.242 \times 10^{-18}} = 9$$

$$n = \sqrt{9} = 3$$

Q22. Bohr's formula for the energy levels of hydrogen atom for any system say  $\text{H}$ ,  $\text{He}^+$ ,  $\text{Li}^{2+}$  etc is

$$E_n = -\frac{mZ^2e^4}{8\epsilon_0^2n^2h^2}$$

$$E_n = -K\left(\frac{Z^2}{n^2}\right)$$

For hydrogen  $Z = 1$  and for  $\text{He}^+$ ,  $Z = 2$ .

(a) Draw an energy level diagram for hydrogen atom and  $\text{He}^+$ .

(b) Thinking that  $K = 2.18 \times 10^{-18} \text{ J}$ , calculate the energy needed to remove the electron from hydrogen atom and from  $\text{He}^+$ .

Solution:

$$K = 2.18 \times 10^{-18} \text{ J}$$

For hydrogen  $Z = 1$

Energy in  $n$ th orbit is given by

$$E_n = -K\left(\frac{Z^2}{n^2}\right)$$

$$\text{For } n = 1 \quad E_1 = -2.18 \times 10^{-18} \left(\frac{1^2}{1^2}\right) = -2.18 \times 10^{-18} \text{ J}$$

$$\text{For } n = \infty \quad E_\infty = -2.18 \times 10^{-18} \left(\frac{1^2}{\infty^2}\right) = 0 \text{ J}$$

Hence, to move an electron from hydrogen's first orbit to an infinite distance, the energy required will be

$$E_\infty - E_1 = 0 - (-2.18 \times 10^{-18}) = 2.18 \times 10^{-18} \text{ J}$$

This is the ionization energy of hydrogen atom



For  $\text{He}^+$  ion  $Z = 2$

Energy in  $n$ th orbit is given by

$$E_n = -K \left( \frac{Z^2}{n^2} \right)$$

$$\text{For } n = 1 \quad E_1 = -2.18 \times 10^{-18} \left( \frac{2^2}{1^2} \right) = -8.72 \times 10^{-18} \text{ J}$$

$$\text{For } n = \infty \quad E_\infty = -2.18 \times 10^{-18} \left( \frac{2^2}{\infty^2} \right) = 0 \text{ J}$$

Hence to move an electron from  $\text{He}^+$  ion's first orbit to an infinite distance, the energy required will be

$$E_\infty - E_1 = 0 - (-8.72 \times 10^{-18}) = \boxed{8.72 \times 10^{-18} \text{ J}}$$

This is the ionization energy of  $\text{He}^+$  ion.

(c) How do you justify that the energies calculated in (b) are the ionization energies of H and  $\text{He}^+$ ?

The amount of energy required to remove an electron from an atom or ion to an infinite distance is called ionization energy.

Hence,  $2.18 \times 10^{-18} \text{ J}$  and  $8.72 \times 10^{-18} \text{ J}$  are the ionization energies of H atom and  $\text{He}^+$  ion respectively.

(d) Use Avogadro's number to convert ionization energy values in  $\text{kJ mol}^{-1}$  or H and  $\text{He}^+$ .

The ionization energy of H-atom in  $\text{kJ/mol}$  is given as

$$E = 2.18 \times 10^{-18} \times \frac{6.02 \times 10^{23}}{1000} = \boxed{1312.36 \text{ kJ/mol}}$$

The ionization energy of  $\text{He}^+$ -ion in  $\text{kJ/mol}$  is given as

$$E = 8.72 \times 10^{-18} \times \frac{6.02 \times 10^{23}}{1000} = \boxed{5249.4 \text{ kJ/mol}}$$

(e) The experimental values of ionization energy of H and  $\text{He}^+$  are  $1331 \text{ kJ mol}^{-1}$  and  $5250 \text{ kJ mol}^{-1}$  respectively. How do you compare your values with experimental values?

The calculated values of ionization energies for H-atom and  $\text{He}^+$ -ion using Bohr's theory are  $1312.36 \text{ kJ/mol}$  and  $5249.4 \text{ kJ/mol}$  respectively.

These results agree well with the experimental results i.e.  $1331 \text{ kJ/mol}$  for H-atom and  $5250 \text{ kJ/mol}$  for  $\text{He}^+$  ion.

Both H-atom and  $\text{He}^+$  ion consists of one electron each and the above results clearly shows that Bohr's theory is perfectly applicable to one electron system.

Q23. Calculate the wave number of the photon when the electron jumps from

(i)  $n = 5$  to  $n = 2$ .

(ii)  $n = 5$  to  $n = 1$ .

In which series of spectral lines these photons will appear.

Solution:

$$\text{Rydberg constant} = R = 1.097 \times 10^7 \text{ m}^{-1}$$

When electron jumps from  $n = 5$  to  $n = 2$ .

The wave number of the photon is given by the eq.

$$\bar{\nu} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = 1.097 \times 10^7 \left( \frac{1}{2^2} - \frac{1}{5^2} \right)$$

$$\bar{\nu} = 1.097 \times 10^7 \left( \frac{1}{4} - \frac{1}{25} \right)$$

$$\bar{\nu} = 1.097 \times 10^7 \times \frac{21}{100} = 2.30 \times 10^6 \text{ m}^{-1}$$

This spectral line is present in visible region (Balmer Series)

When electron jumps from  $n = 5$  to  $n = 1$ .

The wave number of the photon is given by the eq.

$$\bar{\nu} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = 1.097 \times 10^7 \left( \frac{1}{1^2} - \frac{1}{5^2} \right)$$

$$\bar{\nu} = 1.097 \times 10^7 \left( \frac{1}{1} - \frac{1}{25} \right)$$

$$\bar{\nu} = 1.097 \times 10^7 \times \frac{24}{25} = \boxed{1.05 \times 10^7 \text{ m}^{-1}}$$

This spectral line is present in UV region (Lyman Series)

Q24. A photon of a wave number  $102.70 \times 10^5 \text{ m}^{-1}$  jumps from higher to  $n = 1$ .

(a) Determine the number of that orbit from where the electron falls.

Solution:

$$\text{Rydberg constant} = R = 1.097 \times 10^7 \text{ m}^{-1}$$

$$n_1 = 1$$

$$n_2 = ?$$

The wave number of the photon is given by the eq.



$$\bar{\nu} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$102.7 \times 10^5 = 1.097 \times 10^7 \times \left( \frac{1}{1^2} - \frac{1}{n_2^2} \right)$$

$$\frac{102.7 \times 10^5}{1.097 \times 10^7} = 1 - \frac{1}{n_2^2}$$

$$0.93637 = 1 - \frac{1}{n_2^2}$$

$$\frac{1}{n_2^2} = 1 - 0.93637 = 0.0636$$

$$\text{or } n_2^2 = \frac{1}{0.0636}$$

$$n_2 = \sqrt{\frac{1}{0.0636}} = \boxed{3.96 \approx 4}$$

(b) Indicate the name of the series to which this photon belongs.

This spectral line is present in Lyman series

(c) If the electron will fall from higher orbit to  $n = 2$ , then calculate the wave number of the photon emitted. Why this energy difference is so small as compare to above calculations?

When electron jumps from  $n = 4$  to  $n = 2$ .

The wave number of the photon is given by the eq.

$$\bar{\nu} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = 1.097 \times 10^7 \left( \frac{1}{2^2} - \frac{1}{4^2} \right)$$

$$\bar{\nu} = 1.097 \times 10^7 \left( \frac{1}{4} - \frac{1}{16} \right)$$

$$\bar{\nu} = 1.097 \times 10^7 \times \frac{3}{16} = \boxed{2.05646 \times 10^6 \text{ m}^{-1}}$$

Energy difference for  $n=4$  to  $n=1$  can be calculated by the eq.

$$\Delta E = 2.18 \times 10^{-18} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\text{Thus } \Delta E = 2.18 \times 10^{-18} \left( \frac{1}{1^2} - \frac{1}{4^2} \right)$$

$$\Delta E = 2.18 \times 10^{-18} \left( \frac{1}{1} - \frac{1}{16} \right)$$

$$\Delta E = 2.18 \times 10^{-18} \times \frac{15}{16} = \boxed{2.04 \times 10^{-18} \text{ J}}$$

And the energy difference for  $n=4$  to  $n=2$  can be calculated by the eq

$$\text{Thus } \Delta E = 2.18 \times 10^{-18} \left( \frac{1}{2^2} - \frac{1}{4^2} \right)$$

$$\Delta E = 2.18 \times 10^{-18} \left( \frac{1}{4} - \frac{1}{16} \right)$$

$$\Delta E = 2.18 \times 10^{-18} \times \frac{3}{16} = 4 \times 10^{-19} = \boxed{0.4 \times 10^{-18} \text{ J}}$$

The energy difference in second case is small.

It is because electron travel more distance from  $n=4$  to  $n=1$  than  $n=4$  to  $n=2$ . And since energy is directly related to the distance of the electron, hence energy difference in second case is smaller than first case.

Q25. (a) What is de Broglie's wavelength of an electron travelling at half a speed of light?

**Solution:**

$$\text{Mass of electron } = m = 9.1 \times 10^{-31} \text{ kg}$$

$$\text{Velocity of light } = c = 3 \times 10^8 \text{ m/s}$$

$$\text{Velocity of electron } = v = \frac{c}{2} = \frac{3 \times 10^8}{2} = 1.5 \times 10^8 \text{ m/s}$$

$$h = 6.625 \times 10^{-34} \text{ J s}$$

$$\lambda = ?$$

$$10^{-12} \text{ m} = 1 \text{ pm}$$

Wavelength of the electron is given by

$$\lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34}}{9.1 \times 10^{-31} \times 1.5 \times 10^8} = \boxed{4.85 \times 10^{-12} \text{ m} = 4.85 \text{ pm}}$$

(b) Convert the mass of electron into grams and velocity of light into  $\text{cm s}^{-1}$ . Calculate the wavelength of an electron in cm.

**Solution:**

$$m = 9.1 \times 10^{-31} \text{ kg} = 9.1 \times 10^{-31} \times 1000 \text{ g} = 9.1 \times 10^{-28} \text{ g}$$

$$\text{Velocity of light } = c = 3 \times 10^8 \text{ m/s} = 3 \times 10^{10} \text{ cm/s}$$

$$\text{Velocity of electron } = v = \frac{c}{2} = \frac{3 \times 10^{10}}{2} = 1.5 \times 10^{10} \text{ m/s}$$

$$\text{Planck's constant } = h = 6.625 \times 10^{-34} \text{ J s} = 6.625 \times 10^{-34} \times 10^7 \text{ erg s} \\ = 6.625 \times 10^{-27} \text{ erg s}$$

$$1 \text{ J} = 10^7 \text{ erg} \\ 1 \text{ m} = 100 \text{ cm}$$



$$\lambda = ?$$

Wavelength of the electron is given by

$$\lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-27}}{9.1 \times 10^{-28} \times 1.5 \times 10^{10}} = \boxed{4.85 \times 10^{-10} \text{ cm}}$$

(c) Convert the wave length of electron from meters to

(i) nm (ii) Å (iii) pm

$$\lambda = 4.85 \times 10^{-12} \text{ m}$$

**Solution:**

(i)  $1 \text{ m} = 10^9 \text{ nm}$

Therefore

$$\lambda = 4.85 \times 10^{-12} \times 10^9 \text{ nm} = \boxed{4.85 \times 10^{-3} \text{ nm}}$$

(ii)  $1 \text{ m} = 10^{10} \text{ Å}$

Therefore

$$\lambda = 4.85 \times 10^{-12} \times 10^{10} \text{ Å} = 4.85 \times 10^{-2} \text{ Å} = \boxed{0.0485 \text{ Å}}$$

(iii)  $1 \text{ m} = 10^{12} \text{ pm}$

Therefore

$$\lambda = 4.85 \times 10^{-12} \times 10^{12} \text{ pm} = \boxed{4.85 \text{ pm}}$$

HELLO! Mr. Question here!



**OBJECTIVE: Multiple Choice Questions from PAST PAPERS**

- Maximum number of electrons in an orbital is: (Lahore board, 2014)  
(a) 6 (b) 10 (c) 14 (d) 2
- ${}^{66}_{29}\text{Cu} \rightarrow {}^{66}_{30}\text{Zn} + X$  where X is: (Lahore board, 2014)  
(a) Proton (b) Positron (c) Electron (d) Neutron
- Lines of Paschen series are produced when electrons jump from higher orbits to ..... Orbit. (Gujranwala board, 2008)  
(a) 1<sup>st</sup> (b) 2<sup>nd</sup> (c) 3<sup>rd</sup> (d) 4<sup>th</sup>
- The electronic configuration of an atom is  $1s^2 2s^2 2p^4$ . The number of unpaired electrons in this atom is: (Gujranwala board, 2008)  
(a) 0 (b) 2 (c) 4 (d) 6
- Negative charge on cathode rays was established by: (Gujranwala board, 2009)  
(a) William Crook (b) J Perin (c) J.J. Thomson (d) Hittrof
- The  $e/m$  value for positive rays is maximum for: (Gujranwala board, 2009)  
(a) hydrogen (b) helim (c) oxygen (d) nitrogen
- Bombardment of  $\alpha$ -particles on Beryllium (Be) atom emits neutron and this process is called: (Gujranwala board, 2011)  
(a) natural radioactivity (b) artificial radioactivity  
(c) Pauli exclusion principle (d) Hund's rule
- Balmer series in hydrogen spectrum lies in the region: (Gujranwala board, 2011)  
(a) ultraviolet (b) visible (c) infrared (d) microwave
- Positive rays were discovered by: (Multan Board, 2011)  
(a) J.J. Thomson (b) Ruther ford (c) William Crooks (d) Eugene Gold Stein
- Lyman series lies in: (Multan Board, 2011)  
(a) UV region (b) Visible region (c) IR region (d) Microwave region
- Cathode rays cause a chemical change because they have ..... effect. (Rawalpindi Board, 2013)  
(a) Oxidizing (b) Conducting (c) Reducing (d) Diffusing
- After filling of 4f, the entering electron goes into: (Multan Board, 2013)  
(a) 5d (b) 6p (c) 6s (d) 4d
- The positive particle produced in the discharge tube from Hydrogen gas was named Proton by: (Multan Board, 2013)  
(a) Milikan (b) Goldstein (c) Rutherford (d) Chadwick



14. An orbital which is spherical and symmetrical is: (Lahore Board, 2009)  
 (a) s-orbital (b) p-orbital (c) d-orbital (d) f-orbital
15. Angstrom is the unit of (Lahore Board, 2009)  
 (a) time (b) length (c) Mass (d) Frequency
16. Properties of waves are: (Faisalabad Board, 2009)  
 (a) Wave length (b) Wave number (c) Frequency (d) all
17. The nature of anode rays depend on (Rawalpindi Board, 2009)  
 (a) The nature of the electrode (b) The nature of the residual gas  
 (c) The nature of the discharge tube (d) All of above
18. Total number of spectral regions in a spectrum is: (Lahore Board, 2010)  
 (a) 4 (b) 6 (c) 7 (d) 8
19. The value of Plank's constant is (Lahore Board, 2010)  
 (a)  $6.62 \times 10^{-34}$  J.s (b)  $6.62 \times 10^{-27}$  J.s  
 (c)  $6.62 \times 10^{-21}$  J.s (d)  $6.62 \times 10^{-31}$  J.s
20. In discharge tube experiment the pressure of gas was measured at (Bahawalpur Board, 2010)  
 (a) 760 torr (b) 0.1 torr (c) 0.01 torr (d) 10 torr
21. The number of neutron present in  $^{39}_{19}\text{K}$  is (Faisalabad Board, 2011)  
 (a) 39 (b) 18 (c) 20 (d) 19
22. Lyman series occur in: (Lahore Board, 2007)  
 (a) visible region (b) U.V. region (c) I.R. region (d) None of these
23. Balmer series is found in (Faisalabad Board, 2007)  
 (a) I.R. region (b) U.V region (c) visible region (d) None of these
24. Which equation correctly represents the Heisenberg's uncertainty principle? (Faisalabad Board, 2010) (Sargodha Board, 2013)  
 (a)  $\Delta X \times \Delta P = \frac{h}{4\pi}$  (b)  $\Delta X \times \Delta P > \frac{h}{4\pi}$   
 (c)  $\Delta X \times \Delta P \geq \frac{h}{4\pi}$  (d)  $\Delta X \times \Delta P \leq \frac{h}{4\pi}$
25.  $^{65}_{29}\text{Cu} + {}^1_0\text{n} \longrightarrow {}^{65}_{29}\text{Cu} + \text{X}$ . What is "X"? (Faisalabad Board, 2010)  
 (a) electron (b) proton (c) Beta rays (d) gamma rays
26. The wavelength of Lyman series lies in the region. (Sargodha Board, 2010)  
 (a) U.V (b) visible (c) I.R (d) None of the above
27. Number of neutrons present in  $^{39}_{19}\text{K}$  is (D.G. Khan Board, 2010)  
 (a) 20 (b) 19 (c) 39 (d) 18

28. Value of the Redberg's constant is (D.G. Khan Board, 2010)  
 (a)  $1.7904 \times 10^7 \text{ m}^{-1}$  (b)  $1.9768 \times 10^7 \text{ m}^{-1}$   
 (c)  $1.09678 \times 10^7 \text{ m}^{-1}$  (d)  $1.6 \times 10^7 \text{ m}^{-1}$
29. Mass of electron is (Lahore Board, 2011)  
 (a)  $9.1095 \times 10^{31} \text{ kg}$  (b)  $9.1095 \times 10^{-31} \text{ kg}$   
 (c)  $9.1095 \times 10^{-27} \text{ kg}$  (d)  $9.1095 \times 10^{-31} \text{ g}$
30. Neutron was discovered by (Lahore Board, 2011) (Sargodha Board, 2014)  
 (a) Chadwick (b) C.D Andersen (c) Rutherford (d) Goldstein
31. When 4s orbital is complete, the electron goes into (Sargodha Board, 2010)  
 (a) 4p orbital (b) 3d (c) 4d (d) 4f
32. The limiting line of Balmer Series lies in the region (Sargodha Board, 2011)  
 (a) visible (b) U.V. (c) Near I.R. (d) Far I.R.
33. Lyman Series lies in spectral region (Sargodha Board, 2013)  
 (a) Infrared (b) ultraviolet (c) visible (d) none of these

### Answers to Multiple Choice Questions from Past Papers.

Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans
1	(d)	2	(c)	3	(c)	4	(b)	5	(c)
6	(a)	7	(b)	8	(b)	9	(d)	10	(a)
11	(c)	12	(a)	13	(c)	14	(a)	15	(b)
16	(d)	17	(b)	18	(c)	19	(a)	20	(c)
21	(c)	22	(b)	23	(c)	24	(c)	25	(d)
26	(a)	27	(a)	28	(c)	29	(b)	30	(a)
31	(b)	32	(b)	33	(b)				

### Detailed Explanation of Past Papers MCQs & answers to all Past Papers SHORT QUESTIONS in COLLEGE CHEMISTRY OBJECTIVE BOOK-I

#### CATHODE RAYS AND ITS PROPERTIES

##### Short Questions

- (1) How will you prove that cathode rays are material particles with negative charge? (Lahore Board, 2007; Gujranwala Board, 2008; Multan Board, 2009)
- (2) Why cathode rays have reducing effect (or can cause chemical change)? (D.G. Khan Board, 2010; Multan Board, 2011)



- (3) How cathode rays are termed as electrons? (Faisalabad Board, 2009)

**Long Questions**

- (1) Discuss properties of cathode rays. (Faisalabad Board, 2012)

**POSITIVE RAYS AND ITS PROPERTIES**

- (1) Which observation tells the presence of positive rays in discharge tube? (Faisalabad Board, 2008; D.G. Khan Board, 2009)
- (2) Give reason for the production of positive rays. (Lahore Board, 2013)
- (3) Write properties of positive rays. (Gujranwala Board, 2011; Lahore Board, 2013)
- (4) The  $e/m$  value of Positive Rays is less than Cathode Rays. Justify. (Multan Board, 2012)
- (5) Explain the experiment which help us to understand the discovery of protons. (Lahore Board, 2007)

**NEUTRON AND ITS PROPERTIES****Short Questions**

- (1) What particles are formed by the decay of free neutrons? Write balanced equation. (Faisalabad Board, 2008; Sargodha Board, 2007, 2009, 2013; Lahore Board, 2014)
- (2) Write down nuclear reactions involved in the conversion of Cu into Zn. (Gujranwala Board, 2014) OR How the emission of a  $\beta$ -particle results in the increase of atomic number of element? (Rawalpindi Board, 2013)
- (3) Complete (Faisalabad Board, 2011)
- (a)  ${}^4_2\text{He} + {}^9_4\text{Be} \rightarrow ?$  (b)  ${}^{14}_7\text{N} + {}^1_0\text{n} \rightarrow ?$
- (4) How neutrons are used in the treatment of cancer? (Bahawalpur Board, 2012)
- (5) Write two properties of neutron. (Gujranwala Board, 2009; Rawalpindi Board, 2009; Lahore Board, 2014)
- (6) Write balanced equation for any two nuclear reactions (Multan Board, 2008; Faisalabad Board, 2013)

**Long Questions**

- (1) Describe the discovery and Properties of neutron in Chadwick experiment. (D.G. Khan Board, 2010; Gujranwala Board, 2011; Multan Board, 2012)
- (2) Discuss Chadwick's experiment for the discovery of neutron. Compare the properties of electron and proton. (Rawalpindi board 2007; Multan board 2007)

**MEASUREMENT OF CHARGE TO MASS RATIO, CHARGE AND MASS OF ELECTRON****Short Questions**

- (1) Calculate the mass of an electron when  $e/m = 1.7588 \times 10^{11} \text{ C kg}^{-1}$  (Lahore Board, 2014; Faisalabad Board, 2011; Multan Board, 2011, 2013) OR How the mass of electron is calculated by using  $e/m$  value? (Multan Board, 2010; Bahawalpur Board, 2011; Lahore Board, 2011; Rawalpindi Board, 2013)

**Long Questions**

- (1) How  $e/m$  (charge to mass ratio) value of electron was measured. (Sargodha Board, 2012; D.G. Khan Board 2012)
- (2) Explain Millikan's oil drop experiment to determine the charge of an electron. (Multan Board, 2010; Gujranwala Board, 2012; Lahore Board, 2013; Lahore Board, 2013, 2014)

**RUTHERFORD ATOMIC MODEL****Short Questions**

- (1) How did Rutherford's model of an atom first proved the existence of nucleus of the atom? (Gujranwala Board, 2008)
- (2) What are the defects in Rutherford's atomic model? (Rawalpindi Board, 2009; Multan Board, 2007, 2009; Faisalabad Board, 2009, 2013; Gujranwala Board, 2013) Give two defects in Rutherford's atomic model. (Multan Board, 2008; Lahore Board, 2011; D.G. Khan Board, 2010; Sargodha Board, 2010; Rawalpindi Board, 2011; Multan Board, 2011)

**Long Questions**

- (1) Write defects in Rutherford's model of atom. How Bohr removed them? (Sargodha Board, 2011)

**PLANCK'S QUANTUM THEORY, WAVELENGTH, FREQUENCY, WAVENUMBER****Short Questions**

- (1) Give postulates of Planck's theory. OR What is Planck's theory (Rawalpindi Board, 2009; Lahore Board, 2013)
- (2) Derive the formula for frequency of photon (only in two steps) (D.G. Khan Board, 2010)
- (3) Differentiate between (or What is) frequency and wave number. (D.G. Khan Board, 2007; Multan Board, 2010; Gujranwala Board, 2011)
- (4) Give the relationship between energy and frequency. (Bahawalpur Board, 2008)
- (5) The energy associated with violet colour is greater than red colour in visible spectra. Why? (Lahore Board, 2007)

**Long Questions**

- (1) (i) Write three points of Planck's quantum theory. (ii) define frequency and wavelength. (Faisalabad Board, 2010)

**POSTULATES OF BOHR'S ATOMIC MODEL, RADIUS OF ORBIT****Short Questions**

- (1) Why the electrons move faster in an orbit of smaller radius? (Sargodha Board, 2013) OR How do you come to know that the velocities of electrons in higher orbits are less than those of lower orbits.
- (2) The radius of first orbit of hydrogen atom is  $0.529 \text{ \AA}$ . Calculate the radius of 3<sup>rd</sup> orbit of hydrogen atom. (Gujranwala Board, 2013)
- (3) Justify that the distance gaps between different orbits go on increasing from the lower to the higher orbits. (Faisalabad Board, 2007; Sargodha Board, 2009)

**Long Questions**

- (1) Derive radius of revolving electron in n-th orbit of an atom. (Gujranwala Board, 2008, 2009; Faisalabad Board 2009; Bahawalpur Board 2009; Bahawalpur Board, 2010; Rawalpindi Board, 2010; Sargodha Board, 2012, 2013)
- (2) Give Postulates of Bohr's atomic model. (Lahore Board, 2009; D.G. Khan Board, 2011; Multan Board, 2012; Bahawalpur Board, 2012; Gujranwala Board, 2014)

**ENERGY OF ELECTRON (BOHR'S ATOMIC MODEL)****Short Questions**

- (1) Why potential energy of an electron (or bonded electron) is negative in an orbit of atom? (Bahawalpur Board, 2011; Sargodha Board, 2013)



- (2) Total energy of bonded electron is negative. Why? (Gujranwala Board, 2010)
- (3) The energy difference between adjacent levels in an atom goes on decreasing sharply. Why? (Rawalpindi Board, 2007)
- (4) Calculate ionization energy of hydrogen atom by using Bohr's atomic model. (Gujranwala Board, 2010)

**Long Questions**

- (1) Derive the formula for calculating the energy of an electron in  $n$ th orbit using Bohr's model. (Faisalabad Board, 2011; Azad Kashmir Board, 2012)

**SPECTRUM****Short Questions**

- (1) Define spectrum. Name its two types. (D.G. Khan Board, 2012; Multan Board, 2007, 2009; Lahore Board, 2009) OR What is spectrum? Give one example. (Bahawalpur Board, 2009)
- (2) Why atomic spectrum is line spectrum? (Lahore Board, 2010)
- (3) What is atomic emission spectrum? (Sargodha Board, 2014) OR What is the origin of the emission of line spectrum of an atom? (Rawalpindi Board, 2013)
- (4) What is the origin of line spectrum? (Sargodha Board, 2009)
- (5) Differentiate between line spectrum and continuous spectrum. (D.G. Khan Board, 2010; Lahore Board, 2014; Sargodha Board, 2011; Multan Board, 2012)
- (6) Differentiate between atomic emission and atomic absorption spectrum (Bahawalpur Board, 2012)

**Long Questions**

- (1) Describe atomic emission and atomic absorption spectrum with diagram. (Sargodha Board, 2010)
- (2) What is spectrum? Differentiate between continuous and line spectrum. (D.G. Khan board, 2007)
- (3) Define Spectrum. Explain atomic emission and atomic absorption spectrum with diagram. (Bahawalpur Board, 2011)

**EMISSION SPECTRUM OF HYDROGEN ATOM, EXPLANATION BY BOHR'S THEORY****Short Questions**

- (1) What is the origin of hydrogen spectrum? (D.G. Khan Board, 2010)
- (2) Write names of spectral series of hydrogen spectrum. (Lahore Board, 2011)
- (3) What is Lyman series? In which region it lies? (Rawalpindi Board, 2011)
- (4) What is the origin of hydrogen spectrum on the basis of Bohr's model? (Multan Board, 2010)
- (5) Write down the equation for energy difference of two orbits of H-atom (Bahawalpur Board, 2010)

**DEFECTS OF BOHR'S ATOMIC MODEL****Short Questions**

- (1) What are the defects of Bohr's atomic model (Gujranwala Board, 2008; Bahawalpur Board, 2008; D.G. Khan Board, 2009) OR Give two defects of Bohr's atomic model. (D.G. Khan Board, 2007; Multan Board, 2012; Faisalabad Board, 2012; Sargodha Board, 2011, 2014) NOTE: For short question, two defects will be asked preferably.
- (2) What is  $H_\alpha$  line in hydrogen spectrum? Which effect explain these lines? (D.G. Khan Board,

- 2010; Bahawalpur Board, 2010, 2011)
- (3) Differentiate/Describe/Define Stark and Zeeman effects (Faisalabad Board, 2011; Gujranwala Board, 2009, 2010; D.G. Khan Board, 2011; Bahawalpur Board, 2012)
- (4) State Zeeman effect OR What is Zeemann effect? (Rawalpindi Board, 2007; Lahore Board, 2008; D.G. Khan Board, 2008; Multan Board, 2008, 2013; Sargodha Board, 2012, 2013)

**Long Questions**

- (1) Give defects of Bohr's Atomic Model. (Lahore Board, 2011) OR Describe defects in Bohr's atomic model. (Multan Board, 2009, 2013; Lahore Board, 2014)

**X-RAYS, MOSELEY'S LAW****Short Questions**

- (1) What are X-rays? How they are produced? (Sargodha Board, 2007; D.G. Khan Board, 2007; Rawalpindi Board, 2012)
- (2) How the K-series, L-series and M-series of X-rays spectrum are produced? (Lahore Board, 2013)
- (3) What is Moseley's law? Write importance of Moseley's law (Rawalpindi Board, 2007; D.G. Khan Board, 2010; Multan Board, 2010; Lahore Board, 2014) OR Give importance of Moseley law (Azad Kashmir Board, 2012; Rawalpindi Board, 2012) OR Give the Moseley's equation. Also write its importance (or significance). (Faisalabad Board, 2007; Lahore Board, 2009; Multan Board, 2013)
- (4) Define Moseley's law. Give its mathematical expression. (Multan Board, 2007; Gujranwala Board, 2009; D.G. Khan Board, 2012; Faisalabad Board, 2012; Sargodha Board, 2010, 2013) OR What is Moseley's law. (Faisalabad Board, 2008; Lahore Board, 2011, 2012; D.G. Khan Board, 2009)

**Long Questions**

- (1) What are X-rays? Give the conclusions drawn by Moseley from the study of spectral lines. (Faisalabad Board, 2013)

**DE-BROGLIE'S EQUATION, HEISENBERG'S UNCERTAINTY PRINCIPLE, ORBITAL****Short Questions**

- (1) Write and explain de-Broglie's equation. (Multan Board, 2008, 2010)
- (2) Electron has its dual nature. Justify. (Sargodha Board, 2011)
- (3) State Heisenberg's uncertainty principle and write down its mathematical form/equation/formula (Gujranwala Board, 2009; Faisalabad Board, 2012; Multan Board, 2010, 2011, 2012; Bahawalpur Board, 2009; Lahore Board, 2009, 2013; D.G. Khan Board, 2008; Bahawalpur Board, 2011)
- (4) Explain orbital (Lahore Board, 2010)

**DE-BROGLIE'S EQUATION, HEISENBERG'S UNCERTAINTY PRINCIPLE, ORBITAL****Short Questions**

- (1) What is the function of principle quantum number? (Gujranwala Board, 2008; Faisalabad Board, 2009; Sargodha Board, 2013)
- (2) Define quantum numbers. What is the significance of Azimuthal quantum number. (D.G. Khan Board, 2012) OR Define Azimuthal quantum Number and give its importance. (Sargodha Board, 2011)
- (3) State spin quantum number(s) briefly. (Lahore Board, 2013)
- (4) Describe shapes of s and p orbitals (Bahawalpur Board, 2009; Sargodha Board, 2007, 2014)



## Long Questions

- (1) What are quantum numbers? Give the significance of any one quantum number. (D.G. Khan Board, 2009)
- (2) What are quantum numbers? Discuss their significance? (Faisalabad Board 2007; Sargodha board 2007)
- (3) Discuss (i) Azimuthal quantum number (ii) Magnetic quantum number (Sargodha Board, 2013)
- (4) What are quantum numbers? Discuss Principal and Azimuthal quantum numbers. (Sargodha Board, 2014)
- (5) What are quantum numbers? Explain Principal and Magnetic quantum numbers. (Multan Board, 2011)
- (6) Draw and explain shapes of s- and p-orbitals. (Rawalpindi Board, 2009)
- (7) Define orbital. Discuss shapeS of its types. (Lahore Board, 2010)

## AUFBAU PRINCIPLE, PAULI'S EXCLUSION PRINCIPLE, HUND'S RULE

## Short Questions

- (1) What is Aufbau principle? (Bahawalpur Board, 2008) OR Define and explain  $n+l$  rule (Multan Board, 2012) OR Why 4s sub-shell is filled first and 3d afterward. (Sargodha Board, 2013)
- (2) State Pauli's Exclusion principle with an example (Lahore Board, 2007, 2011, 2008, 2012, 2014)
- (3) State Aufbau principle and Pauli's exclusion principle. (Lahore Board, 2010)
- (4) Define/Describe Hund's rule. Explain with example. (Azad Kashmir Board, 2012; D.G. Khan Board, 2010; Sargodha Board, 2012; Lahore Board, 2014; Faisalabad Board, 2013; Multan Board, 2013)
- (5) Define/ State Hund's rule and Pauli's Exclusion principle (Gujranwala Board, 2011; D.G. Khan Board, 2012; Multan Board, 2012; Rawalpindi Board, 2013)

## Long Questions

- (1) Explain the following rules with examples. (i) Pauli's Exclusion principle (ii) Hund's Rule. (D.G. Khan Board, 2012)

## ELECTRONIC CONFIGURATIONS OF ELEMENTS

## Short Questions

- (1) Write electronic configuration for an element with atomic number  $Z = 29$  (Faisalabad Board, 2011)
- (2) Give the electronic configuration of  $\text{Ca}_{20}$  and  $\text{Br}_{35}$  (Faisalabad Board, 2009; D.G. Khan Board, 2011)
- (3) Distribute the electrons in  $\text{Cu}_{29}$  and  $\text{Br}_{35}$  (Faisalabad Board, 2008; Rawalpindi Board, 2011)
- (4) Write electronic configuration of  $_{19}\text{K}$  and  $_{29}\text{Cu}$  OR Write electronic configuration of elements with atomic number 19 and 29 (Lahore Board, 2008; Faisalabad Board, 2013)
- (5) Write down the electronic configuration of  $\text{Fe}(26)$  and  $\text{Br}(35)$  (Lahore Board, 2014)
- (6) Write electronic configuration of elements with atomic number  $z = 24$ ,  $z = 37$  (Sargodha Board, 2012, 2013; Gujranwala Board, 2013)

## TEST YOUR SKILLS

## OBJECTIVE

Marks: 85

Time: 20 Minutes

Note: Over writing, cutting, erasing, using lead pencil will result in loss of marks.

Marks: 17

Q1. Each question has four possible answers. Choose the correct answer and encircle it.

- The wave length of Lyman Series lies in the region  
(a) U.V. (b) Visible (c) I.R. (d) None of above
- How many electrons can be accommodated in a sub-shell for which  $n = 3$ ,  $\ell = 1$ ?  
(a) 8 (b) 6 (c) 18 (d) 32
- The electronic configuration of an atom is  $1s^2, 2s^2, 2p^4$ . The number of unpaired electrons in this atom is  
(a) 2 (b) 0 (c) 4 (d) 6
- The limiting line of Balmer series lies in the region.  
(a) Visible (b) U.V. (c) Near I.R. (d) Far I.R.
- Positive ions are formed from the neutral atom by the loss of  
(a) Positrons (b) protons (c) electrons (d) neutrons
- Cathode rays are deflected by  
(a) an electric field only (b) a magnetic field only (c) by both (d) by none
- $e/m$  value for positive rays is maximum for  
(a) Hydrogen (b) Helium (c) Oxygen (d) Nitrogen
- Neutron possesses  
(a) positive charge (b) negative charge (c) no charge (d) all are corrected
- Lines of Paschen series are produced when electrons jump from higher orbits to \_\_\_\_ orbit.  
(a)  $1^{st}$  (b)  $2^{nd}$  (c)  $3^{rd}$  (d)  $4^{th}$
- When atoms are volatilized, they form  
(a) continuous spectrum (b) line spectrum (c) electromagnetic spectrum (d) none
- In Millikan method for determination of charge on electron the air in the chamber is ionized by  
(a) Protons (b) Electron field (c) X-rays (d)  $\alpha$ -particles
- Smallest charge of electricity that has been measured so far is  
(a) charge on  $\alpha$ -particles (b) charge on electron (c) charge on X-rays (d) charge on gamma rays
- $\alpha$ -particles resembles  
(a)  $\text{He}^{++}$  (b)  $\text{He}^+$  (c) He atom (d)  $\text{He}_2$  molecule
- Splitting of spectral lines of the hydrogen atom under the influence of electric field is called  
(a) Stark effect (b) Zeeman effect (c) Compton effect (d) Photoelectric effect
- According to Bohr's atomic model, radius of second orbit of hydrogen atom is:  
(a)  $0.529 \text{ \AA}$  (b)  $2.116 \text{ \AA}$  (c)  $4.0 \text{ \AA}$  (d)  $5.0 \text{ \AA}$
- An orbital can have maximum two electrons with opposite spins according to  
(a) Heisenberg's principle (b) Auf bau principle (c) Hund's Rule (d) Pauli exclusion principle
- Paschan, bracket and P fund series lie in the  
(a) visible region (b) Ultraviolet region (c) Microwave region (d) Infrared region

## SUBJECTIVE

Marks: 68

Time: 2:10 Hours

Note: Out of Questions 2,3 and 4, Write any TWENTY TWO(22) short answers. While writing answers write question numbers carefully.  $(22 \times 2) = 44$ 

## Section - I

Q2. Answer any Eight parts from the followings.

- Differentiate between line spectrum and continuous spectrum.
- How positive rays are produced?
- Define atomic orbital what is about the probability of finding electron between two orbitals?
- What is the cause of origin of x-rays?



- (v)  $e/m$  value of cathode rays is independent of nature of gas. Why?
- (vi) State Moseley's law and write down its equation.
- (vii) Write down important points of quantum theory.
- (viii) Rutherford's model cannot explain the stability of atom. Why?
- (ix) What is Stark effect?
- (x) What is the origin of line spectrum?
- (xi) How X-rays are analyzed?
- (xii) Calculate the energy of photon travelling with a velocity of  $3 \times 10^8 \text{ m s}^{-1}$  and having a wavelength of 400 nm.

**Q3. Answer any Eight parts from the followings.**

- (i) Why the pressure inside the discharge tube was reduced to 0.01 torr to produce cathode rays?
- (ii) According to de Broglie's idea, only microscopic particles have the waves. Explain?
- (iii) Why the positive rays were called as canal rays?
- (iv) What are slow neutrons? What happens when they are bombarded on nitrogen?
- (v) Why Millikan ionized air in the chamber of his apparatus to determine charge on electron?
- (vi) What is the effect of magnetic field on cathode rays?
- (vii) What are the results of Rutherford's  $\alpha$ -scattering experiment?
- (viii) What is an angular momentum of electron in an orbit?
- (ix) Electron has its dual nature. Justify?
- (x) What is  $(n+1)$  rule?
- (xi) How emission spectrum of hydrogen is obtained?
- (xii) What is Sommerfeld's modification of Bohr Atomic Model?

**Q4. Answer any Six parts from the followings.**

- (i) Justify that the distance gaps between different orbits go on increasing from the lower to the higher orbits?
- (ii) Define Azimuthal quantum Number and give its importance?
- (iii) How is the wave nature of electron verified?
- (iv) Heisenberg uncertainty principle is not applicable to large objects. Why?
- (v) What is the concept of Schrödinger about nature of electron?
- (vi) What information is obtained from azimuthal quantum number?
- (vii) What are degenerate orbitals?
- (viii) How is spinning motion of electron about its axis related to the spectrum of an atom?
- (ix) What is the difference between 1s, 2s and 3s orbitals?

**Section - II (Attempt any three questions)  $(8 \times 3) = 24$**

- Q5.** (a) Derive an expression to calculate the energy of an electron in  $n$ th orbit of H-atom. (04)  
 (b) How did Millikan determine the charge of an electron? (04)
- Q6.** (a) Write a short note on Heisenberg's uncertainty principle. (04)  
 (b) How does spin quantum number explain the doublet structure in the spectrum of H-atom. (03)  
 (c) What is Zeeman effect? (01)
- Q7.** (a) What is Hund's rule. (02)  
 (b) Prove that  $\lambda = \frac{h}{mv}$  (03)  
 (c) How will you demonstrate that cathode rays possess energy and momentum? (03)
- Q8.** (a) Describe J.J. Thomson experiment to calculate the  $e/m$  value of electron. (03)  
 (b) Calculate the wave number of the photon when the electron jumps from (i)  $n = 6$  to  $n = 2$ . (ii)  $n = 6$  to  $n = 1$ . In which series of spectral lines these photons will appear. (03)  
 (c) Draw the shapes of d-orbitals. (02)
- Q9.** (a) Give the main points of Rutherford atomic model and also describe defects of this model. How Bohr removed these defects. (03)  
 (b) A photon of a wave number  $102.70 \times 10^5 \text{ m}^{-1}$  is emitted jumps from higher to  $n = 1$ . Determine the number of that orbit from where the electron falls. (03)  
 (c) Describe Atomic emission and Atomic Absorption spectrum with diagrams? (02)

# Chapter 6

## CHEMICAL BONDING



G.N. Lewis

