

CHAPTER - 05

(*) PROPERTIES OF CHARGE PARTICLES:-

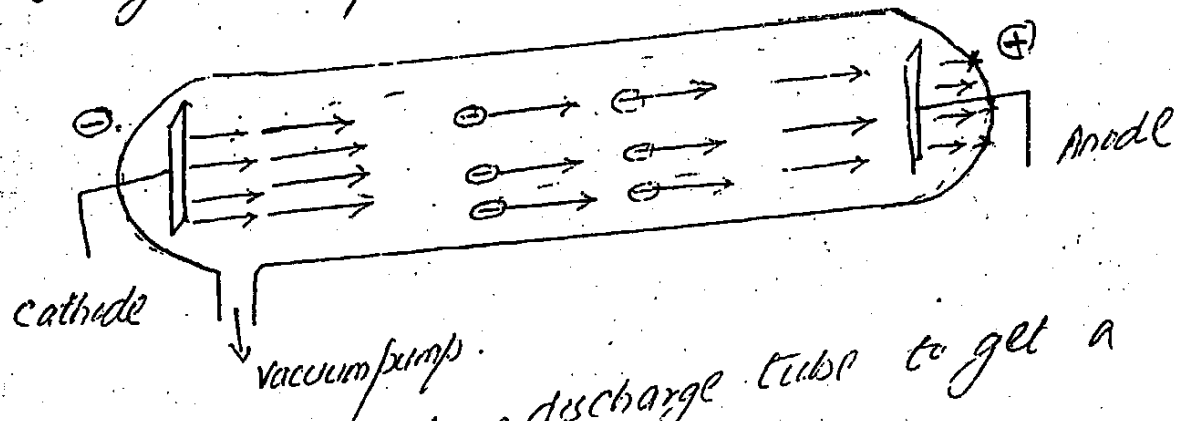
The charged particles possess following general properties

- 1) The electric current is movement of charged particles (electrons) in a conductor.
- 2) Oppositely charged particles attract each other and same charges repel each other.
- 3) When charged particles are passed through an electric field they are attracted towards oppositely charged electrodes. (The positive ion (cation) is attracted towards cathode and negative ion (Anion) is attracted towards Anode (+ve electrode)).
- 4) When charged particles are passed through a magnetic field, they bend at right angle to the line joining the north and south poles of magnet.
- 5) A sharp beam of charged particles could be obtained by using slits or holes.
- 6) Charged particles are not visible. Their presence and direction of movement can be determined by using photographic film or fluorescent material.
- 7) The force of attraction or repulsion between charged particles can be determined by Coulomb's law.

WHAT IS A GAS DISCHARGE TUBE?

A gas discharge tube is a glass tube having two electrodes sealed in it. It may contain a gas, air or vapours of some other substance at very low pressure. The electrodes are connected to a high voltage battery. It may be attached to a

ON SHAPES OF ~~Sphere~~
 um pump so that cona
 ough a gas may be sta. orbital has spherical
 neon sign is also a discharge tube which
 ion gas at a pressure of about 10^{-4} Torr in



A slit may be placed in discharge tube to get a sharp beam of radiations.

WILLIAM CROOKS EXPERIMENT LEADING TO DISCOVERY OF ELECTRON.

William Crooks performed a series of experiments using discharge tube to study passage of discharge through gases. He observed that gases do not conduct electricity at normal pressure even if electrodes are connected to high voltage battery (5000 volts).

But when pressure is reduced in discharge tube by using vacuum pump, gases begin to conduct electric current. A uniform glow is produced in the discharge tube. When pressure in discharge tube is further reduced to 0.01 Torr, the original glow disappears and fluorescence is produced on the side of Anode. This fluorescence is due to the collision of cathode rays on the glass tube. The nature of these rays remains the same for different electrodes and different gases used between two electrodes.

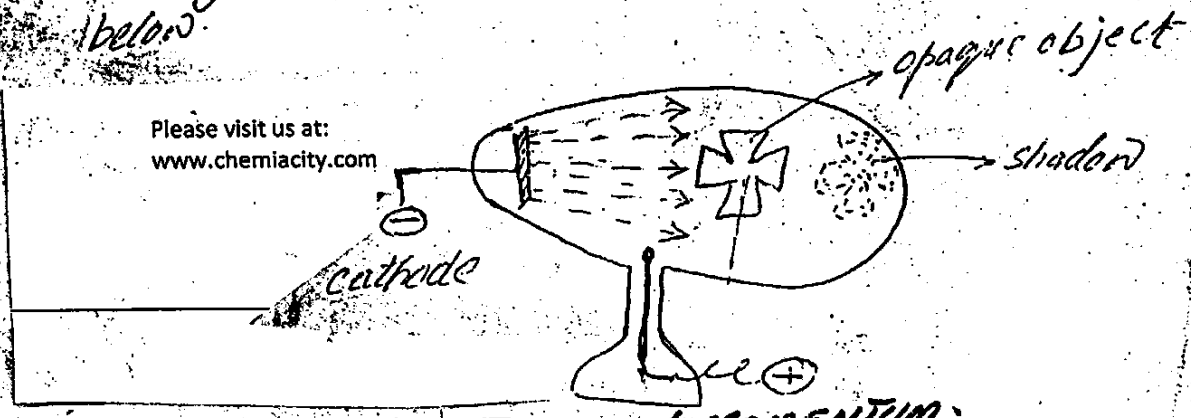
two electrodes. Later experiments showed that these cathode rays are actually moving electrons

EXPERIMENTS LEADING TO PROPERTIES OF CATHODE RAYS.

The characteristic properties of cathode rays have been determined on the basis of several experiments. These experiments have been discussed below.

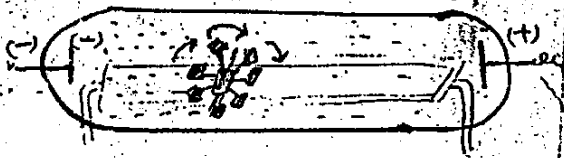
CAST A SHADOW:-

Hittorff observed that cathode rays travel in straight line and produce a sharp shadow when an opaque (non transparent) object is placed in their path. A specially designed discharge tube used for this purpose is shown below.



PARTICLES WITH ENERGY & MOMENTUM:

Crookes in 1870 experimentally proved that cathode rays have energy & momentum. They can move a pin wheel placed in their path. When paddles of pin wheel are hit by the cathode rays it moves towards anode. By reversing the battery the direction of pin wheel is reversed indicating that cathode rays always move from cathode to anode.



CATHODE RAYS ARE NEGATIVELY CHARGED. J. Perrin showed that when cathode rays are passed through an electric field they always bend towards positive plate indicating that they are negatively charged.

DESCRIBE J.J THOMSON EXPERIMENT FOR DETERMINATION OF $\frac{e}{m}$ RATIO OF CATHODE RAYS

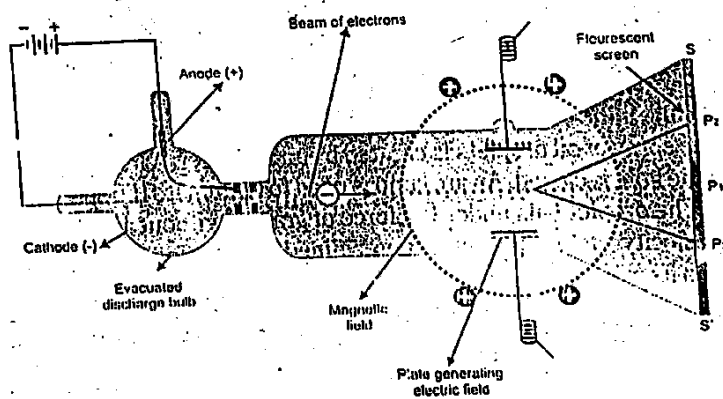
J.J Thomson used a specially designed discharge tube for determination of $\frac{e}{m}$ RATIO of cathode rays.

In absence of any electric or magnetic fields, cathode rays were striking at point P_1 on fluorescent screen.

When only magnetic field is applied, cathode rays strike at P_2 . When only electric field is applied cathode rays strike at point P_3 .

J.J Thomson subjected beam of cathode rays to simultaneous effect of electric and magnetic fields. The strength of these fields was adjusted such that cathode rays again struck at point P_1 .

In this way the electric and magnetic fields were balanced. He determined $\frac{e}{m}$ value of cathode rays and found it to be 1.7528×10^{11} C/kg. He was unable to determine "e" and "m" of cathode rays.



MILLIKAN OIL DROP EXPERIMENT DETERMINATION OF CHARGE & MASS OF ELECTRON.

In 1909 Millikan determined charge on electron by following arrangement.

CONSTRUCTION The apparatus consist of a metallic chamber which consist of two parts. The chamber is filled with air whose pressure can be adjusted.

particles and found was ...
 than 1.6022×10^{-19} Coulomb. This charge is acquired by
 particle when it picks up one electron from air.

MASS OF ELECTRON By using $\frac{e}{m}$ value and charge
 of electron, mass of electron can be calculated.

Putting value of "e"

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

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

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

$$\text{Mass of electron} = 9.1095 \times 10^{-31} \text{ kg} = m$$

PLANCK'S QUANTUM THEORY

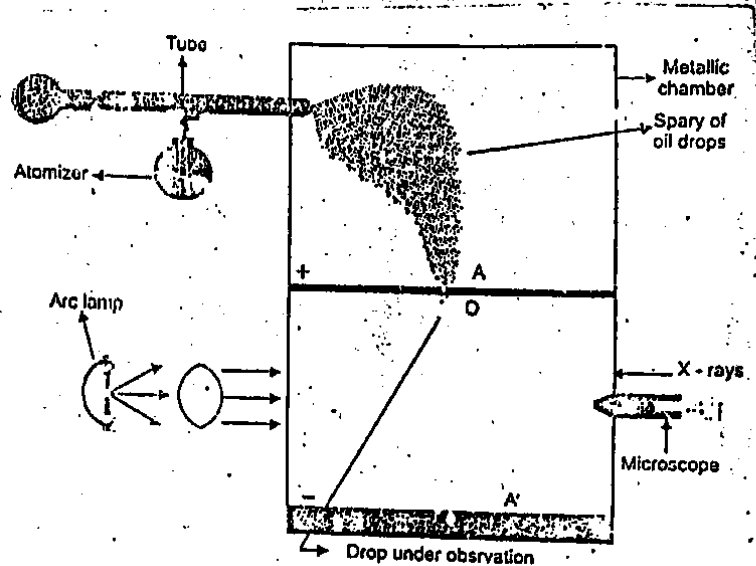
Max plank proposed quantum theory of radiation to explain
 emission and absorption of radiations. The main points of
 this theory are given below.

1. Energy is not absorbed or emitted continuously. It
 is absorbed or emitted in and the form of wave packets
 called quantum. Each quantum is associated with
 definite amount of energy. In case of light this
 quantum of energy is called PHOTON.
2. The energy of quantum is directly proportional to
 frequency of radiation $E \propto \nu$

"h" is called Planck's Constant. $E = h\nu$ — (1)
 $h = 6.625 \times 10^{-34} \text{ J.s.}$
 It is actually ratio of energy and frequency
 of photon.

$$\frac{E}{\nu} = h$$

There are two electrodes enclosed in it. The upper electrode has a hole in it.



A fine spray of oil droplets is introduced between in the chamber by an Atomizer. A few droplets enter in the hole. The hole is closed. An arc lamp is used to illuminate space between two electrodes. In absence of any electric field, the oil droplet falls under force of gravity. The velocity of droplet is determined. This velocity depends upon v_1 of droplet

$$v_1 \propto mg \quad \text{--- (1)}$$

When air between two electrodes is ionized by X-rays. The droplet picks up electrons and gets charged. The plates are connected to battery and an electric field is generated. Let strength of electric field is "H". The droplet moves upward due to electric field. The upward velocity is " v_2 ".

$$v_2 \propto He - mg \quad \text{--- (2)}$$

Dividing eq (1) by eq 2 -

$$\frac{v_1}{v_2} = \frac{mg}{He - mg}$$

When v_1 , v_2 and "H" are known. The mass of droplet can be determined by balancing of forces. Hence charge on droplet can be determined. Millikan determined charge on several thousand

3. A body can absorb or emit energy in terms of integral multiple of quantum (7)

$$E = n h \nu \quad \text{--- (2)} \quad n = 1, 2, 3, \dots$$

Since $c = \nu \lambda$ or $\frac{c}{\lambda} = \nu$

Thus eq. no. 1 could be written as

$$E = \frac{h c}{\lambda} \quad \text{--- (3)}$$

$$E \propto \frac{1}{\lambda}$$

Eq. (3) shows that greater the wavelength lesser is the energy.

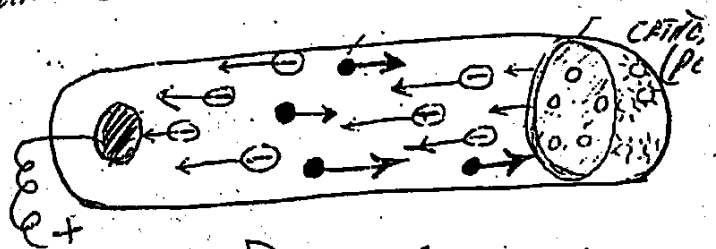
WAVE NUMBER $\bar{\nu}$. It is defined as number of waves per unit length $\bar{\nu} = \frac{1}{\lambda}$ Thus eq (3) can be written as

$$E = h c \bar{\nu} \quad \text{--- (4)}$$

Greater the wave number, greater is the energy of photon $E \propto \bar{\nu}$

Thus energy of photon is related to energy, frequency, wavelength and wave number.

POSITIVE RAYS & DISCOVERY OF PROTONS



Eugene Goldstein in 1886

performed a series of experiments in which he used a special discharge tube with perforated cathode. (Above fig).

He observed fluorescence at the end of tube opposite to anode. This fluorescence is due to rays travelling in a direction opposite to cathode rays. When a perforated cathode is used they pass through these openings hence these are called canal rays. They possess following characteristics.

- 1) They travel in a straight line towards cathode.
- 2) They produce fluorescence on striking walls of discharge.

3. In an applied electric field they bend towards the anode indicating that they are positively charged.
4. These are produced by ionization of gaseous atoms present between two electrodes.
5. The properties of cathode rays depend upon nature of gas present between two electrodes.
6. Their charge over mass ratio (e/m) is less than cathode rays (due to their greater mass).
7. The maximum e/m ratio is obtained for hydrogen gas.
8. The charge on positive rays is never less than that of a proton.
9. The lightest and simplest canal rays are formed when gas discharge tube contains hydrogen gas. The positive charge of this hydrogen ion was found to be $1.6022 \times 10^{-19} \text{ C}$ which is equal to charge of electron.
10. The mass of hydrogen ion was calculated to be $1.6726 \times 10^{-27} \text{ kg}$. This positive ray particle is now called PROTON.

Later on Rutherford showed that the protons are also fundamental particles of atom.

DISCOVERY AND PROPERTIES OF NEUTRONS:

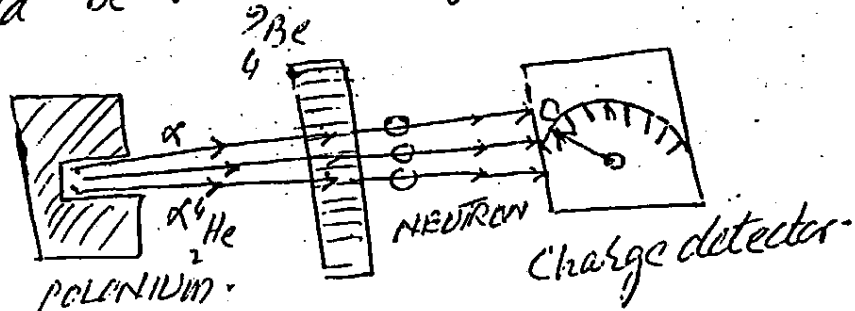
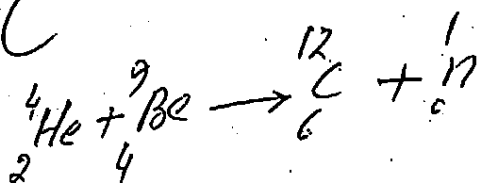
(9)

Upto 1932 it was thought that atom is composed of only protons and electrons. However Rutherford noticed that Atomic masses of atoms could not be explained if it is supposed that it is composed of electrons and protons. Rutherford predicted that some kind of neutral particles having mass equal to mass of proton must be present in atom.

Chadwick in 1935 discovered Neutron in 1935.

EXPERIMENT. Chadwick bombarded a stream of α -particles on Beryllium. Some radiations were given out from Beryllium. The charge detector showed that these radiations are neutral and their mass was equal to mass of proton. These radiations were called NEUTRONS.

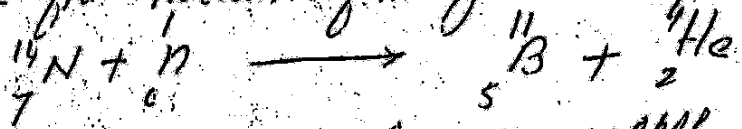
The nuclear reaction could be written as follows



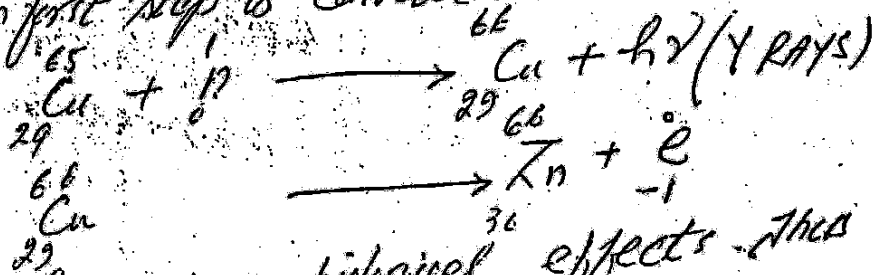
PROPERTIES OF NEUTRONS

1. Free neutrons are unstable and they change into proton, electron and neutrino $\text{n} \rightarrow \text{p} + \text{e} + \bar{\nu}$
2. Neutron cannot ionize gases.
3. Neutrons are highly penetrating kind of particles.
4. They can expel high speed protons from paraffin, paper, cellulose etc.
5. Neutrons with an energy 1.2 MeV are called fast moving neutrons while neutrons with energy less than 1 eV are called slow moving neutrons. Slow neutrons are usually more effective than fast moving neutrons for fission process.

6. When neutrons are used as projectile, they can cause out nuclear reactions. A fast neutron can project Eject an α -particle from nucleus of nitrogen atom and Boron is produced



7. When slow moving neutrons hit the copper metal γ -radiations are produced. The radioactive copper produced in first step is converted into Zinc.

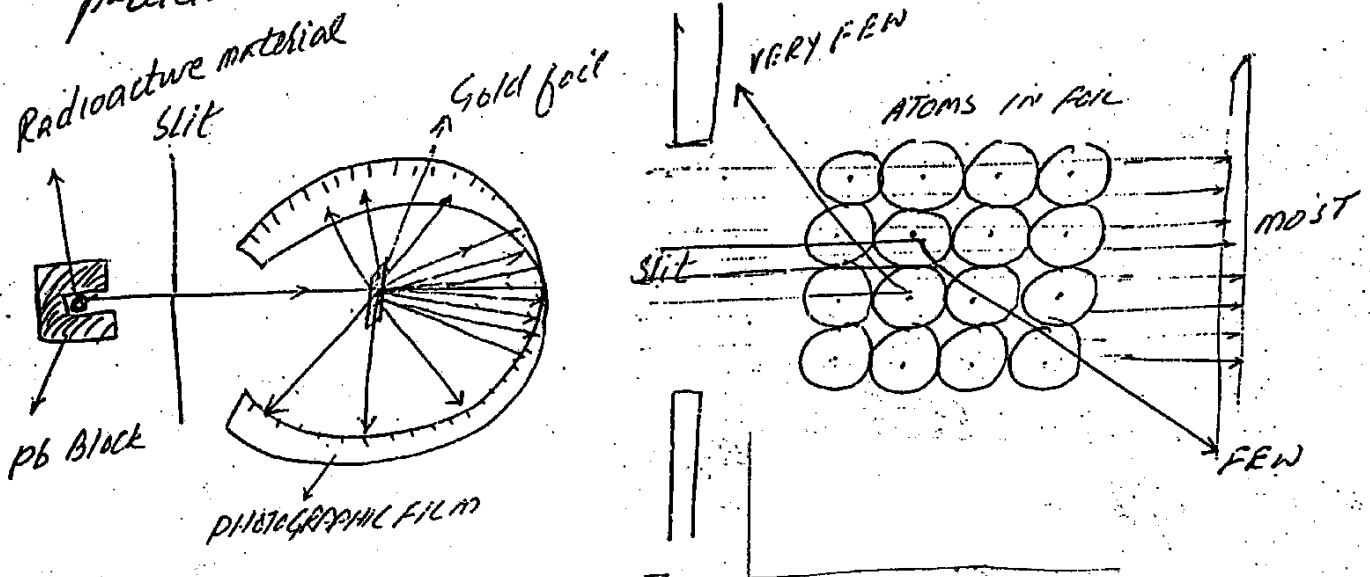


8. Neutrons have intense biological effects. Thus they are being used in treatment of cancer.

DISCOVERY OF NUCLEUS. (RUTHERFORD'S EXPT.)

Rutherford bombarded a thin gold foil with α -particles. These α -particles were obtained from a radioactive element polonium. A slit of lead was used to get a beam of α -particles.

It was observed that most of α -particles passed straight through the foil. A few α -particles were deflected from their path. Very few α -particles were bounced back.



CONCLUSIONS: From this experiment Rutherford concluded that since most of α -particles passed straight through the foil so most of space in an atom is empty. The deflection of a few α -particles from their path indicated that there is positively charged body present in the centre of atom. It is called NUCLEUS. All positive charge and almost all mass of atom is concentrated in nucleus. Only a small portion ($\frac{1}{100000}$ th of atom) of atom is occupied by solid body nucleus. The most of volume is occupied by extranuclear electrons.

RUTHERFORD'S ATOMIC MODEL:

Rutherford on the basis of his experiment proposed following model of an atom, which is similar to solar system.

According to Rutherford's atomic model

1) All positive charge and almost all mass of atom is concentrated in its central body called NUCLEUS.

2) Electrons revolve around nucleus. The number of electrons are equal to number of protons. So atom as a whole is electrically neutral.

3) The negatively charged electrons are revolving around nucleus (like planets around sun). The electrostatic force of attraction between electrons and nucleus provides the centripetal force.

4) All particles of atom except electrons are present in the nucleus, these are called Nucleons.

This Rutherford's atomic model was based upon laws of motion and laws of gravitation.

DEFECTS IN RUTHERFORD'S ATOMIC MODEL:

1) The laws of motion and gravitation are easily applicable to neutral bodies like planets, these could not be applied to the charged bodies like protons and electrons.

2) According to Maxwell theory any electron revolving around nucleus must emit energy continuously. Thus electron should acquire spiral path & into the nucleus and atom should collapse. But it never happens.

3) If electron is continuously revolving, and it emits energy continuously, so a continuous spectrum should be obtained. But in actual practice a line spectrum is obtained.

BOHR'S ATOMIC MODEL

In order to remove defects in Rutherford's atomic model Bohr developed a model of hydrogen atom in 1913. The main points of Bohr's atomic model are given below.

- 1) The electron in hydrogen atom can move around nucleus in a circular pathway called ORBIT.
- 2) As long as an electron remains in its fixed orbit it does not absorb or evolve energy.
- 3) An electron loses energy when it jumps from higher to lower energy orbit. It absorbs energy when it jumps from lower to higher energy orbit. The energy absorbed or evolved is equal to difference of energy between two orbits.

$$\Delta E = E_2 - E_1$$

This energy is emitted as radiations

$$\Delta E = h\nu$$

- 4) The angular momentum of electron is integral multiple of $\frac{h}{2\pi}$. It means angular momentum is quantized.

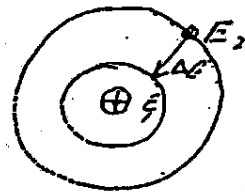
$$mvr = n \frac{h}{2\pi}$$

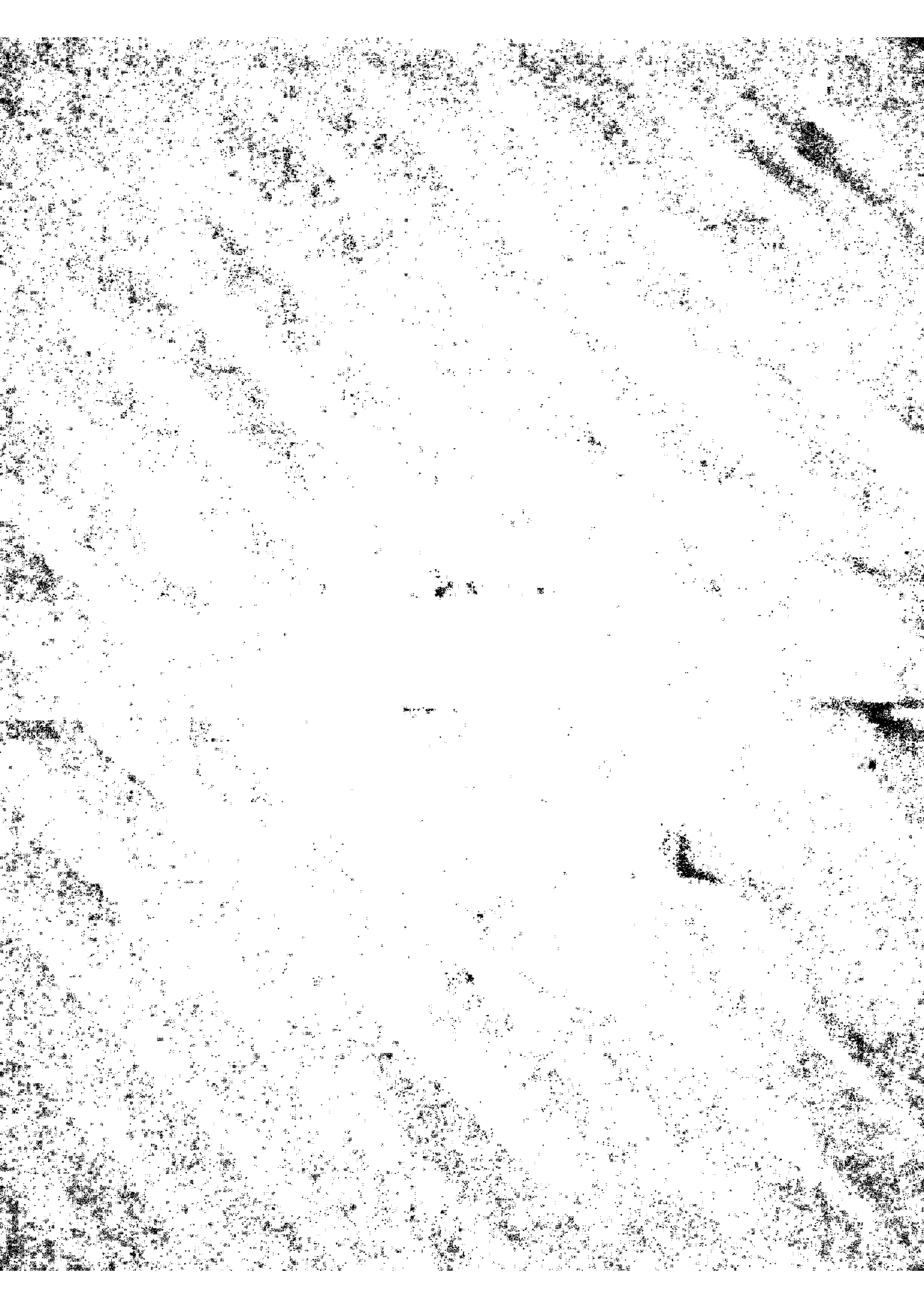
$$n = 1, 2, 3, 4, \dots$$

m = mass of electron, v = velocity of electron
 r = radius of orbit, h = plank's constant.

On the basis of these postulates Bohr not only presented a model of hydrogen atom but also a model for other atoms. He also explain spectrum of hydrogen.

Bohr assumed that nucleus of hydrogen atom which is 1836 times heavier than





For electron of charge " e " and nucleus of charge " Ze " it could be written as

$$F = \frac{Ze \times e}{4\pi\epsilon_0 r^2}$$

$$F_c = \frac{Ze^2}{4\pi\epsilon_0 r^2} \quad \text{--- (2)}$$

Putting value of " F " in equation (1) we get

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

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

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

From Bohr's postulates $mvh = n \frac{h}{2\pi}$
 $v = \frac{n h}{2\pi m r}$

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

Putting value of " v^2 " in equation (4) we get

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

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

$$r = \frac{n^2 h^2 \epsilon_0}{\pi m Ze^2} \quad \text{--- (5)}$$

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

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

$$(a_0 = \frac{\epsilon_0 h^2}{\pi m e^2})$$

For hydrogen $n=1$ $Z=1$

$$r = a_0$$

$$r = 0.529 \text{ \AA} \quad (r = 5.29 \times 10^{-11} \text{ m})$$

" a_0 " is called Bohr radius.

ENERGY OF ELECTRON

The total energy of electron revolving around nucleus is sum of K.E due to its motion and P.E. due to its attraction towards nucleus.

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

Kinetic energy is given by expression $K.E = \frac{1}{2} m v^2$

Putting value of " $m v^2$ " from eq (3) we have

$$K.E = \frac{1}{2} \left(\frac{Z e^2}{4 \pi \epsilon_0 r} \right)$$

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

According to Coulomb's law attraction between electron and nucleus separated by distance " r " is

$$P.E = - \frac{Z e \times e}{4 \pi \epsilon_0 r}$$

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

$$\left[\begin{aligned} P.E &= F \times r \\ &= \frac{Z e^2}{4 \pi \epsilon_0 r^2} \times r \\ P &= \frac{Z e^2}{4 \pi \epsilon_0 r} \end{aligned} \right.$$

The negative sign indicates attraction between electron and nucleus giving algebraically lower energy at a shorter distance

$$E = - \frac{Z e^2}{4 \pi \epsilon_0 r} + \frac{Z e^2}{8 \pi \epsilon_0 r}$$

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

$$E = - \frac{Z e^2}{8 \pi \epsilon_0 r}$$

Putting value of "r" in eq. (6) from eq (5)

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

$$E = \frac{-ze^2}{8\pi\epsilon_0 n^2 h^2 \epsilon_0} \times \pi m e^2 z$$

$$E = \frac{-z^2 e^4 m}{8\epsilon_0^2 h^2 n^2}$$

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

Substituting values of "e", "m", ~~h~~ "h" eq. can be written as $E =$

$$E = -2.18 \times 10^{-18} \text{ J } \frac{z^2}{n^2} \quad \text{--- (8)}$$

When "n = 1" the energy is minimum and it is called ground state. All other states with value of "n" higher than "1" are called excited states -
for hydrogen atom

For hydrogen atom in ground state

$n = 1 \quad z = 1$

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

The energy of electron depends upon value of "n" and is called principle quantum number

CALCULATION OF ENERGY, FREQUENCY, WAVELENGTH, WAVE NUMBER OF PHOTON EMITTED.

According to Bohr's Atomic model when an electron jumps from high energy orbit to low energy orbit, it emits energy in the form of photon.

$$\Delta E = E_2 - E_1$$

From equation (7) " E_2 " and " E_1 " is given by

$$E_2 = -\frac{z^2 e^4 m}{8 \epsilon_0^2 h^2 n_2^2} \quad \phi \quad E_1 = -\frac{z^2 e^4 m}{8 \epsilon_0^2 h^2 n_1^2}$$

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

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

For hydrogen atom

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

Since $\Delta E = h\nu$

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

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

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

WAVE NUMBER CALCULATION

$$\bar{\nu} = c\nu$$

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

$$\bar{\nu} = \frac{z^2 e^4 m}{8 \epsilon_0^2 h^3 c} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \text{--- (11)}$$

$$\bar{\nu} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \text{--- (12)}$$

"R" is called Rydberg constant $= 1.0974 \times 10^7 / \text{m}$

The values of all these wave numbers lie in U.V. region of γ spectrum. This when electron of hydrogen atom jumps from any high energy orbit to first orbit, radiations which are emitted lie in U.V. region.

BALMER SERIES

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

FIRST LINE

$n_1 = 2$ $n_2 = 3$
 $\bar{\nu} = 1.09672 \times 10^7 \left(\frac{1}{2^2} - \frac{1}{3^2} \right)$
 $\bar{\nu} = 15.234 \times 10^5$

SECOND LINE

$n_1 = 2$
 $n_2 = 4$

$\bar{\nu} = 1.09672 \times 10^7 \left(\frac{1}{2^2} - \frac{1}{4^2} \right)$
 $= 20.566 \times 10^5 \text{ m}^{-1}$
 $\bar{\nu} = 23.0 \times 10^5 \text{ m}^{-1}$

THIRD LINE

$n_1 = 2$
 $n_2 = 5$

$\bar{\nu} = 1.09672 \times 10^7 \left(\frac{1}{2^2} - \frac{1}{\infty^2} \right)$

LIMITING LINE

$n_1 = 2$
 $n_2 = \infty$

$\bar{\nu} = 27.421 \times 10^5 \text{ m}^{-1}$

The limiting line lies in U.V. region while remaining lines lie in visible region of spectrum.

Similarly wave numbers of Paschen, Brackett and Pfund series can be calculated (HELP YOURSELF)

NAME OF SERIES	n_1	n_2	FIRST LINE	SECOND LINE	LIMITING LINE
PACHEN SERIES	3	4, 5, ... ∞	_____	_____	_____
BRACKETT SERIES	4	5, 6, ... ∞	_____	_____	_____
P-FUND SERIES	5	6, 7, ... ∞	_____	_____	_____

The values of all these wave numbers lie in U.V. region of spectrum. Thus when electron of hydrogen atom jumps from any high energy orbit to first orbit, radiations which are emitted lie in U.V. region.

BALMER SERIES

FIRST LINE

$n_1 = 2$ $n_2 = 3, 4, 5, \dots$
 $n_1 = 2$ $n_2 = 3$
 $\bar{\nu} = 1.09678 \times 10^7 \left(\frac{1}{2^2} - \frac{1}{3^2} \right)$

SECOND LINE $n_1 = 2$
 $n_2 = 4$

$\bar{\nu} = 1.5234 \times 10^5$
 $\bar{\nu} = 1.09678 \times 10^7 \left(\frac{1}{2^2} - \frac{1}{4^2} \right)$
 $= 20.566 \times 10^5 \text{ m}^{-1}$
 $\bar{\nu} = 23.0 \times 10^5 \text{ m}^{-1}$

THIRD LINE $n_1 = 2$
 $n_2 = 5$

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

LIMITING LINE $n_1 = 2$
 $n_2 = \infty$

$\bar{\nu} = 27.421 \times 10^5 \text{ m}^{-1}$

The limiting line lies in U.V. region while remaining lines lie in visible region of spectrum.

Similarly wave numbers of Paschen, Brackett and Pfund series can be calculated (HELP YOURSELF)

NAME OF SERIES

n_1

n_2

FIRST LINE

SECOND LINE

LIMITING LINE

PASCHEN SERIES

3

4, 5, ... ∞

BRACKETT SERIES

4

5, 6, ... ∞

P-FUND SERIES

5

6, 7, ... ∞

DEFECTS IN BOHR'S ATOMIC MODEL

1. SPECTRUM OF POLYELECTRON SYSTEM Bohr's atomic model can explain origin of spectrum of 'H' atom and ions like He⁺, Li²⁺, Be³⁺ etc. These are one electron systems. But Bohr theory cannot explain origin of spectrum of multielectron or polyelectron systems like He, Li, Be etc

2. FINE STRUCTURE OF H-ATOM when spectrum of H-atom is observed in high resolving power spectrometer, spectral lines are replaced by some fine lines. For example H α -line of hydrogen splits up into fine lines. This is called fine structure or multiple structure. Bohr's atomic model cannot explain multiple structure.

3. THREE DIMENSIONAL STRUCTURE According to Bohr's atomic model, electron revolves around nucleus in circular path called ORBIT. But researches have shown that motion of electron is not in a single plane. It takes place in three dimensional space. Actually atomic model is not FLAT.

4. ZEEMAN EFFECT when excited H-atoms are placed in magnetic field, the spectral lines further split up. This is called ZEEMAN EFFECT. In case of sodium spectrum, is placed in magnetic field, two spectral lines split up into component lines. Bohr's atomic model cannot explain Zeeman effect.

5. STARK EFFECT when ~~spectral lines of~~ excited hydrogen atoms are placed in electrical field then spectral lines undergo splitting. It is called STARK EFFECT. Bohr's atomic model cannot explain Stark effect.

SUMMERFELD MODIFICATION:

Dr Sommerfeld suggested that in addition to circular orbits, electron may revolve in elliptical orbits with nucleus situated at one of foci of ellipse. This elliptical path of e⁻ goes on changing their position in space. Center nucleus buried in by electron cloud from all sides.



WAVE PARTICLE NATURE OF ELECTRON.

In 1905 Einstein in his theory of photoelectric effect showed that light has both wavelike and particle like properties.

LIOWS de-BROGLIE HYPOTHESIS: In 1924 a French scientist predicted that all atomic particles have wave like properties. The wave length of these particles can be calculated as follows. According to Einstein eq. $E = mc^2$ — (1)

According to planks equation $E = h\nu$ — (2)
 Comparing eq (1) and (2) we have $h\nu = mc^2$
 (or since $c = \nu\lambda$ or $\frac{c}{\lambda} = \nu$) $\therefore \frac{hc}{\lambda} = mc^2$

This is an equation for wavelength of photon. For any other particle of mass "m" moving with velocity "v" the wavelength can be written as $\frac{h}{mv} = \lambda$ — (3)

DAVISON and GERMER experimentally proved that electrons were waves with very short wavelength. Electrons were produced from heated tungsten filament and accelerated through charged plates. Davison and Germer showed that accelerated electrons undergo diffraction like waves. When they are allowed to fall on a Nicked Crystal. In this way wave nature of electron was verified.

WAVELENGTH OF ELECTRON/ velocity of electron = 2.122×10^6 m/sec
 $h = 6.625 \times 10^{-34}$ Jsc
 mass of $e^- = 9.1 \times 10^{-31}$ kg
 $\lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34}}{9.1 \times 10^{-31} \times 2.122 \times 10^6} = 0.33 \times 10^{-10}$ m
 $= 0.33 \text{ \AA}$

This wavelength is comparable to wavelength of X-rays. It can be measured via wavelength of proton moving with same velocity is 1836 times less than "e" while λ of α -particles is 7344 times smaller than that of e^- . Let us consider " λ " of a stone of mass "m" = 1g and $v = 10$ m/sec $\lambda = 6.65 \times 10^{-30}$ m. This wavelength is not measurable. Thus we can say that MACROSCOPIC bodies do not have wavelike properties.

HEISENBERG'S UNCERTAINTY PRINCIPLE

It is impossible to determine both position and momentum of a moving body both correct at a time. The more accurately we determine the position, the least accurate is its momentum and vice versa. Suppose uncertainty in position is Δx and uncertainty in momentum is Δp . Then

$$\Delta p \times \Delta x \geq \frac{h}{2\pi}$$

The uncertainty principle is applicable to only microscopic particles like electrons, neutrons etc. It has no significance for large size particles i.e. macroscopic particles.

Heisenberg uncertainty principle can be understood from Compton effect. Suppose we want to locate position of electron. Visible light cannot be used for this purpose because its wavelength is larger than diameter of e^- . X-rays are used for this purpose. When X-ray photon strikes e^- its momentum will change. Thus change in momentum of e^- is responsible for uncertainty of momentum of e^- . The smaller the wavelength of X-rays photon, greater is its energy. This will bring larger change uncertainty in momentum of e^- . Thus in order to locate position of e^- , its momentum is disturbed (becomes uncertain). And if we use photon of longer wavelength to avoid change in its momentum of electron, the position of electron cannot be determined.

Thus due to wave-particle nature of electron, it is not possible to measure both position and momentum of e^- both correct at a time.

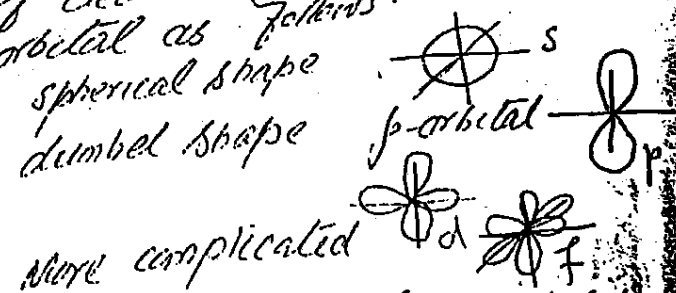
PAGE OR NOTE ON QUANTUM NUMBERS. 25

The properties of electron (eg, energy, shape, orbital and orientation in space) is determined by the values four quantum numbers. These four quantum numbers are: azimuthal quantum number " l ", principle quantum number " n ", magnetic quantum no. " m " and spin quantum number " s ". The first three quantum numbers arise from solution of Schrodinger equation. The fourth quantum number is due to two ways in which an electron may be aligned in an external magnetic field.

PRINCIPLE QUANTUM NUMBER: - " n "
 This quantum number tells the distance of electron from nucleus and its energy. The value " n " may be any integral value 1, 2, 3, 4, ... ∞ . The lower the value of " n " the closer is the electron and the lower is the energy of electron. The higher the value of " n " the greater is the energy of electron and larger is the distance from nucleus. This quantum number is the same as simple integer in Bohr's atomic model. ($mvr = n \frac{h}{2\pi}$)
 $n=1$ K-shell, $n=2$ "L" shell, $n=3$ "M" shell, ...

AZIMUTHAL QUANTUM NUMBER " l "
 This quantum number describes the shape of an orbital. It also contributes to energy of electron but much lesser extent than " n ". Its value may be 0, 1, 2, 3, ... $n-1$. However its value cannot exceed " n " due to limited number of electrons. The value of " l " indicates shape of an orbital as follows:

- $l=0$ s-orbital
- $l=1$ p-orbital
- $l=2$ d-orbital
- $l=3$ f-orbital



For example when $n=1$
 when $n=2$

$l=0$ "1s" Main level and sub-level are same
 $l=0$ 2s
 $l=1$ 2p Two sublevels in second energy level
 $n=3$ $l=0$ 3s
 $l=1$ 3p Three sublevels in third energy level and spin
 $l=2$ 3d

$n = 4$

- $l = 0$ 4s
 1 4p
 2 4d
 3 4f

These are four energy sublevels in fourth level.

Each shell has subshells equal to its principle quantum number "n".

MAGNETIC QUANTUM NUMBER "m" It gives orientation

of an orbital and magnetic properties of electron. The value of "m" varies from $-l$ to $+l$ through zero.

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

Consider following table

n	l	(subshell)	m	Remarks
1	0	(1s)	0	1s One possible orientation i.e. spherical
2	0	(2s)	0	2s } 2p _x } 2p _y } 2p _z } "p" orbital has three possible orientation parallel to three co-ordinate axis x, y, z
	1	(2p)	+1	
			0	
			-1	
3	0	(3s)	0	3s } 3p _x } 3p _y } 3p _z } 3d _{xy} } 3d _{yz} } 3d _{xz} } 3d _{x²-y²} } 3d _{z²} } Five possible orientation of d-orbital.
	1	(3p)	+1	
			0	
			-1	
	2	(3d)	+2	
			+1	
		0		
		-1		
		-2		
			3d _{z²}	

SPIN QUANTUM NUMBER "ms"

This quantum number is associated with spin of electron. All electrons spin either in clockwise or anticlockwise direction.

The direction of spin can be found out by application of an external magnetic field. Since probability of spin in each case is 50% clockwise and 50% anticlockwise therefore spin quantum number has value $+\frac{1}{2}$ or $-\frac{1}{2}$.



$+\frac{1}{2}$



$-\frac{1}{2}$

(Note Draw Table over here from P. No -

TABLE OF QUANTUM NUMBERS.

n	l	m	m _s	No. of electrons	Electron state	Total No. of electrons	Shell	
1	0	0	$\pm \frac{1}{2}$	2	1s	2	K-SHELL	
2	0	0	$\pm \frac{1}{2}$	2	2s } 2p }	8	L-SHELL	
	1	+1	$\pm \frac{1}{2}$	6				
		0	$\pm \frac{1}{2}$					
		-1	$\pm \frac{1}{2}$					
3	0	0	$\pm \frac{1}{2}$	2	3s } 3p } 3d }	18	M-Shell	
	1	0	$\pm \frac{1}{2}$	6				
	2	+1	$\pm \frac{1}{2}$					
		0	$\pm \frac{1}{2}$					
		0	0	$\pm \frac{1}{2}$				10
		+1	$\pm \frac{1}{2}$					
		-1	$\pm \frac{1}{2}$					
	0	$\pm \frac{1}{2}$						
4	0	0	$\pm \frac{1}{2}$	2	4s } 4p } 4d } 4f }	32	N-SHELL	
	1	+1	$\pm \frac{1}{2}$	6				
		0	$\pm \frac{1}{2}$					
		-1	$\pm \frac{1}{2}$					
	2	+2	$\pm \frac{1}{2}$	10				
		+1	$\pm \frac{1}{2}$					
	0	$\pm \frac{1}{2}$						
	-1	$\pm \frac{1}{2}$						
3	+3	$\pm \frac{1}{2}$	14					
	+2	$\pm \frac{1}{2}$						
	+1	$\pm \frac{1}{2}$						
	0	$\pm \frac{1}{2}$						



RULES FOR DISTRIBUTION OF ENERGY SUB-LEVELS

The filling of electrons in energy sub-levels takes place according to following Rules.

"AUF-BAU PRINCIPLE":- According to this rule, "The electron enters in lowest possible energy level." In other words the electrons are placed in orbitals in order of increasing energy values.

It means ^{first} electron will enter in the orbital of lowest energy i.e. 1s orbital. Thus electrons will be filled in the orbitals in following order

1s 2s 2p 3s 3p 4s 3d 4p 5s 4d ...

WISWESSER RULE "(n+l) RULE" According to this rule "The energy of orbital is determined from n+l value. The orbital with least value of n+l will have lowest energy. The orbital with greater value of (n+l) will have higher energy."

Thus electron will first enter in that orbital which has low (n+l) value (low energy). If two orbitals have equal (n+l) value, then electron will enter in that orbital which has low "n" value.

For example there is straight forward filling of electrons up to atomic number "18".

Ar .. 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁰ 4s²

For an element with atomic number "19" (Potassium) the 19th electron may enter in 3d (which is vacant) or 4s (which is also vacant)

For 4s orbital

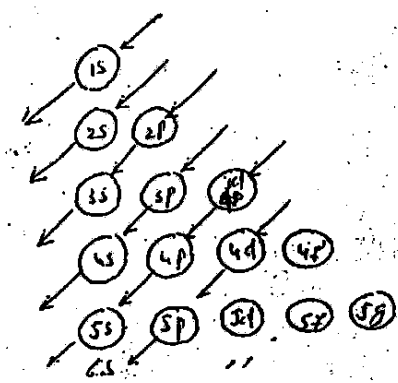
$$n = 4, \quad l = 0$$

$$n + l = 4 + 0 = 4$$

For 3d

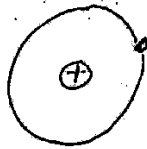
$$n = 3, \quad l = 2$$

$$n + l = 3 + 2 = 5$$



DEFINE AND EXPLAIN FOLLOWING

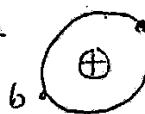
PAULI EXCLUSION PRINCIPLE - It is defined as "No two electrons in the same orbital can have same set of four quantum numbers." It can also be defined as "The spin of two electrons in the same orbital is always opposite." Let us consider electronic config of Hydrogen



For this electron present in "1s" four quantum numbers are

$$n=1, l=0, m=0, s=+\frac{1}{2}$$

If another electron is added to the same shell (as in Helium (1s²)) For second electron "b"



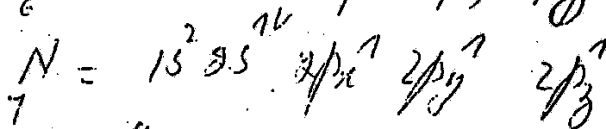
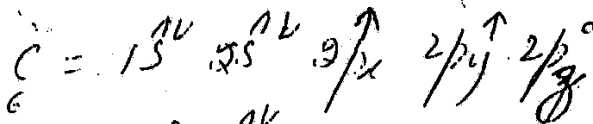
$$n=1, l=0, m=0, s=-\frac{1}{2}$$

The second electron can be accommodated in the same subshell only if its spin is opposite to the first one. Thus for electrons "a" and "b" their quantum numbers are same (n, l, m) but fourth is opposite.

HUND'S RULE :- If two orbitals of equal energy are available to two electrons they will prefer to live separately and have same spin rather than live in same orbital and have opposite spin.

In other words $\uparrow \uparrow$ is more stable than $\uparrow \downarrow$ provided two circles indicate orbitals of equal energy.

According to Hund's Rule Carbon has following configuration



"p_x" "p_y" and "p_z" are orbitals of equal energy.

SPECTRUM

The visual display or dispersion of components of white light is called spectrum. When a radiation of light is passed through a prism, the radiation undergo refraction or bending. The angle of refraction depends upon wavelength. The radiation with smaller wavelength bends the most and least with longer wavelength bends the least.

Ordinary light consist of radiations of all wavelengths thus it splits into radiations of different wavelengths after passing through prism. A complete spectrum can be divided into two main regions

(a) Visible Region

VISIBLE REGION It consist of waves of wavelength 400 nm to 750 nm. It consist of violet, Indigo, blue, green, yellow, orange & red. These radiations are visible to naked eye.

INVISIBLE REGION It can be further divided into two parts

U.V. REGION It includes waves whose wavelength are less than violet. They possess proteins or shorter wavelength and greater energy. The regions below violet are U.V., X-RAYS, γ -RAYS, Cosmic Ray.

I.R. REGION It consist of waves whose wavelength are larger than red coloured waves. It includes I.R., Microwave, radiowaves, T.V. waves. A complete spectrum is shown below.

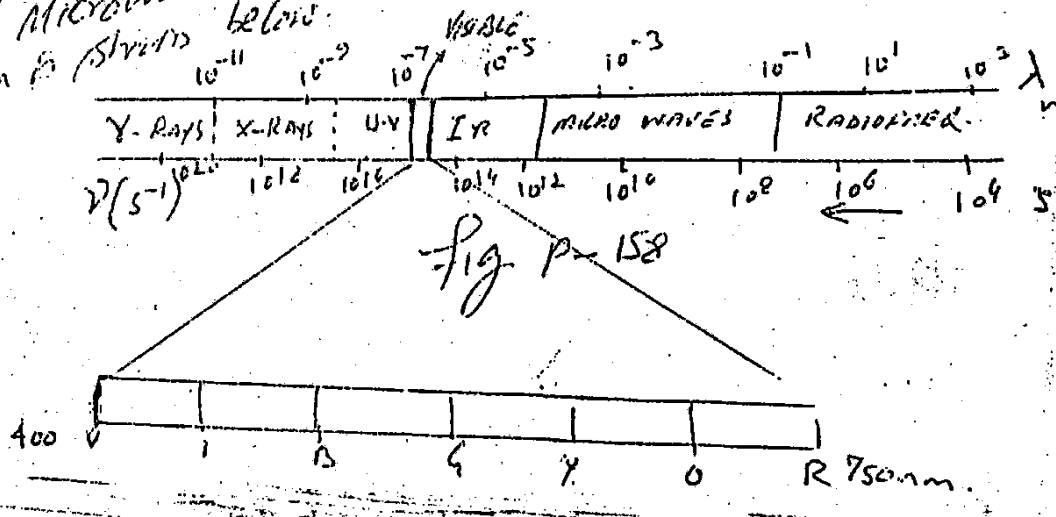


Fig P-158

TYPES OF SPECTRUM

In this type of spectrum the different wavelengths are so close to each other that they are merged into one another. One colour merges into other without any dark space.

The best example of continuous spectrum is Rainbow. It is obtained by light emitted by sun or electric light. It is characteristic of matter in BULK.

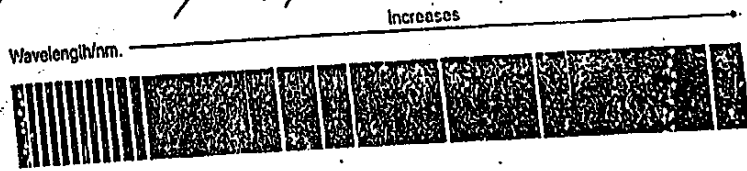
ATOMIC SPECTRUM OR LINE SPECTRUM

The spectrum in which waves corresponding to different wavelengths are separated from each other by dark and bright lines is called LINE SPECTRUM.

For example when an element or compound is volatilized in a flame and light emitted is seen through spectrometer, we can see distinct lines separated by dark spaces. This is called line spectrum or Atomic spectrum.

The number of lines and distance between lines depend upon nature of element volatilized. For example line spectrum of sodium contains two yellow coloured lines separated by definite distance.

Similarly spectrum of hydrogen consist of a number of lines of different colours having different distances. It has been observed that distance between lines decreases with decrease in wavelength. After a certain wavelength spectrum becomes continuous.



Atomic spectrum can also be observed when element in gaseous state is heated at high temperature or subjected to an electric discharge.

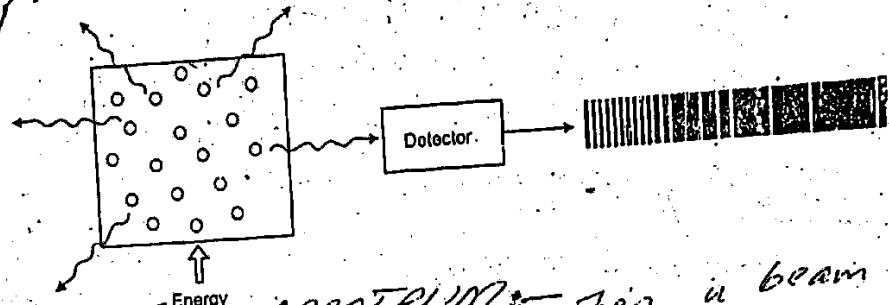
TYPES OF ATOMIC SPECTRUM

(i) Atomic Emission Spectrum

(ii) Atomic Absorption Spectrum

ATOMIC EMISSION SPECTRUM

When solids are volatilized or elements in gaseous state are heated high temp. or subjected to an electrical discharge. Radiations are emitted. The spectrum of these radiations consist of bright lines against dark background. This is called ATOMIC EMISSION SPECTRUM.



ATOMIC ABSORPTION SPECTRUM

When a beam of white light is passed through a gaseous sample of an element, the element absorbs certain wavelengths while some wavelengths pass through it. The spectrum of this radiation is called ATOMIC ABSORPTION SPECTRUM. It consists of dark lines against bright background. Each dark line indicates wavelength which has been absorbed by gaseous elements.

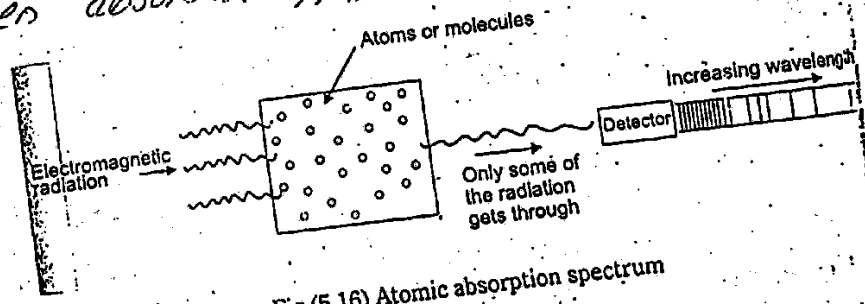
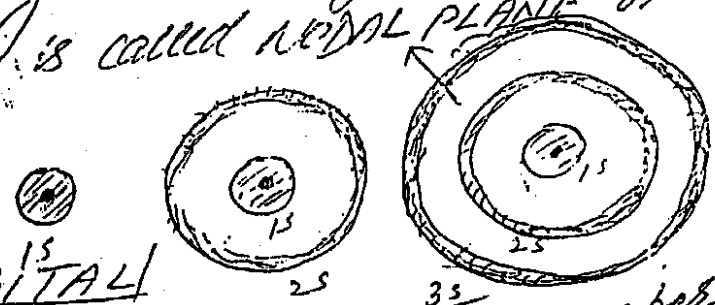


Fig (5.16) Atomic absorption spectrum

It must be noted that absorption spectrum and emission spectrum are identical with respect to position of lines and number of lines. In emission line spectrum each bright line indicates wavelength as emitted by element while in absorption spectrum each line indicates wavelength absorbed by element.

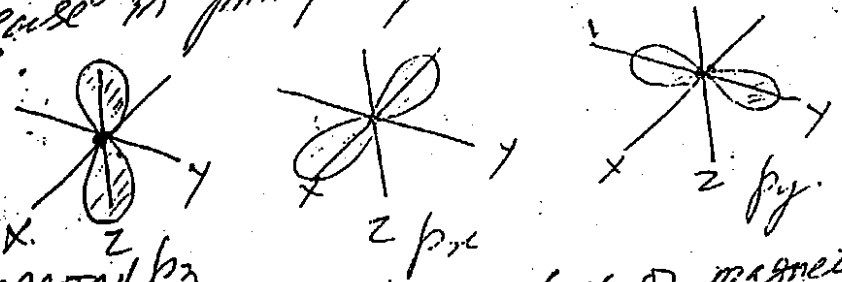
WRITE A NOTE ON SHAPES OF "s" ORBITALS

SHAPE OF "s" - ORBITAL "s" orbital has spherical shape. It is usually represented by a circle which represents a cut of a sphere. With increase in value of principle quantum number "n" the size of s-orbital increases. 2s is larger in size than 1s orbital. Further 2s is farther away from nucleus. The probability of finding electron is zero between two orbitals. This space is called NODAL PLANE or NODAL SURFACE.



SHAPES OF p-ORBITAL

There are three values of magnetic quantum number for p-subshell. Thus p-orbital has three orientations in space i.e. p_x , p_y , p_z . These three are dumb-bell shape. Thus p-orbital has directional character which determines geometry of molecule. All "p" orbitals of all energy levels have similar shapes. But with increase in principle quantum number their sizes increase.



SHAPE OF "d" ORBITAL

There are five values of magnetic quantum number for d-subshell. Thus there are five space orientations along x-axis, y-axis and z-axis. These are designated as d_{xy} , d_{yz} , d_{xz} , $d_{x^2-y^2}$, d_{z^2} . They are not identical in shape. Four d-orbitals contain four lobes each while fifth d-orbital d_{z^2} has only two lobes. In absence of any magnetic field all five d-orbitals are degenerate.