

ATOMIC STRUCTURE

Nothing exists except atoms and empty space: everything else is opinion

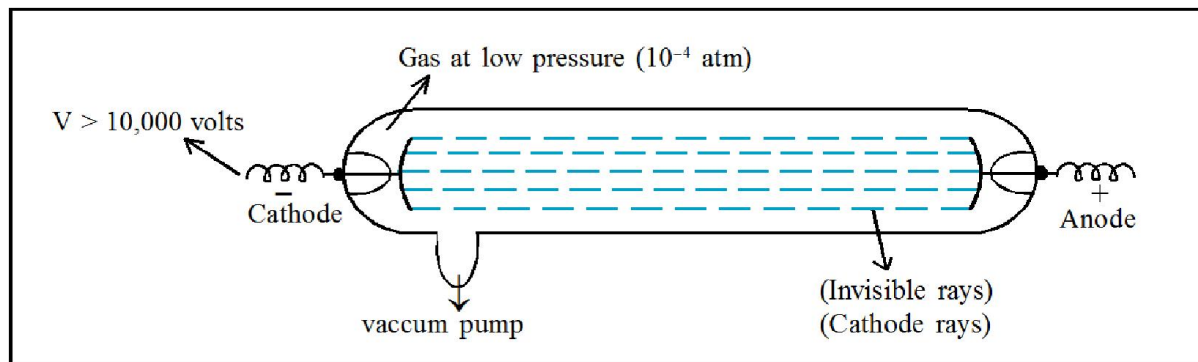
“DEMOCRITUS”

INTRODUCTION

The continued subdivisions of matter would ultimately yield atoms which would not be further divisible. The word atom has been derived from the Greek word ‘a-tomio’ which means uncuttable or non divisible. These earlier ideas were mere speculations and there was no way to test them experimentally. These ideas remained dormant for a very long time and were revived again by scientists in the nineteenth century.

The atomic theory of matter was first proposed on a firm scientific basis by John Dalton, a British school teacher in 1808. His theory, called Dalton’s atomic theory, regarded the atom as the ultimate particle of matter.

In this unit we start with the experimental observations made by scientists towards the end of nineteenth and beginning of twentieth century. These established that atoms can be further divided into sub atomic particles, i.e., electrons, protons and neutrons a concept very different from that of Dalton.

Covering of Fundamental particles of matter / Atoms**(i) 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.
- (3) They produce a green glow when strike 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.
- (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

- (6) They produce heat energy when they collide with the matter. It shows that cathode rays possess 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 :

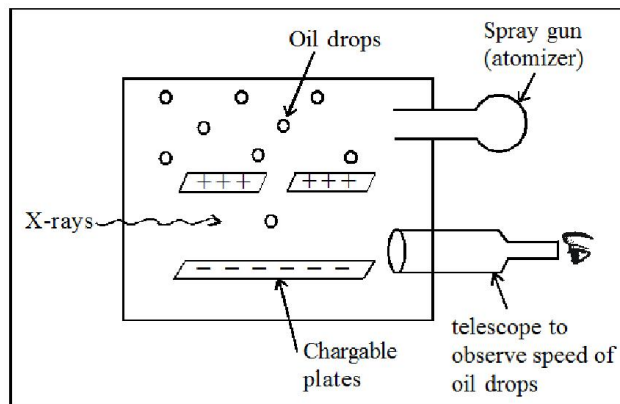
In 1897, J.J. Thomson determined the e/m value (charge/mass) of the electron by studying the deflection of cathode rays in electric & magnetic fields.

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. Millikan in 1909 by the Millikan'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, Millikan 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 $1.59 \times 10^{-19} \text{ C}$. This was recognised as the charge on an e^- . The modern value is $1.602 \times 10^{-19} \text{ C}$.

Mass of the electron :

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

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

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.

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

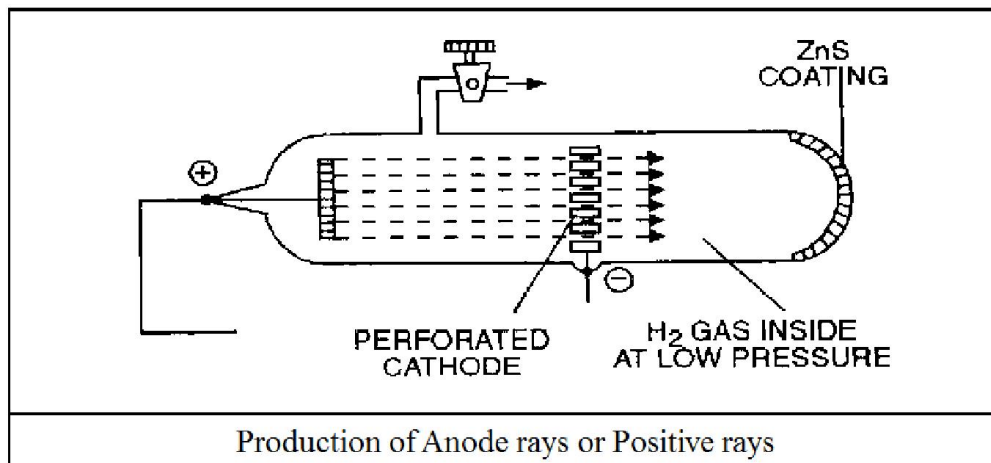
Where v is the velocity of the e^- and c is the velocity of light.

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

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

(ii) 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.



CHEMISTRY FOR NEET & AIIMS

- 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 were recognised :
 - These rays travel in straight lines and cast a shadow of the object placed in their path.
 - Like cathode rays, these rays also rotate the wheel placed in their path and also have heating effect. Thus, the rays possess K.E. i.e. mass particles are present.
 - The rays are deflected by electric and magnetic fields towards the negatively charged plate showing thereby that these rays carry +ve charge.
 - The rays produce flashes of light on ZnS screen
 - These rays can pass through thin metal foil.
 - These rays can produce ionisation in gases.
 - 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.
 - 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 = $+1.602 \times 10^{-19}$ coulomb i.e. one unit +ve charge

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

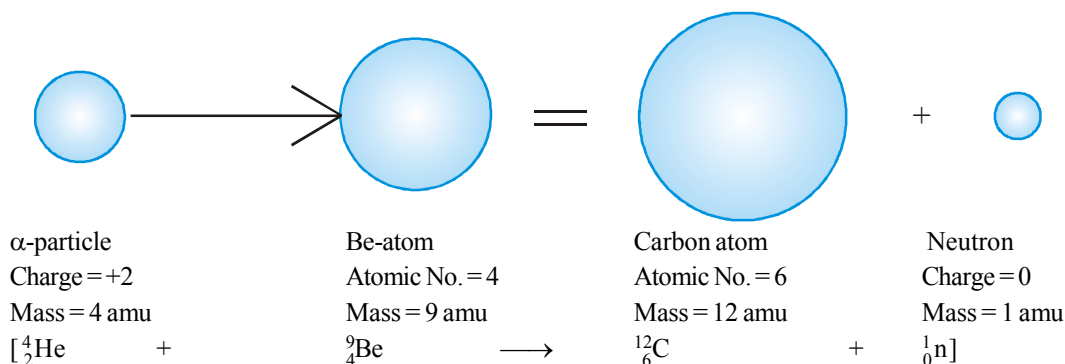
$$\text{Mass of the proton} = \frac{e}{e/m} = \frac{1.602 \times 10^{-19}}{9.579 \times 10^4} = 1.672 \times 10^{-24} \text{ g} = 1.672 \times 10^{-27} \text{ kg}$$

$$\text{Mass of proton in amu} = \frac{1.672 \times 10^{-24}}{1.66 \times 10^{-24}} = 1.0072 \text{ amu.}$$

(iii) Discovery of 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 possess 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



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.**

There are other important fundamental particles in atom also

- Positron** : Particle having mass equal to electron but having a unit positive charge.
- Antiproton** : Particle having mass equal to proton but negative charge.
- Neutrino and antineutrinos** : Particles having no mass and no charge but only spin.
- π -mesons and μ -mesons** : Particles responsible for nuclear stability.
- Antineutrons** : Identical to neutron but spinning in opposite direction.

Density of neutron is 1.5×10^{14} g/cc. Isolated neutron is unstable and disintegrates into electron, proton and neutrino. Of all the elementary particles present in an atom, neutron is the heaviest and least stable particle.

- The radius, r of the nucleus of an atom is related to its mass number A, according to the relation.

$$r = R_0 A^{1/3}$$

$$R_0 = 1.4 \times 10^{-15} \text{ m and A is mass number}$$

- The nuclear radius is about $\frac{1}{10,000}$ of the atomic radius.
- The radii of nuclei are usually expressed in terms of Fermis (1 fermi = 10^{-15} m)

X-rays : X-rays are the high energy electromagnetic radiations which are not deflected by the electric and magnetic fields. These are highly penetrating rays. Therefore, these are employed in clinical laboratories for diagnostic purposes.

Radioactivity : Radioactivity is the phenomenon of emission of radiations by certain elements on their own. The elements which show this phenomenon are known as radioactive elements.

The field of radioactivity was developed by Marie Curie, Pierre Curie, Rutherford and Frederick Soddy. Three kinds of radiation are observed from the radioactive elements.

- Alpha (α) rays** : α -rays consists of α -particles carrying two units of positive charge and four units of atomic mass. α -particles (${}^4_2\text{He}$) are helium nuclei and when combine with two electrons yield helium gas.
- Beta (β) rays** : These rays consist of negatively charged particles (${}^0_{-1}\text{e}$) similar to electrons.
- Gamma (γ) rays** : These rays do not consist of particles. These are neutral electromagnetic radiations.

Penetration power

$$\gamma\text{-rays} > \beta\text{-rays} > \alpha\text{-rays}$$

esu = electrostatic unit

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

amu = atomic mass unit

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

Order of Mass

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

Order of Specific Charge

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

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

CHEMISTRY FOR NEET & AIIMS

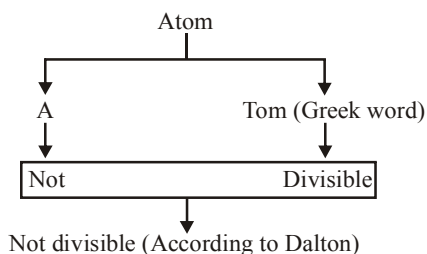
Atomic Structure, atomic number and atomic mass

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	$+1.6 \times 10^{-19}$ coloumb $+4.8 \times 10^{-10}$ esu +1 Unit	1.672×10^{-27} kg 1.672×10^{-24} g 1.00757 amu	9.58×10^4 C/g
Neutron (n^0)	James Chadwick	0	1.675×10^{-27} kg 1.675×10^{-24} g 1.00893 amu	0

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 : ${}_Z X^A$.
Where : A \rightarrow Mass number, Z \rightarrow Atomic number, X \rightarrow 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.

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. ${}_{17}\text{Cl}^{35}$
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. ${}_6\text{C}^{12}$
 $\text{P}^+ \rightarrow 6$ Weight of Proton = 6×1.00750
 $\text{n}^0 \rightarrow 6$ Weight of Neutron = 6×1.00850
 $\text{e}^- \rightarrow 6$ Weight of Electron = 6×0.000549

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. \therefore 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. ${}_6\text{C}^{12}$
 $\text{P}^+ \rightarrow 3$
 $\text{e}^- \rightarrow 12$

e^-	P^+	n^0	
6	6	6	$\text{A} \rightarrow 12$
12	3	6	$\text{A} \rightarrow 9$

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

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. \therefore 12 amu = 150
 \therefore 1 amu = $\frac{150}{12}$
 \therefore 16 amu = $\frac{150}{12} \times 16 = 200$ Unit

Isotopes : 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. ${}_{17}\text{Cl}^{35}$ ${}_{17}\text{Cl}^{37}$
 $\text{n} = 18$ $\text{n} = 20$
 $\text{e} = 17$ $\text{e} = 17$
 $\text{p} = 17$ $\text{p} = 17$

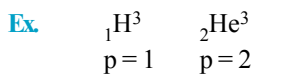
- Isotopes have same chemical property but different physical property.
- Isotopes do not have the same value of $\frac{e}{m} \left(\frac{\text{Number of electron}}{\text{mass}} \right)$ because mass varies.
 (No. of electron are same but mass varies).

Ex. (Protium Deuterium Tritium)
 ${}_1\text{H}^1$ ${}_1\text{H}^2$ ${}_1\text{H}^3$
 $\text{e} = 1$ $\text{e} = 1$ $\text{e} = 1$
 $\text{p} = 1$ $\text{p} = 1$ $\text{p} = 1$
 $\text{n} = 0$ $\text{n} = 1$ $\text{n} = 2$
 e/m 1/1 1/2 1/3

${}_1\text{H}^1$ is the only normal hydrogen which have $\text{n} = 0$ i.e. no neutrons
 Deuterium is also called as heavy hydrogen. It represent by D

CHEMISTRY FOR NEET & AIIMS

Isobars : 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.

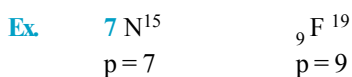


$$\left. \begin{array}{l} e = 1 \\ e = 2 \end{array} \right\}$$

$$\begin{array}{l} n = 2 \quad n = 1 \\ p + n = 3 \quad p + n = 3 \end{array}$$

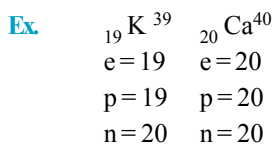
- Isobars do not have the same chemical & physical property
- They do not have the same value of e/m

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

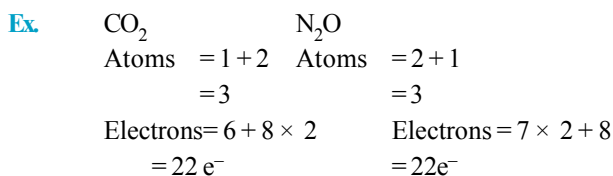


$$\left. \begin{array}{l} n = 8 \\ e = 7 \end{array} \right\} \quad \left. \begin{array}{l} n - p = 1 \quad n = 10 \\ e = 9 \end{array} \right\} \quad n - p = 1$$

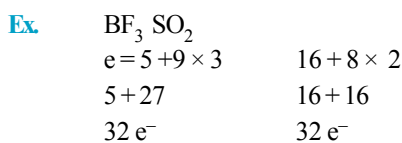
Isotones/ Isoneutronic Species / Isotonic: They are the atoms of different element which have the same number of neutrons.



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



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



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 ${}_6\text{C}^{12}$ and the percent by which it is increased.



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

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

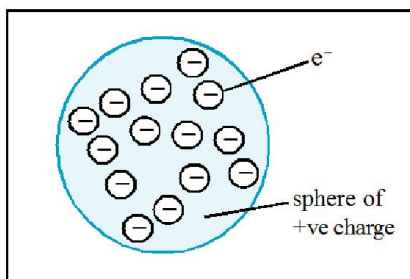
$$\left. \begin{array}{l} n = 12 \text{ amu} \\ p = 6 \text{ amu} \end{array} \right\} = 18 \text{ amu}$$

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

$$\begin{aligned} \text{Step-2 } \% \text{ Increment} &= \frac{\text{Final mass} - \text{Initial mass}}{\text{Initial mass}} \times 100 \\ &= \frac{18 - 12}{12} \times 100 \Rightarrow 50\% \end{aligned}$$

Atomic Models

(I) Thomson's model of atom [1904]



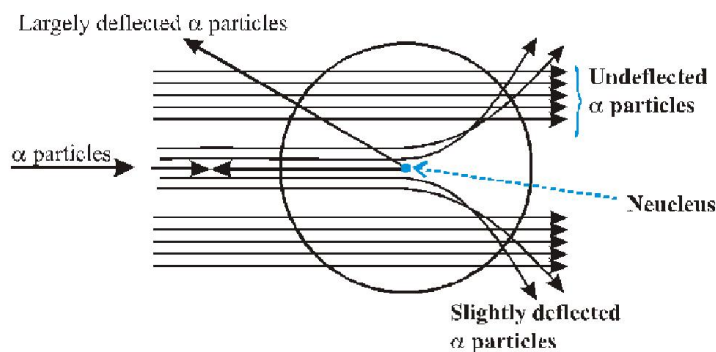
- Thomson was the first to propose a detailed model of the atom.
- Thomson proposed that an atom consists of a uniform sphere of positive charge in which the electrons are present at some places.
- This model of atom is known as '**Plum-Pudding model**'.

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.

(II) RUTHERFORD ATOMIC MODEL

Rutherford Observations :



- Most of the α -particles (nearly 99.9%) went straight without suffering any deflection.
- A few of them got deflected through small angles.
- 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 :

- 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.
- 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.

CHEMISTRY FOR NEET & AIIMS

- 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 or 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 repulsion 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.

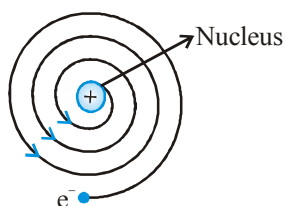
$$\frac{\text{vol. of the atom}}{\text{vol. of the nucleus}} = \frac{\left(\frac{4}{3}\pi r_A^3\right)}{\left(\frac{4}{3}\pi r_N^3\right)} = \frac{(10^{-8})^3}{(10^{-13})^3} = 10^{15}$$

- (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 :

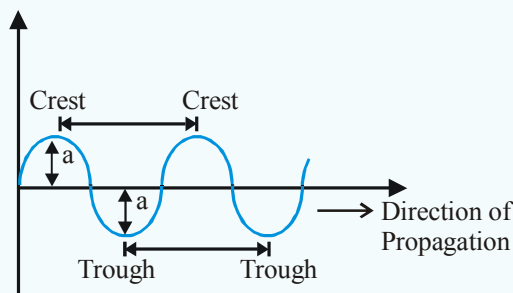
- (1) This theory could not explain the stability of an atom. According to Maxwell electron loses its energy continuously in the form of electromagnetic radiations. As a result of this, the e^- should lose energy at every turn and move closer and closer to the nucleus following a spiral path. The ultimate 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.

Some important characteristics of a wave

A wave is characterized by following six characteristics.



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.

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} .

$$1 \text{ Hz} = 1 \text{ cycle/sec}$$

Velocity of a wave is defined as the linear distance travelled by the wave in one second. It is represented by v and is expressed in cm/sec or m/sec (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

$$v = \nu \times \lambda$$

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 emitted by the transmitter.

Sol. As we know velocity of light (C)

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

Given ν (frequency)

CHEMISTRY FOR NEET & AIIMS

$$\begin{aligned} &= 1368 \text{ kHz} \\ &= 1368 \times 10^3 \text{ Hz} \\ &= 1368 \times 10^3 \text{ sec}^{-1} \end{aligned}$$

$$\therefore \lambda = \frac{c}{\nu} \quad \therefore \lambda = \frac{3 \times 10^8 \text{ msec}^{-1}}{1368 \times 10^3 \text{ sec}^{-1}} \Rightarrow \lambda = 219.3 \text{ m}$$

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

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

$$\bar{\nu} = \frac{1}{5800 \text{ \AA}}$$

$$\bar{\nu} = \frac{1}{5800 \times 10^{-8} \text{ cm}} \quad \{\because 1 \text{ \AA} = 10^{-8} \text{ cm}\}$$

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

$$\begin{aligned} \nu &= c\bar{\nu} \\ &= 3 \times 10^{10} \text{ cm sec}^{-1} \times 1.7 \times 10^4 \text{ cm}^{-1} \\ &= 3 \times 1.7 \times 10^{14} \\ &= 5.1 \times 10^{14} \text{ sec}^{-1} \end{aligned}$$

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 Ist

$$\lambda = \frac{c}{\nu} = \frac{3 \times 10^8 \text{ m sec}^{-1}}{1120 \times 10^3 \text{ sec}^{-1}} = 267.86 \text{ m}$$

Station IInd

$$\lambda = \frac{c}{\nu} = \frac{3 \times 10^8 \text{ m sec}^{-1}}{98.7 \times 10^6 \text{ sec}^{-1}}$$

$$= 3.0395 \text{ m}$$

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

Sol. Distance to be travelled from mars to earth

$$= 8 \times 10^7 \text{ km}$$

$$= 8 \times 10^{10} \text{ m}$$

\therefore Velocity of EM waves

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

$$\begin{aligned} \therefore \text{Time} &= \frac{\text{Distance}}{\text{Velocity}} = \frac{8 \times 10^{10} \text{ m}}{3 \times 10^8 \text{ m/sec}^{-1}} \\ &= 2.66 \times 10^2 \text{ sec.} \end{aligned}$$

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

Sol. Velocity of light in vacuum = $3 \times 10^8 \text{ m sec}^{-1}$

$$\text{Wavelength} = 2225 \times 10^{-10} \text{ meter}$$

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

$$= 1.349 \times 10^{15} \text{ sec}^{-1}$$

(III) Developments leading to the bohr’s model of Atom

After the failure of Rutherford’s atomic model many scientists started working to give an appropriate model which could overcome the flaws of Rutherford’s model. Among such scientists, **Neil Bohr** was successful in giving the answers to the questions which were put forward by the Rutherford’s model of atom.

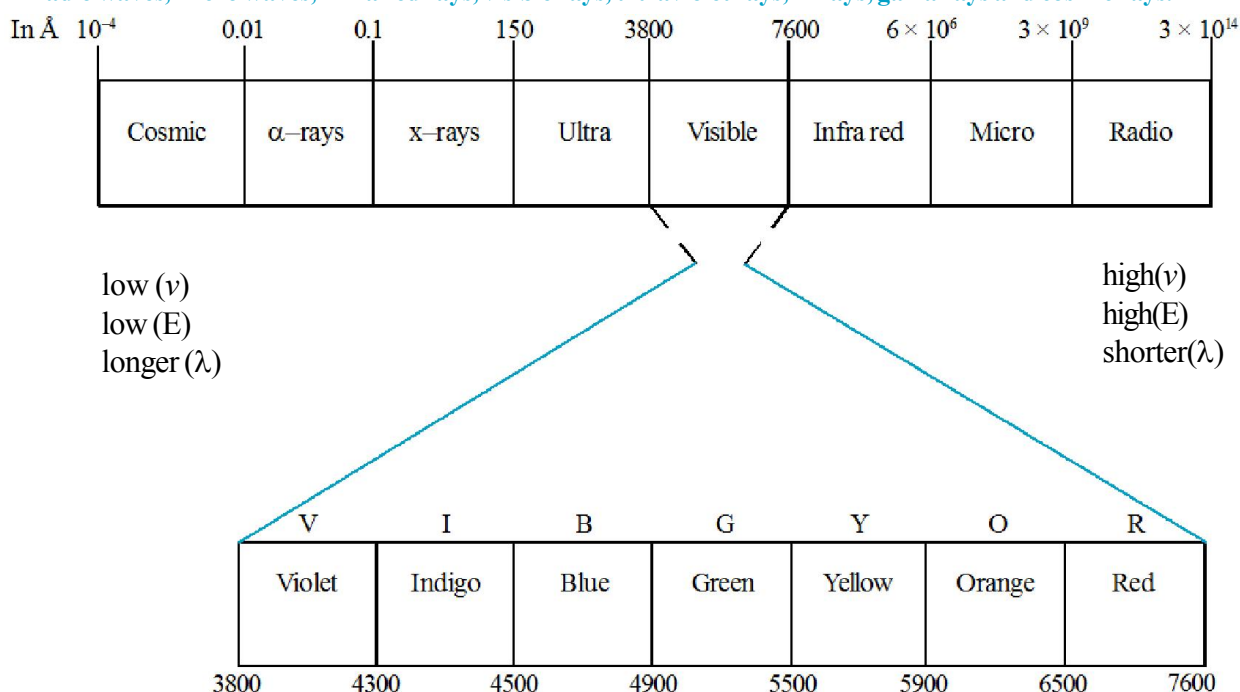
Two developments played a major role in the establishment of Bohr’s model of atom. So before studying Bohr’s model of atom it is important to study these two developments.

- 1. Dual Character of Electromagnetic Radiations :** The electromagnetic radiations have dual character i.e both particle and wave characters.
- 2. Quantisation of Energy :** The results from the atomic spectra gave the evidence that energy is quantised.

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 propagation.

Radio waves, micro waves, Infra red rays, visible rays, ultraviolet rays, x-rays, gama rays and cosmic rays.



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

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

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

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

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

CHEMISTRY FOR NEET & AIIMS

Planck's Quantum Theory

According to planck's quantum theory :

1. The radiant energy emitted or absorbed by a body not continuously but discontinuously in the form of small discrete packets of energy and these packets are called quantum.
2. In case of light, the smallest packet of energy is called as 'photon' but in general case the smallest packet of energy called as quantum.
3. The energy of each quantum is directly proportional to frequency of the radiation i.e.

$$E \propto \nu \quad \Rightarrow \quad E = h\nu \quad \text{or} \quad E = \frac{hc}{\lambda} \left\{ \because \nu = \frac{c}{\lambda} \right\}$$

h is proportionality constant or Planck's constant

$$h = 6.626 \times 10^{-31} \text{ kJ s} \quad \text{or} \quad 6.626 \times 10^{-34} \text{ J s} \quad \text{or} \quad 6.626 \times 10^{-27} \text{ erg s}$$

4. Total amount of energy transmitted from one body to another will be some integral multiple of energy of a quantum.
 $E = nh\nu$ Where n is an integer and n = number of quantum

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

Ex. Calculate the energy of a photon of sodium light of wave length $5.862 \times 10^{-16} \text{ m}$ in Joules.

Sol. $\lambda = 5.886 \times 10^{-16} \text{ m}, \quad c = 3 \times 10^8 \text{ m s}^{-1}$

$$E = nh\nu \quad \text{or} \quad \frac{nhc}{\lambda} \quad \{ \because n = 1 \}$$

$$\therefore E = \frac{hc}{\lambda} = \frac{1 \times 6.6 \times 10^{-34} \text{ J s} \times 3 \times 10^8 \text{ m s}^{-1}}{5.862 \times 10^{-16} \text{ m}} = \frac{6.6 \times 3}{5.862} \times 10^{-10} \text{ J} = 3.38 \times 10^{-10} \text{ J}$$

Ex. Calculate the frequency & energy of a photon of wave length 4000 \AA .

Sol. (a) Calculation of frequency : $\lambda = 4000 \text{ \AA} = 4000 \times 10^{-10} \text{ m}$

$$\therefore \nu = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ m/s}}{4 \times 10^{-7} \text{ m}} = 0.75 \times 10^{15} \text{ s}^{-1} = 7.5 \times 10^{14} \text{ s}^{-1}$$

(b) Calculation of energy : $E = h\nu = 6.626 \times 10^{-34} \text{ joule second} \times 7.5 \times 10^{14} \text{ s}^{-1} = 4.96 \times 10^{-19} \text{ joule}$

Ex. Calculate the λ and frequency of a photon having an energy of 2 electron volt

Sol. $\therefore 1\text{eV} = 1.602 \times 10^{-19} \text{ J} \quad \therefore 2\text{eV} = 3.204 \times 10^{-19} \text{ J} = E$

(a) Calculation of wavelength (λ): $E = \frac{hc}{\lambda}$ or $\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \text{ J s} \times 3 \times 10^8 \text{ m s}^{-1}}{3.204 \times 10^{-19} \text{ J}} = 6.204 \times 10^{-7} \text{ m}$

(b) Calculation of frequency (ν): $\nu = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ m s}^{-1}}{6.204 \times 10^{-7} \text{ m}} = 0.48 \times 10^{15} \text{ s}^{-1} = 4.8 \times 10^{14} \text{ s}^{-1}$

Ex. Which has a higher energy ?

- (a) A photon of violet light with wave length 4000 \AA
- (b) A photon of red light with wave length 7000 \AA

Sol. (a) Violet light : $E_{\text{violet}} = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 3 \times 10^8 \text{ m s}^{-1}}{4000 \times 10^{-10} \text{ m}} = 4.97 \times 10^{-19} \text{ joule}$

(b) Red light : $E_{\text{red}} = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 3 \times 10^8 \text{ m s}^{-1}}{7000 \times 10^{-10} \text{ m}} = 2.8 \times 10^{-19} \text{ joule}$

So, $E_{\text{violet}} > E_{\text{red}}$

Ex. How many photons of lights having a wave length of 5000 Å are necessary to provide 1 joule of energy.

Sol. $\because E = \frac{nhc}{\lambda} \therefore n = \frac{E \times \lambda}{hc} = \frac{1\text{J} \times 5000 \times 10^{-10}\text{m}}{6.626 \times 10^{-34}\text{J s} \times 3 \times 10^8\text{m s}^{-1}} = 2.5 \times 10^{18}$ photons

Units of Energy are

S.I. unit – **Joule (J)**

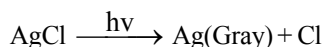
C.G.S. unit – **erg**

Other unit – **electron volt (ev)**

1 ev = 1.6 × 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:



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 × 10³ J/mol

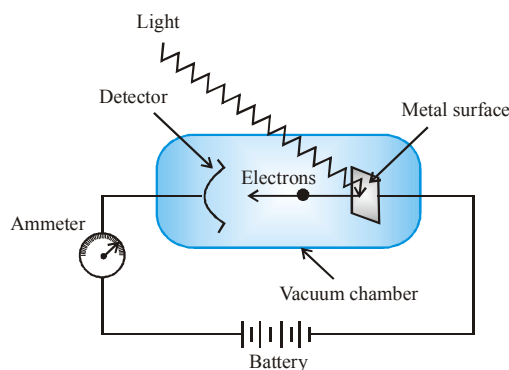
If photon is used for this purpose, then according to Einstein law one molecule absorbs one photon. Therefore,

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

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

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.

CHEMISTRY FOR NEET & AIIMS

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 without 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

Incident energy = Work Function (ϕ) + K.E._{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.
$$\text{K.E.} = \frac{1}{2} m_e v^2 = h(\nu - \nu_0)$$

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

$$\therefore \text{K.E.} = (6.626 \times 10^{-34}) (5 \times 10^{14}) \\ = 3.313 \times 10^{-19} \text{ J}$$

Ex. A photon of wavelength 3000 \AA 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

$$\text{Work function} = 2.20 \text{ eV}$$

$$\text{Therefore, KE} = 4.125 - 2.20 = 1.925 \text{ eV} = 3.08 \times 10^{-19} \text{ J}$$

(iii) Velocity of the photo electron

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

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

BOHR'S ATOMIC MODEL

Some Important formulae :

$$\text{Coulombic force} = \frac{kq_1q_2}{r^2}, \text{ Centrifugal force} = \frac{mv^2}{r}, \text{ Angular momentum} = mvr$$

It is a quantum mechanical model. This model was based on quantum theory of radiation and Classical law of physics.

The important assumption on which Bohr's Model is based are the following :

1st assumption :

- Atoms has a nucleus where all protons and neutrons are present.
- The size of nucleus is very small and it is present at the centre of the atom.

2nd assumption :

- Negatively charged electron are revolving around the nucleus in the same way as the planets are revolving around the sun.
- The path of electron is circular.
- The attraction force (Coulombic or electrostatic force) between nucleus and electron is equal to the centrifugal force on electron.
i.e. Attraction force towards nucleus = centrifugal force.

3rd assumption :

- Electrons can revolve only on those orbits whose angular momentum (mvr) is integral multiple of $\frac{h}{2\pi}$
where h = Planck's constant, π = Constant

$$\text{i.e. } mvr = \frac{nh}{2\pi} \quad (n = \text{Whole number})$$

Angular momentum can have values such as $\frac{h}{2\pi}, 2\frac{h}{2\pi}, 3\frac{h}{2\pi}, 4\frac{h}{2\pi}, 5\frac{h}{2\pi}$ but can not have fractional values such as

- The orbits in which electron can revolve are known as stationary Orbits.

4th assumption:

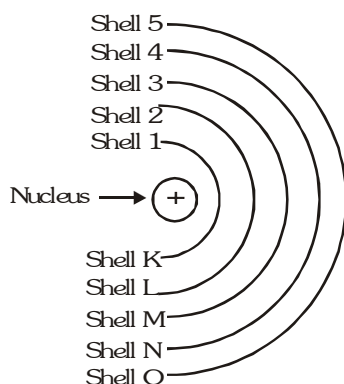
- By the expiry of time, if electrons remains in the stationary state then it does not lose energy. Such a state is called as "GROUND STATE".

5th assumption :

- Each stationary orbit is associated with definite amount of energy therefore these orbits are also called as energy levels and are numbered as 1, 2, 3, 4, 5, or K, L, M, N, O, from the nucleus outwards.

6th assumption :

- The emission or absorption of energy in the form of radiation can only occur when electron jumps from one stationary state to another.



CHEMISTRY FOR NEET & AIIMS

- Energy is absorbed when electron jumps from inner to outer orbit and is emitted when electron moves from outer to inner orbit.
- When electron moves from inner to outer orbit by absorbing definite amount of energy the new state of the e^- is said to be excited state of the electron.
- If electron is in 1st excited state it means now electron is in 2nd orbit. Similarly if electron is in 2nd excited state it means now electron is in 3rd orbit and so on

Ionization energy : The required energy to liberate an electron from the ground state of an isolated atom is called the ionization energy. n_1 to n_2

$$n_1 = 1, n_2 = \infty$$

Separation energy : Required energy to remove an electron from its excited state is called as separation energy.

$$n_1 = 1, 2, 3, 4, 5, \dots, n_2 = \infty$$

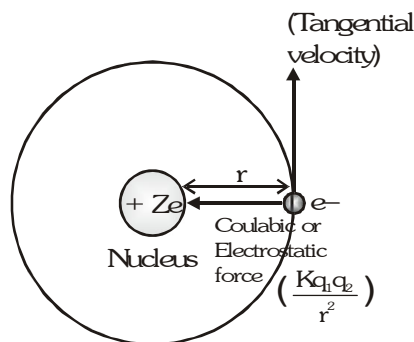
Excitation energy : Required energy to shift an electron from ground state to any excited state is called as excitation energy. $n_1 = 1, n_2 = 2, 3, 4, 5, \dots$

Application of Bohr's Model

1. Radius of various orbits (shell) Excitation energy :

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

Derivation :



$$\text{Coulombic force} = \frac{Kq_1q_2}{r^2} = \frac{K.Ze.e}{r^2} = \frac{KZe^2}{r^2}$$

(Where K is Constant) $K = 9 \times 10^9 \text{ Nm}^2/\text{coulomb}^2$

As we know that Coulombic force = Centrifugal force

$$\frac{KZe^2}{r^2} = \frac{mv^2}{r} \quad \text{or} \quad v^2 = \frac{KZe^2}{mr} \quad \dots(1)$$

$$\text{As we know that } mvr = \frac{nh}{2\pi} \quad \text{or} \quad v = \frac{nh}{2\pi mr} \quad \dots(2)$$

Now putting the value of v from eqⁿ.(2) to eqⁿ.(1)

$$\left(\frac{nh}{2\pi mr}\right)^2 = \frac{KZe^2}{mr} \quad \text{or} \quad \frac{n^2 h^2}{4\pi^2 m^2 r^2} = \frac{KZe^2}{mr}$$

$$r = \frac{n^2 h^2}{4\pi^2 m K Z e^2} \quad \dots(3)$$

Putting the value of $\pi, h, m, K,$ & e (Constants) in the above eqⁿ. (3)

$$r = 0.529 \times 10^{-8} \times \frac{n^2}{Z} \text{ cm} \quad \{ 1 \text{ \AA} = 10^{-10} \text{ m} = 10^{-8} \text{ cm} \}$$

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

This formula is only applicable for hydrogen and hydrogen like species i.e. species contains single electron.

Ex. Calculate the radius of 1st, 2nd, 3rd, 4th Bohr's Orbit of hydrogen.

Sol. Radius of Bohr's orbit $r = 0.529 \times \frac{n^2}{Z} \text{ \AA}$

(a) Radius of Ist orbit : $r = 0.529 \times \frac{1^2}{1} \text{ \AA} = 0.529 \text{ \AA}$

(b) Radius of IInd orbit : $r = 0.529 \times \frac{2^2}{1} = 0.529 \times 4 = 2.116 \text{ \AA}$

(c) Radius of IIIrd orbit : $r = 0.529 \times \frac{3^2}{1} = 0.529 \times 9 = 4.761 \text{ \AA}$

(d) Radius of 4th orbit : $r = 0.529 \times \frac{4^2}{1} = 0.529 \times 16 = 8.464 \text{ \AA}$

Ex. Calculate the radius ratio of 3rd & 5th orbit of He⁺.

Sol. $\therefore r = 0.529 \times \frac{n^2}{Z} \text{ \AA}$ and Atomic Number of He = 2

$$\therefore r_3 = 0.529 \times \frac{(3)^2}{2} = 0.529 \times \frac{9}{2} \quad \text{and} \quad r_5 = 0.529 \times \frac{(5)^2}{2} = 0.529 \times \frac{25}{2}$$

$$\text{Therefore} \quad \frac{r_3}{r_5} = \frac{0.529 \times \frac{(3)^2}{2}}{0.529 \times \frac{(5)^2}{2}} = \frac{9}{25} \quad \text{or} \quad r_3 : r_5 = 9 : 25$$

Ex. Calculate the radius ratio of 2nd orbit of hydrogen and 3rd orbit Li⁺².

Sol. Atomic number of H = 1, Atomic number of Li = 3,

$$2^{\text{nd}} \text{ orbit radius of Hydrogen} \quad (r_2)_H = 0.529 \times \frac{2^2}{1}$$

$$3^{\text{rd}} \text{ orbit radius of Li}^{+2} \quad (r_3)_{\text{Li}^{+2}} = 0.529 \times \frac{3^2}{3}$$

$$\therefore \frac{(r_2)_H}{(r_3)_{\text{Li}^{+2}}} = \frac{0.529 \times \frac{2^2}{1}}{0.529 \times \frac{3^2}{3}} = \frac{4}{3} \quad \therefore (r_2)_H : (r_3)_{\text{Li}^{+2}} = 4 : 3$$

Ex. Calculate the radius ratio of 2nd excited state of H & 1st excited state of Li⁺²

Sol. 2nd excited state, means e⁻ is present in 3rd shell of hydrogen $r_3 = 0.529 \times \frac{(3)^2}{1} = 0.529 \times 9$

1st excited state, means e⁻ exist in 2nd shell of Li⁺² $r_2 = 0.529 \times \frac{(2)^2}{3} = 0.529 \times \frac{4}{3}$

$$\frac{\text{radius of 2}^{\text{nd}} \text{ excited state of hydrogen}}{\text{radius of 1}^{\text{st}} \text{ excited state of Li}^{+2}} = \frac{(r_3)_H}{(r_2)_{\text{Li}^{+2}}} = \frac{0.529 \times \frac{9}{1}}{0.529 \times \frac{4}{3}} = \frac{27}{4}$$

2. Energy of an electron :

Let the total energy of an electron be E. It is the sum of kinetic and potential Energy.

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

$$E = \left(\frac{1}{2}mv^2 \right) + \left(\frac{Kq_1q_2}{r} \right) \left[\text{P.E.} = -\frac{KZe^2}{r} \right]$$

$$E = \frac{1}{2}mv^2 + \frac{K.Z.e.(-e)}{r} = \frac{1}{2}mv^2 - \frac{KZe^2}{r}$$

now putting the value of mv^2 from eq. (1)

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

now putting the value of r from eq. (3)

$$E_n = -\frac{KZe^2 \times 4\pi^2 m KZe^2}{2n^2 h^2} \quad \text{or} \quad \boxed{E_n = -\frac{2\pi^2 m K^2 Z^2 e^4}{n^2 h^2}}$$

now putting the value of π , K, e, m, h, we get :

$$\boxed{E_n = -\frac{21.69 \cdot 10^{-19} Z^2}{n^2} \text{ J/atom}} \quad \text{or} \quad \boxed{E_n = -13.6 \frac{Z^2}{n^2} \text{ eV/atom}}$$

This formula is applicable for hydrogen atom & hydrogen like species i.e. single electron species.

Since n can have only integral values, it follows that total energy of the e⁻ is quantised.

The -ve sign indicates that the e⁻ is under attraction towards nucleus.

Some extra points :

$$(i) \text{ K.E.} = \frac{KZe^2}{2r} \quad \text{i.e.} \quad \text{K.E.} \propto \frac{1}{r}$$

On increasing radius, K.E. decreases.

$$(ii) \text{ P.E.} = -\frac{KZe^2}{r} \quad \text{i.e.} \quad \text{P.E.} \propto -\frac{1}{r}$$

On increasing radius, P.E. increases.

$$(iii) E = -\frac{KZe^2}{2r} \quad \text{i.e.} \quad E \propto -\frac{1}{r}$$

Results : On increasing radius, total energy increases.

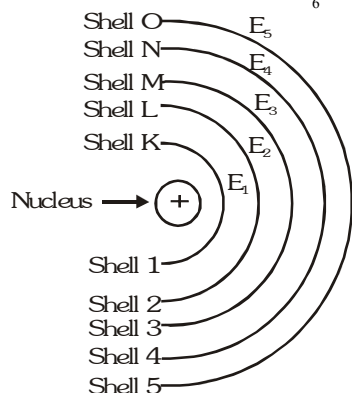
$$\text{P.E.} = (-) 2\text{KE} \quad \text{KE} = (-) E \quad \text{P.E.} = 2E$$

Energy difference between two energy levels :

$$E_{n_2} - E_{n_1} = -13.6 \times Z^2 \left[\frac{1}{n_2^2} - \frac{1}{n_1^2} \right]$$

Energy level for H atom can be represented as follows :

$$n = 6 \text{ or P} \quad E_6 = -0.38 \text{ eV}$$



$$n = 5 \text{ or O} \quad E_5 = -0.54 \text{ eV}$$

$$n = 4 \text{ or N} \quad E_4 = -0.85 \text{ eV}$$

$$n = 3 \text{ or M} \quad E_3 = -1.51 \text{ eV}$$

$$n = 2 \text{ or L} \quad E_2 = -3.4 \text{ eV}$$

$$n = 1 \text{ or K} \quad E_1 = -13.6 \text{ eV}$$

$$E_5 - E_4 = 0.36 \text{ eV}$$

$$E_4 - E_3 = 0.66 \text{ eV}$$

$$E_3 - E_2 = 1.89 \text{ eV}$$

$$E_2 - E_1 = 10.2 \text{ eV}$$

i.e. $(E_2 - E_1) > (E_3 - E_2) > (E_4 - E_3) > (E_5 - E_4) \dots$

Ex. Calculate the energy of Li^{+2} atom for 2nd excited state

Sol. $E = -13.6 \times \frac{Z^2}{n^2}$ $\because Z = 3$ and e^- exist in 2nd excited state, means e^- present in 3rd shell i.e. $n = 3$

$$\therefore E = -13.6 \times \frac{(3)^2}{(3)^2} = -13.6 \text{ eV/atom}$$

Ex. Calculate the ratio of energies of He^+ for 1st & 2nd excited state .

$$\text{Sol.} \quad \frac{\text{Energy of } (\text{He}^+) \text{ 1}^{\text{st}} \text{ Excited state}}{\text{Energy of } (\text{He}^+) \text{ 2}^{\text{nd}} \text{ Excited state}} = \frac{\text{Energy of } (\text{He}^+) \text{ 2}^{\text{nd}} \text{ shell}}{\text{Energy of } (\text{He}^+) \text{ 3}^{\text{rd}} \text{ shell}} = \frac{-13.6 \times \frac{(2)^2}{(2)^2}}{-13.6 \times \frac{(2)^2}{(3)^2}} = \frac{9}{4}$$

Ex. If the P.E. of an electron is -6.8 eV in hydrogen atom then find out K.E., total energy & the orbit where electron exist & radius of orbit.

$$\text{Sol.} \quad 1. \quad \text{K.E.} = -\frac{\text{P.E.}}{2} = \frac{-(-6.8)}{2} = 3.4 \text{ eV}$$

$$2. \quad \text{T.E.} = -\text{K.E.} = -3.4 \text{ eV}$$

$$3. \quad E = -13.6 \times \frac{Z^2}{n^2} \text{ or } 3.4 = -13.6 \times \frac{1^2}{n^2} \Rightarrow n^2 = \frac{-13.6}{-3.4} = 4 \text{ i.e. } n = 2 \text{ i.e. 2}^{\text{nd}} \text{ orbit}$$

$$4. \quad r = 0.529 \times \frac{n^2}{z} \text{ \AA} = 0.529 \times \frac{(2)^2}{1} \text{ \AA} = 0.529 \times 4 \text{ \AA} = 2.116 \text{ \AA}$$

CHEMISTRY FOR NEET & AIIMS

Ex. The ionization energy for the hydrogen atom is 13.6 eV then the required energy in eV to excite it from the ground state to 1st excited state

Sol. Ionization energy = 13.6 eV i.e. Energy in ground state = -13.6 eV
 Energy of 1st excited state i.e. 2nd orbit = -3.4 eV
 so, $E_2 - E_1 = -3.4 + 13.6 = 10.2$ eV

3. Velocity of an electron :

Since

$$\text{Coulombic force} = \text{Centrifugal force or } \frac{KZe^2}{r^2} = \frac{mv^2}{r} \text{ or } KZe^2 = (mvr)(v)$$

$$\text{now putting the value of Angular momentum m.v.r.} = \frac{nh}{2\pi} \Rightarrow KZe^2 = \frac{nh}{2\pi}(v)$$

$$v = \frac{2\pi KZe^2}{nh}$$

now putting the value of π , k , e & h

$$v = 2.188 \times 10^8 \frac{Z}{n} \text{ cm s}^{-1}$$

Ex. If the total energy of an electron is -1.51 eV in hydrogen atom then find out K.E, P.E, orbit, radius and Velocity of the electron in that orbit.

Sol. (i) $KE = -E = 1.51$ eV

(ii) $PE = 2 \times E = -2 \times 1.51 = -2.02$ eV

$$(iii) \because E = -13.6 \times \frac{Z^2}{n^2} \text{ eV} \quad \text{or} \quad -1.51 = -13.6 \times \frac{1^2}{n^2}$$

$$\Rightarrow n^2 = \frac{-13.6}{-1.51} = 9$$

$\therefore n = 3$ i.e. 3rd orbit

$$(iv) r = 0.529 \times \frac{n^2}{Z} = 0.529 \times \frac{3 \times 3}{1} = 0.529 \times 9 = 4.761 \text{ \AA}$$

$$(v) v = 2.188 \times 10^8 \times \frac{Z}{n} = 2.188 \times 10^8 \times \frac{1}{3} \text{ cm/s} = 0.729 \times 10^8 \text{ cm/s}$$

Ex. Calculate velocity of an electron placed in the third orbit of the hydrogen atom. Also calculate the number of revolutions per second that this electron makes around the nucleus.

Sol. Velocity of electron in 3rd orbit :

$$\therefore V_n = 2.182 \times 10^6 \times \frac{Z}{n} \text{ ms}^{-1}$$

$$\therefore V_3 = 2.182 \times 10^6 \times \frac{1}{3} \text{ ms}^{-1} = 7.27 \times 10^5 \text{ ms}^{-1}$$

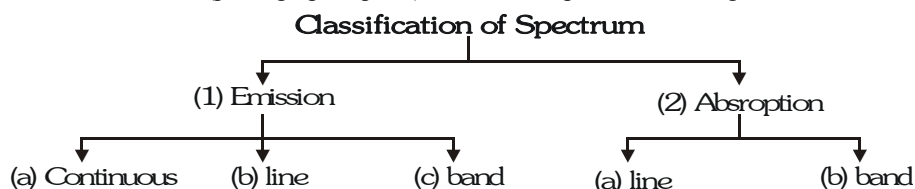
$$\text{No. of revolution per second} = \frac{v_n}{2\pi r^2} = \frac{v_n}{2\pi \left(\frac{n^2 a_0}{z} \right)} = \frac{7.27 \times 10^5}{2 \times 3.14 \times 9 \times 0.529 \times 10^{-10}} = 2.43 \times 10^{14} \text{ r.p.s.}$$

Ex. How much time an e^- will take for one complete revolution in 2nd orbit of He^+ ?

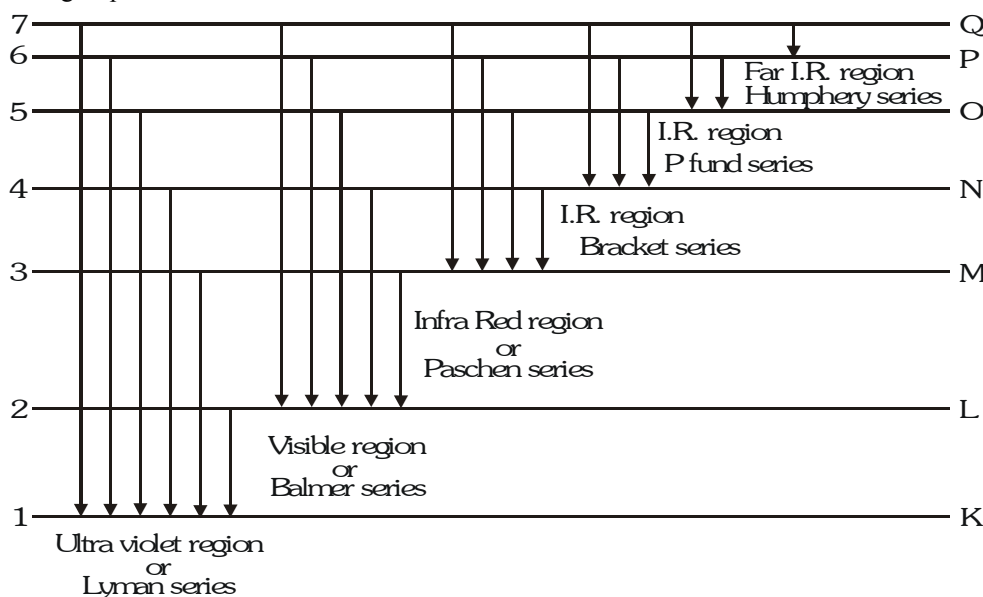
Sol.
$$\text{time taken} = \frac{\text{distance}}{\text{velocity}} = \frac{2\pi r}{v} = \frac{2 \times 3.14 \times 0.529 \times \frac{4}{2} \times 10^{-10} \text{ m}}{2.18 \times 10^6 \times \frac{2}{2} \text{ ms}^{-1}} = 3.05 \times 10^{-16} \text{ s}$$

Spectrum

When a radiation is passed through a spectroscope (prism) for the dispersion of the radiation, the pattern (photograph) obtained on the screen (photographic plate) is called as spectrum of the given radiation



Hydrogen line spectrum or Hydrogen spectrum : When an electric excitation is applied on hydrogen atomic gas at Low pressure, a bluish light is emitted. when a ray of this light is passed through a prism, a spectrum of several isolated sharp line is obtained. The wavelength of various lines show that spectrum lines lie in visible, Ultraviolet and Infra red region. These lines are grouped into different series.



Series	Discovered by	regions $n_2 \rightarrow n_1$	number of lines	
lyman	lyman	U.V. region	$n_2 = 2, 3, 4, \dots / n_1 = 1$	$n_2 - 1$
Balmer	Balmer	Visible region	$n_2 = 3, 4, 5, \dots / n_1 = 2$	$n_2 - 2$
Paschen	Paschen	Infra red (I. R.)	$n_2 = 4, 5, 6, \dots / n_1 = 3$	$n_2 - 3$
Bracket	Bracket	I.R. region	$n_2 = 5, 6, 7, \dots / n_1 = 4$	$n_2 - 4$
Pfund	Pfund	I.R. region	$n_2 = 6, 7, \dots / n_1 = 5$	$n_2 - 5$
Humphery	Humphery	far I.R. region	$n_2 = 7, \dots / n_1 = 6$	$n_2 - 6$

- (i) First line / Starting line / Initial line $(\lambda_{\max.} \text{ and } \nu_{\min.})$
- (ii) Last line / limiting line / marginal line $(\lambda_{\min.} \text{ and } \nu_{\max.})$
- (iii) First line of any series = α line
 Second line of any series = β line
 Third line of any series = γ line

CHEMISTRY FOR NEET & AIIMS

Ex. In a hydrogen spectrum if electron moves from 7 to 1 orbit by transition in multi steps then find out the total number of lines in the spectrum.

Sol. Lyman	=	$(n_1 - 1) = 7 - 1 = 6$
Balmer	=	$(n_2 - 2) = 7 - 2 = 5$
Paschen	=	$(n_2 - 3) = 7 - 3 = 4$
Bracket	=	$(n_2 - 4) = 7 - 4 = 3$
Pfund	=	$(n_2 - 5) = 7 - 5 = 2$
Humphrey	=	$(n_2 - 6) = 7 - 6 = 1$
Total	=	21

Total number of lines can be calculated as follows :

$$\text{Total number of lines} = \frac{(n_2 - n_1)[(n_2 - n_1) + 1]}{2} = \frac{(7 - 1)(6 + 1)}{2} = \frac{42}{2} = 21$$

Ex. In a hydrogen spectrum if electron moves from 6th to 2nd orbit by transition in multi steps then find out the number of lines in spectrum

Sol. Total number of line = 4 + 3 + 2 + 1 = 10

$$\text{or Total number of lines} = \frac{(n_2 - n_1)[(n_2 - n_1) + 1]}{2} = \frac{(6 - 2)(4 + 1)}{2} = \frac{4 \times 5}{2} = 10$$

Ex. In a hydrogen spectrum if electron moves from 6th to 3rd orbit by transition in multi steps then find out the following steps :

- | | |
|---|--|
| (a) Total number of lines in spectrum | (b) Total number of lines in U.V. region |
| (c) Total number of lines in visible region | (d) Total number of lines in IR region |

Sol. (a) Calculation of total number of lines :

$$= \frac{(n_2 - n_1)[(n_2 - n_1) + 1]}{2} = \frac{(6 - 3)[(6 - 3) + 1]}{2} = \frac{3 \times 4}{2} = 6$$

(b) Calculation of number of lines present in U.V. region.

e^- moves from 6th to 3rd orbit in multisteps.

For U.V. region, e^- should be comes into 1st shell. So there is number of lines in U.V. region is zero.

(c) Calculation of total number of lines in visible region.

For visible region, e^- should be comes into 2nd shell, so there is number lines in visible region zero.

(d) Calculation of total number of lines in I.R. region.

In I.R. region, Paschen, Bracket and Pfund series are present.

$$\text{Number of lines in Paschen series} = n_2 - 3 = 6 - 3 = 3$$

$$\text{Number of lines in Bracket series} = n_2 - 4 = 6 - 4 = 2$$

$$\text{Number of lines in Pfund series} = n_2 - 5 = 6 - 5 = 1$$

$$\text{So total number of lines} = 3 + 2 + 1 = 6$$

Ex. In Balmer series of H atom/spectrum which electronic transitions represents 3rd line ?

Sol. In Balmer series	3 rd to 2 nd	→	1 line
	4 th to 2 nd	→	2 line
	5 th to 2 nd	→	3 line
	Infinite to 2 nd	→	Last line or limiting line
So, Ans. is	5 nd to 2 nd line	→	3 rd line

Ex. In H atom if e^- moves, from nth orbit to 1st orbit by transition in multi steps, if there are total number of lines in spectrum are 10 then find out the value of n

Sol. Total number of lines = $\frac{(n_2 - n_1)[(n_2 - n_1) + 1]}{2}$

So, $10 = \frac{(n-1)(n-1+1)}{2}$

or $20 = (n-1)(n)$

$n^2 - n - 20 = 0$

$n^2 - 5n + 4n - 20 = 0$

$n(n-5) + 4(n-5) = 0$

$(n+4)(n-5) = 0 \quad \Rightarrow \quad n = 5$

Rydberg formula : In 1890, Rydberg gave a very simplest theoretical Equation for the calculation of the wavelength of various lines of hydrogen like spectrum and the equation is

$$\bar{\nu} = \frac{1}{\lambda} = RZ^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad \text{where} \quad R = \text{Rydberg constant} = 109678 \text{ cm}^{-1} \simeq 109700 \text{ cm}^{-1}$$

$$\frac{1}{R} = 9.12 \times 10^{-6} \text{ cm} = 912 \text{ \AA}$$

n_1 and n_2 are orbits and for a particular series n_1 is constant and n_2 varies.

for Lyman $n_1 = 1, n_2 = 2, 3, 4, \dots$

for Balmer $n_1 = 2, n_2 = 3, 4, 5, \dots$

for Paschen $n_1 = 3, n_2 = 4, 5, 6, \dots$

for Brackett $n_1 = 4, n_2 = 5, 6, 7, \dots$

for Pfund $n_1 = 5, n_2 = 6, 7, 8, \dots$

for Humphery $n_1 = 6, n_2 = 7, 8, 9, \dots$

Derivations of Rydberg formula :

$$\Delta E = E_{n_2} - E_{n_1}$$

$$\Delta E = \frac{-2\pi^2 m K^2 Z^2 e^4}{n_2^2 h^2} - \left[\frac{-2\pi^2 m K^2 Z^2 e^4}{n_1^2 h^2} \right]$$

$$= \frac{2\pi^2 m K^2 Z^2 e^4}{n_1^2 h^2} - \frac{2\pi^2 m K^2 Z^2 e^4}{n_2^2 h^2} \quad \left(\because \Delta E = h\nu = \frac{hc}{\lambda} \right)$$

$$\frac{hc}{\lambda} = \frac{2\pi^2 m K^2 Z^2 e^4}{h^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad \text{or} \quad \frac{1}{\lambda} = \frac{2\pi^2 m K^2 e^4 Z^2}{ch^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

where $\frac{2\pi^2 m K^2 e^4}{ch^3}$ is a constant which is equal to rydberg constant (R).

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

Ex. Calculate the wavelength of 1st line of Balmer series in Hydrogen spectrum.

Sol. For first line of Balmer series $n_1 = 2, n_2 = 3$

$$\frac{1}{\lambda} = R(1)^2 \left[\frac{1}{4} - \frac{1}{9} \right] = R \left[\frac{9-4}{36} \right] = R \left[\frac{5}{36} \right]$$

$$\Rightarrow \lambda = \frac{36}{5R} = \frac{36}{5} \times \frac{1}{R} = \frac{36}{5} \times 9.12 \times 10^{-6} \text{ cm} = 65.66 \times 10^{-6} \text{ cm}$$

$$= 6566 \text{ \AA}$$

CHEMISTRY FOR NEET & AIIMS

Ex. Calculate the frequency of the last line of the Lyman series in hydrogen spectrum.

Sol. For last line of Lyman series $n_1 = 1, n_2 = \infty$

$$\frac{1}{\lambda} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = R \left(\frac{1}{1} - 0 \right) = R$$

$$\Rightarrow \nu = \frac{c}{\lambda} = c \times \frac{1}{\lambda} = c \times R = 3 \times 10^{10} \text{ cm s}^{-1} \times 109678 \text{ cm}^{-1}$$

$$= 3.29 \times 10^{15} \text{ s}^{-1}$$

Ex. Calculate Wavelength of 3rd line of Bracket series in hydrogen spectrum.

Sol. For 3rd line of Bracket series $n_1 = 4, n_2 = 7$

$$\frac{1}{\lambda} = RZ^2 \left[\frac{1}{(4)^2} - \frac{1}{(7)^2} \right] = R \left[\frac{1}{16} - \frac{1}{49} \right] = R \left[\frac{49 - 16}{16 \times 49} \right] = R \frac{33}{784}$$

$$\text{Therefore, } \lambda = \frac{784}{33R} = \frac{784}{33} \times 912 \text{ \AA} = 21667 \text{ \AA}$$

Ex. The wave number of 1st line of Balmer series of hydrogen spectrum is 15200 cm^{-1} . The wave number of 1st line of Balmer series of Li^{+2} spectrum will be ?

Sol. Wave number of 1st line of Balmer series of hydrogen spectrum. $\bar{\nu} = \frac{1}{\lambda} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

$$(\text{for H, } Z=1) \quad \bar{\nu} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = 15200 \text{ cm}^{-1}$$

Wave number of 1st line of Balmer series of Li^{+2} ion is.

$$\bar{\nu} = Z^2 \times R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \{ \because Z=3 \text{ for } \text{Li}^{+2} \}$$

$$\therefore \bar{\nu} = 3^2 \times 15200 = 9 \times 15200 = 136800 \text{ cm}^{-1}$$

Ex. Calculate the ratio of maximum λ of Lyman & Balmer series ?

Sol. $E \propto \nu \propto \frac{1}{\lambda}$

$$\frac{\text{Maximum } \lambda \text{ of Lyman series}}{\text{Maximum } \lambda \text{ of Balmer series}} = \frac{1^{\text{st}} \text{ line of Lyman series}}{1^{\text{st}} \text{ line of Balmer series}}$$

$$\frac{\lambda_{\text{Lyman}}}{\lambda_{\text{Balmer}}} = \frac{\lambda_{\text{B}}}{\lambda_{\text{L}}} = \frac{R \left[\frac{1}{2^2} - \frac{1}{3^2} \right]}{R \left[\frac{1}{1^2} - \frac{1}{2^2} \right]} = \frac{\frac{1}{4} - \frac{1}{9}}{\frac{1}{1} - \frac{1}{4}} = \frac{\frac{36}{36} - \frac{4}{36}}{\frac{36}{36} - \frac{9}{36}} = \frac{\frac{32}{36}}{\frac{27}{36}} = \frac{32}{27} = \frac{5}{3} \times \frac{4}{3} = \frac{5}{27}$$

Ex. A certain electronic transition from an excited state to Ground state of the Hydrogen atom in one or more steps gives rise of 5 lines in the ultra violet region of the spectrum. How many lines does this transition produce in the Infra red region of the spectrum?

Sol. (Lyman Series) ultra violet region : 5 Lines i.e. e^- is coming from 6th to 1st Orbit

$$n_2 - 1 = 5 \quad \text{or} \quad n_2 = 6$$

Infrared region line

(i) Paschen series = $(6-3) = 3$

(ii) Bracket = $(6-4) = 2$

(iii) Pfund = $(6-5) = 1$

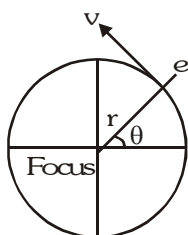
Total Number of lines are = 6

Limitation of the Bohr's model :

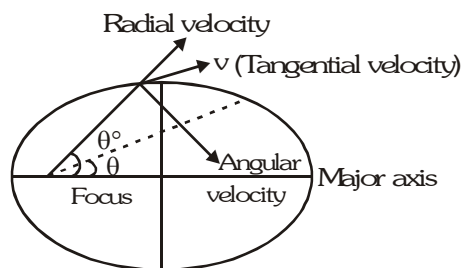
- Bohr's theory does not explain the spectrum of multi electron atom.
- Why the Angular momentum of the revolving electron is equal to $\frac{nh}{2\pi}$, has not been explained by Bohr's theory.
- Bohr interrelate quantum theory of radiation and classical law of physics with out any theoretical explanation.
- Bohr's theory does not explain the fine structure of the spectral lines. Fine structure of the spectral line is obtained when spectrum is viewed by spectroscope of more resolution power.
- Bohr theory does not explain the spiliting of spectral lines in the presence of magnetic field (Zemman's effect) or electric field (Stark's effect)

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



$r = \text{Constant}$
 $\theta = \text{Variable}$



$r = \text{Variable}$
 $\theta = \text{Variable}$

- 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.)
 $[n_r = (n-1) \dots \dots \dots 0]$ $n = \text{Shell number}$

2. **Azimuthal Components:** $J_\phi = \frac{n_\phi h}{2\pi}$ (n_ϕ = Azimuthal quantum number)
 $[n_\phi = 1, 2, 3, 4 \dots \dots \dots n]$ $n = \text{Shell number}$

So total Angular momentum (J_n) = $J_r + J_\phi$

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

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

Ex. Let $n = 4$ then

n	=	$n_r + n_\phi$
4	=	3 + 1
4	=	2 + 2
4	=	1 + 3
4	=	0 + 4

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

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

CHEMISTRY FOR NEET & AIIMS

- If $n = 1$ Then Elliptical path = $(n - 1) = (1 - 1) = 0$
Circular path = 1
- In n^{th} orbit : Number of elliptical path = $(n - 1)$
Number of circular path = 1

Note: Electron in the first orbit always revolve in circular path.

Ex. $(n + 1)$ is the principal quantum number of the energy state for an atom. What are the number of elliptical orbits associated with it :-

- (1) $(n - 1)$ (2) $(n + 1)$ (3) $(n - 2)$ (4) n

Sol. (4)

Quantum Mechanical Model of Atom

(i) 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 .

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

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

$p =$ momentum of electron

\therefore Momentum (p) = Mass (m) \times Velocity (v)

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

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.

Bohr's theory and de-broglie concept :

- (1) According to de-Broglie, the nature of an electron moving around the nucleus is like a wave that flows in circular orbits around the nucleus.
- (2) If an electron is regarded as a wave, the quantum condition as given by Bohr in his theory is readily fulfilled.
- (3) If the radius of a circular orbits is r , then its circumference will be $2\pi r$.

- (4) We know that according to Bohr theory, $mvr = \frac{nh}{2\pi}$

$$\text{or } 2\pi r = \frac{nh}{mv} \quad (\because mv = p \text{ momentum}) \quad \text{or} \quad 2\pi r = \frac{nh}{p}$$

$$\left(\because \frac{h}{p} = \lambda \text{ de-Broglie equation} \right)$$

$\therefore 2\pi r = n\lambda$ (where $n =$ total of waves 1, 2, 3, 4, 5, ... ∞ and $\lambda =$ Wavelength)

- (5) $\therefore 2\pi r = \frac{nh}{mv}$ or $mvr = \frac{nh}{2\pi}$ $\therefore mvr =$ Angular momentum

Thus $mvr =$ Angular momentum, which is a integral multiple of $\frac{h}{2\pi}$.

- (6) It is clear from the above description that according to de-Broglie there is similarity between wave theory and Bohr theory.

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 $p_y = \frac{1}{2} p_x$ (given)

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

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

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

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

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

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.

(II) 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 $m\Delta v$, are related by Heisenberg's relationship as : ($p = mv$, $\Delta p = m\Delta v$)

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

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.

$$\begin{aligned} \Delta x \cdot \Delta v &\geq \frac{6.624 \times 10^{-27}}{4\pi m} \\ &\geq \frac{6.624 \times 10^{-27}}{4 \times 3.14 \times 9.10 \times 10^{-28}} \\ &= 0.57 \text{ erg sec per gram approximately} \end{aligned}$$

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.

CHEMISTRY FOR NEET & AIIMS

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

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

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

(i) de-Broglie wavelength in terms of kinetic energy.

$$\text{Kinetic Energy (K.E.)} = \frac{1}{2}mv^2 \quad \text{or} \quad m \times \text{K.E.} = \frac{1}{2}m^2v^2 \quad \text{or} \quad m^2v^2 = 2m \text{ K.E.} \quad \text{or} \quad mv = \sqrt{2m \text{ K.E.}}$$

$$\text{But } \lambda = \frac{h}{mv} \quad \therefore \quad \lambda = \frac{h}{\sqrt{2m \text{ K.E.}}} \quad (\because mv = \sqrt{2m \text{ K.E.}})$$

- (ii) When a charged particle carrying Q coulomb is accelerated by applying potential difference V then $\text{K.E.} = Q \times V$ Joule

$$\text{But } \lambda = \frac{h}{\sqrt{2m \text{ K.E.}}} \quad \therefore \quad \lambda = \frac{h}{\sqrt{2mQV}} \quad \text{For electron } \left(\lambda = \sqrt{\frac{150}{V}} \text{ \AA} \right) = \frac{12.25}{\sqrt{V}} \text{ \AA}$$

- (iii) Remember $\frac{h}{4\pi} = 0.527 \times 10^{-34}$ Jsec

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.

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

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

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

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

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

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

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

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

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

$$\lambda = \frac{h}{mc} = \frac{6.6252 \times 10^{-34}}{9.1 \times 10^{-31} \times 3 \times 10^7} = \frac{6.6252 \times 10^{-34}}{27.3 \times 10^{-24}}$$

$$\text{or } 0.2426 \times 10^{-10} \text{ metre}$$

$$\text{or } 2.426 \times 10^{-11} \text{ metre}$$

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

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

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

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

Ex. What should be the mass of the sodium photon if its wavelength is 5894 Å, the velocity of light is 3×10^8 metre/second and the value of h is 6.6252×10^{-34} kg m²/sec.?

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

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

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

$$m = \frac{6.652 \times 10^{-34}}{3 \times 10^8 \times 5894 \times 10^{-10}} \text{ or } \frac{6.652}{17682} \times 10^{-32} = 0.0003746 \times 10^{-32}$$

$$\text{or } 3.746 \times 10^{-36} \text{ kg}$$

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
= 5×10^{-12} m

$$\text{Mass of electron (m)} = 9.109 \times 10^{-31} \text{ kg.}$$

$$\therefore \Delta v = \frac{h}{4\pi m \times \Delta x} = \frac{6.6252 \times 10^{-34}}{4 \times 3.14 \times 5 \times 10^{-12} \times 9.109 \times 10^{-31}} \text{ m/sec.}$$

$$\text{or } \Delta v = \frac{6.6252 \times 10^{-34}}{4 \times 3.14 \times 5 \times 9.109 \times 10^{-43}}$$

$$\therefore \Delta v = 1.15816 \times 10^7 \text{ m/sec.}$$

Ex. What should be the uncertainty in velocity of a particle of 1 kg mass if uncertainty in position is 1 Å 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

$$\Delta x = 1 \text{ Å} = 1 \times 10^{-10} \text{ m}$$

$$m = 1 \text{ kg}$$

$$h = 6.6252 \times 10^{-34} \text{ Joule sec.}$$

CHEMISTRY FOR NEET & AIIMS

$$\Delta v = \frac{h}{4\pi \times m \times \Delta x} = \frac{6.6252 \times 10^{-34}}{4 \times 3.14 \times 1 \times 10^{-10}}$$

$$\begin{aligned}\text{or } \Delta v &= \frac{6.6252 \times 10^{-34}}{12.56 \times 10^{-10}} \text{ m/sec.} \\ &= 0.52525 \times 10^{-24} \text{ m/sec.} \\ &= 5.25 \times 10^{-25} \text{ m/sec.}\end{aligned}$$

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

$$\Delta p = 1 \times 10^{-2} \text{ g cm/sec.} = 1 \times 10^{-7} \text{ kg m/sec.}$$

$$h = 6.6252 \times 10^{-34} \text{ Joule sec.}$$

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

$$\text{or } \Delta x = \frac{6.6252 \times 10^{-34}}{4 \times 3.14 \times 10^{-7}} = 0.525 \times 10^{-27} \text{ m}$$

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

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

$$= h \text{ constant}$$

$$= v \text{ Same}$$

\therefore least λ will be SO_2

$$\therefore \lambda \propto \frac{1}{m}$$

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

$$\frac{\Delta x_e \times \Delta p_e \times \frac{h}{4\pi}}{\Delta x_{(\text{He})} \times \Delta p_{\text{He}} \times \frac{h}{4\pi}} = \frac{\Delta p_e}{\Delta p_{\text{He}}} = 1$$

$$\therefore \Delta p_e = \Delta p_{\text{He}}$$

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

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

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

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

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

$$\pi = 3.142$$

According to uncertainty principle

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

$$\begin{aligned} \text{So, } \Delta x &\geq \frac{h}{4\pi} \cdot \frac{1}{\Delta p} \\ &\geq \frac{6.62 \times 10^{-27}}{4 \times 3.142} \times \frac{1}{10^{-3}} \\ &= 0.527 \times 10^{-24} \text{ cm} \end{aligned}$$

(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 $5.27 \times 10^{-24} \text{ ms}^{-1}$ respectively. Calculate the mass of the particle ($h = 6.625 \times 10^{-34} \text{ Joule Sec.}$)

Sol. According to Heisenberg's uncertainty principle,

$$\begin{aligned} \Delta x \cdot m \Delta v &= \frac{h}{4\pi} \quad \text{or} \quad m = \frac{h}{4\pi \Delta x \cdot \Delta v} \\ &= \frac{6.625 \times 10^{-34}}{4 \times 3.143 \times 10^{-10} \times 5.27 \times 10^{-24}} \\ &= 0.099 \text{ kg} \end{aligned}$$

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 1 \AA ($h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$).

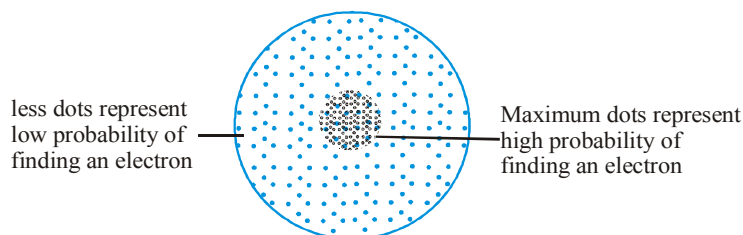
Sol. $\Delta x \cdot m \Delta v = \frac{h}{4\pi}$

$$\begin{aligned} \Delta v &= \frac{h}{4\pi \Delta x \cdot m} \\ &= \frac{6.6 \times 10^{-34}}{4 \times 3.143 \times 10^{-10} \times 0.150} \\ &= 3.499 \times 10^{-24} \text{ ms}^{-1} \end{aligned}$$

Orbit and Orbitals

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 nucleus.



Difference Between Orbit and Orbitals

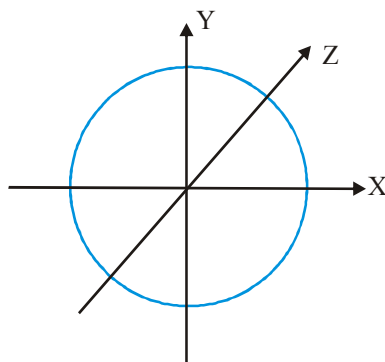
S. No.	Orbit	Orbitals
1	It is well defined circular path followed by revolving electrons around the nucleus	It is the region of space around the nucleus where electron is most likely to be found
2	It represents planar motion of electron	It represents 3 dimensional motion of an electron around the nucleus.
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

$$\text{nodes} = (n - 1)$$

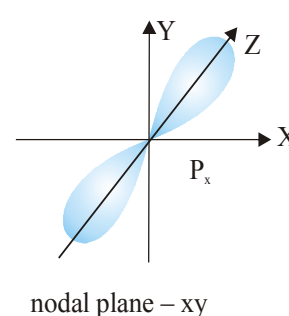
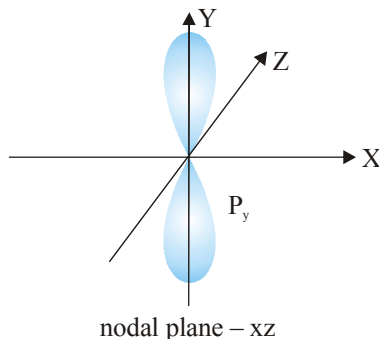
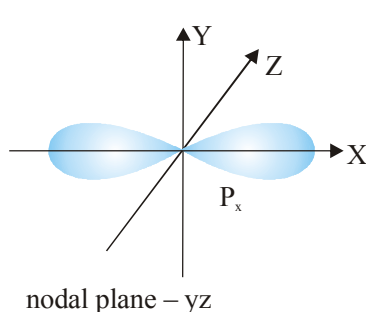


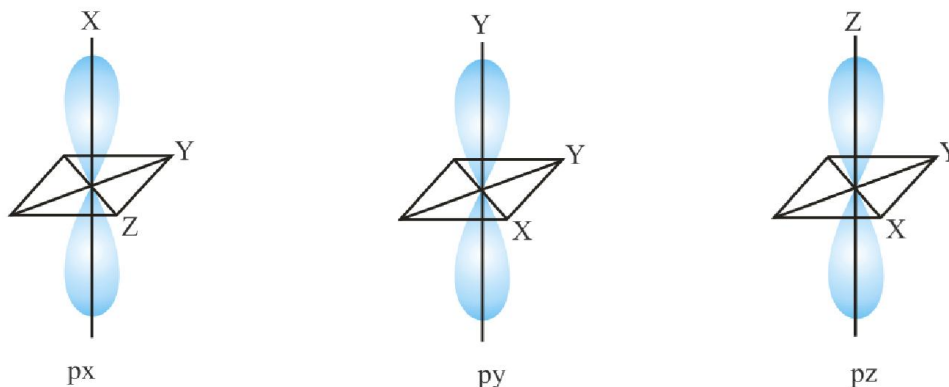
s- orbital is non directional and it is closest to the nucleus, having lowest energy. s-orbital can accomodate maximum no. of two electrons.



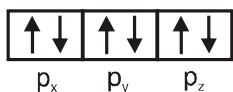
p-Orbital : Shape → dumb bell

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**.

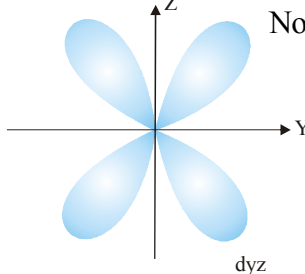
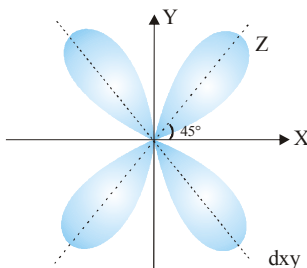




p - subshell can accommodate maximum of six electrons. **Nodal surface = $n - 2$**



d - Orbital : Shape → double dumb bell



Nodal surface = $n - \ell - 1$

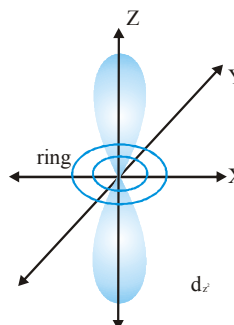
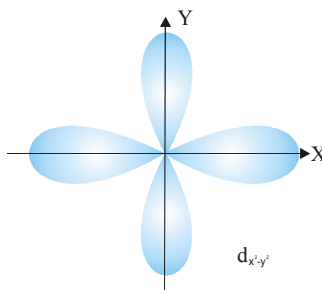
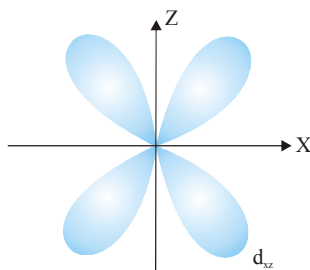
Nodal Plane d_{xy} → xz & yz nodal plane

d_{xz} → xy & zy nodal plane

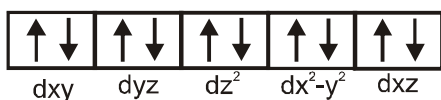
d_{zy} → zx & yx nodal plane

$d_{x^2-y^2}$ → 2 nodal plane

d_{z^2} → 0, nodal plane



d - subshell can accommodate maximum of 10 electrons.



f - Orbital : Shape → leaf like or Complex



f - orbital can accommodate 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.

CHEMISTRY FOR NEET & AIIMS

(i) Principal Quantum Number (n) :

Given by Bohr

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

- Number of subshell present in n^{th} shell = n

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

- Number of orbitals present in n^{th} shell = n^2 .
- The maximum number of electrons which can be present in a principal energy shell is equal to $2n^2$. No energy shell in the atoms of known elements possesses more than 32 electrons.
- Greater the value of n, greater is the distance from the nucleus.

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

$$r_1 < r_2 < r_3 < r_4 < r_5 \text{ -----}$$

- Greater the value of n, greater is the energy of shell

$$E = -13.6 \times \frac{Z^2}{n^2} \text{ eV / atom}$$

$$E_1 < E_2 < E_3 < E_4 \text{ -----}$$

- Velocity of electron $v = 2.18 \times 10^6 \frac{Z}{n} \text{ m/s}$

$$v_1 > v_2 > v_3 \text{}$$

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

- The angular momentum of revolving electron is $mvr = \frac{nh}{2\pi}$

Where n = Principal quantum number.

(ii) Azimuthal Quantum Number (ℓ) :

Given 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	shape
0	s	spherical
1	p	dumb bell shape
2	d	double dumb shape
3	f	complex shape

- If the value of n is same then the order of energy of the various subshell will be $s < p < d < f$

$$\text{Ex. } 4s < 4p < 4d < 4f, \quad 3s < 3p < 3d, \quad 2s < 2p$$

- If Value of ℓ is same but value of n is different then the order of energy will be.

$$\text{Ex. } 1s < 2s < 3s < 4s < 5s < 6s$$

$$3d < 4d < 5d < 6d$$

$$4p < 5p < 6p$$

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

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

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

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

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

- The number of electron in a particular subshell is equal to $2(2\ell + 1)$

(iii) Magnetic Quantum Number (m) :

Given by Linde

- It represents the shape of different orbitals and the orientation of electron cloud (orbital)
- Under the influence of magnetic field each subshell is further subdivided into orbitals (The electron cloud is known as orbital)
- Magnetic quantum number describe these different distribution of electron cloud.
- Value of $m =$ all integral value from $-\ell$ to $+\ell$ including zero.
- i.e. Value of $m = -\ell$ to $+\ell$

Orbital : 3D space around the nucleus in which probability of finding electron is maximum is called an orbital. An orbital can be represented by 3 set of quantum numbers

= $\Psi_{n,\ell,m}$ (classical representation) $n\ell x^*$

Ex. 1 : $2p_x$; $n=2, \ell=1, m=-1$ or $m=+1$

Ex. 2 : $3d_{z^2}$; $n=3, \ell=2, m=0$

Ex. 3 : $\Psi_{(3,2,0)}$; $n=3, \ell=2, m=0$; $3d_{z^2}$

Note : It is point / line / plane / surface in which probability of finding electron is zero.

Total numbers of nodes = $n - 1$

They are of 2 types.

- Radial nodes / spherical nodes number of radial nodes = $n - \ell - 1$
- Angular nodes / number of nodal planes number of angular nodes / nodal planes = ℓ
 - Nucleus and ∞ are not considered as node.

(iv) Spin Quantum Number (s) :

Given by Samuel Goudsmit & Uhlenbeck

- It represents the direction of electron Spin around its own axis
- for clock wise spin/spin up (\uparrow) electron $\rightarrow \pm \frac{1}{2}$
- for anticlock wise spin/spin down (\downarrow) electron $\mp \frac{1}{2}$

Spin angular momentum of an $e^- = \sqrt{s(s+1)} \cdot \frac{h}{2\pi}$ or $\sqrt{s(s+1)} \hbar$

- Each orbital can accommodate 2 electrons with opposite spin or spin paired.



Rules for Filling of Orbitals

(I) Aufbau Principle

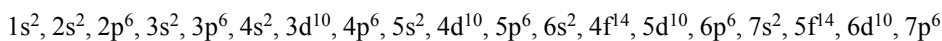
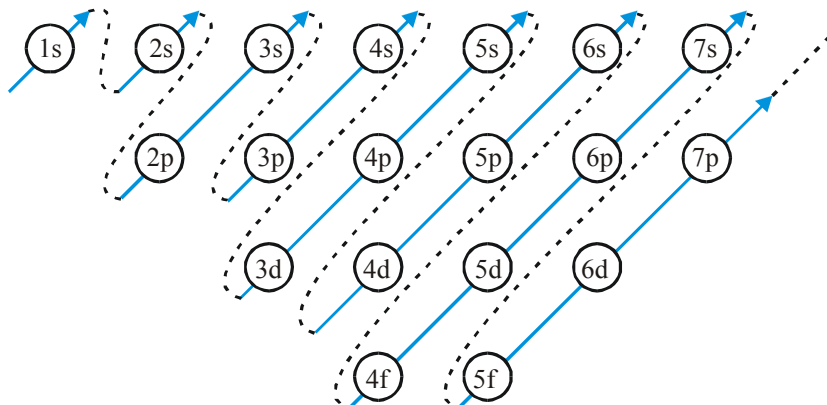
Aufbau is a German word and its meaning 'Building up'

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

CHEMISTRY FOR NEET & AIIMS

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.



(II) $(n + \ell)$ Rule

Given by Bohr-Bury

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

Principle of $(n + \ell)$ rule

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

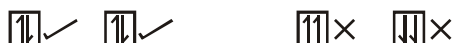
Sub shell	n	ℓ	$n + \ell$	
1s	1	0	1	
2s	2	0	2	
2p	2	1	3	(1)
3s	3	0	3	(2)
3p	3	1	4	(1)
4s	4	0	4	(2)
3d	3	2	5	(1)
4p	4	1	5	(2)
5s	5	0	5	(3)

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

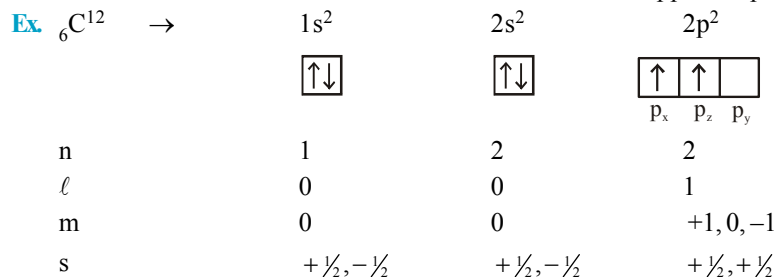
i.e. $1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f \dots\dots\dots$

(III) Pauli's Exclusion Principle

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



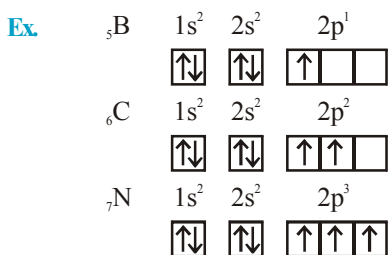
An orbital can accomodates maximum 2 electrons with opposite spin.



(IV) 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.



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

CHEMISTRY FOR NEET & AIIMS

(c) Angular momentum in 4th orbit

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

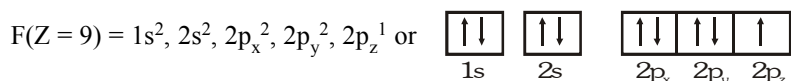
Ex. Given below are the sets of quantum numbers for given orbitals. Name these orbitals.

- (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) $4d_{z^2}$ (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 configuration so obtained can be represented in two ways. As an illustration, let us consider fluorine ($Z = 9$):



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

Sol. ${}_6C : 1s^2, 2s^2 2p^2$

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

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

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

\therefore 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 = ± 3 ; For ${}_{36}Kr$, it is = 0

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

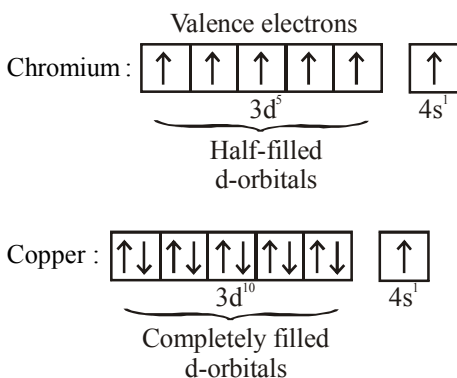
For ${}_7N$, it is = $\sqrt{15}$; For ${}_{24}Cr$, it is = $\sqrt{48}$; For ${}_{36}Kr$, it is = $\sqrt{0}$

Exceptional configurations
Stability of Half Filled and Completely Filled Orbitals :

The electronic configuration of chromium (Cr) and copper (Cu) are different from expected electronic configuration.

	Expected	Actual
Chromium	$[\text{Ar}]3d^44s^2$	$[\text{Ar}]3d^54s^1$
Copper	$[\text{Ar}]3d^94s^2$	$[\text{Ar}]3d^{10}4s^1$

These actual configurations are due to the fact that the half-filled and full-filled orbitals are very stable and nature loves stability and so do the elements. So, the unexpected electronic configurations are acquired to gain stability. As in case of chromium, in its actual electronic configuration, d-orbitals are half-filled.


Causes of Stability of Completely Filled and Half-filled Subshells :

The reasons for the stability of completely filled and half-filled subshells are as follows :

- Symmetrical distribution of electrons :** It is a known fact that the symmetry leads to stability. So, the half-filled and fully-filled orbitals are symmetrical, hence stable. Moreover this type of electronic configuration is even favoured by energy factor. The electrons in the 3d subshell have equal energy, but they just differ in their spacial distribution. This results in less shielding of one another. Due to small shielding, the electrons are pulled closer to the nucleus. And as the electrons move closer to the nucleus, their energy decreases (more negative). Further this decrease in energy leads to stability.
- Exchange energy :** Electrons with the same spin have a tendency to exchange their positions when they are present in the degenerate orbitals of a subshell. The energy released during this exchange is called exchange energy. More are the number of electrons with identical spin, more are the number of ways of exchanging with other electrons, more will be the energy released called exchange energy. Moreover, we know that decrease in energy leads to stability.

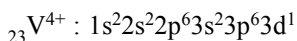
Ex. A compound of vanadium has a magnetic moment of 1.73 BM work out the electronic configuration of the vanadium in the compound.

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

Where n is number of unpaired electrons

$$\therefore 1.73 = \sqrt{n(n+2)} \text{ or } (1.73)^2 = n^2 + 2n, n = 1$$

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



TIPS & FORMULAS

1. Frequency, $\nu = \frac{c}{\lambda}$
2. Energy/photon, $E = h\nu = \frac{hc}{\lambda}$
Also, $E = \frac{12375}{\lambda} \text{ eV}$, 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 n^{th} Bohr orbit of H atom, $r_n = \frac{n^2 h^2}{4\pi^2 m e^2 K}$ (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 n^{th} Bohr orbit of H atom, $v = \frac{2\pi K Z e^2}{nh}$
 $v = 2.18 \times 10^8 \frac{Z}{n} \text{ cm/sec}$.
6. Energy of electron in n^{th} Bohr orbit of H atom, $E = \frac{2\pi^2 m Z^2 e^4 K^2}{n^2 h^2}$
where $n = 1, 2, 3, \dots$
 $[E = -13.6 \times \frac{Z^2}{n^2} \text{ kcal/mole (1 cal = 4.18 J)}]$
 E_1 for H = $-21.72 \times 10^{-12} \text{ erg} = -13.6 \text{ eV}$, E_1 for H like atom = E_1 for H $\times Z^2$
7. Wavelength emitted during transition in H atom,
 $\frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] = \frac{2\pi^2 m e^4}{ch^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$ (in C.G.S.)
8. Photoelectric effect $h\nu = w + \frac{1}{2} m u^2$ or $h\nu = \text{I.E.} + \text{K.E.}$
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 = $n \cdot (h/2\pi)$
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 = ℓ , Total nodes = $(n - \ell)$
15. de Broglie equation : $\lambda = \frac{h}{mu} = \sqrt{\frac{h^2}{2 \times \text{K.E.} \times m}}$
where λ is wavelength, m is mass and u is velocity of particle.
16. Heisenberg uncertainty principle :

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

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

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.