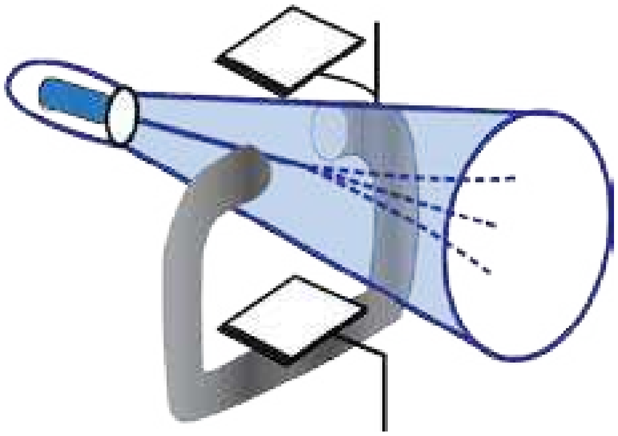
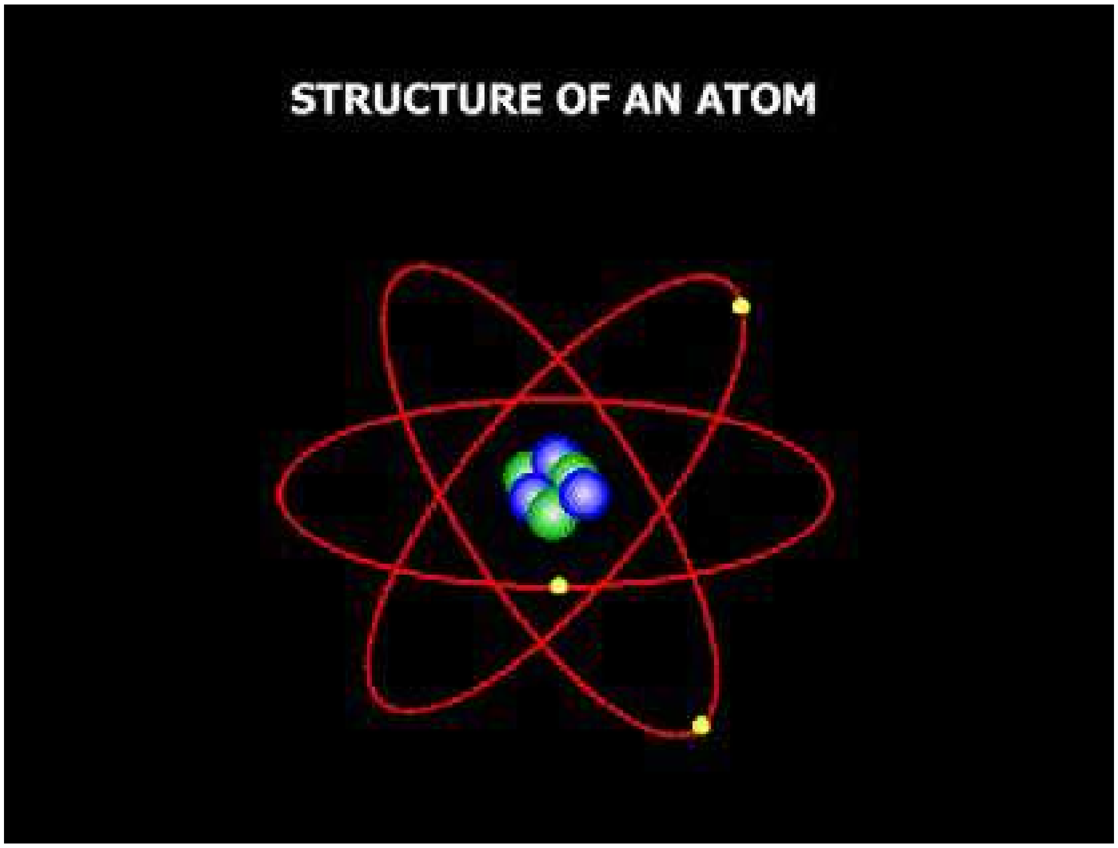


CHAPTER

5

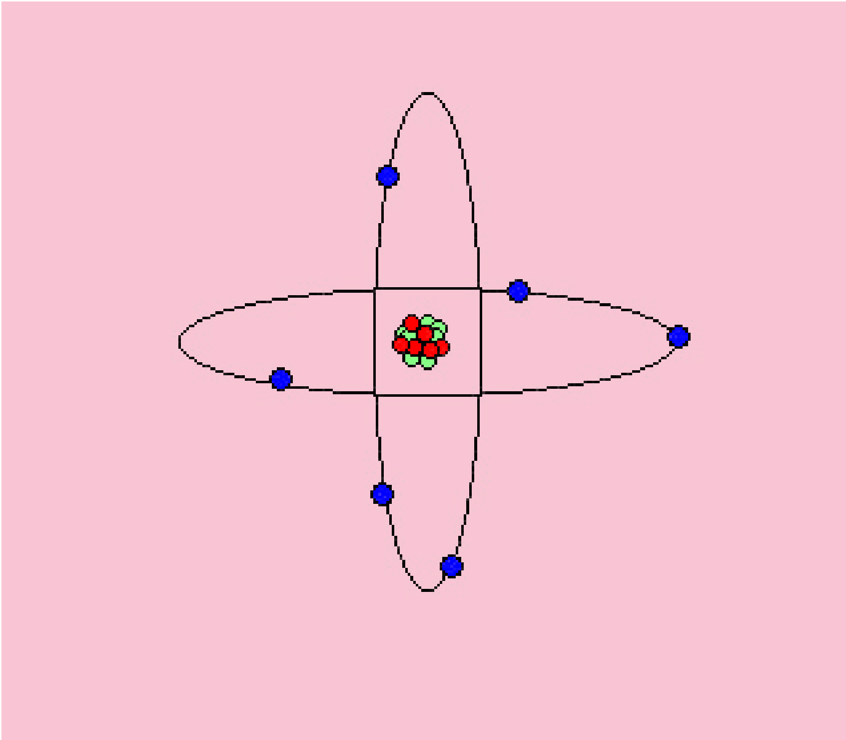
ATOMIC STRUCTURE



Animation 5.1: Atomic Structure
Source & Credit: nuceng

5.1 SUB-ATOMIC PARTICLES OF ATOM

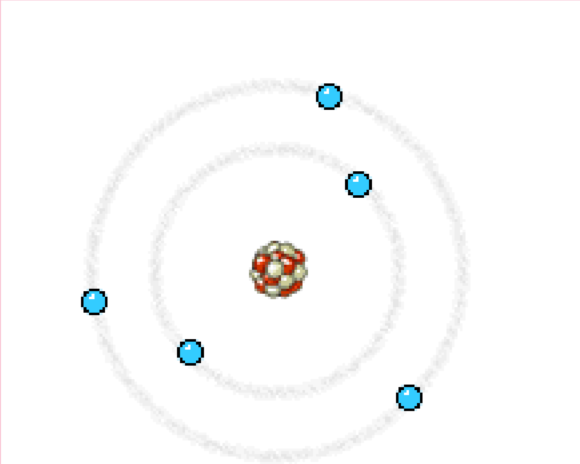
We are familiar with the nature of matter, which is made up of extremely small particles called atoms. According to Dalton's theory, atoms were considered to be ultimate particles which could not be divided any further. Our ideas about structure of atom have undergone radical changes over the years. A number of subatomic particles have been discovered. The experiments which led to the discovery of electron, proton and neutron are described below.



Animation 5.2: Atomic nucleus Model
Source & Credit : myweb.rollins

5.1.1Discovery of Electron (Cathode Rays)

A gas discharge tube is fitted with two metallic electrodes acting as cathode and anode. The tube is filled with a gas, air or vapours of a substance at any desired pressure. The electrodes are connected to a source of high voltage. The exact voltage required depends upon the length of the tube and the pressure inside the tube. The tube is attached to a vacuum pump by means of a small side tube so that the conduction of electricity may be studied at any value of low pressure Fig (5.1).

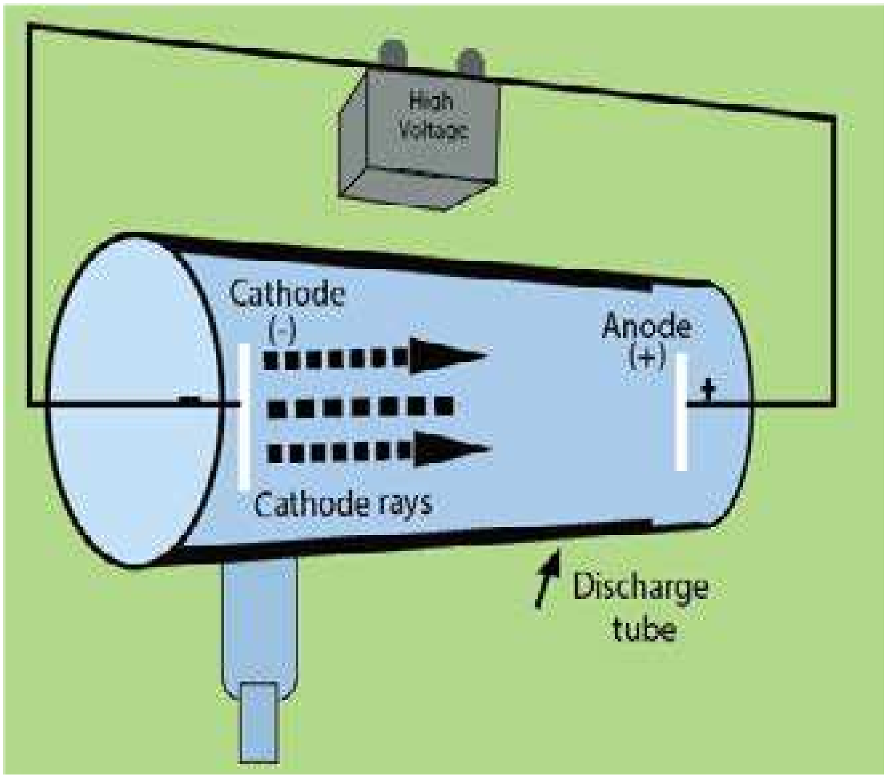


Animation 5.3: Cathode Rays
Source & Credit : wikipedia

It is observed that current does not flow through the gas at ordinary pressure even at high voltage of 5000 volts. When the pressure inside the tube is reduced and a high voltage of 5000-10000 volts is applied, then an electric discharge takes place through the gas producing a uniform glow inside the tube. When the pressure is reduced further to about 0.01 torr, the original glow disappeares. Some rays are produced which create fluorescence on the glass wall opposite to the cathode. These rays are called cathode rays. The colour of the glow or the fluorescence produced on the walls of the glass tube, depends upon the composition of glass.

5.1.2 Properties of Cathode Rays

To study the properties of cathoe rays systematic investigations were made by many scientists. They established the following properties of cathode rays.



Fi g (5.1) Projduct ion of the cath,ode rays

1. Cathode rays are negativelycharged. In 1895, J Perrin showed that when the cathode rays passed between the poles of the magnet, the path of the negatively charged particles was curved downward to point 2 by the magnetic field. Fig (5.2)

In 1897, J. Thomson established their electric charge by the application of electric field, the cathode ray particles were deflected upwards (towards the positive plate) to point 3. Fig. (5.2)

Thomson found that by carefully controlling the charge on the plates when the plates and the magnet were both around the tube, he could make the cathode rays strike the tube at point 1 again Fig.(5.2). In other words, he was able to cancel the effect of the magnetic field by applying an electric field that tended to bend the path of the cathode rays in the opposite direction.

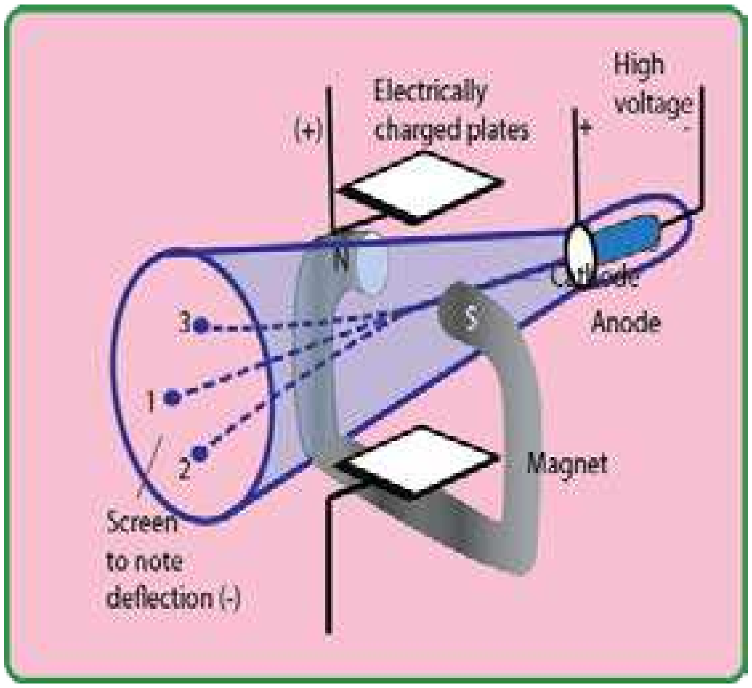


Fig (5.2) Deflection of cathode rays
in electric and magnetic fields

2. They produce a greenish fluorescence on striking the walls of the glass tube. These rays also produce fluorescence in rare earths and minerals. When placed in the path of these rays, alumina glows red and tin stone yellow.

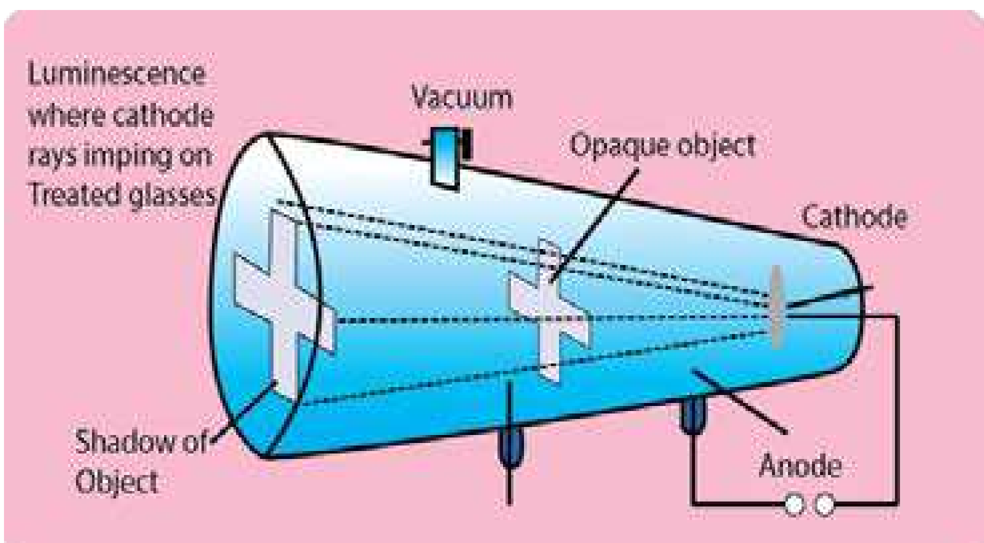
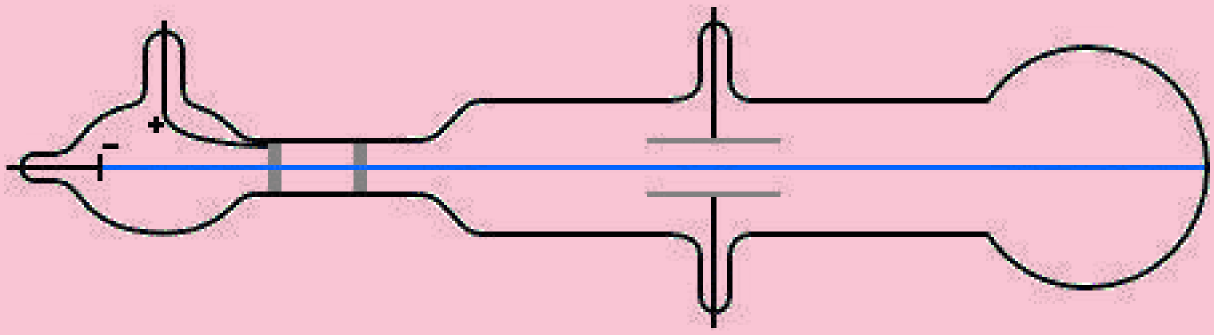


Fig (5.3) Cathode rays cast a shadow of an opaque object



Animation 5.4: X-ray Safety template
Source & Credit : adm.uwaterloo

3. Cathode rays cast a shadow when an opaque object is placed in their path. This proves that they travel q straight line perpendicular to the surface of cathode Fig (5.3).

4. These rays can drive a small paddle wheel placed in their path. This shows that these rays possess momentum. From this observation, it is inferred that cathode rays are not rays but material particles having a definite mass and velocity Fig (5.4).

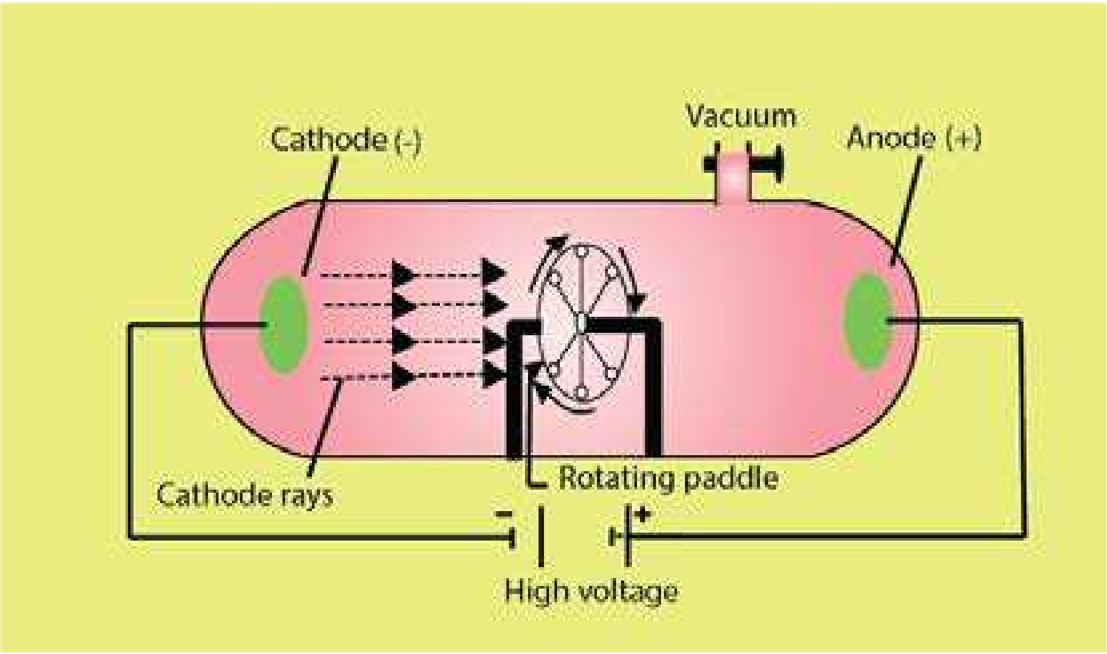


Fig (5.4) cathode rays derive a sman paddle wheel

5. Cathode rays can produce X-rays when they strike an anode particularly with large atomic mass Fig (5.18).
6. Cathode rays can produce heat when they fall on matter e.g. when cathode rays from a concave cathode are focussed on a platinum foil, it begins to glow.
7. Cathode rays can ionize gases.
8. They can cause a chemical change, because they have a reducing effect.
9. Cathode rays can pass through a thin metal foil like aluminum or gold foil.
10. The e/m value of cathode rays shows that they are simply electrons. J.J. Thomson concluded from his experiments that cathode rays consist of streams of negatively charged particles. Stoney named these particles as electrons. Thomson also determined the charge to mass ratio (e/m) of electrons. He found that the e/m value remained the same no matter which gas was used in the discharge tube. He concluded that all atoms contained electrons.

5.1.3 Discovery of Proton (Positive Rays)

In 1886, German physicist, E. Goldstein took a discharge tube provided with a cathode having extremely fine holes in it. When a large potential difference is applied between electrodes, it is observed that while cathode rays are travelling away from cathode, there are other rays produced at the same time. These rays after passing through the perforated cathode produce a glow on the wall opposite to the anode. Since these rays pass through the canals or the holes of cathode, they are called canal rays. These rays are named as positive rays owing to the fact that they carry positive charge Fig (5.5).

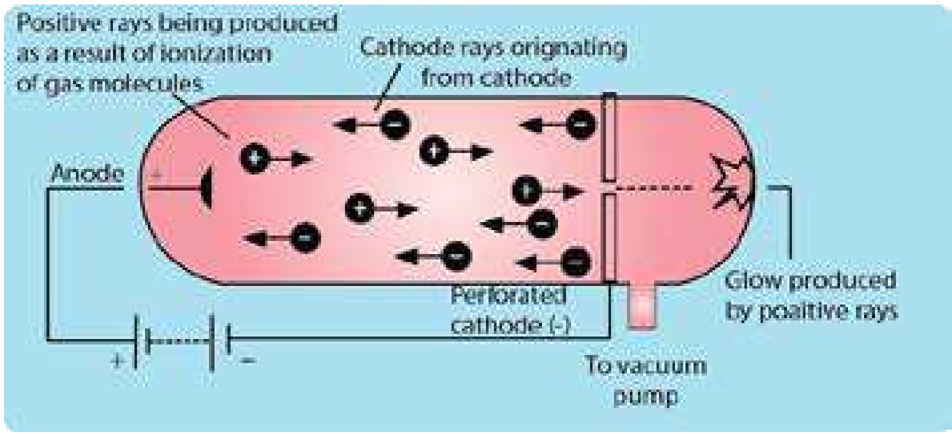
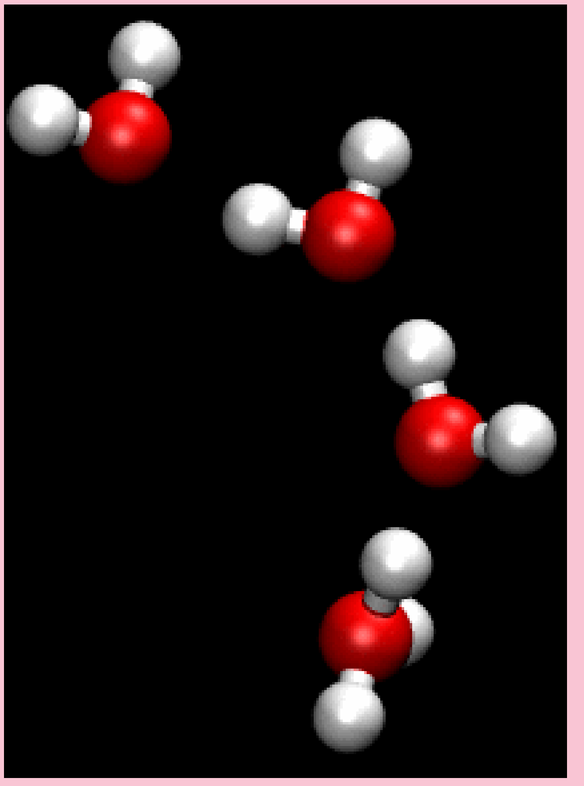


Fig (5.5) Production of positive rays

Reason for the Production of Positive Rays



Animation 5.5: Protons
Source & Credit : wikipedia

These positive rays are produced, when high speed cathode rays (electrons) strike the molecules of a gas enclosed in the discharge tube. They knock out electrons from the gas molecules and positive ions are produced, which start moving towards the cathode Fig (5.5).

$$M + e^- \rightarrow M^+ + 2e^-$$

5.1.4 Properties of Positive Rays

1. They are deflected by an electric as well as a magnetic field showing, that these are positively charged.
2. These rays travel in a straight line in a direction opposite to the cathode rays.
3. They produce flashes on ZnS plate.
4. The e/m value for the positive rays is always smaller than that of electrons and depends upon the nature of the gas used in the discharge tube. Heavier the gas, smaller the e/m value. When hydrogen gas is used in the discharge tube, the e/m value is found to be the maximum in comparison to any other gas because the value of'm' is the lowest for the positive particle obtained from the hydrogen gas. Hence the positive particle obtained from hydrogen gas is the lightest among all the positive particles. This particle is called proton, a name suggested by Rutherford. The mass of a proton is 1836 times more than that of an electron.

5.1.5 Discovery of Neutron

Proton and electron were discovered in 1886 and their properties were completely determined till 1895. It is very strange to know that upto 1932 it was thought that an atom was composed of only electrons and protons. Rutherford predicted in 1920 that some kind of neutral particle having mass equal to that of proton must be present in an atom, because he noticed that atomic masses of atoms could not be explained,if it were supposed that atoms had only electrons and protons. Chadwick discovered neutron in 1932 and was awarded Nobel prize in Physics in 1935.

Experiment

A stream of a-particles produced from a polonium source was directed at beryllium ($^{9}_{4}Be$) target. It was noticed that some penetrating radiation were produced. These radiations were called neutrons because the charge detector showed them to be neutral Fig (5.6). The nuclear reaction is as follows.

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

(a -particle)

Actually a-particles and the nuclei of Be ate re-arranged and extra neutron is emitted.

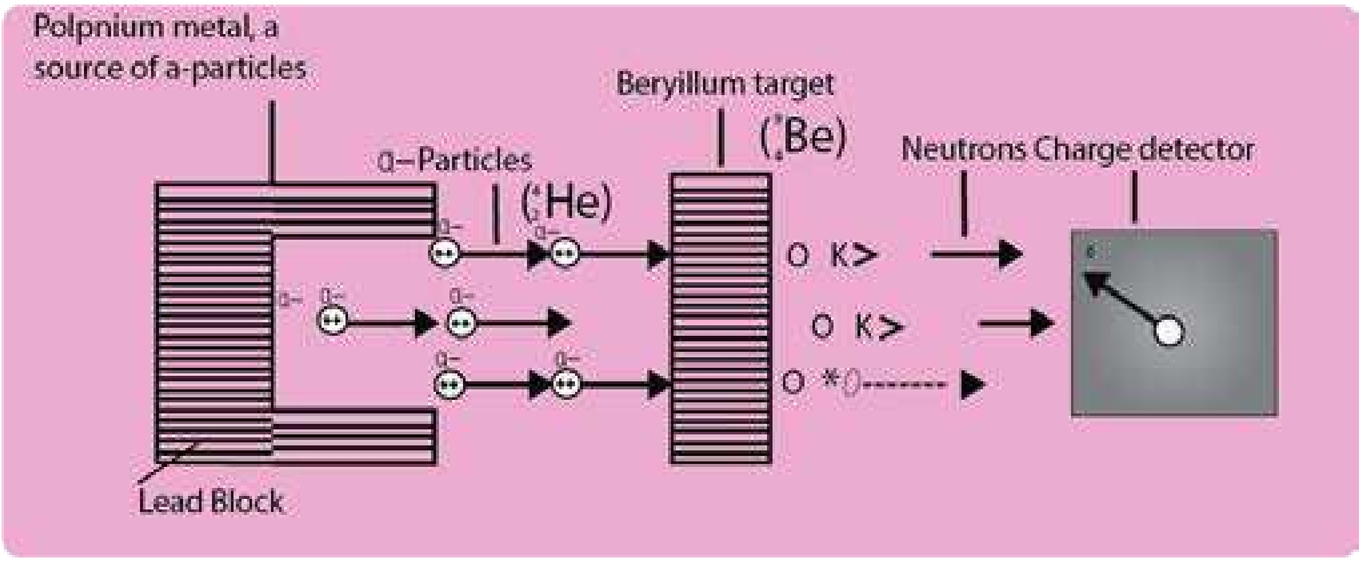
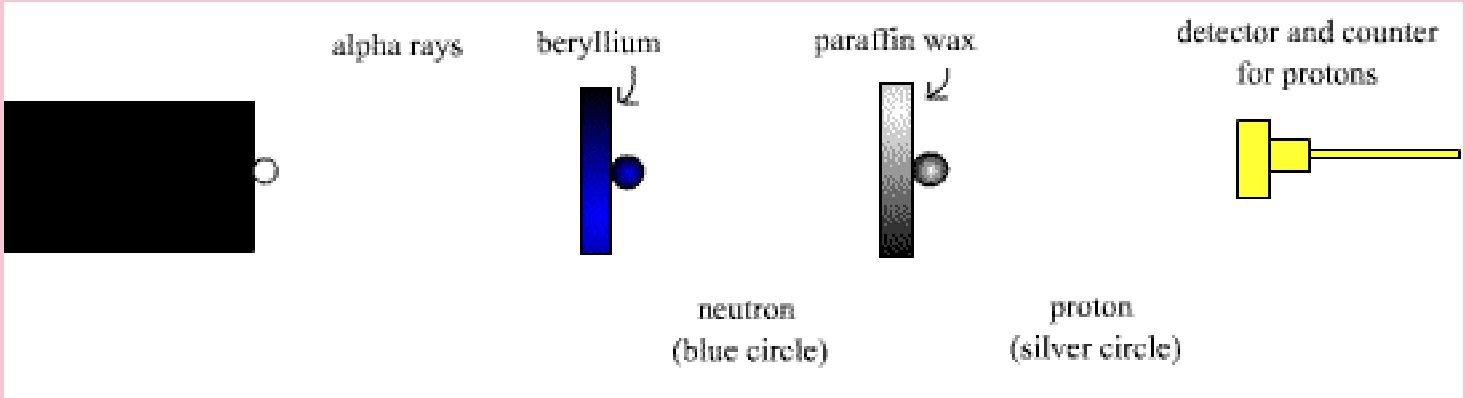


Fig (5.6) Bombardment of Be with α- particles and discovery of neutron



Animation 5.6: chad wicks experiment
Source & Credit : sites.google

5.1.6 Properties of Neutron

1. Free neutron decays into a proton ${}^{1}_{+}P$ with the emission of an electron ${}^{0}_{-1}e$ and a neutrino ${}^{0}_{0}n$.

$$ {}^{1}_{0}n \rightarrow {}^{1}_{+1}P + {}^{0}_{-1}e + {}^{0}_{0}n $$

2. Neutrons cannot ionize gases.
3. Neutrons are highly penetrating particles.
4. They can expel high speed protons from paraffin, water, paper and cellulose.
5. When neutrons travel with an energy 1.2 Mev (Mega electron volt 10^6), they are called fast neutrons but with energy below 1ev are called slow neutrons. Slow neutrons are usually more effective than fast ones for the fission purposes.
6. When neutrons are used as projectiles, they can carry out the nuclear reactions. A fast neutron ejects an a-particle from the nucleus of nitrogen atom and boron is produced, alongwith and a-particles.

$$ {}^{14}_{7}N + {}^{1}_{0}n \rightarrow {}^{11}_{5}B + {}^{4}_{2}He $$

7. When slow moving neutrons hit the Cu metal then γ gamma radiations are emitted. The radioactive ${}^{66}_{29}Cu$ is converted into ${}^{66}_{30}Zn$

$$ {}^{65}_{29}Cu + {}^{1}_{0}n \rightarrow {}^{66}_{29}Cu + hv(\gamma - raditions) $$

$$ {}^{66}_{29}Cu \rightarrow {}^{66}_{30}Zn + {}^{0}_{-1}e \text{ (electron)} $$

Actually, neutron is captured by the nucleus of $^{65}_{29}Cu$ and $^{66}_{29}Cu$ is produced. This radio active $^{66}_{29}Cu$ emits an electron (β-particle) and its atomic number increases by one unit. Because of their intense biological effects they are being used in the treatment of cancer.

5.1.7 Measurement of $\frac{e}{m}$ Value of Electron

In 1897, J.J Thomson devised an instrument to measure the e/m value of electron. The apparatus consists of a discharge tube shown in Fig. (5.7).

The cathode rays are allowed to pass through electric and magnetic fields. When both the fields are off then a beam of cathode rays, consisted of electrons, produces bright luminous spot at P_1 on the fluorescent screen.

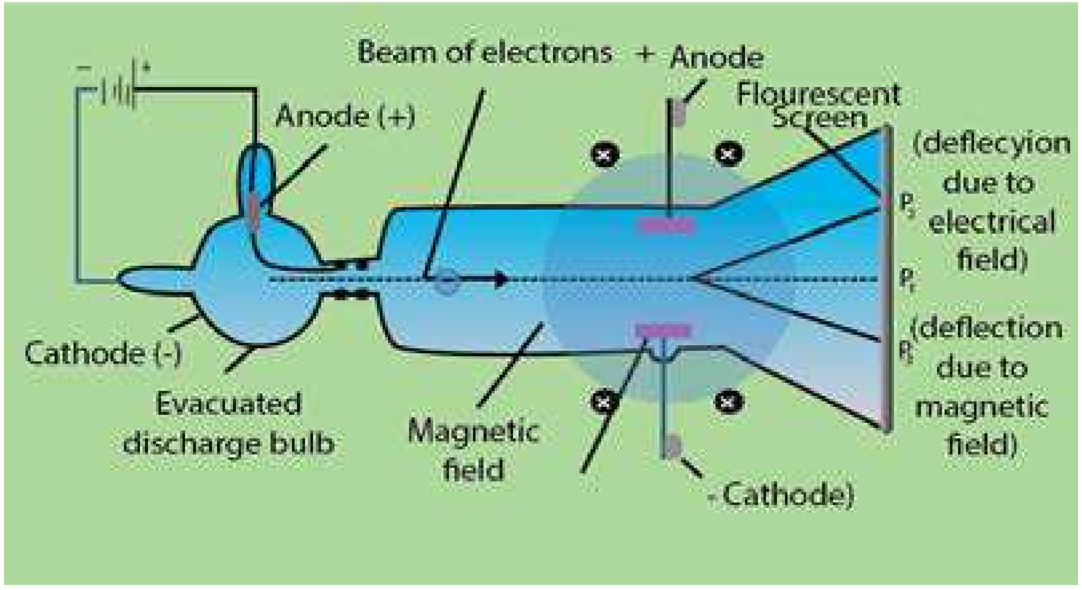


Fig (5.7) Measurement of e/m value of an electron by J.J. Thomson

The north and south poles of magnetic field are perpendicular to the plane of paper in the diagram. The electrical field is in the plane of paper. When only magnetic field is applied, the cathode rays are deflected in a circular path and fall at the point P_3. When only electric field is applied, the cathode rays produce a spot at P_2. Both electric and magnetic fields are then applied simultaneously and their strengths adjusted in such a way that cathode rays again hit the point P_1.
In this way by comparing the strengths of the two fields one can determine the e/m value of ellectrons. It comes out to be 1.7588×10^{11} coulombs kg^{-1}. This means that 1 kg of electrons have 1.7588×10^{11} coulombs of charge.

5.1.8 Measurement of Charge on Electron - Millikan's Oil Drop Method

In 1909, Millikan determined the charge on electron by a simple arrangement. The apparatus consists of a metallic chamber.It has two parts. The chamber is filled with air, the pressure of which can be adjusted by a vacuum pump.

There are two electrodes A and A' These electrodes are used- to generate an electrical field in the space between the electrodes. The upper electrode has a hole in it as shown in Fig (5.8).

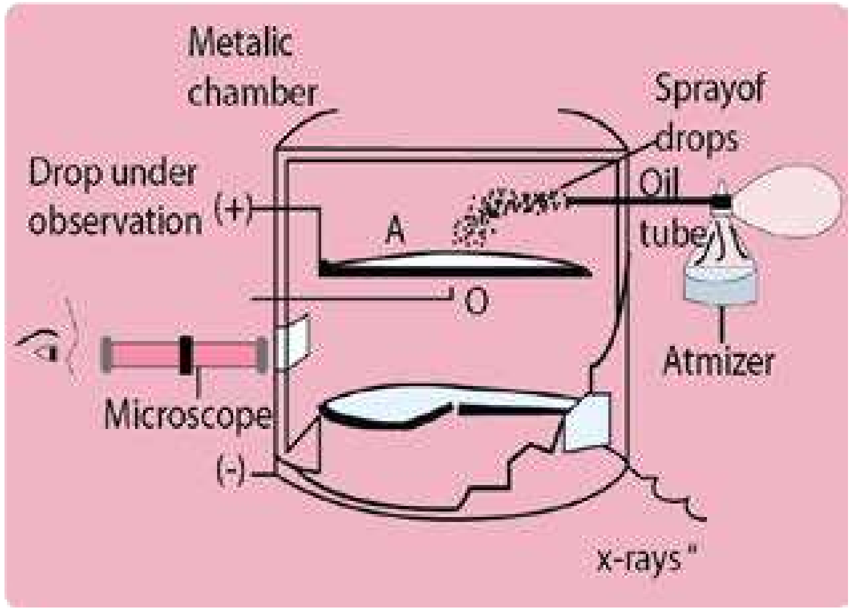


Fig (5.8) Millikan's oil drop method for determination of charge of electron

A fine spray of oil droplets is created by an atomizer. A few droplets passes through the hole in the top plate and into the region between the charged plates, where one of them is observed though a microscope. This droplet, when illuminated perpendicularly to the direction of view, appears in the microscope as bright speck against a dark background. The droplet falls under the force of gravity without applying the electric field. The velocity of the droplet is determined. The velocity of the droplet (V_1) depends upon its weight, mg.

$$v_1 \alpha \ mg \qquad .... \qquad (1)$$

where 'm' is the mass of the droplet and 'g' is the acceleration due to gravity. After that the air between the electrodes is ionized by X-rays. The droplet under observation takes up an electron and gets charged. Now, connect A and A' to a battery which generates an electric field having a strength, E. The droplet moves upwards against the action of gravity with a velocity (v_2).

$$v_2 \alpha \ Ee - mg \qquad .... \qquad (2)$$

where 'e' is the charge on the electron and Ee is the upward driving force on the droplet due to applied electrical field of strength E.

Dividing equation (1) by (2)

$$\frac{v_1}{v_2} = \frac{mg}{Ee\text{-}mg} \qquad .... \qquad (3)$$

The values of v_1 and v_2 are recorded with the help of microscope. The factors like g and E are also known. Mass of the droplet can be determined by varying the electric field in such a way that the droplet is suspended in the chamber. Hence 'e' can be calculated.

By changing the strength of electrical field, Millikan found that the charge on each droplet was different. The smallest charge which he found was 1.59×10^{-19} coulombs, which is very close to the recent value of 1.6022×10^{-19} coulombs. This smallest charge on any droplet is the charge of one electron. The other drops having more than one electron on them, have double or triple the amount of this charge. The charge present on an electron is the smallest charge of electricity that has been measured so far.

Mass of Electron

The value of charge on electron is 1.602×10^{-19} coulombs, while e/m of electron is 1.7588×10^{11} coulombs kg^{-1}. So,

$$\frac{e}{m} = \frac{1.6022\times10^{-19}\text{coulombs}}{\text{Mass of electrons}} = 1.7588\times10^{11} \text{ coulombs kg}^{-1}$$

$$\text{Mass of electron} = \frac{1.6022\times10^{-19}\text{coulombs}}{1.7588\times10^{11}\text{coulombs kg}^{-1}}$$

Rearranging

$$\text{Mass of electron} = 9.1095\times10^{-31} \text{ kg}$$

Properties of Fundamental Particles

The Table (5.1) shows the properties of three fundamental particles electron, proton and neutron present in an atom.

Table (5.1) Properties of three fundamental particles

Particle	Charge (coul)	Relative charge	Mass (kg)	Mass (amu)
Proton	$+1.6022 \times 10^{-19}$	+1	1.6726×10^{-27}	1.0073
Neutron	0	0	1.6750×10^{-27}	1.0087
Electron	-1.6022×10^{-19}	-1	9.1095×10^{-31}	5.4858x10-4

5.2 Rutherford's Model of Atom (Discovery of Nucleus)

In 1911, Lord Rutherford performed a classic experiment. He studied the scattering of high speed α-particles. which were emitted from a radioactive metal (radium or polonium)

A beam of a-partides was directed onto a gold foil of 0.00004 cm thickness as target through a pin-hole in lead plate, Fig (5.9).

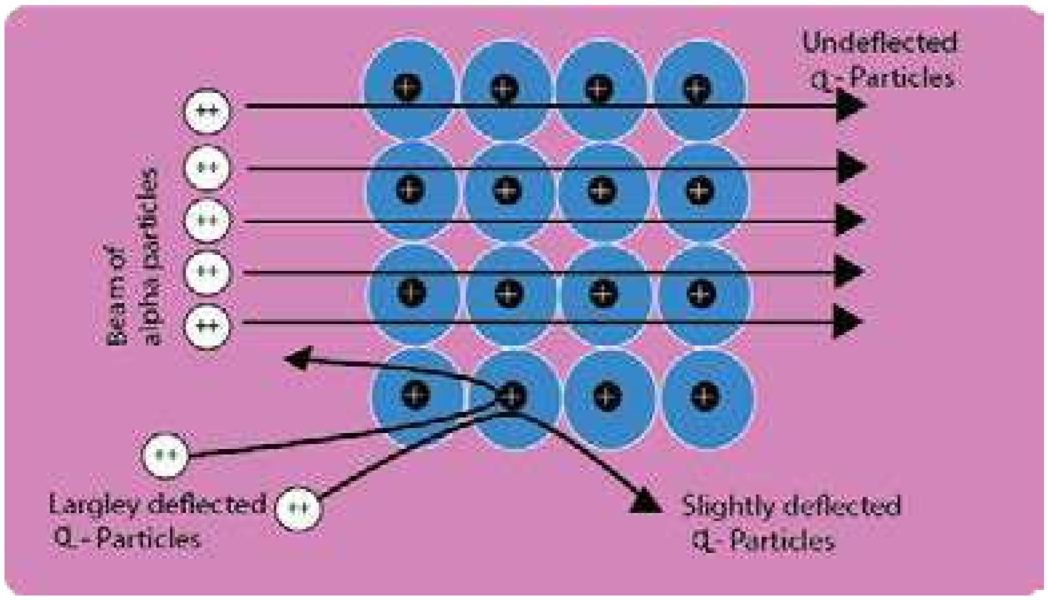


Fig (5.9) Rutherford's experiment for scattering 0f α -partices

A photographic plate or a screen coated with zinc sulphide was used as a detector. Whenever, an a-partide struck the screen, flash of light was produced at that point. It was observed that most of the particles went through the foil undeflected. Some were deflected at fairly large angles and a few were deflected backward. Rutherford proposed that the rebounding particles must have collided with the central heavy portion of the atom which he called as nucleus.

On the basis of these experimental observations, Rutherford proposed the planetary model (similar to the solar system) for an atom in which a tiny nucleus is surrounded by an appropriate number of electrons. Atom as a whole being neutral, therefore, the nucleus must be having the same number of protons as there are number of electrons surrounding it.

In Rutherford's model for the structure of an atom, the outer electrons could not be stationary. If they were, they would gradually be attracted by the nucleus till they ultimately fall into it. Therefore, to have a stable atomic structure, the electrons were supposed to be moving around the nucleus in closed orbits. The nuclear atom of Rutherford was a big step ahead towards understanding the atomic structure, but the behaviour of electrons remained unexplained in the atom.

Rutherford's planet-like picture was Electron defective and unsatisfactory because the moving electron must be accelerated towards the nucleus Fig (5.10).

Therefore, the radius of the orbiting electron should become smaller and smaller and the electron should fall into the nucleus. Thus, an atomic structure as proposed by Rutherford would collapse.

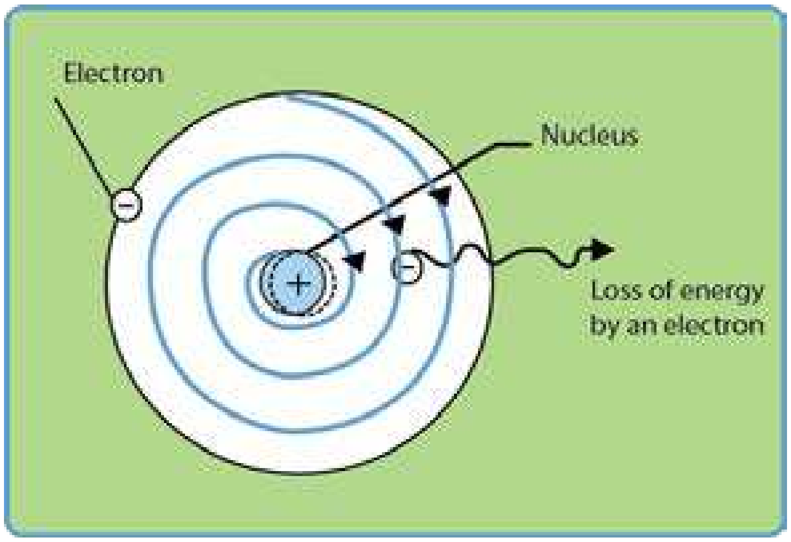


Fig (5.10) Rotation of electron around the nucleus and expected spiral path

5.3 PLANCK'S QUANTUM THEORY

Max Planck proposed the quantum theory in 1900 to explain the emission and absorption of radiation. According to his revolutionary' theory, energy travels in a discontinuous manner and it is composed of large number of tiny discrete units called quanta. The main points of his theory are:

(i) Energy is not emitted or absorbed continuously. Rather, it is emitted or absorbed in a discontinuous manner and in the form of wave packets. Each wave packet or quantum is associated with a definite amount of energy. In case of light, the quantum of energy is often called photon.

(ii) The amount of energy associated with a quantum of radiation is proportional to the frequency (v) of the radiation. Frequency is the number of waves passing through a point per second.

$$E \propto v$$

$$E = hv \qquad \text{.............................} \qquad (4)$$

Where 'h' is a constant known as Planck's constant and its value is 6.626×10^{-34} Js. It is, in fact, the ratio of energy and the frequency of a photon.

(iii) A body can emit or absorb energy only in terms of quanta.

$$E = hv$$

The frequency 'v' is related to the wavelength of the photon as

$$v = c/\lambda$$

Greater the wavelength, smaller the frequency of photon

So, $E = hc/\lambda$ ....(5)

Wavelength is the distance between the two adjacent crests or troughs and expressed in $\mathring{A}$, nm or pm. ($1\mathring{A} = 10^{-10}$m, 1nm = 10^{-9}m, 1pm=10^{-12}m)

Greater the wavelength associated with the photon, smaller is its energy. Wave number ($\bar{v}$) is the number of waves per unit length, and is reciprocal to wavelength.

$$\bar{v} = 1/\lambda$$

Putting the value of λ in equation (5)

$$E = hc\bar{v} \quad ....(6)$$

So, the energy of a photon is related to frequency, wavelength and wave number. Greater the wave number of photons, greater is the energy associated with them. The relationships of energy, frequency, wavelength, wave number about the photon of light are accepted by scientists and used by Bohr in his atomic model.

5.4 BOHR'S MODEL OF ATOM

Bohr made an extensive use of the quantum theory of Planck and proposed that the electron, in the hydrogen atom, can only exist in certain permitted quantized energy levels. The main postulates of Bohr's theory are:

(i) Electron revolves in one of the circular orbits outside the nucleus. Each orbit has a fixed energy and a quantum number is assigned to it.

(ii) Electron present in a particular orbit neither emits nor absorbs energy while moving in the same fixed orbits. The energy is emitted or absorbed only when an electron jumps from one orbit to another.

(iii) When an electron jumps, the energy change AE is given by the Planck's equation

$$\Delta E = E_2 - E_1 = hv \qquad \text{..................} \quad (7)$$

Where ΔE is the energy difference of any two orbits with energies E_1 and E_2 Energy is absorbed by the electron when it jumps from an inner orbit to an outer orbit and is emitted when the electron jumps from outer to inner orbit. Electron can revolve only in those orbits having a fixed angular momentum (mvr). The angular momentum of an orbit depends upon its quantum number and it is an integral multiple of the factor h/2 π i.e.

$$mvr = \frac{nh}{2\pi} \qquad \text{............................} \qquad (8)$$

Where n = 1,2,3,.............

The permitted values of angular momenta are, therefore, $\frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi}$ ....

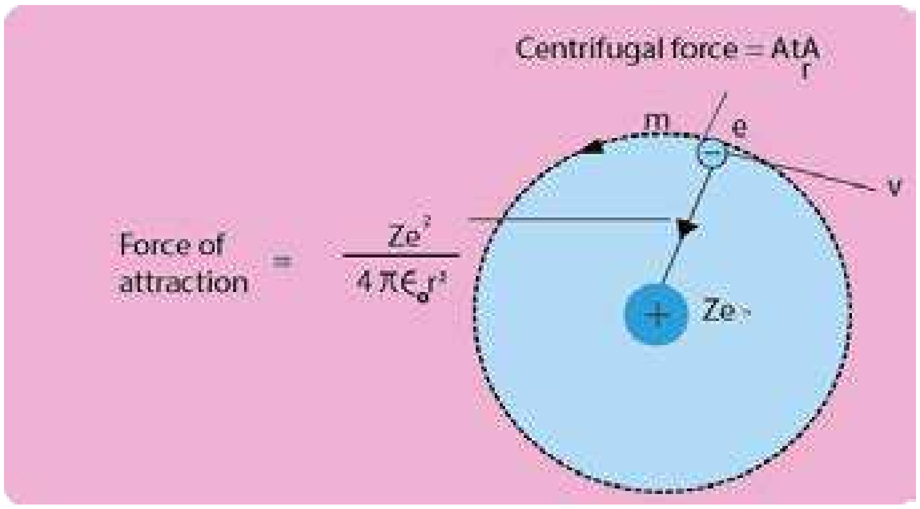
The electron is bound to remain in one of these orbits and not in between them. So, angular momentum is quantized.

Derivation of Radius and Energy of Revolving Electron in nth Orbit.

By applying these ideas, Bohr derived the expression for the radius of the nth orbit in hydrogen atom.

For a general atom, consider an electron of charge 'e' revolving around the nucleus having charge Ze^+. Z being the proton number and e^+ is the charge on the proton Fig (5.11).

Let m be the mass of electron, r the radius of the orbit and v the velocity of the revolving electron. According to Coulombs law, the electrostatic force of attraction between the electron and the nucleus will be given by the f ollowing formula .



Fi'g (5.11) .E, lectr.o n rev. olvingv +m an atom with nuclear charge Ze (If Z=l, then the picture is for H-atom)

$$\frac{Ze^{+}.e^{-}}{4\pi \in_0 r^2} = \frac{Ze^2}{4\pi \in_0 r^2}$$

$\in_0$ is the vacuum permittivity and its value is 8.84 x $10^{-12}C^2J^{-1}m^{-1}$. This force of attraction is balanced by the $\frac{mv^2}{r}$ Therefore, for balanced conditions, we can write

or $$\frac{mv^2}{r} = \frac{Ze^2}{4\pi \in_0 r^2}$$

$$mv^2 = \frac{Ze^2}{4\pi \in_0 r} \quad .... \quad (9)$$

Rearranging the equation (9)

$$r = \frac{Ze^2}{4\pi \in_0 mv^2} \quad .... \quad (10)$$

According to equation (10), the radius of a moving electron is inversely proportional to the square of its velocity. It conveys the idea, that electron should move faster nearer to the nucleus in an orbit of smaller radius. It also tells, that if hydrogen atom has many possible orbits, then the promotion of electron to higher orbits makes it move with less velocity.

The determination of velocity of electron is possible while moving in the orbit. In order to eliminate the factor of velocity from equation (10), we use Bohr's postulate (iv). The angular momentum of the electron is given by.

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

Rearranging the equation of angular momentum

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

Taking square

$$v^2 = \frac{n^2h^2}{4\pi^2m^2r^2} \quad .... \quad (11)$$

Substituting the value of v^2 from eq. (11) into eq. (10), we get

$$r = \frac{Ze^2 \times 4\pi^2 m^2 r^2}{4\pi\varepsilon_0 mn^2h^2}$$

Rearranging the above equation, we get

$$r = \frac{\varepsilon_0 n^2 h^2}{\pi m Z e^2} \quad \text{..............................} \quad \textbf{(12)}$$

For hydrogen atom Z = 1, so the equation for radius of H-atom is

$$r = \frac{\varepsilon_0 n^2 h^2}{\pi m e^2} = (\frac{\varepsilon_0 h^2}{\pi m e^2})n^2 \quad \text{............................} \quad \textbf{(13)}$$

According to the equation (13), the radius of hydrogen atom is directly proportional to the square of number of orbit (n). So, higher orbits have more radii and vice versa. The collection of parameters $(\frac{\varepsilon_0 h^2}{\pi m e^2})$ in equation (13) is a constant factor.

When we put the value of $\in_0$, h^2 π, m and e^2 alongwith the units then the calculations show that it is equal to 0.529 x 10^{-10} m or 0.529 Å.(10^{-10} m = l Å)

Hence r=0.529 Å (n^2) .... (14)

By putting the values of na s 1,2.3,4............ the radii of orbits of hydrogen atom are

n=1	r_1=0.529 Å	n=4	r_4=8.4 Å
n=2	r_2=2.11 Å	n=5	r_5=13.22 Å
3 n=	r $_3$=4.75 Å		

The comparison of radii shows that the distance between orbits of H-atom goes on increasing as we move from 1st orbit to higher orbits. The orbits are not equally spaced.

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

The second orbit is four times away from the nucleus than first orbit, third orbit is nine times away and similarly fourth orbit is sixteen times away.

Energy of Revolving Electron

The total energy of an electron in an orbit is composed of two parts, the kinetic energy which is equal to $\frac{1}{2}mv^2$ and the potential energy. The value of potential energy can be calculated as follows.

The electrostatic force of attraction between the nucleus and the electron is given by $\frac{Ze^2}{4\pi\varepsilon_0 r^2}$. If the electron moves through a small distance dr, then the work done for moving electron is given by

$$\frac{Ze^2}{4\pi\varepsilon_0 r^2}dr \quad \text{because work=(force x distance)}$$

In order to calculate the potential energy of the electron at a distance r from the nucleus, we calculate the total work done for bringing the electron from infinity to a point at a distance r from the nucleus. This can be obtained by integrating the above expression between the limits of infinity and r.

$$\int_{\infty}^{r}\frac{Ze^2 dr}{4\pi\epsilon_0 r^2} = \frac{Ze^2}{4\pi\epsilon_0}\int_{\infty}^{r}\frac{dr}{r^2} = \frac{Ze^2}{4\pi\epsilon_0}\left[\frac{-1}{r}\right]_{\infty}^{r} = \frac{Ze^2}{4\pi\epsilon_0}\left[\frac{-1}{r}\right] = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

The work done is the potential energy of electron, so

$$\text{Work done} = E_{potential} = -\frac{Ze^2}{4\pi\varepsilon_0 r} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (15)$$

The minus sign indicates that the potential energy of electron decreases, when it is brought from infinity to a point at a distance 'r' from the nucleus. At infinity, the electron is not being attracted by any thing and the potential energy of the system is zero. Whereas at a point nearer the nucleus, it will be attracted by the nucleus and the potential energy becomes less than zero. The quantity less than zero is negative. For this reason, the potential energy given by equation (15) is negative.

The total energy (E) of the electron, is the sum of kinetic and potential charges.

So, $E = E_{kinetic} + E_{potential}$

$$= \frac{1}{2} mv^2 - \frac{Ze^2}{4\pi\varepsilon_o r} \quad \text{..............................} \quad (16)$$

Now, we want to eliminate the factor of velocity from equation (16). So, from equation (9), substitute the value of mv^2 in eq. (16)

Since $mv^2 = \frac{Ze^2}{4\pi \in_0 r}$ .... (9)

$$E = \frac{Ze^2}{8\pi \in_0 r} - \frac{Ze^2}{4\pi \in_0 r}$$

Simplifying it, $E = -\frac{Ze^2}{8\pi \in_0 r}$ .... (17)

Now substitute the value of r from eq (12) into eq (17) we get

Since $\frac{\in \; n^2h^2}{mZe}$ .... (12)

$$E_n = \frac{-mZ^2e^4}{8 \in_0^2 n^2h^2} \quad \text{..............................} \quad (18)$$

Where E_n is the energy of nth orbit.

For hydrogen atom , the number of protons in nucleus is one, so (Z = 1).

$$E_n = -\frac{me^4}{8 \in_0^2 h^2}\left[\frac{1}{n^2}\right] \quad \text{...............................} \quad (19)$$

Eq.(19) gives the energy of electron revolving around the nucleus of hydrogen atom.

The factors outside the brackets in equation (19) are all constants. When the values of these constants are substituted along with their units, then it comes out to be 2.178 x 10^{-18} J. The equation (19) can be written as,

$$E_n = -2.178\text{x}10^{-18}\left[\frac{1}{n^2}\right]\text{J} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \qquad (20)$$

This equation (20) gives the energy associated with electron in the nth orbit of hydrogen atom. Its negative value shows that electron is bound by the nucleus i.e. electron is under the force of attraction of the nucleus. Actually, the electron has been brought from infinity to distance r from the nucleus.

The value of energy obtained for the electron is in joules/atom. If, this quantity is multiplied by Avogadro's number and divided by 1000, the value of E_n will become

$$E_n = \frac{6.02\times10^{23}\times2.18\times10^{-18}}{1000}\left[\frac{1}{n^2}\right]\text{kJmol}^{-1}$$

$$E_n = -\frac{1313.315}{n^2}\text{kJmol}^{-1} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \qquad (21)$$

This energy is associated with 1.008g of H-atoms i.e. with Avogadro's number of atoms of hydrogen.

Substituting, the values of n as 1,2,3,4,5, etc. in equation (21), we get the energy associated with an electron revolving in 1st, 2nd, 3rd, 4th and 5th orbits of H-atom.

$$E_1 = -\frac{1313.31}{1^2} = -1313.31\text{ kJmol}^{-1}$$

$$E_2 = -\frac{1313.31}{2^2} = -328.32\text{ kJmol}^{-1}$$

$$E_3 = -\frac{1313.31}{3^2} = -145.92\text{ kJmol}^{-1}$$

$$E = -\frac{1313.31}{} = -82.08 \text{ kJmol}^{-1}$$

$$E_5 = -\frac{1313.31}{5^2} = -52.53 \text{ kJmol}^{-1}$$

$$E_\infty = -\frac{1313.31}{\infty^2} = 0 \text{ kJmol}^{-1}$$ (electron is free from the nucleus)

The values of energy differences between adjacent orbits can be calculated as follows

E_2-E_1 = (-328.32)-(-1313.31) = 984.99 kJmol^{-1}

E_3-E_2 = (-145.92)-(-328.32) = 182.40 kJmol^{-1}

E_4-E_3 = (-82.08)-(-145.92) = 63.84 kJmol^{-1}

The differences in the values of energy go on decreasing from lower to higher orbits.

$E_2-E_1 > E_3-E_2 > E_4-E_3 >$.........................

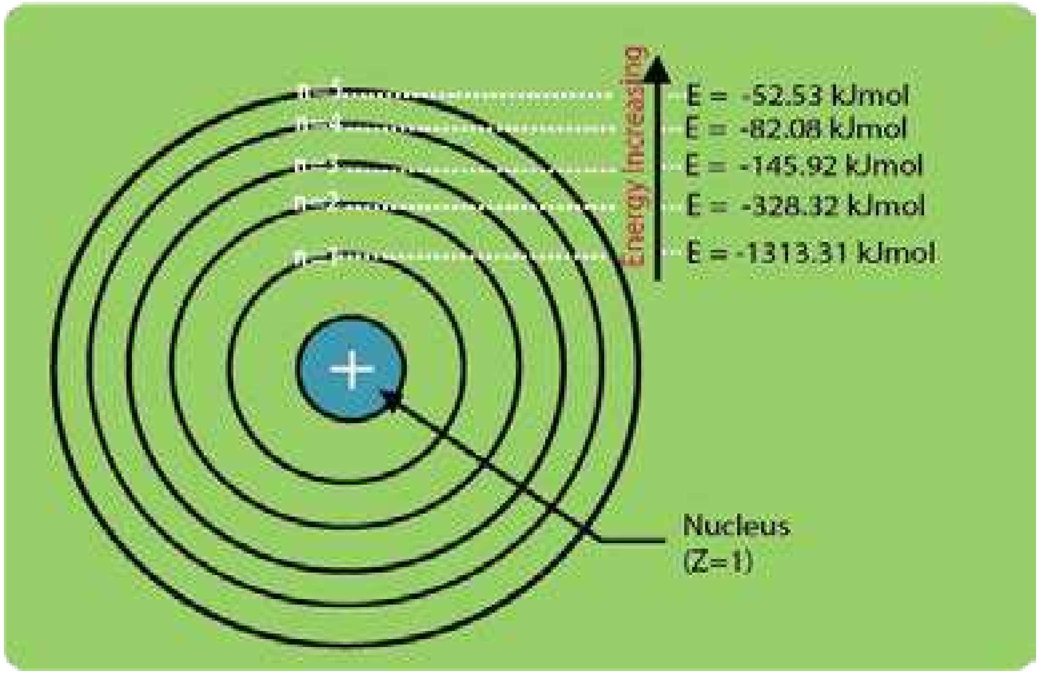


Fig (5.12) Energy values associated with an electron in vanous orbits in hydrogen atom

The energy difference between first and infinite levels of energy is calculated as:

E„ - E_1 = 0 - (-1313.31) = 1313.31 kJmol^{-1}

1313.31 kJmol^{-1} is the ionization energy of hydrogen. This value is the same as determined experimentally. These values show that the energy differences between adjacent orbits of Bohr's model of hydrogen atom go on decreasing sharply.

Keep in mind, that distances between adjacent orbits increase. The Fig (5.12) makes the idea clear.

5.5 SPECTRUM

When a radiation of light is passed through a prism, the radiation undergoes refraction or bending. The extent of bending depends upon the wavelength of the photons. A radiation of longer wavelength is bent to a smaller degree than the radiation of a shorter wavelength. Ordinary, white light consists of radiation of all wavelengths, and so after passing through the prism, white light is splitted up into radiations of different wavelengths.

The colours of visible spectrum are violet, indigo, blue, green, orange, yellow and red and their wavelengths range from 400 nm to 750 nm. In addition to the visible region of the spectrum, there are seven other regions. Ultraviolet, X-rays, y-rays and cosmic rays are towards the lower wavelength end of the spectrum and they possess the photons with greater energies. On the other side of the visible region, there lies infrared, microwave and radio frequency regions. Fig. (5.13) shows the continuity of wavelengths for all types of regions of spectrum. Hence, a visual display or dispersion of the components of white light, when it is passed through a prism is called a spectrum.

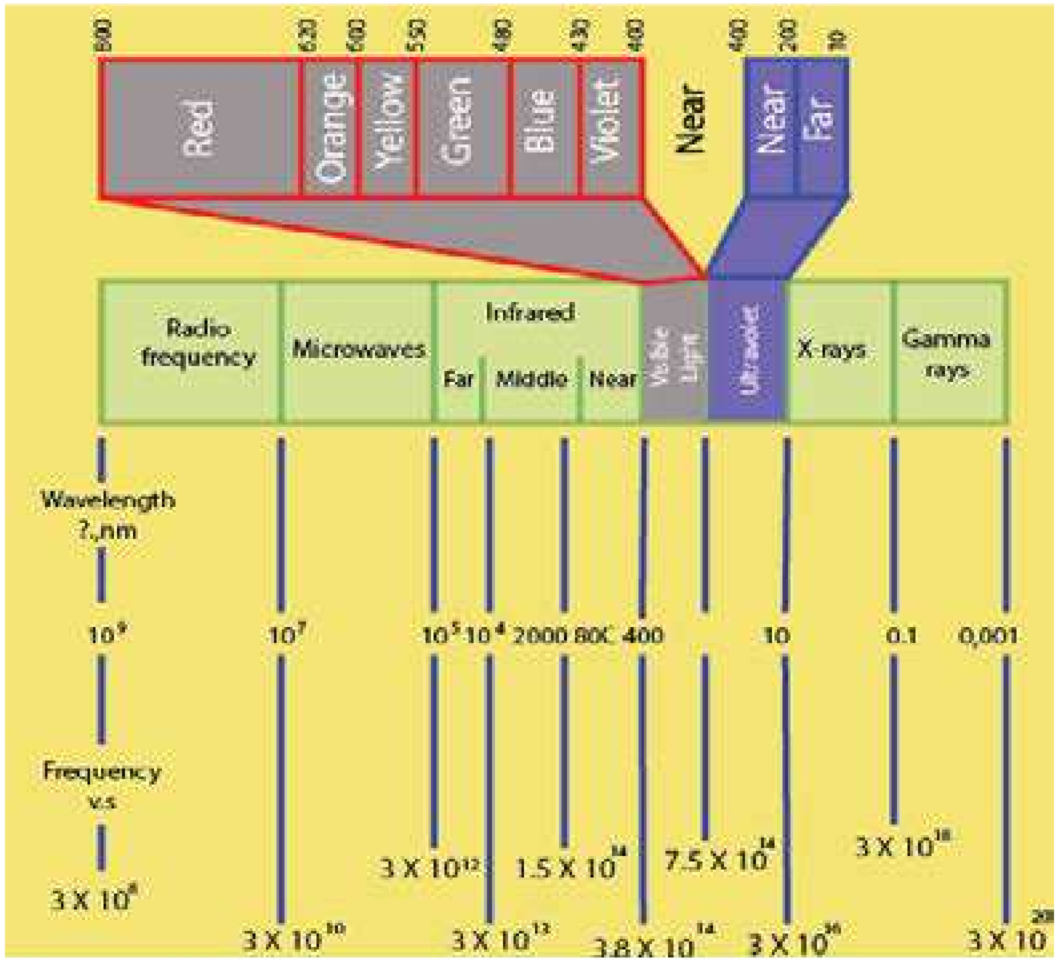


Fig (5.13) The visible and other regions of spectrum

Spectrum is of two types.

(i) Continuous spectrum (ii) Line spectrum

5.5.1 Continuous Spectrum

In this type of spectrum, the boundry line between the colours cannot be marked. The colours diffuse into each other. One colour merges into another without any dark space. The best example of continuous spectrum is rainbow. It is obtained from the light emitted by the sun or incandescent (electric light) solids. It is the characteristic of matter in bulk.

5.5.2 Atomic or Line Spectrum

When an element or its compound is volatilized on a flame and the light emitted is seen through a spectrometer, We see distinct lines separated by dark spaces. This type of spectrum is called line spectrum or atomic spectrum. This is characteristic of an atom. The number of lines and the distance between them depend upon the element volatilized. For example, line spectrum of sodium contains two yellow coloured lines separated by a definite distance. Similarly, the spectrum of hydrogen consists of a number of lines of different colours having different distances from each other. It has also been observed that distances between the lines for the hydrogen spectrum decrease with the decrease in wavelength and the spectrum becomes continuous after a certain value of wavelength Fig (5.14).

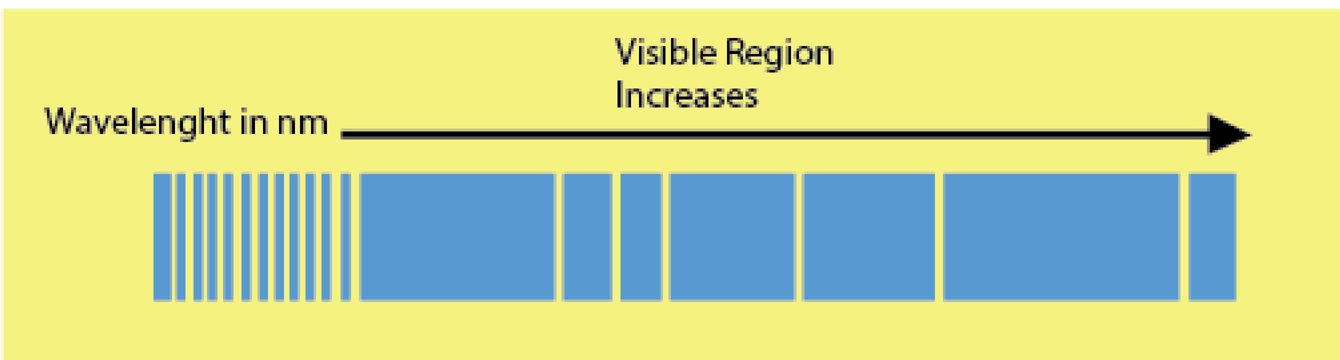


Fig (5.14) Atomic spectrum of hydrogen

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

There are two ways in which an atomic spectrum can be viewed.

(i) Atomic emission spectrum

(ii) Atomic absorption spectrum

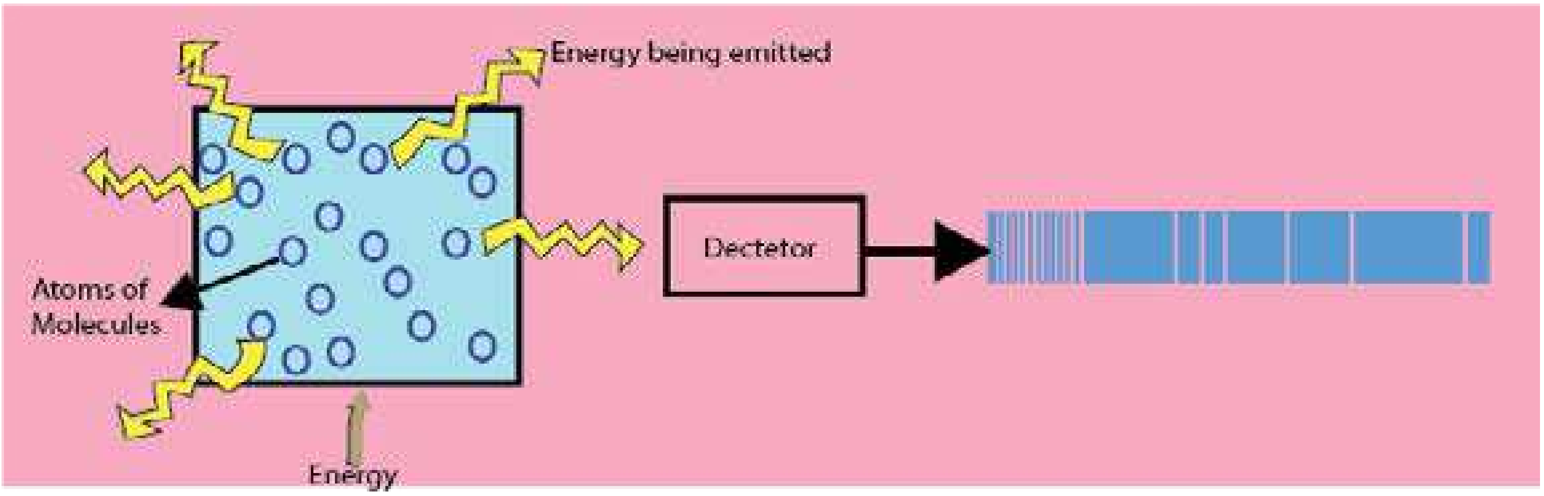


Fig (5.15) Atomic emission spectrum

5.5.3 Atomic Emission Spectrum

When solids are volatilized or elements in their gaseous states are heated to high temperature or subjected to an electrical discharge, radiation of certain wavelengths are emitted. The spectrum of this radiation contained bright lines against a dark background. This is called atomic emission spectrum. Fig (5.15)

5.5.4 Atomic Absorption Spectrum

When a beam of white light is passed through a gaseous sample of an element, the element absorbs certain wavelengths while the rest of wavelengths pass through it. The spectrum of this radiation is called an atomic absorption spectrum. The wavelengths of the radiation that have been absorbed by the element appear as dark lines and the background is bright, Fig (5.16).

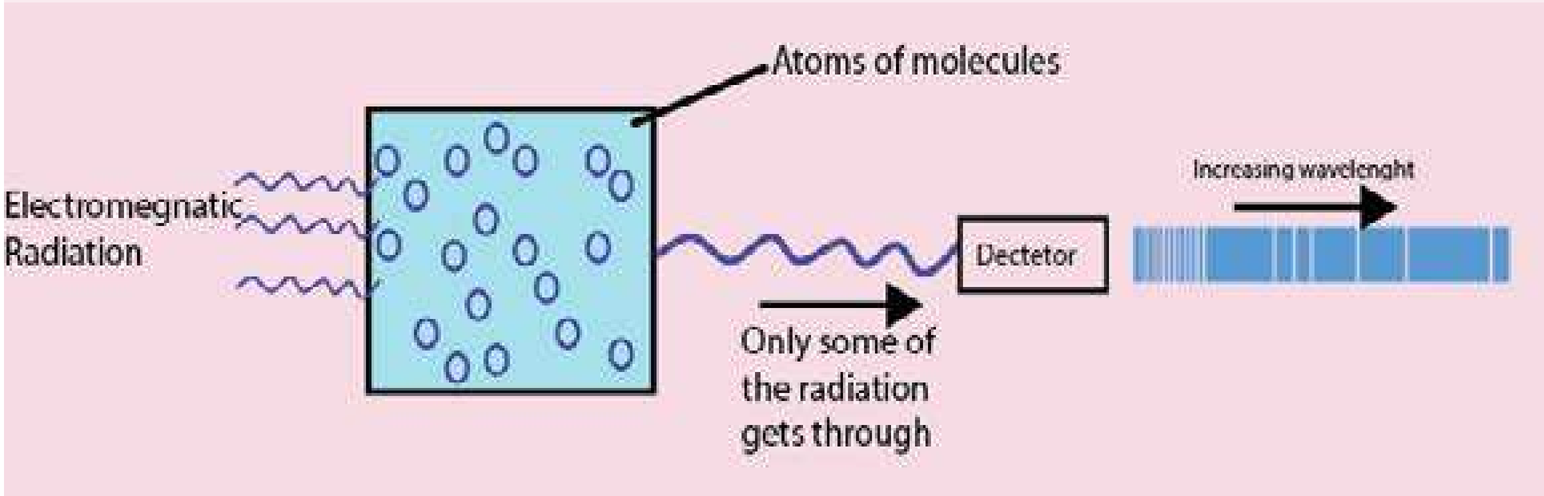


Fig (5.16) Atomic absorption spectrum

It is interesting to note that the positions or the wavelengths of lines appearing in both emission and absorption spectra are exactly the same. In emission spectrum, these lines appear bright because the corresponding wavelengths are being emitted by the element, whereas they appear dark in absorption spectrum because the wavelengths are being absorbed by the element.

5.5.5 Hydrogen Spectrum

Hydrogen-spectrum is an important example of atomic spectrum. Hydrogen is filled in a discharge tube at a very low pressure a bluish light is emitted from the discharge tube. This light when viewed through a spectrometer shows several isolated sharp lines.

These are called spectral lines. The wavelengths of these lines lie in the visible, ultraviolet and infrared regions. These spectral lines can be classified into five groups called spectral series. These series are named after their discoverers as shown below.

(i) Lyman series (U.V region)
(ii) Balmer series (visible region)
(iii) Paschen series (LR region)
(iv) Brackett series (I.R region)
(v) Pfund series (I.R region)

The first four series were discovered before Bohr's atomic model (1913). The wave numbers (m^{-1}) of the series of lines in hydrogen spectrum are given in Table (5.2).

It is seen from the Table (5.2) that as we proceed from Lyman series to Pfund series, the wave numbers (m^{-1}) of spectral lines decrease. The lines of Balmer series have been given specific names as H_{α}, H_{β}........, etc.

Table (5.2)Wave numbers (m^{-1}) of various series of hydrogen spectrum.

Lyman series (U.V. region)	Balmer series (Visible region)	Paschen series (I.R. region)	Brackett series (I.R. region)	Pfund series (I.R. region)
82.20×10^5	15.21×10^5 ($H_{á}$ line)	5.30×10^5	2.46×10^5	1.34×10^5
97.20×10^5	20.60×10^5 ($H_{â}$ line)	7.80×10^5	3.80×10^5	2.14×10^5
102.20×10^5	23.5×10^5 ($H_{ã}$ line)	9.12×10^5	4.61×10^5	
105.20×10^5	24.35×10^5 ($H_{ä}$ line)	9.95×10^5		
106.20×10^5	25.18×10^5			
107.20×10^5				

5.5.6 Origin of Hydrogen Spectrum on the Basis of Bohr's Model

According to Bohr, electron in hydrogen atom may revolve in any orbit depending upon its energy. When hydrogen gas is heated or subjected to an electric discharge, its electron moves from one of the lower orbit to higher orbit, absorbing particular wavelength of energy. Subsequently, when it comes back, the same energy is released. This energy is observed as radiation of particular wavelengths in the form of bright lines seen in the certain region of the emission spectrum of hydrogen gas.

The spectral lines of Lyman series are produced when the electron jumps from n_2= 2, 3,4,5, to, n_1 = 1 (Lyman did not know this reason). Similarly, spectral lines of Balmer series discovered in 1887 originated when an electron jumps from n_2 = 3, 4, 5, 6,................ to n_1= 2orbit.

In the same way, Paschen, Brackett and Pfund series of lines are produced as a result of electronic transitions from higher orbits to 3rd, 4th and 5th orbits, respectively Fig (5.17).

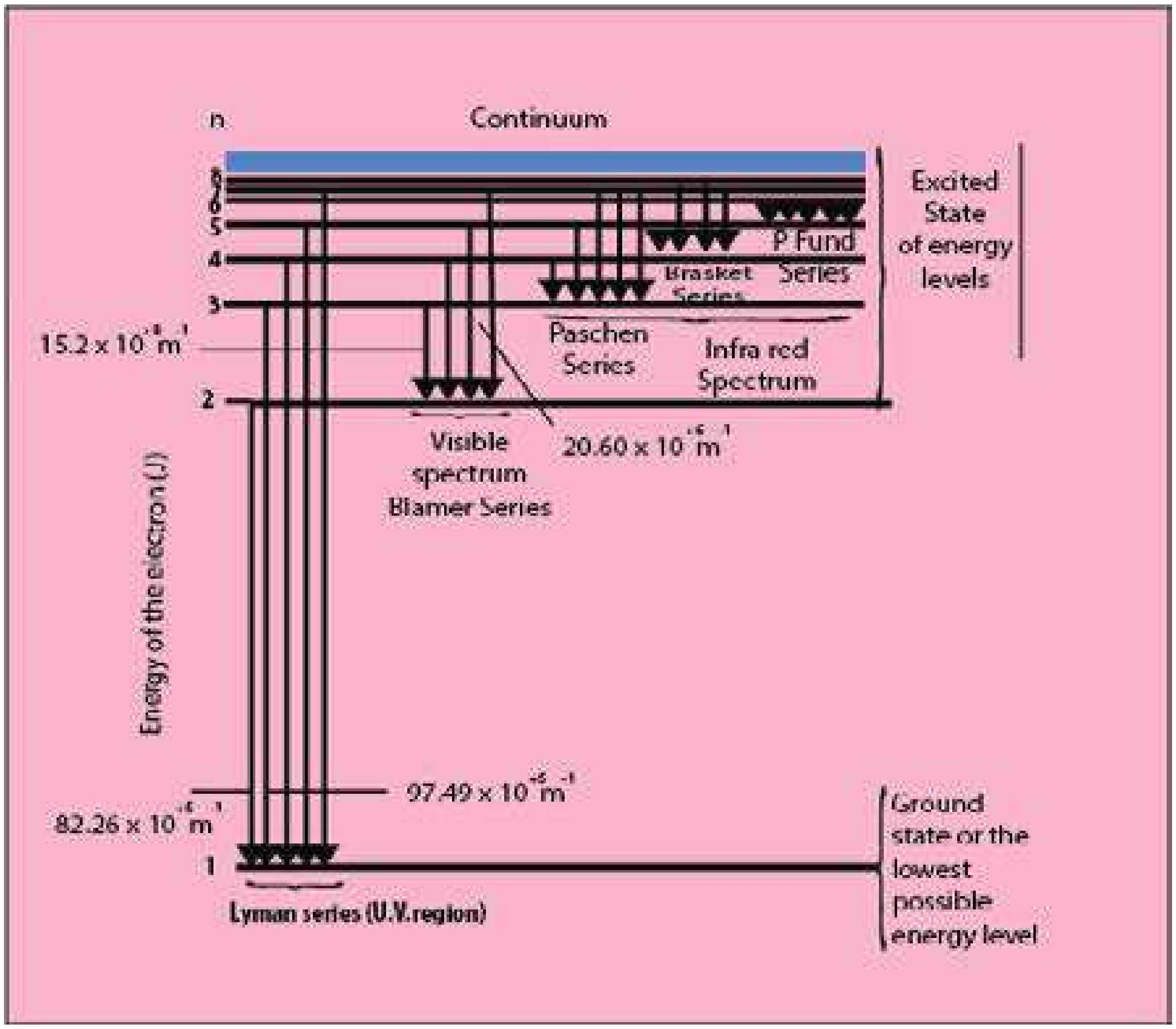


Fig (5.17) Electronic transitions in hydrogen atom and series of spectral lines, justified by Bohr's model atom

Calculations of Wave Numbers of Photons of Various Spectral Series by Bohr's Theory

The wavelength (λ) or wave number ($\bar{v}$) of a spectral line depends on the quantity of energy emitted by the electron. Suppose, an electron jumps from n_2 to n_1 and emits a photon of light. According to Bohr's equation of energy

$$E_1 = \frac{-Z^2me^4}{8\in_0^2 n^2{}_1 h^2}$$

$$E_2 = \frac{-Z^2me^4}{8\in_0^2 n^2{}_2 h^2}$$

E_1 and E_2 are the energies of electrons in n_1 and n_2 respectively. The energy difference between the two can be calculated as follows: $\Delta E = E_2 - E_1 = \frac{Z^2me^4}{8\in_0^2 h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$Joules .... (22)

For H-atom; Z - 1

and $\frac{me^4}{8\in_0^2 h^2} = 2.18 \text{ x } 10^{-18}$J (by putting the values of constants)

$$\ddot{A}E = 2.18x10^{-18}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]\text{Joules} \quad .... \quad (23)$$

With the help of equation (23), the energy difference between any two orbits of Hatom can be calculated where n_t is the lower level and n_2 is higher level. It is not necessary that n_1 and n_2 are adjacent orbits.

Since $\ddot{A}E = hv$

Therefore $hv = \frac{me^4}{8\in_0^2 h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

$$v = \frac{me^4}{8\in_0^2 h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]\text{Hz} \quad .... \quad (24)$$

Frequency (v) has the units of the cycles s^{-1} or Hz. (1 Hz = 1 cycle s^{-1})

Equation (24) gives us the frequency of a photon emitted, when electron jumps from higher orbit to lower orbit in H-atom. The frequency values go on decreasing between adjacent levels.

Calculation of Wave Number

Since $v = c\bar{v}$

Putting in equation (24)

Therefore $c\bar{v} = \frac{Z^2me^4}{8\epsilon_0^2h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

$$\bar{v} = \frac{Z^2me^4}{8\epsilon_0^2h^3c}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]m^{-1} \qquad \text{.............................} \qquad (25)$$

The value of the factor $\frac{me^4}{8\epsilon_0^2h^3c}$ in eq. (25) has been calculated to be 1.09678 x $10^7 m^{-1}$

This is called Rydberg constant. Putting Z = 1 for hydrogen atom, the equation (25)becomes.

$$\bar{v} = 1.09678 \times 10^7\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]m^{-1} \qquad \text{.........................} \qquad (26)$$

Equation (26) gives the values of wave number of photons emitted or absorbed when the electron jumps between n_1 and n_2 orbits.

Let us calculate, the wave numbers of lines of various series.

Lyman Series: Fig. (5.17)

Fitrst line n_1 = 1(lower orbit), n_2 = 2 (higher orbit)

$$\bar{v} = 1.09678 \times 10^7 \left[\frac{1}{1^2} - \frac{1}{2^2}\right] = 82.26\text{x}10^5 \text{m}^{-1}$$

Second line n_1 = 1 n_2 = 3

$$\bar{v} = 1.09678 \times 10^7 \left[\frac{1}{1^2} - \frac{1}{3^2}\right] = 97.49\text{x}10^5 \text{m}^{-1}$$

Limiting line n_1 = 1 n_2 = ∞

$$\bar{v} = 1.09678 \times 10^7 \left[\frac{1}{1^2} - \frac{1}{\infty^2}\right] = 109.678\text{x}10^5 \text{m}^{-1}$$

Limiting line is developed, when electron jumps from infinte orbit to, n = 1

The values of all these wave numbers lie in the U.Y region of the spectrum. It means that when electron of H-atom falls from all the possible higher levels to n = 1, then the photons of radiation emitted lie in the range of U.V region.

Balmer Series: Fig (5.17)

Fitrst line n_1 = 2, n_2 = 3

$$\bar{v} = 1.09678 \times 10^7 \left[\frac{1}{2^2} - \frac{1}{3^2}\right] = 15.234\text{x}10^5 \text{m}^{-1}$$

Second line $n_1 = 2$ $n_2 = 4$

$$\bar{v} = 1.09678 \times 10^7 \left[\frac{1}{2^2} - \frac{1}{4^2}\right] = 20.566 x 10^5 m^{-1}$$

Third line $n_1 = 2$ $n_2 = 5$

$$\bar{v} = 1.09678 \times 10^7 \left[\frac{1}{2^2} - \frac{1}{5^2}\right] = 23.00 x 10^5 m^{-1}$$

Limiting line $n_1 = 2$ $n_2 = \infty$

$$\bar{v} = 1.09678 \times 10^7 \left[\frac{1}{2^2} - \frac{1}{\infty^2}\right] = 27.421 x 10^5 m^{-1}$$

The limiting line of Balmer series lies in U.V region, while other lines fall in visible region. Similarly, we can calculate the wave numbers for all the lines of Paschen, Brackett and Pfund series. These three series of lines lie in the infrared region.

5.5.7 Defects of Bohr's Atomic Model

1. Bohr's theory can successfully explain the origin of the spectrum of H-atom and ions like He^{+1}, Li^{+2} and Be^{+3}, etc. These are all one electron systems. But this theory is not able to explain the origin of the spectrum of multi-electrons or poly-electrons system like He, Li and Be, etc.

2. When the spectrum of hydrogen gas is observed by means of a high resolving power spectrometer, the individual spectral lines are replaced by several very fine lines, i.e. original lines are seen divided into other lines. The H_α- line in the Balmer series is found to consist of five - component lines. This is called fine structure or multiple structure. Actually, the appearance of several lines in a single line suggests that only one quantum number is not sufficient to explain the origin of various spectral lines.

3. Bohr suggested circular orbits of electrons around the nucleus of hydrogen atom, but researches have shown that the motion of electron is not in a single plane, but takes place in three dimensional space. Actually, the atomic model is not flat.

4. When the excited atoms of hydrogen (which give an emission line spectrum) are placed in a magnetic field, its spectral lines are further split up into closely spaced lines. This type of splitting of spectral lines is called Zeeman effect. So, if the source which is producing the Na - spectrum is placed in a weak magnetic field, it causes the splitting of two lines of Na into component lines. Similarly, when the excited hydrogen atoms are placed in an electrical field, then similar splitting of spectral lines takes place which is called "Stark effect". Bohr's theory does not explain either Zeeman or Stark effect.

However, in 1915, Sommorfeld suggested the moving electrons might describe in addition to the circular orbits elliptic orbits as well wherein the nucleus lies at one of the focii of the ellipse.

5.6 X-RAYS AND ATOMIC NUMBER

X-rays are produced when rapidly moving electrons collide with heavy metal anode in the discharge tube. Energy is released in the form of electromagnetic waves when the electrons are suddenly stopped. In the discharge tube, the electrons produced by a heated tungsten filament are accelerated by high voltage Fig. (5.18). It gives them sufficient energy to bring about the emission of X-rays on striking the metal target. X-rays are emitted from the target in all directions, but only a small portion of them is used for useful purposes through the windows. The wavelength of X-rays produced depends upon the nature of the target metal. Every metal has its own characteristic X-rays.

The X-rays are passed through a slit in platinum plate and then emerged through aluminum window. This is thrown on a crystal of $K_4[Fe(CN)_6]$, which analyses the X-ray beam. The rays are diffracted from the crystal and are obtained in the form of line spectrum of X-rays. This is allowed to fall on photographic plate. This line spectrum is the characteristic of target material used. This characteristic X-rays spectrum has discrete spectral lines. These are grouped into K-series, L-series and M-series, etc. Each series has various line as K_α, K_β, L_α, L_β, M_α, M_β etc.

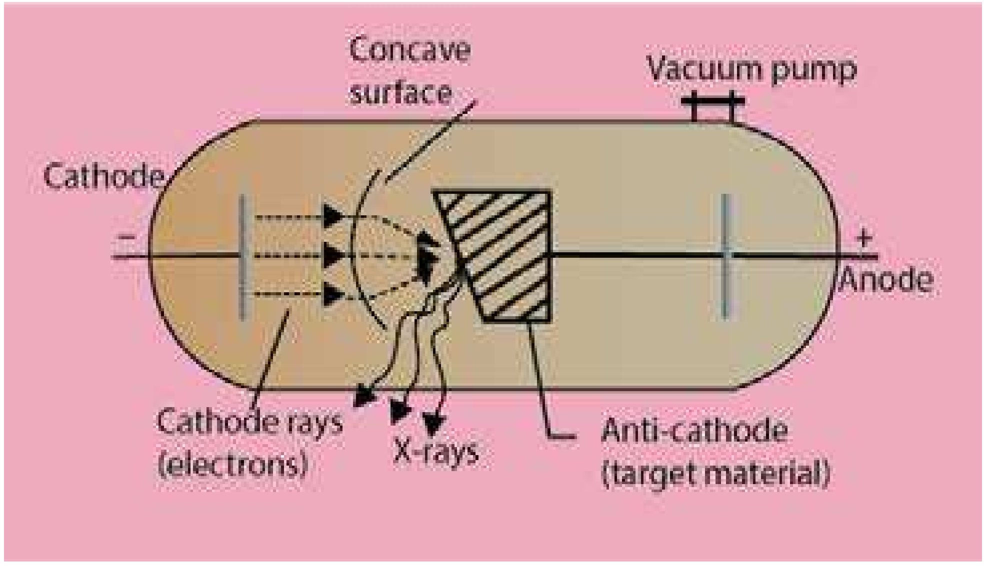


Fig (5.18) Production of X-rays

A systematic and comprehensive study of X-rays was undertaken by Moseley in 1913-1914. His researches covered a range of wavelengths 0.04 - 8 A. He employed thirty eight different elements from aluminium to gold, as target in X-rays tube. Moseley was able to draw the following important conclusions from a detailed analysis of the spectral lines which he obtained.

(i) The spectral lines could be classified into two distinct groups. One of shorter wavelengths are identified by K-series and the other of comparatively longer wavelengths are identified by L-series.

(ii) If the target element is of higher atomic number the wavelength of X-rays becomes shorter.

(iii) A very simple relationship was found between the frequency (v) of a particular line of X-rays and the atomic number Z of the element emitting it.

$$\sqrt{v} = a(Z-b) \qquad \text{..................} \qquad (27)$$

Here 'a' and 'b' are the constants characteristic of the metal under consideration. This linear equation (27) is known as Moseley's Law. 'a" is proportionality constant and 'b' is called screening constant of the metals.
This law states that the frequency of a spectral line in X-ray spectrum varies as the square of atomic number of an element emitting it. This law convinces us that it is the atomic number and not the atomic mass of the element which determines its characteristic properties, both physical and chemical. If value of $\sqrt{v}$ for K-series are plotted against Z, then a straight line is obtained.

Importance of Moseley Law

(i) Moseley arranged K and Ar, Ni and Co in a proper way in Mendeleev's periodic table.
(ii) This law has led to the discovery of many new elements like Tc(43), Pr(59), Rh(45).
(iii) The atomic number of rare earths have been determined by this law.

5.7 WAVE-PARTICLE NATURE OF MATTER (DUAL NATURE OF MATTER)

Planck's quantum theory of radiation tells us that light shows a dual character. It behaves both as a material particle and as a wave. This idea was extended to matter particles in 1924 by Louis de- Broglie. According to de-Broglie, all matter particles in motion have a dual character. It means that electrons, protons, neutrons, atoms and molecules possess the characteristics of both the material particle and a wave.
This is called wave-particle duality in matter. de-Broglie derived a mathematical equation which relates the wavelength (λ) of the electron to the momentum of electron.

$$\lambda = \frac{h}{mv} \quad \text{......................} \quad (28)$$

Here λ = de-Broglie's wavelength,
m = mass of the particle
v = velocity of electron

According to this equation, the wavelength associated with an electron is inversely proportional to its momentum (mv).

This equation is derived as follows.

According to Planck's equation

$$E = h\nu \quad ....$$

According to Einstein's mass energy relationship

$$E = mc^2 \quad .... \quad (29)$$

Where 'm' is the mass of the material particle which has to convert itself into a photon; 'and c' is the velocity of photon. Equating two values of energy;

$$h\nu = mc^2$$

Since

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

So, $\frac{hc}{\lambda} = mc^2$ or $\lambda = \frac{h}{mc}$ .... (30)

According to equation (30), the wavelength of photon is inversely proportional to the momentum of photon. Considering that nature is symmetrical, we apply this equation (30) to the moving electron of mass'm' and velocity V. This idea gives us the de-Broglie's equation (28)

$$\lambda = \frac{h}{mv} \quad .... \quad (28)$$

According to equation (28), the wavelength of electron is inversely proportional to momentum of electron. Now, consider an electron which is moving with a velocity of $2.188 \times 10^{6}\ ms^{-1}$ in the first orbit of Bohr's model of hydrogen atom. Then, wavelength associating with it, can be calculated with the help of equation(28)

h = 6.626×10^{-34} Js

m_e = 9.108×10^{-31} kg

$$\lambda = \frac{6.626 \times 10^{-34}\, Js}{9.108 \times 10^{-31}\, kg \times 2.188 \times 10^{6}\, ms^{-1}}$$ Since $(J = kg\ m^2\ s^{-2})$

$\lambda = 0.33 \times 10^{-9}$m $(10^{-9}m = 1mm)$

$\lambda = 0.33$ nm

This value of wavelength (λ)of electron while moving in the first orbit of H-atom is comparable to the wavelength of X-rays and can be measured.

If we imagine a proton moving in a straight line with the same velocity as mentioned for electron, it's wavelength will be 1836 times smaller than that of electron. Similarly, an α-particle moving with the same velocity should have a wavelength 7344 times smaller as compared to that of ejectron. Now, consider a stone of mass one gram moving with a velocity of 10 ms^{-1}, then its wavelength will be:

$$\lambda = \frac{6.626 \times 10^{-34}\,\text{Js}}{10^{-3}\,\text{kg} \times 10\,\text{ms}^{-1}}$$

$$= 6.626\text{x}10^{-30}\ \text{m}$$

This wavelength is so small, that it cannot be measured by any conceivable method. It means that heavy material particles have waves associated with them, but they cannot be captured and we say that the macroscopic bodies don't have the waves.

5.7.1 Experimental Verification of Dual Nature of Matter

In 1927, two American scientists, Davisson and Germer did an experiment to verify the wave nature of moving electron. Electrons were produced from heated tungsten filament and accelerated by applying the potential difference through charged plates. Davisson and Germer proved that the accelerated electrons undergo diffraction, like waves, when they fall on a nickel crystal. In this way, the wave nature of electron got verified. Davisson ahd Germer got the nobel prize for inventing an apparatus to prove the matter waves and de Broglie got the separate nobel prize for giving the equation of matter wave.

5.8 HEISENBERG'S UNCERTAINTY PRINCIPLE

According to Bohr's theory, an electron is a material particle and its position as well as momentum can be determined with great accuracy. But with the advent of the concept of wave nature of electron, it has not been possible for us to measure simultaneously the exact position and velocity of electron. This was suggested by Heisenberg, in 1927.

Suppose, that Δx is the uncertainty in the measurement of the position and Δp is the uncertainty in the measurement of momentum of an electron, then

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

This relationship is called uncertainty principle. This equation shows that if Δx is small then Δp will be large and vice versa. So, if one quantity is measured accurately then the other becomes less accurate. Hence, certainty in the determination of one quantity introduces uncertainty in the determination of the other quantity.

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

Compton's effect can help us understand the uncertainty principle, Suppose, we wish to determine the position of electron. Visible light cannot help us, because the wavelength of visible light is millions time large as compared to the diameter of electron. For this purpose, we have to use X-rays which have very short wavelength as compared to that of visible light. When this photon of X-rays strikes an electron, the momentum of electron will change. In other words, uncertainty of momentum will appear due to change of velocity of electron. Smaller the wavelength of X-rays, greater will be the energy of the photon. Hence, the collision of X-rays with electron will bring about the greater uncertainty in momentum. So, an effort to determine the exact position of electron has rendered its momentum uncertain. When we use the photons of longer wavelength to avoid the change of momentum, the determination of the position of electron becomes impossible.

Concept of Orbital

Following this principle, the Bohr's picture of an atom does not appear to be satisfactory. In Bohr's atom, the electrons are moving with specific velocities in orbits of specified radii, and according to uncertainty principle, both these quantities cannot be measured experimentally. A theory involving quantities, which cannot be measured does not follow the tradition of scientific work.

In order to solve this difficulty, Schrodinger, Heisenberg and Dirac worked out wave theories of the atom. The best known treatment is that of Schrodinger. He set up a wave equation for hydrogen atom. According to Schrodinger, although the position of an electron cannot be found exactly, the probability of finding an electron at a certain position at any time can be found.

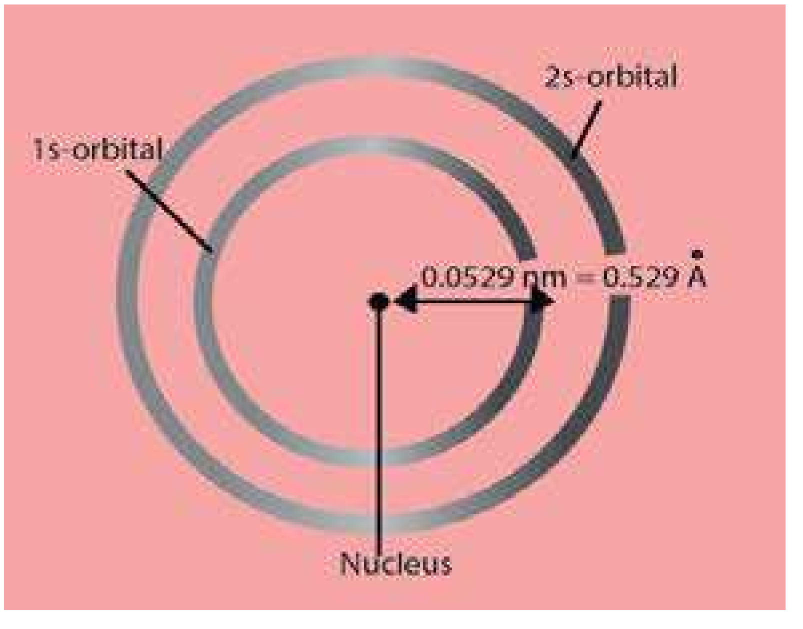


Fig (5.19) Probable electron density diagram for hydrogen atom.

The solution of the wave equation gives probability of finding an electron present in a given small region of space. When the probability of finding the electron at a distance r from the nucleus is calculated for the hydrogen atom in the ground state, Fig (5.19) is obtained.

The maximum probability of finding the electron is at a distance of 0.053 nm. It is the same radius as calculated for the Bohr's first orbit. There is a possibility that the electron is either closer to the nucleus or outside the radius of 0.053 nm, where probability of finding electron decreases sharply.

The volume of space in which there is 95% chance of finding an electron is called atomic orbital. The term orbital should not be confused with the term orbit as used in the Bohr's theory. The orbital can be regarded as a spread of charge surrounding the nucleus. This is often called the "electron cloud".

5.8.1 Quantum Numbers

Schrodinger wave equation, has been solved for hydrogen atom. It may have different solutions. Quantum numbers are the sets of numerical values which give the acceptable solutions to Schrodinger wave equation for hydrogen atom. An electron in an atom is completely described by its four quantum numbers. You know that a complete address of a person comprises his name, city in which he lives, the block, street and the house number. On the similar grounds, quantum numbers serve as identificatio numbers or labels, which completely describe an electron. These quantum numbers specify position of electron in an atom.

There are four quantum numbers which can describe the electron completely.

(1) Principal quantum number (n)
(2) Azimuthal quantum number (ℓ)
(3) Magnetic quantum number (m)
(4) Spin quantum number (s) Let us discuss these quantum numbers one by one.

Principal Quantum Number (n)

The different energy levels in Bohr's atom are represented by 'n'. This is called principal quantum number by Schrodinger. Its values are non-zero, positive integers upto infinity.

n = 1, 2, 3, 4, 5,........................, The value of n represents the shell or energy level in which the electron revolves around the nucleus. Letter notations K, L, M, N, etc are also used to denote the various shells. For example, when n =1, it is called K shell, for n = 2, it is L shell and so on. The values of n also determine the location of electron in an atom, i.e the distance of electron from the nucleus, greater the value of 'n' greater will be the distance of electron from the nucleus. It is a quantitative measure of the size of an electronic shell, 'n' also provides us the energy of electron in a shell. Bohr's results help us to know the relationships of distance and energy of electron.

Azimuthal Quantum Number (ℓ)

It has already been mentioned in the defects of Bohr's model that a spectrometer of high resolving power shows that an individual line in the spectrum is further divided into several very fine lines. This thing can be explained by saying that each shell is divided into subshells. So, only principal quantum number (n) is not sufficient to explain the line spectrum. There is another subsidiary quantum number called azimuthal quantum number and is used to represent the subshells. The values of azimuthal quantum number (ℓ) are

$$\ell = 0, 1, 2, 3, \ldots\ldots\ldots\ldots\ldots\ldots\ldots (n-1)$$

Its value depends upon n. These values represent different subshells, which are designated by small letters, s, p, d, f. They stand for sharp, principal, diffused and fundamental, respectively. These are the spectral terms used to describe the series of lines observed in the atomic spectrum. The values of azimuthal quantum number always start from zero.

A subshell may have different shapes depending upon the value of (' ℓ '). It may be spherical, dumb-bell, or some other complicated shapes. The value of ' ℓ ' is related to the shape of the subshell as follows:

$\ell = 0$	s-subshell	spherical
$\ell = 1$	p-subshell	dumb-bell
$\ell = 2$	d-subshell	(complicated shape)

The relationship between principal and azimuthal quantum numbers is as follows.

n = 1	K-shell	{ℓ = 0	{s-subshell	should be called as	1s
n = 2	L-shell	$\ell = 0$	s-subshell		2s
		$\ell = 1$	p-subshell		2p
n = 3	M-shell	$\ell = 0$	s-subshell		3s
		$\ell = 1$	p-subshell		3p
		$\ell = 2$	d-subshell		3d
n = 4	N-shell	$\ell = 0$	s-subshell		4s
		$\ell = 1$	p-subshell		4p
		$\ell = 2$	d-subshell		4d
		$\ell = 3$	f-subshell		4f

In 1s, 2s, ..., etc, the digit represents the value of principal quantum number.'ℓ' values also enable us to calculate the total number of electrons in a given subshell. The formula for calculating electrons is 2 (2ℓ + 1).

when	ℓ = 0	s-subshell	total electrons = 2
	ℓ = 1	p-subshell	total electrons = 6
	ℓ = 2	d-subshell	total electrons = 10
	ℓ = 3	f-subshell	total electrons = 14

Magnetic Quantum Number (m)

In the defects of Bohr's model, it has been mentioned that strong magnetic field splits the spectral lines further. In order to explain this splitting, a third quantum number called the magnetic quantum number (m) has been proposed.

Its values are

$$m = 0, \pm 1, \pm 2, \pm 3, \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

The value of'm' depends upon values of 'ℓ'

when	ℓ = 0	s-subshell	m=0
	ℓ = 1	p-subshell	m=0, ±1(p-subshell has three degenerate orbitals)
	ℓ = 2	d-subshell	m=0,±1, ±2(d-subshell has five degenerate orbitals)
	ℓ = 3	f-subshell	m=0,±1, ±2, ±3(f-subshell has seven degenerate orbitals)

This above description shows that for a given value of 'ℓ' the total values of'm' are (2ℓ +1).

Actually, the value of m gives us the information of degeneracy of orbitals in space. It tells us the number of different ways in which a given s, p, d or f-subshell can be arranged along x, y and z-axes in the presence of a magnetic field. Thus, different values of'm' for a given value of 'ℓ', represent the total number of different space orientations for a subshell.

In case of s-subshell ℓ = 0, so, m = 0. It implies that s-subshell of any energy level has only one space orientation and can be arranged in space only in one way along x, y and z-axes. So s-subshell is not sub-divided into any other orbital. The shape of's' orbital is such that the probability of finding the electron in all the directions from the nucleus is the same. It is a spherical and symmetrical orbital. Fig (5.20).

For p-subshell, ℓ = 1 and m = 0, ±1. These values of'm' imply that p-subshell of any energy level has three space orientations and can be arranged in space along x, y, and z axes Fig. (5.21). These three orbitals are perpendicular to each other and named as p_x, p_y, and p_z. They have egg shaped lobes which touch each other at the origin. They are disposed symmetrically along one of the three axes called orbital axis. In the absence of the magnetic field, all the three p-orbitals have the same energy and are called degenerate orbitals. Since, they are three in number, so these orbitals are said to be 3-fold degenerate or triply degenerate.

For d-subshell ℓ = 2 m = 0, ±1, ±2. It implies that it has five space orientations and are designated as d_{xy} (m = -2), d_{yz} (m = -1), d_{zx}(m = +1), $d_{x^2-y^2}$(m = +2) and d_{z^2}(m - 0) Fig. (5.22).

All these five d-orbitals are not identical in shape. In the absence of a magnetic field, all five d-orbitals have the same energy and they are said to be five fold degenerate orbitals.

For f-subshell, ℓ = 3 and m = 0, ±1, ±2, ±3. They have complicated shapes.

The whole discussion shows that magnetic quantum number determines the orientation of orbitals, so it is also called orbital orientation quantum number.

Spin Quantum Number (s)

Alkali metals have one electron in their outermost shell. We can record their emission spectra, when the outermost electron jumps from an excited state to a ground state. When the spectra are observed by means of high resolving power spectrometer, each line in the spectrum is found to consist of pair of lines, this is called doublet line structure. We should keep it in mind, that doublet line structure is different from the fine spectrum of hydrogen (as we have discussed in azimuthal quantum number).

It should be made clear that lines of doublet line structure are widely separated from each other, while those of fine structure are closely spaced together.

In 1925, Goudsmit and Uhlenbech suggested that an electron while moving in an orbital around the nucleus also rotates or spins about its own axis either in a clockwise or anti-clockwise direction. This is also called self-rotation. This spinning electron is associated with a magnetic field and hence a magnetic moment. Hence, opposite magnetic fields are generated by the clockwise and anti-clockwise spins of electrons. This spin motion is responsible for doublet line structure in the spectrum.

The four quantum numbers of all the electrons in the first four shells are summarized in Table (5.3). Notice, that each electron has its own set of quantum numbers and this set is different for each electron.

Table (5.3) Quantum Numbers of Elections

Principal Quantum Number 'n'	Azimuthal Quantum number ' ℓ '	Magnetic Quantum number 'm'	Spin Quantum number 's'	Number of electrons accommodated
1 K	0 s	0	+½,-½	2
2 L	0 s 1 p	0 +1, 0, −1	+½,-½ +½,-½	2 6 } 8
3 M	0 s 1 p 2 d	0 +1, 0, −1 +2, +1, 0, −1, −2	+½,-½ +½,-½ +½,-½	2 6 } 18 10
4 N	0 s 1 p 2 d 3 f	0 +1, 0, −1 +2, +1, 0, −1, −2 +3, +2, +1, 0, −1, −2, −3	+½,-½ +½,-½ +½,-½ +½,-½	2 6 } 32 10 14

5.8.2 Shapes of Orbitals

In section 5.8.1, we were introduced to the four types of orbitals depending upon the values of azimuthal quantum number. These orbitals are s, p, d and f having azimuthal quantum number values as ℓ = 0,1, 2,3, respectively. Let us, discuss the shapes of these, orbitals.

Shapes of s-Orbitals

s-orbital has a spherical shape and is usually represented by a circle, which in turn, represents a cut of sphere, Fig. (5.20). With the increase of value of principal quantum number (n), the size of s-orbital increases. 2s-orbital is larger in size than ls-orbital. 2s-orbital is also further away form the nucleus Fig. (5.20). The probability for finding the electron is zero between two orbitals. This place is called nodal plane or nodal surface.

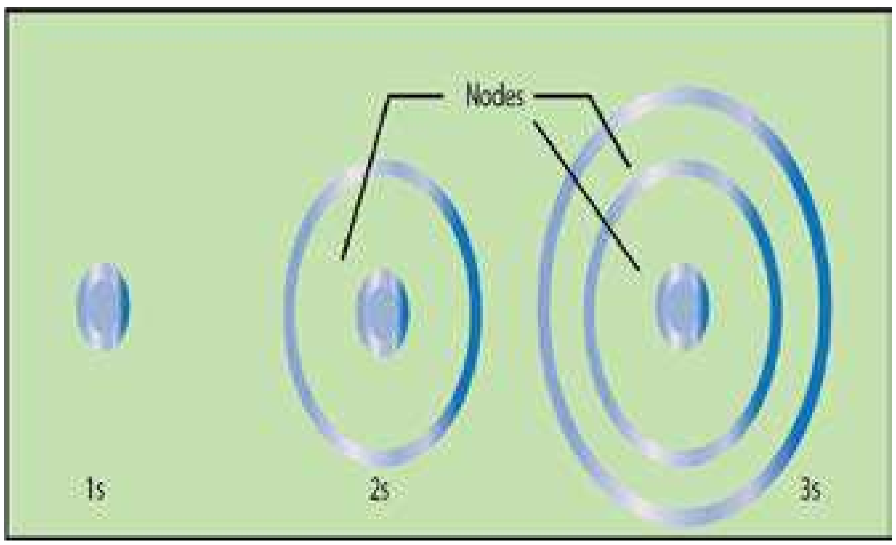


Fig (5.20) Shapes of s-orbitals with increasing principal quantum number

Shapes of p-Orbitals

There are three values of magnetic quantum numbef for p-subshell. So, p-subshell has three orientations in space i.e. along x, y and z-axes. All the three p-orbitals namely, p_x, p_y and p_z have dumb-bell shapes, Fig. (5.21). So, p-orbitals have directional character which determines the geometry of molecules. All the p-orbitals of all the energy levels have similar shapes, but with the increase of principal quantum number of the shell their sizes are increased.

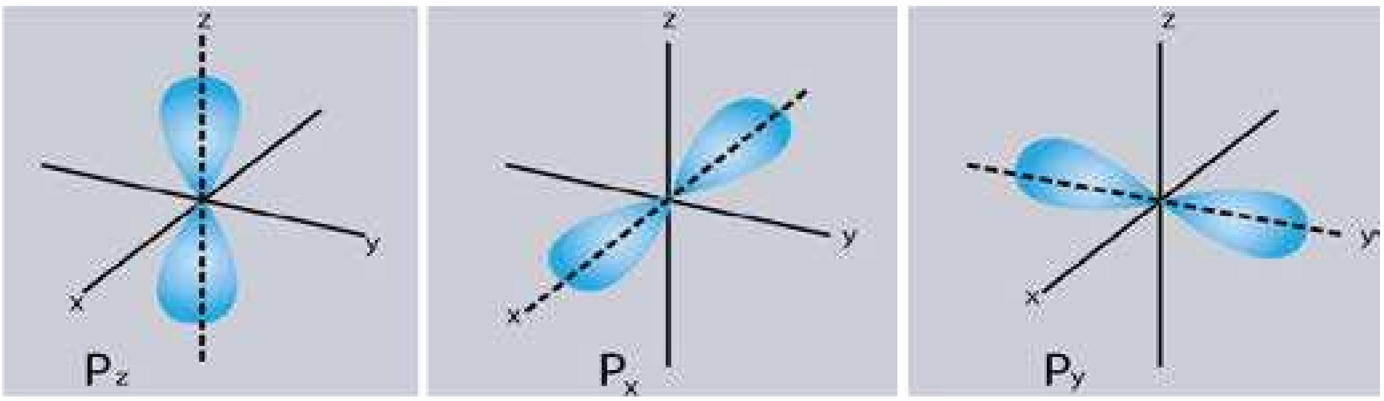
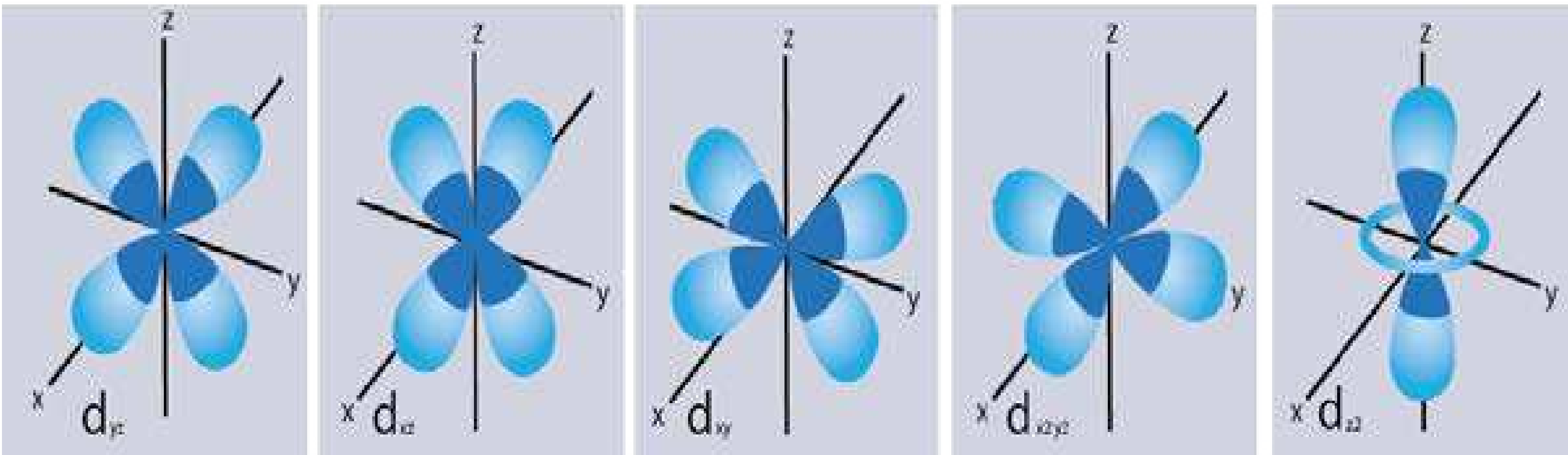


Fig (5.20) Shapes of p-orbitals

Shapes of d-Orbitals

For d subshell there are five values of magnetic quantum number. So, there are five space orientations along x, yand z-axes. Fig (5.22). They are designated as d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$, d_{z^2} .The lobes of first three d-orbitals lie between the axis. The other lie on the axis.
They are not identical in shape. Four d-orbitals out of these five contain four lobes each, while the fifth orbital d_{z^2} consists of only two lobes, Fig (5.22). In the absence of magnetic field, all the five d-orbitals are degenerate. The shape of f-orbital is very complicated.



Fig(5.22)Shapesofd-orbitals

5.9 ELECTRONIC DISTRIBUTION

In order to understand the distribution of electrons in an atom, we should know the following facts.

1. An orbital like s, p_x, p_y, p_z and d_{xy}, etc. can have at the most two electrons.
2. The maximum number of electrons that can be accommodated in a shell is given by $2n^2$ formula where n is principal quantum number and it cannot have zero value.

Moreover, following rules have been adopted to distribute the electrons in subshells or orbitals.

1. Aufbau principle
2. Pauii's exclusion principle
3. Hand's rule

But, before we use these rules, the subshells should be arranged according to $(n + \ell)$ rule, Table(5.4). This rule says that subshells are arranged in the increasing order of $(n + \ell)$ values and if any two subshells have the same $(n + \ell)$ values, then that subshell is placed first whose n value is smaller.

The arrangement of subshells in ascending order of their energy may be as follows: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s and so no.

Aufbau Principle

The electrons should be filled in energy subshells in order of increasing energy values. The electrons are first placed in Is, 2s, 2p and soon.

Table (5.4) Arrangement of orbitals according to (n+1) rule

	n	ℓ	n + ℓ
1s	1	0	1 + 0 = 1
2s	2	0	2 + 0 = 2
2p	2	1	2 + 1 = 3
3s	3	0	3 + 0 = 3
3p	3	1	3 + 1 = 4
3d	3	2	3 + 2 = 5
4s	4	0	4 + 0 = 4
4p	4	1	4 + 1 = 5
4d	4	2	4 + 2 = 6
4f	4	3	4 + 3 = 7
5s	5	0	5 + 0 = 5
5p	5	1	5 + 1 = 6
5d	5	2	5 + 2 = 7
5f	5	3	5 + 3 = 8
6s	6	0	6 + 0 = 6
6p	6	1	6 + 1 = 7
6d	6	2	6 + 2 = 8
6f	6	3	6 + 3 = 9
7s	7	0	7 + 0 = 7

Pauli's Exclusion Principle

This principle can be stated as follows:

It is impossible for two electrons residing in the same orbital of a poly-electron atom to have the same values of four quantum numbers, or Two electrons in the same orbital should have opposite spins (↓↑).

Hund's Rules

If, degenerate orbitals are available and more than one electrons are to be placed in them, they should be placed in separate orbitals with the same spin rather than putting them in the same orbital with opposite spins.

According to the rule, the two electrons in 2p subshell of carbon will be distributed as follows.

$$_{6}C = \overset{\downarrow\uparrow}{1s}\ \overset{\downarrow\uparrow}{2s}\ \overset{\uparrow}{2p_x}\ \overset{\downarrow}{2p_y}\ \overset{o}{2p_z}$$

The three orbitals of 2p subshell are degenerate.

5.9.1 Electronic Configuration of Elements

Keeping in view the rules mentioned above, the electronic configurations of first thirty six elements are given in Table (5.5).

Table (5.5) Electron configurations of elements

Element	Atomic number	Electron Configuration Notation
Hydrogen	1	$\overset{\uparrow}{1s}$
Helium	2	$1s^2$
Lithium	3	$1s^2\overset{\uparrow}{2s}$
Beryllium	4	$1s^22s^2$

Table (5.5) continued

Element	Atomic number	Electron Configuration Notation
Boron	5	$1s^2 2s^2 2\overset{\uparrow}{p}_x 2\overset{0}{p}_y 2\overset{0}{p}_z$
Carbon	6	$1s^2 2s^2 2\overset{\uparrow}{p}_x 2\overset{\uparrow}{p}_y 2\overset{0}{p}_z$
Nitrogen	7	$1s^2 2s^2 2\overset{\uparrow}{p}_x 2\overset{\uparrow}{p}_y 2\overset{\uparrow}{p}_z$
Oxygen	8	$1s^2 2s^2 2p^2_x 2\overset{\uparrow}{p}_y 2\overset{\uparrow}{p}_z$
Fluorine	9	$1s^2 2s^2 2p^2_x 2p^2_y 2\overset{\uparrow}{p}_z$
Neon	10	$1s^2 2s^2 2p^2_x 2p^2_y 2p^2_z$
Sodium	11	$[Ne]\, 3\overset{\uparrow}{s}$
Magnesium	12	$[Ne]\, 3\overset{\uparrow\downarrow}{s}$
Aluminum	13	$[Ne]\, 3s^2 3\overset{\uparrow}{p}_x 3\overset{0}{p}_y 3\overset{0}{p}_z$
Silicon	14	$[Ne]\, 3s^2 3\overset{\uparrow}{p}_x 3\overset{\uparrow}{p}_y 3\overset{0}{p}_z$
Phosphorus	15	$[Ne]\, 3s^2 3\overset{\uparrow}{p}_x 3\overset{\uparrow}{p}_y 3\overset{\uparrow}{p}_z$
Sulphur	16	$[Ne]\, 3s^2 3p^2_x 3\overset{\uparrow}{p}_y 3\overset{\uparrow}{p}_z$
Chlorine	17	$[Ne]\, 3s^2 3p^2_x 3p^2_y 3\overset{\uparrow}{p}_z$
Argon	18	$[Ne]\, 3s^2 3p^2_x 3p^2_y 3p^2_z$
Potassium	19	$[Ar]\, 4\overset{\uparrow}{s}$
Calcium	20	$[Ar]\, 4s^2$

(continued on next page)

Element	Atomic number	Electron Configuration Notation
Scandium	21	$[Ar]\ 4s^2\ \overset{\uparrow}{3d_{xy}}\ \overset{0}{3d_{yz}}\ \overset{0}{3d_{xz}}\ \overset{0}{3d_{x^2-y^2}}\ \overset{0}{3d_{z^2}}$
Titanium	22	$[Ar]\ 4s^2\ \overset{\uparrow}{3d_{xy}}\ \overset{\uparrow}{3d_{yz}}\ \overset{0}{3d_{xz}}\ \overset{0}{3d_{x^2-y^2}}\ \overset{0}{3d_{z^2}}$
Vanadium	23	$[Ar]\ 4s^2\ \overset{\uparrow}{3d_{xy}}\ \overset{\uparrow}{3d_{yz}}\ \overset{\uparrow}{3d_{xz}}\ \overset{0}{3d_{x^2-y^2}}\ \overset{0}{3d_{z^2}}$
Chromium	24	$[Ar]\ \overset{\uparrow}{4s}\ \overset{\uparrow}{3d_{xy}}\ \overset{\uparrow}{3d_{yz}}\ \overset{\uparrow}{3d_{xz}}\ \overset{\uparrow}{3d_{x^2-y^2}}\ \overset{\uparrow}{3d_{z^2}}$
Manganese	25	$[Ar]\ 4s^2\ 3d^2_{xy}\ \overset{\uparrow}{3d_{yz}}\ \overset{\uparrow}{3d_{xz}}\ \overset{\uparrow}{3d_{x^2-y^2}}\ \overset{\uparrow}{3d_{z^2}}$
Iron	26	$[Ar]\ 4s^2\ 3d^2_{xy}\ 3d^2_{yz}\ \overset{\uparrow}{3d_{xz}}\ \overset{\uparrow}{3d_{x^2-y^2}}\ \overset{\uparrow}{3d_{z^2}}$
Cobalt	27	$[Ar]\ 4s^2\ 3d_{xy}\ 3d_{yz}\ 3d_{xz}\ \overset{\uparrow}{3d_{x^2-y^2}}\ \overset{\uparrow}{3d_{z^2}}$
Nickel	28	$[Ar]\ 4s^2\ 3d_{xy}\ 3d_{yz}\ 3d_{xz}\ 3d_{x^2-y^2}\ \overset{\uparrow}{3d_{z^2}}$
Copper	29	$[Ar]\ \overset{\uparrow}{4s}\ 3d^2_{xy}\ 3d^2_{yz}\ 3d^2_{xz}\ 3d^2_{x^2-y^2}\ 3d^2_{z^2}$
Zinc	30	$[Ar]\ 4s^2\ 3d^2_{xy}\ 3d^2_{yz}\ 3d^2_{xz}\ 3d^2_{x^2-y^2}\ 3d^2_{z^2}$
Gallium	31	$[Ne]\ 4s^2\ 3d^{10}\ \overset{\uparrow}{4p_x}\ \overset{0}{4p_y}\ \overset{0}{4p_z}$
Germanium	32	$[Ne]\ 4s^2\ 3d^{10}\ \overset{\uparrow}{4p_x}\ \overset{\uparrow}{4p_y}\ \overset{0}{4p_z}$
Arsenic	33	$[Ne]\ 4s^2\ 3d^{10}\ \overset{\uparrow}{4p_x}\ \overset{\uparrow}{4p_y}\ \overset{\uparrow}{4p_z}$
Selenium	34	$[Ne]\ 4s^2\ 3d^{10}\ 4p^2_x\ \overset{\uparrow}{4p_y}\ \overset{\uparrow}{4p_z}$
Bromine	35	$[Ne]\ 4s^2\ 3d^{10}\ 4p^2_x\ 4p^2_y\ \overset{\uparrow}{4p_z}$
Krypton	36	$[Ne]\ 4s^2\ 3d^{10}\ 4p^2_x\ 4p^2_y\ 4p^2_z$

KEY POINTS

1. Matter is made up of extremely small particles called atoms.
2. Cathode rays and positive rays were discovered during discharge tube experiments. The properties of cathode rays showed them to be negatively charged particles called electrons, whereas, the positive rays were found to contain positively charged particles called protons.
3. Neutron was discovered through artificial radioactivity.
4. Electrons, protons and neutrons are regarded as the fundamental particles of an atom.
5. Rutherford discovered the nucleus and successfully explained the presence of moving electrons around the nucleus.
6. In 1905, Planck put forward his famous Planck's quantum theory.
7. Neil Bohr explained the structure of hydrogen atom by using Planck's quantum theory. He also calculated the radius and energy of electron in the nth shell of hydrogen atom.
8. Bohr's atomic model successfully explained the origin of line spectrum and the lines present in the spectrum of hydrogen atom in the visible and invisible regions.
9. X-rays are produced when rapidly moving electrons collide with heavy metal anode in the discharge tube.
10. Moseley discovered a simple relationship between the frequency of X-rays and the atomic number of the target element.
11. de-Broglie discovered wave particle duality of material particles. According to him, all material particles in motion have a dual character. Davisson and Germer experimentally verified the wave concept of an electron.
12. Heisenberg pointed out that it is not possible for us, to measure the exact position and the exact momentum of electron simultaneously.
13. After the failure of Bohr's atomic model, Schrodinger developed the wave mechanical model of hydrogen atom. According to him, although the position of an electron cannot be found exactly, the probability of finding an electron at a certain position at any time can be calculated.
14. An electron in an atom is completely described by its four quantum numbers. Three out of these four quantum numbers, have been derived from Schrodinger wave equation, when it is solved for hydrogen atom.

EXERCISE

Q1. Select the most suitable answer for the given one.

(i) The nature of the positive rays depend on
- (a) the nature of the electrode (b) the nature of the discharge tube
- (c) the nature of the residual gas (d) all of the above

(ii) The velocity of photon is
- (a) independent of its wavelength (b) depends on its wavelength
- (c) equal to square of its amplitude (d) depends on its source

(iii) The wave number of the light emitted by a certain source is $2 \times 10^6\ m^{-1}$. The wavelength of this light will be
- (a) 500 nm (b) 500 m (c) 200nm (d) 5×10^7m

(iv) Rutherford's model of atom failed because
- (a) the atom did not have a nucleus and electrons
- (b) it did not account for the attraction between protons and neutrons
- (c) it did not account for the stability of the atom
- (d) there is actually no space between the nucleus and the electrons

(v) Bohr model of atom is contradicted by
- (a) Planck's quantum theory (b) dual nature of matter
- (c) Heisenberg's uncertainty principle (d) all of the above

(vi) Splitting of spectral lines when atoms are subjected to strong electric field is called,
- (a) Zeeman effect (b) Stark effect
- (c) Photoelectric effect (d) Compton effect

(vii) In the ground state of an atom, the electron is present
- (a) in the nucleus (b) in the second shell
- (c) nearest to the nucleus (d) farthest from the nucleus

(viii) Quantum number values for 2p orbitals are
- (a) n = 2, ℓ = 1 (b) n = 1, ℓ = 2
- (c) n = 1, ℓ = 0 (d) n = 2, ℓ = 0

(ix) Orbitals having same energy are called
- (a) hybrid orbitals (b) valence orbitals
- (c) degenerate orbitals (d) d-orbitals

(x) When 6d orbital is complete, the entering electron goes into
- (a) 7f (b) 7s (c) 7p (d) 7d

Q2. Fill in the blanks with suitable words.

(i) β-particles are nothing but __________ moving with a very high speed.

(ii) The charge on one mole of electrons is__________coulombs.

(iii) The mass of hydrogen atom is____________ grams.

(iv) The mass of one mole of electrons is______________ .

(v) Energy is __________ when electron jumps from higher to a lower orbit.

(vi) The ionization energy of hydrogen atom can be calculated from_____model of atom.

(vii) For d-subshell, the azimuthal quantum number has value of __________.

(viii) The number of electrons in a given subshell is given by formula_________ .

(ix) The electronic configuration of H^+ is__________ .

Q3. Indicate true or false as the case may be.

(i) A neutron is slightly lighter particle than a proton.

(ii) A photon is the massless bundle of energy but has momentum.

(iii) The unit of Rydberg constant is the reciprocal of unit of length.

(iv) The actual isotopic mass is a whole number.

(v) Heisenberg's uncertainty principle is applicable to macroscopic bodies.

(vi) The nodal plane in an orbital is the plane of zero electron density.

(vii) The number of orbitals present in a sublevel is given by the formula $(2\ell + 1)$.

(viii) The magnetic quantum number was introduced to explain Zeeman and Stark effect.

(ix) Spin quantum number tells us the direction of spin of electron around the nucleus.

Q 4: Keeping in mind the discharge tube experiment, answer the following questions.

(a) Why is it necessary to decrease the pressure in the discharge tube to get the cathode rays?

(b) Whichever gas is used in the discharge tube, the nature of the cathode rays remains the same. Why?

(c) Why e/m value of the cathode rays is just equal to that of electron?

(d) How the bending of the cathode rays in the electric and magnetic fields shows that they are negatively charged?

(e) Why the positive rays are also called canal rays?

(f) The e/m value of positive rays for different gases are different but those for cathode rays the e/m values are the same. Justify it.

(g) The e/m value for positive rays obtained from hydrogen gas is 1836 times less than that of cathode rays. Justify it.

Q5 (a) Explain Millikan's oil drop experiment to determine the charge of an electron.

(b) What is J.J Thomson's experiment for determining e/m value of electron?

(c) Evaluate mass of electron from the above two experiments.

Q6 (a) Discuss Chadwick's experiment for the discovery of neutron. Compare the properties of electron, proton and neutron.

(b) Rutherford's atomic model is based on the scattering of α-particles from a thin gold foil. Discuss it and explain the conclusions.

Q7. (a) Give the postulates of Bohr's atomic model. Which postulate tells us that orbits are stationary and energy is quantized?

(b) Derive the equation for the radius of nth orbit of hydrogen atom using Bohr's model.

(c) How does the above equation tell you that

(i) radius is directly proportional to the square of the number of orbit.

(ii) radius is inversely proportional to the number of protons in the nucleus.

(d) How do you come to know that the velocities of electrons in higher orbits, are less than those in lower orbits of hydrogen atom?

(e) Justify that the distance gaps between different orbits go on increasing from the lower to the higher orbits.

Q8 Derive the formula for calculating the energy of an electron in nth orbit using Bohr's model. Keeping in view this formula explain the following:

(a) The potential energy of the bounded electron is negative.

(b) Total energy of the bounded electron is also negative.

(c) Energy of an electron is inversely proportional to n^2, but energy of higher orbits are always greater than those of the lower orbits.

(d) The energy difference between adjacent levels goes on decreasing sharply.

Q9. (a) Derive the following equations for hydrogen atom, which are related to the

(i) energy difference between two levels, n_1 and n_2.

(ii) frequency of photon emitted when an electron jumps from n_2 to n_1.

(iii) wave number of the photon when the electron jumps from n_2 to n_1.

(b) Justify that Bohr's equation for the wave number can explain the spectral lines of Lyman, Balmer and Paschen series.

Q10. (a) What is spectrum. Differentiate between continuous spectrum and line spectrum.

(b) Compare line emission and line absorption spectra.

(c) What is the origin of line spectrum?

Q11. (a) Hydrogen atom and He^+ are mono-electronic system, but the size of He^+ is much smaller than H^+, why?

(b) Do you think that the size of Li^{+2} is even smaller than He^+? Justify with calculations.

Q12. (a) What are X-rays? What is their origin? How was the idea of atomic number derived from the discovery of X-rays?

(b) How does the Bohr's model justify the Moseley's equation?

Q13. Point out the defects of Bohr's model. How these defects are partially covered by dual nature of electron and Heisenberg's uncertainty principle?

Q14. (a) Briefly discuss the wave mechanical model of atom. How has it given the idea of orbital. Compare orbit and orbital.

(b) What are quantum numbers? Discuss their significance.

(c) When azimuthal quantum number has a value 3, then there are seven values of magnetic quantum number. Give reasons.

Q15. (a) Discuss rules for the distribution of electrons in energy subshells and in orbitals.

(b) What is (n + ℓ) rule. Arrange the orbitals according to this rule. Do you think that this rule is applicable to degenerate orbitals?

(c) Distribute electrons in orbitals of $_{57}La$, $_{29}Cu$, $_{79}Au$, $_{24}Cr$, $_{53}1$, $_{86}Rn$.

Q16 Draw the shapes of s, p and d-orbitals. Justify these by keeping in view the azimuthal and magnetic quantum numbers.

Q17 A photon of light with energy 10^{-19} J is emitted by a source of light.

(a) Convert this energy into the wavelength, frequency and wave number of the photon in terms of meters, hertz and m^{-1}, respectively.

(Ans:$1.51xl0^{14}s^{-1}$; $1.98x10^{-6}m$; $5xl0^{5}m^{-1}$)

(b) Convert this energy of the photon into ergs and calculate the wavelength in cm, frequency in Hz and wave number in cm^{-1}.

[h = $6.626x\ 10^{-34}$ Js or $6.625x\ 10^{-27}$ ergs, c = $3x10^{8}\ ms^{-1}$ or $3x\ 10^{+10}\ cms^{-1}$]

(Ans:$1.51xl0^{14}s^{-1}$; $1.98xl0^{-4}cm$; $5xl0^{3}cm^{-1}$)

Q18 The formula for calculating the energy of an electron in hydrogen atom given by Bohr's model

$$E_n = \frac{-m^2e^4}{8\varepsilon_0^2h^2n^2}$$

Calculate the energy of the electron in first orbit of hydrogen atom. The values of various parameters are same as provided in Q19.

(Ans:$-2.18xlO^{-18}$J)

Q 19 Bohr's equation for the radius of nth orbit of electron in hydrogen atom is

$$r_n = \frac{\epsilon_0 h^2n^2}{\pi e^2m}$$

(a) When the electron moves from n = 1 to n = 2, how much does the radius of the orbit increases.

(Ans: 1.587 Å)

(b) What is the distance travelled by the electron when it goes from n=2 to n=3 and n=9 ton=10?

[ε_0 = 8.85x 10^{-12} $c^2J^{-1}m^{-1}$, h = 6.624 x.10^{-34} js, π = 3.14, m = 9.108x 10^{-31} kg, e = 1.602 x 10^{-19}c] while doing calculations take care of units of energy parameter.

[J = $kgm^2 s^{-2}$, c = $kg^{1/2} m^{3/2} s^{-1}$]

(Ans: 2.65 Å; 10.05 Å)

Q 20 Answer the following questions, by performing the calculations.

(a) Calculate the energy of first five orbits of hydrogen atom and determine the energy differences between them.

(b) Justify that energy difference between second and third orbits is approximately five times smaller than that between first and second orbits.

(c) Calculate the energy of electron in He+ in first five orbits and justify that the energy differences are different from those of hydrogen atom.

(d) Do you think that groups of the spectral lines of He^+ are at different places than those for hydrogen atom? Give reasons.

Q 21 Calculate the value of principal quantum number if an electron in hydrogen atom revolves in an orbit of energy- 0.242 xlO^{-18} J.

(Ans:n=3)

Q 22 Bohr's formula for the energy levels of hydrogen atom for any system say H, He^+,Li^{2+} ,etc. is

$$E_n = \frac{-Z^2e^4m}{8\varepsilon_0{}^2h_2n^2}$$

or

$$E_n = -K\left[\frac{Z^2}{n^2}\right]$$

For hydrogen:Z = 1 and for He^+, Z = 2.

(a) Draw an energy level diagram for hydrogen atom and He^+ .

(b) Thinking that K = 2.18 x 10^{-18}J, calculate the energy needed to remove the electron from hydrogen atom and from He^+.

(Ans: 2.18 x 10^{-18}J; 8.72x10^{-18}J)

(c) How do you justify that the energies calculated in (b) are the ionization energies of H and He^+?

(d) Use Avogadro's number to convert ionization energy values in $kJmol^{-1}$ for H and He^+.

(Ans: 1313.3$kJmol^{-1}$; 5249.4$kJmol^{-1}$)

(e) The experimental values of ionization energy of H and He^+ are 1331 $kJmol^{-1}$ and 5250 $kJmol^{-1}$, respectively. How do you compare your values with experimental values?

(Ans: 5249kJ mol^{-1})

Q 23 Calculate the wave number of the photon when the electron jumps from

(i) n = 5 to n = 2. (Ans:$2.3 \times 10^6 m^{-1}$)

(ii) n = 5 to n = 1 (Ans: $1.05 \times 10^7 m^{-1}$)

In which series of spectral lines and spectral regions these photons will appear.

(Ans: (i) Balmer Series (ii) Lyman Series)

Q 24 A photon of a wave number 102.70 x 10 m is emitted when electron jumps from higher to n = 1.

(a) Determine the number of that orbit from where the electron falls.

(Ans: n=4)

(b) Indicate the name of the series to which this photon belongs.

(Ans: Lyman series)

(c) If the electron will fall from higher orbit to n = 2, then calculate the wave number of the photon emitted. Why this energy difference is so small as compared to that in part (a)?

(Ans: $20.5 \times 10^5 m^{-1}$)

Q 25. (a) What is de-Broglie's wavelength of an electron in meters travelling at half a speed of light?

[$m = 9.109 \times 10^{-31}$ kg , $c = 3 \times 10^8 ms^{-1}$]

(Ans: λ=0.048 $\mathring{A}$)

(b) Convert the mass of electron into grams and velocity of light into cms^{-1} and then calculate the wavelength of an electron in cm. (Ans:0.048×10^{-8} cm)

(c) Convert the wavelength of electron from meters to

(i) nm (ii) $\mathring{A}$ (iii) pm.

(Ans: 0.0048nm; 0.048; 4.85$\mathring{A}$ pm)