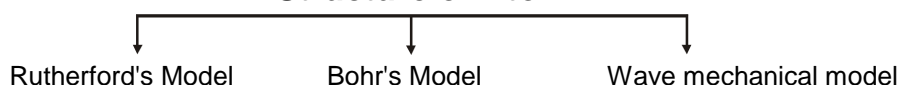


# Atomic Structure

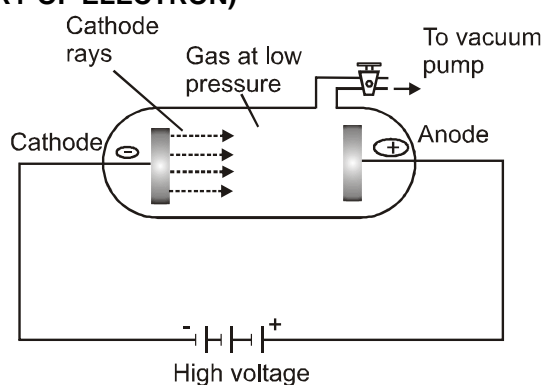
## INTRODUCTION :

### Structure of Atom



Dalton's concept of the indivisibility of the atom was completely discredited by a series of experimental evidences obtained by scientists. A number of new phenomenon were brought to light and man's idea about the natural world underwent a revolutionary change. The discovery of electricity and spectral phenomena opened the door for radical changes in approaches to experimentation. It was concluded that atoms are made of three particles : electrons, protons and neutrons. These particles are called the fundamental particles of matter.

## CATHODE RAYS (DISCOVERY OF ELECTRON)



In 1859 **Julius Plucker** started the study of conduction of electricity through gases at low pressure ( $10^{-4}$  atm) in a discharge tube. When a high voltage of the order of 10,000 volts or more was impressed across the electrodes, some sort of invisible rays moved from the negative electrode to the positive electrode. These rays are called as cathode rays.

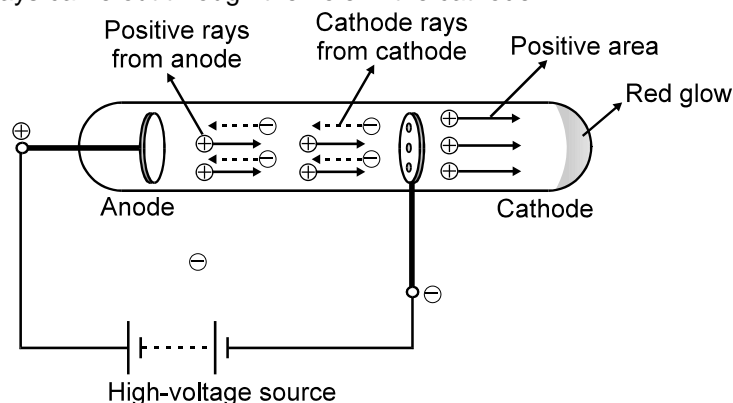
## PROPERTIES OF CATHODE RAYS :

- Path of travelling is straight from the cathode with a very high velocity as it produces shadow of an object placed in its path.
- Cathode rays produce mechanical effects. If a small paddle wheel is placed between the electrodes, it rotates. This indicates that the cathode rays consist of material particles.
- When electric and magnetic fields are applied to the cathode rays in the discharge tube, the rays are deflected, thus establishing that they consist of charged particles. The direction of deflection showed that cathode rays consist of negatively charged particles called **electrons**.
- They produce a green glow when they strike the glass wall beyond the anode. Light is emitted when they strike the zinc sulphide screen.
- Cathode rays penetrate through thin sheets of aluminium and metals.
- They affect photographic plates.
- The ratio of charge ( $e$ ) to mass ( $m$ ) i.e. charge/mass is the same for all cathode rays irrespective of the gas used in the tube.  $e/m = 1.76 \times 10^{11} \text{ C kg}^{-1}$

Thus, it can be concluded that electrons are basic constituents of all atoms.

### ANODE RAYS (DISCOVERY OF PROTON) :

Goldstein (1886) repeated the experiment with a discharge tube filled with a perforated cathode and found that new type of rays came out through the hole in the cathode.



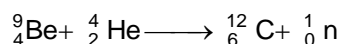
When this experiment is conducted, a faint red glow is observed on the wall behind the cathode. Since these rays originate from the anode, they are called anode rays.

### PROPERTIES OF ANODE RAYS :

- **Anode rays travel along straight paths** and hence they cast shadows of object placed in their path.
- **They rotate a light paddle wheel placed in their path.** This shows that anode rays are made up of material particles.
- They are deflected towards the negative plate of an electric field. This shows that these rays are positively charged.
- For different gases used in the discharge tube, the charge to mass ratio ( $e/m$ ) of the positive particles constituting the positive rays is different. When hydrogen gas is taken in the discharge tube, the  $e/m$  value obtained for the positive rays is found to be maximum. Since the value of charge ( $e$ ) on the positive particle obtained from different gases is the same, the value of  $m$  must be minimum for the positive particles obtained from hydrogen gas. Thus, the positive particle obtained from hydrogen gas is the lightest among all the positive particles obtained from different gases. This particle is called the proton.

### DISCOVERY OF NEUTRON :

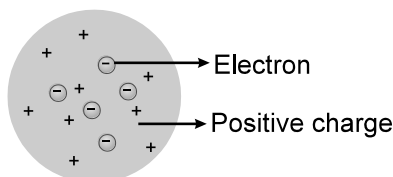
Later, a need was felt for the presence of electrically neutral particles as one of the constituent of atom. These particles were discovered by **James Chadwick** in 1932 by bombarding a thin sheet of Beryllium with  $\alpha$ -particles, when electrically neutral particles having a mass slightly greater than that of the protons were emitted. He named these particles as neutrons.



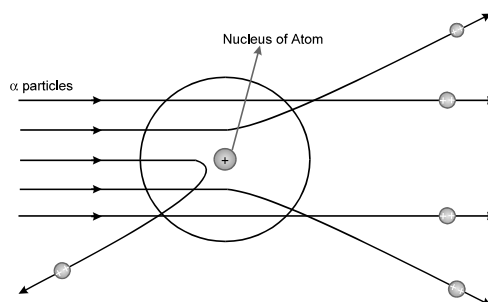
### ATOMIC MODELS :

#### THOMSON'S MODEL OF THE ATOM :

An atom is electrically neutral. It contains positive charges as well as negative charges (due to the presence of electrons). Hence, J J Thomson assumed that an atom is a uniform sphere of positive charges with electrons embedded in it. The magnitude of total positive charge on sphere is equal to total negative charge of embedded electrons.



### RUTHERFORD'S EXPERIMENT :



- Most of the  $\alpha$ -particles passed straight through the gold foil without suffering any deflection from their original path.
- A few of them were deflected through small angles, while a very few were deflected to a large extent.
- A very small percentage (1 in 100000) was deflected through angles ranging from  $90^\circ$  to  $180^\circ$ .

### Rutherford's nuclear concept of the atom.

- The atom of an element consists of a small positively charged 'nucleus' which is situated at the centre of the atom and which carries almost the entire mass of the atom.
- The electrons are distributed in the empty space of the atom around the nucleus in different concentric circular paths, called orbits.
- The number of electrons in orbits is equal to the number of positive charges (protons) in the nucleus. Hence, the atom is electrically neutral.
- The volume of the nucleus is negligibly small as compared to the volume of the atom.
- Most of the space in the atom is empty.

### NUCLEUS :

Electrons, protons & neutrons are the fundamental particles present in all atoms, (Except hydrogen)

Particles	Symbol	Mass	Charge	Discoverer
Electron	${}_{-1}e^0$ or $\beta$	$9.1096 \times 10^{-31}$ kg 0.000548 amu	$-1.602 \times 10^{-19}$ Coulombs $-4.803 \times 10^{-10}$ esu	J.J. Thompson Stoney Lorentz 1887
Proton	${}_1H^1$	$1.6726 \times 10^{-27}$ kg 1.00757 amu	$+1.602 \times 10^{-19}$ Coulombs $+4.803 \times 10^{-10}$ esu	Goldstein Rutherford 1907
Neutron	${}_0n^1$	$1.6749 \times 10^{-27}$ kg 1.00893 amu $1 \text{ amu} \approx 1.66 \times 10^{-27} \text{ kg}$	Neutral 0	James Chadwick 1932

**Uncommon Fundamental Particles :-** Other less important fundamental particles of atom are positrons, neutrinos and mesons.

**(A) Positron (Positive electron,  ${}^1_1e^0$ )** :- It is the positive counterpart of electron, discovered by Anderson in 1932. It is very unstable and combines with electron producing  $\gamma$ -rays (energy radiations). Positron is symbolised as  ${}^1_1e^0$  or  $e^+$

**(B) Neutrino** :- These are particles of small ( $\cong 0$ ) mass and zero charge. These were postulated by Paulling in 1934.

**(C) Antineutrino** :- These are particles of small ( $\cong 0$ ) mass and zero charge. These were postulated by Fermi in 1934. "Identical to neutrino but opposite spin"

**(D) Mesons** :- (postulated by Yukawa in 1935) Mesons may be either positively or negatively charged or neutral. Their mass is intermediate between that of electron and proton.

MESONS	CHARGE	MASS
$\mu$	+/-	286 $m_e$
$\pi$	+/-/0	270 $m_e$
k	+/-/0	970 $m_e$

**(E) Anti proton** :- Discovered by Segre (1955) its mass equal to proton and charge equal to electron.

**(F) Anti neutron** :- Discovered by Cork (1956) its mass equal to neutron and charge equal to zero. "Identical to neutron but opposite spin"

#### ATOMIC NUMBER AND MASS NUMBER :

##### ○ Atomic number of an element

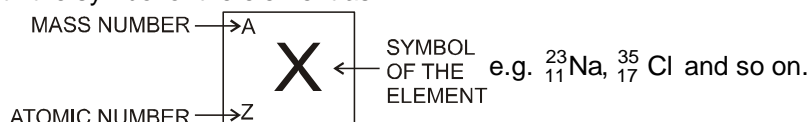
= Total number of protons present in the nucleus

= Total number of electrons present in the atom

- Atomic number is also known as proton number because the charge on the nucleus depends upon the number of protons.
- Since the electrons have negligible mass, the entire mass of the atom is mainly due to protons and neutrons only. Since these particles are present in the nucleus, therefore they are collectively called **nucleons**.
- As each of these particles has one unit mass on the atomic mass scale, therefore the sum of the number of protons and neutrons will be nearly equal to the mass of the atom.

##### ○ Mass number of an element = No. of protons + No. of neutrons.

- The mass number of an element is nearly equal to the atomic mass of that element. However, the main difference between the two is that mass number is always a whole number whereas atomic mass is usually not a whole number.
- The atomic number (Z) and mass number (A) of an element 'X' are usually represented alongwith the symbol of the element as

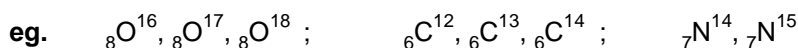


#### IMPORTANT DEFINATIONS :

##### 1. ISOTOPES :

- (i) First proposed by soddy.

- (ii) The isotopes have same atomic number but different atomic weight.  
 (iii) They have same chemical properties because they have same atomic number.  
 (iv) They have different physical properties because they have different atomic masses.



eg. ${}_1\text{H}^1$	${}_1\text{H}^2$	${}_1\text{H}^3$
Protium	deuterium	Tritium
Z = 1	1	1
A = 1	2	3

## 2. ISOBAR :

The different atoms which have same atomic masses but different atomic number are called as Isobar.

eg.	${}_{18}\text{Ar}^{40}$	${}_{19}\text{K}^{40}$	${}_{20}\text{Ca}^{40}$
Atomic mass	40	40	40
Atomic number	18	19	20

## 3. ISOTONE :

Elements which contain same no. of neutron are called as Isotones.

eg.	${}_{14}\text{Si}^{30}$	${}_{15}\text{P}^{31}$	${}_{16}\text{S}^{32}$
Number of neutrons	16	16	16

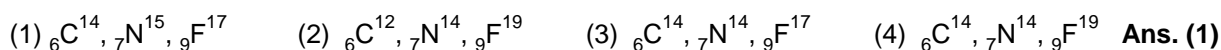
## 4. ISOELECTRONIC :

Ion or atom or molecule or species which have the same number of electrons are called as isoelectronic species.

eg.	${}_{17}\text{Cl}^-$	${}_{18}\text{Ar}$	${}_{19}\text{K}^+$	${}_{20}\text{Ca}^{+2}$
No. of electron	18	18	18	18

## Solved Examples

1. The triad of nuclei that is isotonic -



2. Complete the following table :

Particle	Mass No.	Atomic No.	Protons	Neutrons	Electrons
Nitrogen atom	—	—	—	7	7
Calcium ion	—	20	—	20	—
Oxygen atom	16	8	—	—	—
Bromide ion	—	—	—	45	36

**Sol.** For nitrogen atom.

No. of electron = 7 (given)

No. of neutrons = 7 (given)

$\therefore$  No. of protons =  $Z = 7$  ( $\therefore$  atom is electrically neutral)

Atomic number =  $Z = 7$

Mass No. (A) = No. of protons + No. of neutrons  
 $= 7 + 7 = 14$

**For calcium ion.**

No. of neutrons = 20 (Given)

Atomic No. (Z) = 20 (Given)

$\therefore$  No. of protons =  $Z = 20$  ;

No. of electrons in calcium atom =  $Z = 20$

But in the formation of calcium ion, two electrons are lost from the extranuclear part according to the equation  $\text{Ca} \rightarrow \text{Ca}^{2+} + 2e^-$  but the composition of the nucleus remains unchanged.

$\therefore$  No. of electrons in calcium ion

$$= 20 - 2 = 18$$

Mass number (A) = No. of protons + No. of neutrons

$$= 20 + 20 = 40.$$

**For oxygen atom.**

Mass number (A) = No. of protons + No. of neutrons

$$= 16 \text{ (Given)}$$

Atomic No. (Z) = 8 (Given)

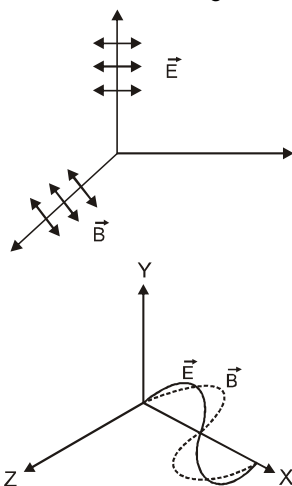
No. of protons =  $Z = 8$ ,

No. of electrons =  $Z = 8$

No. of neutrons =  $A - Z = 16 - 8 = 8$

**ELECTROMAGNETIC RADIATIONS :**

The oscillating electrical/magnetic field are electromagnetic radiations. Experimentally, the direction of oscillations of electrical and magnetic field are perpendicular to each other.



$\vec{E}$  = Electric field,  $\vec{B}$  = Magnetic field

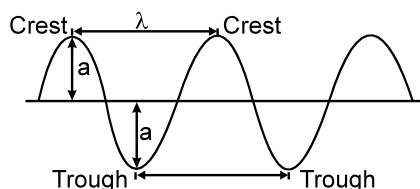
Direction of wave propagation.

**WAVE NATURE OF LIGHT :**

- **Wavelength** of a wave is defined as the distance between any two consecutive crests or troughs. It is represented by  $\lambda$  (lambda) and is expressed in  $\text{\AA}$  or m or cm or nm (nanometer) or pm (picometer).

$$1 \text{ \AA} = 10^{-8} \text{ cm} = 10^{-10} \text{ m}$$

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



- **Frequency** of a wave is defined as the number of waves passing through a point in one second. It is represented by  $\nu$  (nu) and is expressed in Hertz (Hz) or cycles/sec or simply  $\text{sec}^{-1}$  or  $\text{s}^{-1}$ .  
 $1 \text{ Hz} = 1 \text{ cycle/sec}$
- **Velocity** of a wave is defined as the linear distance travelled by the wave in one second. It is represented by  $v$  and is expressed in cm/sec or m/sec ( $\text{ms}^{-1}$ ).
- **Amplitude** of a wave is the height of the crest or the depth of the trough. It is represented by 'a' and is expressed in the units of length.
- **Wave number** is defined as the number of waves present in 1 cm length. Evidently, it will be equal to the reciprocal of the wavelength. It is represented by  $\bar{\nu}$  (read as nu bar).

$$\bar{\nu} = \frac{1}{\lambda}$$

If  $\lambda$  is expressed in cm,  $\bar{\nu}$  will have the units  $\text{cm}^{-1}$ .

**Relationship between velocity, wavelength and frequency of a wave.** As frequency is the number of waves passing through a point per second and  $\lambda$  is the length of each wave, hence their product will give the velocity of the wave. Thus

$$c = v \times \lambda$$

#### Order of wavelength in electromagnetic spectrum

Cosmic rays <  $\gamma$  – rays < X-rays < Ultraviolet rays < Visible < Infrared < Micro waves < Radio waves.

#### PARTICLE NATURE OF LIGHT (PLANK'S QUANTUM THEORY)

The smallest quantity of energy that can be emitted or absorbed in the form of electromagnetic radiation is called as quantum of light.

According to Planck, the light energy coming out from any source is always an integral multiple of a smallest energy value called quantum of light.

Let quantum of light be  $= E_0(\text{J})$ , then total energy coming out is  $= nE_0$  ( $n = \text{Integer}$ )

Quantum of light = Photon (Packet or bundle of energy)

Energy of one photon is given by

$$E_0 = h\nu \quad (\nu - \text{Frequency of light})$$

$$h = 6.625 \times 10^{-34} \text{ J-Sec} \quad (h - \text{Planck const.})$$

$$E_0 = \frac{hc}{\lambda} \quad (c - \text{speed of light})$$

( $\lambda$  - wavelength)

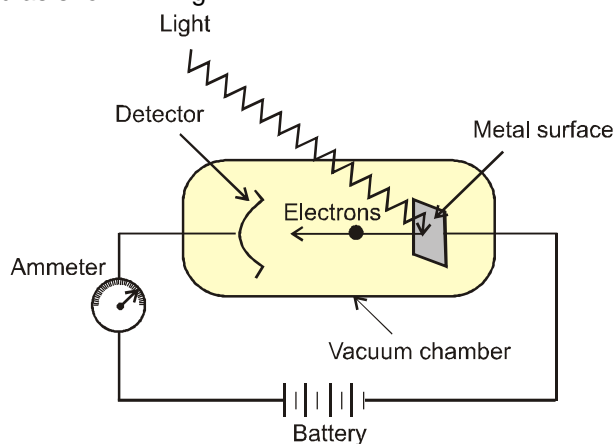
$$\text{Order of magnitude of } E_0 = \frac{10^{-34} \times 10^8}{10^{-10}} = 10^{-16} \text{ J}$$

Some of the experimental phenomenon such as diffraction and interference can be explained by the wave nature of the electromagnetic radiation. However, following are some of the observations which could not be explained

- (i) the nature of emission of radiation from hot bodies (black - body radiation)
- (ii) ejection of electrons from metal surface when radiation strikes it (photoelectric effect)

### Photoelectric Effect :

When certain metals (for example Potassium, Rubidium, Caesium etc.) were exposed to a beam of light electrons were ejected as shown in Fig.



The phenomenon is called **Photoelectric effect**. The results observed in this experiment were :

- (i) The electrons are ejected from the metal surface as soon as the beam of light strikes the surface, i.e., there is no time lag between the striking of light beam and the ejection of electrons from the metal surface. This phenomenon is called SINGLE COLLISION event. The electron at the surface collides with only one photon once.
- (ii) The number of electrons ejected is proportional to the intensity or brightness of light.
- (iii) For each metal, there is a characteristic minimum frequency,  $\nu_0$  (also known as **threshold frequency**) below which photoelectric effect is not observed. At a frequency  $\nu > \nu_0$ , the ejected electrons come out with certain kinetic energy. The kinetic energies of these electrons increase with the increase of frequency of the light used.

When a photon of sufficient energy strikes an electron in the atom of the metal, it transfers its energy instantaneously to the electron during the collision and the electron is ejected without any time lag or delay. Greater the energy possessed by the photon, greater will be transfer of energy to the electron and greater the kinetic energy of the ejected electron. In other words, kinetic energy of the ejected electron is proportional to the frequency of the electromagnetic radiation. Since the striking photon has energy equal to  $h\nu$  and the minimum energy required to eject the electron is  $h\nu_0$  (is also called work function,  $W_0$ ) then the difference in energy ( $h\nu - h\nu_0$ ) is transferred as the kinetic energy of the photoelectron. Following the conservation of energy principle, the kinetic energy of the ejected electron is given by the equation

$$h\nu = h\nu_0 + \frac{1}{2} m_e v^2$$

where  $m_e$  is the mass of the electron and  $v$  is the velocity associated with the ejected electron.

#### Example 1.

The threshold frequency  $\nu_0$  for a metal is  $6 \times 10^{14} \text{ s}^{-1}$ . Calculate the kinetic energy of an electron emitted when radiation of frequency  $\nu = 1.1 \times 10^{15} \text{ s}^{-1}$  hits the metal.



**Sol.**  $K.E. = \frac{1}{2} m_e v^2 = h(\nu - \nu_0)$

$\therefore K.E. = (6.626 \times 10^{-34}) (1.1 \times 10^{15} - 6 \times 10^{14})$

$\therefore K.E. = (6.626 \times 10^{-34}) (5 \times 10^{14})$

$= 3.313 \times 10^{-19} \text{ J}$

**Example 2.**

When electromagnetic radiation of wavelength 310 nm fall on the surface of Sodium, electrons are emitted with K.E. = 1.5 eV. Determine the work function ( $W_0$ ) of Sodium.

**Sol.**  $h\nu = \frac{12400}{3100} = 4 \text{ eV}$

$\frac{1}{2} m_e v^2 = 1.5 \text{ eV}$

$\therefore h\nu_0 = W_0 = h\nu - \frac{1}{2} m_e v^2 = 4 - 1.5 = 2.5 \text{ eV}$

**SOME IMPORTANT FORMULAE :**

1.  $A = Z + N$  (Number of neutrons)
2. dynamic mass of particle  $m = m_0 / [1 - (v/c)^2]^{1/2}$
3. Radius of nucleus  $R = R_0 (A)^{1/3}$ ,  $R_0 = 1.2 \times 10^{-15} \text{ m}$
4.  $c = \nu \lambda$
5. wave number  $\bar{\nu} = 1 / \lambda$
6.  $E = h\nu = hc / \lambda = hc \bar{\nu}$
7.  $F = K \frac{q_1 q_2}{r^2}$  ;  $K = \frac{1}{4\pi\epsilon_0} = 9.0 \times 10^9 \text{ Nm}^2/\text{C}^2$
8.  $\Delta E = h\nu = E_2 - E_1$

*Solved Examples*

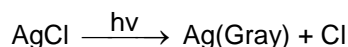
**Ex-3.** Calculate number of photon coming out per sec. from the bulb of 100 watt. If it is 50% efficient and wavelength coming out is 600 nm.

**Sol.** Energy = 100J

$$\text{Energy of one photon} = \frac{hc}{\lambda} = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{600 \times 10^{-9}} = \frac{6.625}{2} \times 10^{-19}$$

$$\text{no. of photon} = \frac{100}{6.625} \times 10^{19} = 15.09 \times 10^{19}$$

**Ex-4.** Certain sun glasses having small of AgCl incorporated in the lenses, on exposers to light of appropriate wavelength turns to gray colour to reduce the glare following the reactions:



If the heat of reaction for the decomposition of AgCl is 248 kJ mol<sup>-1</sup>, what maximum wavelength is needed to induce the desired process?

**Sol.** Energy needed to change = 248 × 10<sup>3</sup> J/mol

If photon is used for this purpose, then according to Einstein law one molecule absorbs one photon.

$$\text{Therefore, } \therefore N_A \cdot \frac{hc}{\lambda} = 248 \times 10^3$$

$$\lambda = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^8 \times 6.023 \times 10^{23}}{248 \times 10^3} = 4.83 \times 10^{-7} \text{ m}$$

**Ex-5.** Sodium street lamp gives off a characteristic yellow light of wavelength 588 nm. Calculate the energy mole (in kJ/mol) of these photons.

**Sol.**  $\lambda = 588 \text{ nm} = 588 \times 10^{-9} \text{ m}$

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

$$E = N_0 h\nu = N_0 h \frac{c}{\lambda}$$

$$= \frac{6.02 \times 10^{23} \times 6.63 \times 10^{-34} \times 3 \times 10^8}{588 \times 10^{-9}}$$

$$= 2.04 \times 10^5 \text{ J mol}^{-1} = 2.04 \times 10^2 \text{ kJ mol}^{-1}$$

**Ex-6.** Find the wavelength of 100 g particle moving with velocity 100 ms<sup>-1</sup>

$$\text{Sol. } \lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{0.1 \text{ kg} \times 100 \text{ ms}^{-1}}$$

$$= 6.626 \times 10^{-35} \text{ m.}$$

**Ex-7.** A bulb emits light of wavelength 4500 Å. The bulb is rated as 150 watt and 8% of the energy is emitted as light. How many photons are emitted by the bulb per second.

**Sol.** A 150 watt bulb emits 150 J of energy per second.

The energy emitted by the bulb as light

$$= 150 \times \frac{8}{100} = 12 \text{ J}$$

suppose the bulb emits n photons per second

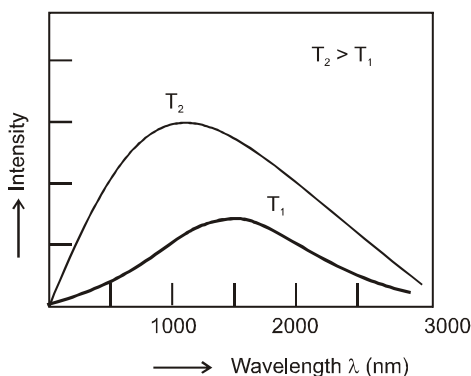
$$E = nh\nu = \frac{nhc}{\lambda}$$

$$n = \frac{E \times \lambda}{c \times h} = \frac{12 \text{ J} \times 4500 \times 10^{-10} \text{ m}}{3 \times 10^8 \text{ ms}^{-1} \times 6.63 \times 10^{-34} \text{ Js}} = 2.715 \times 10^{19}$$

### BLACK BODY RADIATION :

When solids are heated they emit radiation over a wide range of wavelengths.

The ideal body, which emits and absorbs all frequencies, is called a black body and the radiation emitted by such a body is called black body radiation. The exact frequency distribution of the emitted radiation (i.e., intensity versus frequency curve of the radiation) from a black body depends only on its temperature.



The above experimental results cannot be explained satisfactorily on the basis of the wave theory of light. Planck suggested that atoms and molecules could emit (or absorb) energy only in discrete quantities and not in a continuous manner.

**BOHR'S ATOMIC MODEL :** It is based on quantum theory of light.

It is applicable only for Hydrogen like species, for example  $\text{He}^+$ ,  $\text{Li}^{2+}$ ,  $\text{Be}^{3+}$ , etc.

**Assumptions of Bohr's model :**

- There are certain orbits around the nucleus such that if electron will be revolving in these orbit, then it does not emit any electromagnetic radiation. These are called stationary orbit for the  $e^-$ . The necessary centripetal force is produced by attraction forces of nucleus.

$$\frac{mv^2}{r} = \frac{Ke^2Z}{r^2}$$

- Angular momentum of the electron in these stationary orbit is always an integral multiple of  $\frac{h}{2\pi}$

$$mvr = \frac{nh}{2\pi}$$

- Electron can make jump from one stationary orbit to another stationary orbit by absorbing or emitting a photon of energy equal to difference in the energies of the stationary orbit i.e. energy change does not take place in continuous manner.

$$\frac{hc}{\Delta} = \Delta E$$

$\Delta E$  – difference in the energy of orbit

$$v = \frac{\Delta E}{h}$$

This is Bohr's frequency rule.

**Mathematical forms of Bohr's Postulates :**

**Calculation of the radius of the Bohr's orbit :** Suppose that an electron having mass 'm' and charge 'e' revolving around the nucleus of charge 'Ze' (Z is atomic number & e = charge) with a tangential/linear velocity of 'v'. Further consider that 'r' is the radius of the orbit in which electron is revolving.

According to Coulomb's law, the electrostatic force of attraction (F) between the moving electron and nucleus is :

$$F = \frac{KZe^2}{r^2} \quad \text{where : } K = \text{constant} = \frac{1}{4\pi\epsilon_0} = 9 \times 10^9 \text{ Nm}^2/\text{C}^2$$

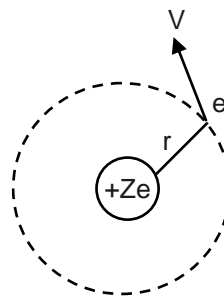
$$\text{and the centrifugal force } F = \frac{mv^2}{r}$$

For the stable orbit of an electron both the forces are balanced.

$$\text{i.e. } \frac{mv^2}{r} = \frac{KZe^2}{r^2}$$

then  $v^2 = \frac{KZe^2}{mr}$  ..... (i)

From the postulate of Bohr,



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

On squaring  $v^2 = \frac{n^2 h^2}{4\pi^2 m^2 r^2}$  ..... (ii)

From equation (i) and (ii)

$$\frac{KZe^2}{mr} = \frac{n^2 h^2}{4\pi^2 m^2 r^2}$$

On solving, we will get

$$r = \frac{n^2 h^2}{4\pi^2 m K Z e^2}$$

On putting the value of  $e$ ,  $h$ ,  $m$ , the radius of  $n^{\text{th}}$  Bohr orbit is given by :

$$r_n = 0.529 \times \frac{n^2}{Z} \text{ \AA}$$

### Solved Examples

**Ex-8.** Calculate radius ratio for 2<sup>nd</sup> orbit of He<sup>+</sup> ion & 3<sup>rd</sup> orbit of Be<sup>+++</sup> ion.

**Sol.**  $r_1$  (radius of 2<sup>nd</sup> orbit of He<sup>+</sup> ion) =  $0.529 \left( \frac{2^2}{2} \right) \text{ \AA}$

$$r_2 \text{ (radius of 3<sup>rd</sup> orbit of Be<sup>+++</sup> ion)} = 0.529 \left( \frac{3^2}{4} \right) \text{ \AA}$$

$$\text{Therefore } \frac{r_1}{r_2} = \frac{0.529 \times 2^2 / 2}{0.529 \times 3^2 / 4} = \frac{8}{9}$$

#### Calculation of velocity of an electron in Bohr's orbit :

Angular momentum of the revolving electron in  $n^{\text{th}}$  orbit is given by

$$mvr = \frac{nh}{2\pi}$$

$$v = \frac{nh}{2\pi mr} \text{ ..... (iii)}$$

put the value of 'r' in the equation (iii)

$$\text{then, } v = \frac{nh \times 4\pi^2 m Z e^2 K}{2\pi m n^2 h^2}$$

$$v = \frac{2\pi Ze^2 K}{nh}$$

on putting the values of  $\pi$ ,  $e^-$ ,  $h$  and  $K$

velocity of electron in  $n^{\text{th}}$  orbit  $v_n = 2.18 \times 10^6 \times \frac{Z}{n} \text{ m/sec}$  ;  $v \propto Z$  ;  $v \propto \frac{1}{n}$

$T$ , Time period of revolution of an electron in its orbit =  $\frac{2\pi r}{v}$

$f$ , Frequency of revolution of an electron in its orbit =  $\frac{v}{2\pi r}$

### Calculation of energy of an electron :

The total energy of an electron revolving in a particular orbit is

$$T.E. = K.E. + P.E.$$

where : P.E. = Potential energy , K.E. = Kinetic energy , T.E. = Total energy

The K.E. of an electron =  $\frac{1}{2}mv^2$

and the P.E. of an electron =  $-\frac{KZe^2}{r}$

Hence, T.E. =  $\frac{1}{2}mv^2 - \frac{KZe^2}{r}$

we know that,  $\frac{mv^2}{r} = \frac{KZe^2}{r^2}$  or  $mv^2 = \frac{KZe^2}{r}$

substituting the value of  $mv^2$  in the above equation :

$$T.E. = \frac{KZe^2}{2r} - \frac{KZe^2}{r} = -\frac{KZe^2}{2r}$$

$$\text{So, } T.E. = -\frac{KZe^2}{2r}$$

substituting the value of 'r' in the equation of T.E.

$$\text{Then } T.E. = -\frac{KZe^2}{2} \times \frac{4\pi^2 Ze^2 m}{n^2 h^2} = -\frac{2\pi^2 Z^2 e^4 m}{n^2 h^2} K^2$$

Thus, the total energy of an electron in  $n^{\text{th}}$  orbit is given by

$$T.E. = E_n = -\frac{2\pi^2 m e^4 k^2}{h^2} \left( \frac{Z^2}{n^2} \right) \quad \dots (iv)$$

Putting the value of  $m, e, h$  and  $\pi$  we get the expression of total energy

$$E_n = -13.6 \frac{Z^2}{n^2} \text{ eV / atom } n \uparrow T.E. \uparrow ; \quad Z \uparrow T.E. \downarrow$$

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

$$T.E. = \frac{1}{2} P.E.$$

$$T.E. = -K.E.$$

Note : - The P.E. at the infinite = 0

The K.E. at the infinite = 0

**Conclusion from equation of energy :**

- (a) The negative sign of energy indicates that there is attraction between the negatively charged electron and positively charged nucleus.
- (b) All the quantities on R.H.S. in the energy equation [Eq. iv] are constant for an element having atomic number  $Z$  except 'n' which is an integer such as 1,2,3, etc. i.e. the energy of an electron is constant as long as the value of 'n' is kept constant.
- (c) The energy of an electron is inversely proportional to the square of 'n' with negative sign.
- (d) Negative charge of the energy of  $e^-$  in the atom indicates that the energy of  $e^-$  in the atom is at lower energy than the energy of a free  $e^-$  at rest (which is taken to be zero).

### Solved Examples

**Ex-9** What are the frequency and wavelength of a photon emitted during a transition from  $n = 5$  state to the  $n = 2$  state in the hydrogen atom ?

**Sol.** Since  $n_i = 5$  and  $n_f = 2$ , this transition gives rise to a spectral line in the visible region of the Balmer series.

$$\Delta E = 2.18 \times 10^{-18} \text{ J} \left[ \frac{1}{5^2} - \frac{1}{2^2} \right] = -4.58 \times 10^{-19} \text{ J}$$

It is an emission energy

The frequency of the photon (taking energy in terms of magnitude) is given by

$$\nu = \frac{\Delta E}{h} = \frac{4.58 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ Js}} = 6.91 \times 10^{14} \text{ Hz}$$

$$\lambda = \frac{c}{\nu} = \frac{3.0 \times 10^8 \text{ ms}^{-1}}{6.91 \times 10^{14} \text{ Hz}} = 434 \text{ nm}$$

**Ex-10.** If the energy of an electron in 3rd Bohr orbit is  $-E$ , what is the energy of the electron of the electron in (i) 1st Bohr orbit (ii) 2nd Bohr orbit ?

**Sol.** According to Bohr's model,

$$E_n = \frac{E_1}{n^2}$$

$$E_3 = \frac{E_1}{(3)^2} = -E \text{ (given)}$$

$$\therefore E_1 = -9E$$

$$E_2 = \frac{E_1}{(2)^2} = -\frac{9E}{4} = 2.25 E$$

**Ex-11.** The ratio of  $(E_2 - E_1)$  to  $(E_4 - E_3)$  for  $\text{He}^+$  ion is approximately equal to (where  $E_n$  is the energy of  $n^{\text{th}}$  orbit) (1) 10 (2) 15 (3) 17 (4) 12

Sol. 
$$\frac{13.6 (2)^2 \left[ \frac{1}{(1)^2} - \frac{1}{(2)^2} \right]}{13.6 (2)^2 \left[ \frac{1}{(3)^2} - \frac{1}{(4)^2} \right]} = 15$$

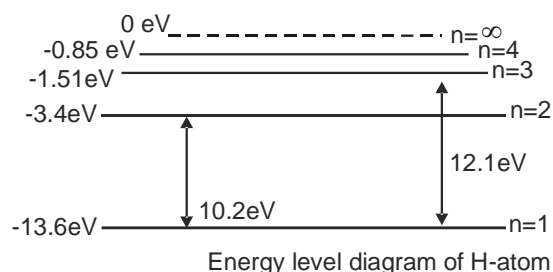
Ans. (2)

**Failures / limitations of Bohr's theory:**

- (a) He could not explain the line spectra of atoms containing more than one electron.
- (b) He also could not explain the presence of doublet i.e. 2 closely spaced lines.
- (c) He was unable to explain the splitting of spectral lines in magnetic field (Zeeman effect) and in electric field (Stark effect)
- (d) No conclusion was given for the principle of quantisation of angular momentum.
- (e) He was unable to explain the de-Broglie's concept of dual nature of matter.
- (f) He could not explain Heisenberg's uncertainty principle.
- (g) Could't explain the ability of atoms to form molecules by chemical bonds.

**Energy Level Diagram :**

- (i) Orbit of lowest energy is placed at the bottom, and all other orbits are placed above this.
- (ii) The gap between two orbits is proportional to the energy difference of the orbits.

**DEFINITION VALID FOR SINGLE ELECTRON SYSTEM :****(i) Ground state :**

Lowest energy state of any atom or ion is called ground state of the atom. For it  $n = 1$ .

Ground state energy of H-atom = - 13.6 eV

Ground state energy of  $\text{He}^+$  Ion = - 54.4 eV

**(ii) Excited State :**

States of atom other than the ground state are called excited states :

$n = 2$	first excited state
$n = 3$	second excited state
$n = 4$	third excited state
$n = n + 1$	$n^{\text{th}}$ excited state

**(iii) Ionisation energy (IE) :**

Minimum energy required to move an electron from ground state to  $n = \infty$  is called ionisation energy of the atom or ion.

Ionisation energy of H-atom = 13.6 eV

Ionisation energy of  $\text{He}^+$  ion = 54.4 eV

Ionisation energy of  $\text{Li}^{+2}$  ion = 122.4 eV

**(iv) Ionisation Potential (I.P.) :**

Potential difference through which a free electron must be accelerated from rest, such that its kinetic energy becomes equal to ionisation energy of the atom is called ionisation potential of the atom.

I.P. of H atom = 13.6 V, I.P. of He<sup>+</sup> Ion = 54.4 V

**(v) Excitation Energy :**

Energy required to move an electron from ground state of the atom to any other state of the atom is called excitation energy of that state.

Excitation energy of 2<sup>nd</sup> state = excitation energy of 1<sup>st</sup> excited state = 1<sup>st</sup> excitation energy = 10.2 eV.

**(vi) Excitation Potential :**

Potential difference through which an electron must be accelerated from rest to so that its kinetic energy become equal to excitation energy of any state is called excitation potential of that state.

Excitation potential of third state = excitation potential of second excited state = second excitation potential = 12.09 V.

**(vii) Binding Energy 'or' Separation Energy :**

Energy required to move an electron from any state to  $n = \infty$  is called binding energy of that state.

Binding energy of ground state = I.E. of atom or Ion.

### Solved Examples

**Ex-12** A single electron system has ionization energy 11180 kJ mol<sup>-1</sup>. Find the number of protons in the nucleus of the system.

**Sol.**  $I.E. = \frac{Z^2}{n^2} \times 21.69 \times 10^{-19} \text{ J}$

$$\frac{11180 \times 10^3}{6.023 \times 10^{23}} = \frac{Z^2}{1^2} \times 21.69 \times 10^{-19} \quad \text{Ans. } Z = 3$$

**Ex-13.** The ionization energy of He<sup>+</sup> is  $19.6 \times 10^{-18} \text{ J/atom}$ . Calculate the energy of the first stationary state of Li<sup>2+</sup>.

**Sol.** For H-like species

$$I.E. = I.E._{(H)} \times Z^2$$

$$\therefore I.E._{(He^+)} = Z^2 \times I.E._{(H)}$$

$$19.6 \times 10^{-18} \text{ J} = (2)^2 \times I.E._{(H)}$$

$$I.E._{(H)} = \frac{19.6 \times 10^{-18}}{4} \text{ J}$$

$$I.E._{(Li^{2+})} = Z^2 \times I.E._{(H)}$$

$$= \frac{(3)^2 \times 19.6 \times 10^{-18}}{4}$$

$$= 4.41 \times 10^{-17} \text{ J/atom}$$

$$I.E._{(Li^{2+})} = E_{\infty} - E_1$$

$$4.41 \times 10^{-17} = 0 - E_1$$

$$E_1 = -4.41 \times 10^{-17} \text{ J/atom.}$$

**Ex-14.** If the binding energy of 2<sup>nd</sup> excited state of a hydrogen like sample is 24 eV approximately, then the ionisation energy of the sample is approximately

- (1) 54.4 eV                      (2) 24 eV                      (3) 122.4 eV                      (4) 216 eV



Sol.  $\frac{13.6(Z)^2}{(3)^2} = 24$

I.E. =  $13.6(Z)^2 = (24 \times 9) = 216 \text{ eV}$

Ans. (4)

**Ex-15.** The ionisation energy of H atom is  $21.79 \times 10^{-19} \text{ J}$ . Then the value of binding energy of second excited state of  $\text{Li}^{2+}$  ion

(1)  $3^2 \times 21.7 \times 10^{-19} \text{ J}$

(2)  $21.79 \times 10^{-19} \text{ J}$

(3)  $\frac{1}{3} \times 21.79 \times 10^{-19} \text{ J}$

(4)  $\frac{1}{3^2} \times 21.79 \times 10^{-19} \text{ J}$

Sol. B.E. =  $\frac{21.79 \times 10^{-19} (3)^2}{(3)^2} = 21.79 \times 10^{-19} \text{ J}$

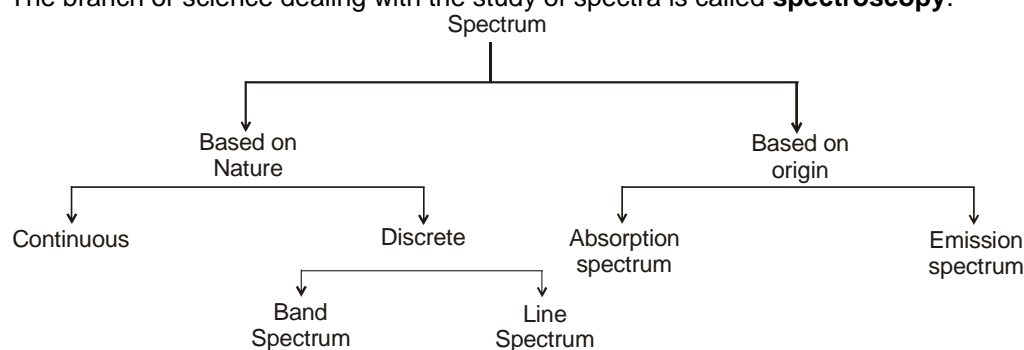
Ans. (2)

## HYDROGEN SPECTRUM :

### Study of Emission and Absorption Spectra :

An instrument used to separate the radiation of different wavelengths (or frequencies) is called spectroscope or a spectrograph. Photograph (or the pattern) of the emergent radiation recorded on the film is called a spectrogram or simply a spectrum of the given radiation.

The branch or science dealing with the study of spectra is called **spectroscopy**.



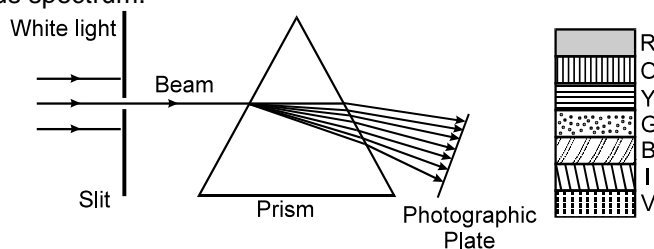
### Emission spectra :

When the radiation emitted from some source e.g. from the sun or by passing electric discharge through a gas at low pressure or by heating some substance to high temperature etc, is passed directly through the prism and then received on the photographic plate, the spectrum obtained is called 'Emission spectrum'.

Depending upon the source of radiation, the emission spectra are mainly of two type :

#### (a) Continuous spectra :

When white light from any source such as sun, a bulb or any hot glowing body is analysed by passing through a prism it is observed that it splits up into seven different wide band of colours from violet to red. These colours are so continuous that each of them merges into the next. Hence the spectrum is called continuous spectrum.



**(b) Discrete spectra :** It is of two type

#### (i) Band spectrum

Band spectrum contains colourful continuous bands separated by some dark space. Generally, molecular spectrum are band spectrum.

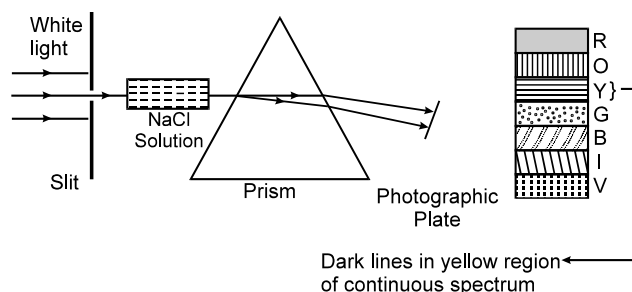
**(ii) Line Spectrum :**

This is the ordered arrangement of lines of particular wavelength separated by dark space eg. hydrogen spectrum.

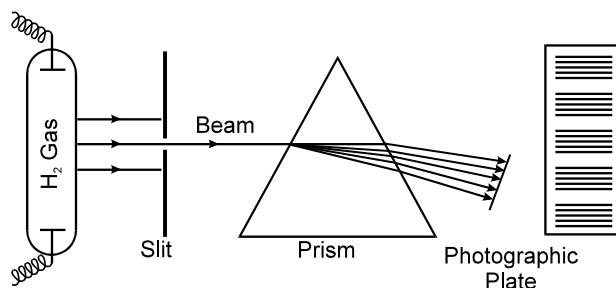
Line spectrum can be obtained from atoms.

**Absorption spectra :**

When white light from any source is first passed through the solution or vapours of a chemical substance and then analysed by the spectroscope, it is observed that some dark lines are obtained in the continuous spectrum. These dark lines are supposed to result from the fact that when white light (containing radiations of many wavelengths) is passed through the chemical substance, radiations of certain wavelengths are absorbed, depending upon the nature of the element.



**EMISSION SPECTRUM OF HYDROGEN :**

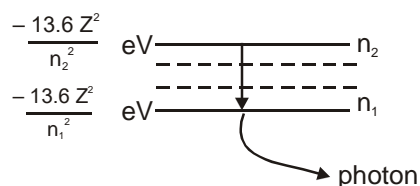


When hydrogen gas at low pressure is taken in the discharge tube and the light emitted on passing electric discharge is examined with a spectroscope, the spectrum obtained is called the emission spectrum of hydrogen.

**Line Spectrum of Hydrogen :**

Line spectrum of hydrogen is observed due to excitation or de-excitation of electron from one stationary orbit to another stationary orbit

Let electron make transition from  $n_2$  to  $n_1$  ( $n_2 > n_1$ ) in a H-like sample



$$\text{Energy of emitted photon} = (\Delta E)_{n_2 \rightarrow n_1} = \frac{-13.6Z^2}{n_2^2} - \left( \frac{-13.6Z^2}{n_1^2} \right) = 13.6Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Wavelength of emitted photon

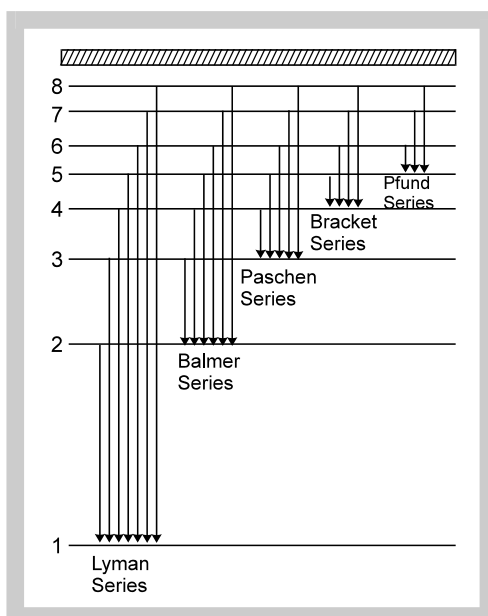
$$\lambda = \frac{hc}{(\Delta E)_{n_2 \rightarrow n_1}}$$

$$\lambda = \frac{hc}{13.6Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)}$$

$$\frac{1}{\lambda} = \frac{(13.6)Z^2}{hc} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\text{Wave number, } \frac{1}{\lambda} = \bar{\nu} = RZ^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$R = \text{Rydberg constant} = 1.09678 \times 10^7 \text{ m}^{-1}; R \approx 1.1 \times 10^7 \text{ m}^{-1}; R = \frac{13.6 \text{ eV}}{hc}; R h c = 13.6 \text{ eV}$$



### Solved Examples

**Ex-16** Calculate the wavelength of a photon emitted when an electron in H- atom makes a transition from  $n = 2$  to  $n = 1$

**Sol.** 
$$\frac{1}{\lambda} = RZ^2 \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\therefore \frac{1}{\lambda} = R(1)^2 \left[ \frac{1}{1^2} - \frac{1}{2^2} \right]$$

$$\therefore \frac{1}{\lambda} = \frac{3R}{4} \text{ or } \lambda = \frac{4}{3R}$$

### SPECTRA LINES OF HYDROGEN ATOM : LYMAN SERIES

\* It is first spectral series of H.

- \* It was found to be in ultraviolet region by Lyman in 1898.
- \* For it value of  $n_1 = 1$  and  $n_2 = 2, 3, 4$  where ' $n_1$ ' is ground state and ' $n_2$ ' is called excited state of electron present in a H - atom.

$$\frac{1}{\lambda} = R_H \left[ \frac{1}{1^2} - \frac{1}{n_2^2} \right] \text{ where } n_2 > 1 \text{ always.}$$

$$\text{The wavelength of marginal line (i.e. } n_2 = \infty) = \frac{n_1^2}{R_H} \text{ for all series. So for lyman series } \lambda = \frac{1}{R_H}.$$

\* 1<sup>st</sup> line of lyman series  $\Rightarrow 2 \rightarrow 1$

II<sup>nd</sup> line of lyman series  $= 3 \rightarrow 1$

Last line of lyman series  $= \infty \rightarrow 1$

$$[10.2 \text{ eV} \leq (\Delta E)_{\text{lyman}} \leq 13.6 \text{ eV}]$$

$$\frac{12400}{13.6} \leq \lambda_{\text{lyman}} \leq \frac{12400}{10.2} \text{ A}^\circ$$

$$\text{* Longest line : longest wavelength line } \lambda_{\text{longest}} \text{ or } \lambda_{\text{max.}} = \frac{12400}{(\Delta E)_{\text{min}}}$$

$$\text{* Shortest line : shortest wavelength line } \lambda_{\text{shortest}} \text{ or } \lambda_{\text{min}} = \frac{12400}{(\Delta E)_{\text{max}}}$$

\* First line of any spectral series is the longest ( $\lambda_{\text{max}}$ ) line.

\* Last line of any spectral series is the shortest ( $\lambda_{\text{min}}$ ) line.

#### Series limit :

It is the last line of any spectral series.

$$\text{Wave no of 1<sup>st</sup> line of Lyman series} = \frac{1}{\lambda} = \bar{\nu} = R \times 1^2 \left( \frac{1}{1^2} - \frac{1}{2^2} \right)$$

$$\bar{\nu} = R \times 1^2 \left( \frac{4-1}{4} \right)$$

$$\bar{\nu} = \frac{R \times 3}{4} = \frac{3}{4} R$$

$$\therefore \left[ \lambda = \frac{4}{3R} \right]$$

Wave no of last line of Lyman series

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

$$\bar{\nu} = R$$

For Lyman series,

$$\lambda_{\text{longest}} = \frac{12400}{(\Delta E)_{2 \rightarrow 1}}, \lambda_{\text{shortest}} = \frac{12400}{(\Delta E)_{\infty \rightarrow 1}}$$

#### BALMER SERIES :

- \* It is the second series of H-spectrum.
- \* It was found to be in visible region by Balmer in 1892.
- \* For it value of  $n_1 = 2$  and  $n_2 = 3, 4, 5, \dots$

$$\text{* The wavelength of marginal line of Balmer series} = \frac{n_1^2}{R_H} = \frac{2^2}{R_H} = \frac{4}{R_H}$$

$$* \quad \frac{1}{\lambda} = R_H \left( \frac{1}{2^2} - \frac{1}{n_2^2} \right) \text{ where } n_2 > 2 \text{ always.}$$

$$1.9 \leq (\Delta E)_{\text{balmer}} \leq 3.4 \text{ eV.}$$

All the lines of balmer series in H spectrum are not in the visible range. Infact only 1<sup>st</sup> 4 lines belongs to visible range.

$$\frac{12400}{3.4} \text{ Å} \leq \lambda_{\text{balmer}} \leq \frac{12400}{1.9} \text{ Å}$$

$$3648 \text{ Å} \leq \lambda_{\text{balmer}} \leq 6563 \text{ Å}$$

Lines of balmer series (for H atom) lies in the visible range.

1<sup>st</sup> line of balmer series =  $3 \rightarrow 2$

last line of balmer series =  $\infty \rightarrow 2$

$$(\bar{\nu}) \text{ 1<sup>st</sup> line} = R \times 1 \left( \frac{1}{2^2} - \frac{1}{3^2} \right) = \frac{5R}{36}$$

$$(\bar{\nu}) \text{ last line} = R \left( \frac{1}{2^2} - \frac{1}{\infty^2} \right) = \frac{R}{4}$$

#### PASCHEN SERIES :

(a) It is the third series of H - spectrum.

(b) It was found to be in infrared region by Paschen.

(c) For it value of  $n_1 = 3$  and  $n_2 = 4, 5, 6, \dots$

$$(d) \text{ The wavelength of marginal line of Paschen series} = \frac{n_1^2}{R_H} = \frac{3^2}{R_H} = \frac{9}{R_H}.$$

$$(e) \quad \frac{1}{\lambda} = R_H \left[ \frac{1}{3^2} - \frac{1}{n_2^2} \right] \text{ where } n_2 > 3 \text{ always.}$$

#### BRACKETT SERIES :

(a) It is fourth series of H - spectrum.

(b) It was found to be in infrared region by Brackett.

(c) For it value of  $n_1 = 4$  and  $n_2 = 5, 6, 7, \dots$

$$(d) \text{ The wavelength of marginal line of brackett series} = \frac{n_1^2}{R_H} = \frac{4^2}{R_H} = \frac{16}{R_H}$$

$$(e) \quad \frac{1}{\lambda} = R_H \left[ \frac{1}{4^2} - \frac{1}{n_2^2} \right] \text{ where } n_2 > 4 \text{ always.}$$

#### PFUND SERIES :

(a) It is fifth series of H- spectrum.

(b) It was found to be in infrared region by Pfund.

(c) For it value of  $n_1 = 5$  and  $n_2 = 6, 7, 8, \dots$  where  $n_1$  is ground state and  $n_2$  is excited state.

$$(d) \text{ The wavelength of marginal line of Pfund series} = \frac{n_1^2}{R_H} = \frac{5^2}{R_H} = \frac{25}{R_H}$$

$$(e) \quad \frac{1}{\lambda} = \left[ \frac{1}{5^2} - \frac{1}{n_2^2} \right] R_H \text{ where } n_2 > 5 \text{ always.}$$

#### HUMPHRY SERIES :

(a) It is the sixth series of H-spectrum.

(b) It was found to be in infrared region by Humphry.

(c) For it value of  $n_1 = 6$  and  $n_2 = 7, 8, 9$  .....

(d) The wavelength of marginal line of Humphry series  $= \frac{n_1^2}{R_H} = \frac{6^2}{R_H} = \frac{36}{R_H}$

(e)  $\frac{1}{\lambda} = R_H \left[ \frac{1}{6^2} - \frac{1}{n_2^2} \right]$  where  $n_2 > 6$ .

### Solved Examples

**Ex-17** Electron in hydrogen atom is in fourth stationary state. What is the maximum number of spectral lines that can be observed as it de-excites.

**Sol.** Maximum number of spectral lines from  $n^{\text{th}}$  state  $= \frac{n(n-1)}{2}$

$$n = 4$$

$$\frac{n(n-1)}{2} = \frac{4(4-1)}{2} = 6$$

**Ans. 6**

**Ex-18** Calculate wavelength for 2<sup>nd</sup> line of Balmer series of  $\text{He}^+$  ion

**Sol.**  $\frac{1}{\lambda} = R(2)^2 \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$

$$n_1 = 2 \quad n_2 = 4$$

$$\frac{1}{\lambda} = R(2^2) \left[ \frac{1}{2^2} - \frac{1}{4^2} \right]$$

$$\frac{1}{\lambda} = \frac{3}{4} R \quad \lambda = \frac{4}{3} R \quad \text{Ans.}$$

**Ex-19.** calculate the wavelength and energy of radiation emitted for the electronic transition from infinity to stationary state one of the hydrogen atom.

**Sol.**  $\frac{1}{\lambda} = 109678 \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$

$$= 109678 \left[ \frac{1}{(1)^2} - \frac{1}{\infty} \right] = 109678 \text{ cm}^{-1}$$

$$\lambda = \frac{1}{109678} \text{ cm} = 9.1 \times 10^{-6} \text{ cm}$$

$$= 9.1 \times 10^{-8} \text{ m} = 91 \text{ nm.}$$

$$E = \frac{hc}{\lambda} = \frac{6.63 \times 10^{-34} \text{ J.s} \times 3 \times 10^8 \text{ ms}^{-1}}{9.1 \times 10^{-8} \text{ m}}$$

$$= 2.186 \times 10^{-18} \text{ J}$$

**Ex-20.** Calculate the wavelength of the radiation emitted, producing a line in the Lyman series when an electron falls from fourth stationary state in hydrogen atom ( $R_H = 1.1 \times 10^7 \text{ m}^{-1}$ )

**Sol.** For Lyman series  $n_1 = 1$

$$\frac{1}{\lambda} = R_H \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] = 1.1 \times 10^7 \text{ m}^{-1} \left[ \frac{1}{(1)^2} - \frac{1}{(4)^2} \right]$$

$$= 1.1 \times 10^7 \times \frac{15}{16}$$

$$\lambda = 9.7 \times 10^{-8} \text{ m} = 97 \text{ nm}$$

**Ex-21.** Calculate the wave number for the shortest wavelength transition in the Balmer series of atomic hydrogen.

**Sol.** The shortest wavelength transition corresponds to  $n_2 = \infty$  to  $n_1 = 2$  transition

$$\bar{\nu} = 109678 \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ cm}^{-1}$$

$$= 109678 \left[ \frac{1}{(2)^2} - \frac{1}{\infty} \right]$$

$$= \frac{109678}{4} = 27419.5 \text{ cm}^{-1}$$

**Ex-22.** The energy of the electron in the second and third Bohr orbits of hydrogen atom is  $-5.42 \times 10^{-12}$  ergs and  $-2.41 \times 10^{-12}$  ergs respectively. Calculate the wavelength of the emitted radiation when electron drops from third to second orbits.

**Sol.**  $\Delta E = E_3 - E_2$

$$= -2.41 \times 10^{-12} - (-5.42 \times 10^{-12}) \text{ ergs}$$

$$= -2.41 \times 10^{-12} + 5.42 \times 10^{-12} \text{ ergs}$$

$$= 3.01 \times 10^{-12} \text{ ergs}$$

$$\text{Now } h = 6.63 \times 10^{-27} \text{ ergs s,}$$

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

$$\Delta E = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{6.63 \times 10^{-27} \text{ ergs.s} \times 3 \times 10^{10} \text{ cms}^{-1}}{3.01 \times 10^{-12} \text{ ergs}} = 6.6 \times 10^{-5} \text{ cm} = 6.6 \times 10^3 \text{ \AA}$$

**Ex-23.** Calculate the energy emitted when electrons of 1.0 g atom of hydrogen undergo transition giving the spectral line of lowest energy in the visible region of its atomic spectrum. ( $R_H = 1.1 \times 10^7 \text{ m}^{-1}$ )

**Sol.**  $\frac{1}{\lambda} = R_H \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$

$$= 1.1 \times 10^7 \text{ m}^{-1} \left[ \frac{1}{(2)^2} - \frac{1}{(3)^2} \right]$$

$$= 1.1 \times 10^7 \times \frac{5}{36} \text{ m}^{-1}$$

$$\lambda = 6.545 \times 10^{-7} \text{ m.}$$

$$\text{Energy emitted per atom, } E = \frac{hc}{\lambda}$$

$$= \frac{6.62 \times 10^{-34} \text{ J.s} \times 3 \times 10^8 \text{ ms}^{-1}}{6.545 \times 10^{-7} \text{ m}}$$

$$= 3.03 \times 10^{-19} \text{ J}$$

1.0 g atom hydrogen contains 1 mole hydrogen atoms

Energy emitted by 1.0 g atom of hydrogen

$$N_A \times 3.03 \times 10^{-19} \text{ J}$$

$$= 6.02 \times 10^{23} \times 3.03 \times 10^{-19} \text{ J}$$

$$= 1.82 \times 10^5 \text{ J}$$

**Ex-24.** The wave number of the first line in the Balmer series of hydrogen is  $15200 \text{ cm}^{-1}$ . What would be the wavenumber of the first line in the Lyman series of the  $\text{Be}^{3+}$  ion?

- (1)  $2.4 \times 10^5 \text{ cm}^{-1}$       (2)  $24.3 \times 10^5 \text{ cm}^{-1}$       (3)  $6.08 \times 10^5 \text{ cm}^{-1}$       (4)  $1.313 \times 10^6 \text{ cm}^{-1}$

**Sol.** Given  $15200 = R(1)^2 \left[ \frac{1}{(2)^2} - \frac{1}{(3)^2} \right]$  ..... (1)

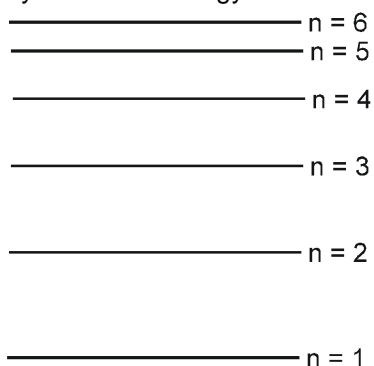
Then  $\bar{\nu} = R(4)^2 \left[ \frac{1}{(1)^2} - \frac{1}{(2)^2} \right]$  ..... (2)

from (1) and (2) equation

$$\bar{\nu} = 1.313 \times 10^6 \text{ cm}^{-1}$$

**Ans. (4)**

**Ex-25.** What would be the maximum number of emission lines for atomic hydrogen that you would expect to see with the naked eye if the only electronic energy levels involved are those as shown in the Figure?



Hint : Balmer series lines lies in visible region.

- (1) 4      (2) 6      (3) 5      (4) 15

**Sol.** Only four lines are present in visible region,  $6 \rightarrow 2$ ,  $5 \rightarrow 2$ ,  $4 \rightarrow 2$  &  $3 \rightarrow 2$ .

### No. of photons emitted by a sample of H atom :

If an electron is in any higher state  $n = n_2$  and makes a transition to ground state, then total no. of different photons emitted is equal to  $\frac{n \times (n-1)}{2}$ .

If an electron is in any higher state  $n = n_2$  and makes a transition to another excited state  $n = n_1$ , then total no. of different photons emitted is equal to  $\frac{\Delta n (\Delta n + 1)}{2}$ , where  $\Delta n = n_2 - n_1$

**Note :** In case of single isolated atom if electron make transition from  $n^{\text{th}}$  state to the ground state then max. number of spectral lines observed =  $(n-1)$

### Solved Examples



**Ex-26** If electron make transition from 7<sup>th</sup> excited state to 2<sup>nd</sup> state in H atom sample find the max. number of spectral lines observed.

**Sol.**  $\Delta n = 8 - 2 = 6$

$$\text{spectral lines} = 6 \left( \frac{6+1}{2} \right) = 6 \times \frac{7}{2} = 21$$

### Dual nature of electron (de-Broglie Hypothesis):

(a) Einstein had suggested that light can behave as a wave as well as like a particle i.e. it has dual character.

(b) In 1924, de-Broglie proposed that an electron behaves both as a material particle and as a wave.

(c) This proposed a new theory, the wave mechanical theory of matter. According to this theory, the electrons protons and even atom when in motion possess wave properties.

(d) According to de-Broglie, the wavelength associated with a particle of mass  $m$ , moving with velocity  $v$  is given by the relation,

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

where  $h$  is Planck's constant

(e) This can be derived as follows according to Planck's equation.

$$E = h\nu = \frac{h.c}{\lambda}$$

Energy of photon on the basis of Einstein's mass energy relationship

$$E = mc^2 \quad \text{or} \quad \lambda = \frac{h}{mc}$$

Equating both we get

$$\frac{h.c}{\lambda} = mc^2$$

$$\text{or} \quad \lambda = \frac{h}{mc}$$

Which is same as de - Broglie relation.

$$\begin{array}{c} \lambda = \frac{h}{p} \\ \downarrow \\ \lambda = \frac{h}{mv} \quad \lambda = \frac{h}{\sqrt{2mKE}} \quad \lambda = \frac{h}{\sqrt{2mqV}} \end{array}$$

\* If an electron is accelerated through a potential difference of 'V' volt from rest then :

$$\Rightarrow \lambda = \frac{h}{\sqrt{2m_e(eV)}}$$

$$\Rightarrow \lambda = \sqrt{\left( \frac{150}{V} \right)} \text{ \AA} \quad (\text{on putting values of } h, m_e \text{ and } e)$$

$$\lambda = \frac{12.3}{\sqrt{V}} \text{ \AA} \quad (V \text{ in volt})$$

$$* \quad mvr = n \times \frac{h}{2\pi}$$

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

$$mv = \frac{h}{\lambda} \text{ putting this in } mvr = \frac{nh}{2\pi}$$

$$\therefore \frac{h}{\lambda} r \frac{nh}{2\pi} \Rightarrow \left[ \lambda = \frac{2\pi r}{n} \right] = \text{de Broglie wavelength}$$

### Solved Examples

**Ex-27** What will be the wavelength of a ball of mass 0.1 kg moving with a velocity of 10 m s<sup>-1</sup> ?

**Sol.** According to de Broglie equation

$$\lambda = \frac{h}{mv} = \frac{(6.626 \times 10^{-34} \text{ Js})}{(0.1 \text{ kg}) (10 \text{ m s}^{-1})} = 6.626 \times 10^{-34} \text{ m (J = kg m}^2 \text{ s}^{-2}).$$

**Ex-28.** A moving electron has  $5 \times 10^{-25}$  J of kinetic energy. What is the de-broglie wavelength ?

**Sol.** Mass of the electron  $m = 9.1 \times 10^{-31}$  kg

$$\text{K.E.} = \frac{1}{2} mv^2 = 5 \times 10^{-25} \text{ J}$$

$$\lambda = \frac{h}{\sqrt{2m \times \text{K.E.}}}$$

$$= \frac{6.626 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 5 \times 10^{-25}}}$$

$$= 6.95 \times 10^{-7} \text{ m.}$$

**Ex-29.** The de Broglie wavelength of an electron moving in a circular orbit is  $\lambda$ . The minimum radius of orbit is

- (1)  $\frac{\lambda}{\pi}$                       (2)  $\frac{\lambda}{2\pi}$                       (3)  $\frac{\lambda}{4\pi}$                       (4)  $\frac{\lambda}{3\pi}$

**Sol.** We know  $2\pi r = n\lambda$   
For minimum radius  $n = 1$

$$2\pi r_{\min} = \lambda \quad ; \quad r_{\min} = \frac{\lambda}{2\pi}$$

**Ans. (2)**

**Ex-30.** An electron, practically at rest, is initially accelerated through a potential difference of 100 volts. It then has a de Broglie wavelength =  $\lambda_1$  Å. It then get retarded through 19 volts and then has a wavelength  $\lambda_2$

Å. A further retardation through 32 volts changes the wavelength to  $\lambda_3$ , What is  $\frac{\lambda_3 - \lambda_2}{\lambda_1}$  ?

- (1)  $\frac{20}{41}$                       (2)  $\frac{10}{63}$                       (3)  $\frac{20}{63}$                       (4)  $\frac{10}{41}$

**Sol.**  $\lambda_1 = \sqrt{\frac{150}{100}} \text{ \AA} \quad \dots (1) \quad \lambda_2 = \sqrt{\frac{150}{81}} \text{ \AA} \quad \dots (2)$

$$\lambda_3 = \sqrt{\frac{150}{49}} \text{ \AA} \quad \dots (3)$$

From (1), (2) and (3)

$$\frac{\lambda_3 - \lambda_2}{\lambda_1} = \frac{20}{63}$$

Ans. (3)

### HEISENBERG'S UNCERTAINTY PRINCIPLE :

It is impossible to measure simultaneously both the position and velocity (or momentum) of a microscopic particle with absolute accuracy or certainty.

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi} \quad \text{or} \quad m \Delta x \cdot \Delta v \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$$

where,  
 $\Delta x$  = uncertainty in position  
 $\Delta p$  = uncertainty in momentum  
 $h$  = Planck's constant  
 $m$  = mass of the particle  
 $\Delta v$  = uncertainty in velocity

- In terms of uncertainty in energy  $\Delta E$ , and uncertainty in time  $\Delta t$ , this principle is written as,

$$\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$$

- Heisenberg replaced the concept of definite orbits by the concept of probability.

### Solved Examples

**Ex-31.** Alveoli are the tiny sacs of air in the lungs whose average diameter is 50 pm. Consider an oxygen molecule trapped within a sac. Calculate uncertainty in the velocity of oxygen molecule?

- (1)  $1.98 \times 10^{-2} \text{ ms}^{-1}$       (2\*)  $19.8 \text{ ms}^{-1}$       (3)  $198 \times 10^{-4} \text{ ms}^{-1}$       (4)  $19.8 \times 10^{-6} \text{ ms}^{-1}$

**Sol.**  $\Delta x = 50 \text{ pm}$

$$\begin{aligned} \text{So } \Delta v &= \frac{h}{4\pi \cdot m \Delta x} = \frac{6.625 \times 10^{-34} \times 6.022 \times 10^{23}}{4 \times 3.14 \times 32 \times 10^{-3} \times 50 \times 10^{-12}} \text{ m/sec} \\ &= 0.0019853 \times 10^4 \text{ m/sec} \\ &= 19.853 \text{ m/sec} \end{aligned}$$

**Ex-32.** Determine the de-Broglie wavelength associated with an electron in the 3<sup>rd</sup> Bohr's orbit of  $\text{He}^+$  ion?

- (1)  $10 \text{ \AA}$       (2)  $2 \text{ \AA}$       (3\*)  $5 \text{ \AA}$       (4)  $1 \text{ \AA}$

**Sol.**  $n\lambda = 2\pi r$

$$\text{so } \lambda = \frac{2\pi r}{3} = \frac{2\pi}{3} \times (53 \text{ pm}) \times \frac{9}{2} \approx 5 \text{ \AA}$$

**Ex-33.** If the light of wavelength  $5.77 \times 10^{-10} \text{ cm}$  is used to detect an electron then the uncertainty in velocity (approximately) will be ( $h = 6.6 \times 10^{-34} \text{ Js}$ ,  $m_e = 9.1 \times 10^{-31} \text{ kg}$ ).

- (1)  $10^6 \text{ m/s}$       (2)  $10^6 \text{ m/s}$       (3\*)  $10^7 \text{ m/s}$       (4) None of these

$$\text{Sol. } \Delta V = \frac{h}{4\pi m \Delta x} = \frac{6.6 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31} \times 5.77 \times 10^{-12}} = 10^7 \text{ m/s}$$

**Ex-34.** The uncertainty in position and velocity of the particle are  $0.1 \text{ nm}$  and  $5.27 \times 10^{-24} \text{ ms}^{-1}$  respectively then the mass of the particle is : ( $h = 6.625 \times 10^{-34} \text{ Js}$ )

- (1)  $200 \text{ g}$       (2)  $300 \text{ g}$       (3\*)  $100 \text{ g}$       (4)  $1000 \text{ g}$

**Sol.**  $m = \frac{h}{4\pi\Delta x} = \frac{6.6 \times 10^{-34}}{4 \times 3.14 \times 10^{-10} \times 5.27 \times 10^{-24}}$   
 $\approx 100 \text{ gm.}$

**Ex-35.** Uncertainty in position of a hypothetical subatomic particle is  $1 \text{ \AA}$  and uncertainty in velocity is  $\frac{3.3}{4\pi} \times 10^5$

m/s then the mass of the particle is approximately [ $h = 6.6 \times 10^{-34} \text{ Js}$ ]

(1)  $2 \times 10^{-28} \text{ kg}$  (2)  $2 \times 10^{-27} \text{ kg}$  (3)  $2 \times 10^{-29} \text{ kg}$  (4)  $4 \times 10^{-29} \text{ kg}$

**Sol.**  $\Delta x \times m \times \Delta v \geq h/4\pi$

$$1 \times 10^{-10} \times m \times \frac{3.3}{4\pi} \times 10^5 \geq \frac{6.6 \times 10^{-34}}{4 \times \pi} \quad m = 2 \times 10^{-29} \text{ kg}$$

**Ans. (3)**

### THE SCHRODINGER EQUATION :

This equation determines the probability of position and energy of electron which is moving around the nucleus.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad \text{or} \quad \nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

Where  $\nabla^2$  = Laplacian operator.

E = Total energy of the electron.

V = Potential energy of the electron

$\psi$  = Wave function or wave amplitude

$\psi^2$  = Probability density (probability of finding an electron in an atom)

#### Important features of the quantum mechanical model of atom

Quantum mechanical model of atom is the picture of the structure of the atom, which emerges from the application of the Schrodinger equation to atoms. The following are the important features of the quantum mechanical model of atom :

1. The energy of electrons in atoms is quantized (i.e. can only have certain specific values), for example when electron are bound to the nucleus in atoms.
2. The existence of quantized electronic energy levels is a direct result of the wave like properties of electrons and are allowed solutions of schrodinger wave equation.
3. Both the exact position and exact velocity of an electron in an atom cannot be determined simultaneously (Heisenberg uncertainty principle). The path of an electron in an atom therefore, can never be determined or known accurately. That is why, as you shall see later on, one talks of only probability of finding the electron at different points in an atom .
4. An atomic orbital is the wave function  $\psi$  for an electron in an atom. Whenever an electron is described by a wave function, we say that the electron occupies that orbital
5. The probability of finding an electron at a point within an atom is proportional to the square of the orbital wave function i.e.  $|\psi|^2$  at that point.  $|\psi|^2$  is known as probability density and is always positive.

#### Hydrogen atom and the schrodinger Equation :

When Schrodinger equation is solved for hydrogen atom. The solution gives the possible energy levels the electron can occupy and the corresponding wave function(s) ( $\psi$ ) of the electron associated with each energy level. These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (**principal quantum number n, azimuthal quantum number  $\ell$  and magnetic quantum number  $m_\ell$** ) arise as a natural consequence in the solution of the Schrodinger equation.

Application of Schrodinger equation to multi-electron atoms presents a difficulty : the Schrodinger equation cannot be solved exactly for a multi electron system. This difficulty can be overcome by using approximate methods such as calculation with the aid of modern computers show that orbitals in atoms other than hydrogen do not differ in any radical way from the hydrogen orbitals discussed above. The principle difference lies in the consequence of increased nuclear charge. Because of this all the orbitals are somewhat contracted. Unlike orbitals of hydrogen or hydrogen like species, whose energies depend only on the quantum number  $n$ , the energies of the orbitals in multi-electron atoms depend on quantum numbers  $n$  and  $\ell$ .

### QUANTUM NUMBERS :

The set of four numbers required to define an electron completely in an atom are called quantum numbers. The first three have been derived from Schrodinger wave equation.

#### (i) Principal quantum number ( $n$ ) : (Proposed by Bohr)

It describes the size of the electron wave and the total energy of the electron. It has integral values 1, 2, 3, 4 ..., etc., and is denoted by K, L, M, N. ..., etc.

\* Number of subshell present in  $n^{\text{th}}$  shell =  $n$

$n$	subshell
1	s
2	s, p
3	s, p, d
4	s, p, d, f

\* Number of orbitals present in  $n^{\text{th}}$  shell =  $n^2$ .

\* The maximum number of electrons which can be present in a principal energy shell is equal to  $2n^2$ . No energy shell in the atoms of known elements possesses more than 32 electrons.

\* Angular momentum of any orbit =  $\frac{nh}{2\pi}$

#### (ii) Azimuthal quantum number ( $\ell$ ) : (Proposed by Sommerfield)

It describes the shape of electron cloud and the number of subshells in a shell.

\* It can have values from 0 to  $(n - 1)$

value of $\ell$	subshell
0	s
1	p
2	d
3	f

\* Number of orbitals in a subshell =  $2\ell + 1$

\* Maximum number of electrons in particular subshell =  $2 \times (2\ell + 1)$

\* Orbital angular momentum  $L = \frac{h}{2\pi} \sqrt{\ell(\ell + 1)} = \hbar \sqrt{\ell(\ell + 1)} \quad \left[ \hbar = \frac{h}{2\pi} \right]$

i.e. Orbital angular momentum of s orbital = 0, Orbital angular momentum of p orbital =  $\sqrt{2} \frac{h}{2\pi}$ ,

Orbital angular momentum of d orbital =  $\sqrt{3} \frac{h}{2\pi}$

#### (iii) Magnetic quantum number ( $m$ ) : (Proposed by Linde)

It describes the orientations of the subshells. It can have values from  $-\ell$  to  $+\ell$  including zero, i.e., total  $(2\ell + 1)$  values. Each value corresponds to an orbital. s-subshell has one orbital, p-subshell three orbitals ( $p_x$ ,  $p_y$  and  $p_z$ ), d-subshell five orbitals ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ,  $d_{x^2-y^2}$ ,  $d_{z^2}$ ) and f-subshell has seven orbitals. The total number of orbitals present in a main energy level is ' $n^2$ '.

**(iv) Spin quantum number (s) : (Proposed by Goldschmidt & Uhlenbeck)**

It describes the spin of the electron. It has values  $+1/2$  and  $-1/2$ . (+) signifies clockwise spinning and (–) signifies anticlockwise spinning.

\* Spin magnetic moment  $\mu_s = \frac{eh}{2\pi mc} \sqrt{s(s+1)}$  or  $\mu = \sqrt{n(n+2)}$  B.M. (n = no. of unpaired electrons)

\* It represents the value of spin angular momentum which is equal to  $\frac{h}{2\pi} \sqrt{s(s+1)}$

\* Maximum spin of atom =  $\frac{1}{2} \times$  No. of unpaired electron.

- Total no. of  $e^-$  in main energy shell =  $2n^2$   
Total no. of  $e^-$  in a subshell =  $2(2\ell + 1)$   
Maximum no. of  $e^-$  in an orbital = 2  
Total no. of orbitals in a subshell =  $(2\ell + 1)$   
No. of subshells in main energy shell = n  
No. of orbitals in a main energy shell =  $n^2$
- Orbital angular momentum  $L = \frac{h}{2\pi} \sqrt{\ell(\ell + 1)}$
- Spin angular momentum  $S = \frac{h}{2\pi} \sqrt{S(S + 1)}$  ;  $S = \frac{1}{2}$   
 $\mu = \sqrt{n(n + 2)}$  B.M. (n = no. of unpaired electrons)
- Orbital magnetic moment  $\mu_s = \frac{eh}{4\pi m_e} \times \sqrt{\ell(\ell + 1)}$

## ELECTRONIC CONFIGURATION

### Pauli's exclusion principle :

No two electrons in an atom can have the same set of all the four quantum numbers, i.e., an orbital cannot have more than 2 electrons because three quantum numbers (principal, azimuthal and magnetic) at the most may be same but the fourth must be different, i.e., spins must be in opposite directions.

### Aufbau principle :

Aufbau is a German word meaning building up. The electrons are filled in various orbitals in order of their increasing energies. An orbital of lowest energy is filled first. The sequence of orbitals in order of their increasing energy is : 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, ....

The energy of the orbitals is governed by  $(n + \ell)$  rule.

### (n + l) Rule :

This rule states that electrons are filled in orbitals according to their  $(n + \ell)$  values. Electrons are filled in increasing order of their  $(n + \ell)$  values. When  $(n + \ell)$  is same for sub energy levels, the electrons first occupy the sublevels with lowest 'n' value.

### Energy level diagram :

The representation of relative energy levels of various atomic orbital is made in terms of energy level diagrams.

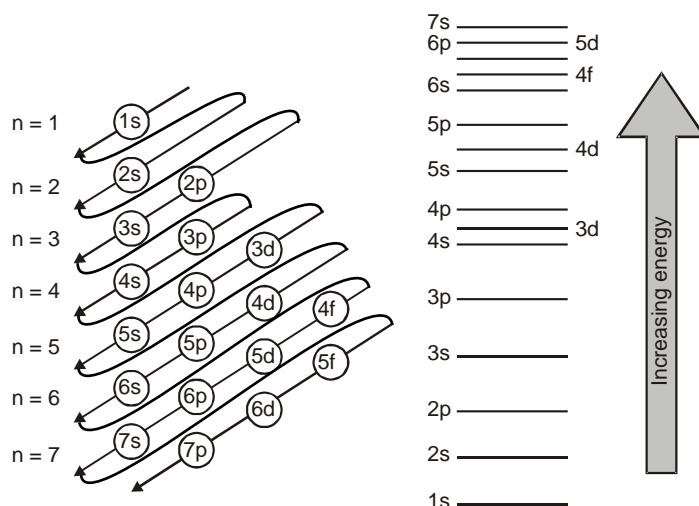


Fig. Sequence of filling of electrons in orbitals belonging to different energy levels

### Hund's rule :

No electron pairing takes place in the orbitals in a subshell until each orbital is occupied by one electron with parallel spin. Exactly half filled and fully filled orbitals make the atoms more stable, i.e.,  $p^3$ ,  $p^6$ ,  $d^5$ ,  $d^{10}$ ,  $f^7$  and  $f^{14}$  configuration are most stable.

### Solved Examples

**Ex-36.** Calculate total spin, magnetic moment for the atoms having at. no. 7, 24 and 36.

**Sol.** The electronic configuration are

${}_7\text{N}$	: $1s^2, 2s^2, 2p^3$	unpaired electron = 3
${}_{24}\text{Cr}$	: $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$	unpaired electron = 6
${}_{36}\text{Kr}$	: $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6$	unpaired electron = 0

$\therefore$  Total spin for an atom =  $\pm 1/2 \times \text{no. of unpaired electron}$

For  ${}_7\text{N}$ , it is =  $\pm 3/2$  ; For  ${}_{24}\text{Cr}$ , it is =  $\pm 3$  ; For  ${}_{36}\text{Kr}$ , it is = 0

Also magnetic moment =  $\sqrt{n(n+2)}$

For  ${}_7\text{N}$ , it is =  $\sqrt{15}$  ; For  ${}_{24}\text{Cr}$ , it is =  $\sqrt{48}$  ; For  ${}_{36}\text{Kr}$ , it is =  $\sqrt{0}$

**Ex-37.** Write down the four quantum numbers for fifth and sixth electrons of carbon atom.

**Sol.**  ${}_6\text{C}$  :  $1s^2, 2s^2, 2p^2$

fifth electron :  $n = 2$  ,  $\ell = 1$  ,  $m = -1$  or  $+1$  ,  $s = +\frac{1}{2}$  or  $-\frac{1}{2}$

sixth electron :  $n = 2$   $\ell = 1$   $m = 0$   $s = +\frac{1}{2}$  or  $-\frac{1}{2}$

**Ex-38.** Given below are the sets of quantum numbers for given orbitals. Name these orbitals.

- |                           |                           |                           |                           |                           |
|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| (a) $n = 3$<br>$\ell = 1$ | (b) $n = 5$<br>$\ell = 2$ | (c) $n = 4$<br>$\ell = 1$ | (d) $n = 2$<br>$\ell = 0$ | (e) $n = 4$<br>$\ell = 2$ |
|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|

**Ans.** 3p, 5d, 4p, 2s, 4d

**Sol.** (a)  $n = 3, \ell = 1 \Rightarrow 3p$  (b)  $n = 5, \ell = 2 \Rightarrow 5d$  (c)  $n = 4, \ell = 1 \Rightarrow 4p$   
(d)  $n = 2, \ell = 0 \Rightarrow 2s$  (e)  $n = 4, \ell = 2 \Rightarrow 4d$

**Ex-39.** Which of the following set of quantum numbers is not valid.

- |   |  |
|---|--|
| (1) $n = 3, \ell = 2, m = 2, s = +\frac{1}{2}$  | (2) $n = 2, \ell = 0, m = 0, s = -\frac{1}{2}$ |
| (3) $n = 4, \ell = 2, m = -1, s = +\frac{1}{2}$ | (4) $n = 4, \ell = 3, m = 4, s = -\frac{1}{2}$ |

**Sol.** Not valid

**Ans.** (4)

**Ex-40.** What is the total spin value in case of  ${}_{26}\text{Fe}^{3+}$  ion

- |              |              |                  |              |
|--------------|--------------|------------------|--------------|
| (1) +1 or -1 | (2) +2 or -2 | (3) +2.5 or -2.5 | (4) +3 or -3 |
|--------------|--------------|------------------|--------------|

**Sol.** Total spin = no. of unpaired  $e^- \times \left(\pm \frac{1}{2}\right)$

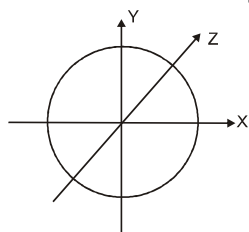
$$= 5 \times \left(\pm \frac{1}{2}\right) = \pm \frac{5}{2}$$

**Ans.** (3)

## Shape of the orbitals :

Shape of the orbitals are related to the solutions of Schrodinger wave equation and gives the space in which the probability of finding an electron is maximum.

**s-orbital :** Shape  $\rightarrow$  spherical



s-orbital is non directional and it is closest to the nucleus, having lowest energy.

s-orbital can accommodate maximum no. of two electrons.

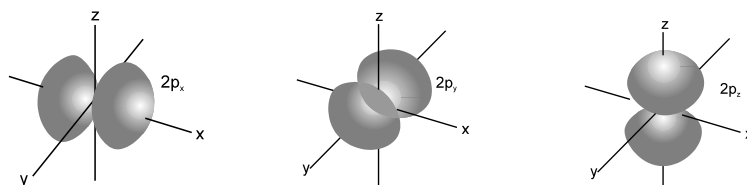


n s

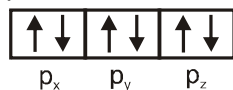
**p-orbital :** Shape  $\rightarrow$  dumb bell

Dumb bell shape consists of two loops which are separated by a region of zero probability called node.

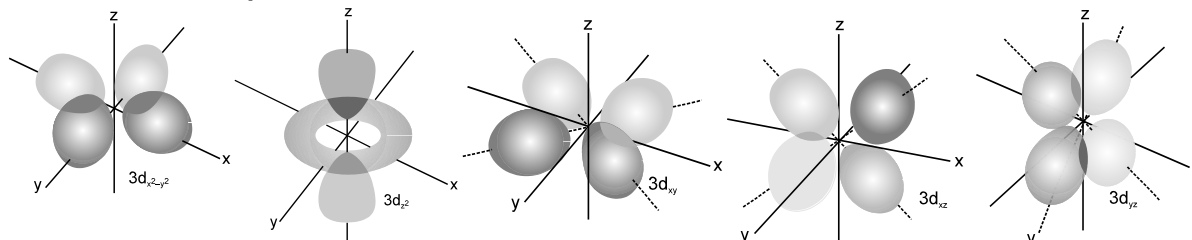




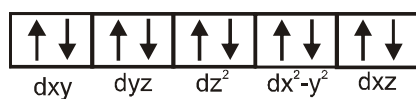
p - orbital can accommodate maximum no. of six electrons.



**d - Orbital :** Shape double → dumb bell



d - orbital can accommodate maximum no. of 10 electrons.



**f - orbital :** Shape leaf like



f - orbital can accommodate maximum no. of 14 electrons.

### Nodes in orbitals

- (i) total nodes =  $n - 1$ ,
- (ii) angular nodes =  $\ell$ ,
- (iii) radial nodes =  $n - \ell - 1$ .

## Nuclear Chemistry

Spontaneous disintegration of nuclei due to emission of radiations like  $\alpha$ ,  $\beta$ ,  $\gamma$  is called radioactivity.

Radioactivity is a nuclei phenomenon.

Radioactivity is not dependent on external conditions like temperature, pressure etc.

Radioactivity of a substance is independent to its physical state.

$x(s)$ ,  $x(l)$ ,  $x(g)$ ,  $(x)^+(g)$ ,  $(x)^-(g)$  in all form, x is radioactive.

$^{14}\text{CO}_2$ ,  $^{14}\text{C}(s)$ ,  $^{14}\text{C}(g)$  is radioactive.

### Radiations :

$\alpha$  :  ${}_2\text{He}^4$  ( ${}_2^4\text{He}^{2+}$ ) (nucleus of He-atom)

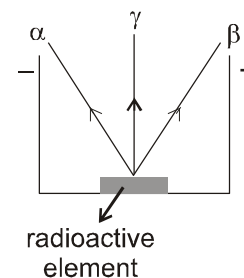
$\beta$  or  $\beta^-$  :  ${}_{-1}e^0$  (fast moving electron emitted from nucleus)

$\gamma$  :  ${}_0\gamma^0$  (electromagnetic radiation (waves) of high frequency)

speed :  $\gamma > \beta > \alpha$

penetrating power :  $\gamma > \beta > \alpha$

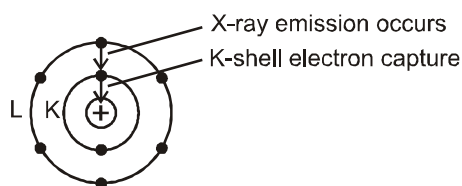
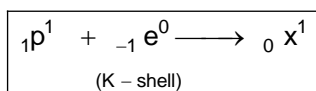
ionisation power :  $\alpha > \beta > \gamma$



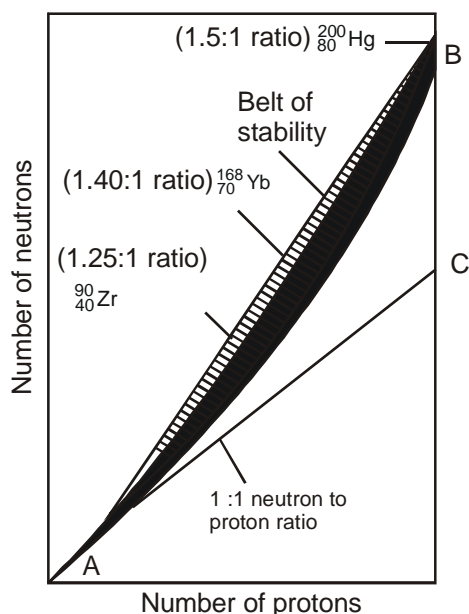
Emission of rays	Usual condition	Effect	Process representation / example
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1.  $\alpha$   $Z > 83$   $\frac{n}{p}$  ratio increases  ${}_Z X^A \rightarrow {}_{Z-2} X'^{A-4} + {}_2 \text{He}^4$   
 ${}_{92} \text{U}^{238} \rightarrow {}_{90} \text{Th}^{234} + {}_2 \text{He}^4$
2.  $\beta$  If  $\frac{n}{p}$  ratio is high.  $\frac{n}{p}$  ratio decreases  ${}_Z Y^A \rightarrow {}_{Z+1} Y'^{A-4} + {}_{-1} e^0$   
 eg.  ${}_6 \text{C}^{12}$  (stable)  $\frac{n}{p} = \frac{6}{6}$   ${}_6 \text{C}^{14} \rightarrow {}_7 \text{N}^{14} + {}_{-1} e^0$   
 ${}_6 \text{C}^{14}$  (radioactive)  $\frac{n}{p} = \frac{8}{6}$  (high)  $\frac{n}{p} = \frac{8}{6}$   $\frac{n}{p} = \frac{7}{7}$   
 eg.  ${}_{11} \text{Na}^{24}$  (radioactive)  $\frac{n}{p} = \frac{13}{11}$  (high)  ${}_0 n^1 \rightarrow {}_1 p^1 + {}_{-1} e^0$  (from nucleus)  
 ${}_{11} \text{Na}^{23}$  (stable)  $\frac{n}{p} = \frac{12}{11}$   
 ${}_{11} \text{Na}^{22}$   $\frac{n}{p} = \frac{11}{11}$  ( $\frac{n}{p}$  ratio low)
3.  $\gamma$  If nucleus energy level is high nucleus energy level decreases  ${}_{43} \text{Tc}^{99} \rightarrow {}_{43} \text{Tc}^{99} + \gamma$   
 high nucleus energy (metastable) low nucleus energy
4. (a) Positron emission  $({}_{+1} e^0)$  If  $\frac{n}{p}$  ratio is low  $\frac{n}{p}$  ratio increases  ${}_Z Y^A \rightarrow {}_{Z-1} Y'^A + {}_{+1} e^0$   
 ${}_{11} \text{Na}^{22} \rightarrow {}_{10} \text{Ne}^{22} + {}_{+1} e^0$   
 ${}_1 p^1 \rightarrow {}_0 n^1 + {}_{+1} e^0$  (from nucleus)
- (b) Electron capture If  $\frac{n}{p}$  ratio is low  $\frac{n}{p}$  ratio increases  ${}_Z X'^A + {}_{-1} e^0_{\text{K-shell}} \rightarrow {}_{Z-1} X''^A$   
 (EC) or K-shell  ${}_{80} \text{Hg}^{197} + {}_{-1} e^0 \rightarrow {}_{79} \text{Au}^{197}$

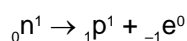
**Electron capture**



**Nuclear stability belt :**



### $\beta$ -emission



- \* Z upto 20 : nuclei stable with n/p ratio nearly 1 : 1
- \* Z > 20 : n/p ratio increases with Z in stable nuclei region.
- \* More number of neutrons are required to reduce repulsion between protons.
- \*  ${}_{83}\text{Bi}^{209}$  : Stable with largest n/p ratio

$$\frac{n}{p} = \frac{1.52}{1}$$

### Even - odd rule :

no. of n	no. of p	no. of stable nuclei
even	even	155 (max)
even	odd	55
odd	even	50
odd	odd	5 (min)

\* Expected pairing of nucleus

### Magic Numbers :

Nuclei in which nucleons have magic no. (2, 8, 20, 28, 50 ....) are more stable.

e.g.  ${}_2\text{He}^4$ ,  ${}_8\text{O}^{16}$

### Group displacement law : (Given by Soddy and Fajan)

- \* When  $1\alpha$  emission takes place from a nucleus, new formed nucleus occupy two position left in periodic table.
- \* When  $1\beta$  emission takes place from a nucleus, new formed nucleus occupy one position right in periodic table.

Due to emission of  $1\beta$  particle; isobars are formed.

Due to emission of  $1\alpha$  particle; isodiaphers are formed.

Due to emission of  $1\alpha$  and  $2\beta$  ; isotopes are formed.



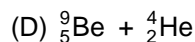
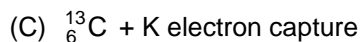
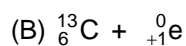
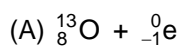
$$\therefore c = b + 4m \quad \dots\dots(i)$$

$$\text{and } a = d + 2m - n \quad \dots\dots(ii)$$

by (i) & (ii)

$$n = d + \left( \frac{c-b}{2} \right) - a. \text{ Ans. (C)}$$

**Ex-43.** The decay product of  ${}^{13}_7\text{N}$  is :



**Sol.**  ${}^{13}_7\text{N}$  is positron emitter ;  $\frac{n}{p}$  ratio is low. **Ans. (B)**

**Ex-44.** A radioactive element X has an atomic numbers of 100. It decays directly into an element Y which decays directly into an element Z. In both processes a charged particle is emitted. Which of the following statement would be true?

(A) Y has an atomic number of 102.

(B) Z has an atomic number of 101.

(C) Z has an atomic number of 97.

(D) Z has an atomic number of 99.

**Sol.** X and Y can decay one  $\alpha$  each or one  $\beta$  each or X-decays, 1  $\alpha$ , Y-decays 1  $\beta$  or X-decays 1  $\beta$  or Y-decays 1  $\alpha$ . In either case (A), (B) and (C) cannot be true. **Ans. (D)**