CHAPTER - 04
STRUCTURE OF ATOM

INTRODUCTION

Atoms are the smallest particle of matter which are having either the same property or different property of it. John Dalton introduced the word atom from the Greek word (Atomio or Atomos). It's meaning is indivisible (cannot be sub-divided)

Fundamental sub atomic particles

There are 36 sub atomic particles are present those are:-

Proton $\left({}_{1}^{1}P\right)$; Neutron $\left({}_{0}^{1}n\right)$; Electron $\left({}_{-1}^{0}e\right)$; Positron $\left({}_{+1}^{0}e\right)$; Antiproton $\left({}_{-1}^{1}P\right)$; μ mesons $(\mu\pm)$; π meson $(\pi\pm)$; Pions (O). Neutrino and Antineutrino etc. Among these proton, electron and neutron are the fundamental sub atomic particles.

I. DISCOVERIES OF FUNDAMENTAL SUB ATOMIC PARTICLES

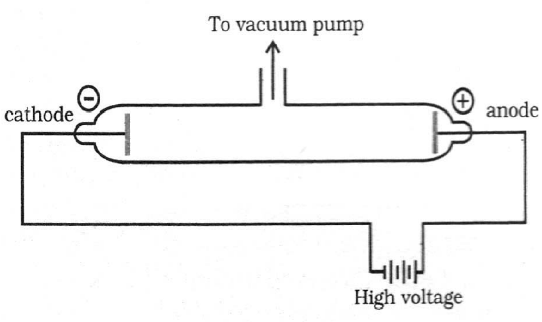
(CATHODE RAY EXPERIMENT)/DISCHARGE TUBE EXPERIMENT (JULIUS PLUCKER)

DISCOVERY OF ELECTRON

Julius Plucker (1889) and J.J. Thomson (1898) studied the discharge of electricity through partially evacuated tubes (cathode ray discharge tube).

They observed that when a high voltage electric current is passed through a gas at low pressure, negatively charged particles (called cathode rays) travelled from the cathode towards the anode.

A cathode ray discharge tube, Crooks tube, consists of a long glass tube fitted with metal electrodes on both ends across which a high voltage can be applied. The tube is connected to a vacuum pump for controlling the pressure of gas inside.

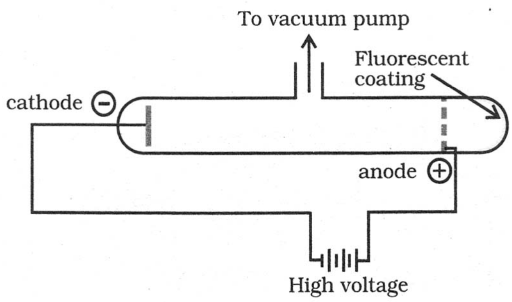


Cathode ray discharge tube

Electrical discharge through gases is possible only at very low pressures and very high voltages.

When the pressure of gas inside the tube is reduced to about 10^{-4} atmospheres and a potential difference of 10000 volts is applied, (the tube glows with a faint greenish light) current starts flowing through a stream of particles moving in the tube from the negative electrode (cathode) towards the positive electrode (anode).

The flow of current was further checked by making a hole in the anode and coating the tube behind the anode with a phosphorescent material (zinc sulphide). These rays, after passing through the anode developed a bright spot on the zinc sulphide coating.



Cathode ray discharge tube with perforated anode

<u>Characteristic features of cathode rays</u>

1. These rays are negatively charged and move along straight line
2. They are massive particles and deflect in magnetic and electric field.
3. They affect photographic plate
4. These rays ionise gases, which kept inside the discharge tube.
5. They produce heat and light, when hit on the tungsten filament.
6. They produce X-rays, when it hit on the tungsten metal.
7. They produce fluorescence and phosphorescence, when it hit on the corresponding material.
8. The e/m value of cathode rays doesn't depend on the nature of the gas.

<u>Millikans oil drop experiment</u>

- This experiment is used to find the quantity of electronic charge (q)
- The Principle behind of the experiment is comparing the terminal velocities of oil drop which is adsorbed with electron, with electric field and without electric field.

Charge on the Electron

Thomson's experiment led to the determination of e/m_e value of the electron. The charge (e) on the electron was determined by American scientist, Robert Millikan in 1909, by his 'oil drop' experiment.

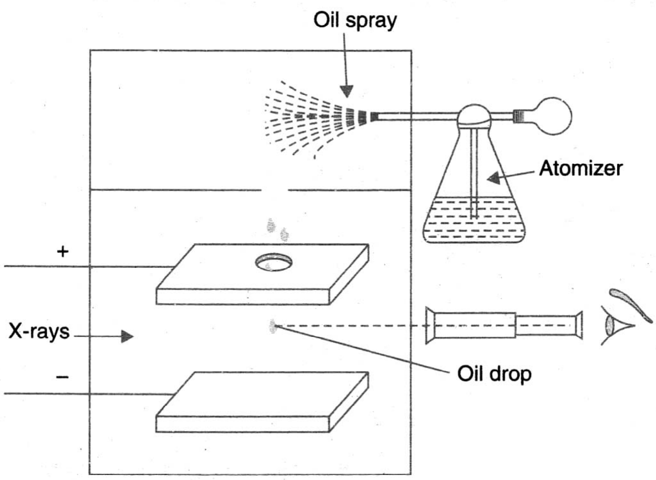
Millikan's oil drop apparatus consists of a chamber containing two charged plates, anode with a hole in the centre and a cathode placed below. The chamber is provided with an atomiser, a telescope and a source of X-rays. The downward motion of oil droplets produced by the atomiser and entering through the small hole can be viewed with the microscope. By measuring the rate of fall of the drops, it is possible to measure the mass of the oil droplets.

The air between the electrodes is ionised by passing X-rays. Oil drops acquire one or more electrons to become negatively charged which are attracted by the positive plate which affects their fall. The rate of fall of the charged ions can be controlled by varying the applied voltage.

Millikan found that the magnitude of charge 'q' on the droplets is always an integral multiple of the electrical charge, e (1.60×10^{-19}C).

$$q = ne$$

where n = 1, 2, 3.......(quantized)



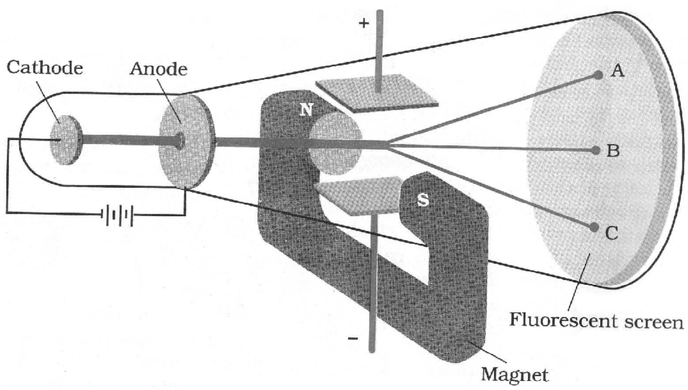
Millikan's oil drop apparatus

J.J. Thomson experiment to determine the specific charge of electron (e/m)

CHARGE TO MASS RATIO OF ELECTRON

In 1897, British physicist J.J. Thomson measured the ratio of charge (e) to mass of electron(m_e) using cathode ray tube by applying electrical and magnetic fields perpendicular to each other and the path of the electrons. He observed that deviation of the particles from their path depended on the magnitude of negative charge on the particle, mass of the particle and strength of the electrical or magnetic field.

1. Greater the magnitude of charge, greater is the interaction with the field and hence higher the deviation.
2. Heavier the particle lesser the deviation
3. Greater the strength of the magnetic field or the voltage applied, greater will be the deviation.



Apparatus to determine charge to mass ratio of electron

The magnetic and electric fields deflect the beam in opposite directions (A and C) from point B. From the amount of charge required to balance the effect of the magnetic field, Thomson calculated the e/m_e of cathode ray particle as 1.758820 × 10^{11} C kg^{-1}.

$$\frac{e}{m_e} = 1.758820 \times 10^{11}\,C\,kg^{-1}$$

The e/m_e ratio for cathode rays was found to be the same irrespective of the nature of the cathode or the gas taken in the discharge tube, thus indicating that electrons are basic constituents of all atoms.

- e/m value of cathode rays independent of gases inside the discharge tube.
- e/m value of electron is the highest one among all particles
- From the experimental observations, e/m value obtained from the relation

$$\boxed{\frac{e}{m} = \frac{E}{rB^2}}$$

Where E and B are the electric and magnetic field strength and r is the radius of an arc developed on a photographic plate.

- e/m value of electron = $1.76 \times 10^{11} C / kg$

Mass of the Electron

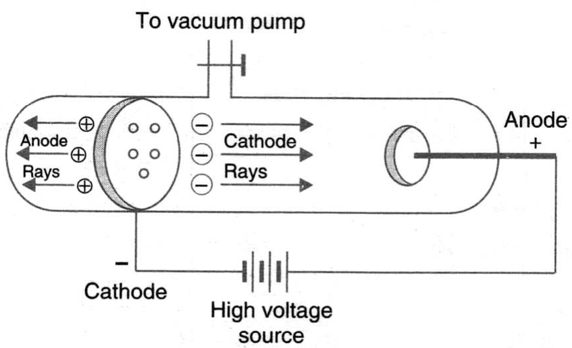
The mass of the electron was calculated by combining these results with Thomson's e/m_e value

$$m_e = \frac{e}{e/m_e} = \frac{1.6022 \times 10^{-19}\,C}{1.75882 \times 10^{8}\,C^{-1}g} = 9.1094 \times 10^{-28}\,g$$

$$= 9.1094 \times 10^{-31}\,kg$$

The mass of the electron is approximately 1/1837 of the mass of the hydrogen atom.

<u>Anode ray experiemnt / Discovery of canal rays</u>



- Origin of anode rays are the gases present in the discharge tube.
- e/m value of anode rays depend on gases inside the discharge tube and its value was found to be $9.58 \times 10^7 C / kg$, when H_2 gas is taken in the discharge tube.

- Mass of proton = 1.673×10^{-27} kg

Characteristic features of anode rays

- Unlike the charge all the properties of cathode rays are similar to anode rays.

Discovery of Neutrons/James Chadwick experiment

α-particles bombarded on a beryllium foil, it transmutted to carbon atom and releasing chargeless and massive particles are known as neutrons.

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

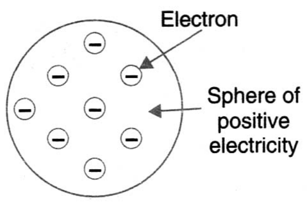
Mass of neutron = 1.675×10^{-27} Kg

Characteristic features of Neutron

1. They are highly penetrating
2. They remain unaffected in electric and mangetic field
3. Neutrons mainly take part in nuclear reactions.

J.J. THOMSON'S MODEL

- Plum pudding model or watermelon model / Raisin pudding model



MERITS

He could clearly explained:-

1. Neutrality of atom
2. When metal is heated, only electrons are emitted
3. Positive sphere is immovable
4. Mass of an atom is uniformly distributed

DEMERIT

1. This model could not satisfy the facts obtained from the Rutherford experiments.

RADIOACTIVITY

Wilhalm Roentgen in 1895 observed that when electrons strike a material in the cathode ray tube produce fluorescence due to X-rays. It was noticed that X-rays were produced more effectively when cathode rays strike dense metal anode (target). X-rays are not deflected by electric or magnetic fields and have very high penetrating power. They have very short wavelengths (≈ 0.1 nm) and are electromagnetic in character. In 1896, French physicist, Henry Baqueral discovered radioactivity, which is the spontaneous emission of radiations by certain elements like uranium. Such elements are said to be radioactive.

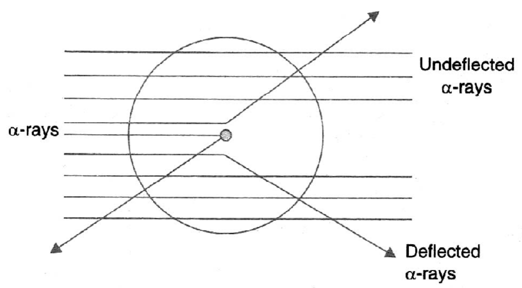
Further investigations by Marie Curie, Piere Curie, Rutherford and Fredrick Soddy showed that three types of rays, i.e. α, β and γ emanated from radioactive elements.

Characteristics of α, β particles and γ – rays

	α – rays	β – rays	γ – rays
Mass	6.67×10^{-27} kg	9.11×10^{-31} kg	
Charge	+2	–1	0
Type/nature	Helium nucleus (He^{2+})	Electron	High energy Radiation
Velocity	Nearly $\frac{1}{10}$th of that of light	Nearly the same as that of light	Same as that of light
Effect of electric field	Deflected towards negative plate	Deflected towards positive plate	No effect
Penetrating power	Low	High (100 times that of α-rays)	Very high (1000 times that of α– rays)

RUTHERFORD MODEL OF AN ATOM

α - scattering experiment



- Inference of this experiment is the most of the space in an atom is empty.

Rutherford Model

- Planetary model/solar system model
- Atom is sub divided into two parts :-

  Nuclear part and Extra nuclear part

Nuclear part :

- Nucleus : It is positive centre core which contain positive charge. Most of the mass is concentrated in it.

- Radius of nucleus : $r_n = R_0 \times A^{1/3}$, R_0 is the proportionally constant and is equal to 1.3×10^{-15}

- Radio of radius of nucleus to atom = $\frac{10^{-15}}{10^{-10}} = 10^{-5}$

- Density of nucleus is remains constant for all elements and is equal to $2.3 \times 10^{17}\ kgm^{-3}$

Extra nuclear part

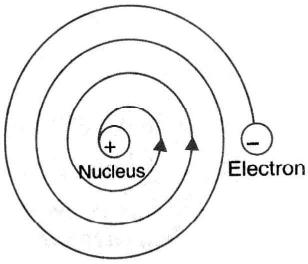
- Other than the nucleus in an atom is extra nuclear part. In which electrons are revolving round the nucleus in a circular path

- Centrifugal force is counter balanced by electrostatic force of attraction between nucleus and electron.

Limitations

1. Stability of atom could not clearly explained.

   According to the classical theory of electromagnetism proposed by Maxwell, every accelerated charged particle must emit radiations in the form of electromagnetic waves and lose its total energy. Since energy of electrons keep on decreasing, the radius of the circular path should also decrease (a spiral path) and ultimately it should fall into the nucleus.



Electron emitting energy and spiralling into the nucleus.

Calculations showed that it will take only 10^{-8} seconds for the electron to spiral into the nucleus.

2. Spectrums of atoms could not clearly explained

3. He could not clearly explain the electronic arrangement of atoms.

Atomic number (Z) = Number of protons = Number of electrons

Mass number

The mass of the atom is mainly concentrated in the nucleus. The nucleus contains protons and neutrons which are collectively called nucleons.

The total number of protons and neutrons in the nucleus is called mass number of the atom.

Mass number (A) = Number of protons + Number of neutrons = Number of nucleons.

The atomic number (Z) and mass number (A) of an element are usually represented along with the symbol of that element as shown below:

$$^{A}_{Z}X$$

3.1 ISOTOPES, ISOBARS AND ISOTONES

Isotopes: All atoms of an element have the same number of protons in their nuclei, however, the number of neutrons may vary. Atoms having same atomic number but different mass numbers are known as isotopes. For example, hydrogen has three isotopes namely protium $\left(^{1}_{1}H\right)$, deuterium $\left(^{2}_{1}D\right)$ and tritium $\left(^{3}_{1}T\right)$.

Similarly, the three isotopes of carbon are ${}^{12}_{6}C$, ${}^{13}_{6}C$ and ${}^{14}_{6}C$. Chlorine has two isotopes, ${}^{35}_{17}Cl$ and ${}^{37}_{17}Cl$.

Chemical properties of atoms are controlled by the number of electrons and therefore, all isotopes of a given element exhibit same chemical behaviour.

Isotones: Sometimes atoms of different elements contain the same number of neutrons. Such atoms are known as isotones. Thus, isotones are atoms of different elements containing the same number of neutrons. E.g. ${}^{13}_{6}C$ and ${}^{14}_{7}N$; ${}^{30}_{14}Si$, ${}^{31}_{15}P$ and ${}^{32}_{16}S$.

Isodiaphers: They are atoms of different elements which have the same difference between the number of neutrons and protons (same n - p value). Eg. ${}^{11}_{5}B$ and ${}^{13}_{6}C$, ${}^{15}_{7}N$ and ${}^{19}_{9}F$

Isosters: Molecules which have the same number of atoms and electrons are alled isosters. E.g. CO and N_2O, CaO and KF, OF_2 and HClO.

LIGHT

I. **Newtons Corpusular Theory :** Particle nature could clearly explained by Newtons corpusular theory.

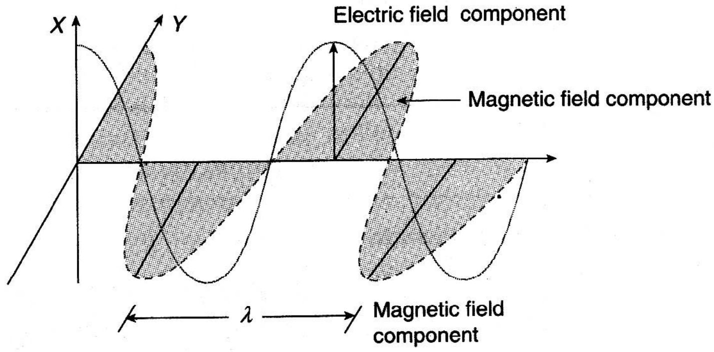
- *Limitations of Newtons corpusular theory*

  Diffraction, Interference etc could not clearly explained.

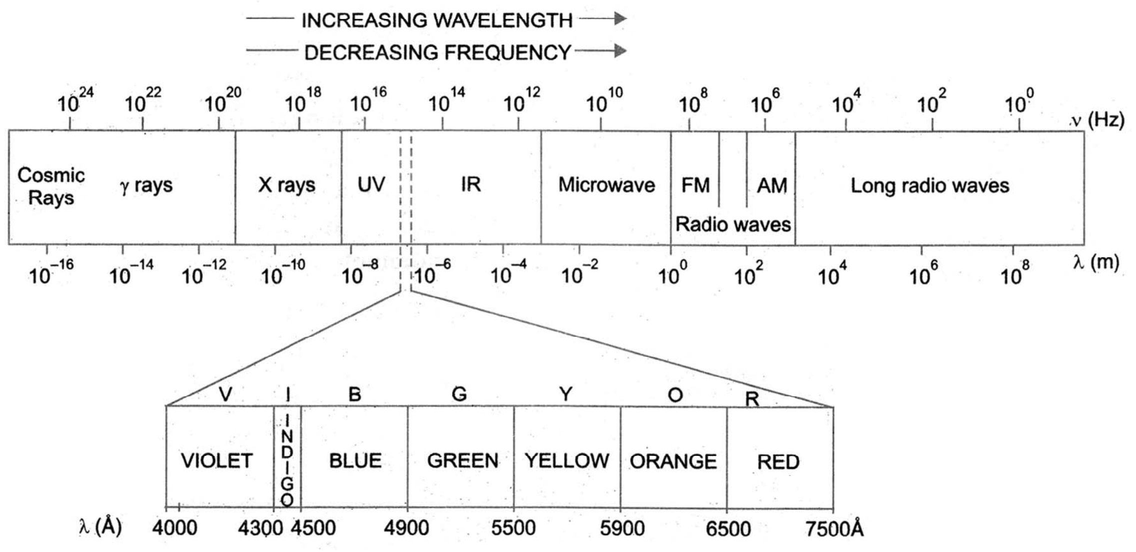
II. **Wave theory**

Electromagnetic wave theory :

Accelerated charged particles like electron which emit radiation/energy in the form of wave component. Which resolve into two component, ie., electrical component wave and magnetic component wave. Those waves are mutually particular to each other and are perpendicular to the propagation.



The electric and magnetic field components of electromagnetic wave



The electromagnetic spectrum (visible region is only a small part of the spectrum)

Characteristic features of wave

1. Wavelength (λ) : Distance between the two consecutive crests or troughs

2. Frequency (υ) : Number of waves passing through a point per second.

$\upsilon = \frac{c}{\lambda}$; c is the velocity of light

$$\upsilon = \frac{1}{T}$$

3. Amplitude A : The maximum height of crests or the maximum depth of trough.

$\upsilon = 1/T$, T = Time in second.

4. Wave number $\bar{\upsilon}$ = Number of waves passing per unit length .

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

Relation between υ and $\bar{\upsilon}$

$$\upsilon = c\bar{\upsilon}$$

2. **Plancks quantum theory**

Postulate

1. Atom absorbs and liberate energy not continuously discontinuously in the form of small packets called quanta (photon)
2. E = $h\upsilon$ - (1 photon or 1 quanta)
3. E = $\frac{hc}{\lambda}$
4. E = n $\frac{hc}{\lambda}$ n = no. photons

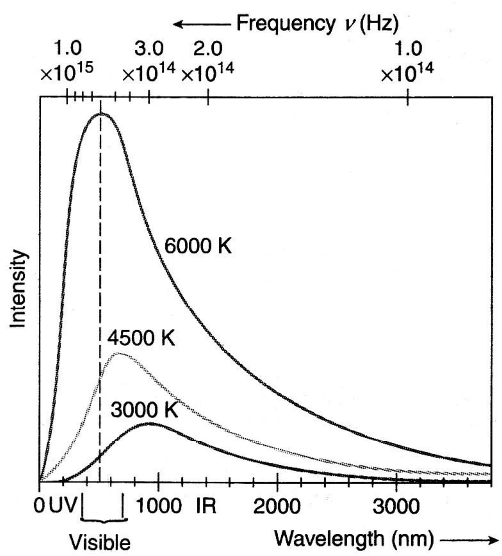
♦ 1 Photon breaks 1 molecule where as 1 mole photon breaks 1 mole molecule.

Limitations of wave theory

1. Black body radiation

An ideal black body is expected to absorb completely the radiant energy falling on it is known as a black body. The radiation emitted by a black body kept at high temperature is called black body radiation. A black body radiation is the visible glow that the solid object gives off, when heated.

A graph is obtained by plotting the intensity of radiation against wave length gives the following details.



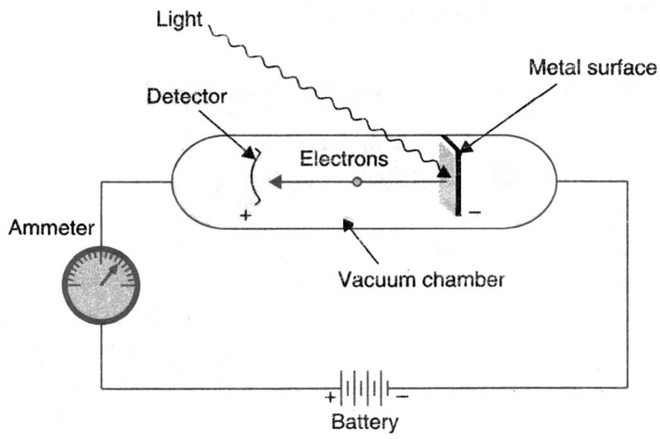
Wave length - intensity relationship.

1. The naure of the radiation depends upon the Temperature of the black body.
2. At given temperature, the intensity of radiation increases with the wavelength, reaches maximum and then decreases.
3. As the temperature increases peak of maximum intensity shifts towards the shorter wavelength.

Photo electric effect

When light fall on low ionisation energised metals like Cs and K electrons are ejected

E - incident energy , E_0 threshold energy



Equipment for studying photoelectric effect.

$\left(E_0 = h\upsilon_0\right)$ υ_0 = Threshold frequency

$E_1 = E_0 \rightarrow$ photoelectric effect is formed

$E_1 < E_0 \rightarrow$ No photo electric effect

$E_1 > E_0 \rightarrow$ K.E. of photoelectrons are present

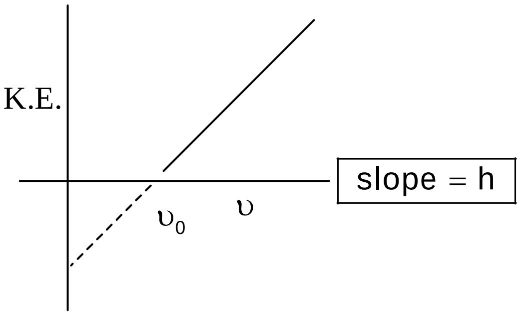
$$\Delta E = E_1 - E_0 = KE = h\upsilon - h\upsilon_0$$

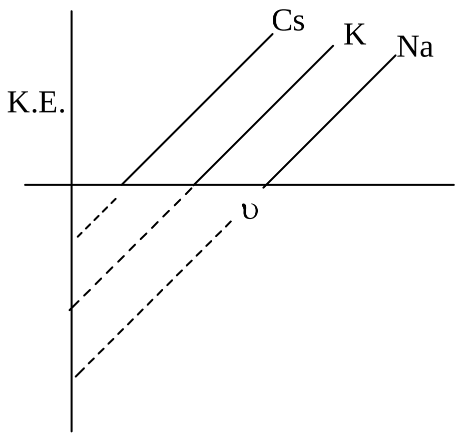
$$KE = h\left(\upsilon - \upsilon_0\right)$$

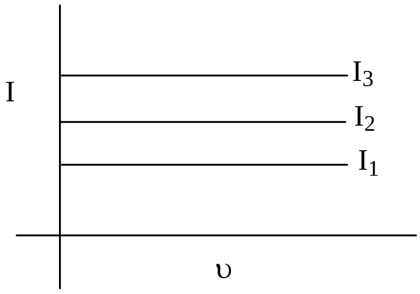
$$\boxed{KE \ \alpha \ \upsilon}$$

$$\boxed{I_{\text{incident light}} \ \alpha \ \text{no ejected electrons}}$$

Graphical explanation of photoelectric effect







Stopping potential :

The external potential is required to stop the K.E. of ejected electrons.

$KE = h\upsilon - h\upsilon_0$

$eV = h\upsilon - h\upsilon_0$

$$V = \frac{h\upsilon}{e} - \frac{h\upsilon_0}{e}$$
$$y = mx + c$$

Where V is the stopping potential.

Bohr atomic model

Bohr's atomic theory

Postulates

1. Electron is revolving round the nucleus in a circular stationary energy path called **Orbit.**
2. As long as electron revolve round the nucleus in a circular path, it neither loose energy nor absorb.
3. Angular momentum of an orbit is quantised. It is integral multiple of some constant values $mvr_n = \frac{nh}{2\pi}$

   or $mVr_n = n\hbar$

4. When an electron absorb energy from external source, it get excited to the higher energy level. That electron has no stability, it de-excited to lower levels by releasing absorbed energy. That energy corresponds to the spectrum.

MERITS

1. He could clearly derived the relations of K.E., P.E., E_n (total) velocity of electron in the n^{th} Bohr orbit and radius of n^{th} Bohr orbit.

1. Relation of KE and PE

1. $K.E. = \frac{KZe^2}{2r_n}$, $K = \frac{1}{4\pi\varepsilon_0}$; $\varepsilon_0 \rightarrow$ permitivity in free space

2. $P.E. = \frac{-KZe^2}{r_n}$

If KE is x, PE = –2x.

♦ Hydrogen like species are He^{+1}, Li^{+2}, Be^{+3} . Those species contain one electron in ground state.

2 Relation of Radius of Bohr orbit

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

$$r_n = 0.529\frac{n^2}{Z}A^0 \text{ or } r_n = 52.9\frac{n^2}{Z}pm$$

$$\boxed{r_{nx} = r_1H \times \frac{n^2x}{Zx}}$$ x = Hydrogen like species

3. Relations of total energy of Bohr orbit

K.E. + P.E. = E_n

$$E = \frac{-2\pi^2me^4z^2k^2}{n^2h^2}$$

$$E_n = -1312\frac{Z^2}{n^2}kJ/mol$$

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

$$E_n = -2.18\times10^{-18}\frac{Z^2}{n^2}J/atom$$

$$E_n = -313.6\frac{Z^2}{n^2}Kcal/mol$$

$$\boxed{E_n x = E_1 H \times \frac{Z^2 x}{n^2 x}}$$; Where x is the hydrogen like species.

4. Relation of velocity of Bohr orbit

$$V = \frac{nh}{2\pi m r_n}; \quad V_n = \frac{2\pi KZe^2}{nh}$$

$$\boxed{V_n = 2.18 \times 10^6 \frac{Z}{n} \text{ m / s}}$$

$$\boxed{V_{nx} = V_1 H \times \frac{Z_x}{N_x}}$$; where x is the Hydrogen like species

Ionisation energy

The energy required to eject electron from the outermost shell of neutral gaseous atom in a ground state.

5. Relations of ionisation energy of Bohr orbit

$$E_\infty - E_1 = \Delta E = -\left(-E_1\right) = +E$$

$$E_n = 1312 \frac{Z^2}{n^2} \text{ kJ / mol}$$

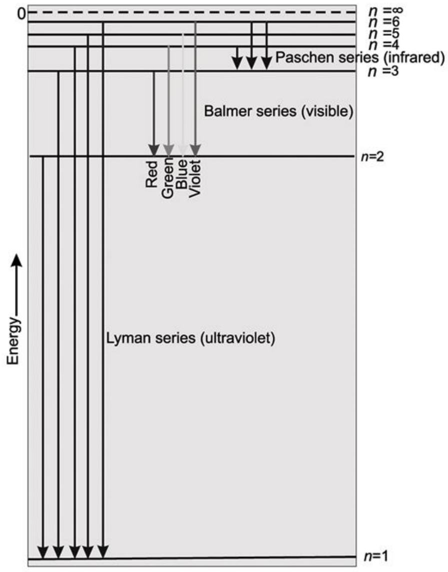
$$E_n = 13.6 \frac{Z^2}{n^2} \text{eV / atom}$$

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

$$E_n = 313.6 \frac{Z^2}{n^2} \text{Kcal / mol}$$

$$\boxed{I.E_{nx} = I.E_{1H} \times \frac{Z_x^2}{n_x^2}}$$ where x is the H like species.

HYDROGEN SPECTRUM



1. Number of possible spectral lines obtained from the de excitation of electron from excited (n) level to ground level = $\frac{n(n-1)}{2}$

2. Number of possible spectral lines obtained from the de excitation of electron from excited (n) level to lower level other than the ground level = $\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$

3. Number of spectral lines obtained from the excited level (n) to

   1. U.V. region only = n – 1

   2. Visible region only = n – 2

   3. I.R. region only = $\frac{(n-3)(n-3+1)}{2}$

Rydberg equation (Ritz combination principle)

1. The principle states that, spectral lines of any element include frequencies that are either the sum or the difference of the frequencies of two other lines.

$$\bar{\upsilon} = 1/\lambda = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]Z^2 \quad ; \quad n_1 = 1; \; n_2 = 2, 3, 4 \text{ etc}$$

$$R_H = 109677 \text{ cm}^{-1} \text{ or } 1.09677 \times 10^7 \text{ m}^{-1} \; ; \; n_1 = 1; \; n_2 = 1, 2, 3 \text{ etc}$$

♦ Ionisation energy in terms of R_H

$\boxed{\text{I.E.} = R_H . hc \times Z_x^2}$; x = H like species

Spectrum

- Emission spectrum
  - Continuous spectrum (Solar spectrum)
  - Discontinuous spectrum
    - (Atomic spectrum) Line spectrum
    - Finger print of an atom
- Absorption spectrum

Limitations

1. Fine spectrum could not clearly explained.

   Fine spectrum is the normal spectral line split in several by observing the spectrum through fine spectro scope.

2. Multi electron spectrums could not clearly explained

3. Zeeman effect and Stark effect could not clearly explained.

   Zeeman effect - Splitting of spectral line, when magnetic field is introduced.

   Stark effect - Splitting of spectral line, when electric field is introduced.

4. Dualism of sub-atomic particle could not clearly explained.

5. Uncertainities are the inherent property of the system that results from the dualism of matter. Those uncertainities could not clearly explained.

Davisson and Germer experiment

This experiment could clearly proved that wave nature of electron in the nth Bohr orbit by the x-ray diffraction experiment conducted on Nickel metal.

Mosley's experiment

He could clearly proved that, the identity of element is the atomic number by an x-ray diffraction experiment and derived relations.

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

υ = frequency of radiation

Z = atomic number

a = proportionality constant

b = constant for lines of X-ray

De-brogle relation

According to Einstein's mass energy relation and Planck's quantum theory . He derived a relation

$\lambda = \frac{h}{mc}$............(1) for light wave

$\lambda = \frac{h}{mv}$............(2) for matter wave

Relation between KE and λ

$$\boxed{\lambda = \frac{h}{\sqrt{2mKE}}}$$

- Number of waves or wavelength produced by an electron when it is revolve round the nucleus in the n^{th} Bohr orbit is equal to its principle quantum number $\frac{2\pi r_n}{\lambda} = n$
- Number of revolutions made by electron in the n^{th} orbit per sec $\upsilon = \frac{V_n}{2\pi r_n}$
- The time required for the revolution of electron in the n^{th} Bohr orbit T = $1/\upsilon = \frac{2\pi r_n}{V_n}$
- Relation between λ and potential = $\lambda_{\mathring{A}} = \sqrt{\frac{150}{V}}$

Heinsenbergs uncertainity principle

It is impossible to determine both position and momentum of sub atomic particles simultaneously with accuracy.

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

$\Delta x.m\Delta v \geq \frac{h}{4\pi}$; where Δx and Δp are uncertainity position and uncertainity momentum respectively.

$\Delta E.\Delta t \geq \frac{h}{4\pi}$; where ΔE uncertainity energy and Δt uncertainity in time

Quantum mechanical model of an atom (Erwin Schrodinger)

Based on De-Broglie relation and Heisenberg uncertainity principle, Erwin Schrodinger put forward an equation,. Through that equation he could clearly explained the quantum mechanical model of an atom.

Schrodinger wave equation

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

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - v)\psi = 0$$

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

$$\left.\begin{array}{l} \hat{H} - \text{Hamiltonion} \\ \nabla^2 - \text{Laplacian} \end{array}\right\} \text{Mathematical operator}$$

Significance of ψ

ψ has no independent significance. ψ is a solution of Schrodinger equation. ψ is a wave function only.

ψ^2 has significance, it is the region in space where the probability of finding electron is maximum.

ie orbital.

ie. $\psi = \psi_{radial} \cdot \psi_{angular}$; $\psi_{(nlm)} = \psi_r \cdot \psi_{(\theta.\phi)}$

	Orbit	Orbital
1	Electrons revolving round the nucleus in a stationary circular path	It is the region in space where the probability of finding of electron is maximum
2	It is 2-Dimensional	It is 3-Dimensional
3	It is circular in shape	Orbitals have:- S-orbital - spherically symmetrical P-orbital - dumb bell d-orbital - double dumb bell f - Three dimensional complicated structure
4	It doesn't obey Heisenberg's uncertainity principle	It obeys Heisenberg's uncertainity principle

Quantum numbers

These are the numbers which designate size/energy of orbit, shape of orbitals, orientation /direction of orbitals and spinning of electrons in its own axis.

Mainly three quantum number n, *l*, m are used to construct an orbital.

I. Principal quantum number (n) Bohr

It gives the size or energy of shell or orbit

It denoted by the letter n

n can have values 1, 2, 3, 4 etc represents K, L, M, N shells.

- ♦ Maximum number of subshells present in shell = n
- ♦ Maximum number of orbitals present in shell = n^2
- ♦ Maximum number of electrons can occupy in the shell = $2n^2$

II. Azimuthal Quantum number / Subsidiary quantum number - Angular Quantum Number (Somerfield)

- ♦ It gives shapes of sub shells
- ♦ Its value is obtained by l = 0 to n – 1
- ♦ It denoted by l

l = O - s = subshell

l = 1 - p - subshell

l = 2 - d - subshell

l = 3 - f - subshell

- ♦ If n = 1, K shell; l = 0 1s subshell

  n = 2, L shell; l = 0 2s subshell

l = 1 2p subshell

So on

Angular momentum of orbital = $\sqrt{\ell(\ell+1)}\ h/2\pi$

Sommerfield model of an atom

- He could clearly explained atom with sub shells

ie. motion of electron in closed circular orbit is influenced by its own nucleus and is set up into closed elliptical path.

III. Magnetic Quantum Number (m_ℓ) Lande / Zeeman

- It gives orientation or direction of orbitals
- Its value obtained by the relation $-\ell, 0, +\ell$
- It denoted by the letter m_ℓ

$n = 1$ K shell $\ell = 0$ 1s subshell 1s orbital
(l = 0) $(m_l = 0)$

$n = 2$ $\ell = 0$ 2s subshell $m_\ell = 0$ 2s orbital

$\ell = 1$ 2p subshell m_ℓ =

-1	0	+1
P_x	P_z	P_y

n = 3 $l = 0$ s subshells $m_l = 0$ 3s orbital

$l = 1$ p subshell m_l =

-1	0	+1
$3P_y$	$3P_z$	P_x

$l = 2$ d

m_l = -2	-1	0	+1	+2
3dxy	3dyz	$3dz^2$	3dxz	$3dx^2$-y^2

- Maximum number of orbitals in subshell = $(2\ell+1)$
- Maximum number of electron can occupy the sub shell = $2(2\ell+1) = 4\ell+2$

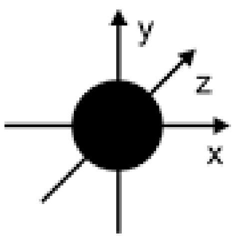
IV. Spin quantum number ($m_{(s)}$) (Uhlenbeck Goudsmit)

- ♦ It gives the spinning of electron in its own axis
- ♦ Its values are –1/2, +1/2
- ♦ Maximum two electrons with opposite spin can be placed in an orbital.

$\boxed{\uparrow\downarrow}$

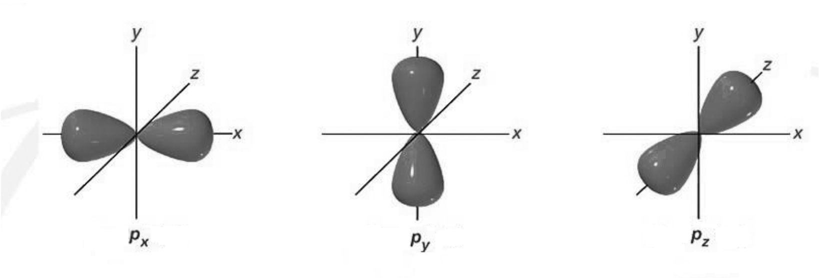
SHAPES OF SUB SHELLS

S-orbital

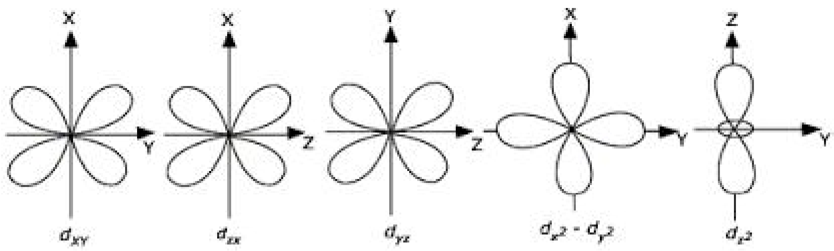


S

p-orbital



d-orbital



Node:

The region space where the probability of finding electron is zero. There are two types of nodes:-

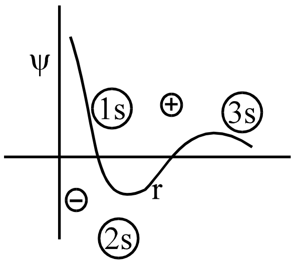
1. Radial node / spherical node

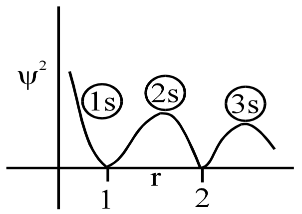
2. Nodal plane / angular node

- Radial node or spherical node = $n - \ell - 1$
- Angular node/nodal plane = ℓ value
- Total number of nodes = n – 1

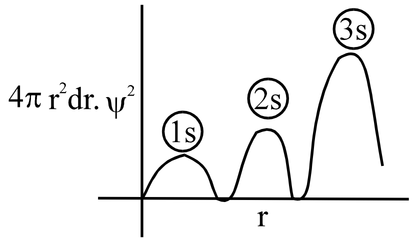
<u>Radial Probability Distrubution Curves</u>

ψ = radial wavefunction, ψ^2 radial probability density $4\pi r^2 dr\ \psi^2$ -radial probability function





radial node, radial node



Number of minima = no.of radial node = $n - \ell - 1$

Number of maxima = no.of radial node + 1 = $n - \ell$

<u>Rules for writing the electronic configuration</u>

1. **Pauli's exclusion principle :** No two electrons in an atom can have same set of 4 quantum numbers.
2. **Aufbau principle:** Electrons are filling in the increasing order of energy of atomic orbitals. It is based on $(n + \ell)$ rule

Rule-I : The orbitals having higher $(n + \ell)$ value higher will be the energy.

Rule-II : If the orbitals having same $(n + \ell)$ value, higher the n value orbital higher will be the energy.

In single electron system (Orbit is considered) : 1s < 2s = 2p < 3s = 2p = 3d

In multiple electron system : 1s < 2s < 2p < 3s < 3p < 3d (orbital is considered)

<u>Hunds rule of maximum multiplicity</u>

In a degenerate orbitals like p, d and f, electrons are filling first singly occupied after that pairing will occur.

For example : p^4 $\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$

Exceptional configuration

$Cr = 24\ \underset{18}{[Ar]}4s^1 3d^5$

$Cu = 29\underset{18}{[Ar]}4s^1 3d^{10}$

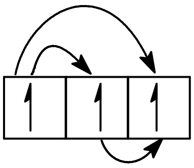
This is due to half filled and fully filled stable configuration

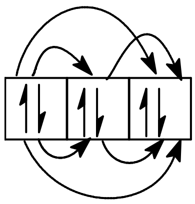
Reason for half filled and fully filled stable configuration

1. Symmetrical arrangement
2. Exchange energy

The energy released, when electrons are exchange in orbitals. Exchange energy increases, stability increases. Number of exchanges directly proportioal to stability.

Number of exchanges increases also stability increases.

P^3 

P_6 

No of exchanges = 3 No.of exchanges = 6

- Stability order of half filled/fully filled orbitals : $d^5 < p^3 < d^{10} < p^6$

Reason

First consider the orbital stability then exchange energy.

- Spectrum will not produce, when an electron exchange takes place in degenerate orbitals.