

CHAPTER - 3

THE ATOMIC STRUCTURE

INTRODUCTION

The theory that matter was made from small indivisible particles called atoms dates back to some five centuries B.C. to Democritos and a century B.C. to a Roman Poet Leukippos. This theory was put on a sound scientific basis by John Dalton in 1808.

Today it is well established that atoms are complex organizations of matter and energy. Many particles have been discovered within the atom. These sub-atomic particles include electron, proton, neutron, positron, neutrino and several types of mesons and hyperons etc. Since electrons, protons and neutrons in atom play a major role in determining the chemical and physical properties of matter, we will, therefore, restrict ourselves to the study of these particles.

Evidence for the presence of electrons, protons and neutrons in the atom is derived through many experiments such as:

- (i) Faraday's experiment indicates the existence of electrons.
- (ii) Crooke's tube experiments show the presence of electron and protons in the atoms.
- (iii) Radioactivity further confirms the presence of electrons and protons.

- (iv) Chadwick experiment shows the presence of neutrons.
- (v) Spectroscopic experiments reveal the electronic structure of atoms. These are discussed one by one.

3.1 FARADAY'S EXPERIMENT—Passage of Electricity through solutions

Clue about Electrons: We first consider the passage of electricity through chemical solutions called *electrolytes*. Earlier Davy had noticed that electric charges appear when solutions decompose by the passage of an electric current. Later this phenomenon was studied in greater details by Faraday.

Faraday observed that, when two metal plates called electrodes, are placed in an electrolytic solution and an electric current is passed, the solution breaks up into charged particles called ions. There are positive ions and negative ions, depending upon the type of charge they carry. These ions travel to the oppositely charged electrodes, give up their charge and are liberated as neutral particles. He also determined the charges carried by different ions and also the amount of different elements liberated from the electrolytic solution when a given amount of charge passes through different electrolytic solutions. What is of interest here, is that there is some elementary unit of electric charge associated with these ions which can be calculated. The ions were observed to carry some integral multiple of this charge. The basic unit of electric charge was later named by Stoney (1891), as "ELECTRON".

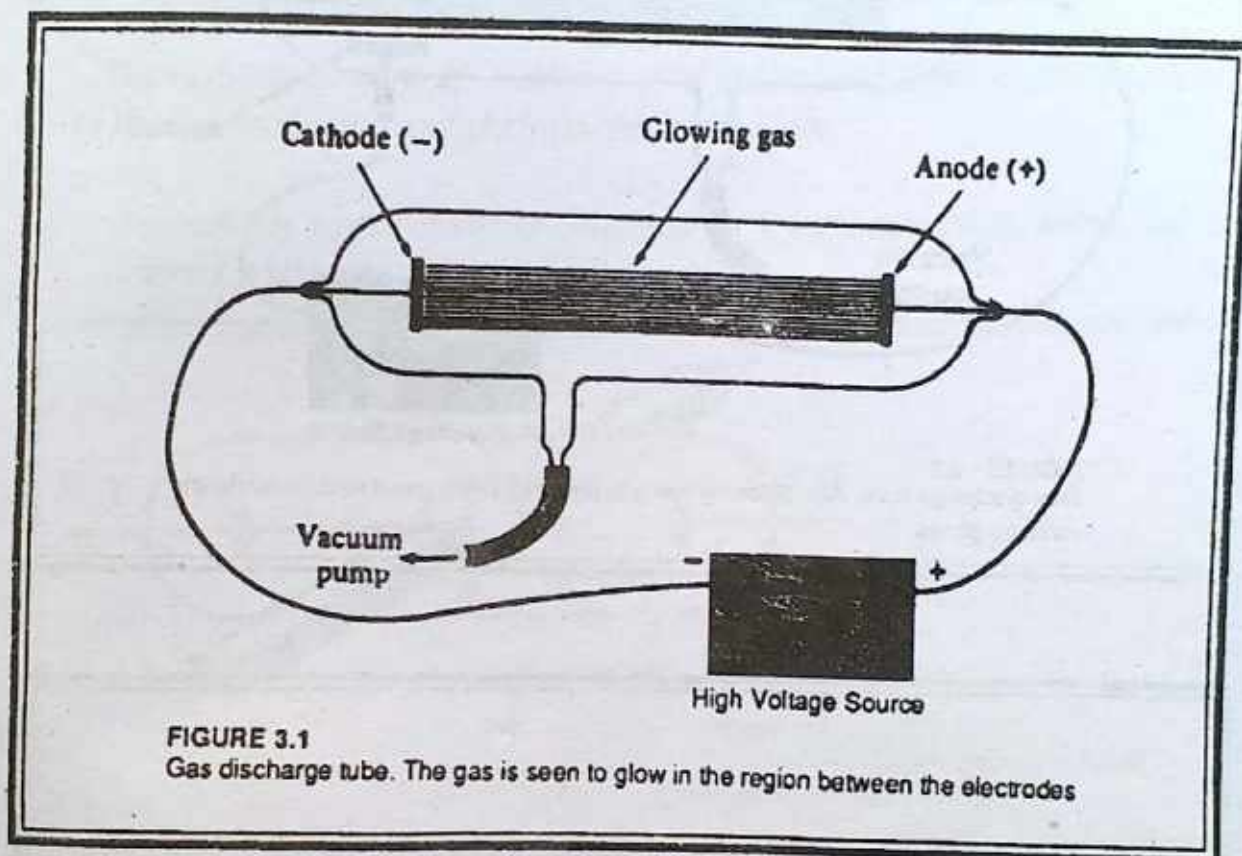
3.2 CROOKES'S TUBE OR DISCHARGE TUBE EXPERIMENTS—Passage of electricity through gases at low pressure

Discovery of Electrons and Protons : We know that air or gases normally do not conduct electricity, unless a very high voltage is applied. The work on the passage of electricity through gases was initiated by a German instrument maker Heinrich Geissler. This work was later extended by W. CROOKES.

To appreciate what happens when an electric current passes through some gas, imagine two metal plates, known as electrodes sealed in a glass tube containing some gas. The tube is provided with an outlet through which gas inside the tube can be evacuated at will. At ordinary pressure, unless very high potential difference is applied, there would be no discharge, and the electric spark cannot be made to pass from one electrode to the other. If the gas inside is gradually pumped out of the tube, the number of molecules of gas present inside is reduced,

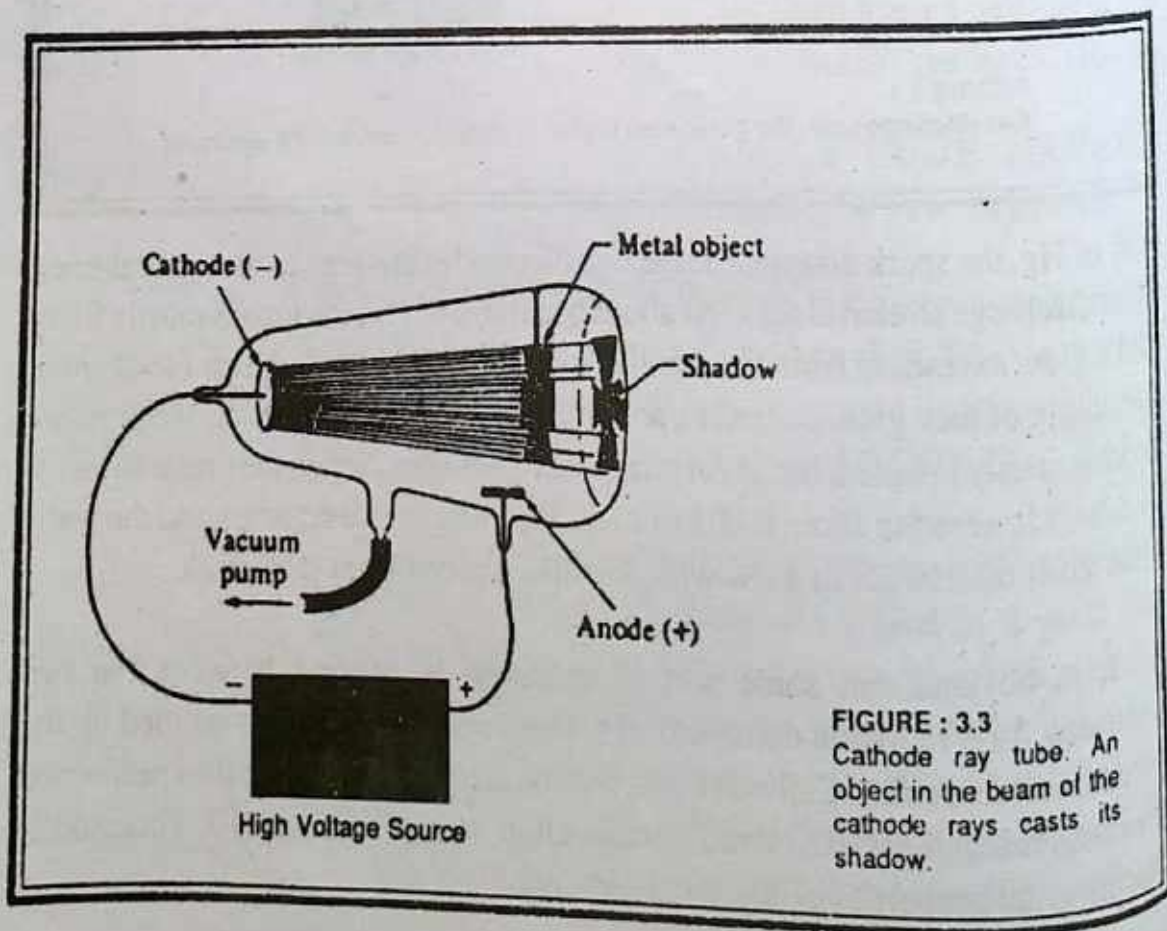
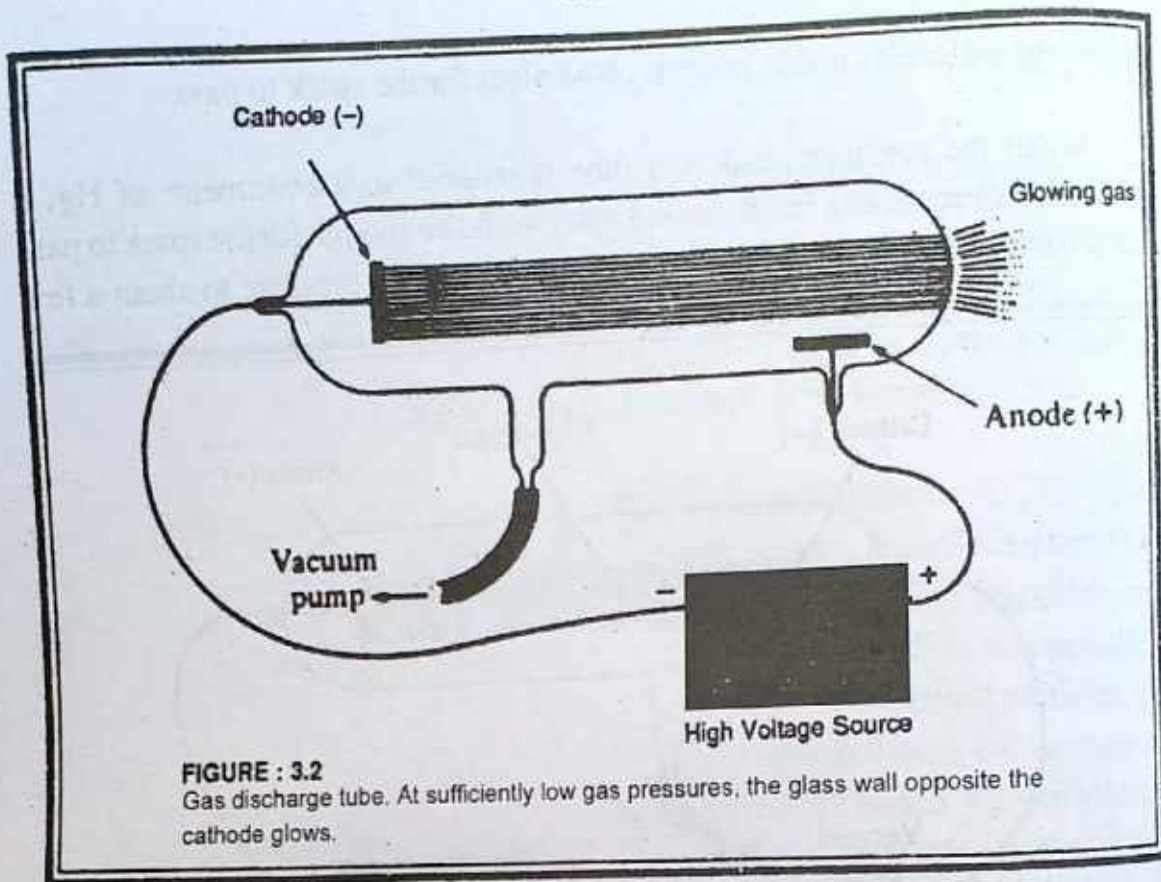
and fewer molecules inside make it convenient for the spark to pass.

When the pressure inside the tube is reduced to a centimetre of Hg, a potential difference of a few thousand volts would be enough for the spark to pass like a flash of lightening (Fig: 3.1) At further reducing pressure to about a few



m.m of Hg, the spark disappears, the two electrodes are seen to glow and the rest of the discharge stream is dark. At about one m.m. of Hg, the tube is mostly filled with a glow extending from the positive electrode and is called positive column. The colour of this glow depends upon the gas filled in the tube. As the pressure is continuously lowered, beautiful phenomena are seen. When the pressure inside the tube is lowered to about 0.001 m.m of Hg, the glow disappears and the walls of the glass tube begin to glow with a brilliant green light (Fig. 3.2)

It is obvious that some sort of radiation is passing between the two electrodes. This radiation consisted of a vast swarm of particles emitted by the cathode and were called Cathode Rays. Various experiments were thus performed by various researchers like Hertz, Lenard, Goldstein, Perrin and J.J. Thomson to determine the properties of these cathode rays.



The cathode rays were seen to possess the following properties:

1. The rays travel in straight lines, as they produce sharp shadows of objects placed in their path.
2. The rays emerge normally from the cathode and can be focused by using a concave cathode.
3. The rays penetrate small thicknesses of matter, like aluminium or gold foil without producing any perforations in the foils.
4. The cathode rays are easily deflected by a magnetic field, which can be shown by bringing a magnet close to them.

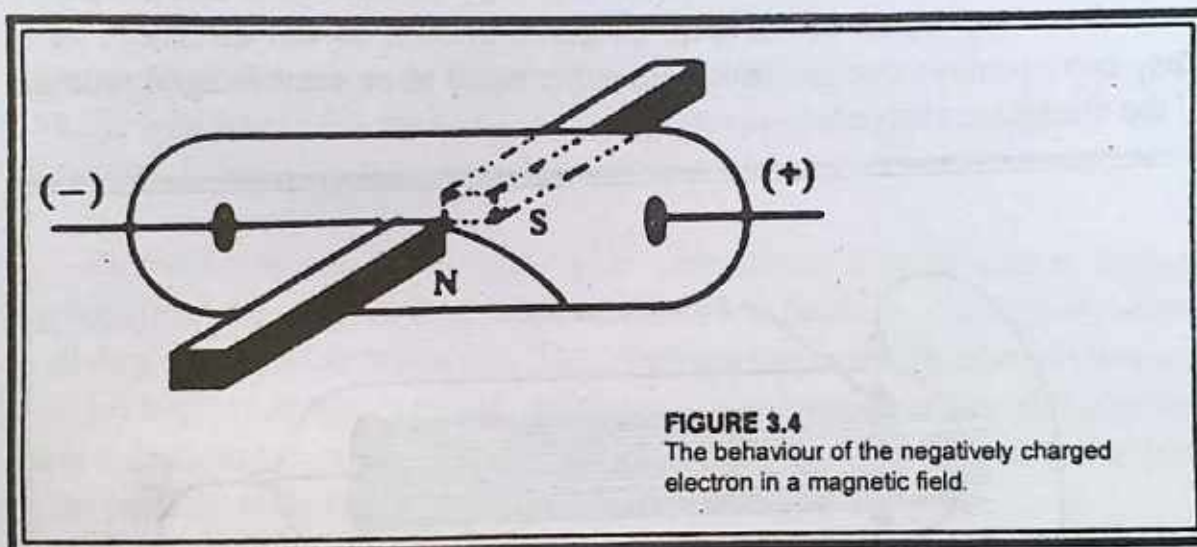


FIGURE 3.4
The behaviour of the negatively charged electron in a magnetic field.

5. The rays carry a negative charge.
6. The rays can also be easily deflected by an electrostatic field.
7. The rays can exert mechanical pressure, showing they possess kinetic energy.
8. The rays were seen neither to depend upon the material of which the electrodes were made nor upon the gas which is filled in the tube.
9. These rays consist of particles now called *Electrons* carrying a fixed unit of charge and a fixed mass.

Different discharge tubes with different electrodes and residual gases were tried by a number of workers besides Thomson. All the experiments gave the same value for charge to mass ratio (e/m). This shows that electrons could be produced from any kind of matter and hence perhaps were constituent of all matter.

3.3 POSITIVE RAYS – Protons

During the study of the passage of electricity through gases at low pressure, it was observed by Goldstein that if thin holes are made in the cathode, then some radiations appear behind the cathode (Fig. 3.5). These rays were found to be positively charged and hence called positive rays. It was found that these rays consist of atoms and ions of the various gases present in the discharge tube. They carry positive charges which are either equal to or some integral multiple of the electronic charge 'e'.

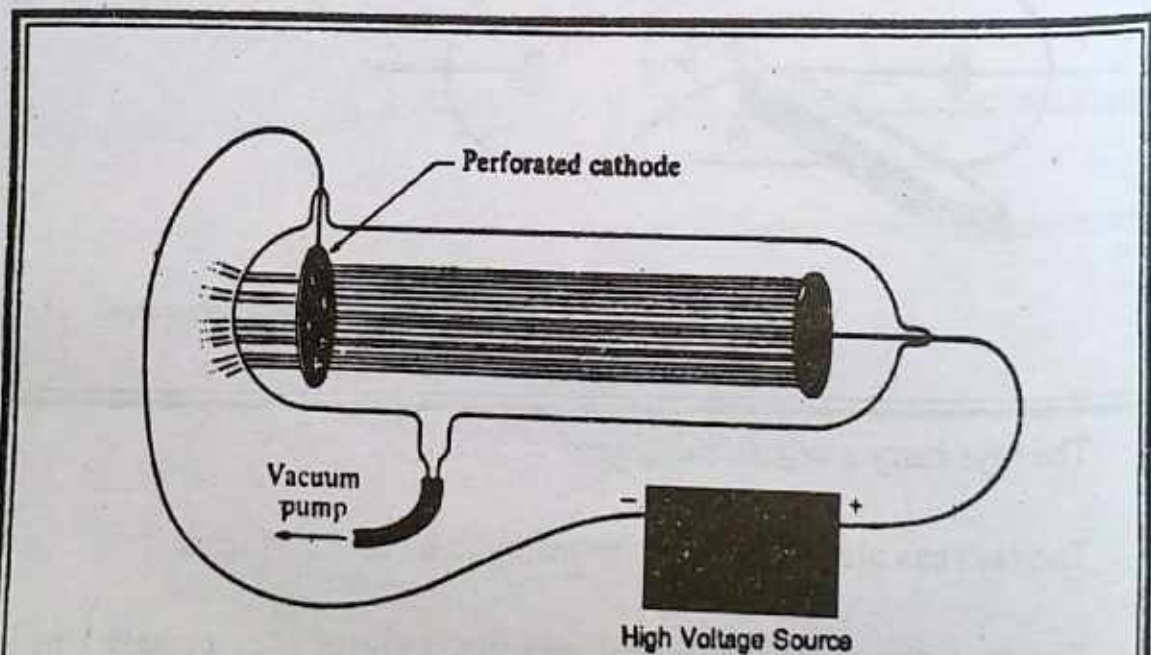


FIGURE 3.5

Cathode ray tube with a perforated cathode. Positive canal rays pass through the cathode and cause the glass wall to glow.

J.J. Thomson discovered that positive rays, unlike cathode rays, have values of e/m dependent on the gas present in the Crookes's tube. The lightest particle found, was that from hydrogen. This particle, which has a mass

1836 times that of the electron is now known as proton (Greek, "first").

3.4 RADIOACTIVITY – Confirmation of Electrons and Protons

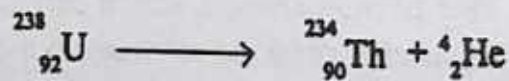
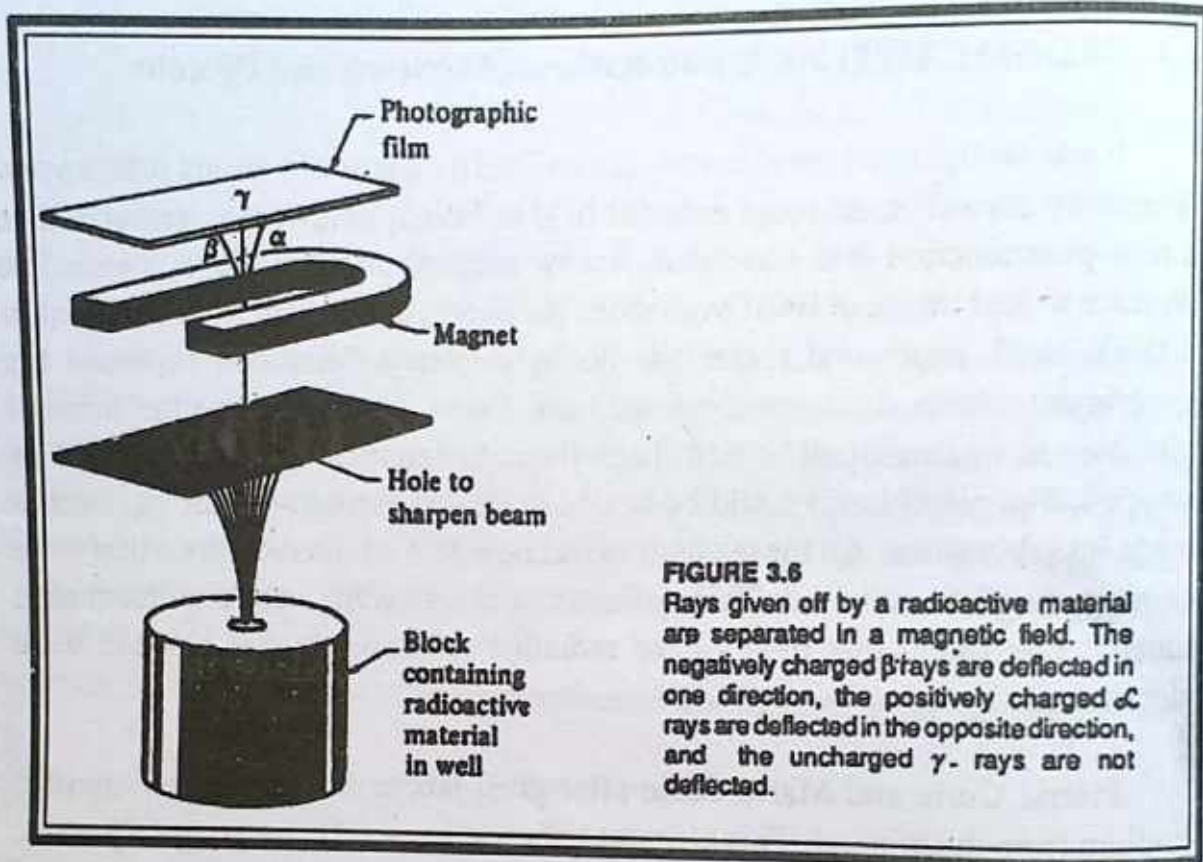
It was thought that the electrons are emitted by atoms of various substances. When they are subjected to an external field or heated to high temperatures then a new phenomenon was observed. A new mineral pitchblende was found to produce a clear image of itself even when the photographic plate was wrapped in a thick black paper and there was no light. Henry Becquerel repeated his experiments under different conditions and found that only when the mineral pitchblende was wrapped in lead sheet, the radiation coming out of it could be stopped. The pitchblende could be heated or cooled, it might be compressed or made into thin sheet. All these changes had no effect on the radiations that were coming out of this mineral. This emission of charge went on at a uniform rate. Later it was found that most of the radiation given out by pitchblende were electrons.

Pierrie Curie and Marie Curie after great labour isolated a new element Radium from the mineral. This element radium was found to be extremely active in giving out invisible radiations. This phenomenon in which certain elements emit invisible radiation is called *radioactivity* and the elements which give out these radiations are called *radioactive elements*. Most of the elements after lead in the periodic table are naturally radioactive.

The radiation emitted by radium was subjected to a magnetic field perpendicular to the direction of emission. If the magnetic field was strong enough, the radiations emitted were found to split up into three different streams of rays, which were labelled α , β and γ - rays.

The α -rays were found to carry positive charge and the β -rays a negative charge. The third, the γ -rays, remained undeflected no matter how strong was the magnetic field and hence were considered to be uncharged. The γ -rays were found to be extremely penetrating and hence identified with x-rays.

An element after giving out radiations breaks down to a more stable element. For example ${}_{92}^{238}\text{U}$ on emission of α - particles would be converted to ${}_{90}^{234}\text{Th}$



α - Particle

The emission of radiation would continue until the formation of lead as stable end product.

Properties of these radiations are summarized below :

1. α -rays are fast moving helium nuclei. They ionize air i.e. they knock out electrons from other atoms. They produce bright flashes on fluorescent screen and have a very small range (1-2 cm) in air, before they are completely stopped.
2. β -rays are fast moving electrons with a range of (1-2 m) in air and can pass through small thickness of matter.

3. γ -rays are very penetrating. These are short wave electro-magnetic radiations like x-rays, only that these are much more penetrating. These rays will pass through (15-20 cm) of lead. On passing through matter, γ -rays would eject high speed electrons from the matter.

The evidence of radioactivity shows that the atom is not an indivisible particle. If it can emit electrons and helium nuclei, it must have a sub structure of its own.

3.5 CHADWICK EXPERIMENT — Discovery of Neutron

Chadwick investigated the effect of the radiation on other elements both in the solid and in the gaseous form. During his studies with beryllium, Chadwick found that very penetrating radiations were given out when beryllium was bombarded with α - particles. Chadwick put forward the suggestion that these penetrating radiations were due to material particles with mass comparable with that of an atom of hydrogen but carrying no charge. These particles were called neutrons. The neutrons must have come out from atoms on disintegration of the bombarded element. This is indicated by the equation.



We have so far seen three particles which come out of atoms on their disintegration and these are:

- (a) Electrons, which carry a negative charge of 4.803×10^{-10} esu
 $= 1.602 \times 10^{-19}$ coulombs with $e/m = 1.758 \times 10^8$ C/g
 and $m_e = 9.115 \times 10^{-31}$ Kg = 0.000550 amu.
- (b) Proton carries a positive charge equal to that of an electron
 $m_p = 1.008$ amu
- (c) Neutron carries no charge but has a mass $m_n = 1.009$ amu

3.6 SPECTROSCOPIC EXPERIMENTS — Spectroscopy

Electronic Structure of Atom:

Once the presence of fundamental particles was established, the next question concerned the electronic structure of atom. This objective was mainly achieved through *spectroscopic experiments* which investigate the electromagnetic radiation emitted or absorbed by the substances. At this point, it is appropriate to describe briefly the *Planck's Quantum Theory* which had tremendous impact on the development of the theory of structure of atom.

3.7 PLANCK'S QUANTUM THEORY - Quantization of Energy

This theory was proposed in 1900 by the German physicist *Max Planck* to account for the observed radiations from heated bodies.

Max Planck suggested that the energy could not be absorbed or emitted by the atoms in any arbitrary quantity, but only in specified amounts called *quanta*. That is to say, an atom cannot change its energy continuously but only by a series of steps. The amount of energy depends upon the frequency (ν) of radiation absorbed or emitted. It is given by relation:

$$E = h \nu \text{ where } h = \text{Planck's constant } (6.625 \times 10^{-34} \text{ J.S.} \\ = 6.625 \times 10^{-27} \text{ erg.S})$$

The main consequence of Planck's quantum theory is that the amount of energy gained or lost is quantized i.e., energy change occurs in small packets or multiple of those packets, $h\nu, 2h\nu, 3h\nu$ and so on.

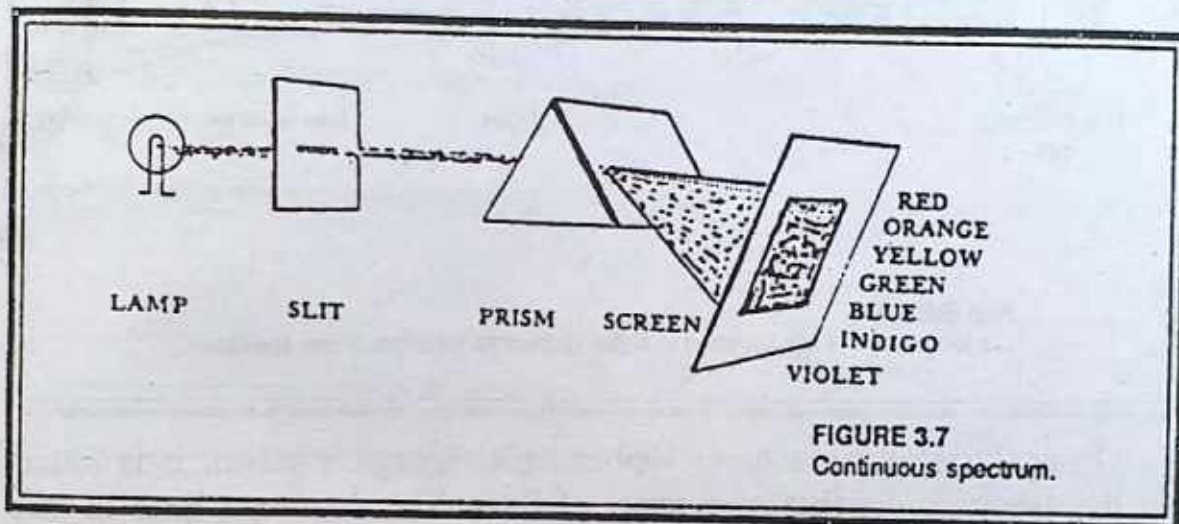
3.8 SPECTRA

Our knowledge of the way in which electrons are distributed in atoms comes largely from the evidence of spectra.

When an element absorbs sufficient energy, for example, from a flame or an electric arc, it emits radiant energy. When this radiation is passed through a prism in a spectroscope, it is separated into component wave lengths to form an image

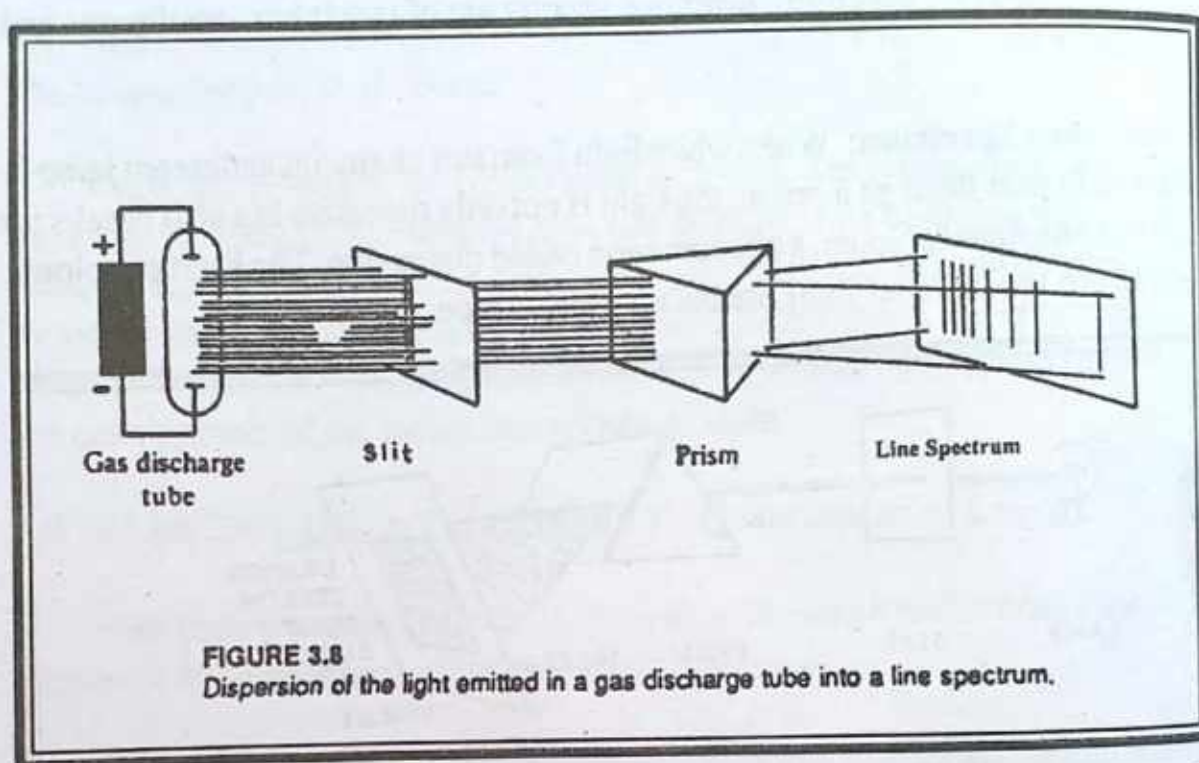
called an Emission spectrum. Emission spectra are of two types, continuous and line spectrum.

Continuous Spectrum: When white light from sun or any incandescent lamp is allowed to pass through a prism, the light is not only deviated, but also breaks up into its constituent colours, a phenomenon called dispersion. The band of colours into which the incident light breaks up is called spectrum.



The white light gives a continuous band of colours. On one end the least deviated is red and at the other end is violet which suffers the maximum deviation. The colours of the spectrum are so mixed up that there is no line of demarcation between different colours. Such spectrum is called continuous spectrum. It is given not only by sunlight but also by the light from any hot solid or liquid body. The colour of light depends on its wave length. Violet has the shortest wave length (about $4000 \text{ \AA}$), and red light the longest (about $7000 \text{ \AA}$). Light of a single wave length is called monochromatic.

Line Spectrum : A different kind of spectrum may be obtained when light emitted from a gas source passes through a prism. In order to emit light, the gas must be excited in some way. A common way of doing this is to pass an electric current through the gas at low pressure (Crookes's tube experiment). The neon lights used in advertisement make use of this method for producing light and so do sodium vapour street lights. If the light from the discharge tube is allowed to pass through a prism, some discrete sharp lines on an otherwise completely dark back ground are obtained. Such spectrum is called *line spectrum*. Each line corresponds to a definite wave length.



On analysis of the sodium vapour light through a prism, it is found that the spectrum consists of a series of lines. The dominant lines in this area are the two yellow lines which give sodium vapour lamps their characteristic colour. Each element produces a characteristic set of lines, so *line spectra came to serve as "finger prints"* for the identification of elements.

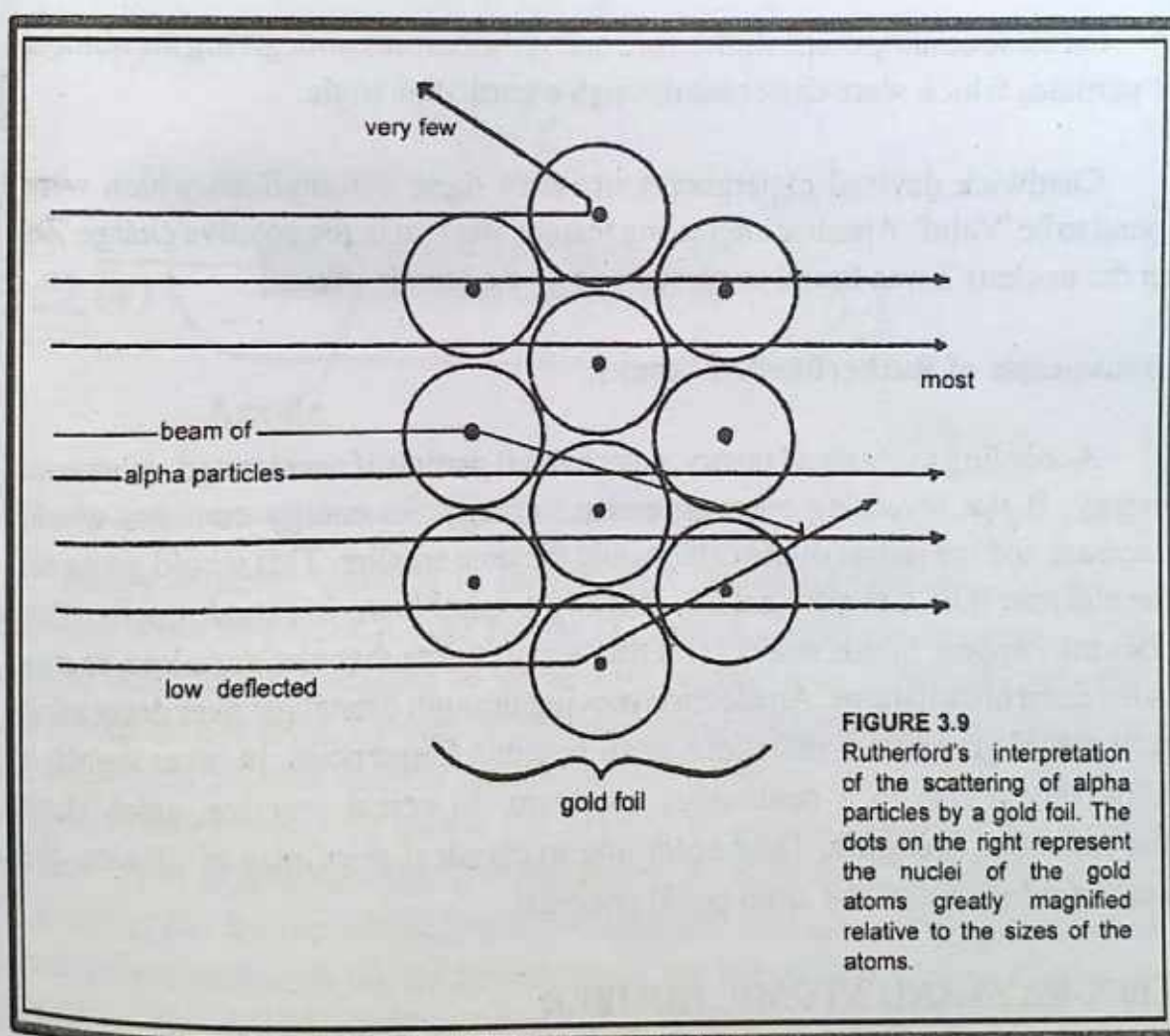
The facts are that (1) samples of the same element always emit the same wave lengths of radiation and (2) under the right conditions only certain wave lengths are emitted by any one element. This leads to the belief that electrons are arranged around the nucleus in definite energy levels, E_1 and when they are excited they go to definite excited levels E_2 . This means that the difference in the energy of electrons, $E_2 - E_1$ is same for a given transition and this explains the fact that the energies emitted by a given excited element always have the same wave lengths.

3.9 RUTHERFORD'S MODEL OF AN ATOM – Evidence for Nucleus and Arrangement of Particles.

Though the nature of the proton was well established by 1900, the role of this positive particle in the structure of atom was uncertain. A clue to the

arrangement of positive and negative particles within atoms was finally provided by the experiments of Rutherford.

Rutherford and his co-workers performed several experiments on the scattering of α -particles by thin films. In one of such experiments α -particles emitted from polonium bombarded on thin gold foil, it was found that most of the α -particles penetrated the foil and emerged undeflected on the other side. However, one particle in 8000 suffered a deflection greater than 90° and remerged on the same side. A number of particles suffered deflections of varying degrees.



To explain this scattering of α -rays, Rutherford made some basic assumptions:

- (a) The mass of the atom is concentrated in its nucleus, the dimensions of which are negligible in comparison with the radius of the atom.
- (b) The nucleus carries a positive charge, '+ Ze'
- (c) There must be 'z' number of negatively charged electrons outside the nucleus and at fairly large distances, arranged in some manner.
- (d) The greater part of the atomic volume comprises of empty space in which the electrons revolve and spin.

On these assumptions, Rutherford derived an expression, giving the number of particles which were deflected through a particular angle.

Chadwick devised experiments to verify these assumptions which were found to be 'Valid'. Another interesting feature was that in the positive charge 'Ze' on the nucleus Z was found to be nearly half the atomic mass.

Weaknesses of Rutherford's Theory :

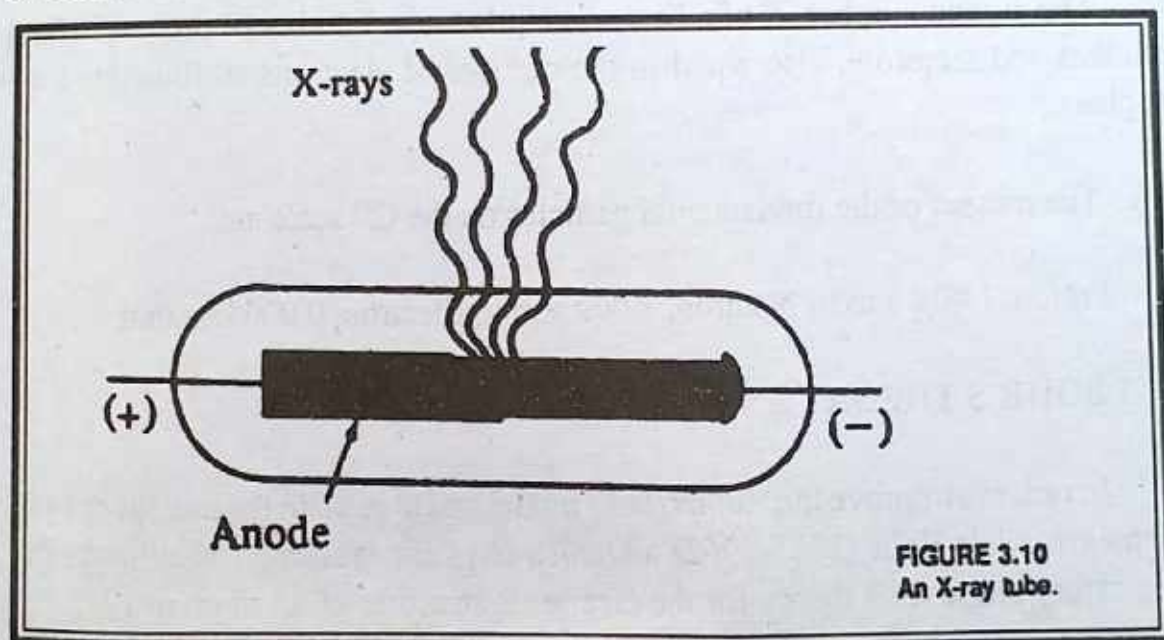
According to classical theory, any charged particle if accelerated, must emit energy. If the revolving electron emits energy, its energy contents would decrease and the radius of the orbit would become smaller. This would go on till the electron falls into the nucleus, charting a spiral path. In actual practice this does not happen. In this respect it is necessary to note that electrons lose energy in the form of radiations. An electron moving through orbitals of ever decreasing radii would give rise to radiations of all possible frequencies. In other words, it would give rise to a continuous spectrum. In actual practice, atom gives discontinuous spectrum. Thus according to classical principles of physics, the Rutherford model of the atom could not exist.

3.10 X-RAYS AND ATOMIC NUMBER

W. Roentgen in 1895 found that a photographic plate he developed had been struck by invisible radiation coming from a cathode ray tube (Crookes's tube expt.). These previously unknown rays were labelled X-rays. These rays are

some times known as Roentgen rays (after the discoverer). These rays had the ability to penetrate paper, rubber, glass, metal and human flesh. X-rays were soon identified as short wave, high energy electromagnetic radiation. They were put to medical uses immediately.

The X-rays arise from the anode of the Crookes's tube experiment as it is struck by the fast moving electrons from the cathode. X-rays have played a vital part in the determination of structure at subatomic levels.



Henry Moseley working in Rutherford's laboratory in 1911 studied the different wave lengths of X-rays produced from anodes of different metals. He noticed that the wave lengths of the X-rays emitted decreased regularly with increasing atomic mass. On careful examination of his data, Moseley found that the number of positive charges on the nucleus increases from atom to atom by single electronic unit. He called the number of positive charges the atomic number. Thus atomic number of an element is the number of protons present in its nucleus. For the first time, it became apparent that what distinguishes one element from another is not the atomic mass, but the nuclear charge, that is, the atomic number. It is denoted by 'Z'.

It is worth mentioning here that Rutherford's theory of the nuclear atom was supported by the Moseley's experiment.

We now have a picture of the atom which can be summarized:

- (a) The atom consists of a small, dense, positively charged nucleus, containing protons.
- (b) The nucleus is surrounded by a number of electrons equal to the number of protons in the nucleus.
- (c) The atomic number 'Z' of an atom is equal to the number of protons in the nucleus and therefore, also equal to the number of electrons surrounding the nucleus.
- (d) The masses of the fundamental particles on the C^{12} scale are:

Proton, 1.008 a.m.u, Neutron, 1.009 a.m.u, Electron, 0.00055 a.m.u.

3.11 BOHR'S THEORY

In order to improve the Rutherford's model and to explain the line spectra of elements, Niels Bohr (1885-1962) a Danish physicist working in Rutherford's laboratory proposed a theory for the electronic structure of an atom in 1913.

Bohr assumed that on the basis of the quantum theory, there exists the possibility that electron in certain orbits may not give out radiation and an electron revolving in any one of such orbits would be completely stable. Such orbits were called '*Stationary states*.' Bohr envisioned the stationary states as circular orbits around the nucleus. He considered that an electron in a certain orbit has a certain energy and as long as it keeps revolving in that orbit, it neither absorbs nor radiates energy. If the electron absorbs energy equal to the energy difference between the two orbits, the electron is excited, i.e. it jumps to higher energy state. If it falls back to lower level, it must emit energy equal to the energy difference between the two orbits. (Fig: 3.11). If this energy is absorbed or emitted as light, a single photon (quantum) of absorbed or emitted light must account for the required energy differences, so that

$$h \nu = \Delta E$$

Where ΔE is the difference between the energies of the final and initial orbits, h = Planck's constant (6.625×10^{-34} J.S.) which has the dimensions of energy $\times$ time.

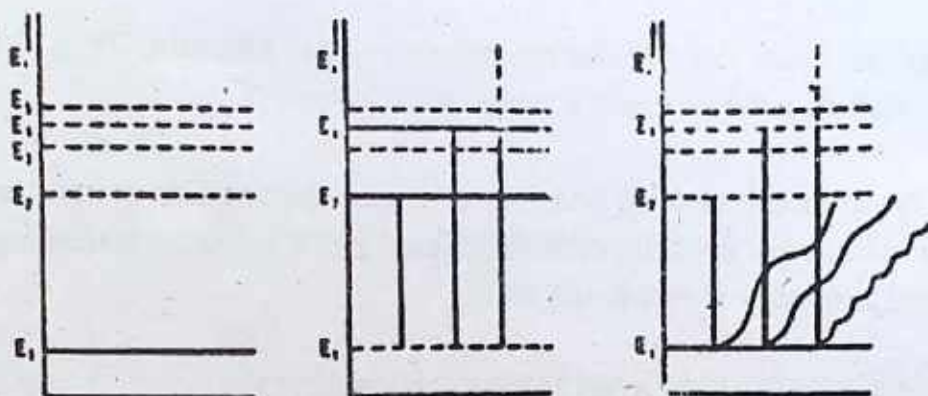


FIGURE 3.11

Excitation of electrons from low energy levels to higher energy levels is a process that requires energy. When electrons fall from the excited levels, e.g., E_4 , E_3 , or E_2 , radiant energy is given off, possibly as visible light.

Bohr assumed that all the transitions that electrons make between two orbits, yield a single unique spectral line.

Bohr further assumed that the stationary states were only those orbits in which the product momentum (mv) $\times$ circumference ($2\pi r$), sometimes called the 'action', was equal to the Planck's constant ' h ' or some integral multiple of ' h ' therefore for the first possible orbit.

$$\text{momentum} \times \text{circumference} = h$$

$$mv \times 2\pi r = h$$

or for any other orbit,

$$mv \times 2\pi r = nh$$

Where 'n' was a simple integer, $n = 1$ for first orbit, $n = 2$ for the second and so on.

This equation could be re-written as,

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

Here 'mvr' becomes the angular momentum of the electron. Thus Bohr's first condition defining the stationary states could be stated as,

"Only those orbits were possible in which the angular momentum of the electrons would be an integral multiple of $h/2\pi$ ". These stationary states correspond to energy levels in the atom.

3.12 BOHR'S THEORY AND HYDROGEN ATOM

The truth of the basic assumptions of Bohr was established when applied to hydrogen atom. The hydrogen atom consists of a single electron revolving around a single positively charged nucleus, each of which would behave as a point charge, and hence exact calculations of the stationary orbits can be made. Let 'e' be the charge, m mass of electron, 'Ze' the positive charge on the nucleus, 'r' the radius of the orbit in which electron is moving with a velocity 'V'

If we equate the centrifugal force, mv^2/r to the centripetal force which is due to the attraction between the electrons and the nucleus.

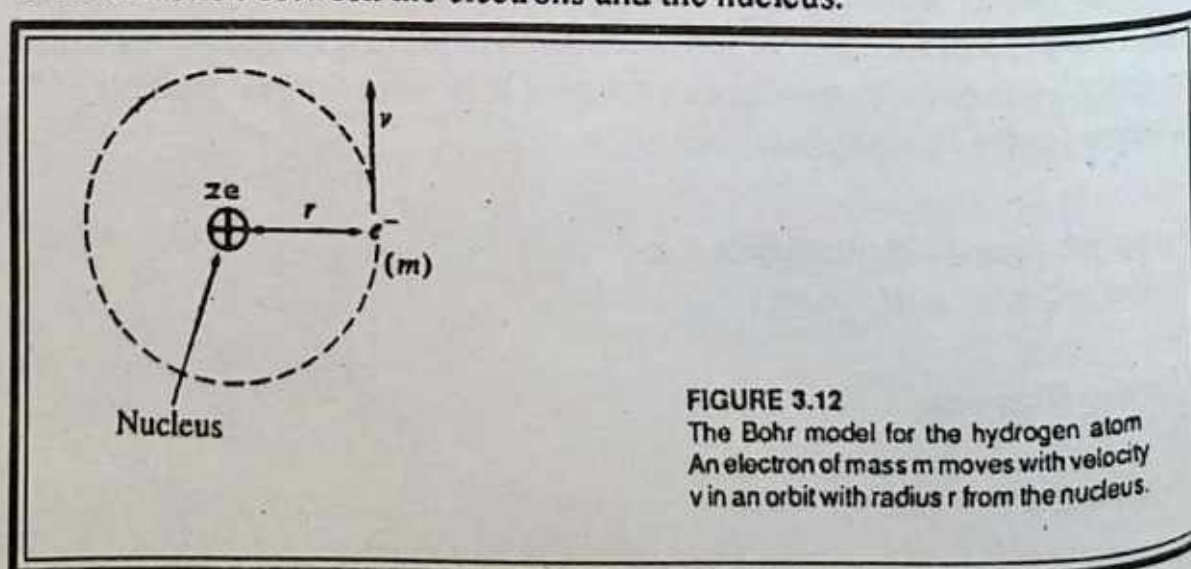


FIGURE 3.12

The Bohr model for the hydrogen atom. An electron of mass m moves with velocity v in an orbit with radius r from the nucleus.

$$\frac{mv^2}{r} = \frac{Ze.e}{r^2} \dots(1)$$

The Bohr's postulate states that only those orbits are possible in which:

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

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

Substituting the value of 'v' in the above equation, we get

$$\frac{m}{r} \left(\frac{nh}{2\pi mr} \right)^2 = \frac{Ze^2}{r^2}$$

$$\frac{m}{r} \left(\frac{n^2 h^2}{4\pi^2 m^2 r^2} \right) = \frac{Ze^2}{r^2}$$

$$\therefore r = \frac{n^2 h^2}{4\pi^2 m Ze^2} \dots(2)$$

This equation gives the radii of all the possible stationary states. All the quantities on the right hand side of the equation are known and if we substitute $Z = 1$ for hydrogen atom, $n = 1$ for the first orbit.

If we put the values of the constants,

$h = 6.625 \times 10^{-27}$ erg. sec. (or 6.625×10^{-34} J.S. which is the S.I. unit).

$m_e = 9.11 \times 10^{-28}$ g (or 9.11×10^{-31} Kg which is the S.I. unit).

$e = 4.802 \times 10^{-10}$ esu (or 1.602×10^{-19} C which is the S.I. unit).

We get, $r = 0.529 \times 10^{-8}$ cm (10^{-8} cm = $1 \text{ \AA}$)

$\therefore r = 0.529 \text{ \AA}$

$r_1 = 0.529 \text{ \AA}$ as the radius of the first stationary state for the hydrogen atom.

We can also write the equation 2 for the radius as

$$r = n^2 \left(\frac{h^2}{4\pi^2 m Z e^2} \right) = n^2 a_0 \dots (3)$$

For the first orbit $n = 1$ and $r = 0.529 \text{ \AA}$. This is the value of the terms in the bracket sometimes written as a_0 , called Bohr's radius. For the second, third and so on orbitals, we would take $n = 2, 3, \dots$

Thus we see that the radii of the orbits are proportional to the squares of the first natural numbers. To test the validity of these values, the spectrum of the hydrogen atom offers the best example.

3.13 DETERMINATION OF ENERGY

The single electron of hydrogen atom with mass ' m ' revolves around the nucleus, its kinetic energy is given by the expression $\frac{1}{2} mv^2$, ' v ' being the velocity of electron in circular motion. The potential energy possessed due to the position of isolated electron from the nucleus at a distance ' r ' is given by the expression $-\frac{Ze^2}{r}$ (the energy of electron at infinity being zero) Fig: 3.12.

E, the total energy is given by:

$$E = \frac{1}{2} mv^2 - \frac{Ze^2}{r} \dots (4)$$

From equation (1) we have

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2} \quad \therefore mv^2 = \frac{Ze^2}{r}$$

Substituting the value of mv^2 in equation (4) we get,

$$E = \frac{1}{2} \frac{Ze^2}{r} - \frac{Ze^2}{r}$$

$$\therefore E = -\frac{Ze^2}{2r} \quad \text{---(5)}$$

Substituting the value of $r = \left(\frac{n^2 h^2}{4\pi^2 m Z e^2} \right)$ from equation (2) in equation (5), we get,

$$E = -\frac{Ze^2}{2 \left(\frac{n^2 h^2}{4\pi^2 m Z e^2} \right)} = \frac{-2\pi^2 m Z^2 e^4}{n^2 h^2} \quad \text{---(6)}$$

This is the expression of energy of an electron in any orbit.

Expression for frequency and wave number:

Energy of an electron in a lower orbit (n_1) and higher orbit (n_2) can be expressed as follows:

$$E_1 = -\frac{2\pi^2 m Z^2 e^4}{n_1^2 h^2}$$

and $E_2 = -\frac{2\pi^2 m Z^2 e^4}{n_2^2 h^2}$

When an atom or gas is electrically heated, its electrons jump to higher orbit. In this state, it is said to be excited.

The excited state is unstable. Electron has to come back to original ground level by radiating energy equal to the difference of energies of the excited and ground state. Then

$$\text{Energy emitted } \Delta E = E_2 - E_1 = h\nu$$

$$E_2 - E_1 = -\frac{2\pi^2 m Z^2 e^4}{n_2^2 h^2} - \left(-\frac{2\pi^2 m Z^2 e^4}{n_1^2 h^2} \right)$$

Rearranging

$$E_2 - E_1 = \frac{2\pi^2 m Z^2 e^4}{n_1^2 h^2} - \frac{2\pi^2 m Z^2 e^4}{n_2^2 h^2}$$

or

$$E_2 - E_1 = \frac{2\pi^2 m Z^2 e^4}{h^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{-----(7)}$$

According to Bohr's postulate

$$E_2 - E_1 = h\nu$$

$$h\nu = \frac{2\pi^2 m Z^2 e^4}{h^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\boxed{\nu = \frac{2\pi^2 m Z^2 e^4}{h^3} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{-----(8)}}$$

This is the expression for frequency of emitted wave or photons therein.

Now $\nu = c\bar{\nu}$ where $\bar{\nu}$ is called wave number and is defined as number of waves per unit distance.

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

or

$$\bar{\nu} = \frac{2\pi^2 m Z^2 e^4}{ch^3} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{-----(9)}$$

Putting

$$\frac{2\pi^2 m e^4}{ch^3} = R_H$$

Where R_H is called Rydberg constant. Its value is 109678 cm^{-1}

$$\therefore \bar{\nu} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{-----(10)}$$

This is the expression for wave number. Where for hydrogen $Z=1$.

3.14 HYDROGEN SPECTRUM

Historical background:- It is well known that when a gas is heated in a discharge tube at low pressure, it emits radiation. Balmer in 1885, studied the spectrum of hydrogen gas. He found a series of lines in visible region (i.e, having λ between 4000 to 7000 $\text{\AA}$). They were called Balmer series. He proposed an empirical formula to find wave number $\bar{\nu}$ of each line.

$$\bar{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

R_H is called Rydberg constant where $n_2=3,4,5,6,\text{----etc.}$

Lyman later on discovered another series in ultraviolet region. Wave number of each line was found by a formula similar to that given by Balmer.

$$\bar{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Where $n_2 = 2,3,4,5,\text{---etc.}$

Paschen discovered an other such series in infrared region. $\bar{\nu}$ of each line was given by:

$$\bar{\nu} = R_H \left(\frac{1}{3^2} - \frac{1}{n_2^2} \right)$$

Where $n_2 = 4,5,6,7,\text{---etc.}$

Brackett found another series in far-infrared region.

Pfund also found another series in far-infrared region.

General expression:— A general expression can give wave number of each line of each series. It is:

$$\bar{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Where n_1 is fixed for each series. n_2 keeps increasing (value of $R_H = 109678 \text{ cm}^{-1}$)

BOHR'S THEORY AND HYDROGEN SPECTRUM

Bohr's theory success lies in the fact that it provided logical proof and reason for the formation of hydrogen spectrum. According to Bohr's theory, "At ordinary temperature, the electron in hydrogen atom resides in lowest energy level i.e. first orbit or ground state. When electrically it is heated at low pressure in a discharge tube, the electrons of different hydrogen atoms absorb different amount of energy and jump to an appropriate high energy level. They are now said to be in excited state.

All the atoms in excited state, due to their high energy, are unstable. So now the electrons jump back to the original first orbit directly or to some other level of lower energy. In doing so they emit energy equal to the difference of energies of two levels. These energetic waves are separated by a prism according to their wavelength and thus hydrogen spectrum is obtained.

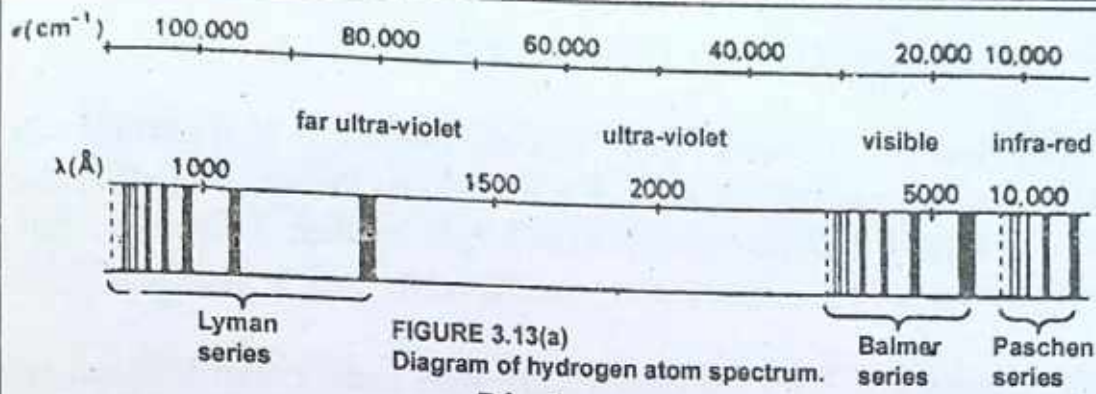


FIGURE 3.13(a)
Diagram of hydrogen atom spectrum.

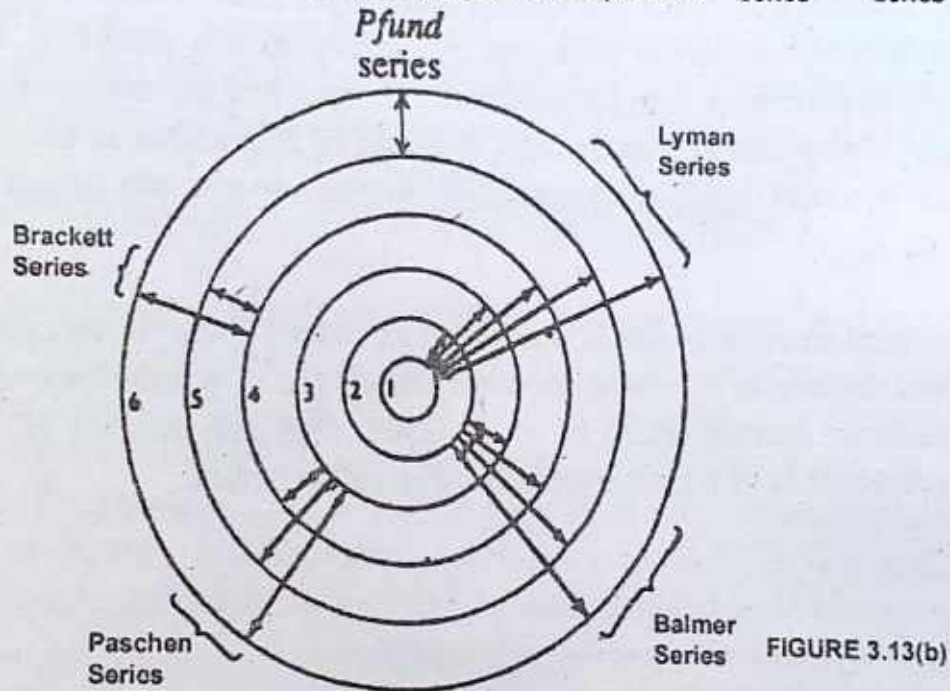


FIGURE 3.13(b)

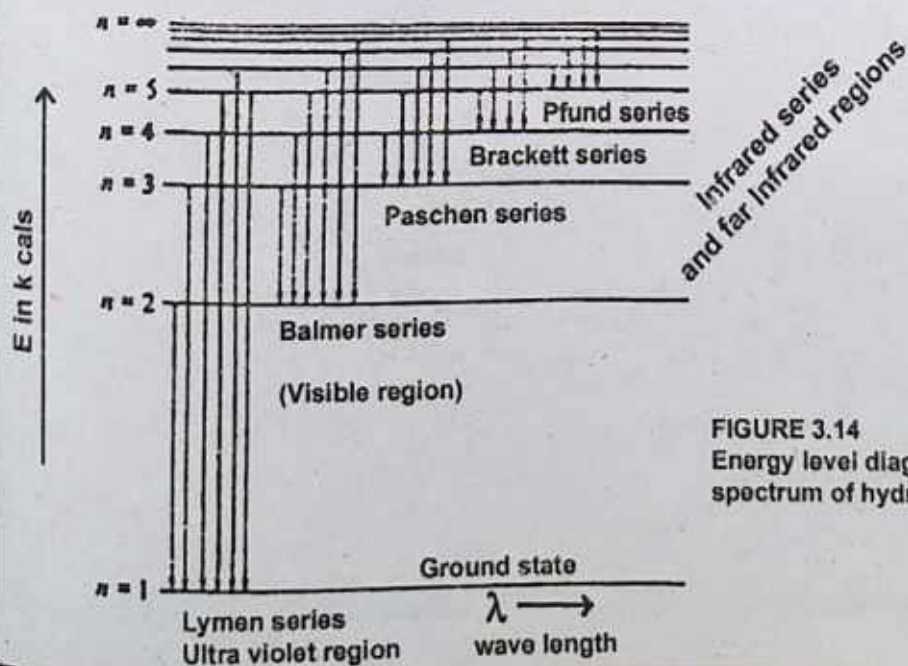


FIGURE 3.14
Energy level diagram for the
spectrum of hydrogen

3.15 HEISENBERG'S UNCERTAINTY PRINCIPLE

An electron in Bohr's theory was considered to be a particle whose momentum and the path along which it moved was known precisely. Electron also behaves as a wave, according to *de Broglie* concept. Thus dual nature of an electron makes the concept of the circular orbits unclear and meaningless.

Heisenberg in 1925 enunciated a principle known after him and called Heisenberg's Uncertainty principle. According to this principle, it was not possible to determine simultaneously the position and momentum of a moving particle. If one was known exactly, it would be impossible to know the other exactly. It would therefore be impossible to chase an electron around its path or to locate it.

In mathematical terms, it was stated as under : If Δp_x is the uncertainty in the determination of the momentum of a particle and Δx was the uncertainty in the simultaneous determination of its position, then the product of these two uncertainties was of the order of h , the Planck's constant.

$$\Delta p_x \cdot \Delta x \simeq h$$

Thus if one of the two i.e. p_x or x was known exactly, then the uncertainty in its determination could be zero and that of the other would become infinite. As a matter of fact, it is applicable to a very small particle when the ordinary laws of mechanics are not obeyed.

On this principle, it is impossible to think of an electron or any other particle to be at rest or to say it possesses zero energy and is at a particular location. The Bohr's orbits thus lose meaning as a circular path. The Heisenberg's principle, therefore explains the basic incompleteness of the Bohr-model of atom.

3.16 ENERGY LEVELS AND ENERGY SUB-LEVELS

Bohr suggested the existence of certain circular orbits at definite distance from the nucleus. These orbits are associated with definite energy of the electron increasing outwards from the nucleus. Its evidence is given by the line spectra. The Bohr's circular orbits are usually referred to as "Energy levels" or "Shells". These are designated as 1, 2, 3, 4, etc. or K, L, M, N, etc. The maximum possible number of electrons a shell 'n' can accommodate is given by $2n^2$, i.e. 2, 8, 18, and 32 respectively in the first, second, third and fourth energy level. It may be pointed

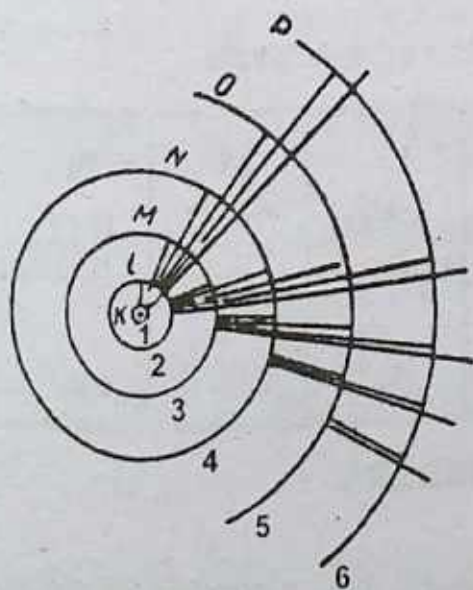


FIGURE 3.15
Electron orbits or
Energy levels.

out that in the outer most shell of any atom, the maximum number of electrons possible is 8 (Except hydrogen whose outer most orbit being first orbit, is to be filled by "2" electrons).

Table 3.1 Energy Levels and Maximum Electrons.

n	1	2	3	4
Designation	K	L	M	N
Maximum electrons	2	8	18	32

The spectral lines, which correspond to the transition of an electron from one energy level to another, have for the most part, a fine structure, i.e. each line actually consists of several separate, close lying lines as doublets, triplets and so on indicating that some of the electrons of the given energy level have different energies. That is to say, that the electrons belonging to same energy level may differ in their energy. The energy levels are accordingly divided into sub energy levels denoted by the letters s, p, d, f.... for the first four series of lines in the spectra of the alkali metals, based on the terms Sharp, Principal, Diffuse and Fundamental. The number of sub level in a given energy level or shell is equal to its value of 'n' for example, with in a principal energy level ($n=2$) i.e. second energy level, two sub levels are possible which are s and p.

Table 3.2 Energy levels and sub levels

ENERGY LEVEL	K ($n=1$)	L ($n=2$)	M ($n=3$)	N ($n=4$)
SUB-LEVEL	s	s, p	s, p, d	s, p, d, f.

3.17 ORBITALS AND QUANTUM NUMBERS

Although the spectroscopic data indicate that electrons in atoms have various energies and that these energies may be described as main energy levels and sub-levels, these data do not give information about the movement of

electrons in atoms. Bohr's concept of circular path was disproved by the Heisenberg's Uncertainty principle.

Through the use of mathematical methods known as wave mechanics, Schrodinger in 1926 was able to calculate the probability of locating the electron in a region of space about the nucleus. Thus on the basis of wave mechanics, it would not be proper to have a picture of an orbit or to think of an electron following a specific path. At best what can be said is that around the nucleus there are certain regions of space, where the likelihood of finding an electron is maximum. Such regions around the nucleus are called *orbitals*.

Each orbital in an atom is completely described by four quantum numbers. The *principal quantum number* specifies the size of orbital. This is given the symbol 'n'. As the value of 'n' increases, the size and also the energy of orbital increases. The *azimuthal* or *subsidiary* quantum number, symbol ' l ' governs the shape of the orbital. This can have values $l=0$ to $(n-1)$. When value of $l=0$, the orbital is called s orbital, when $l=1$, it is 'p' orbital, when $l=2$, d orbital and $l=3$, it is 'f' orbital. The third quantum number is the *magnetic quantum number*, symbol 'm'. The value of $m = -l$ to $+l$ through zero e.g. when $l=1$ (p orbital), $m = -1, 0, +1$ and if $l=2$, $m = -2, -1, 0, +1, +2$ and so on. In fact the magnetic quantum number gives different orientations of an orbital in space in applied magnetic field. Finally, the spin quantum number, Symbols can have value of either $+\frac{1}{2}$ or $-\frac{1}{2}$ it specifies the spin of electron in an orbital.

3.18 PAULI'S EXCLUSION PRINCIPLE.

It is an empirical rule but agrees fully with experimental observations. It was enunciated by Wolfgang Pauli in 1925 and states that:

"In an atom no two electrons can have the same set of four quantum numbers"

In an atom, therefore, two electrons may have a maximum of three same quantum numbers of same values but the fourth would be different. Thus in any orbital, when the values of n, l and m are same, two electrons can occupy the same orbital only if their spins are opposed or paired, $\uparrow\downarrow$.

Table : 3.3 SUB-DIVISION OF ENERGY LEVELS

Energy Level 'n'	Sub-Level 'l' (0 to n-1)	Orientations of orbitals 'm' (+l to -l)	Number of orbitals (n ²)	Number of electrons (Pauli's principle)	Maximum number of electrons (2n ²)
n=1 (K)	l=0 (s)	m=0	1	s ²	2
n=2 (L)	l=0 (s) l=1 (p)	m=0 m=1, 0, -1	1 (s) 3p <u>4 (Total orbitals)</u>	s ² p ⁶	8
n=3 (M)	l=0 (s) l=1 (p) l=2 (d)	m=0 m=1, 0, -1 m=2, 1, 0, -1, -2	1 (s) 3 (p) 5 (d) <u>9 (Total orbitals)</u>	s ² p ⁶ d ¹⁰	18
n=4 (N)	l=0 (s) l=1 (p) l=2 (d) l=3 (f)	m=0 m=1, 0, -1 m=2, 1, 0, -1, -2 m=3, 2, 1, 0, -1, -2, -3	1 (s) 3 (p) 5 (d) 7 (f) <u>16 (Total orbitals)</u>	s ² p ⁶ d ¹⁰ f ¹⁴	32

The first energy level (K) contains only one orbital; therefore it does not contain more than two electrons, it is not strictly speaking divided into sub levels.

The second energy level (L) consists of four orbitals and maximum of eight electrons. One of the four orbitals is an s orbital and the other three are p orbitals. Thus the second energy level consists of two sub levels, the 2s sub level and 2 p sub level, the 2s sub level consists of a single s orbital and the 2p sub level consists of three orbitals.

The third energy level (M), with a maximum of 18 electrons, contains three sub levels consisting of nine orbitals, one s orbital, three p orbitals, five d orbitals.

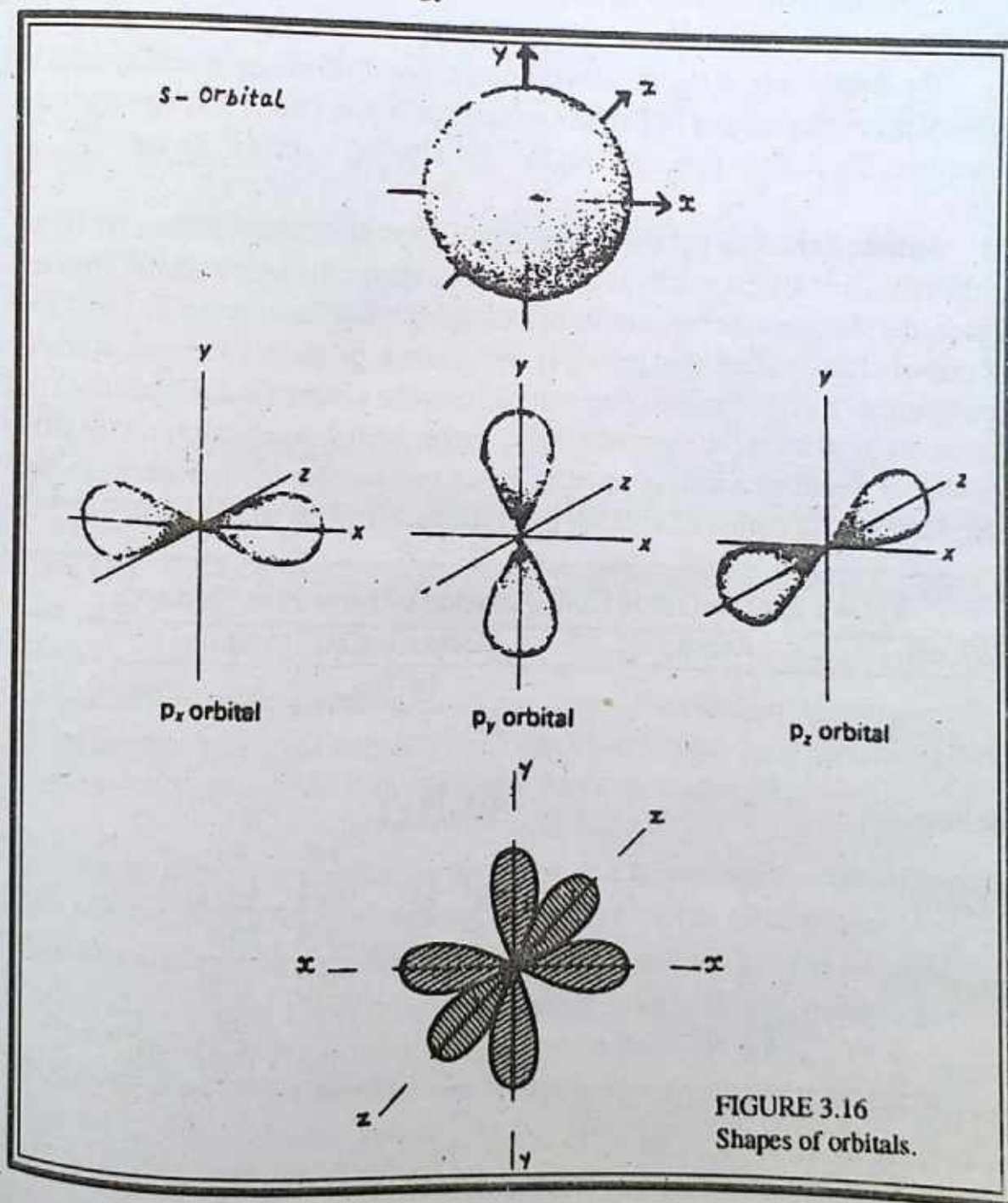
The fourth energy level (N) consisting of four sub levels, contains 16 orbitals: one s, three p, five d and seven f orbitals. The maximum number of electrons in the fourth level is 32.

3.19 SHAPES OF ORBITALS

All 's' orbitals are spherical in shape with the nucleus at the centre. Therefore in an 's' orbital, the probability of finding the electron is uniformly

distributed around the nucleus. It has only one possible orientation in space in the magnetic field because it spreads over all the three axes uniformly. It has no nodal plane.

The p orbitals are dumb-bell-shaped and they are oriented in space along the three mutually perpendicular axes (x, y, z), and are called p_x , p_y and p_z orbitals. All the three p orbitals are perpendicular to each other. These are degenerate orbitals, that are of equal energy.



Each p orbital has two lobes. One of which is labelled (+) and the other (-). Each lobe is like a pear. It is worthwhile to note that it would be wrong to imagine an electron moving along from one lobe to another. The point when the two lobes meet each other is usually referred to as the nodal plane along which the probability of finding the electron is zero. Here we are not concerned with the shapes of d and f orbitals which are rather more complicated.

3.20 ELECTRONIC CONFIGURATION

The distribution of electrons in the available orbitals is governed by certain rules or principles such as (i) Pauli's exclusion principle (which has already been described) (ii) Aufbau principle (iii) $(n + l)$ Rule, (iv) Hund's Rule etc.

(i) **Aufbau Principle** : It states that for any given atom, the electrons are filled to the orbitals of lowest energy in sequence, two electrons to each orbital. In other words, the electrons are fed in order of increasing orbital energy starting with the 1s orbital. Pauli called this principle the Aufbau principle (German Aufbau "building up"). Hypothetically we can build up the electronic configurations of the atoms by placing the electrons in the lowest available orbitals until the total number of electrons added is equal to the atomic number 'Z'. For example, the electronic configuration of the first five elements is given in table 3.4.

Table : 3.4 Electronic Configuration of First Five Elements

Element	Atomic No. 'Z'	Electronic Configuration
Hydrogen	1	$1s^1$ 
Helium	2	$1s^2$ 
Lithium	3	$1s^2 2s^1$  
Beryllium	4	$1s^2 2s^2$  
Boron	5	$1s^2 2s^2 2p^1$   

The sequence of increasing orbital energy is:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, ...

The scheme for the order of the filling of orbitals is shown in the table 3.5 :

The same order of the building up of orbitals may be simplified as shown in the table 3.6

Table 3.5 Order of filling of orbitals	Table 3.6 Order of filling orbitals

(ii) **$(n + \ell)$ Rule** : The order of the filling of orbitals in elements is guided by $(n + \ell)$ rule.

"In building up the electronic configuration of the elements, the orbital with the lowest value of $(n + \ell)$ fills first; when two orbitals have the same value of $(n + \ell)$, the orbital with the lower value of 'n' fills first"

Here 'n' and ' ℓ ' stand for the principal and azimuthal quantum numbers respectively. This useful rule reminds us that the energy of an orbital of multi electron atoms depends upon the value of both the quantum numbers, n and ℓ , but mainly on the value of n. For example, which fills first 3d or 4s orbital? For the 3d orbital ($n = 3$; $\ell = 2$); the value of $(n + \ell) = 5$; for the 4s orbital ($n = 4$; $\ell = 0$), the value of $(n + \ell) = 4$. Hence 4s which has the lower value of $(n + \ell)$ and thus lower energy fills first. Likewise, 4p orbital fills before 5s although the $(n + \ell)$ value for both is same, but 4p orbital has the lower value of the principal quantum number 'n'.

(iii) **Hund's Rule of Maximum Multiplicity:** The orbitals which are degenerated (having equal energy) like p, d, f, where these begin to fill up, they do so according to a Rule called the Hund's Rule of Maximum Multiplicity. It states:

- The electrons tend to avoid being in the same orbital. Thus as electrons are successively added, a maximum number of electrons will try to occupy orbitals singly. Only when all the orbitals are singly occupied only then the pairing of electrons commences.
- In the ground state, the electrons occupying the orbitals singly will have their spin parallel.

Making use of the above mentioned principles, we could consider in the table 3.7 the electronic configuration of the first 11 elements.

Table : 3.7 Electronic Configurations of Elements 1 to 11.

Atomic No. Z	Element	1s	2s	2p _x	2p _y	2p _z	3s	Electronic configuration
1	H	1						1s ¹
2	He	1↓						1s ²
3	Li	1↓	1					1s ² 2s ¹
4	Be	1↓	1↓					1s ² 2s ²
5	B	1↓	1↓	1				1s ² 2s ² 2p _x ¹
6	C	1↓	1↓	1	1			1s ² 2s ² 2p _x ¹ 2p _y ¹
7	N	1↓	1↓	1	1	1		1s ² 2s ² 2p _x ¹ 2p _y ¹ 2p _z ¹
8	O	1↓	1↓	1↓	1	1		1s ² 2s ² 2p _x ² 2p _y ¹ 2p _z ¹
9	F	1↓	1↓	1↓	1↓	1		1s ² 2s ² 2p _x ² 2p _y ² 2p _z ¹
10	Ne	1↓	1↓	1↓	1↓	1↓		1s ² 2s ² 2p _x ² 2p _y ² 2p _z ²
11	Na	1↓	1↓	1↓	1↓	1↓	1	1s ² 2s ² 2p ⁶ 3s ¹

From the above studies, it is gathered that :

- The maximum number of orbitals in a particular energy level is equal to n^2 . For example K, L, M and N contain 1, 4, 9, 16 orbitals.
- An orbital cannot contain more than two electrons (Pauli's principle).

- (c) The maximum number of electrons that a particular energy level specified by 'n' can hold, is given by $2n^2$. For example, K, L, M and N energy levels can hold 2, 8, 18 and 32 electrons respectively.
- (d) The number of sub levels in an energy level specified by 'n' is equal to n.e.g. energy level with $n = 2$ has two sub levels.
- (e) The number of orbitals in each sub energy level specified by 'l' is given by $(2l + 1)$. For example s, p, d and f energy sub levels contain 1, 3, 5 and 7 orbitals respectively.
- (f) The maximum number of electrons which can be accommodated in an energy sub level is given by $2(2l + 1)$. Thus s, p, d and f sublevels contain 2, 6, 10 and 14 electrons respectively: $s^2 p^6 d^{10} f^{14}$
- (g) The orbitals given by a particular value of 'l' if 'n' is same, have the same energy and such orbitals are called *degenerate*. Like $l = 1$ gives three p orbitals specified as p_x, p_y, p_z and the p orbitals are said to be three fold degenerate. These orbitals are filled according to Hund's Rule.
- (h) The notation used to indicate the number of electrons present in a given energy level is $n l^x$, where 'n' may be 1, 2, 3, ...; 'l' may be s, p, d... and 'x' represents the number of electrons actually present for example, Na has $Z = 11$; these electrons are distributed as $1s^2 2s^2 2p^6 3s^1$. This indicates that the inner three orbitals 1s, 2s and 2p are full while the outer most orbital is 3s and contain only one electron.

3.21 ATOMIC RADIUS

According to wave mechanics, an electron could be any where around the nucleus, hence it would be improper to talk of a fixed radius of an atom. The presence of other atoms also affects the outer charge distribution. Still it is useful to talk about the radius of an atom. The radius of an atom is taken as half the bond length between two homonuclear diatomic molecules like $H-H$; $O=O$; $Cl-Cl$

etc. The values of the distances between the two nuclei are determined from the spectroscopic data and X-ray diffraction measurements. For example the distance between two atoms of carbon in diamond is $1.54\text{\AA}$, giving the radius of carbon atoms as $0.77\text{\AA}$ ($1\text{\AA} = 10^{-8}\text{ cms}$). Similarly the internuclear distance between two sulphur atoms is $2.06\text{\AA}$, thereby giving the radius of sulphur atom as $1.03\text{\AA}$. Some atomic and ionic sizes are shown in the table 3.8

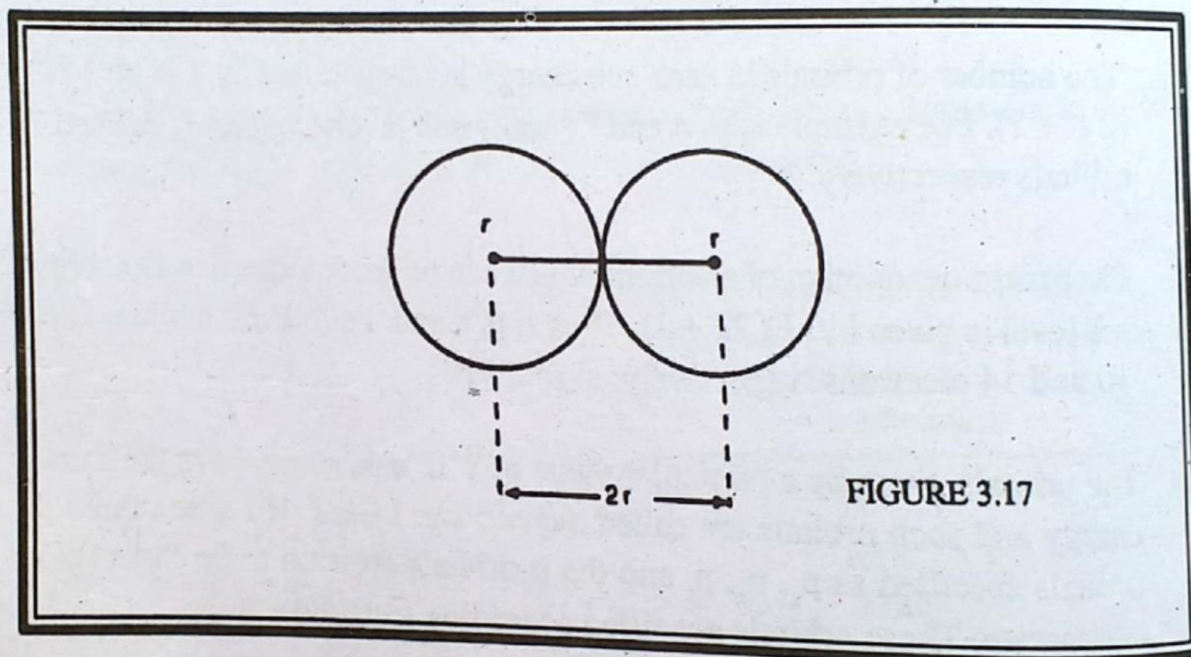


FIGURE 3.17

In case of heterogeneous diatomic molecules i.e. where two different kinds of atoms A, B are joined together, the bond length is $(r_A + r_B)$ and if any one of the radii is known, the other can be found. The knowledge of the atomic radii is useful in predicting chemical behaviour, e.g. phosphorus combines with chlorine to give PCl_5 , but does not combine with iodine to give PI_5 . The reason is that the iodine atom is much bigger than the Cl atom and 5 of the iodine atoms cannot be accommodated around a single phosphorus atom.

TABLE 3.8

Sizes of the atoms and their ions

atoms	C	N	O	F	Na	Mg	Al	Si
size	0.77	0.70	0.66	0.64	1.51	1.36	1.25	1.17
ions	C ⁴⁻	N ³⁻	O ²⁻	F ⁻	Na ⁺	Mg ⁺²	Al ³⁺	Si ⁴⁺
size	2.60	1.71	1.40	1.36	0.95	0.65	0.50	0.41

IONIC RADII

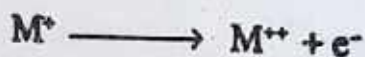
	H ⁻	Li ⁺	Be ²⁺	B ³⁺	C ⁴⁺			
	1.54	0.60	0.31	0.20	0.15			
O ⁻	F ⁻	Na ⁺	Mg ²⁺	Al ³⁺	Si ⁴⁺	P ⁵⁺	S ⁶⁺	Cl ⁷⁺
1.40	1.36	0.95	0.65	0.50	0.41	0.31	0.29	0.26
S ⁻	Cl ⁻	K ⁺	Ca ²⁺	Sc ³⁺	Ti ⁴⁺	V ⁵⁺	Cr ⁶⁺	Mn ⁷⁺
1.84	1.81	1.33	0.99	0.81	0.68	0.59	0.52	0.46
Se ⁻	Br ⁻	Rb ⁺	Sr ²⁺	Y ³⁺	Zr ⁴⁺	Nb ⁵⁺	Mo ⁶⁺	Tc ⁷⁺
1.98	1.95	1.48	1.13	0.93	0.80	0.70	0.62	—
Te ⁻	I ⁻	Cs ⁺	Ba ²⁺	La ³⁺	Hf ⁴⁺	Ta ⁵⁺	W ⁶⁺	Re ⁷⁺
2.21	2.16	1.69	1.35	1.15	0.79	0.71	0.65	0.50

3.22 IONIC RADIUS.

When an electron is removed from a neutral atom, the atom is left with an excess of positive charge called a positive ion or cation. Instead of a neutral atom takes up an electron it becomes a negative ion or anion.



The magnitude of the charge on the ion depends upon the number of electrons removed or added to the neutral atom.



As in case of atomic radius, the ionic radii are known from X-ray analysis. The ionic radii are also deduced from the way the ions are packed together. The monoatomic ions are considered as spheres and their radii are determined from the packing in crystals. The value of the ionic radius also depends on the ions that surround it.

(i) Ionic radii show that the cations have smaller radii than neutral atoms. On removal of an electron the effective charge on the nucleus increases and pulls the remaining electrons more firmly e.g.

$$\begin{aligned} \text{radius of Na atom} &= 1.57 \text{ \AA} \\ \text{radius of Na}^+ \text{ ion} &= 0.95 \text{ \AA} \end{aligned}$$

(ii) Anions have a larger radii than the neutral atoms as an excess of negative charge results in greater electron repulsion e.g.

$$\begin{aligned} \text{radius of Cl atom} &= 0.99 \text{ \AA} \\ \text{radius of Cl}^- \text{ ion} &= 1.81 \text{ \AA} \end{aligned}$$

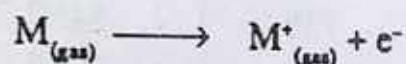
- (iii) In case of ions which have the same electronic configuration like Na^+ , Mg^{++} , Al^{+++} , ($1s^2, 2s^2, 2p^6$) the radii decrease with increasing nuclear charge.

Element	Na^+	Mg^{++}	Al^{+++}
Atomic No.	11	12	13
Ionic radius in Å	0.95	0.65	0.50

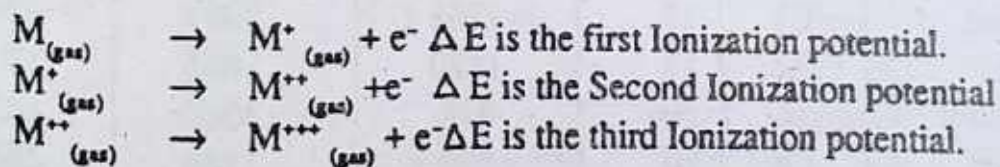
The ions which have the same electronic configuration, as given above, are called isoelectronic. The ionic sizes are shown in table 3.8.

3.23 IONIZATION POTENTIAL

It is defined as the minimum amount of energy required to remove the least strongly bound electron from a neutral gaseous atom, ion or molecule. It is called Ionization potential or ionization Energy.



It is possible to remove more than one electron from an atom or ion, giving doubly or triply charged ions and the energies needed are called:



The ionization potential is measured in Kilo-Joules per mole and is determined from spectroscopic methods or by measurement of current passing through a discharge tube. The ionization potential depends upon the distance of the electron from the nucleus. Farther the electron is from the nucleus, more easily it is removed. When one electron is removed, the positive charge on the nucleus becomes unbalanced and binds the remaining electrons more firmly. It is therefore, becomes more and more difficult to remove the second and then the third electron. Due to their larger distance, it is easier to remove an electron from 'f' shell than a 'd' shell and removal from a 'd' shell is easier than a 'p' shell. The first, second and third ionization potentials of first 20 elements are given in Table 3.9.

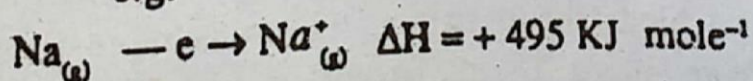
Table 3.9 Ionization Potentials (KJ mol⁻¹)

Element	Symbol	At. No:	1st	2nd	3rd
Hydrogen	H	1	1312		
Helium	He	2	2372	5250	
Lithium	Li	3	520	7297	11,810
Beryllium	Be	4	900	1757	14,850
Boron	B	5	800	2427	3658
Carbon	C	6	1086	2352	4619
Nitrogen	N	7	1403	2858	4578
Oxygen	O	8	1314	3391	5300
Fluorine	F	9	1681	3381	6046
Neon	Ne	10	2081	3964	6150
Sodium	Na	11	495	4563	6912
Magnesium	Mg	12	738	1450	7730
Aluminium	Al	13	577	1816	2745
Silicon	Si	14	787	1577	3230
Phosphorus	P	15	1060	1896	2908
Sulphur	S	16	1000	2258	3381
Chlorine	Cl	17	1255	2297	3849
Argon	Ar	18	1520	2665	3947
Potassium	K	19	418	3069	4439
Calcium	Ca	20	590	1146	4941

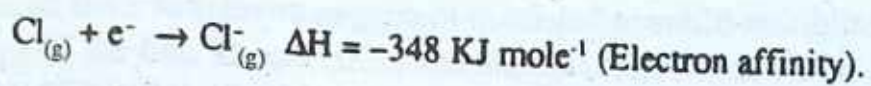
3.24 ELECTRON AFFINITY

It is easy to remove an electron from a metal to form a positive ion according to the equation $M - e \rightarrow M^+$

e.g.



The non metals on the other hand try to gain an electron to complete their shells. The energy change accompanying the gain of an electron by a neutral gaseous atom to form a negative ion is called its electron affinity. The addition of electron to an atom, is mostly an exothermic change. For example;



Some non-metallic elements particularly halogens of VIIA group evolve large amounts of energy, that is, their electron affinities are large and negative. (Refer Table 3.10). The large values of the electron affinity show that these elements are very strong oxidizing agents. The large electron affinities of halogens are attributed to their small atomic radii and greater attraction for the electrons. Moreover, the addition of an electron produces the stable inert gas configuration (i.e. Octet). The value for fluorine is anomalous, probably because the fluorine atom is very small and the incoming electrons are repelled by the electrons already present.

Table 3.10 **Electron Affinities (KJ mole⁻¹)***

IA	IIA	IIIA	IVA	VA	VIA	VIIA	ZERO
H							He
-73							+54
Li	Be	B	C	N	O	F	Ne
-57	+66	-15	-123	+31	-141	-333	+99
Na	Mg	Al	Si	P	S	Cl	
-21	+67	-26	-135	-60	-196	-348	
						Br	
						-340	
						I	
						-297	

*Positive values signify that the reaction $A + e^- \rightarrow A^{-1}$ is endothermic.

Looking at the table 3.10 you might note that the electron affinities of group IA elements are somewhat negative, even though these elements have very little attraction for the electron. The elements of group IIA, Beryllium and Magnesium have positive electron affinities (change is endothermic) because the electron is being added to higher energy p-level. In VA group elements such as Nitrogen, the value is positive because the electron must enter the half filled p-orbital and becomes paired, a process which is not energetically favourable.

The addition of second electron to oxygen or sulphur must overcome the repulsion of the negative charge already present on O^- and S^- . The process is, therefore, endothermic e.g. for O^{2-} it is + 844 and for S^{2-} it is + 532 KJ mole⁻¹

3.25 ELECTRONEGATIVITY (E.N)

In a molecule the tendency or power of an atom to attract a shared pair of electrons to itself, is called the electronegativity of that atom. The polarity of covalent bond depends upon the electronegativities of held atoms. The electronegativity values of elements are listed in table 3.11.

The numerical values of the electronegativity of fluorine is fixed as 4 which is the highest value from the values listed in table 3.11. It is clear that the E.N. values in general, increase as we go from left to right in any horizontal period, while they decrease as we go down from top to bottom a group in the periodic table.

TABLE 3.11
Electronegativities of representative Elements

H 2.1							He —
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne —
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar —
K 0.8	Ca 1.0	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr —
Rb 0.8	Sr 1.0	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe —
Cs 0.7	Ba 0.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn —
Fr 0.7	Ra 0.9						

On the basis of electronegativity values. It is *predictable* that what type of bond will be formed. If the difference between E.N. values of any two bonded atoms is less than 1.7 the bond will be covalent. The polarity of covalent bond also depends upon the E.N. values, that is, the covalent bond between two similar atoms ($\text{H}-\text{H}$, $\text{O}=\text{O}$, $\text{N}=\text{N}$ etc), the E.N. are equal, the covalent bond is non-polar in character. The covalent bond between dissimilar atoms is always polar in nature, the polarity increase with difference in their E.N. values. For example, bond between N and H is more polar than bond between C and H, because E.N. difference in case of N and H is more than E.N. difference between C and H.

PROGRESS TEST 3

1. What is the experimental evidence for the presence of small nucleus containing most of the mass and all of the positive charge in the atom?
2. What information about the structure of atom is obtained from the experiments on the passage of electricity through gases under low pressure?
3. Criticize the following statement, "An electron moves about the nucleus of an atom in a manner analogous to the movement of a planet about the sun"?
4. What information about the electron in the atom is obtained from the fact that the emission spectra of the elements are frequently discontinuous?
5. Explain quantized energy states in terms of Bohr's orbits and electron transition between the orbits.
6. What principles and rules are followed in the electronic configuration of atoms?
7. Explain the origin of X-rays and relationship between their wave length and nuclear charge in the atoms from which they originate.
8. (a) State the restrictions placed on our ability to know the position and momentum of an electron.

- (b) Explain the significance of Pauli's Exclusion principle in relation to the electronic structure of atoms.
- (c) Write down the electronic configuration for the ground states of each of the following (i) Na ($Z = 11$) (ii) Ca ($Z = 20$) (iii) Sc ($Z = 21$) (iv) Mg^{2+} ($Z = 12$) (v) Cl^- ($Z = 17$).
9. Explain the distinction between the following:
- (a) α and β - Particles (b) Orbit and orbital (c) Ground state and excited state (d) Continuous and discontinuous spectrum.
10. Describe the contribution made by the following individuals toward the structure of atom (a) Rutherford (b) Bohr (c) Moseley.
11. Give the number of protons, neutrons and electrons in each of the following:
 (a) $^{19}_{39}K$ (b) $^8_{16}O$ (c) ^3_7Li (d) $^9_{19}F^-$ (e) $^{11}_{23}Na$
 Also write down their electronic configuration.
12. What do you understand by the terms:
 (a) Atomic Radius (b) Ionization potential (c) Electron affinity (d) Electronegativity.
13. List the four quantum numbers that define the energy state of the electrons in a hydrogen atom along with their possible values and explain their significance in terms of orbitals.
14. (a) The ionization potential of Lithium and potassium are 5.4 and 4.3 eV. what do you predict for the I.P. of Na.
 (b) What is the shape of orbital for which $l = 0$? Those for which $l = 1$?
15. (a) How is emission of radiation from an atom explained by Bohr's model?
 (b) Why was the nucleus of hydrogen atom was assumed to be a fundamental particle?