ATOMIC STRUCTURE

INTRODUCTION

The existence of atoms has been propsed by ancient Indian and Greek philosophers (400 B.C.) who believed that all matter consisted of very small indivisible particles called atoms. According to them, atoms were the fundamental building blocks of matter. The continued subdivision of matter would yield atoms, which could not be further subdivided. This means that atom is the fundamental unit of matter. So these ideas remained dominant for a very long time and were reviewed again by scientists in 19th century.

In 1808, an English scientist John Dalton formulated a precise definition of the indivisble blocks of matter i.e. atoms. His theory, called Dalton's atomic theory, regarded atom as the ultimate particle of matter. The postulates are as follows :

(a) Every matter is composed of very minute particles called as atoms which take part in chemicals reactions.

(b) Atoms can not be further subdivided.

(c) The atoms of different elements differ from each other in their properties and masses. while atoms of same elements are identical in all aspects.

(d) The atoms of different elements can combine in simple ratios to form compounds. The massed combined elements represents the masses of combined atoms.

(e) Atoms can neither be created nor be destroyed.

Although Dalton was pretty much successful in explaining the law of conservation of mass, law of constant proportion, law of multiple proportion, however he failed to explain many properties as well. The drawbacks are as follows :

(a) It failed to explain the internal structure of atoms and assumed atoms do not have any structure.

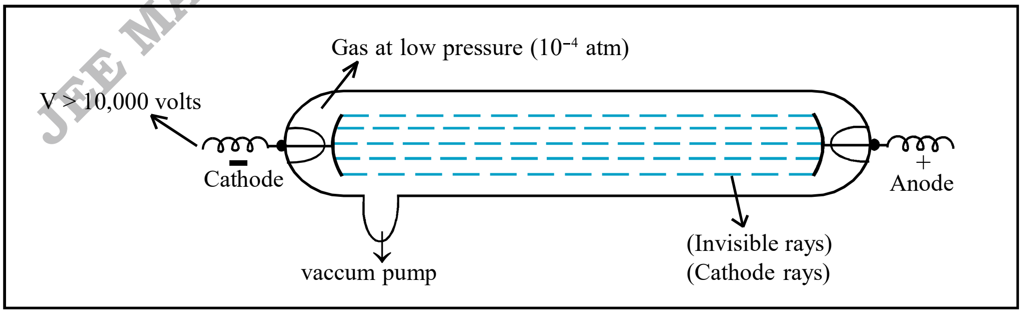
(b) It could not explain how atoms of different elements differ from one another.

(c) It could not explain how atoms of different elements combine with one other.

ATTEMPTS FOR DISCOVERING FUNDAMENTAL PARTICLES OF MATTER / ATOMS

Earlier Efforts to Reveal Structure of Atom

CATHODE RAYS (Discovery of e^-)

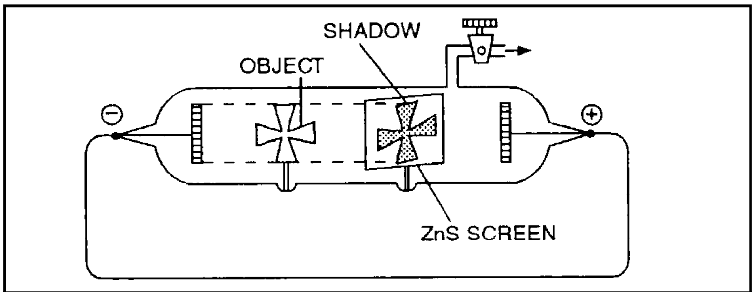


In 1859, **Julius plucker** started the study of conduction of electricity through gases at low pressure in a discharge tube. When a high voltage of the order 10, 000 volts or more was applied across the electrodes, some sort of invisible rays moved from the –ve electrode to the +ve electrode. Since the –ve electrode is referred to as cathode, these rays were called cathode rays.

- **Properties of Cathode Rays**

(1) They travel in straight lines away from cathode with very high velocity (about one - tenth of velocity of light).

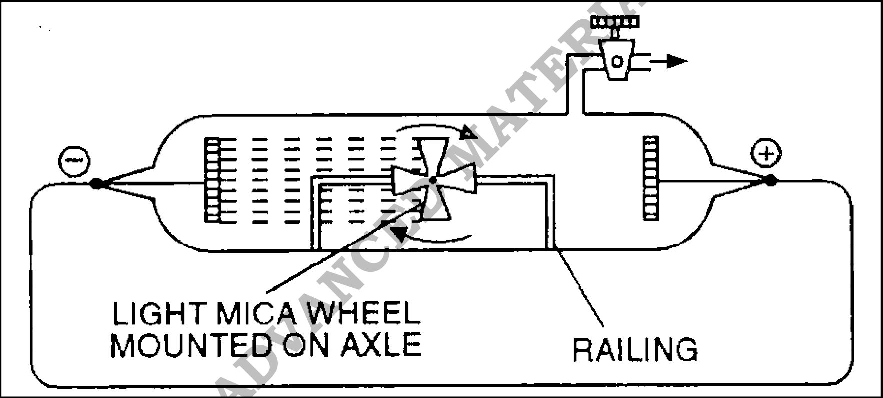
(2) A shadow of metallic object placed in the path is cast on the wall opposite to the cathode.



Production of a shadow of the solid object by cathode rays

(3) They produce a green glow when strick the glass wall matter. Light is emitted when they strike the zinc-sulphide screen.

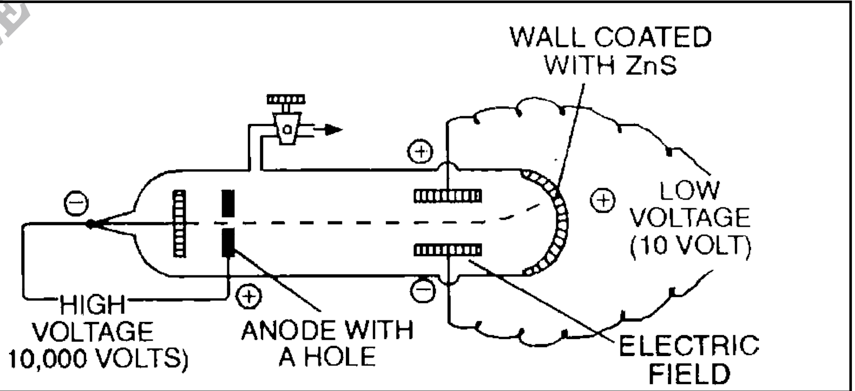
(4) When a small pin wheel is placed in their path, the blades of the wheel are set in motion. Thus the cathode rays consist of material particles which have mass and velocity.



Rotation of light paddle wheel by cathode rays

(5) They are deflected by the electric and magnetic fields. When the rays are passed between two electrically charged plates, these are deflected towards the positively charged plate. It shows that cathode rays carry -ve charge. These particles carrying negative charge were called negatrons by Thomson.

The name negatron was changed to 'electron' by Stoney



Deflection of cathode rays towards positive plate of the electric field

(6) They produce heat energy when they collide with the matter. It shows that cathode rays posses Kinetic energy which is converted into heat energy when stopped by matter.

(7) These rays affect the photographic plate.

(8) Cathode rays can penetrate the thin foil of solid materials.

(9) Cathode rays can ionize the gases through which they pass.

(10) The nature of cathode rays is independent of

(a) The nature of cathode and

(b) The gas in discharge tube.

MEASUREMENT OF E/M FOR ELECTRON

In 1897, J.J. Thomson determined the e/m value (charge/mass) of the electron by studying the deflection of cathode rays in electric & magnetic fields.

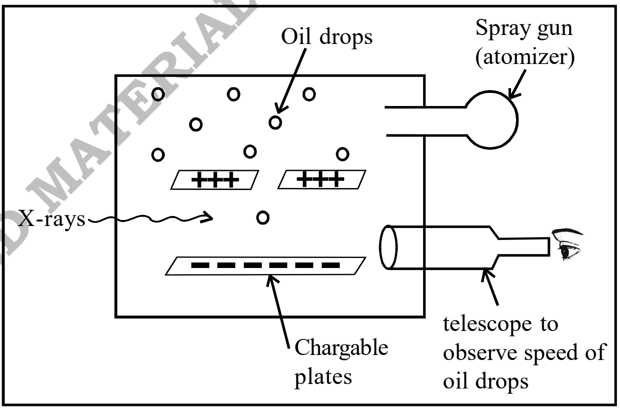
The value of e/m has been found to be -1.7588×10^8 coulomb/g.

- By performing a series of experiments, Thomson proved that whatever gas be taken in the discharge tube and whatever be the material of the electrodes the value of e/m is always the same.
- Electrons are thus common universal constituents of all atoms.

DETERMINATION OF THE CHARGE ON AN ELECTRON

The absolute value of the charge on an e^- was measured by R.A. Milikan in 1909 by the Milikan's oil drop experiment.

- The apparatus used by him is shown in fig.
- An oil droplet falls through a hole in the upper plate. The air between the plates is then exposed to X-rays which eject electrons from air molecules. Some of these e^- are captured by the oil droplet and it acquires a negative charge.



The metal plates were given an electric charge, and as the electric field between the plates was increased, it was possible to make some of the drops travel upwards at the same speed as they were previously falling. By measuring the speed, and knowing things like the strength of the field and the density of the oil, radius of oil drops, Milikan was able to calculate the magnitude of the charge on the oil drops. He found that the smallest charge to be found on them was approximately **1.59×10^{-19} C**. This was recognised as the charge on an e^-. The modern value is **1.602×10^{-19} C**.

MASS OF THE ELECTRON

Mass of the e^- can be calculate from the value of e/m and the value of e

$$m = \frac{e}{e/m} = \frac{-1.602 \times 10^{-19}}{-17588 \times 10^{8}} = 9.1096 \times 10^{-28}\ g \quad \text{or} \quad = 9.1096 \times 10^{-31}\ kg$$

This is termed as the rest mass of the electron i.e. mass of the electron when moving with low speed. The mass of a moving e^- may be calculate by applying the following formula.

$$\text{Mass of moving } e^- = \frac{\text{rest mass of } e^-}{\sqrt{1-(v/c)^2}}$$

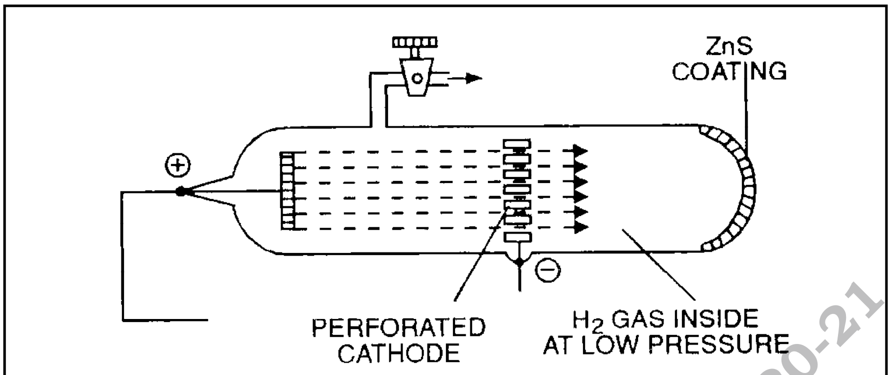
Where v is the velocity of the e^- and c is the velocity of light.

When $v = c \Rightarrow$ mass of $e^- = \infty$

$v > c \Rightarrow$ mass of e^- = imaginary

ANODE RAYS OR POSITIVE RAYS - (DISCOVERY OF PROTON)

- The first experiment that lead to the discovery of the +ve particle was conducted by 'Goldstein'.
- He used a perforated cathode in the modified cathode ray tube.



Production of Anode rays or Positive rays

- It was observed that when a high potential difference was applied b/w the electrodes, not only cathode rays were produced but also a new type of rays were produced simultaneously from anode moving towards cathode and passed through the holes or canals of the cathode. These rays were termed canal rays since these passed through the canals of the cathode.These were also named anode rays as these originated from anode.
- When the properties of these rays were studied by Thomson, he observed that these rays consisted of positively charged particles and named them as positive rays.
- The following characteristics of the positive rays we recognised :

(i) These rays travel in straight lines and cast a shadow of the object placed in their path.

(ii) Like cathode rays, these rays also rotate the wheel placed in their path and also have heating effect. Thus, the rays passess K.E. i.e. mass particles are present.

(iii) The rays are deflected by electric and magnetic fields towards the negatively charged plate showing thereby that these rays carry +ve charge.

(iv) The rays produce flashes of light on ZnS screen

(v) These rays can pass through thin metal foil.

(vi) These rays can produce ionisation in gases.

(vii) Positive particles in these rays have e/m value much smaller than that of e^-. For a small value of e/m, it is definite that positive particles possess high mass.

(viii) e/m value is dependent on the nature of the gas taken in the discharge tube, i.e. +ve particles are different in different gases.

- Accurate measurements of the charge and the mass of the particles in the discharge tube containing hydrogen, the lightest of all gases, were made by J.J. Thomson in 1906. These particles were found to have the e/m value as $+9.579 \times 10^4$ coulomb/g. This was the maximum value of e/m observed for any +ve particle.
- It was thus assumed that the positive particle given by the hydrogen represents a fundamental particle of +ve charge. This particle was named proton by Rutherford in 1911. Its charge was found to be equal in magnitude but opposite in sign to that of electron.

Thus

charge on proton = $+ 1.602 \times 10^{-19}$ columb i.e. one unit +ve charge

- The mass of the proton, thus can be calculated.

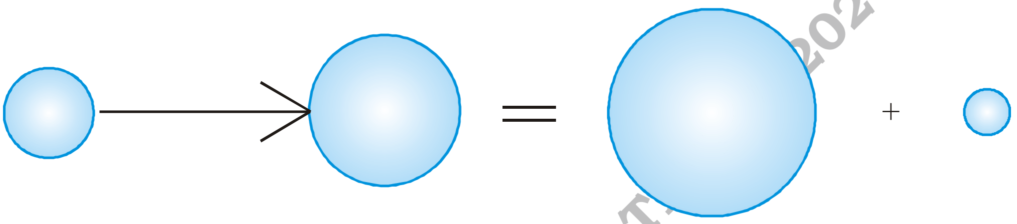
$$\text{Mass of the proton} = \frac{e}{e/m} = \frac{1.602\times10^{-19}}{9.579\times10^{4}} = 1.672\times10^{-24}\ \text{g} \quad = 1.672\times10^{-27}\ \text{kg}$$

$$\text{Mass of proton in amu} = \frac{1.672\times10^{-24}}{1.66\times10^{-24}} = 1.00757\ \text{amu.}$$

NEUTRON

In 1920, Rutherford suggested that in an atom, there must be present at least a third type of fundamental particles which should be electrically neutral and posses mass nearly equal to that of proton. He proposed the name for such fundamental particles as neutron.

In 1932, chadwick bombarded beryllium with a stream of α-particles. He observed that penetrating radiations were produced which were not affected by electric & magnetic fields. These radiations consisted of neutral particles, which were called neutrons. The nuclear reaction can be shown as



α-particle	Be-atom	Carbon atom	Neutron
Charge = +2	Atomic No. = 4	Atomic No. = 6	Charge = 0
Mass = 4 amu	Mass = 9 amu	Mass = 12 amu	Mass = 1 amu

$$[{}^{4}_{2}\text{He} + {}^{9}_{4}\text{Be} \longrightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}\text{n}]$$

Thus a neutron is a sub atomic particle which has a mass 1.675×10^{-24} g approximately 1amu, or nearly equal to the mass of proton or hydrogen atom and carrying no electrical charge.

- The e/m value of a neutron is zero.

ATOMIC STRUCTURE

Atom is actually made of 3 fundamental particles

1. Electron
2. Proton
3. Neutron

Fundamental Particle	Discovered By	Charge	Mass	$\frac{\text{Charge}}{\text{mass}}$ (specific Charge)
Electron (e^- or β)	J.J.Thomson	-1.6×10^{-19} coloumb -4.8×10^{-10} esu -1 Unit	9.1×10^{-31} kg 9.1×10^{-28} g 0.000548 amu	1.76×10^{8} C/g
Proton (P) (Ionized H atom, H^+)	Goldstein	$+1.6\times10^{-19}$ coloumb $+4.8\times10^{-10}$ esu +1 Unit	1.672×10^{-27} kg 1.672×10^{-24} g 1.00757 amu	9.58×10^{4} C/g
Neutron (${}_0n^1$)	James Chadwick	0	1.675×10^{-27} kg 1.675×10^{-24} g 1.00893 amu	0

KEY POINTS

1. esu = electrostatic unit

$(1\ \text{C} = 3 \times 10^9\ \text{esu})$

amu = atomic masss unit

$1\ \text{amu} = 1.6 \times 10^{-24}\ \text{g} = 1.6 \times 10^{-27}\ \text{kg}$

2. **Order of Mass**

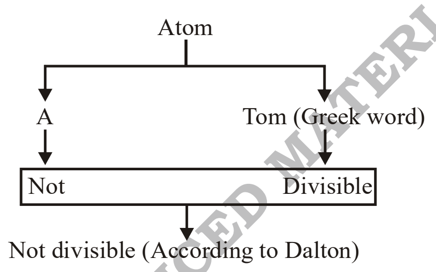
$m_{e^-} < m_p < m_n$

- **Order of Specific Charge**

$$\left(\frac{e}{m}\right)_n < (e/m)_p < (e/m)_{e^-}$$

$$\left(\frac{\text{mass of proton}}{\text{mass of electron}}\right)\frac{m_p}{m_{e^-}} = 1837$$

INTRODUCTION



- **Atom is a Greek Word**

and its meaning Indivisible i.e. an ultimate particles which cannot be further subdivided.

John Dalton (1803 - 1808) considered that " all matter was composed of small particle called atom.

ACCORDING TO DALTON'S THEORY

(1) Atom is the smallest indivisible part of matter which takes part in chemical reaction.

(2) Atom is neither created nor destroyed.

(3) Representation of atom : $_ZX^A$.

Where : A → Mass number, Z → Atomic number, X → Symbol of atom.

- **Mass Number**

It is represented by capital A. The sum of number of neutrons and protons is called the mass number. of the element. It is also known as number of nucleons because neutron & proton are present in nucleus.

$$\boxed{\text{A = number of protons + number of neutrons}}$$

Note : It is always a whole number.

- **Atomic Number**

It is represented by Z. The number of protons present in the Nucleus is called atomic number of an element. It is also known as nuclear charge.

For Neutral Atom : Number of proton = Number of electron

For Charged Atom : Number of e^- = Z – (charge on atom)

Z= number of protons only

For Ex. $_{17}Cl^{35}$

$n = 18$

$p = 17$

$e = 17$

Two different elements can not have the same Atomic Number

Number of Neutrons = Mass number – Atomic number

$= A - Z$

$= (p + n) - p$

$= n$

- **Method for Analysis of Atomic Weight**

Ex. $_{6}C^{12}$

$P^{+} \rightarrow 6$ Weight of Proton $= 6 \times 1.00750$

$n^{0} \rightarrow 6$ Weight of Neutron $= 6 \times 1.00850$

$e^{-} \rightarrow 6$ Weight of Electron $= 6 \times 0.000549$

Weight of C atom = 12.011 a.m.u.

Mass no. of C atom = 12 [P and n]

Note : Mass no. of atom is always a whole no. but atomic weight may be in decimal.

Ex. If no. of protons in X^{-2} is 16. then no. of e^{-} in X^{+2} will be–

(1) 14 **(2)** 16 **(3)** 18 **(4)** None

Sol. $\because$ No. of proton in X^{-2} is = 16

$\therefore$ No. of electron in X^{+2} is = 14

Ex. In C^{12} atom if mass of e^{-} is doubled and mass of proton is halved, then calculate the percentage change in mass no. of C^{12}.

Sol. $_{6}C^{12}$

$P^{+} \rightarrow 3$

$e^{-} \rightarrow 12$

e^{-}	P^{+}	$n°$	
6	6	6	$A \rightarrow 12$
12	3	6	$A \rightarrow 9$

$$\% \text{ change} = \frac{3}{12} \times 100 = 25\%$$

Ex. Assuming that atomic weight of C^{12} is 150 unit from atomic table, then according to this assumption, the weight of O^{16} will be :-

Sol. $\because$ 12 amu = 150

$\therefore$ $1 \text{ amu} = \frac{150}{12}$

$\therefore$ $16 \text{ amu} = \frac{150}{12} \times 16 = 200$ Unit

Isotopes : Given by Soddy

They are the atoms of a given element which have the same atomic number (Z) but different mass number (A) i.e. They have same Nuclear charge (Z) but different number of Neutrons (A–Z).

Ex.

$_{17}Cl^{35}$	$_{17}Cl^{37}$
$n = 18$	$n = 20$
$e = 17$	$e = 17$
$p = 17$	$p = 17$

- Isotopes have same chemical property but different physical property.
- Isotopes do not have the same value of $\frac{e}{m}\left(\frac{\text{Number of electron}}{\text{mass}}\right)$ because mass varies.

  (No. of electron are same but mass varies).

Ex. (Proteium Deuterium Tritium)

	$_1H^1$	$_1H^2$	$_1H^3$
	$e = 1$	$e = 1$	$e = 1$
	$p = 1$	$p = 1$	$p = 1$
	$n = 0$	$n = 1$	$n = 2$
e/m	1/1	1/2	1/3

$_1H^1$ is the only normal hydrogen which have n = 0 i.e. no nuetrons

Deuterium is also called as heavy hydrogen. It represent by D

Ex.

$_6C^{12}$	$_6C^{13}$	$_6C^{14}$
$e = 6$	$e = 6$	$e = 6$
$p = 6$	$p = 6$	$p = 6$
$n = 6$	$n = 7$	$n = 8$

Isobars : Given by Aston

They are the atoms of different element which have the same mass number (A) but different Atomic number (Z) i.e They have different number of Electron, Protons & Neutrons But sum of number of neutrons & Protons i.e. number of nucleons remains same.

Ex.

$_1H^3$	$_2He^3$
$p = 1$	$p = 2$
$e = 1$	$e = 2$
$n = 2$	$n = 1$
$p + n = 3$	$p + n = 3$

- Isobars do not have the same chemical & physical property
- They do not have the same value of e/m

Ex.

$_{19}K^{40}$		$_{20}Ca^{40}$	
$p = 19$		$p = 20$	
$n = 21$	$n + p = 40$	$n = 20$	$n + p = 40$
$e = 19$		$e = 20$	
$19 + 21 = 40$		$20 + 20 = 40$	

$n + p = 40$

Number of Nucleons same

Isodiaphers

They are the atoms of different element which have the same difference of the number of Neutrons & protons.

Ex.

$_5B^{11}$		$_6C^{13}$	
$p = 5$		$p = 6$	
$n = 6$	$n - p = 1$	$n = 7$	$n - p = 1$
$e = 5$		$e = 6$	

Ex.

$_7N^{15}$		$_9F^{19}$	
$p = 7$		$p = 9$	
$n = 8$	$n - p = 1$	$n = 10$	$n - p = 1$
$e = 7$		$e = 9$	

Isotones/ Isoneutronic Species / Isotonic

They are the atoms of different element which have the same number of neutrons.

Ex.

$_1H^3$	$_2He^4$
$p = 1$	$p = 2$
$n = 2$	$n = 2$
$e = 1$	$e = 2$

Ex.

$_{19}K^{39}$	$_{20}Ca^{40}$
$e = 19$	$e = 20$
$p = 19$	$p = 20$
$n = 20$	$n = 20$

Isosters

They are the molecules which have the same number of atoms & electrons.

Ex.

	CO_2		N_2O
Atoms	$= 1 + 2$	Atoms	$= 2 + 1$
	$= 3$		$= 3$
Electrons	$= 6 + 8 \times 2$	Electrons	$= 7 \times 2 + 8$
	$= 22\ e^-$		$= 22e^-$

Ex.

	CaO	KF
Atoms	2	2
Electrons	$20 + 8$	$19 + 9$
	$28\ e^-$	$28\ e^-$

Ex.

	OF_2	$HClO$
Atoms	$= 3$	3
Electrons	$= 8 + 18$	$1 + 17 + 8$
	$= 26\ e^-$	$17 + 9$
		$26\ e^-$

Isoelectronic Species

They are the atoms, molecules or ions which have the same number of electrons.

Ex.

	Cl^-	Ar
Electron	$18\ e^-$	$18\ e^-$

Ex.

H_2O	NH_3
$e = 2 + 8$	$e = 7 + 3$
$10\ e^-$	$10\ e^-$

Ex.

BF_3	SO_2
$e = 5 + 9 \times 3$	$16 + 8 \times 2$
$5 + 27$	$16 + 16$
$32\ e^-$	$32\ e^-$

Nuclear Isomer

Nuclear isomers (isomeric nuclei) are the atoms with the same atomic number and same mass number but with different radioactive properties.

Example of nuclear isomers is

Uranium–X (half–life 1.4 min) and

Uranium–Z (half–life 6.7 hours)

The reason for nuclear isomerism is the different energy states of the two isomeric nuclei.

Other examples are

${}^{69}_{30}Zn$	${}^{69}_{30}Zn$	$(T_{1/2} = 13.8\text{ hr})$	$(T_{1/2} = 57\text{ min})$
${}^{80}_{35}Br$	${}^{80}_{35}Br$	$(T_{1/2} = 4.4\text{ hour})$	$(T_{1/2} = 18\text{ min})$

EXAMPLE BASED ON NUCLEAR STRUCTURE

Ex. If the mass of neutrons is doubled & mass of electron is halved then find out the atomic mass of ${}_6C^{12}$ and the percent by which it is increased.

Sol. **Step-1** ${}_6C^{12}$

$e = 6$

$$\left.\begin{array}{l} p = 6 = 6\text{ amu} \\ n = 6 = 6\text{ amu} \end{array}\right] = 12\text{ amu}$$

If the mass of neutrons is doubled and mass of e^- is halved then.

$$\left.\begin{array}{l} n = 12\text{ amu} \\ p = 6\text{ amu} \end{array}\right] = 18\text{ amu}$$

Imp. Note : mass of e^- is negligible, so it is not considered in calculation of atomic mass.

Step-2

$$\%\text{ Increment} = \frac{\text{Final mass - Initial mass}}{\text{Initial mass}} \times 100$$

$$= \frac{18 - 12}{12} \times 100 \Rightarrow 50\%$$

Ex. If mass of neutron is doubled, mass of proton is halved and mass of electron is doubled then find out the change in At. wt of ${}_6C^{12}$

1. Remain same
2. Increased by 25%
3. Increased by 37.5%
4. None of them

Sol. **Step-1** ${}_6C^{12}$

$e = 6$

$$\left.\begin{array}{l} p = 6 \\ n = 6 \end{array}\right] = 12\text{ amu}$$

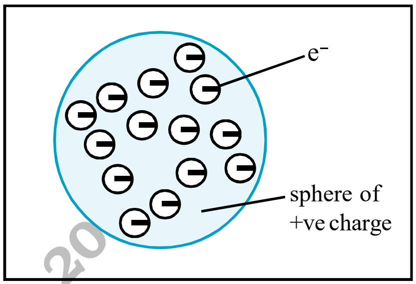
If mass of neutron is doubled, mass of proton is halved and mass of electron is doubled,then new atomic mass will be :

$$\left.\begin{array}{l} n = 12\text{ amu} \\ p = 3\text{ amu} \end{array}\right] = 15\text{amu}$$

Step-2 $\% \text{ Increment} = \dfrac{\text{Final mass - Initial mass}}{\text{Initial mass}} \times 100 = \dfrac{15 - 12}{12} \times 100 \Rightarrow 25\%$

ATOMIC MODELS

THOMSON'S MODEL OF ATOM [1904]



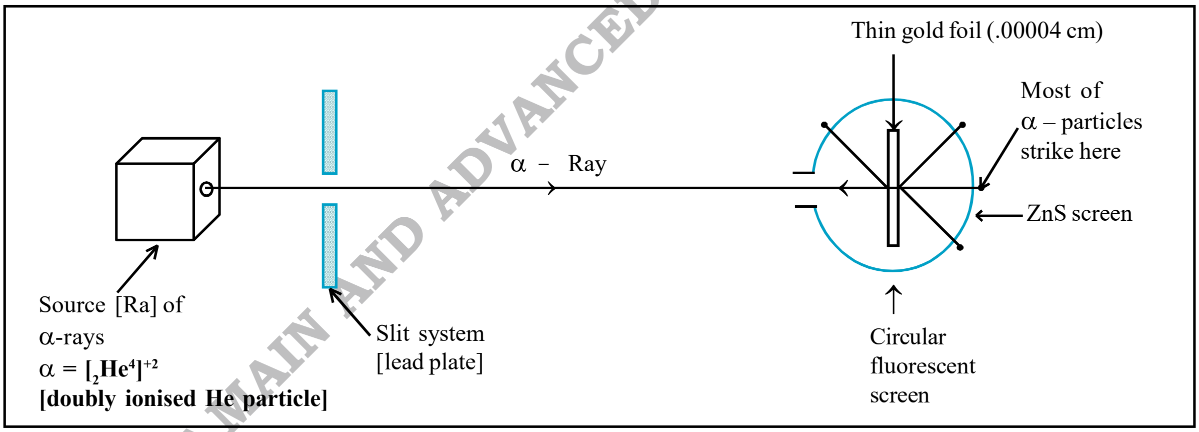
- Thomson was the first to propose a detailed model of the atom.
- Thomson proposed that an atom consists of a uniform sphere of positive charge in which the electrons are present at some places.
- This model of atom is known as **'Plum-Pudding model'**.

Drawbacks

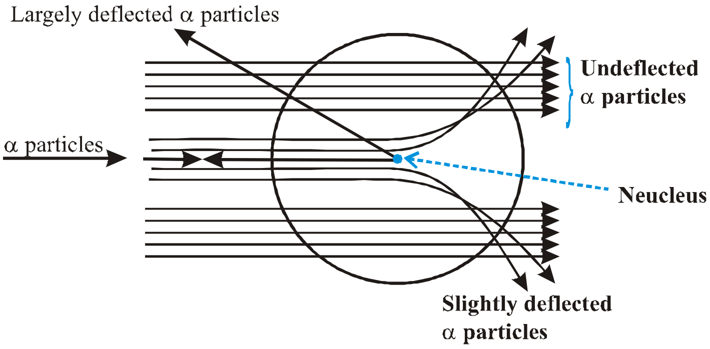
- An important drawback of this model is that the mass of the atoms is considered to be evenly spread over that atom.
- It is a static model. It does not reflect the movement of electron.

RUTHERFORD'S α- SCATTERING EXPERIMENT

α-Scattering Experiment



Rutherford Observed That



(i) Most of the α-particles (nearly 99.9%) went straight without suffering any deflection.

(ii) A few of them got deflected through small angles.

(iii) A very few α-particles (about one in 20,000) did not pass through the foil at all but suffered large deflections (more than 90°) or even come back in the direction from which they have come i.e. a deflection of 180°.

Following Conclusions were Drawn from the Above Observations

(1) Since most of the α-particle went straight through the metal foil undeflected, it means that there must be very large empty space within the atom.

(2) Since few of the α-particles were deflected from their original path through moderate angles; it was concluded that whole of the +ve charge is concentrated and the space occupied by this positive charge is very small in the atom.

- Whenever α-particles come closer to this point, they suffer a force of repulsion and deviate from their paths.
- The positively charged heavy mass which occupies only a small volume in an atom is called nucleus. It is supposed to be present at the centre of the atom.

(3) A very few of the α-particles suffered strong deflections on even returned on their path indicating that the nucleus is rigid and α-particles recoil due to direct collision with the heavy positively charged mass.

(4) The relation between number of deflected particles and deflection angle θ is

$$\mu = \frac{1}{\sin^4\frac{\theta}{2}} \quad [\theta \text{ increases } \mu \text{ decreases}]$$

where μ = deflected particles θ = deflection angle

- As atomic number increases, the number of protons increases which increases the repulstion and so deflection angle θ increases.

APPLICATIONS OF RUTHERFORD MODEL

On the basis of scattering experiments, Rutherford proposed the model of an atom, which is known as nuclear atomic model. According to this model -

(i) An atom consists of a heavy positively charged nucleus where all the protons are present.

(ii) The volume of the nucleus is very small and is only a minute fraction of the total volume of the atom. Nucleus has a radius of the order of 10^{-13} cm and the atom has a radius of the order of 10^{-8} cm

$$\frac{r_A}{r_N} = \frac{\text{radius of the atom}}{\text{radius of the nucleus}} = \frac{10^{-8}}{10^{-13}} = 10^5, \quad r_A = 10^5 r_N$$

Thus radius (size) of the atom is 10^5 times the radius of the nucleus.

- The radius of a nucleus is proportional to the cube root of the mass no. of the nucleus.

$$R \propto A^{1/3} \Rightarrow R = R_0 A^{1/3} \text{ cm}$$

Where $R_0 = 1.33 \times 10^{-13}$(a constant) and, A = mass number (p + n)

R = radius of the nucleus.

$$R = 1.33 \times 10^{-13} A^{1/3} \text{ cm}$$

(iii) There is an empty space around the nucleus called extra nuclear part. In this part electrons are present. The no. of electrons in an atom is always equal to no. of protons present in the nucleus. As the nuclear part of atom is responsible for the mass of the atom, the extra nuclear part is responsible for its volume. The volume of the atom is about 10^{15} times the volume of the nucleus.

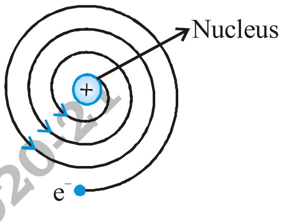
$$\frac{\text{vol. of the atom}}{\text{vol. of the nucleus}} = \frac{\left(\frac{4}{3}\pi r_A^3\right)}{\left(\frac{4}{3}\pi r_N^3\right)} = \frac{\left(10^{-8}\right)^3}{\left(10^{-13}\right)^3} = 10^{15}$$

(iv) Electrons revolve round the nucleus in closed orbits with high speeds.

- This model was similar to the solar system, the nucleus representing the sun and revolving electrons as planets.

Drawbacks of Rutherford Model

(1) This theory could not explain the stability of an atom. According to Maxwell electron loses it's energy continuously in the form of electromagnetic radiations. As a result of this, the e⁻ should loss energy at every turn and move closer and closer to the nucleus following a spiral path. The ultimate result will be that it will fall into the nucleus, thereby making the atom unstable.

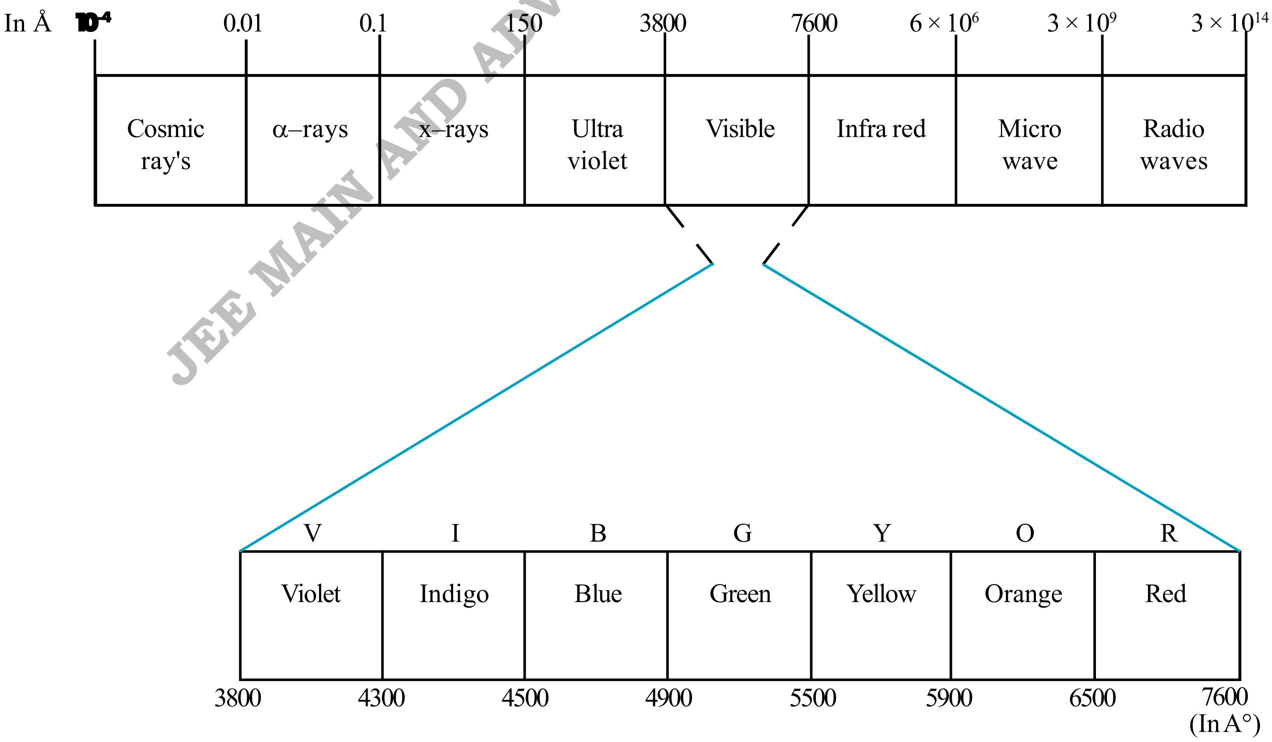


(2) If the electrons loose energy continuously, the observed spectrum should be continuous but the actual observed spectrum consists of well defined lines of definite frequencies (discontinuous). Hence, the loss of energy by electron is not continuous in an atom.

Electromagnetic Waves (EM waves) or Radiant Energy/Electromagnetic Radiation

- It is the energy transmitted from one body to another in the form of waves and these waves travel in the space with the same speed as light (3×10^8 m/s) and these waves are known as Electromagnetic waves or radiant energy.
- The radiant Energy do not need any medium for propogation.

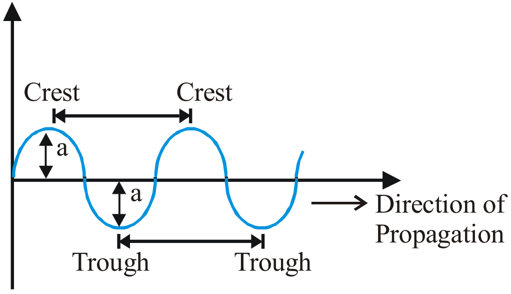
Ex : Radio waves, micro waves, Infra red rays, visible rays, ultraviolet rays, x–rays, gama rays and cosmic rays.



A wave is characterized by following six characterstics.

The upper most point of the wave is called crest and the lower most point is called trough.

Some of the terms employed in dealing with the waves are described below.



KEY POINTS

Some important characteristics of a wave

Wavelength of a wave is defined as the distance between any two consecutive crests or troughs. It is represented by λ (lambda) and is expressed in Å or m or cm or nm (nanometer) or pm (picometer).

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

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

Frequency of a wave is defined as the number of waves passing through a point in one second. It is represented by ν (nu) and is expressed in Hertz (Hz) or cycles/sec or simply sec^{-1} or s^{-1}.

1 Hz = 1 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 (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 λ is expressed in cm, $\bar{\nu}$ will have the units 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 λ is the length of each wave, hence their product will give the velocity of the wave. Thus

$$\boxed{v = \nu \times \lambda}$$

Order of wavelength in Electromagnetic spectrum

Cosmic rays < γ – rays < X-rays < Ultraviolet rays < Visible < Infrared < Micro waves < Radio waves.

Ex. The vividh Bharti station of All India Radio broadcast on a frequency of 1368 Kilo Hertz. Calculate the wave length of the Electromagnetic waves emited by the transmitter.

Sol. As we know velocity of light (C)

$C = 3 \times 10^8$ m/sec.

Given ν (frequency)

= 1368 kHz

$= 1368 \times 10^3$ Hz

$= 1368 \times 10^3\ \text{sec}^{-1}$

$\because \quad \lambda = \frac{C}{\nu} \qquad \therefore \quad \lambda = \frac{3\times10^{8}\,\text{msec}^{-1}}{1368\times10^{3}\,\text{sec}^{-1}} \Rightarrow \lambda = 219.3\text{ m}$

Ex. Calculate $\bar{\nu}$ in cm^{-1} and ν of yellow radiations having wavelength of 5800 Å

Sol. As we known $\bar{\nu} = \frac{1}{\lambda}$

$$\bar{\nu} = \frac{1}{5800\,\text{Å}}$$

$$\bar{\nu} = \frac{1}{5800\times10^{-8}\,\text{cm}} \quad \{\because \ 1\text{Å} = 10^{-8}\text{ cm}\}$$

$$= \frac{10^{8}}{5800}\,\text{cm}^{-1} = 17241.4\text{ cm}^{-1}$$

$$\nu = c\bar{\nu}$$
$$= 3\times10^{10}\,\text{cm sec}^{-1}\times 1.7\times10^{4}\,\text{cm}^{-1}$$
$$= 3\times1.7\times10^{14}$$
$$= 5.1\times10^{14}\,\text{sec}^{-1}$$

Ex. A particular radiostation broadcast at a frequency of 1120 Kilo Hertz another radio station broadcast at a frequency of 98.7 mega Hertz. What are the wave length of radiations from each station.

Sol. Station I$^{\text{st}}$

$$\lambda = \frac{C}{\nu} = \frac{3\times10^{8}\,\text{m sec}^{-1}}{1120\times10^{3}\,\text{sec}^{-1}} = 267.86\text{ m}$$

Station II$^{\text{nd}}$

$$\lambda = \frac{C}{\nu} = \frac{3\times10^{8}\,\text{m sec}^{-1}}{98.7\times10^{6}\,\text{sec}^{-1}}$$

$$= 3.0395\text{ m}$$

Ex. How long would it take a radio wave of frequency 6×10^{3} sec^{-1} to travel from mars to the earth, a distance of 8×10^{7} km ?

Sol. Distance to be travelled from mars to earth

$= 8\times10^{7}$ km

$= 8\times10^{10}$ m

$\because$ Velocity of EM waves

$= 3\times10^{8}$ m/sec

$$\therefore \quad \text{Time} = \frac{\text{Distance}}{\text{Velocity}} = \frac{8\times10^{10}\,\text{m}}{3\times10^{8}\,\text{m / sec}^{-1}}$$

$= 2.66\times10^{2}$ sec.

Ex. What will be the frequency of photon of wavelength 2225 Å traveling in vacuum ?

Sol. Velocity of light in vacuum $= 3\times10^{8}$ m sec^{-1}

Wavelength $= 2225\times10^{-10}$ meter

$$\text{Frequency} = \frac{\text{Velocity}}{\text{Wavelength}} = \frac{3\times10^{8}\,\text{meter / sec}}{2225\times10^{-10}\,\text{meter}} = \frac{3000}{2225}\times10^{5}\,\text{sec}^{-1}$$

$= 1.349\times10^{15}$ sec^{-1}

Particle Nature of Electromagnetic Radiation : Planck's Quantum Theory

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

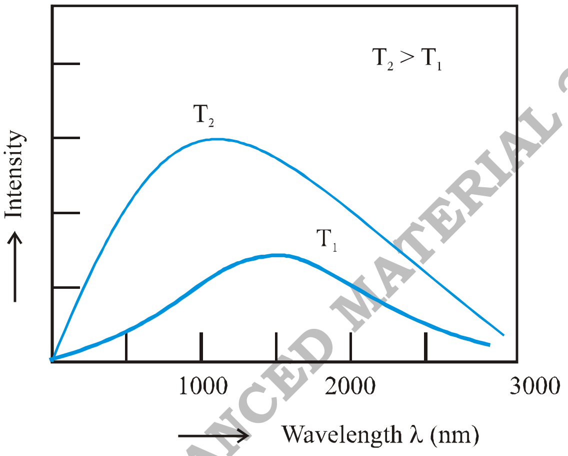
(i) the nature of emission of radiation from hot bodies (black - body radiation)

(ii) ejection of electrons from metal surface when radiation strikes it (photoelectric effect)

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.

Quantum Theory of Light

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(J), then total energy coming out is = nE_0 (n = Integer)

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

Energy of one photon is given by

$E_0 = h\nu$ (ν- Frequency of light)

$h = 6.626 \times 10^{-34}$ J-Sec (h - Planck const.)

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

(λ - wavelength)

Order of magnitude of $E_o = \dfrac{10^{-34} \times 10^{8}}{10^{-10}} = \mathbf{10^{-16}\ J}$

KEY POINTS

Units of Energy are

S.I. unit – **Joule (J)**
C.G.S. unit – **erg**
Other unit – **electron volt (ev)**

$$\boxed{\mathbf{1\ ev = 1.6 \times 10^{-19}\ J,\ 1\ erg = 10^{-7}\ J}}$$

while using the formula $E_0 = \frac{hc}{\lambda}$ use **hc = 1240 ev - nm = 12400 ev - Å**

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

$$AgCl \xrightarrow{hv} Ag(Gray) + Cl$$

If the heat of reaction for the decomposition of AgCl is 248 kJ mol^{-1}, what maximum wavelength is needed to induce the desired process?

Sol. Energy needed to change = 248×10^3 J/mol

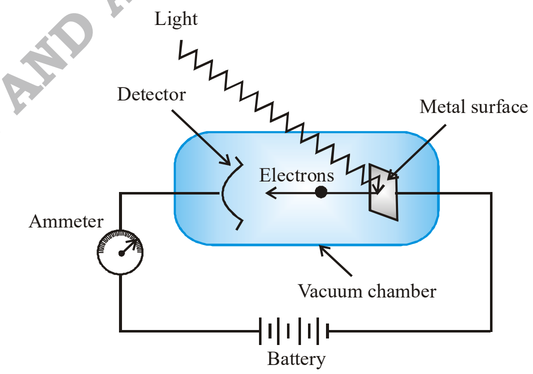
If photon is used for this purpose, then according to Einstein law one molecule absorbs one photon.

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

$$\lambda = \frac{6.626 \times 10^{-34} \times 3.0 \times 10^8 \times 6.023 \times 10^{23}}{248 \times 10^3} = 4.83 \times 10^{-7}\ m$$

PHOTOELECTRIC EFFECT (P.E.E.)

The ejection of electrons when light of certain minimum frequency called as threshold frequency is incident on a matel surface is called as 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.



Some important terms regarding P.E.E.

Threshold Frequency : Threshold frequency is defined as the minimum frequency of incident light which can cause photo electric emission i.e. this frequency is just able to eject electrons with out giving them additional energy.

Work Function : The minimum quantity of energy which is required to remove an electron to infinity from the surface of a given solid, usually a metal.

Threshold frequency is the minimum frequency required and work function is the minimum energy required.

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.

(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, ν_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.

Photoelectric Effect Equation

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

$$\text{Incident energy} = \text{Work Function } (\phi) + \text{K.E.}_{\text{max}}$$

$$E_i = \phi + (\text{K.E.})_{\text{max}}$$

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

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

Ex. The threshold frequency ν_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. $$\text{K.E.} = \frac{1}{2} m_e V^2 = h(\nu - \nu_0)$$

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

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

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

Ex. A photon of wavelength 3000 Å strikes a metal surface, the work function of the metal being 2.20 eV. Calculate (i) The energy of the photon in eV (ii) the kinetic energy of the emitted photo electron and (iii) the velocity of the photo electron.

Sol. (i) Energy of the photon

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.6 \times 10^{-34}\ \text{Js})(3 \times 10^8\ \text{ms}^{-1})}{3 \times 10^{-7}\ \text{m}} = 6.6 \times 10^{-19}\ \text{J}$$

$$1\text{eV} = 1.6 \times 10^{-19}\ \text{J}$$

$$\text{Therefore } E = \frac{6.6 \times 10^{-19}\ \text{J}}{1.6 \times 10^{-19}\ \text{J / ev}} = 4.125\ \text{eV}$$

(ii) Kinetic energy of the emitted photo electron

Work function = 2.20 eV

Therefore, KE = 2.475 – 2.20 = 1.925 eV = 3.08×10^{-19} J

(iii) Velocity of the photo electron

$$\text{KE} = \frac{1}{2} mv^2 = 3.08 \times 10^{-19}\ \text{J}$$

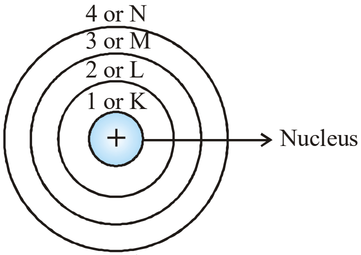
$$\text{Therefore, velocity (v)} = \sqrt{\frac{2 \times 3.08 \times 10^{-19}}{9.1 \times 10^{-31}}} = 8.22 \times 10^5\ \text{ms}^{-1}$$

BOHR'S ATOMIC MODEL

It is based on quantum theory of light. It is applicable only for single electron species. Ex. H, He^+, Li^{2+}, etc.

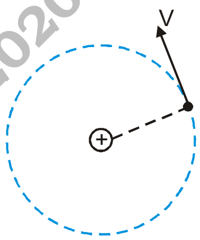
Assumptions of Bohr's Model

- The electron in the hydrogen atom revolves around the nucleus in a circular path of fixed radius and energy. These paths are called orbits, stationary states, energy shells, or allowed energy states. these stationary states for electrons are numbered as n = 1, 2, 3, ... or designated as K, L, M, N, ..., etc. shells (Fig.) These integral numbers are known as principal quantum numbers. These orbits are arranged concentricallly around the nucleus.



Bohr's orbit

- Electrons revolve only in those orbits where the angular momentum of the electron is quantized. Thus an electron can move only in those orbits for which its angular momentum is an integral multiple of $h/2\pi$.



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

where n = 1, 2, 3, ..., n ; h is Planck's constant; m is mass of electron ; v is the velocity of electron; and r is the radius of the orbit.

- The energy of an electron in the orbit does not change with time. This means that the eneryg of an electron in a particular orbit remains constant; it does not lose or gain energy.

- The electron will move from a lower stationary state to a higher stationary state when the required amount of energy is absorbed by the electron. When the electron jumps back to the lower energy level, it emits the same amount of energy. The energy change does not take place in a continuous manner.

- The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE is given by

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$$

where E_1 and E_2 are the energies of the lower and higher allowed energy states, respectively. This expression is called 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 –

$$F = \frac{KZe^2}{r^2} \qquad \text{where : } K = \text{constant} = \frac{1}{4\pi\varepsilon_0} = 9 \times 10^9\ Nm^2/C^2$$

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

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

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

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

From the postulate of Bohr,

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

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

From equation (i) and (ii)

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

On solving, we will get

$$\boxed{r = \frac{n^2h^2}{4\pi^2mKZe^2}}$$

On putting the value of e , h , m, the radius of nth Bohr orbit is given by :

$$\boxed{r_n = 0.529 \text{ x } \frac{n^2}{Z} \text{ Å}} \Rightarrow \because r \propto \frac{n^2}{Z} \Rightarrow \boxed{\frac{r_1}{r_2} = \frac{n_1^2}{n_2^2} \times \frac{Z_2}{Z_1}}$$

Ex. Calculate radius ratio for 2nd orbit of He^+ ion & 3rd orbit of Be^{+++} ion.

Sol. r_1 (radius of 2nd orbit of He^+ ion) $= 0.529\left(\frac{2^2}{2}\right)$ Å

r_2 (radius of 3rd orbit of Be^{+++} ion) $= 0.529\left(\frac{3^2}{4}\right)$ Å

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 nth orbit is given by

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

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

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

then, $$v = \frac{nh \times 4\pi^2mZe^2K}{2\pi mn^2h^2}$$

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

on putting the values of π, e^-, h and K

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

$$\because \quad v \propto \frac{Z}{n} \Rightarrow \frac{v_1}{v_2} = \frac{Z_1}{Z_2} \times \frac{n_2}{n_1}$$

T, Time period of revolution of an electron in its orbit = $\frac{2\pi r}{v}$ substituting the value of 'r' and 'v' we get

$$\text{Time Period, } T = 1.52 \times 10^{-16} \times \frac{n^3}{Z^2} \Rightarrow \boxed{T \propto \frac{n^3}{Z^2} \Rightarrow \frac{T_1}{T_2} = \frac{n_1^3}{n_2^3} \times \frac{Z_2^2}{Z_1^2}}$$

f, Frequency of revolution of an electron in its orbit = $\frac{v}{2\pi r} = \frac{1}{T}$

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 $mv^2 = \frac{KZe^2}{r} \Rightarrow$ K.E. = $\frac{1}{2}\frac{KZe^2}{r}$

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

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

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

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

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

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

$$\text{T.E.} = E_n = -\frac{2\pi^2 me^4 k^2}{h^2}\left(\frac{z^2}{n^2}\right) \quad \text{... (iv)}$$

Putting the value of m,e,h and π we get the expression of total energy

$$\boxed{E_n = -13.6\,\frac{Z^2}{n^2}\ \text{eV / atom}}$$

as the value of n increases , energy of an electron in the orbit increases.

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

KEY POINTS

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.

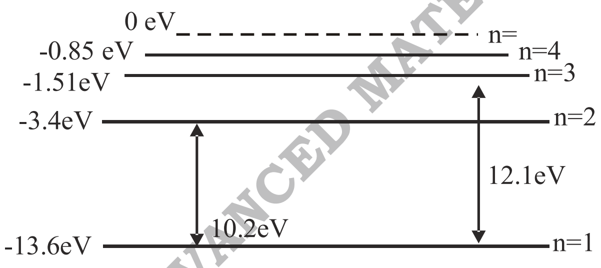
(b) All the quantities on R.H.S. in the energy equation [Eq. iv] are constant for an element having atomic number Z except ‘n’ which is an integer such as 1,2,3, etc . i.e. the energy of an electron is constant as long as the value of ‘n’ is kept constant.

(c) The energy of an electron is inversely proportional to the square of ‘n’ with negative sign.

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.



Energy level diagram of H-atom

Definition Valid for Single Electron System

(i) Ground state

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

Ground state energy of H–atom = – 13.6 ev

Ground state energy of 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^{th} excited state

(iii) Ionisation Energy (IE)

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

$\boxed{\text{I.E.} = \text{Energy of first shell.}}$

Ionisation energy of H–atom = 13.6 ev

Ionisation energy of He^+ ion = 54.4 ev

Ionisation energy of 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^+ 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 2nd state = excitation energy of 1st excited state = 1st 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 exicited state = second excitation potential = 12.09 V.

(vii) Binding Energy 'or' Seperation 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.

Ex. A single electron system has ionization energy 11180 kJ mol^{-1} . Find the number of protons in the nucleus of the system.

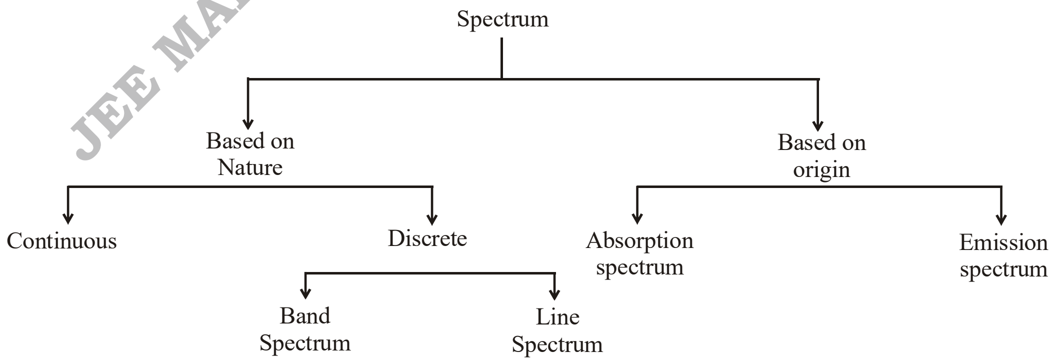
Sol. $\text{I.E.} = \frac{Z^2}{n^2} \times 21.69 \times 10^{-19}$ J

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

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.



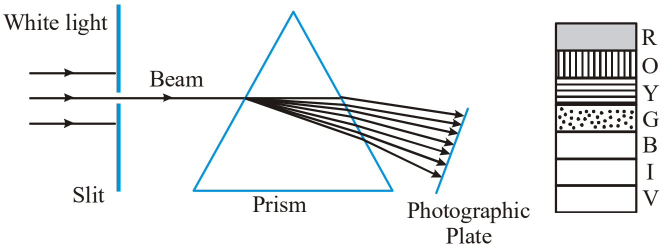
Emission Spectra

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 :

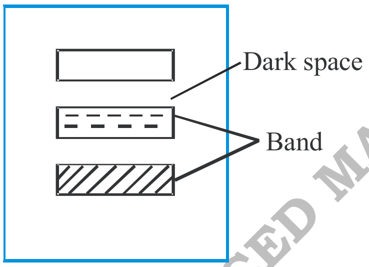
(a) Continuous Spectra

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.



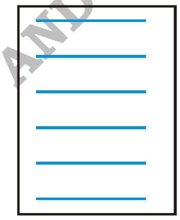
(b) Discrete Spectra : It is of two type

(i) Band Spectrum



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

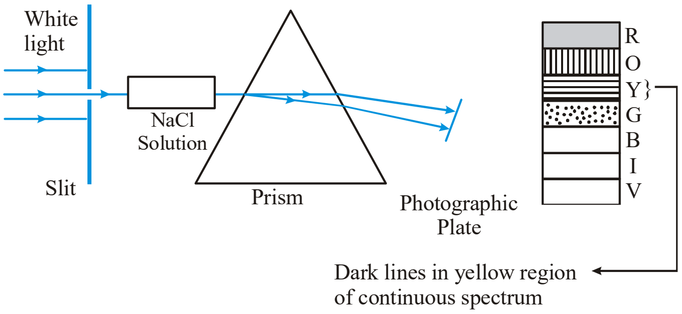
(2) Line Spectrum



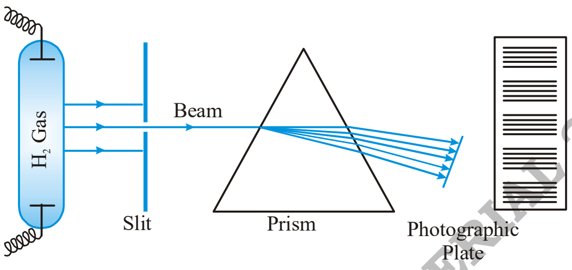
This is the ordered arrangement of lines of particular wavelength seperated by dark space eg. hydrogen spectrum. Line spectrum can be obtained from atoms.

2. 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

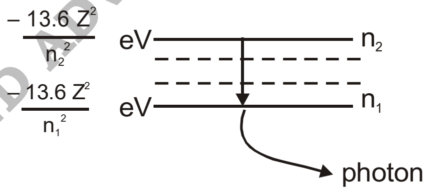


When hydrogen gas at low pressure is taken in the discharge tube and the light emitted on passing electric discharge is examined with a spectroscope, the spectrum obtained is called the emission spectrum of hydrogen.

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



Energy of emitted photon $= (\Delta E)_{n2 \to n1} = \dfrac{-13.6Z^2}{n_2^2} - \left(\dfrac{-13.6Z^2}{n_1^2}\right) = 13.6Z^2\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$

Wavelength of emitted photon

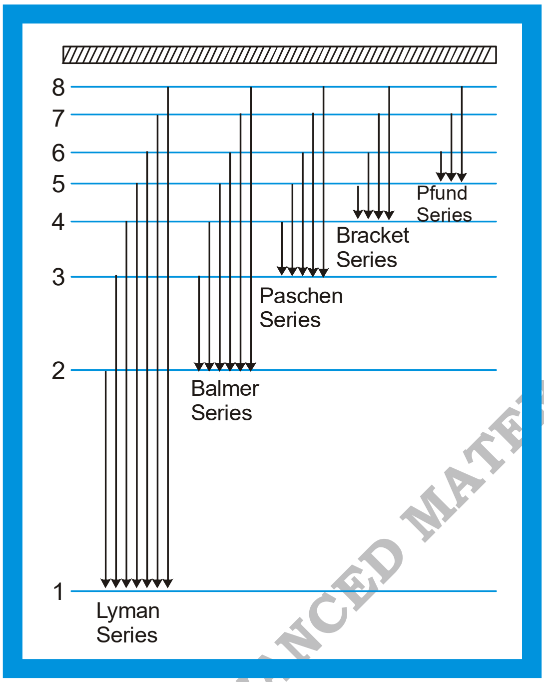
$$\lambda = \frac{hc}{(\Delta E)_{n_2 \to n_1}}$$

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

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

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

R = Rydberg constant = $1.09678 \times 10^7 m^{-1}$; $R \simeq 1.1 \times 10^7 m^{-1}$; $R = \frac{13.6eV}{hc}$; R ch = 13.6 eV



Ex. Calculate the wavelength of a photon emitted when an electron in H- atom maker a transition from n = 2 to n = 1

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

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

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

Spectra Lines of Hydrogen Atom

LYMAN SERIES

- It is first spectral series of H.
- It was found out in ultraviolet region in 1898 by Lyman.
- It's 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.
- $\frac{1}{\lambda} = R_H\left[\frac{1}{1^2} - \frac{1}{n_2^2}\right]$ where $n_2 > 1$ always.

- The wavelength of marginal line = $\frac{n_1^2}{R_H}$ for all series. So for lyman series $\lambda = \frac{1}{R_H}$.
- I^{st} line of lyman series $\Rightarrow 2 \rightarrow 1$
  II^{nd} line of lyman series $= 3 \rightarrow 1$
  Last line of lyman series = $\infty \rightarrow 1$
  $[10.2\text{ eV} \le (\Delta E)_{lyman} \le 13.6\text{ eV}]$
  $\frac{12400}{13.6} \le \lambda_{lyman} \le \frac{12400}{10.2}\ A^o$
- **Longest Line :** longest wavelength line $\lambda_{longest}$ or $\lambda_{max.} = \frac{12400}{(\Delta E)_{min}}$
- **Shortest Line :** shortest wavelength line $\lambda_{shortest}$ or $\lambda_{min} = \frac{12400}{(\Delta E)_{max}}$
- First line of any spectral series is the longest (λ_{max}) line.
- Last line of any spectral series is the shortest (λ_{min}) line.

Series Limit

It is the last line of any spectral series.

Wave no of I^{st} line of Lyman series

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

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

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

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

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,

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

BALMER SERIES

- It is the second series of H-spectrum.
- It was found out in 1892 in visible region by Balmer.
- It's value of $n_1 = 2$ and $n_2 = 3,4,5,$.............

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

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

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

  All the lines of balmer series in H spectrum are not in the visible range. Infact only Ist 4 lines belongs to visible range.

  $\frac{12400}{3.4}\text{A}^\circ \le \lambda_{\text{balmer}} \le \frac{12400}{1.9}\text{Å}$

  $3648\ \text{Å} \le \lambda_{\text{balmer}} \le 6536\ \text{Å}$

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

  Ist line of balmer series = $3 \to 2$

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

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

  $(\bar{\nu})$ 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 out in infrared region by Paschen.

(c) It's value of $n_1 = 3$ and $n_2 = 4,5,6$ ....

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

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

BRACKETT SERIES

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

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

(c) It's value of $n_1 = 4$ and $n_2 = 5,6,7$ ....

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

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

PFUND SERIES

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

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

(c) It's value of $n_1 = 5$ and $n_2 = 6,7,8$ .... where n_1 is ground state and n_2 is excited state.

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

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

HUMPHRY SERIES

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

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

(c) It's 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 $n_2 > 6$.

Ex. Calculate wavelength for 2nd line of Balmer series of He^+ ion

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

$n_1 = 2 \quad n_2 = 4$

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

$$\frac{1}{\lambda} = \frac{3R}{4} \qquad \lambda = \frac{4}{3R}$$ **Ans.**

No. of Photons Emitted by a Sample of H Atom

If an electron is in any higher state n = n 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 $\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$

Note : In case of single isolated atom if electron make transition from nth state to the ground state then max. number of spectral lines observed = (n–1)

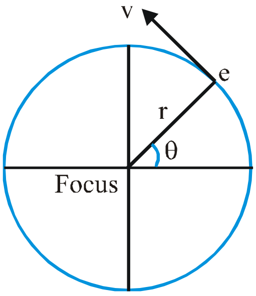
Ex. If electron make transition from 7th excited state to 2nd state in H atom sample find the max. number of spectral lines observed.

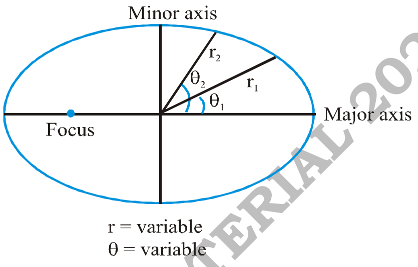
Sol. $\Delta n = 8 - 2 = 6$

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

SOMMERFELD EXTENSION OF THE BOHR'S MODEL

- According to sommerfeld electron revolve around the nucleus in the Elliptical Orbits.
- Circular orbit is a special case of elliptical orbit when the length of major axis becomes equal to the length of minor axis then the shape of orbit will be circular.





- If electrons revolve in elliptical orbit then its angular momentum shows two components

1. **Radial Component**

$$J_r = \frac{n_r h}{2\pi}$$

where n_r = radial quantum number.

$[n_r = (n-1)................0]$

n = Shell number

2. **Azimuthal Components**

$$J_\phi = n_\phi \frac{h}{2\pi}$$

n_ϕ = Azimuthal quantum number

$[\,n_\phi = 1, 2, 3, 4............n]$

n = Shell number

So total Angular momentum = J_n

$$J_n = J_r + J_\phi$$

$$\frac{nh}{2\pi} = \frac{n_r h}{2\pi} + n_\phi \frac{h}{2\pi}$$

$n = n_r + n_\phi$ where n = principal quantum number

Ex. Let $n = 4$ $\quad n = n_r + n_\phi$

Then $\quad 4 = 3 + 1$

$4 = 2 + 2$

$4 = 1 + 3$

$4 = 0 + 4$

- The length of major axis indicates by $n_r + n_\phi$ i.e. n and length of minor axis indicates by n_ϕ
- The path of electron

$$K = \frac{n_r + n_\phi}{n_\phi} = \frac{n}{n_\phi} = \frac{\text{Length of major axis}}{\text{Length of minor axis}}$$

n_ϕ varies is from 1 to n.

- If n = 4 then $n_\phi = 1, 2, 3, 4$

$$K = \frac{4}{1}, \frac{4}{2}, \frac{4}{3}, \qquad \frac{4}{4}$$

3 Elliptical path circular path

- If n = 5 then $n_\phi = 1, 2, 3, 4, 5$
- $$K = \frac{5}{1}, \frac{5}{2}, \frac{5}{3}, \frac{5}{4}, \qquad \frac{5}{5}$$

4 Elliptical path Circular path

- If n = 1 Then Elliptical path = $(n-1) = (1-1) = 0$

  Circulars path = 1

In nth Orbit : Number of elliptical path = $(n-1)$

Number of circular path = 1

In every atom, 1st orbit is always circular.

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 multiple spectral 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.

THE DUAL NATURE OF MATTER (THE WAVE NATURE OF ELECTRON)

1. In 1924. a French physicist, Louis De Broglie suggested that if the nature of light is both that of a particle and of a wave, then this dual behavior should be true for the matter also.
2. According to De Broglie, the wavelength λ of an electron is inversely proportional to its momentum p.

$$\lambda \propto \frac{1}{p} \quad \text{or} \quad \lambda \propto \frac{1}{mv}$$

$$\lambda = \frac{h}{p}$$ Here h = Planck's constant

p = momentum of electron

∴ Momentum (p) = Mass (m) × Velocity (c)

- $$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2m(K.E.)}}$$

From the de-Broglie equation it follows that wavelength of a particle decrease with increase in velocity of the particle. Moreover, lighter particles would have longer wavelength than heavier particles, provided velocity is equal.

- If a charged particle Q is accelerated through potential difference V from rest then de-broglie wavelength is

$$\lambda = \frac{h}{\sqrt{2mQV}} \qquad \text{for an electron } \lambda = \sqrt{\frac{150}{V}}\,\text{Å} = \frac{12.25}{\sqrt{V}}\,\text{Å}$$

- de-Broglie concept is more significant for microscopic or sub-microscopic particles whose wavelength can be measured.
- The circumference of the n^{th} orbit is equal to n times the De-broglie wavelength of the electron revolving around the nucleus.

$$2\pi r_n = n\lambda \qquad \text{where n = no. of shells or no. of waves.}$$

Ex. Two particles X and Y are in motion. If the wavelength associated with particle X is 4×10^{-8} m, calculate the wavelength associated with particle Y if its momentum is half of X.

Sol. According to de Broglie equation

$$\lambda_x = \frac{h}{p_x} \text{ and } \lambda_y = \frac{h}{p_y}$$

$$\frac{\lambda_x}{\lambda_y} = \frac{p_y}{p_x}$$

But $p_y = ½\ p_x$ (given)

$$\frac{\lambda_x}{\lambda_y} = \frac{1/2p_x}{p_x} = ½$$

$\lambda_B = 2\lambda_A = 2 \times 4 \times 10^{-8}\text{m} = 8 \times 10^{-8}\text{m}$

Ex. Calculate the de Broglie wavelength of a ball of mass 0.1 kg moving with a speed of 30 ms^{-1}.

Sol. $\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34}}{0.1 \times 30}$

$\lambda = 2.2 \times 10^{-34}$ m

This is apparent that this wavelength is too small for ordinary observation.

Although the de Broglie equation is applicable to all material objects but it has significance only in case of microscopic particles.

Since, we come across macroscopic objects in our everyday life, de Broglie relationship has no significance in everyday life.

HEISENBERG UNCERTAINTY PRINCIPLE

Bohr's theory considers an electron as a material particle. Its position and momentum can be determined with accuracy. But, when an electron is considered in the form of wave as suggested by de-Broglie, it is not possible to ascertain simultaneously the exact position and velocity of the electron more precisely at a given instant since the wave is extending throughout a region of space.

In 1927, Werner Heisenberg presented a principle known as Heisenberg uncertainty principle which states as : "It is impossible to measure simultaneously the exact position and exact momentum of a body as small as an electron."

The uncertainty of measurement of position, Δx, and the uncertainty of momentum Δp or mΔv, are related by Heisenberg's relationship as : (p = mv, Δp = mΔv)

$$\Delta x\,.\,\Delta p \geq \frac{h}{4\pi} \qquad \text{or} \qquad \Delta x\,.\,m\Delta v \geq \frac{h}{4\pi} \qquad \text{or} \qquad \Delta x.\Delta v \geq \frac{h}{4\pi m}$$

where h is Planck's constant.

$\Delta x\ \Delta v$ = uncertainty product

For an electron of mass m (9.10×10^{-28} g), the product of uncertainty is quite large.

$$\Delta x\,.\,\Delta v \geq \frac{6.624 \times 10^{-27}}{4\pi m}$$

$$\geq \frac{6.624 \times 10^{-27}}{4 \times 3.14 \times 9.10 \times 10^{-28}}$$

$$= 0.57 \text{ erg sec per gram approximately}$$

When $\Delta x = 0, \Delta v = \infty$ and vice-versa.

In the case of bigger particles (having considerable mass), the value of uncertainty product is negligible. If the position is known quite accurately, i.e., Δx is very small, Δv becomes large and vice-versa.

- In terms of uncertainty in energy ΔE, and uncertainty in time Δt, this principle is written as,

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

- Heisenberg replaced the concept of definite orbits by the concept of probability. According to Heisenberg we can only define the probability of finding electrons around the nucleus.

Ex. Why electron cannot exist inside the nucleus according to Heisenberg's uncertainty principle ?

Sol. Diameter of the atomic nucleus is of the order of 10^{-15} m

The maximum uncertainty in the position of electron is 10^{-15} m.

Mass of electron = 9.1×10^{-31} kg.

$$\Delta x.\ \Delta p = \frac{h}{4\pi}$$

$$\Delta x \times (m.\Delta v) = h/4\pi$$

$$\Delta v = \frac{h}{4\pi} \times \frac{1}{\Delta x.m} = \frac{6.63 \times 10^{-34}}{4 \times \frac{22}{7}} \times \frac{1}{10^{-15} \times 9.1 \times 10^{-31}}$$

$\Delta v = 5.80 \times 10^{10}\ \text{ms}^{-1}$

This value is much higher than the velocity of light and hence not possible.

DE BROGLIE RELATIONSHIP & HEISENBERG'S UNCERTAINTY PRINCIPLE

Ex. The mass of a particle is 1 mg and its velocity is 4.5×10^5 cm per second. What should be the wavelength of this particle if $h = 6.652 \times 10^{-27}$ erg second.

(1) 1.4722×10^{-24} cm (2) 1.4722×10^{-29} cm (3) 1.4722×10^{-32} cm (4) 1.4722×10^{-34} cm

Sol. Given that

$m = 1 \text{ mg} = 1 \times 10^{-3}$ g

$c = 4.5 \times 10^5$ cm/sec.

$h = 6.652 \times 10^{-27}$ erg sec.

$$\therefore \quad \lambda = \frac{h}{mc} = \frac{6.652 \times 10^{-27}}{1 \times 10^{-3} \times 4.5 \times 10^{5}} = \frac{6.652 \times 10^{-29}}{4.5} \text{ cm} = 1.4722 \times 10^{-29} \text{ cm}$$

Ex. Which of the following should be the wavelength of an electron if its mass is 9.1×10^{-31} kg and its velocity is 1/10 of that of light and the value of h is 6.6252×10^{-24} joule second?

(1) 2.446×10^{-7} metre **(2)** 2.246×10^{-9} metre **(3)** 2.246×10^{-11} metre **(4)** 2.246×10^{-13} metre

Sol. Given that

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

$c = \frac{1}{10}$ of velocity of light

or $c = \frac{1}{10} \times 3 \times 10^8$ metre/second i.e. 3×10^7 metre/second

$h = 6.6252 \times 10^{-34}$ joule second

$$\lambda = \frac{h}{mc} = \frac{6.6252\times10^{-34}}{9.1\times10^{-31}\times3\times10^{7}} = \frac{6.6252\times10^{-34}}{27.3\times10^{-24}}$$

or 0.2426×10^{-10} metre

or 2.426×10^{-11} metre

Ex. What should be the momentum (in gram cm per second) of a particle if its De Broglie wavelength is 1 Å and the value of h is 6.6252×10^{-27} erg second ?

(1) 6.6252×10^{-19} **(2)** 6.6252×10^{-21} **(3)** 6.6252×10^{-24} **(4)** 6.6252×10^{-27}

Sol. Given that

$\lambda = 1$ Å $= 1 \times 10^{-8}$ cm

$h = 6.6252 \times 10^{-27}$ erg second

or $p = \frac{6.6252\times10^{-27}}{1\times10^{-8}} = 6.6252 \times 10^{-19}$ gram cm/sec.

Ex. What should be the mass of the sodium photon if its wavelength is 5894Å, the velocity of light is 3×10^8 metre/second and the value of h is 6.6252×10^{-34} kg m^2/sec.?

(1) 3.746×10^{-26} **(2)** 3.746×10^{-30} **(3)** 3.746×10^{-34} **(4)** 3.746×10^{-36}

Sol. $\lambda = \frac{h}{m\times c} \Rightarrow m = \frac{h}{c\lambda}$

($\because \lambda = 5894$Å $= 5894 \times 10^{-10}$ m)

$$m = \frac{6.652\times10^{-34}}{3\times10^{8}\times5894\times10^{-10}} \text{ or } \frac{6.652}{17682}\times10^{-32} = 0.0003746 \times 10^{-32}$$

or 3.746×10^{-36} kg

Ex. What should be the uncertainty in the velocity of an electron if the uncertainty in its position is 0.005 nm, the mass of electron is 9.109×10^{-31} kg and the value of h is 6.6252×10^{-34} joule/second?

(1) 2.316×10^5 **(2)** 1.158×10^7 **(3)** 2.316×10^9 **(4)** 2.316×10^{11}

Sol. Uncertainty in position (Δx) = 0.005 nm = 0.005×10^{-9} m

$= 5 \times 10^{-12}$ m

Mass of electron (m) = 9.109×10^{-31} kg.

$$\therefore \quad \Delta v = \frac{h}{4\pi m \times \Delta x} = \frac{6.6252\times10^{-34}}{4\times3.14\times5\times10^{-12}\times9.109\times10^{-31}} \text{ m/sec.}$$

or $$\Delta v = \frac{6.6252\times10^{-34}}{4\times3.14\times5\times9.109\times10^{-43}}$$

$\therefore$ $\Delta v = 1.15816\times10^{7}$ m/sec.

Ex. What should be the uncertainty in velocity of a particle of 1 kg mass if uncertainty in position is 1Å and the value of h is 6.6252×10^{-34} Joule sec.?

(1) 1.055×10^{-22} **(2)** 1.055×10^{22} **(3)** 5.25×10^{-25} **(4)** 1.055×10^{24}

Sol. Given that

$\Delta x = 1Å = 1\times10^{-10}$ m

m = 1 kg

$h = 6.6252\times10^{-34}$ Joule sec.

$$\Delta v = \frac{h}{4\pi\times m\times\Delta x} = \frac{6.6252\times10^{-34}}{4\times3.14\times1\times10^{-10}}$$

or $$\Delta v = \frac{6.6252\times10^{-34}}{12.56\times10^{-10}}\ \text{m/sec.}$$

$= 0.52525\times10^{-24}$ m/sec.

$= 5.25\times10^{-25}$ m/sec.

Ex. What should be the uncertainty in position if uncertainty in momentum is 1×10^{-2} g cm/sec. and value of h is 6.6252×10^{-34} Joule sec. ?

(1) 1.054×10^{-22} m **(2)** 1.054×10^{-25} m **(3)** 0.525×10^{-27} m **(4)** 1.054×10^{-32} m

Sol. Given that

$\Delta p = 1\times10^{-2}$ g cm/sec. $= 1\times10^{-7}$ kg m/sec.

$h = 6.6252\times10^{-34}$ Joule sec.

$$\Delta x\times\Delta p = \frac{h}{4\pi} \qquad \therefore\ \Delta x = \frac{h}{4\pi\times\Delta p}$$

or $$\Delta x = \frac{6.6252\times10^{-34}}{4\times3.14\times10^{-7}} = 0.525\times10^{-27}\ \text{m}$$

Ex. A ball weighs 25 g moves with a velocity of 6.6×10^{4} cm/sec then find out the De Broglie λ associated with it.

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

$$= \frac{6.6\times10^{-34}\times10^{7}}{25\times6.6\times10^{4}\ \text{cm / sec}}\ \text{ergsec} = 1\times\frac{10^{-38}}{25}$$

$= 0.04\times10^{-38}\times10^{7}$

$= 0.04\times10^{-31}$ cm

$= 4\times10^{-33}$ cm

Ex. Which of the following has least De Broglie λ if they have same velocity.

1. e^- **2.** p **3.** CO_2 **4.** SO_2

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

∴ mass of SO_2 is greater than the mass of e^-, p, CO_2

= h constant

= v Same

∴ least λ will be SO_2

∴ $\lambda \propto \frac{1}{m}$

Ex. If uncertainty in position of an e^- is same as the Δx of He atom. If Δp of e^- is 32×10^5 then find Δp in He atom.

Sol. $\Delta x \times \Delta p = \frac{h}{4\pi}$

Since Δx is same for both.

therefore Δp will be same by

$$\frac{\Delta x_e \times \Delta p_e {}^{3} \frac{h}{4\pi}}{\Delta x_{(He)} \times \Delta P_{He} {}^{3} \frac{h}{4\pi}} = \frac{\Delta Pe}{\Delta P_{He}} = 1$$

∴ $\Delta P_e = \Delta P_{He}$

$32 \times 10^5 = 32 \times 10^5$

$\Delta P_{He} = 32 \times 10^5$

Ex. Calculate the uncertainty in the position of a particle when the uncertainty in momentum is (a) 1×10^{-3} g cm sec^{-1} (b) Zero.

Sol. Given

$\Delta p = 1 \times 10^{-3}$ g cm sec^{-1}

$h = 6.62 \times 10^{-27}$ erg sec.

$\pi = 3.142$

According to uncertainty principle

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

So,
$$\Delta x \geq \frac{h}{4\pi} . \frac{1}{\Delta p}$$

$$\geq \frac{6.62 \times 10^{-27}}{4 \times 3.142} \times \frac{1}{10^{-3}}$$

$$= 0.527 \times 10^{-24} \text{ cm}$$

(b) When the value of $\Delta p = 0$, the value of Δx will be infinity.

Ex. The uncertainty in position and velocity of a particle are 10^{-10} m and 5.27×10^{-24} ms^{-1} respectively. Calculate the mass of the particle ($h = 6.625 \times 10^{-34}$ Joule Sec.)

Sol. According to Heisenberg's uncertainty principle,

$$\Delta x . m\, \Delta v = \frac{h}{4\pi} \quad \text{or} \quad m = \frac{h}{4\pi \Delta x . \Delta v}$$

$$= \frac{6.625 \times 10^{-34}}{4 \times 3.143 \times 10^{-10} \times 5.27 \times 10^{-24}}$$

$$= 0.099 \text{ kg}$$

Ex. Calculate the uncertainty in velocity of a cricket ball of mass 150 g if the uncertainty in its position is of the order of 1Å ($h = 6.6 \times 10^{-34}$ kg m^2 s^{-1}).

Sol. $\Delta x\ .\ m\ \Delta v = \frac{h}{4\pi}$

$$\Delta v = \frac{h}{4\pi \Delta x . m}$$

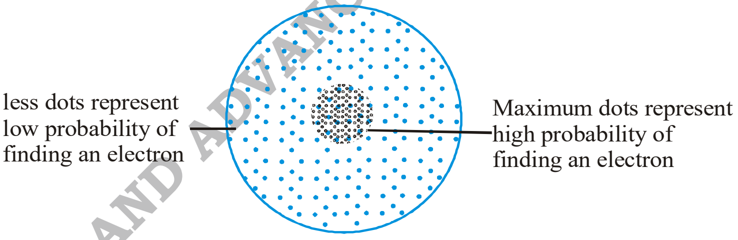
$$= \frac{6.6 \times 10^{-34}}{4 \times 3.143 \times 10^{-10} \times 0.150}$$

$$= 3.499 \times 10^{-24} \text{ ms}^{-1}$$

Orbital

An orbital may be defined as the region of space around the nucleus where the probability of finding an electron is maximum (90% to 95%)

Orbitals do not define a definite path for the electron, rather they define only the probability of the electron being in various regions of space around the nucles.



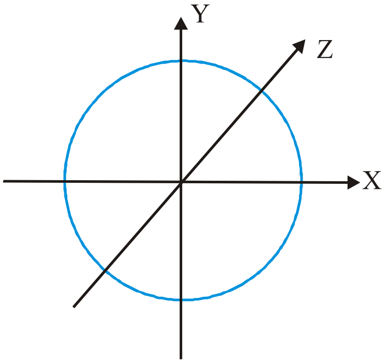
Difference Between Orbit and Orbitals

S. No.	Orbit	Orbitals
1	It is well defined circular path followed by revolving electrons around the nucleus	It is the region of space around the nucleus where electron is most likely to be found
2	It represents planar motion of electron	It represents 3 dimensional motion of an electron around the nucleus.
3	The maximum no. of electron in an orbits is $2n^2$ where n stands for no. of orbit.	Orbitals can not accomodate more than 2 electrons.
4	Orbits are circular in shape.	Orbitals have different shape e.g. s-orbital is spherical, p - orbital is dumb- bell shaped.
5	Orbit are non directional in character. Hence, they cannot explain shape of molecules	Orbitals (except s-orbital) have directional character. Hence, they can account for the shape of molecules.
6	Concept of well defined orbit is against Heisenberg's uncentainty principle.	Concept of orbitals is in accordance with Heisenberg's principle

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 → spherical



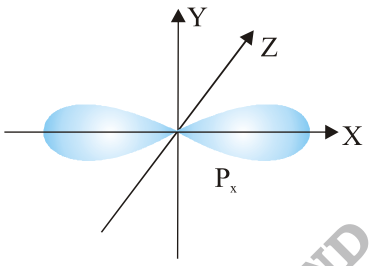
s- orbital is non directional and it is closest to the nucleus, having lowest energy.
s-orbital can accomodate maximum no. of two electrons.

↑↓
n s

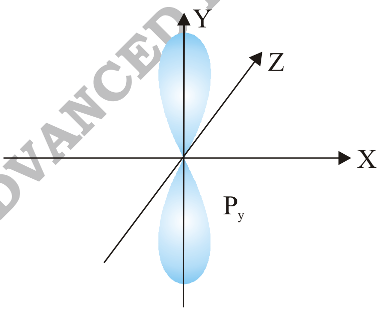
p-Orbital : Shape → dumb bell

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

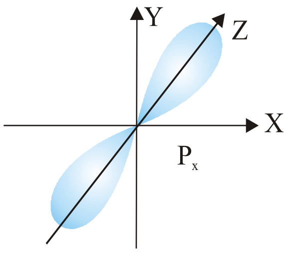
Nodal Plane – The imaginary plane where probability of finding an electron is **zero**.



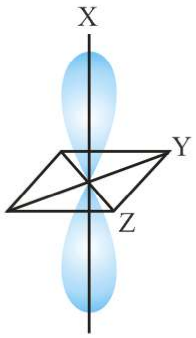
nodal plane – yz



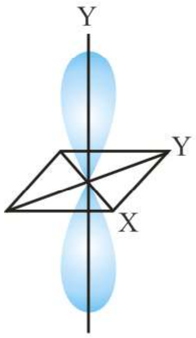
nodal plane – xz



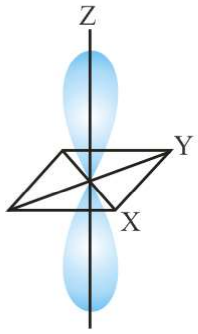
nodal plane – xy



px



py

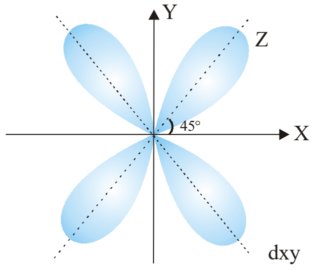


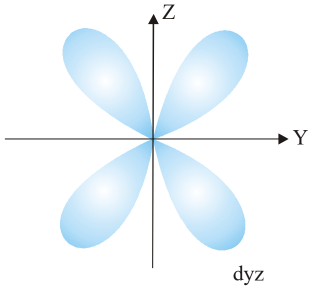
pz

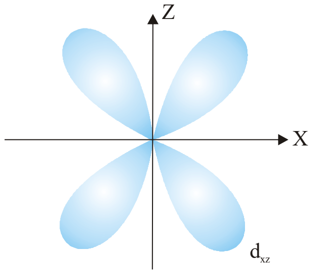
p - subshell can accomodate maximum of six electrons.

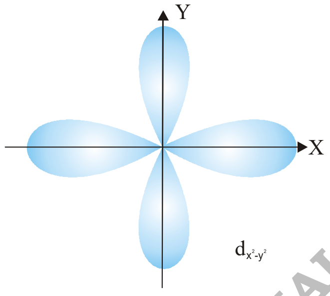
↑↓	↑↓	↑↓
p_x	p_y	p_z

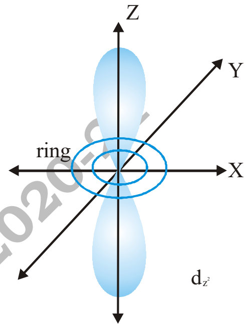
d - Orbital : Shape → double dumb bell











d - subshell can accomodate maximum of 10 electrons.

↑↓	↑↓	↑↓	↑↓	↑↓
dxy	dyz	dz^2	dx^2-y^2	dxz

f - Orbital : Shape → leaf like or Complex

↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

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

Quantum Numbers

The set of four numbers required to define the possible location of an electron 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 nth shell = n

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

- Number of orbitals present in nth 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 (ℓ) : (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). Each value of ℓ represents a subshell.
-

value of ℓ	**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 $L = \frac{h}{2\pi}\sqrt{\ell(\ell+1)} = \hbar\sqrt{\ell(\ell+1)}$ $\left[\hbar = \frac{h}{2\pi}\right]$

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 Samuel Goudsmit & Uhlenbeck)

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

(i) 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)

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

(iii) Maximum spin of atom = $\frac{1}{2}$ x No. of unpaired electron.

Rules for Filling of Orbitals

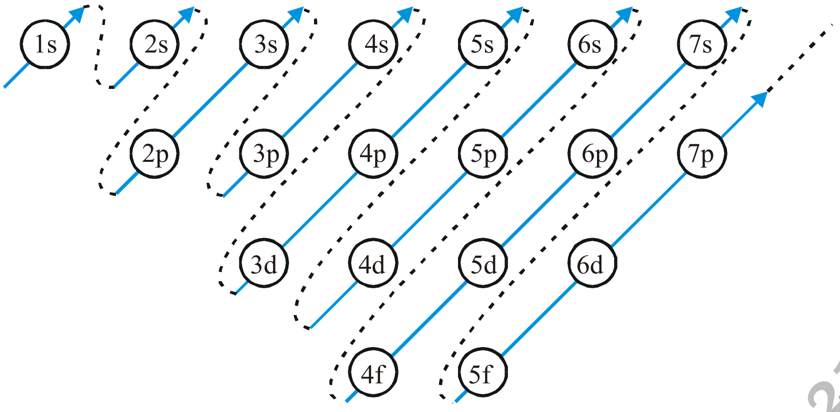
1. Aufbau Principle

Aufbau is a German word and its meaning 'Building up'

Aufbau principle gives a sequence in which various subshell are filled up depending on the relative order of the Energies of various subshell.

- **Principle :** The subshell with minimum energy is filled up first and when this subshell obtained maximum quota of electrons then the next subshell of higher energy starts filling.

- The sequence in which various subshell are filled is the following.



$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{14}, 6d^{10}, 7p^6$

2. (n + ℓ) Rule

According to it the sequence in which various subshell are filled up can also be determined with the help of (n + ℓ) value for a given subshell.

PRINCIPLE OF (n + ℓ) RULE

The subshell with lowest(n + ℓ) value is filled up first, when two or more subshell have same (n+ℓ) value then the subshell with lowest value of n is filled up first.

Sub Shell	n	ℓ	n +ℓ	
1s	1	0	1	
2s	2	0	2	
2p	2	1	3	(1)
3s	3	0	3	(2)
3p	3	1	4	(1)
4s	4	0	4	(2)
3d	3	2	5	(1)
4p	4	1	5	(2)
5s	5	0	5	(3)
4d	4	2	6	(1)
5p	5	1	6	(2)
6s	6	0	6	(3)

KEY POINTS

For H atom the energy of orbital depends only on the value of n.

i.e. 1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f.................

3. Pauli's Exclusion Principle

In 1925 Pauli stated that no two electron in an atom can have same values of all four quantum numbers.

- An orbital can accomodates maximum 2 electrons with opposite spin.

4. Hund's Maximum Multiplicity Rule

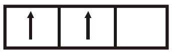
(Multiplicity : Many of the same kind)

- According to Hund's rule electrons are distributed among the orbitals of subshell in such a way as to give maximum number of unpaired electron with parallel spin. i.e. in a subshell pairing of electron will not start until and unless all the orbitals of that subshell will get one electron each with same spin.

SPIN MULTIPLICITY

It is given by 2S + 1 where S is the total spin.

(a) 

(b) 

For (a), $S = +\frac{1}{2} - \frac{1}{2} = 0$

Spin multiplicity $= 2S + 1 = 0 + 1 = 1$ (singlet)

For (b), $S = +\frac{1}{2} + \frac{1}{2} = 1$

Spin multiplicity $= 2S + 1 = 2 \times 1 + 1 = 3$ (triplet)

Ex. Find out the angular momentum of an electron in

(a) 4s orbital (b) 3p orbital (c) 4th orbital

Sol. Angular momentum in an orbital $= \frac{h}{2\pi}\sqrt{\ell(\ell+1)}$

(a) $\ell = 0$ for 4s orbital, hence orbital angular momentum = 0

(b) $\ell = 1$ for 3p orbital

$\therefore$ Angular momentum $= \frac{h}{2\pi}\sqrt{(1+1)\times 1} = \frac{h}{\sqrt{2}\pi}$

(c) Angular momentum in 4th orbit

$= \frac{nh}{2\pi} = \frac{4h}{2\pi} = \frac{2h}{\pi}$

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

(i) $n = 4, \ell = 2, m = 0$ (ii) $n = 3, \ell = 1, m = \pm 1$

(iii) $n = 4, \ell = 0, m = 0$ (iv) $n = 3, \ell = 2, m = \pm 2$

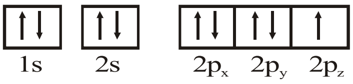
Sol. (i) $4dz^2$ (ii) $3p_x$ or $3p_y$

(iii) 4s (iv) $3d_{x^2-y^2}$ or $3d_{xy}$

ELECTRONIC CONFIGURATION OF ELEMENTS

Based on the rules, we can easily determine the electronic configurations of most element. We just need to know the atomic number of an element, the order in which orbitals are to be filled and the maximum number of electrons in a shell, sub-shell or orbital. The configurtion so obtained can be represented in two ways. As an illustration, let us consider fluorine (Z = 9) :

F(Z = 9) = $1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$ or



Importance of knowing the exact electronic configuration of an element lies in the fact that the chemical properties of an element are dependent on the behaviour and relative arrangement of its electrons.

Electronic configurations of heavier elements (beyond Z = 56) deviate a little from the order mentioned previously. These are listed below :

Lanthanides	La (Z = 57)	:	$[Xe]6s^2 5d^1$ (not $4f^1$)
	Ce (Z = 58)	:	$[Xe]6s^2 5d^1 4f^1$
	Pr (Z = 59)	:	$[Xe]6s^2 5d^1 4f^2$
Actinides	Ac (Z = 89)	:	$[Rn]7s^2 6d^1$ (not $5f^1$)
	Th (Z = 90)	:	$[Rn]7s^2 6d^1 5f^1$
	Pa (Z = 91)	:	$[Rn]7s^2 6d^1 5f^2$
Beyond Z = 103	Z = 104	:	$[Rn]5f^{14} 6d^2 7s^2$
	Z = 105	:	$[Rn]5f^{14} 6d^3 7s^2$
	Z = 106	:	$[Rn]5f^{14} 6d^4 7s^2$
	Z = 112	:	$[Rn]5f^{14} 6d^{10} 7s^2$

Ex. Write the electronic configuration and find the no. of unpaired electrons as well as total spin for the following atoms

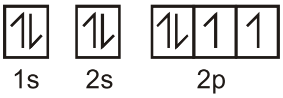
(1) $_6C$
(2) $_8O$
(3) $_{15}P$
(4) $_{21}Sc$
(5) $_{26}Fe$
(6) $_{10}Ne$

Sol. (i) $_6C \rightarrow 1s^2, 2s^2, 2p^2$

No. of unpaired electrons → 2.

Total spin = $\frac{+2}{2}$ or $\frac{-2}{2}$

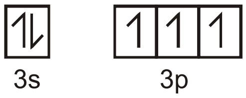
(ii) $_8O \rightarrow 1s^2, 2s^2, 2p^4$



∴ No. of unpaired electrons = 2

Total spin = $\frac{+2}{2}$ or $\frac{-2}{2}$

(iii) $_{15}P \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^3$

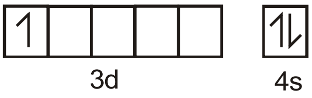


∴ No. of unpaired electrons = 3

Total spin = $\frac{+3}{2}$ or $\frac{-3}{2}$

(iv) $_{21}Sc \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^1$

or [Ar] $4s^2\ 3d^1$



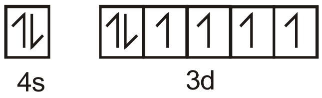
[Ar] $3d^1\ 4s^2$

∴ No. of unpaired electrons = 1

∴ Total spin = $\frac{+1}{2}$ or $\frac{-1}{2}$

(v) $_{26}Fe \rightarrow 1s^2,\ 2s^2\ 2p^6, 3s^2, 3p^6, 4s^2\ 3d^6$

or [Ar] $4s^2, 3d^6$



No. of unpaired electrons = 4

∴ Total spin = $\frac{+4}{2}$ or $\frac{-4}{2}$

(vi) $_{10}Ne \rightarrow 1s^2, 2s^2\ 2p^6$

No. of unpaired electrons = 0

Total spin = 0

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

Sol. $_6C : 1s^2, 2s^2\ 2p^2$

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

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

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

Sol. The electronic configuration are

$_7N$	:	$1s^2, 2s^2\ 2p^3$	unpaired electron = 3
$_{24}Cr$	:	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^5, 4s^1$	unpaired electron = 6
$_{36}Kr$	:	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^6$	unpaired electron = 0

∴ Total spin for an atom $= \pm 1/2 \times$ no. of unpaired electron

For $_7N$, it is $= \pm 3/2$; For $_{24}Cr$, it is $= \pm 3$; For $_{36}Kr$, it is $= 0$

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

For $_7N$, it is $= \sqrt{15}$; For $_{24}Cr$, it is $= \sqrt{48}$; For $_{36}Kr$, it is $= \sqrt{0}$

EXCEPTIONAL CONFIGURATIONS

Stability of Half Filled and Completely Filled Orbitals

Cu has 29 electrons. its expected electronic configuration is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^9$.

But a shift of one electron from lower energy 4s orbital to higher energy 3d orbital will make the distribution of electron symmetrical and hence will impart more stability.

Thus the electronic configuration of Cu is $1s^2, 2s^2, 2p^6, 3s^2, 2p^6, 4s^1, d^{10}$

Fully filled and half filled orbital are more stable.

Ex. We know that fully filled and half filled orbital are more stable. Can you write the electronic configuration of Cr(Z = 24) ?

Sol. Cr (Z = 24)

$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$.

Since half filled orbital is more stable, one 4s electron is shifted to 3d orbital.

Ex. A compound of vanadium has a magnetic moment of 1.73 BM work out the electronic configuration of the vanadium in the compound.

Sol. Magnetic moment = $\sqrt{n\left(n+2\right)}$

Where n is number of unpaired electrons

∴ $1.73 = \sqrt{n\left(n+2\right)}$ or $(1.73)^2 = n^2 + 2n, n = 1$

Vanadium atom must have the unpaired electron and thus its configuration is :

$_{23}V^{4+} : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$

WAVE MECHANICAL MODEL OF ATOM

Schrodinger Wave Equation

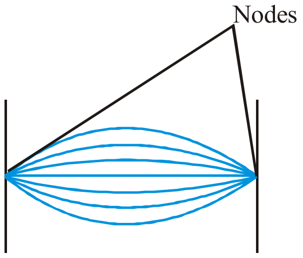
General wave equation

$y = A \sin \omega t$

where, y = displacement

A = amplitude

t = time



Developed by schrodinger, this model is based on the particle and wave nature of electron is known as WAVE MECHANICAL MODEL of atom. The motion of electron around nucleus is round motion and may be considered to be analogous to the STANDING WAVES, the waves which are generated by plucking the stretched string. The amplitude of the standing wave is independent of time and is a function of the distance from one fixed end. The derived eq. by schrodinger is

Schrodinger wave equation ⇒ $\boxed{\frac{\delta^2\psi}{\delta x^2}+\frac{\delta^2\psi}{\delta y^2}+\frac{\delta^2\psi}{\delta z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0}$

where ψ = Amplitude of e^- wave (or wave function)

m = mass of e^-

E = Total energy

V = Potential energy

or $\nabla^2\psi+\frac{8\pi^2 m}{h^2}(E-V)\psi=0$

where ∇^2 = Laplacian operator = $\left(\frac{\delta}{\delta x^2}\right)+\left(\frac{\delta}{\delta y^2}\right)+\left(\frac{\delta}{\delta z^2}\right)$

$$\frac{h^2}{8\pi^2 m}\nabla^2\psi+(E-V)\psi=0$$

$$\left(\frac{-h^2}{8\pi^2 m}\nabla^2+V\right)\psi=E\psi$$

$$\boxed{H\psi=E\psi}$$

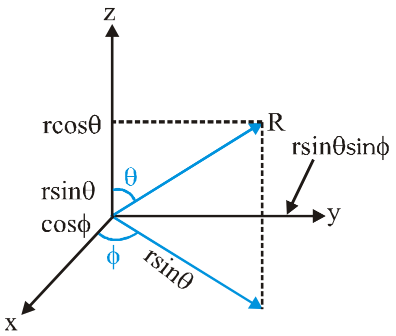
$\therefore$ $\boxed{H=\frac{-h^2}{8\pi^2 m}\nabla^2+V}$ Hemiltonion operator

SCHRODINGER EQUATION IN CARTESIAN COORDINATE

$Z = r\cos\theta$

$y = r\sin\theta\sin\phi$

$x = r\sin\theta\cos\phi$



The schrodinger equation can be written in terms of cartesian coordinates (x, y, z) or in terms of spherical polar coordinates (r, θ, ϕ). However for most calculations it is simpler to solve the wave equation in polar coordinates. When Schrodinger wave equation in polar coordinates is solved for hydrogen atom the solution obtained can be factorized into 2 separate parts, one being the function of r and other the function of θ and ϕ.

$\psi(r,\theta,\phi)=R(r)\,f(\theta,\phi)$

$R(r)$ = Radial function

$f(\theta,\phi)$ = Angular function

SIGNIFICANCE OF (ψ)

The wave function may be regarded as amplitude of electron wave expressed in terms of coordinates (x, y, z) or (r, θ, ϕ). The wave function may have +ve or –ve values depending on the values of coordinates. As such there is no physical significance of ψ.

SIGNIFICANCE OF $(\psi)^2$

In classical theory of electromagnetic radiation, the square of amplitude is proportional to the intensity of light. A very similar concept was suggested by MAX BORN in QUANTUM MECHANICS according to which the square of function ψ at any point is proportional to the probability of finding an electron at that point ψ^2 is known as PROBABILITY DENSITY and is always +ve.

The region of space in which there is maximum probability of finding an electron (say 90%) is termed as an orbital.

QUANTUM NUMBERS

In an atom, a large no of orbitals are permissible. These orbitals are designated by a set of 3 numbers known as QUANTUM NUMBERS (principle, azimuthal, magnetic) which arise as a natural consequence in the solution of schrondinger wave equation. These quantum numbers describe energies of electron in an atom, information about shapes and orientation of orbitals. In order to designate the electron an additional quantum number called as SPIN QUANTUM NUMBER is needed to specify spin of the electron.

GRAPHICAL REPRESENTATION OF ψ

ψ = Amplitude of wave

ψ^2 = probability density → It gives us probability of finding an electron at a point or per unit volume.

$$\boxed{\text{Probability} = \psi^2 \times dv}$$

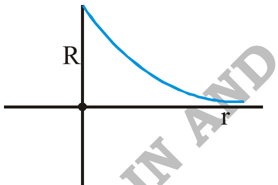
$\psi = \psi\,(x, y, z) = \psi\,(r, \theta, \phi)$

$\psi = R(r) \sim (\theta, \phi)$

R^2 = radial probability density, r = radius

R^2 = radial probability density of finding an electron at a distance R from the nucleus in any direction.

(i)

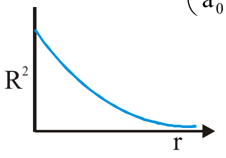


Hyperbola

$$\boxed{R(r)_{1s} = 2\left(\frac{1}{a_0}\right)e^{\frac{-\sigma}{2}}} \quad \text{where } \sigma = \frac{2r}{na_0}$$

$a_0 = 0.529$ Å n = principal quantum number

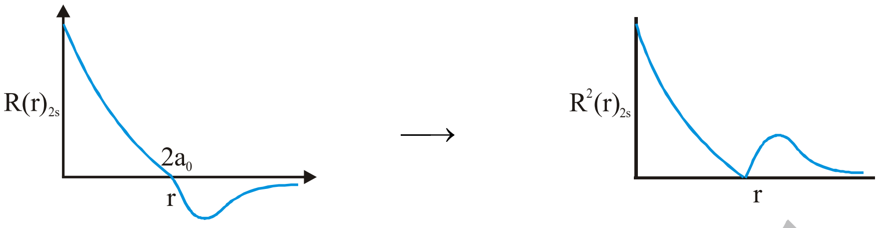
$$R(r)_{1s} = 2\left(\frac{1}{a_0}\right)^{\frac{3}{2}} e^{-\frac{r}{a_0}}$$



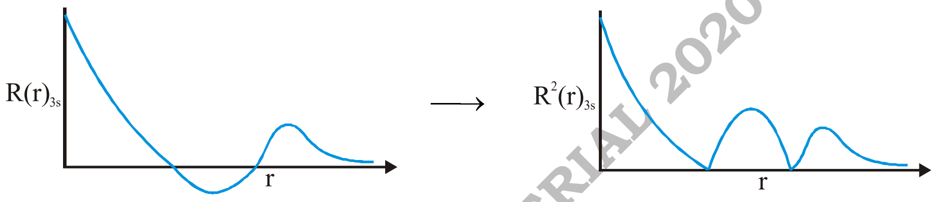
Graph between R^2 and r will be same hyperbolic.

(ii) $$\boxed{R(r)_{2s} = \frac{1}{2\sqrt{2}}\left(\frac{1}{a_0}\right)^{\frac{3}{2}}(2-\sigma)e^{-\frac{\sigma}{2}}}$$

After reaching $2a_0$ now curve would start decreasing and again goes up to cut at ∞.

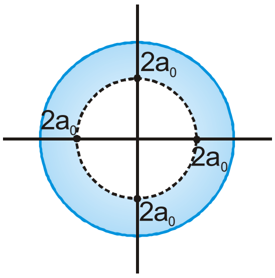


(iii) R(r)$_{3s}$ vs r



RADIAL NODES : Points at which the probability of finding an electron is zero is known as radial nodes.

No. of radial nodes = n – ℓ – 1

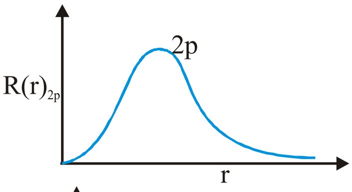


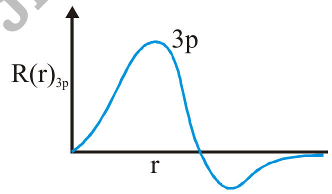
Electron cannot be present at $2a_0$ distance from nucleus. If we join all $2a_0$ points to form a sphere, we can say that electron cannot be present on surface of sphere, however it may be present inside or outside. At $2a_0$ distance probability of presence of electron is zero. Since a sphere is formed radial nodes are also called SPHERICAL NODES.

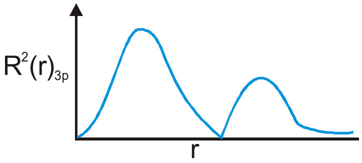
Radial nodes are spherical in shape also known as spherical nodes or nodal sphere.

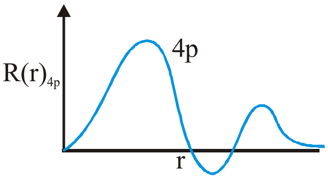
GRAPHS FOR P-ORBITALS

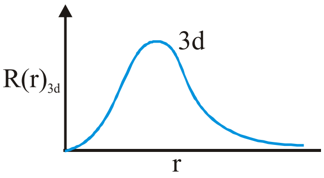
$$\boxed{R(r)_{2p} = \frac{1}{2\sqrt{6}}\left(\frac{1}{a_0}\right)^{\frac{3}{2}}\sigma e^{-\frac{\sigma}{2}}}$$



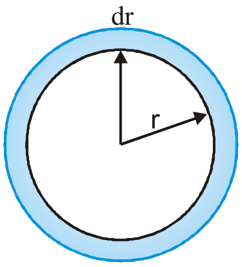








RADIAL PROBABLITY DISTRIbUTION FUNCTION



dr is very very less

$$\text{volume} = \frac{4}{3}\pi((r+dr)^3 - r^3) \text{ shell}$$

$$= \frac{4}{3}\pi((r^3 + 3r^2dr + 3r\,dr^2 + dr^3 - r^3)$$

dr^2 and dr^3 are neglected

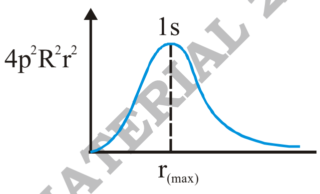
$$= \frac{4}{3}\pi(3r^2dr) = 4\pi r^2dr$$

Radial probability in given shell $= 4\pi r^2drR^2$

Radial probability function $= 4\pi r^2R^2$

The probability of finding an electron at a distance r from the nucleus in all the direction is called radial probability function (RPF).

GRAPHS BETWEEN R PF AND r



$$R(r)_{1s} = Ce^{\frac{-\sigma}{2}}$$

$$4\pi^2R^2r^2 = 4\pi r^2C^2e^{\frac{-\sigma}{2}}$$

$$= C'r^2e^{-\frac{2r}{a_0}}$$

$$4\pi^2R^2r^2 = C'r^2e^{-\frac{2r}{a_0}}$$

For s-orbital, R and R^2 at nucleus is not zero but probability is almost equal to zero because of very small size.

$R^2dv \approx 0$ as $dv \approx 0$ for nucleus

$r_{max} \rightarrow$ distance at which the probability of finding an electron is max.

$$\boxed{P = 4\pi R_{1s}^2r^2} \qquad \boxed{R_{1s} = 2\left(\frac{1}{a_0}\right)^{3/2} e^{\frac{-r}{a_0}}}$$

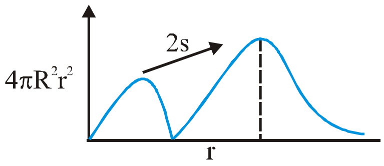
now differentiate eq. by putting value of R_{1s}

$$P = 4\pi r^2 \times 4\left(\frac{1}{a_0}\right)^3 e^{\frac{-2r}{a_0}}$$

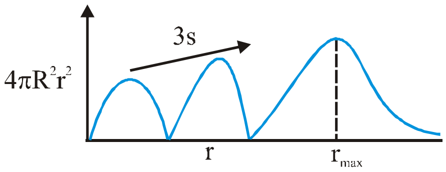
$$P = Cr^2e^{\frac{-2r}{a_0}} \qquad \frac{dP}{dr} = C(2re^{\frac{-2r}{a_0}} + r^2e^{\frac{-2r}{a_0}})$$

$$\frac{dP}{dr} = Cre^{\frac{-2r}{a_0}} + \left(2 - \frac{2r}{a_0}\right) = 0$$

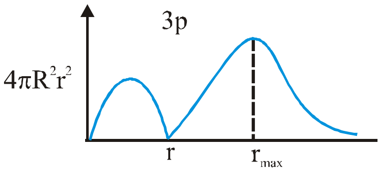
$\therefore$ $\boxed{r = a_0}$ Maxima



Peaks of the curves are increasing



Here 1st peak is smaller than 2nd and 2nd smaller than 3rd.



ANTINODE POINT - Point at which probability of finding an electron is max.

COMPARISON OF $r_{max.}$ & r_{avg} FOR DIFFERENT ORBITALS

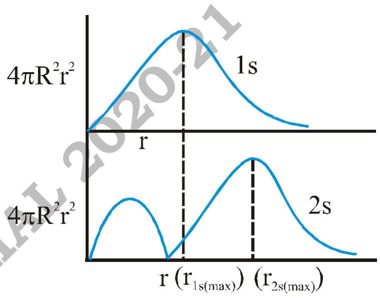
Note : r_{avg} is always greater than r_{max}

Case I - when ℓ is same but n is different.

As value of n increases r_{max} increases.

Peaks are numbered according to value of $(n - \ell)$.

As n increases r_{avg} increases if r_{avg} is more, electron will be more away from nucleus.



PENETRATION POWER : Penetration power of orbital is a measure of its closeness to the nucleus.

1s > 2s > 3s

Case II - When 'n' is same but 'ℓ' different.

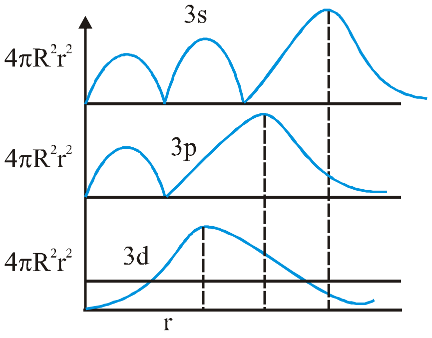
As value of 'ℓ' increases, r_{avg} increases

As value of 'ℓ' increases, r_{max} decreases

$\ell \uparrow \quad r_{max.} \downarrow$

$\ell \uparrow \quad r_{avg.} \uparrow$

Closeness to nucleus - 3s > 3p > 3d



ENERGY COMPARISON

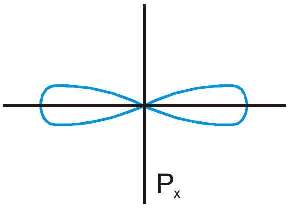
For energy comparison Aufbau rule should be used. But for hydrogen atom, subshell belonging to particular shell possess equal energy.

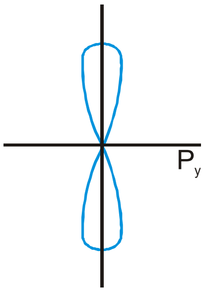
2p = 2s, 3s = 3p = 3d

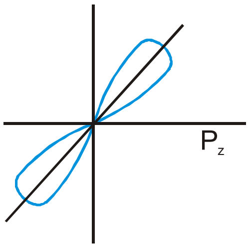
ANGULAR FUNCTION

It gives us an idea about the shape, orientation of an orbital

Ex. $\ell = 1 \Rightarrow m = -1, 0, +1$







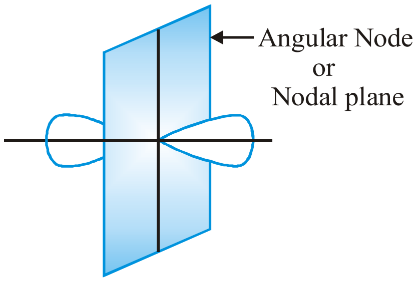
For s orbital, angular part is independent of θ and ϕ.

$\therefore$ There would be zero angular nodes for s-orbital.

$$\boxed{\text{No. of angular nodes for any orbital} = \ell}$$

SHAPE OF ANGULAR NODE

For P_x :



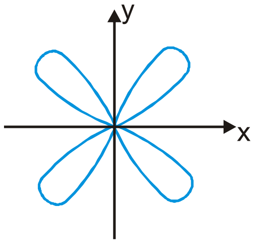
Angular node or nodal plane

$\therefore$ $P_x \rightarrow$ yz plane

$P_y \rightarrow$ xz plane

$P_z \rightarrow$ xy plane

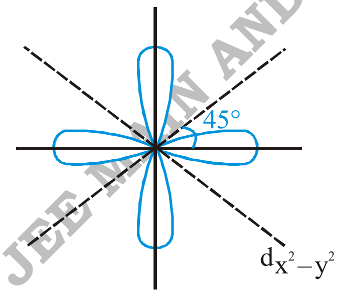
For d_{xy} :



$\therefore$ $d_{xy} \rightarrow$ xz and yz

$d_{yz} \rightarrow$ xz and xy

$d_{zx} \rightarrow$ xy and yz



We cannot predict the designation of angular nodes but can be said that at an angle of 45° with axis.

Nuclear Chemistry

Spontaneous disintegration of nuclei due to emission of radiations like α, β, γ is called radioactivity.

Radioactivity is a nuclei phenomenon.

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

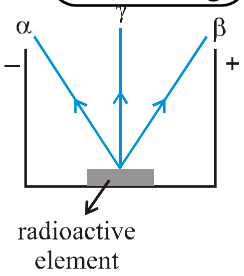
Radioactivity of a substance is independent to its physical state.

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

$^{14}CO_2$, $^{14}_{6}C(s)$, $^{14}_{6}C(g)$ is radioactive.

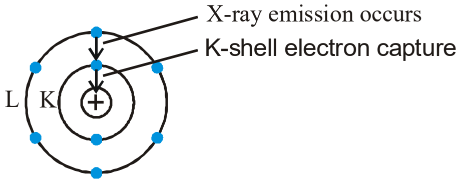
Radiations

$\alpha : {}_2He^4$	$({}_2^4He^{2+})$ (nucleus of He-atom)
β 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 :	$\alpha > \beta > \gamma$

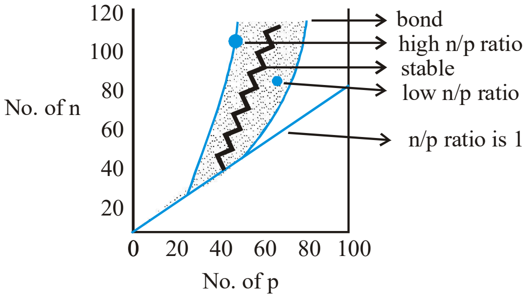


Emission of rays	Usual condition	Effect	Process representation / example
1. α	$Z > 83$	$\frac{n}{p}$ ratio increases	${}_ZX^A \rightarrow {}_{Z-2}X'^{A-4} + {}_2He^4$ ${}_{92}U^{238} \rightarrow {}_{90}Th^{234} + {}_2He^4$
2. β	If $\frac{n}{p}$ ratio is high.	$\frac{n}{p}$ ratio decreases	${}_ZY^A \rightarrow {}_{Z+1}Y'^{A-4} + {}_{-1}e^0$
Ex.	${}_6C^{12}$ (stable) $\frac{n}{p} = \frac{6}{6}$		${}_6C^{14} \rightarrow {}_7N^{14} + {}_{-1}e^0$
	${}_6C^{14}$ (radioactive) $\frac{n}{p} = \frac{8}{6}$ (high)		$\frac{n}{p} = \frac{8}{6}$ $\frac{n}{p} = \frac{7}{7}$
Ex.	${}_{11}Na^{24}$ (radioactive) $\frac{n}{p} = \frac{13}{11}$ (high)		${}_0n^1 \rightarrow {}_1p^1 + {}_{-1}e^0$ (from nucleus)
	${}_{11}Na^{23}$ (stable) $\frac{n}{p} = \frac{12}{11}$		
	${}_{11}Na^{22}$ $\frac{n}{p} = \frac{11}{11}$ ($\frac{n}{p}$ ratio low)		
3. γ	If nucleus energy level is high	nucleus energy level decreases	${}_{43}Tc^{99} \rightarrow {}_{43}Tc^{99} + \gamma$ 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	${}_ZY^A \rightarrow {}_{Z-1}Y'^A + {}_{+1}e^0$ ${}_{11}Na^{22} \rightarrow {}_{10}Ne^{22} + {}_{+1}e^0$ ${}_1p^1 \rightarrow {}_0n^1 + {}_{+1}e^0$ (from nucleus)
(b) Electron capture (EC) or K-shell electron capture	If $\frac{n}{p}$ ratio is low	$\frac{n}{p}$ ratio increases	${}_ZX'^A + \underset{\text{K–shell}}{{}_{-1}e^0} \rightarrow {}_{Z-1}X''^A$ ${}_{80}Hg^{197} + {}_{-1}e^0 \rightarrow {}_{79}Au^{197}$

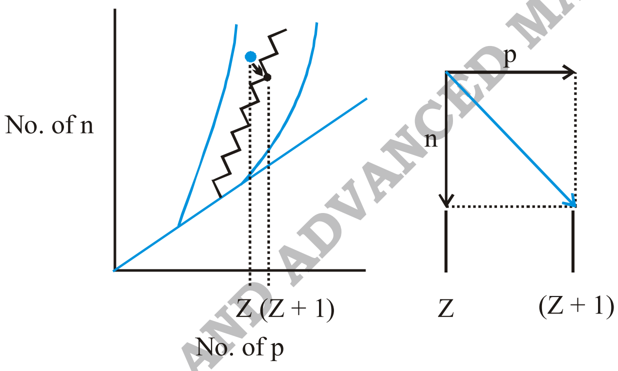
$$_1p^1 + \underset{\text{(K – shell)}}{_{-1}e^0} \longrightarrow {_0x^1}$$



Nuclear Stability Belt



β-Emission



$$_0n^1 \to {_1p^1} + {_{-1}e^0}$$

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

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

Even - Odd Rule : (Out of syllabus)

no. of n	**no. of p**	**no. of stable nucleic**
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.

Ex. $_2He^4$, $_8O^{16}$

Group Displacement Law : (Given by Soddy and Fajan)

- When 1α emission takes place from a nuclie, new formed nuclie occupy two position left in periodic table.
- When 1β emission takes place from a nuclie, new formed nuclie occupy one position right in periodic table.

Due to emission of 1β particle; isobars are formed.

Due to emission of 1α particle; isodiaphers are formed.

Due to emission of 1α and 2β ; isotopes are formed.

Isotopes :	same number of proton	eg. $_6C^{14}$ and $_6C^{12}$
Isobars :	same mass number	eg. $_6C^{14}$ and $_7N^{14}$
Isotones :	same number of neutron	eg. $_2He^4$ and $_1H^3$

Isodiaphers : Same (n – p) difference

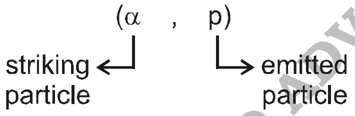
Ex. $_9F^{19}$ and $_{19}K^{39}$; (n – p) = 10

Isosters : Same number of atoms and electrons

Ex. N_2 and CO

N_2O and CO_2

Artifical Nuclear Reaction



- specific nuclei + striking particle ⟶ New nuclei + emitted particle

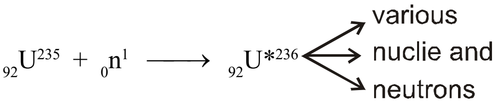
Ex.

1. (α, p type) $_7N^{14} + \underset{\text{(s.p.)}}{_2He^4} \longrightarrow {_8O^{17}} + \underset{\text{(e.p.)}}{_1p^1}$ (or $_1H^1$)
2. (n, γ type) $_{11}N^{23} + {_1n^0} \longrightarrow {_{11}Na^{24}} + \gamma$
3. (D, p type) $_{13}Al^{27} + {_1H^2} \longrightarrow {_{13}Al^{28}} + {_1H^1}$
4. (p, α type) $_3Li^7 + {_1H^1} \longrightarrow {_2He^4} + {_2He^4}$

Nuclear Fission and Nuclear Fusion

In both processes, large amount of heat evolved due to conversion of some mass into energy.

Nuclear Fission : Is a process where heavy nuclei splits into large nuclei.


$_{92}U^{235} + {_0n^1} \longrightarrow {_{92}U^{*236}}$

Ex. atom bomb is based on fission.

Nuclear Fusion

Is a process where light nuclei fused together to form heavy nuclei.

$$_1H^2 + {}_1H^3 \longrightarrow {}_2He^4 + {}_0n^1$$

$$_1H^2 + {}_1H^2 \longrightarrow {}_2He^4$$

Hydrogen bomb is based on fusion. Very high temperature is required in this process.

For Objective Questions

Total time (T) = no. of halves (n) × Half life ($t_{1/2}$)

$$\boxed{T = n \times t_{1/2}}$$

No. of half life	Int. wt.	Final weight
1	w	w/2
2	w/2	$w/4 = w/2^2$
3	w/4	$w/8 = w/2^3$

$$\text{Amount of substance left in n halves (wt / mole)} = \frac{\text{Initial amount (wt / mole)}}{2^n}$$

Radioactive Disintegration Series

A series of continued disintegrations starting from an unstable nucleus (radioactive elements) and ending at a stable nucleus, is known as radioactive disintegration series.

Mainly Radioactive Disintegration Series are of Four Type -

(1) Thorium series (4n series) :

$$^{232}_{90}Th \text{ (Starting element)} \xrightarrow{-6\alpha,-4\beta} {}^{208}_{82}Pb \text{ (last element)}$$

(2) Neptunium series (4n + 1 series):

$$^{237}_{93}Np \text{ (Starting element)} \xrightarrow{-7\alpha,-4\beta} {}^{209}_{83}Bi \text{ (last element)}$$

(3) Uranium Series (4n + 2 series) :

$$^{238}_{92}U \text{ (Starting element)} \xrightarrow{-8\alpha,-6\beta} {}^{206}_{82}Pb \text{ (last element)}$$

(4) Actinium Series (4n + 3 series) :

$$^{235}_{92}U \text{ (Starting element)} \xrightarrow{-7\alpha,-4\beta} {}^{207}_{82}Pb \text{ (last element)}$$

* Thorium series (4n series), Uranium Series (4n + 2 series), Actinium Series (4n + 3 series) are naturally series. But Neptunium series (4n + 1 series) is artificial series because Neptunium–237 is prepared artificial and the only member of this series found in nature is the stable end product Bi–209.

Ex. ^{23}Na is the most stable isotope of Na. Find out the process by which $^{24}_{11}Na$ can undergo radioactive decay.

Sol. n/p ratio of ^{24}Na is 13/11 and thus greater than one. It will therefore decay following β-emission.

$$^{24}_{11}Na \longrightarrow {}^{24}_{12}Mg + {}^{0}_{-1}e$$

Ex. The number of β-particle emitted during the change ${}^{c}_{a}X \longrightarrow {}^{b}_{d}Y$ is :

(A) $\frac{a-b}{4}$ **(B)** $d+\left(\frac{a-b}{2}\right)+c$ **(C)** $d+\left(\frac{c-b}{2}\right)-a$ **(D)** $d+\left(\frac{a-b}{2}\right)-c$

Sol. ${}^{c}_{a}X \longrightarrow {}^{b}_{d}Y + m\,{}^{4}_{2}He + n\,{}^{0}_{-1}e$

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

and $a = d + 2m - n$ ......(ii)

by (i) & (ii)

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

Ex. The decay product of ${}^{13}_{7}N$ is :

(A) ${}^{13}_{8}O + {}^{0}_{-1}e$ **(B)** ${}^{13}_{6}C + {}^{0}_{+1}e$

(C) ${}^{13}_{6}C$ + K electron capture **(D)** ${}^{9}_{5}Be + {}^{4}_{2}He$

Sol. ${}^{13}_{7}N$ is positron emitter ; $\frac{n}{p}$ ratio is low. **Ans. (B)**

Ex. 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 α each or one β each or X-decays, 1 α, Y-decays 1 β or X-decays 1 β or Y-decays 1 α. In either case (a), (b) and (c) cannot be true. **Ans. (D)**

Tips

1. Frequency, $\nu = \frac{c}{\lambda}$

2. Energy/photon, $E = h\nu = \frac{hc}{\lambda}$

Also, $E = \frac{12375}{\lambda} eV$, if λ is in Å

3. Electronic energy change during transition, $\Delta E = E_{n_2} - E_{n_1}$

$n_2 > n_1$, emission spectra if electron jumps from n_2 to n_1 shell and absorption spectra if electron excites from n_1 to n_2 shell.

4. Radius of nth Bohr orbit of H atom, $r_n = \frac{n^2h^2}{4\pi^2me^2K}$ (where $K = 9 \times 10^9$)

r_1 for H = 0.529 Å ; r_n for H like atom $r_n = 0.529 \times \frac{n^2}{Z}$ Å

5. Velocity of electron in nth Bohr orbit of H atom, $v = \frac{2\pi KZe^2}{nh}$

$v = 2.18 \times 10^8 \frac{Z}{n} cm/sec$.

6. Energy of electron in nth Bohr orbit of H atom, $E = \frac{2\pi^2mZ^2e^4K^2}{n^2h^2}$

where n = 1, 2, 3..........

$[E = -13.6 \times \frac{Z^2}{n^2}$ kcal/mole (1 cal = 4.18 J)]

E_1 for H = – 21.72×10^{-12} erg = – 13.6 eV, E_1 for H like atom = E_1 for H $\times Z^2$

7. Wavelength emitted during transition in H atom,

$$\frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = \frac{2\pi^2me^4}{ch^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{ (in C.G.S.)}$$

8. Photoelectric effect $h\nu = w + \frac{1}{2}mu^2$ or $h\nu$ = I.E. + K.E.

9. Possible transitions for a jump from n_2 to n_1 = $\sum(n_2 - n_1)$

10. Angular momentum of electron in an orbit = n. $(h/2\pi)$

11. Angular momentum of electron in an orbital = $(nh/2\pi)\sqrt{[\ell(\ell+1)]}$

12. Total spin = $\pm\left(\frac{1}{2}\times n\right)$; where n is no. of unpaired electrons.

13. Magnetic moment of an atom $\sqrt{n(n+2)}$ B.M.; where n is no. of unpaired electrons.

14. Nodal planes : Radial nodes = $n - \ell - 1$, Angular nodes = 1, Total nodes = $(n - \ell)$

15. de Broglie equation : $\lambda = \frac{h}{mu} = \sqrt{\frac{h^2}{2 \times K.E. \times m}}$

where λ is wavelength, m is mass and u is velocity of particle.

16. Heisenberg uncertainty principle :

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

$$\Delta u.\Delta x \geq \frac{h}{4\pi m}$$

where Δp, Δu and Δx are uncertainties in momentum, velocity and position respectively. Planck's constant is h and m is mass of subatomic particle.