CHAPTER

1 Structure of the Atom (i)

(*Quantum Mechanical Approach : Dalton to Bohr-Sommerfeld*)

Dalton's Atomic Theory

An English Chemist, Dalton in 1803 put forward atomic theory, known as *Dalton's Atomic Theory* according to which all matter is composed of extremely indivisible particles which he named *atoms* (*Greek* : atom = cannot be cut *i.e.*, indivisible.)

However this concept of indivisibility of atom did not hold long and it was proved by the experiments made by brilliant research workers like *J.J. Thomson* (1897), *Rutherford* (1911), *Neils Bohr* (1912), *Chadwick, Mosely* and others that the *atom itself has a complex structure, i.e.,* the atom consists of several particles, called *sub-atomic particles* like *electron, proton, neutron, positron, neutrino, meson* etc. Out of these, electrons, protons and neutrons are very important. The atom, of course, remains indivisible in all physical and chemical changes.

Cathode (or Negative) Rays—Discovery of Electron

Production of Cathode Rays.

The first indication of the complex nature of atom was obtained from a study of *conduction of electricity through gases at reduced pressure* by Julius Plucker (1859). He took a cylindrical glass tube, called *discharge tube* which was 30 cm long and 4 cm in diameter, closed at both ends, provided with metallic electrodes and a side tap meant for connecting the tube with a high vacuum pump and low pressure gauge. To obtain very low pressures, molecular pump and charcoal cooled by liquid air that has the property of absorbing most of the residual gas were used. The two electrodes were connected to a high voltage battery (voltage was of the order of 10,000 volts and more). The electrode connected to the negative terminal of the battery is known as *cathode* (–) while that connected to the positve terminal is called anode (+) or *anticathode.* Plucker pumped out most of the gas of the tube by means of high vacuum pump and low pressure gauge and thus reduced the pressure of the gas in the tube to about 0.001 mm Hg. Now he observed that when he applied a high voltage of the order of 10,000 volts across the metallic electrodes, the walls of the tube began to glow with a bluish or greenish light depending on the composition of the glass of which the tube is made. It thus appeared that the invisible rays of light were emitted from the cathode and moved towards anode at right angles and with large velocity (Fig. 1.1). These rays were called *cathode rays* by Goldstein (1876), since these originated from the cathode.

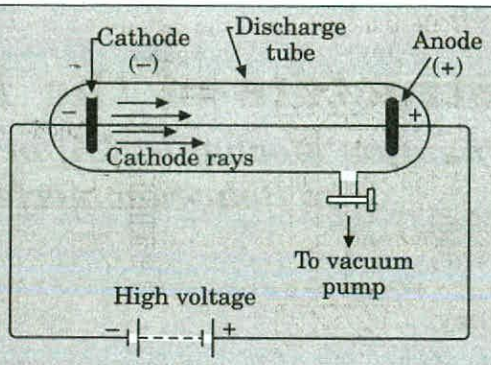


Fig. 1.1. Production of cathode rays in a discharge tube.

Properties of Cathode Rays.

Systematic investigations made by W. Crooks, J. J. Thomson, J. Perrin and others have established the following properties of cathode rays.

1. *The particles constituting the cathode rays are negatively charged.* This fact is confirmed by the following experiments.

(*a*) In 1897 J.J. Thomson showed that when cathode rays are passed through an electric field (*i.e,* when the rays are passed between two electrically charged plates), they are deflected towards the positively charged plate [Fig. 1.2 (*a*)], showing thereby that the particles constituting the cathode rays are negatively charged. These negatively charged particles were called **electrons** by Thomson.

(*b*) In 1895 J. Perrin showed that if a magnetic field is applied on cathode rays from top to bottom, perpendicular to the plane of the paper as shown in Fig. 1.2 (*b*), cathode rays are deflected upwards in the plane of the paper. This experiment also shows that the particles constituting the cathode rays are negatively charged.

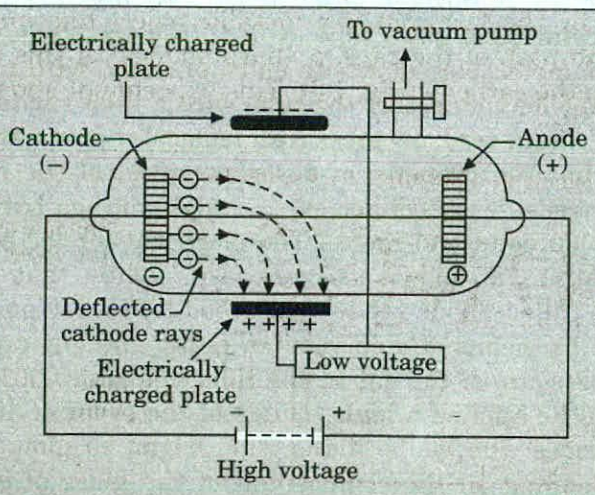


Fig. 1.2 (*a*) Cathode rays are deflected in an electric field, showing that the particles (*i.e.* electrons) constituting the cathode rays are negatively charged.

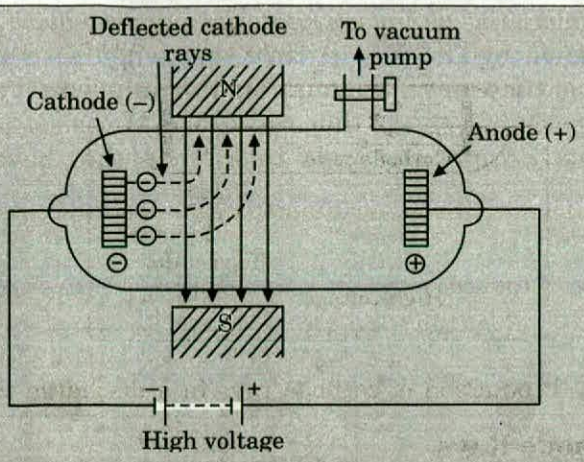


Fig. 1.2 (*b*) Cathode rays are deflected in a magnetic field, showing that the particles (*i.e.*, electrons) constituting the cathode rays are negatively charged.

Fig. 1.2. Experiment to show that the particles (*i.e.* electrons) constituting the cathode rays are negatively charged.

2. *They produce a greenish fluorescence on the walls of the glass tube.* They also produce flourescence in barium pentacyanide. rare earths (cerium etc.) natural minerals, sulphides and sulphates. When placed in path of these rays, *alumina glows red, tin stone yellow* and *willemite green.* The minerals which show fluorescence are called *phosphors.*

3. *The rays are shot out normally from the cathode.* The direction of the rays is not affected by the position of the anode.

4. *These rays travel in straight line perpendicular to the surface of the cathode.* This can be shown by the fact that if a metallic object like hinged aluminium cross is placed in the path of the rays, a sharp shadow of this object is cast on the walls opposite to the cathode (Fig. 1.3). This experiment shows that electrons have *particle properties.*

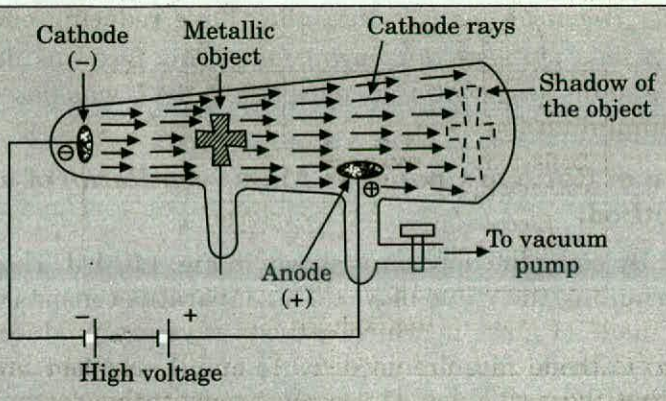


Fig. 1.3. Cathode ray cast shadow of the object placed in their path, showing thereby that these rays travel in straight line and hence electrons of which these rays are composed have particle properties.

5. *Cathode rays consist of moving material particles with definite mass and velocity.* It was shown by Crookes in 1870 that when a small paddle wheel is placed in the path of these rays, the mica blades of the wheel are set into motion (Fig. 1.4). This experiment shows that cathode rays consist of *moving material particles which have definite mass and velocity i.e.* they have *momentum.*

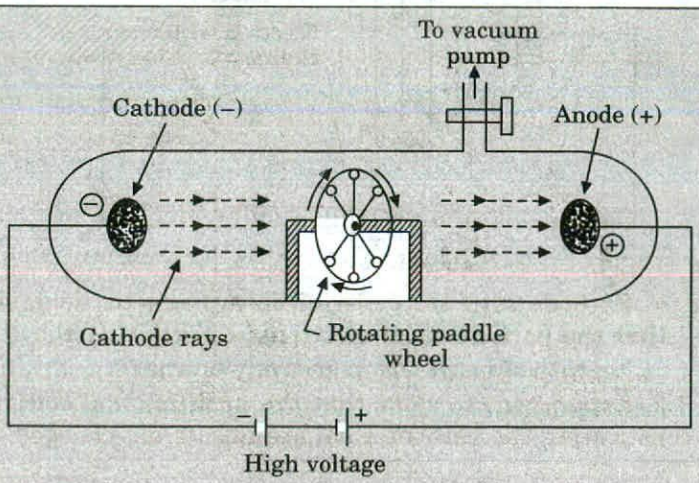


Fig. 1.4. Cathode rays rotate a small paddle wheel placed in their path, showing thereby that cathode rays consist of moving material particles with defenite mass and velocity.

6. *Cathode rays produce heat when they fall on matter.* When cathode rays from a concave cathode are focussed on a platinum foil, it begins to glow. The kinetic energy of the cathode rays is transformed into heat energy by their stoppage.

7. *Cathode rays produce X-rays.* When cathode rays strike a solid substance, particularly one with a large atomic weight, they give rise to penetrating radiations, called X-rays which have the same nature as light does.

8. *They ionise the gas through which they pass.*

9. *They couse chemical changes, e.g.,* they have reducing effect.

10. *They can pass through thin metal foils.* This fact was demonstrated by Heinrich Hertz and his assistant, P. Lenard (1862-1947) who passed cathode rays through thin aluminium foils.

Determination of Ratio of Change to Mass (*e/m Ratio*) of an Electron by Thomson's Method.

Apparatus. By using the apparatus shown in Fig. 1.5, J. J. Thomson succeeded in 1897 in determining the value of *e/m*. The apparatus consists of an evacuated discharge bulb made of glass in which cathode rays are produced from cathode which consists of a small aluminium disc. A_1 and A_2 are two brass discs which contain very narrow central holes. These holes convert the eletron beam into very fine beam beyond A_2. This beam strikes the fluorescent screen, SS' on which the deflections of the beam in electric and magnetic fields are noted. The surface of

the screen is coated with some fluorescent material like ZnS. The plates P and P' between which an electric field in the plane of the paper is generated are placed on either side of the beam. Magnetic field is applied at the same place in a direction of the electric field, *i.e.* perpendicular to the plane of the paper.

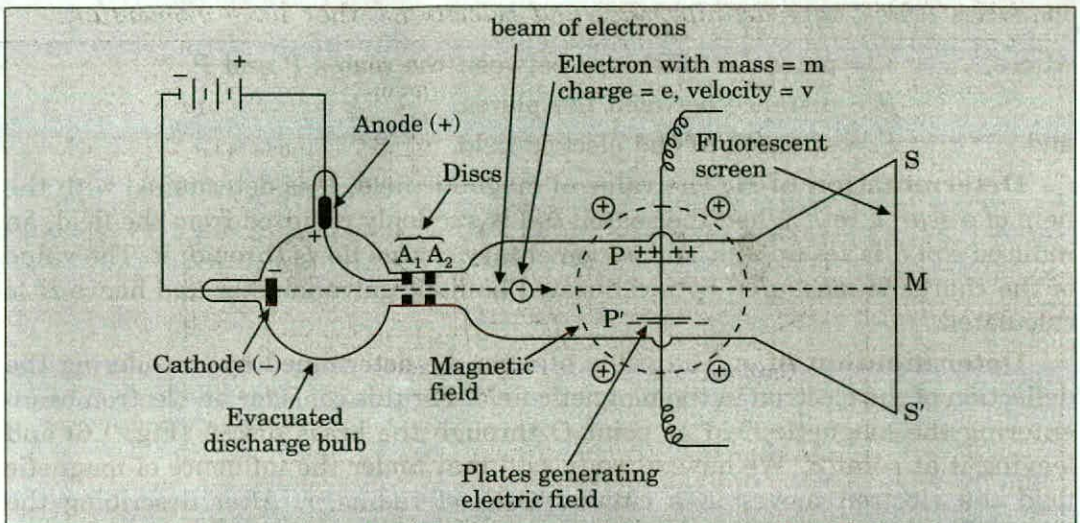


Fig. 1.5. Apparatus used in the determination of *e/m* value of the electron.

Working. A beam of electrons produced from cathode is first passed through a magnetic field of strength H which is being applied at right angles to the direction of the motion of electrons. Let the charge, mass and velocity of each electron be e, m and v respectively. Magnetic force acting on each of the electrons will then be equal to Hev. Under the influence of megnetic field the electron moves in a circular path. Let the radius of this circular path be r. After describing a circular path, the electron leaves the magnetic field and then moves in a straight line with the same velocity (= v) and ultimately strikes the screen at a point. In this case the centripetal (centrifugal) force (= mv^2/r) which is required for the orbital motion of the electron is supplied by the magnetic force (= Hev) acting on the eletron. Thus here both these forces are in equilibrium, *i.e.*

$$\frac{mv^2}{r} = Hev$$

or

$$\frac{e}{m} = \frac{v}{rH}$$

Knowing the values of v, H and r, the ratio e/m can be determined.

Determination of *v*. To find out the value of velocity v, apply the magnetic and electric fields on the electron beam *simultaneously at the right angles to each other*. Under this condition, according to Fleming's left-hand rule the electron will be deflected *downwards* by the magnetic field and *upwards* to the same extent by the electric field between the two plates and consequently the vertical deflection suffered by the electron would be zoo. Thus the electron would go straight (*i.e.* undeviated) and would strike the screen at point M. Since the deflection is zero,

the downward magnetic force (= Hev) acting on the electron will be equal to the upward electric force (= eE) acting on the electron. Thus :

$$eE = Hev$$

or $$v = \frac{E}{H} = \frac{V/d}{H} = \frac{V}{dH},$$

where V = potential difference between the plates P and P'

d = distance between the plates.

and E = strength of the electric field.

Determination of H. The value of magnetic field, H is determined with the help of a *search coil.* When the search coil is suddenly removed from the field, an induced *e.m.f.* is set up in it and a momentary charge flows through it. The value of the charge is measured by a calibrated ballistic galvanometer and hence H is calculated.

Determination of *r*. The value of r can be determined by considering the deflection of the electron in the magnetic field. For this consider an electron beam entering the magnetic field at point O through the brass disc A (Fig. 1.6) and leaving it at point R. We have already said that under the influence of magnetic field the electron moves in a circular path of radius, r. After describing the circular path, the electron leaves the magnetic field and then flies in a straight line with the same velocity and ultimately strikes the screen, MN at point N. Draw OC perpendicular on OM. Let RC and RN meet OM at S and L points respectively. Thus C is the centre of the circular path namely OR which is the length of the region in which magnetic field is applied.

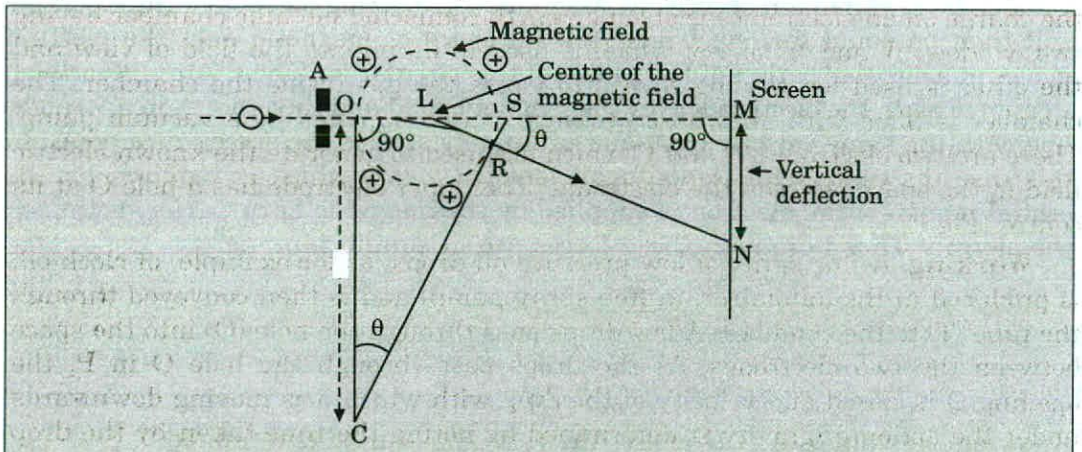


Fig. 1.6. Deflection of cathode rays in magnetic field and determination of the radius of the circular path described by the electron in the magnetic field.

Now $$\angle OCR = \angle NLM = \theta$$

$\therefore$ $$\tan\theta = \frac{OS}{OC} = \frac{MN}{ML}$$

or $$\frac{OS}{OC} = \frac{MN}{ML}$$

or $$\frac{OS}{r} = \frac{MN}{ML}$$

or $$r = \frac{OS \times ML}{MN}$$

OS is very nearly equal to the length of the region, OR in which the magnetic field is applied. ML is equal to the distance between M and the centre of the magnetic field (*i.e.* L point) and MN is the vertical deflection suffered by the electron. The first two quantities *viz.* OS and ML are constants and are given by the makers of the apparatus and the third one can be easily measured.

Thomson carried out a number of experiments for the determination of *e/m* value of an electron in which he varied the metal forming the cathode as well as the gas in the evacuated discharge bulb. In every case he found the value of *e/m* to be equal to -1.758×10^8 coulomb/*g*.

Thomson's method suffers from the following two errors :

(*i*) Vertical deflection MN is very small.

(*ii*) There is lack of uniformity in the velocity of electrons constituting the cathode rays.

Determination of Charge on an Electron (*e value*) by Millikan's Oil Drop Method.

Apparatus. The apparatus used by Millikan (1909) for the determination of the charge on an electron consists of an earth connected metallic chamber having two window, *W* and *W'* one of which is used to illuminate the field of view and the other is used for passing X-rays to ionise the gas inside the chamber. The chamber is filled with air whose pressure can be adjusted by a vacuum pump. There are two electrodes, P and P' which are used to generate the known electric field in the space between the electrodes. The upper electrode has a hole O at its centre (Fig. 1.7).

Working. A fine spray of low pressure oil drops, as for example, of clock oil, is produced in the automiser, (a fine spray pump) and is then conveyed through the tube (T) to the chamber. A few drops pass through the hole (O) into the space between the two electrodes. As the drops pass through the hole O in P, the opening O is closed and velocity of the drop with which it is moving downwards under the action of gravity is determined by noting the time taken by the drop in moving down between the two points fiexed by cross hairs of a meter eye-piece having a scale. This eye piece is fitted in a microscope. An are lamp is used to illuminate the space between the electrodes through window, *W*. Evidently the velocity of the drop, v_1, with whcih it is moving downwards by the action of gravity is proportional to its weight, *mg* (*m* = mass of the drop, and *g* = acceleration due to gravity = 981 cm/sec^2), *i.e.*

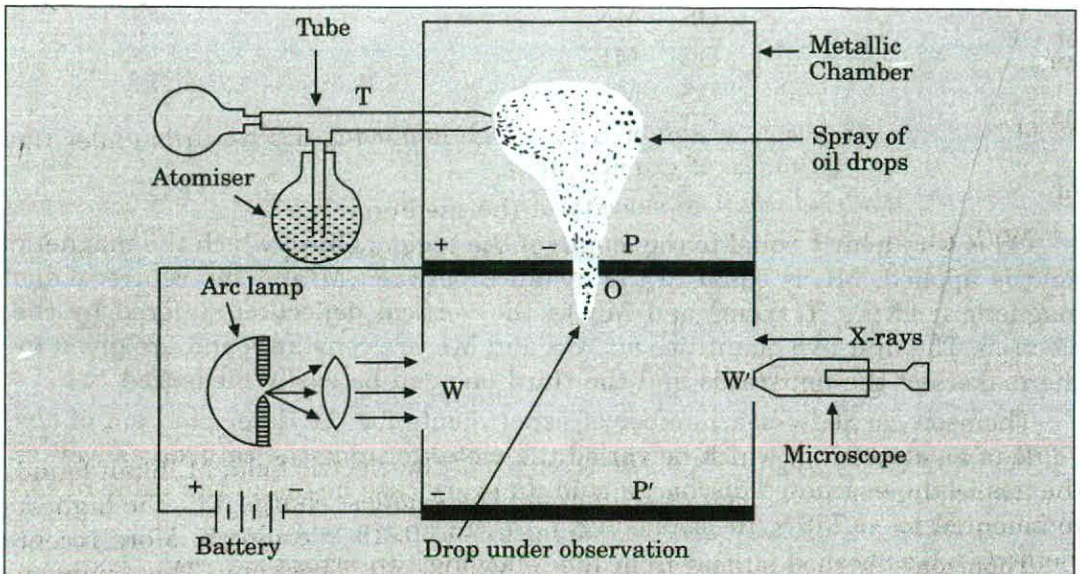


Fig. 1.7. Millikan's oil drop method for the dotermination of charge on an electron.

$$v_1 \propto mg \qquad ...(i)$$

Now the air space between the electrodes is ionised by X-rays passing into the chamber through the window, W'. The drop which is under observation, frequently takes up a gas ion and, thus gets charged. If now the electrodes, P and P′ are connected to a battery, electric field of strength, E comes into action and the drop moves upwards instead of downwards against the action of gravity with a uniform velocity, v_2. In this case the velocity, v_2 is proportional to $Ee—mg$, *i.e.*

$$v_2 \propto Ee - mg \qquad ...(ii)$$

Here e is the charge on the electron

From equations (i) and (ii), we get

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

The values of v_1 and v_2 are noted by means of the telescope and E is the strength of the applied electric fleld. Thus v_1, v_2 and E are the known quantities and, if the mass; m of the drop is determined, e can be calculated by equation (iii)

Determination of *m*. If oil drop is assumed to be a spherical particle, its mass, m is given by :

$$m = \frac{4}{3}\pi r^3 \rho$$

where r = radius of the spherical oil drop.

ρ = density of the oil of which the drop is composed of

The value of r to be used in the above equation can be known from the following relation, called *Stokes's relation,*

$$v_1 = \frac{2gr^2\rho}{9\eta}$$

or $$r = \left(\frac{9v_1\eta}{2g\rho}\right)^{1/2}$$

where v_1 = velocity of the oil drop which is moving down-wards under the influence of gravity alone.

η = coefficient of velocity of the medium.

With the help of the above two equations m is given by :

$$m = \frac{4}{3}\pi r^3\rho$$

$$= \frac{4}{3}\pi\left(\frac{9v_1\eta}{2g\rho}\right)^{3/2} \cdot \rho$$

By varying the magnitude of the strength of the electric field, Millikan found that the charge on each drop was different. The smallest charge (*i.e.*, the highest common factor of all the values) is equal to -1.59×10^{-19} coulomb. More recent methods have shown that the value of $e = -1.602\times 10^{-19}$ coulomb. This quantity is taken to be equal to one unit of negative charge (–1). Thus the electron is said to carry one unit of negative charge on it. The charge taken by an electron is the smallest charge of electricity that has been measured so far. In *a.m.u.* and *e.s.u.* the charge carried by an electron is equal to 1.602×10^{-20} *a.m.u.* and 4.8×10^{-10} *e.s.u.* respectively.

Importance of the Determination of Charge on the Electron

The determination of the charge on an electron has enabled us to determine the following :

1. Determination of Avagadro's number. Avogadro's number is defined as the number of molecules per gram molecule of a substance or it is the number of atoms per gram atom of a substance. Now we know that the charge required to liberate one gm ion of H^+ ion is equal to 96,500 coulomb and the charge on one H^+ ion is equal (though of opposite sign) to that carried by an electron, *i.e.* 1.602×10^{-19} coulomb. Hence :

$$\text{Avogadro s number} = \frac{96,500 \text{ coulomb}}{1.602\times10^{-19} \text{ coulomb}}$$

$$= 6.023\times10^{23}$$

2. Mass of an electron in grams. The value of the electronic charge (e) and e/m enables us to determine the mass (m) of an electron as follows :

$$m = \frac{e}{e/m} = \frac{1.602\times10^{-19} \text{ coulomb}}{1.758\times10^{8} \text{ coulomb}/g}$$

$$= 9.108\times10^{-28} g$$

This is the mass of an electron moving at *low speed.* It is called its **rest mass** which is defined *as the mass of the electron when it is moving with a velocity much smaller than that of light.*

3. Mass of an electron relative to that of hydrogen atom. It has been found that the number of atoms in one mole of any element is equal to Avogadro's number, 6.023×10^{23}. Therefore :

The weight of 6.023×10^{23} atoms of hydrogen

= At. wt of hydrogen = 1.008 g

$\therefore$ The weight of one atom of hydrogen

$$= \frac{1.008}{6.023\times10^{23}}\text{ g}$$

$$= 1.67\times10^{-24}\text{ g}$$

Now we know that the mass of an electron = 9.1×10^{-28}g

$$\therefore \frac{\text{Mass of hydrogen atom}}{\text{Mass of an electron}} = \frac{1.67\times10^{-24}\text{ g}}{9.1\times10^{-28}\text{g}}$$

$$= 1.835\times10^{3} = 1835$$

or Mass of hydrogen atom = 1835 × Mass of an electron

or $$\text{Mass of an electron} = \frac{1}{1835}\times\text{Mass of hydrogen atom} \qquad ...(i)$$

Thus we see that an atom of hydrogen is 1835 times heavier than an electron. In other words. *the mass of an electron is* $\frac{1}{1835}$*th of the mass of a hydrogen atom.*

4. Mass of an electron in atomic mass units. On atomic weight scale, the mass of hydrogen atom has been found to be equal to 1.008 *amu*. Hence from equation (*i*), we have

On atomic weight scale, the mass of an electron

$$= \frac{\text{Mass of hydrogen atom in } amu}{1835}$$

$$= \frac{1.008\ amu}{1835} = 0.0005493\ amu$$

This mass is taken to be equal to zero. Thus an electron is said to be a massless particle.

5. Radius of an electron. Considering the whole mass of an electron to be electrical in nature it has been proved by J. J. Thomson that the mass, m ($= 9.108\times10^{-28}$ g) of an electron is related to its radius, r as follows :

$$m = \frac{2}{3}\cdot\frac{\mu e^2}{r}$$

where μ = permeability of the medium = 1

e = charge on the electron = 1.602×10^{-20} *a.m.u.*

Thus :

$$r = \frac{2\mu e^2}{3m} = \frac{2\times 1\ (1.602\times 10^{-20})^2}{3\times 9.108\times 10^{-28}}$$
$$= 1.879\times 10^{-13}\ cm$$

Definition of Electron

Having known the mass and charge on an electron, it can be defined as *a subatomic particle which bears mass equal to 0.0005493 amu (which is taken to be equal to zero)* and negative charge equal to *–1 on it.* In other words *an electron is a massless particle which bears one unit of negative charge on it.* An electron is indicated as $_{-1}e^0$ where zero indicates that it has no mass and –1 stands to show the presence of one unit of negative charge on it.

Electrons are the Common Universal Constituents of all Atoms

It has been shown by Thomson that the electrons emitted in the cathode rays have the same *e/m* value (= -1.758×10^8 coulomb g.), irrespective of the nature of the material of the cathode and that of the gas taken in the discharge tube. Similarly it has been shown by Millikan that the value of *e* for the electrons is also the same (= -1.602×10^{-19} coulomb), irrespective of the gas used in the experiment. From these observations it can be concluded that *electrons are present in all forms of matter and are common or universal constituents of all atoms.*

Anode (or Positive) Rays–Discovery of Proton

Production of Positive Rays.

We have seen that since an atom, as a whole, is electrically neutral and it has negatively charged particles known as electrons, it should have some particles which should be positively charged. In order to show the presence of positively charged particles in an atom, attempts were made by many scientists. In 1886, German physicist, E. Goldstrein took a discharge tube provided with a cathode perforated with extremely fine holes and observed that when a large potential difference was applied between the electrodes, not only cathode rays of electrons were originated from the cathode, moving from cathode towards anode, but also new type of coloured rays were also simultaneously originated from the anode, moving from anode towards cathode through the fine holes or canals in the cathode (Fig. 1.8), and causing a glow on the wall opposite to anode.

Initially these rays were called canal rays, since they pass through the canals or holes of the cathode. These are also called *anode rays* as they seem to originate from the anode. J. J. Thomson has shown that these rays are positively-charged and hence he has called them *positive rays.*

The origin of these rays can easily be understood. In a discharge tube when gas atoms (say H atoms) lose negatively charged electrons, they acquire a positive charge. These positively charged particles then move from anode to cathode. (Fig. 1.8).

Properties of Positive Rays.

Some properties of these rays as investigated by J. J. Thomson are given below :

1. *The particles constituting the anode rays are positively charged.* This property can be shown by the following experiments :

(*a*) When these rays are passed through an electric field, they are deflected towards the negatively charged plate, showing thereby that these rays consist of positively-charged particles.

(*b*) In presence of magnetic field, these rays are deflected in a direction opposite to that of cathode. These anode rays consist of particles which are positively-charged.

2. The charge-to-mass ratio (*e*/*m*) for positive rays is smaller than that for an electron.

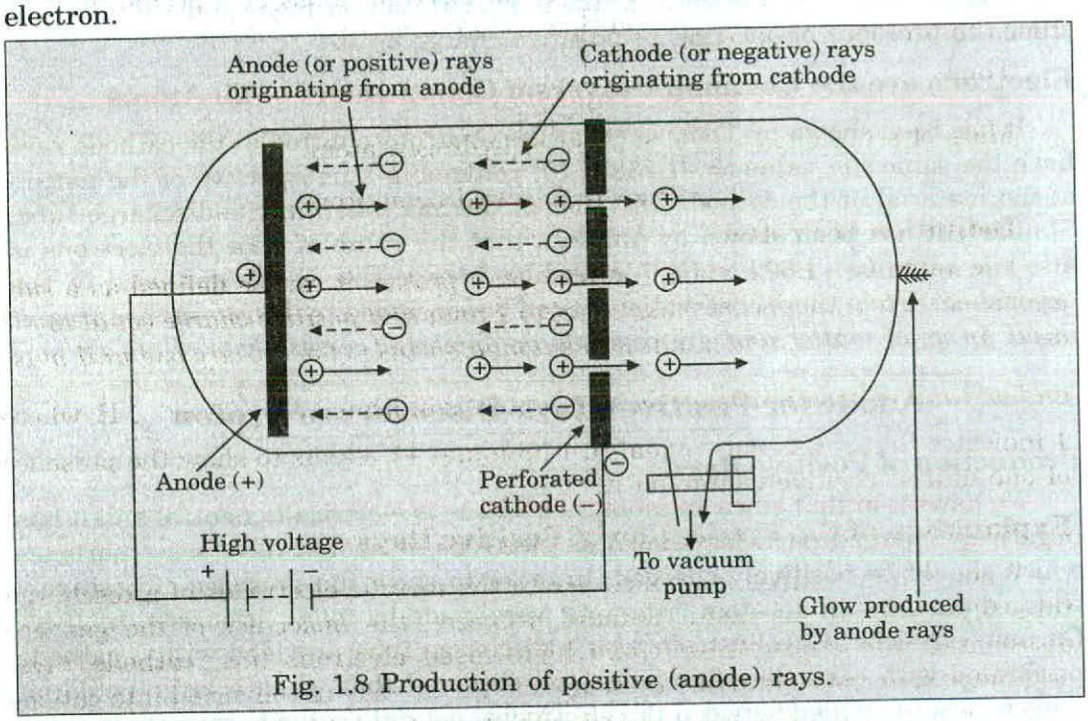


Fig. 1.8 Production of positive (anode) rays.

3. Positive rays produce flashes on ZnS plate.

4. These rays travel in a straight line in a direction opposite to the cathode.

5. *Charge-to-mass ratio* (*e*/*m*) *value.* For a number of gases charge-to-mass ratio (*e*/*m*) of positive particles constituting the positive rays has been determined and it has been found that *e*/*m* ratio for the positive rays is different for different gases. When hydrogen gas is used in the discharge tube, *e*/*m* value for the positive rays obtained from hydrogen gas has been found to be the maximum. Since the value of charge (*e*) on the positve particle obtained from all gases is the same, the value of *m* should be lowest for the positive particle obtained from hydrogen gas. Thus positive particle obtained from hydrogen gas is the lightest among all the positive particles obtained from different gases. This particle is called **proton**. Thus the positively-charged particle obtained from hydrogen gas is called a proton.

$$H - e^- \rightarrow \underset{\text{Proton}}{H^+}$$

This name was given by Rutherford.

6. *Charge on a proton.* Charge on a proton is equal in magnitude but opposite in sign to that of an electron. Thus the charge carried by a proton is equal to $+1.602 \times 10^{-19}$ coulombs which is taken to be equal to one unit of positive charge (+1). Thus a proton is said to carry one unit of positive charge on it.

7. *Mass of a proton.* The mass of a proton has been found by Thomson and it is equal to 1.672×10^{-24}g. On the relative scale its mass is equal to 1.005757 *amu* which is taken to be equal to 1 *amu* Thus a proton is said to have one unit mass. The mass of a proton is about 1837 times the mass of an electron, *i.e.*

Mass of a proton = 1837 × Mass of an electron. Mass of a proton is $\frac{1835}{1837}$ times that of hydrogen atom.

Thus :

$$\text{Mass of a proton} = \frac{1835}{1837} \times \text{Mass of hydrogen atom.}$$
$$= 0.9989 \times \text{Mass of hydrogen atom.}$$

Definition of Proton

Having known the mass and charge on a proton, it can be defined as a *subatomic particle which bears mass equal to 1 amu and positive charge equal to + 1 on it.* In other words, a *proton is a subatomic particle which bears one unil mass and one unit of positive charge on it.* A proton is indicated as ${}^{1}_{+1}p$ or ${}^{1}_{+1}\text{H}$ where 1 indicates that it has mass equal to 1 *amu* and +1 stands to show the presence of one unit of positive charge on it.

Explanation of the Production of Positive Rays

When a high voltage is applied across the metallc electrodes of a discharge tube filled with a gas under reduced pressure, the molecules of the gas are dissociated into atoms. Now when high speed electrons (*i.e.,* cathode rays) originated from cathode strike these atoms, the atoms are converted into cations which pass through the holes of the cathode and constitute positive rays. The electrons obtained in the conversion of the gaseous atoms into cations move towards anode as negative rays (Fig. 1.9).

$$\underset{\text{Gaseous atoms}}{M} + e^{-}(\textit{originated from cathode}) \rightarrow \underset{\substack{\downarrow \\ \textit{Pass through the perforated cathode as positive rays}}}{M^{+}} + \underset{\substack{\downarrow \\ \textit{Move towards anode as negative rays}}}{2e^{-}}$$

Now it is believed that *the protons like electrons are also the common universal constituents of all atoms, excepting hydrogen which has no neutron.*

Thomson's Atomic Model

On the basis of the properties of positive rays as discussed above, Thomson, in 1893, proposed that an atom can be regarded as a heavy positively charged

sphere which consists of a positively charged substance distributed uniformly throughout the whole sphere. The electrons are embedded in the sphere so that the atom becomes electrically neutral. The electrons are embedded in the sphere as the seeds are embedded in a water melon. The mutual repulsion existing between different eletrons keeps them changed in the form of circular shells. (Fig. 1.10).

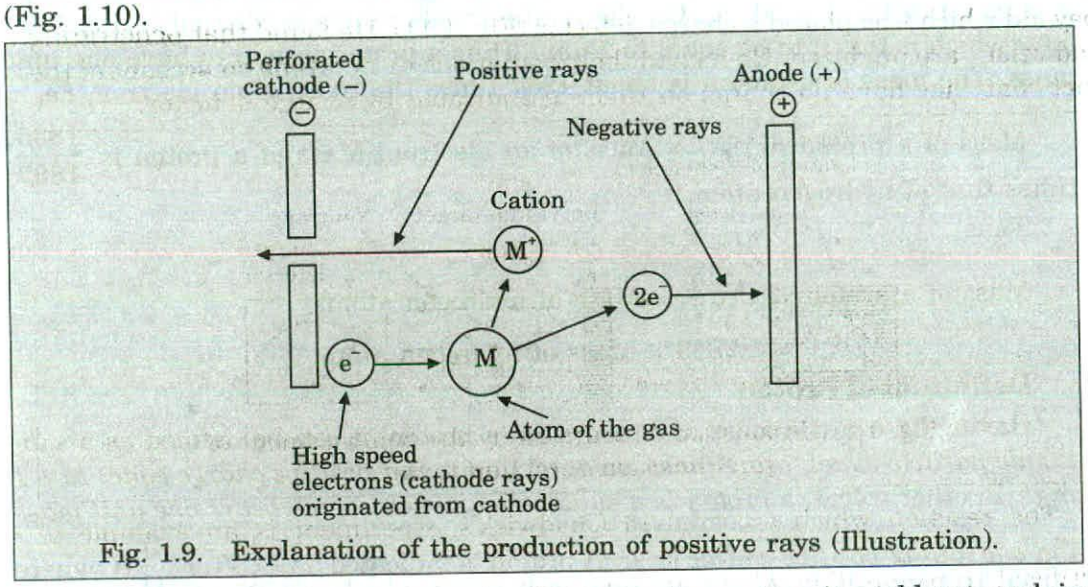


Fig. 1.9. Explanation of the production of positive rays (Illustration).

This atomic model was given up after some time, since it could not explain the large deflection suffered by α-particles in Rutherford's experiment which is described below.

Discovery of Noutron

Upto 1932 it was postulated than an atom is composed of only protons and electrons, and that the mass of an atom is due to the mass of protons present in the nucleus, since the mass of electrons is negligible. Mass of each proton is equal to 1.00375 atomic mass unit (*a.m.u*).

Rutherford noticed that the atomic masses of different atoms could not be explained if it is supposed that the atom is composed only of protons and electrons and, therefore, he predicted in 1920 that some kind of neutral particles having mass equal to protons must be present in an atom.

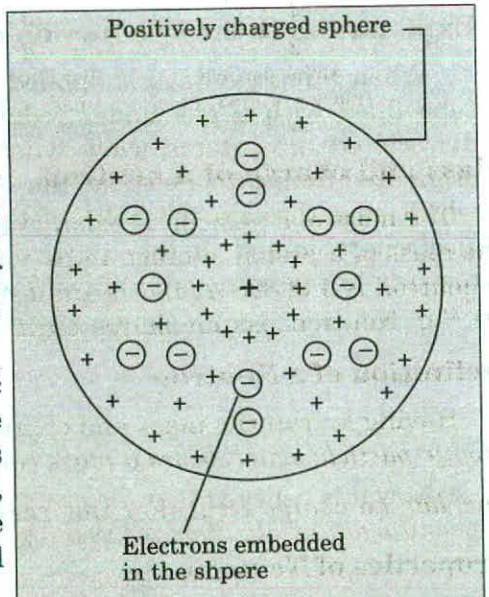


Fig. 1.10. Thomson's a atomic model.

It was in 1932 that Chadwick discoved these neutral particles for which he was awarded the Nobel Prize in Physics in 1935. He obtained these neutral particles by bombarding light nuclei like Li and

Be with α-particles. He named these particles as **neutrons** on account of their neutral nature.

Experiment. In his experiment, Chadwick directed a stream of α-particles $\left(\begin{matrix}4\\2\end{matrix}\mathrm{He}\right)$ produced from polonium source at a berrylium target $\left(\begin{matrix}9\\4\end{matrix}\mathrm{Be\ isotope}\right)$ beyond which was placed a charge detector (Fig. 1.11). He found that penetrating radiations are produced. He named these radiations as neutrons on account of the fact that they have no charge on them as indicated by charge detector.

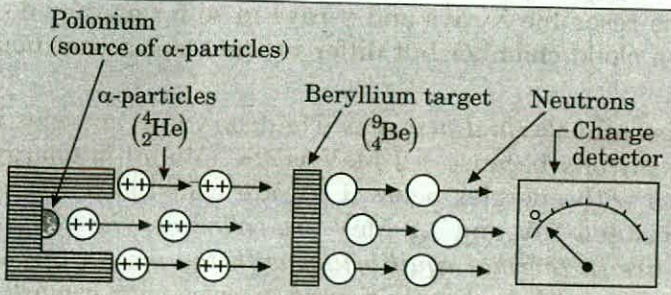


Fig. 1.11. Production of neutrons by the bombardment of α-particles on beryllium target.

The reaction which occurred in Chadwick's experiment is an example of artificial transmutation where an atom of beryllium $\left(\begin{matrix}9\\4\end{matrix}\mathrm{B\ isotope}\right)$ is converted into a carbon atom through the nuclear reaction shown below :

$$\underset{\substack{\text{Alpha particle}\\(\text{mass} = 4\ amu,\ \text{at. no.} = 2)}}{\begin{matrix}4\\2\end{matrix}\mathrm{He}} + \underset{\substack{\text{Beryllium atom}\\(\text{mass} = 9\ amu,\\ \text{at. no.} = 4)}}{\begin{matrix}9\\4\end{matrix}\mathrm{Be}} \rightarrow \begin{matrix}12\\6\end{matrix}\mathrm{C} + \begin{matrix}1\\0\end{matrix}n$$

Mass and charge of a neutron

The mass of a neutron is equal to that of a proton. On the relative scale, since the mass of a proton is taken to be equal to 1 *a.m.u.,* although the exact mass of a neutron is 1.00898 *a.m.u.* In grams, the mass of a neutron is equal to 1.672×10^{-24} g. Neutron has no charge on it.

Definition of a Neutron

Having known the mass and charge of a neutron, it can be defined as a *sub-atomic particle which bears a mass equal to that of a proton (i.e.* equal to 1 *amu) and has no charge on it.* For this reason a neutron is represented as $\begin{matrix}1\\0\end{matrix}n$.

Properties of Neutron

(*i*) *Decay of neutron.* A free neutron $({}_0n^1)$ decays into a *proton* $\left(\begin{matrix}1\\+1\end{matrix}p\right)$ with the emission of an *electron* $\left(\begin{matrix}0\\-1\end{matrix}e\right)$ and a *neutrino* $\left(\begin{matrix}0\\0\end{matrix}v\right)$

$$\underset{\text{Neutron}}{{}_0n^1} \rightarrow \underset{\text{Proton}}{{}_{+1}p^1} + \underset{\text{Electron}}{{}_{-1}e^0} + \underset{\text{Neutrino}}{{}_0\upsilon^0}$$

(*ii*) *The neutrons are very penetrating.* Their intensity of penetration is reduced to one-half in passing through lead of thickness of about 1.5 cm. Neutrons are less penetrating than cosmic rays.

(*iii*) Neutrons have the property of expelling high speed protons from hydrogenous matter like paraffin, water, paper, cellophane etc. From the rang of protons knocked out from paraffin the energy of neutrons has been calculated.

(*iv*) Neutrons resemble X-rays and γ–rays in so far as they do not produce a track in a Wilson cloud chamber but differ in one respect that neutrons produce no ionisation.

(*v*) *Fast, slow and thermal neutrons.* Neutrons with energies above 1.2 MeV are called *fast neutrons* because 1.2 MeV is the minimum energy for fission of ${}_{92}U^{235}$. Neutrons with energies below 1 eV are called *slow neutrons.* Neutrons with energies between 1eV and 1.2 MeV are called *epi-thermal neutrons. Those neutrons which are in thermal equilibrium with the matter through which they pass and have a Maxwellian distribution of energies with a most probable value depending upon temperature are called thermal neutrons.* The most probable energy of thermal neutrons at 27°C is 0.00260 eV.

Slow neutrons are usually more effective than fast ones, because high-speed neutrons may pass through a neucleus without bringing about transmutation.

Uses of Neutrons

(*i*) Almost all the elements can be transmulated by neutrons Some of the elements require fast neutrons whereas other require slow ones. Thus a fast neutron ejects an α-particle from a nitrogen nucleus, thereby converting it into a boron nucleus.

$${}_7N^{14} + {}_0n^{10} \rightarrow {}_5B^{11} + {}_2He^4$$

When slow moving neutrons fall on certain substances, they are captured with the emission of high energy γ-particle from a nitrogen nucleus, thereby converting it into a boron nucleus.

$${}_{29}Cu^{65} + {}_0n^1 \rightarrow \underset{\text{Radioactive}}{{}_{29}Cu^{66}} + h\upsilon$$

$${}_{29}Cu^{66} \rightarrow + {}_{30}Zn^{11} + {}_{-1}e^0.$$

(*ii*) The neutrons are now being widely used in biological and medical sciences. Because of their intense biological effects they are now being used in the treatment of cancer.

Summary of the Important Properties of Sub-atomic Particles : Electron, Proton and Neutron.

We have hitherto studied important properties of the three principal fundamental particles of the atom which are *electron, proton* and *neutron.* Their properties are summarised in table 1.1 given on page 17.

Nearly all of the ordinary properties of matter can be explained on the basis of the properties of these fundamental subatomic particles.

Table 1.1 Important properties of electron, proton and neutron

Particle	Mass			Charge		Charge units	Symbol	Discoverer	Location
	In g. (C.G.S. units)	In kg (S.I. units)	In a.m.u.	In e.s.u. (C.G.S. units)	In Coulomb (C) (S.I. units)				
Electron	9.108×10^{-28} g	9.108×10^{-31} kg	0.005493 a.m.u. ≈ 0.00 a.m.u.	4.8×10^{-10} e.s.u.	1.602×10^{-19} C	− 1	$_{-1}e^{0}$	J.J. Thomson	Outside the nucleus
Proton	1.672×10^{-27} g	1.672×10^{-27} kg	1.005757 a.m.u. ≈ 1.00 a.m.u.	—	1.602×10^{-19}C	+ 1	$_{+1}p^{1}$ or $_{+1}H^{1}$	J.J.Thomson	In the nucleus
Neutron	1.672×10^{-24} g	1.672×10^{-27} kg	1.00898 a.m.u. ≈ 1.00 a.m.u.	0	0	0	$_{0}n^{1}$	Chadwick	In the nucleus

Rutherford's Nuclear Atomic Model—Discovery of Nucleus

We have been that, according to Thomson's atomic model, an atom consists of electrons and protons. In order to test Thomson's model and to know as to how and where the electrons are located in the atom, Rutherford (1911), a British scientist, performed some experiments on the scattering of α-particles by a thin metal foil. Here it may be mentioned that α-particle is a helium nucleus which consists of two units of positive charge and its mass number is equal to 4. Hence it is represented by the symbol, $_{+2}\alpha^4$ or $_{+2}He^4$.

The pictorial representation, of Rutherford's experiment is given in Fig. 1.12. In his experiment he produced a narrow beam of α-particles from a radioactive substance like radium placed in a lead block and directed it at a thin sheet of gold foil of thickness of 0.00004 cm. A movable circular screen coated with ZnS was placed on the other side of the foil. This screen helped in detecting the direction in which the α-particles moved. When these particles struck the screen, a flash of light was observed.

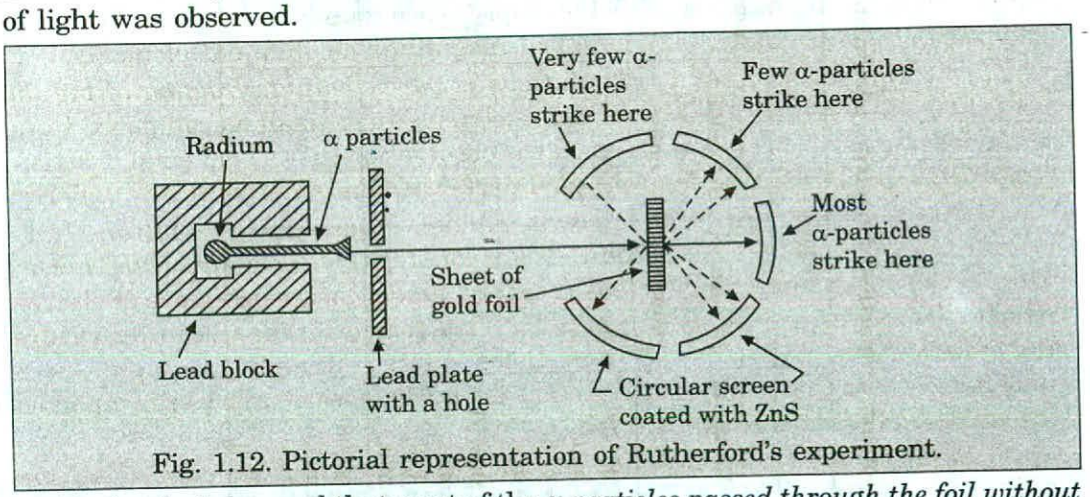


Fig. 1.12. Pictorial representation of Rutherford's experiment.

Rutherford observed that most of the α-*particles passed through the foil without any deflection from their path* and struck the screen at its centre, causing illuminations. *A few of them* were deflected at *some angles* (90^0 or wider angles) after passing through the foil. *Very few* (not more than one in 10,000) *turned back on their original path.* All the three types of deflections are shown in Fig. 1.13.

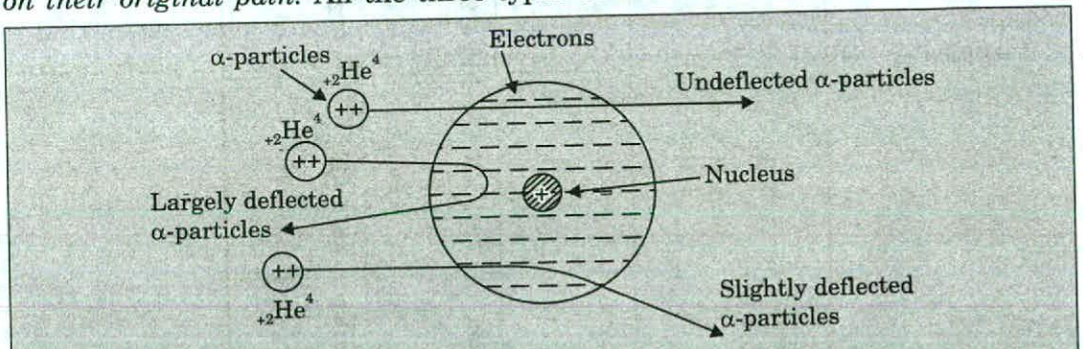


Fig. 1.13. Three types of deflection of α-particles by a thin metal foil shown in a simpler way.

On the basis of the observations made by Rutherford in his experiments, combined with the discovery of neutron made by Chadwick in 1932, he proposed a complete model of the atom which is named as *Rutherford's nuclear atomic model* after his name. This is also called *nuclear atom*. According to this model :

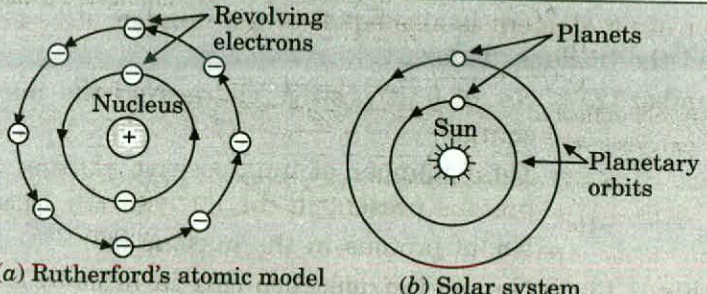
Postulates of Rutherford's Model

1. *Atom contains a massive (heavy) and positively charged part at its centre. This central part of the atom is called* **nucleus.** The presence of the nucleus at the central part of the atom is based on the observation that a few α-particles are deflected back. It is this positively charged nucleus which repells the positively charged α-particles to go back. All the protons and neutrons are present in the nucleus of the atom. Although the nucleus is small in size, it is heavy due to the presence of all protons and neutrons in it. Thus the entire mass of the atom resides in its nucleus and is equal to the sum of the masses of protons and neutrons, since the mass of the electrons is negligible. The remaining part of the atom round the nucleus is left empty. Thus the atom contains a lot of empty space round the nucleus. The nucleus has positive charge which is different in magnitude for different elements.

2. *The volume occupied by the nucleus is only a minute fraction of the total volume of the atom, i.e.* the size of the nucleus is very small as compared to that of the whole atom. This fact is based on the observation that a very small fraction of α-particles turned back on their original parts without undergoing any deflection.

3. Atom is not all solid, as was earlier suggested by Dalton, but is *extraordinarily hollow, since it consists of a lot of empty space round the nucleus.* Most of the space round the nucleus is empty, except for the presence of electrons which themselves are extremely minute. This conclusion has been drawn from the observation that most of α-particles passed straight through the foil undeflected. It is this empty space around the nucleus which allows the α-particles to pass undeflected through the foil.

4. *Electrons are revolving round the nucleus in closed orbits with a fast speed and hence almost all the space round the nucleus is occupied by the revolving electrons.* (Fig 1.14). The electrons keep revolving in orbits round the uncleus as the planets revolve round the sun. Thus Rutherford's model of atom bears a close resemblance with the solar system in which the massive sun plays the role of the massive nucleus and the planets play the role of the revolving electrons. It is because of the close resemblance of Rutherford's model with solar system that the electrons revolving round the nucleus are generally referred to as *planetary electrons.*



(*a*) Rutherford's atomic model (*b*) Solar system

Fig. 1.14. Comparison of Rutherford's atomic model with solar system.

Drawbacks of Rutherford's Nuclear Atomic Model

We have seen that according to Rutherford's nuclear atomic model the electrons are revolving around the nucleus in orbits with a fast speed. The speed of orbiting electrons is so high that each of the electrons is accelerated. Now according to the *classical electromagnetic theory* (electrodynamics), if a charged particle (here this particle is electron) is accelerating around an oppositely charged particle (here this particle is nucleus), it (*i.e.* electron) would continuously lose or radiate energy and its speed will decrease and hence will gradually come closer to the nucleus by a spiral path. The ultimate result of this spiral path will be that the electron will fall into the nucleus as shown in Fig. 1.15, thereby making the atom unstable, *i.e.* according to Rutherford's model the atom should not exist. In actual practice this does not happen. Thus we see that Rutherford's model cannot explain the stability of the atom. This dilemma was solved in 1913 by Neils Bohr who proposed an improved form of Rutherford's atomic model.

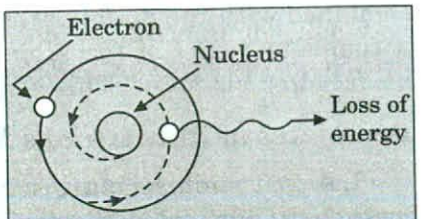


Fig. 1.15. An electron while revolving round the nucleus loses energy and its speed is decreased, and ultimately the electron falls into the nucleus by a spiral path.

What is Atomic Number (Z) ?

We have seen that, according to Rutherford, the atom has a nucleus which carries positive charge on it. The positive charge carried by the nucleus is called *nuclear charge* which is equal to the total number of positive charges on the nucleus of the atom of that element. *This total number of unit positive charges on the nucleus is called the atomic number of the element.* Now since each proton has +1 charge and neutron has no charge, the total number of unit positive charges carried by the nucleus is equal to the number of protons present in the nucleus of the atom. Thus atomic number of an element can also be defined *as the number of protons present in the nucleus. Thus* :

Atomic number of an element is defined as the number of unit positive charges on the nucleus (nuclear charge) of the atom of that element or as the number of protons present in the nucleus.

Now since the atom as a whole is electrically neutral, the number of protons (positively charged particles) in the nucleus is equal to the number of electrons (negatively charged particles) revolving in orbits around the nucleus. Consequently atomic number of an element is also equal to the number of electrons revolving in orbits round the nucleus. Thus :

Atomic number (Z) = No. of unit positive charges on the nucleus (Nucleus charge)
= Total number of unit positive charges carried by all protons present in the nucleus.
= No. of protons in the nucleus (p)
= No. of electrons revolving in orbits (e)

or $\boxed{Z = p = e}$

Atomic number of an element is also defined *as the serial number of its position in the periodic table, starting from hydrogen as the first element.*

Mosley's Law

Roentgen while making some experiments with a discharge tube in 1895, found that when cathode rays are allowed to fall on a metal target called *anti-cathode* or *target material* placed in their path, new type of radiations are produced. These radiations are called X-rays. These rays are also electromagnetic in character and are comparable to light waves. The common form of X-ray tube used for producing X-rays is shown in Fig. 1.16. The stream of cathode rays (*i.e.* electrons) produced from the cathode converges to a point through a concave surface on the anti-cathode and gives rise to X-rays.

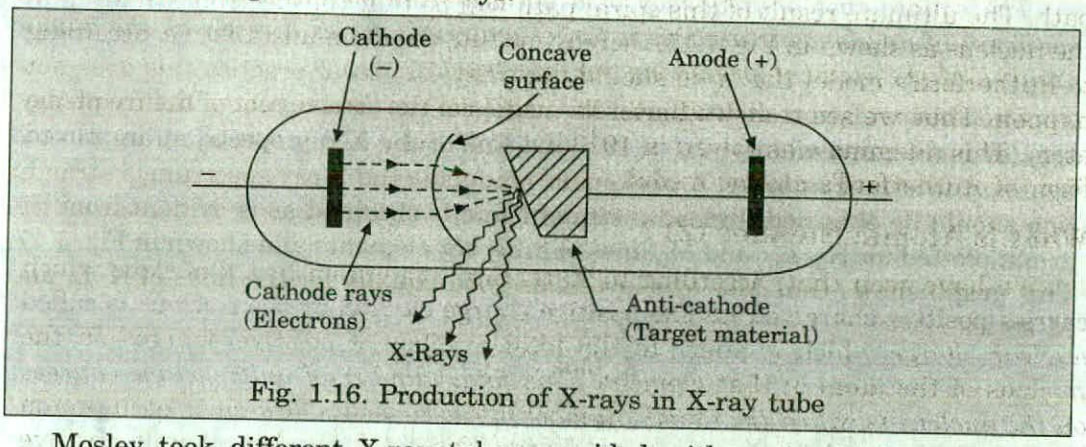


Fig. 1.16. Production of X-rays in X-ray tube

Mosley took different X-ray tubes provided with anti-cathode made from different elements. He found that when cathode rays are allowed to fall on the anti-cathode, X-rays are emitted the wave lengths of which are characteristic of the element of which the anti-cathode is made.

X-rays were passed through a slit in platinum plate and then emerged from X-ray apparatus through aluminium window. The emergent beam led on to the cleavage face of a crystal of potassium ferrocyanide (used as diffraction grating) which analysed the X-ray beam. The rays thus diffracted by the crystal were obtained in the form of *line X-ray spectrum* and were allowed to fall on a photographic plate. Line spectrum is characteristic of the target material used. In fact X-rays constituting the line spectrum are called *characteristic X-rays.* The characteristic X-ray spectrum consists of discrete spectral lines which can be grouped into K-series, L-series, M-series etc. Each of these series consists of various lines as shown below :

K-series $\rightarrow K_\alpha, K_\beta, K_\gamma$ *etc. lines (called K-lines).*

L-series $\rightarrow L_\alpha, L_\beta, L_\gamma$ *etc. lines (called L-lines).*

M-series $\rightarrow M_\alpha, M_\beta, M_\gamma$ *etc. lines (called M-lines).*

The number of the lines present in the spectrum depends both on the nature of the target material and the excitation voltage.

Mosley showed that the square root of the frequency $\sqrt{\upsilon}$ of a line of a given series of characteristic X-rays spectrum is related to the atomic number (Z) of the element used as anti-cathode (target material) by the following expression :

$$\sqrt{\upsilon} = a\,(Z-b) \qquad ...(i)$$

where a = proportionality constant

and b = a constant whose value is the same for all the lines of a given series. For K_α and K_β lines of K-series, $b = 1$. b is called *screening constant* which takes into account the screening effect of electrons.

The values of a and b vary from one series to the other. *i.e.,* their values for the lines of K series are different from those for the lines of L-series, etc.

The relation represented by equation (i) is called *Mosley's law* which can be stated as :

The square root of frequency of a spectral line on the characteristic X-ray spectrum of an element (used as a target material) varies directly as the atomic number of the element producing the spectrum.

The above relation shows that if the values of the square root of the frequency, $\sqrt{\upsilon}$ (or more conveniently $\sqrt{\upsilon} \times 10^8$) of a line of the X-ray spectrum are plotted against the atomic number, Z, of element producing the X-ray spectrum, a straight line should be obtained. Indeed a straight line is obtained as is evident from the graph plotted for K_α, L_α, and M_α lines of different elements and shown in Fig. 1.17. This graph shows that Mosley's law holds good equally for the lines of K, L, and M series.

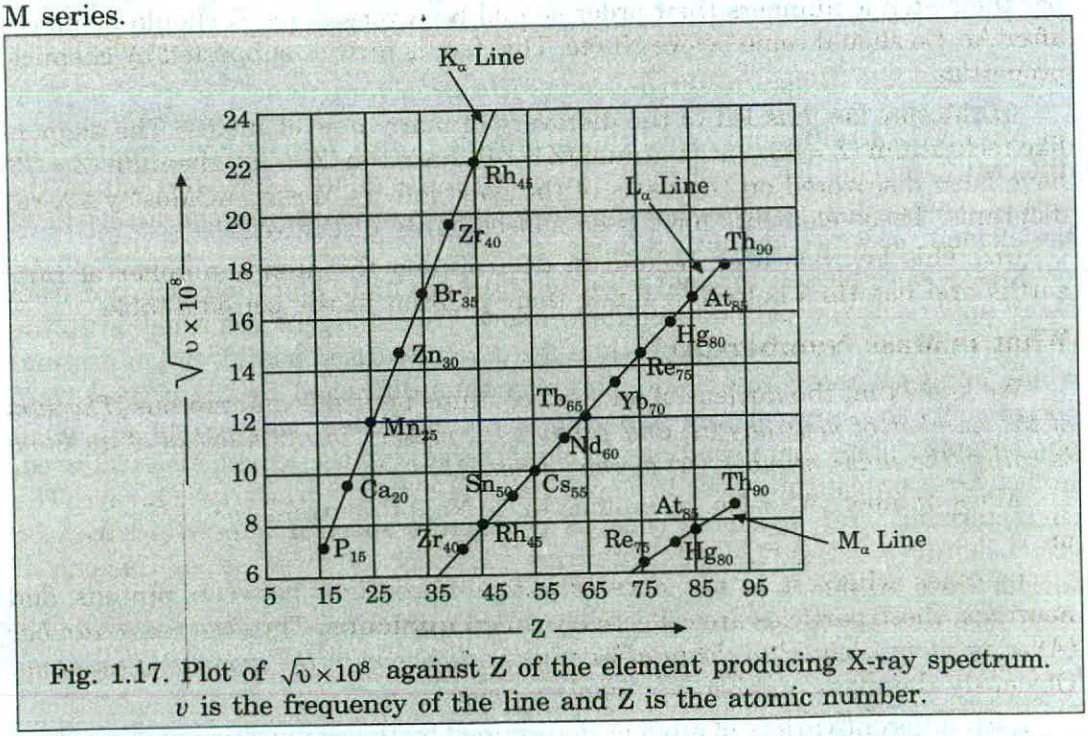


Fig. 1.17. Plot of $\sqrt{\upsilon} \times 10^8$ against Z of the element producing X-ray spectrum. υ is the frequency of the line and Z is the atomic number.

For the K_α and K_β lines of K-series for which $b = 1$, the above relation becomes :

$$\sqrt{\upsilon} = a(Z-1)$$

Thus for K_α and K_β lines Mosley law becomes *that the square root of the frequency is proportional to the atomic number of the element reduced by one.*

The integer, Z, which is called atomic number of the element, determines the exact position of the element in the periodic table. The atomic number of an element can be directly determined from the X-ray spectrum of the element and is equal to the number of unit positive charges on the nucleus of the atom concerned.

Importance of Mosley's Law

Mosley law has been found to be very useful. The improtance of this law is evident from the following points :

(*i*) We have seen that this law his established that the atomic number is always numerically equal to the number of electrons revolving round the nucleus. According to this law *it is the atomic number and not atomic weight on which the properties of the elements (both physical and chemical) depend.* It thus says that *the elements must be arranged in the periodic table in the increasing order of their atomic number and not atomic weight as originally enunciated by Mendeleef.* Accordingly, Mosley's law has been used to place elements in their proper order in the periodic table in certain questionable cases, *e.g.,* if the elements are placed according to their increasing atomic weight, K(Z = 19) should come before Ar (Z = 10); Ni (Z = 28) shold precede Co (Z = 27) etc. But Mosley law says that as per their atomic numbers their order should be reversed, *i.e.* K should be placed after Ar, Co should come before Ni etc. This fact is further supported by chemical properties.

(*ii*) Mosley law has led to the discovery of many new elements. The element like technitium (Z = 43), promethium (Z = 61), hafnium (Z = 72), rhenium (Z = 75) have been discovered on the basis of the gaps left by Mosley in Mosley's X-ray diagrams. These elements have been subsequently discovered.

(*iii*) This law has been helpful in determining the atomic number of rare-earths and has thus helped in fixing their position in the periodic table.

What is Mass Number (A) ?

We know that the nucleus of an atom contains neutrons and protons. *The sum of the number of neutrons (n) and protons (p) present in the nucleus of an atom is called the mass number (A) of that atom, i.e.*

Mass number (A) = No. of protons (p) + No. of neutrons (n)

or $$A = p + n$$

In cases where it is not necessary to differentiate between protons and neutrons, these particles are collectively called **nucleons.** Thus *the mass number (A) of an atom is equal to the tatal number of nucleons in the nucleus of an atom.* Obviously the mass number is a *whole number.*

Each different variety of atom as determined by the composition of its nucleus is called a **nucleide.**

Determination of the Composition of an Atom (Nucleide) in terms of Number of Electrons, Protons, and Neutrons

Using the relations namely :

Atomic number (Z) = *No. of protons* (p) = *No. of electrons* (e) ...(i)

Mass number (A) = *No. of protons* (p) = *No. of neutrons* (n) ...(ii),

we can find out the number of electrons, protons and neutrons in an atom. The composition of the atoms of first twenty elements (H to Ca) in terms of the number of electrons, protons and neutrons is shown in Table 1.2.

Table 1.2. Composition of the atoms of the first twenty elements in terms of the protons, neutrons and electrons.

Element	At. No. (Z)	Mass number (A) of the isotope having the maximum abundence	Protons (p) = Z	Nuetrons (n) = (A – Z) = (A – p)	Electrons (e) = Z = p
H	1	1	1	0	1
He	2	4	2	2	2
Li	3	7	3	4	3
Be	4	9	4	5	4
B	5	11	5	6	5
C	6	12	6	6	6
N	7	14	7	7	7
O	8	16	8	8	8
F	9	19	9	10	9
Ne	10	20	10	10	10
Na	11	23	11	12	11
Mg	12	24	12	12	12
Al	13	27	13	14	13
Si	14	28	14	14	14
P	15	31	15	16	15
S	16	32	16	16	16
Cl	17	35	17	18	17
Ar	18	40	18	22	18
K	19	39	19	20	19
Ca	20	40	20	20	20

Bohr's Atomic Model

We have seen that according to Rutherford's nuclear atomic model, an atom has a nucleus and negative electrons which are revolving round the nucleus in the same way as the planets revolve round the sun in the solar system. This model could not say anything as to how and where these electrons were arranged.

This model could also not explain how the spectral lines are produced by the simplest atoms like hydrogan atom when an electron jumps from one orbit to the other.

In order to explain why an electron revolving round the nucleus does not lose energy and consequently does not fall into the nucleus and how the spectral lines of the emission spectrum of H-atom are produced when an electron jumps from one energy level to the other, Niels Bohr, a Danish Physicist, in 1913, put forward a new atomic model which is based on Planck's quantum theory of radiation.

Before, we could deal with Bohr's atomic model we should have a clear understanding of the follwing topics :

(*i*) *Electromagnetic radiations (or waves) and nature of radiations emitted by electron.*

(*ii*) *Emission spectrum, continuous spectrum and line spectrum of hydrogen atom.*

(*iii*) *Plancks' quantum theory of radiation, and its application in explaining photoelectric effect and Compton effect.*

Electromagnetic Radiations or Electromagnetic Waves—Nature of Radiations Emitted by Electron

When an object moves up and down or vibrates continuously, energy, in the form of a wave, is sent or transmitted (or propagated) by the vibrating object to a distant place. The wave travels at right angle to the vibratory motion of the vibrating object and away from it (Fig. 1.18). Wave produced by a vibrating object can be represented by a wavy curve. One such wavy curve is shown in Fig. 1.18. The tops (*i.e.* maxima) of the wavy curve are called *crests* and the bottoms (*i.e.* minima) are called *troughs* (Fig. 1.18). When a stone is thrown in a pond of water, water molecules start to vibrate up and down and transmit their energy as waves on water surface which are seen travelling towards the bank of the pond.

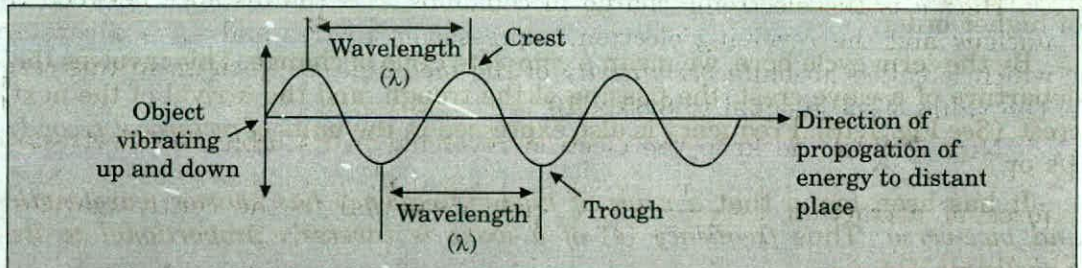


Fig. 1.18. Production of a wave by a vibrating object and definition of crests, troughs and wavelength in a wave.

In 1864 James Clark Maxwell showed that when an electric current is passed through a circuit (*e.g.* through a tungsten filament), it radiates energy in the form of waves. The energy radiated is called **radiate energy** and the waves produced are called **electromagnetic waves** or **electromagnetic radiations.** These waves are so called because similar sort of waves can also be obtained by moving a charged body as well as a magnet *to* and *fro* in a magnetic field. These waves do not require any medium for propagation or transmission; *e.g.*, light and radio waves (which are electromagnetic waves) from the sun and stars reach the earth by travelling through nonmaterial medium *i.e.*, through empty space. All these waves travel with the speed of light.

The radiations (or waves) emitted by the vibratory motion of an electron are also electromagnetic radiations. These radiations also travel with that speed of light.

Properties of Waves—Waves Parameters

Waves are characterised by the following properties :

(*i*) *Wavelength* (λ) (*ii*) *Frequency* (υ) (*iii*) *Speed or velocity* (c) (*iv*) *Wave number* (υ) These properties are called *wave parameters.*

Now let us discuss these wave parameters, one by one, as follows :

(*i*) Wave length (λ). *The wave length of a wave is defined as the distance between two successive crests or two successive troughs of a wave* (Fig. 1.18). It is represented by *lambda* (λ) and is measured in terms of *centimetre* (*cm*) or *Angstrom* (A^0) *units* (*in C.G.S. units*) or *meters* (*m*) or *Angstrom units* (*in S.I. units*). Wavelengths are also expressed in *micrometers* (μm) *and nanometers* (*nm*). Various units are related to meter as follows :

$1\ A^0 = 10^{-10}$ m $= 10^{-8}$ cm

$1\ \mu m = 10^{-6}$ m

$1\ nm = 10^{-9}$ m

All the above mentioned units are related to each other as follows :

$1\ cm = 10^{-2}\ m = 10^8 A^0 = 10^4\ \mu m = 10^7\ nm$

(*ii*) Frequency (υ) and velocity (c). *Frequency is defined as the number of waves or cycles which pass a given point on the wave in one second.* It is represented by *nu* (υ) and is measured in terms of *cycles* (*or waves*) *per second* (*cps*) or *Hertz* (Hz) *units.* A frequency of 100 hertz means 100 cycles (or waves) per second. *Kilocycles per second* (ke/s), *megacycles per second* (Mc/s) and *kilomegacycles per second* (kMc/s) are the terms used to express the frequencies of higher order.

By the term cycle here, we mean a complete cycle of change. This involves the departure of a wave crest, the passing of the trough, and the arrival of the next crest. (*See* Fig. 1.18). Frequency is also expressed in the units of *reciprocal second,* 1/s or s^{-1}.

It has been found that *a wave of higher frequency has shorter wavelength and vice-versa.* Thus *frequency* (υ) *of a wave is inversely proportional to its wavelength* (λ), *i.e.*

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

$$\text{or} \qquad \upsilon = \frac{c}{\lambda}, \qquad \ldots(1)$$

where c is a constant which is called the *velocity of the wave. Velocity of a wave is defined as the distance travelled by the wave in one second.* It is, therefore, expressed in $cm.s^{-1}$ (in C.G.S. units) or in $m.s^{-1}$ (in S.I. units). Its value has been found to be constant for all types of electromagnetic radiations. Its experimental value has been found to be equal to 3×10^{10} $cm.s^{-1}$ or 3×10^8 $m.s^{-1}$. As a matter of fact this value is the velocity of light in air. Thus c is equal to the velocity of light ($=3\times10^{-10}$ $cm.s^{-1}$ or 3×10^8 $m.s^{-1}$) for all types of electromagnetic radiations.

Equation (1) clearly shows that :

$$\textit{Velocity } (c) = \textit{Wavelength } (\lambda) \times \textit{Frequency } (\nu)$$

$$\textit{or} \qquad c = \lambda \nu \qquad \ldots(2)$$

The validity of equation (2) has been shown in Fig. 1.19, from which it is evident that the product of wavelength (λ) and frequency (υ) for all the waves shown is constant (= 120), *i.e.* all types of radiations travel with the same speed or velocity.

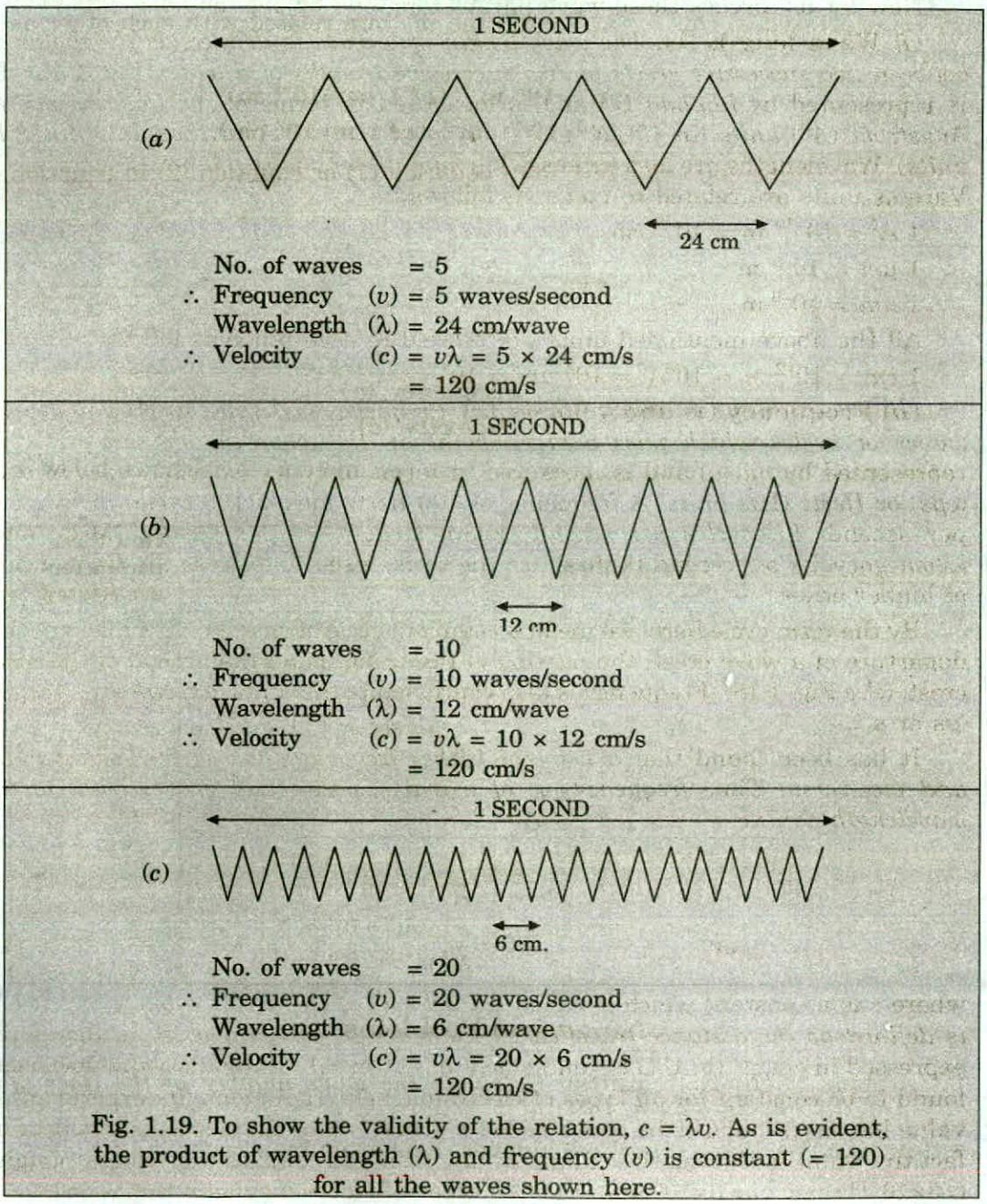


Fig. 1.19. To show the validity of the relation, $c = \lambda\upsilon$. As is evident, the product of wavelength (λ) and frequency (υ) is constant (= 120) for all the waves shown here.

***(iii)* Wave number** $(\bar{\upsilon})$, In spectroscopy, frequency of light is generally expressed in terms of wave number $(\bar{\upsilon})$ which is defined as the number of wavelengths per meter and is equal to the reciprocal of wavelength (λ). It is denoted by *nu bar* $(\bar{\upsilon})$. Thus :

$$\textbf{Waver number } (\bar{\upsilon}) = \frac{1}{\lambda} \qquad ...(3)$$

Since $\bar{\upsilon}$ is the reciprocal of wavelength and wavelength is expressed in cm or m, $\bar{\upsilon}$ is expressed in cm^{-1} or m^{-1}. cm^{-1} and m^{-1} are related with each other as follows :

$$1 cm^{-1} = 10^2 m^{-1} \ (cf\ 1\ cm = 10^{-2}\ m)$$
$$\textbf{and} \qquad 1 m^{-1} = 10^{-2} cm^{-1} \ (cf\ 1\ m = 10^2\ cm)$$

On substituting the value of λ from equation (1) or equation (2) in equation (3), we get :

$$\bar{\upsilon} = \frac{1}{c/\upsilon}$$

or

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

$$\textbf{or} \qquad \textbf{\textit{Wave number}}\ (\bar{\upsilon}) = \frac{\textbf{\textit{Frequency}}\ (\upsilon)}{\textbf{\textit{Velocity}}\ (c)} \qquad ...(4)$$

The abbreviations, relations between these parameters etc. is shown below in a tabular form :

Wave parameter	Abbreviation	Unit	How these parameters are related.
(*i*) Wavelength	λ (Lambda)	cm or m or A° or *nm* [1 cm = 10^{-2} m = 10^8 A° = 10^7 *nm*]	$\bar{\upsilon} = \frac{1}{\lambda} = \frac{\upsilon}{c}$
(*ii*) Frequency	υ (Nu)	cycles/sec or Hz or s^{-1}.	
(*iii*) Velocity	c (Velocity of light) $c = 3 \times 10^{10}$ cm/sec $= 3 \times 10^8$ m/sec	cm/sec or m/sec	
(*iv*) Wave number	$\bar{\upsilon}$ (Nu bar)	cm^{-1} or m^{-1} [1 cm^{-1} = 10^2 m^{-1}; 1 m^{-1} = 10^{-2} cm^{-1}]	

Numerical Problems

Problem 1. (In S. I. units). *Calculate the wave number of the lines of frequencies 4×10^{14} Hz and 5×10^{16} Hz.*

Solution. We know that wave number, $\bar{\upsilon}$ is given by :

$$\bar{v} = \frac{1}{\lambda} = \frac{v}{c}$$

(*a*) Here $v = 4 \times 10^{14}$ Hz and $c = 3 \times 10^{8}$ ms^{-1}

$$\therefore \quad \bar{v} = \frac{4\times10^{14}\ \text{Hz}}{3\times10^{8}\ m.s^{-1}} = \frac{4\times10^{14}\ s^{-1}}{3\times10^{8}\ m.s^{-1}} \qquad (\because \text{Hz} = s^{-1})$$

$$= 1.33\times10^{6}\ \text{m}^{-1}$$

(*b*) Here $v = 5\times10^{16}$ Hz and $c = 3\times10^{8}\ m.s^{-1}$

$$\therefore \quad \bar{v} = \frac{5\times10^{16}\ \text{Hz}}{3\times10^{8}\ m.s^{-1}} = \frac{5\times10^{16}\ s^{-1}}{3\times10^{8}\ m.s^{-1}} \qquad (\therefore \text{Hz} = s^{-1})$$

$$= 1.66\times10^{8}\ m^{-1}.$$

Problem 2 (In S.I. units). *Calculate the wavelength of a wave of frequency 10^{11} Hz travelling with the speed of light = 3×10^{8} $m.s^{-1}$.*

Solution. Here $\lambda = 10^{11}$ Hz and $c = 3\times10^{8}\ ms^{-1}$

$$\therefore \quad \lambda = \frac{c}{v} = \frac{3\times10^{8}\ ms^{-1}}{10^{11}\ \text{Hz}} = \frac{3\times10^{-3}\ ms^{-1}}{s^{-1}}$$

$$= 3\times10^{-3}\ \text{m}$$

Problem 3 (In S.I. units). *Calculate the frequency and wave number of yellow light having wavelength of 580 nm.*

Solution. Here $\lambda = 580\ nm = 580 \times 10^{-9}\ m$

and $c = 3 \times 10^{8}\ ms^{-1}$

$$\therefore \quad \lambda = \frac{c}{\lambda} = \frac{3\times10^{8}\ ms^{-1}}{580\times10^{-9}\ m} = \frac{3\times10^{17}}{580}\ s^{-1}$$

$$= \frac{3\times10^{17}}{580}\ \text{Hz} = 0.005172\times10^{17}\ \text{Hz}$$

$$= 5.172\times10^{14}\ \text{Hz}$$

$$v = \frac{1}{\lambda} = \frac{1}{580\times10^{-9}\ m} = \frac{1}{580}\times10^{9}\ m^{-1}$$

$$= 0.001724\times10^{9}\ m^{-1}$$

$$= 1.724\times10^{6}\ m^{-1}$$

Problem 4 (In S.I. units). *What is the frequency and wave number associated with light of wavelength equal to 6000 A° ?*

Solution. Here $\lambda = 6000$ A° $= 6000 \times 10^{-10}\ m$

and $c = 3 \times 10^{8}\ m.s^{-1}$

$\therefore$ Wave number, $\bar{v} = \frac{1}{\lambda}$

$$= \frac{1}{6000\times10^{-10}\,\text{m}}$$

$$= \frac{1}{6\times10^{3}\times10^{-10}}\ \text{m}^{-1}$$

$$= \frac{10^7}{6} \text{ m}^{-1} = 0.1666 \times 10^7 \text{ m}^{-1}$$

$$= 1.666 \times 10^6 \text{ m}^{-1}$$

Frequency, $$\upsilon = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ m.s}^{-1}}{6000 \times 10^{10} \text{ m}}$$

$$= \frac{10^8}{2 \times 10^{-7}} s^{-1} = 0.5 \times 10^{15} \text{ s}^{-1}$$

$$= 5.0 \times 10^{14} \text{ s}^{-1}$$

Problem 5 (In S.I. units). *The wavelength of a certain wave is 6m and 30 waves pass a fixed point per minute. What is the speed of the waves ?*

Solution. Here $\lambda = 6$ m

and $\upsilon = 30$ cycles/minute

$$= \frac{30}{60} \text{ cycles .s}^{-1}$$

$$= \tfrac{1}{2} \text{ cycles .s}^{-1}$$

$\therefore$ Speed (c) of the wave

$$= \upsilon.\lambda$$

$$= \tfrac{1}{2} \times 6 \text{ m.s}^{-1}$$

$$= 3 \text{ m.s}^{-1}$$

Spectrum

What is Spectrum ?

A spectrum is an array of waves or particles which is spread out according to the increasing or decreasing of some property such as wavelength or frequency.

Types of Spectra

Depending on the nature of the source emitting the radiation, there are two types of spectra.

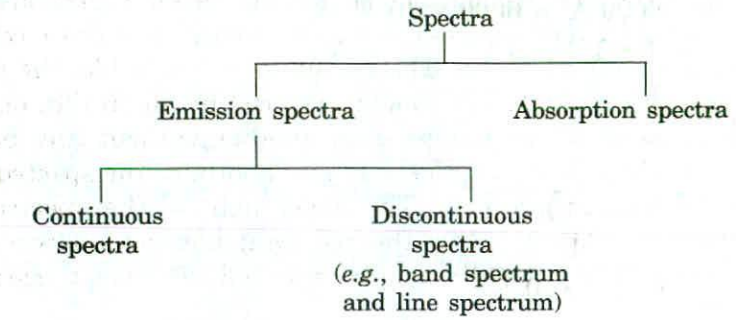
I. *Emission spectra*

II. *Absorption spectra.*

Emission spectra are further of two types :

(*a*) *Continuous spectrum*

(*b*) *Discontinuous spectrum* which may be a *band spectrum or line spectrum.* Line spectrum is also called *atomic spectrum.* Thus :



I. Emission Spectra

Emission spectra can be obtained from the substances which emit light on excitation. Their excitation can be done-as follows :

(*i*) By heating the liquid or solid substances in a flame at high temperature. These substances become incandescent at high temperature, *i.e.,* when these substances are heated at high temperature, they emit light. Electric light, lime light, arc light are the examples of such solid substances.

(*ii*) By passing an electric discharge through a gas at low pressure.

(*iii*) By passing electric current through thin filament of a high melting point metal like tungsten, when the filament becomes incandescent.

Types of Emission Spectra

Emission spectra are of the following two types :

1. **Continuous spectrum.** When a narrow beam of sun light or any white light (*e.g.* an arc lamp) is allowed to pass through a prism and then allowed to fall on a screen, it gets resolved into seven colours *viz, violet, indigo, blue, green, yellow, orange* and *red* (VIBGYOR) (Fig. 1.20). This phenomenon is called **dispersion** and the band of seven colours observed on the screen is called **visible spectrum.** Each of the seven colours of the spectrum has got a characteristic wavelength as shown in the figure. It may be seen that the wavelengths of different radiations of the visible spectrum lie in the range : 4000—7500Å.

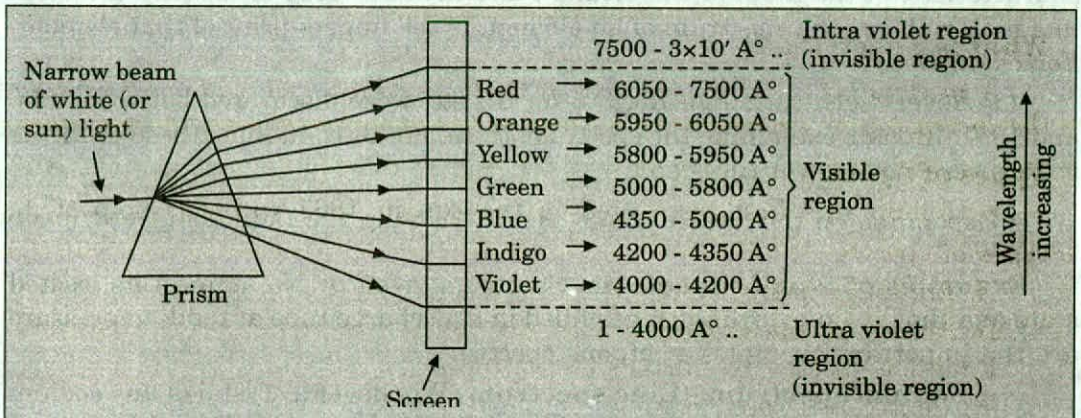


Fig. 1.20. The continuous spectrum of sun light (solar spectrum).

Since the wavelengths and frequencies of all the seven radiations of the spectrum can be detected by human eye, the region consisting of these colours is called *visible region or visible spectrum.* The visible spectrum is like the rainbow often seen in the sky after a rainfall or colour produced by an oil film on water. In the spectrum, since one colour merges into another without any break or discontinuity (*i.e.*, one colour changes gradually into another), the spectrum thus obtained is called *continuous spectrum.* The violet light of the spectrum has shortest wavelength (λ = 4000 Å) while the red light has longest wavelength (λ = 7500 Å). The region below the violet light is called *ultraviolet region.* The

radiations of this region, have *lower wavelengths* (*i.e.* higher frequencies) than that of the violet rediaton (λ = 1—4000 Å). Similarly the region below the red radiation is called *infra-red region.* The radiations of this region have *higher wavelengths* (*i.e.* lower frequencies) than that of red radiation (λ = 7500—3 × 10^7 Å). Ultraviolet and infra-red regions are not visible to the human eye and hence are collectively called *invisible region or invisible spectra.* Our eyes are not sensitive to the radiations of invisible spectra.

2. **Discontinuous spectrum.** It may be band spectrum or line spectrum.

(*i*) **Band spectrum. (Molecular spectrum)** Band spectrum is the property of molecules and generally given by the compounds or gases like N_2 and O_2 molecules at low temperature and pressure. The band spectrum consists of a number of bright bands, separated by dark spaces. Each band is sharp at one end and fades gradually as we approach the other end. Due to its *fluted appearance,* band spectrum is sometimes referred to as *fluten spectrum.* Since this spectrum is characteristic of molecules, it is also called *molecular spectrum.*

(*ii*) **Atomic spectrum.** When an atom of an element, whether free or in combination, absorbs energy, it gets *excited.* The excited atom emits light radiations of a characteristic colour. When this emitted radiation is allowed to pass through a prism, it is resolved into individual components. The pattern of different components of the radiation is called *atomic spectrum.* It is so called because this spectrum is given by the atoms of the element This kind of spectrum is characteristic of the atom of the element and hence is used to identify the atom in a material. *i.e.,* the spectrum of an element is the fingers-print of that element. For example :

(*a*) Several elements like Rb, Cs, In, Ga etc. were discovered between 1860 and 1897 through, examining the spectra of the minerals containing these elements which were not known till then.

(*b*) Helium was first discovered in the sun in 1868 with the help of its spectrum.

Examples of atomic spectrum. Spectrum given by Na atom in its excited state and that given by hydrogen gas filled in a discharge tube at reduced pressure are the important examples of atomic spectra.

(*i*) **Sodium spectrum. (Line spectrum)** Whenever a crystal of any sodium salt is vaporised in a bunsen flame, a bright light is emitted. When this emitted light is passed through a prism and then allowed to fall on a photographic plate as shown in Fig. 1.21 (or when examined through a spectroscope), two bright isolated yellow lines, D_1 and D_2, separated by a dark space are found in the spectrum. The wavelength of these lines are found to be 5893 Å and 5896 Å. D_1 and D_2 lines appearing in the atomic spectrum constitute the *emission spectrum* of sodium. Line spectrum (or emission spectrum) given by sodium differs from that given be other elements.

Since the atomic spectrum consists of two isolated lines separated by a dark space, the atomic spectrum is also called *line spectrum.* Atomic spectrum is also known by other names like *line emission spectrum* or *atomic emission spectrum.*

(*ii*) **Hydrogen spectrum.** As mentioned above hydrogen spectrum is also an important example of atomic spectrum. This spectrum, like the atomic spectrum given by other elements, is also known by other names like *line emission spectrum* or *atomic emission spectrum of hydrogen.*

How is hydrogen spectrum obtained ?

When an electric discharge is passed through hydrogen gas filled in a discharge tube at a very low pressure, a bluish light is emitted from the discharge tube. When the ray of this bluish emitted light is passed through a prism (Fig. 1.21), a *discontinous line spectrum consisting* of several isolated sharp lines with dark area in between is obtained. Such a spectrum is called *line spectrum* of hydrogen. This spectrum gives a useful idea about the atomic structure.

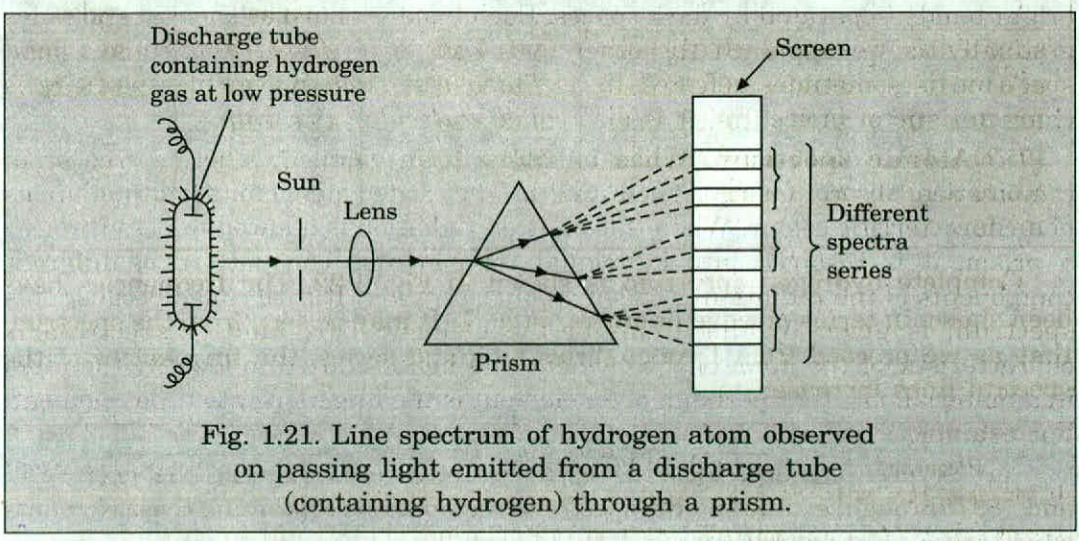


Fig. 1.21. Line spectrum of hydrogen atom observed on passing light emitted from a discharge tube (containing hydrogen) through a prism.

When an electric discharge is passed through hydrogen, the molecules of hydrogen break into atom. These absorb energy from the electric spark and get *excited.* The excited atoms give the extra energy in the form of emitted light (bluish light). When this emitted light is allowed to pass through a prism line spectrum of hydrogen is obtained. This spectrum is also called *line emission spectrum.* Here since it is the atom (of hydrogen) which is the source of the spectrum, hydrogen spectrum is also called *atomic spectrum of hydrogen.*

Classification of Spectral Lines in Hydrogen Spectrum.

As already said, hydrogen spectrum consists of several isolated sharp lines with dark area in between. The wavelengths of various spectral lines seen in hydrogen spectrum show that these lines lie in *visible, ultraviolet* and *infra-red regions* of the spectrum. All these spectral lines can be classified into five groups or series called **spectral series** which are named after the names of their discoverers as shown below :

Spectral series	***Discovered by***	***Appearing in***
(*i*) *Lyman series*	*Lyman*	*Ultraviolet region*
(*ii*) *Balmer series*	*Balmer*	*Visible region*

(*iii*) *Paschen series*	*Paschen*	*Infra-red region*
(*iv*) *Brackett series*	*Brackett*	*Infra-red region*
(*v*) *Pfund series*	*Pfund*	*Infra-red region*

The values of frequencies in terms of wave number, υ (in m^{-1}) of various spectral lines, as determined experimentally by Ritz, are given in Table 1.3.

Table 1.3 Experimental values of frequencies in terms of wave numbers, $\bar{\upsilon}$ (in m^{-1}) of various spectral lines seen in hydrogen spectrum

Lyman series (Ultraviolet region)	Balmer series (Visible region)	Paschen series (Infra-red series)	Brackett series (Infra-red region)	Pfund series (Infra-red region)
82.20×10^5	15.21×10^5 (H_α line)	5.30×10^5	2.46×10^5	1.34×10^5
97.60×10^5	20.60×10^5 (H_β line)	7.80×10^5	3.80×10^5	2.14×10^5
102.70×10^5	23.05×10^5 (H_γ line)	9.12×10^5	4.61×10^5	
105.20×10^5	24.35×10^5 (H_δ line)	9.95×10^5		
106.20×10^5	25.18×10^5			
107.10×10^5				

Complete hydrogen spectrum is shown in Fig. 1.22. The frequencies have been shown in terms of wave numbers, $\bar{\upsilon}(m^{-1})$. It may be seen from the spectrum that as we proceed from Lyman series to Pfund series, the frequencies of the spectral lines increase.

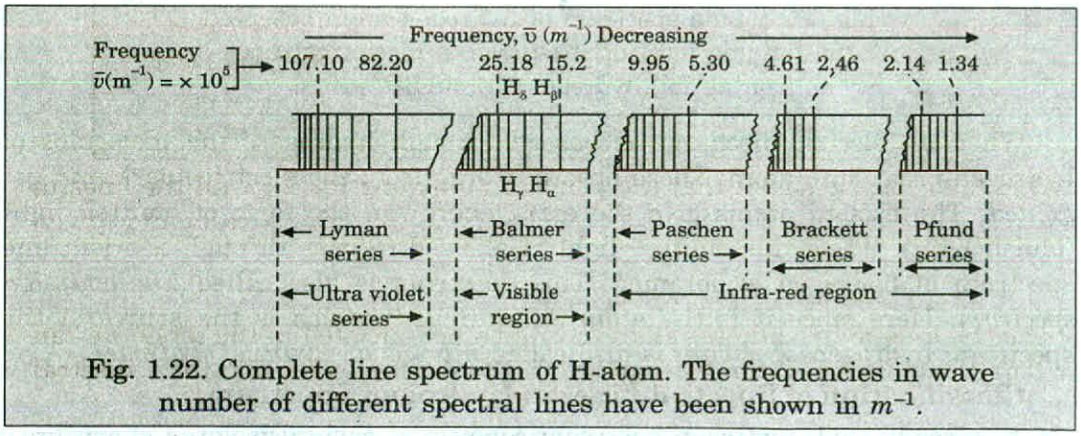


Fig. 1.22. Complete line spectrum of H-atom. The frequencies in wave number of different spectral lines have been shown in m^{-1}.

How to Calculate the Frequencies of Spectral Lines by Rydberg's Equation.

By measuring the wavelength of a large number of lines observed in different spectral series of hydrogen spectrum, Rydberg gave an empirical equation with the help of which the frequency in terms of wave number, $\bar{\upsilon}$ (reciprocal of wavelength, λ), of any line of a given series of hydrogen spectrum can be calculated. According to this equation the wave number of any line of a particular series appearing in the H-spectrum is represented as a difference of two terms. For a

given series one of the two terms remains constant while the other varies from line to line in the same series. This equation can be written as :

$$\bar{v} = \frac{1}{\lambda} = \text{constant}\left(\frac{1}{x^2} - \frac{1}{y^2}\right)m^{-1}$$

$$= R\left(\frac{1}{x^2} - \frac{1}{y^2}\right)m^{-1},$$

where $\bar{v}$ = frequency in wave number (in m^{-1}) ; λ = wavelength ; R = a universal constant which is called **Rydberg's constant.** Its experimental value, as determined by Ritz, is $109.678 \times 10^5\ m^{-1}$, and x and y are simple whole numbers which are called Rydberg's integers. Equation given above is called **Rydberg's equation.**

For a given spectral series x remains constant while y varies from line to line in the same series. For example the frequency of H_α ($= 15.21 \times 10^5\ m^{-1}$), H_β ($= 20.60 \times 10^5\ m^{-1}$), H_γ ($= 23.05 \times 10^5\ m^{-1}$) and H_δ ($= 24.35 \times 10^5\ m^{-1}$) spectral lines appearing in the Balmer series can be obtained by putting $x = 2$ and $y = 3, 4, 5$ and 6 respectively in Rydberg's equation in which $R = 109.687 \times 10^5\ m^{-1}$. The values of x for various series and those of y for successive lines in the same series are given below in Table 1.4.

Table 1.4. Values of *x* and *y* for various spectral observed in hydrogen spectrum.

Spectral series	*x*	*y* = (*x* + 1), (*x* + 2)... ∞	Spectral region
Lyman	*1*	*2, 3, 4, 5, 6.....∞*	*Ultraviolet region*
Balmer	*2*	*3, 4, 5, 6, ...∞*	*Visible region*
Paschen	*3*	*4, 5, 6 .....∞*	*Infra-red region*
Brackett	*4*	*5, 6, ...∞*	*Infra-red region*
Pfund	*5*	*6, ...∞*	*Infra-red region*

This table clearly shows that the value of x remains fixed for all the lines in a particular series while y varies from line to line in the same series and is given by :

$$y = (x + 1), (x + 2).....\text{etc.}$$

Thus by assigning suitable values to x and y as indicated in the table, we can calculate the values of the wave number ($\bar{v}$) and wavelength (λ) of the spectral lines.

The table also makes it evident that Rydberg's equation for the five sectral series can be written as :

For Lyman series : $x = 1$ and $y = 2, 3, 4, 5, 6, \ldots \infty$

$$\bar{v} = \frac{1}{\lambda} = R\left(\frac{1}{1^2} - \frac{1}{y^2}\right)m^{-1} = R\left(1 - \frac{1}{y^2}\right)m^{-1}$$

For Balmer series : $x = 2$ and $y = 3, 4, 5, 6 \ldots \infty$

$$\bar{v} = \frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{y^2}\right)m^{-1} = R\left(\frac{1}{4} - \frac{1}{y^2}\right)m^{-1}$$

For Paschen series : $x = 3$ and $y = 4, 5, 6 \ldots \infty$

$$\bar{v} = \frac{1}{\lambda} = R\left(\frac{1}{3^2} - \frac{1}{y^2}\right)m^{-1} = R\left(\frac{1}{9} - \frac{1}{y^2}\right)m^{-1}$$

For Brackett series : $x = 4$ and $y = 5, 6 \ldots \infty$

$$\bar{v} = \frac{1}{\lambda} = R\left(\frac{1}{4^2} - \frac{1}{y^2}\right)m^{-1} = R\left(\frac{1}{16} - \frac{1}{y^2}\right)m^{-1}$$

For Pfund series : $x = 5$ and $y = 6, 7, \ldots \infty$

$$\bar{v} = \frac{1}{\lambda} = R\left(\frac{1}{5^2} - \frac{1}{y^2}\right)m^{-1} = R\left(\frac{1}{25} - \frac{1}{y^2}\right)m^{-1}$$

II. Absorption Spectra

If, in the arrangement to get a continuous spectrum of white light, a substance is placed between the white light source (*e. g.* sun) and the prism (or spectroscope), we get an **absorption spectrum.** This spectrum appears in the form of dark lines in a particular region of the continuous spectrum of white light. For example, if a solution of NaCl is placed between the sun (white light source) and prism, the continuous spectrum of white light is found to be crossed by two *dark lines* in the yellow region of the spectrum (Fig. 1.23). If the white light source is removed, the whole of the continuous spectrum disappears leaving behind only two, bright yellow lines. These lines are located at exactly the same place where two D_1 and D_2 lines of line spectrum of sodium were located. These dark lines are known as **absorption line spectrum.**

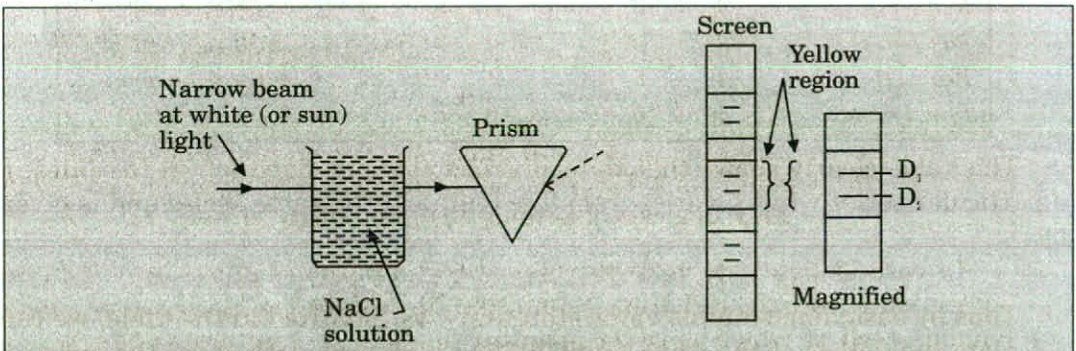


Fig. 1.23. Absorption spectrum.

Planck's Quantum Theory of Radiation : Quantisation of Energy.

In 1900 Max Planck studied the spectral lines obtained from thermal radiations emitted by a hot (black) body at different temperatures and put forward a theory which, after his name, is known as *Planck's quantum theory of radiation* (*quantum* is a Latin word which means *how much*).

Postulates of Plank's Quantum Theory of Radiation

Theory of Radiation. Various postulates of this theory are :

1. *A hot body emits radiant energy not continuously* (*i.e.* not as continous waves as suggested by the classical Max well's wave theory) *but discontinuously* (*discretely*). In other words this means that a *hot body emits radiant energy not as continuous waves but as small packets or bundles or discrete* (*separate*) *units of the waves.* Each of these units is called a **quantum** (plural is **quanta**) which can exist independently. Thus a quantum can be defined as follows :

A quantum is the smallest unit of waves in the form of which a hot body emits radiant energy and which can exist independently.

The emission of radiant energy in continuous waves and in discontinuous waves as individual quantum from a heated iron ball is shown in Fig. 1.24.

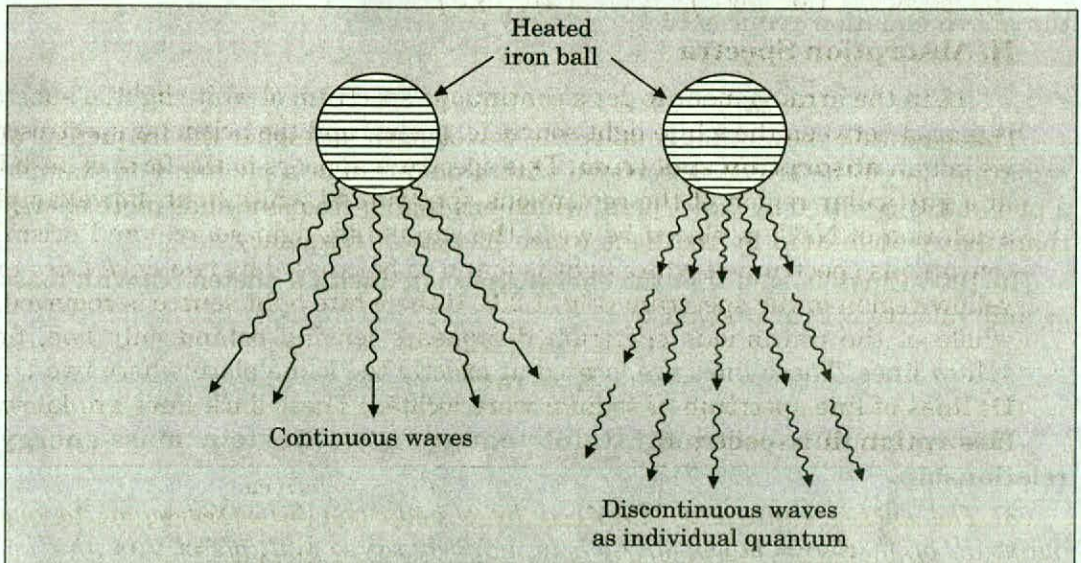


Fig. 1.24. Emission of radiant energy from a heated iron ball in (*a*) continuous waves (according to classical Maxwell's theory—old theory) and (*b*) discontinuous waves as individual quantum (according to Max Planck's quantum theory—modern theory).

In case of light which is also a form of radiation, light energy (*i.e.*, energy associated with light radiation) is emitted or absorbed in the form of packets or bundles each of which is called **photon** (instead of quantum). *Photon is not a material body.* It is considered to be a *massless bundle of energy.*

Thus we see that, according to this theory, *light is composed of massless particles which are called photons.* The presence of photons in light cannot be detected readily under normal conditions, since even light of low intensity consists of billions of photons. It was in 1905 when Einstein, while explaining the photoelectric effect, could prove the existence of photons.

2. *The energy* (E) *associated with each quantum or photon* (*in case of light*) *of a given radiation or light is proportional to the frequency* (υ) *of the emitted radiation or light, i.e.*

$$E \propto \upsilon$$

or

$$E = h\upsilon,$$

where h = a constant known as **Planck's constant** whose numerical value is 6.624×10^{-27} erg. s (in C.G.S. units) or 6.624×10^{-34} j-s (in S.I units).

E = energy associated with each quantum or photon of a given radiation. E is in ergs (in C.G.S. units) or in kJ (in S.I. units).

υ = frequency of the emitted radiation or light.

This equation is applicable to all types of radiation and is called **planck's equation**. This equation shows that the energy associated with a quantum or a photon, E is equal to $h\upsilon$.

Now since $\upsilon = \frac{c}{\lambda}$, ($c$ = velocity of radiation and λ = wave length of radiation), the above equation reduces to :

$$E = h.\frac{c}{\lambda}$$

This equation shows that smaller the wavelength (or higher the frequency) of radiation, large the energy associated with a quantum or a photon. For example a photon transmitted by violet light, which has higher frequency has more energy than that transmitted by red light which has lower frequency.

In 1905 Einstein said that the energy associated with a photon (E) with mass m and velocity c is also given by :

$$\boxed{E = mc^2}$$

This equation is called **Einstein's equation** or **Einstein mass-energy relationship.**

3. *The energy emitted or absorbed by a body can be either equal to one quantum of energy (= $h\upsilon$) or any whole number, say n multiple of this unit i.e.*

Energy emitted or absorbed = $n \times h\upsilon$.

Thus the energy emitted or absorbed by a body can be equal to 1 $h\upsilon$, 2 $h\upsilon$, 3 $h\upsilon$, etc. but never equal to any fractional value of $h\upsilon$ like 1.5 $h\upsilon$, 2.5 $h\upsilon$, 4.9 $h\upsilon$. Thus we find that the energy emitted or absorbed by a body is quantised and this is called the **concept of quantisation of energy.**

It is clear from the study of quantum theory of radiation as given above that the atoms would transfer energy in photon units. The absorption of a photon by an atom increases its energy by a definite quantity which is equal to $h\upsilon$. An atom which has absorbed energy in this way is said to be an *excited atom* or in the *excited state.* When an excited atom radiates energy, energy is given out in photon units.

The description given above makes it evident that this theory is also known as **photon theory**, *since according to the theory, light radiations are supposed to be composed of photons each of which is associated with energy equal to $h\upsilon$.*

Applications of Planck's Quantum Theory of Radiation

This theory has been used to explain many phenomena. For example :

(*i*) In 1905 Einsten applied this theory to explain the photoelectric effect.

(*ii*) In 1913 Bohr used this theory to explain the structure of the atom (See *Bohr's Model of Atomic Structure*) and the origin of spectral lines seen in hydrogen spectrum.

(*iii*) In 1922 Compton applied this theory to explain the phenomena of scattering of X-rays (*Compton Effect*).

Numerical Problems

Problem 1 (In S.I. units). *Two lines one voilet and the other red, in a spectrum, have wavelengths equal to 4000 and 6000 Å respectively. Calculate the energies of photons transmitted by them* ($h = 6.626 \times 10^{-39}$ *J-s*; $c = 3 \times 10^8$ $m.s^{-1}$.)

Solution (*a*) *Energy of photon transmitted by violet light.*

Here $\lambda = 4000 \text{ Å} = 4000 \times 10^{-10} \text{ m}$

$$\therefore \quad E = h\nu = \frac{h.c}{\lambda}$$

$$= \frac{(6.626\times10^{-34} \text{ J.s})\times(3\times10^8 \text{ ms}^{-1})}{4000\times10^{-10} \text{ m}}$$

$$= \frac{6.626\times3\times10^{-16}}{4000} \text{ J}$$

$$= \frac{6.626\times3\times10^{-19}}{4} \text{ J}$$

$$= 4.9695\times10^{-19} \text{ J.}$$

(*b*) *Energy of photon transmitted by red light.*

Here $\lambda = 6000 \text{ Å} = 6000 \times 10^{-10} \text{ m}$

$$\therefore \quad E = h\nu = \frac{h.c}{\lambda}$$

$$= \frac{(6.626\times10^{-34} \text{ J.s})\times(3\times10^8 \text{ ms}^{-1})}{6000\times10^{-10} \text{ m}}$$

$$= \frac{6.626\times3\times10^{-19}}{6} \text{ J}$$

$$= 3.313\times10^{-19} \text{ J.}$$

Problem 2. (In S.I. units) *Calculate the magnitude of the energy of the photon (or quantum) associated with light of wavelength* 6057.8 Å ($h = 6.6256 \times 10^{-44}$ *J-s*, $c = 3 \times 10^8$ ms^{-1})

Solution. Here $\lambda = 6057.8 \text{ A} = 6057.8 \times 10^{-10}$ m. Now according to Planck's equation :

$$E = h\nu = \frac{h.c}{\lambda}$$

$$= \frac{(6.6256\times10^{-34} \text{ J.s})\times(3\times10^8 \text{ ms}^{-1})}{6057.8\times10^{-16} \text{ m}}$$

$$= 0.0032811\times10^{-16} \text{ J}$$

$$= 3.2811\times10^{-19} \text{ J}$$

Problem 3 (In S.I. units). *Electromagnetic radiation of wave length 242 nm is just sufficient to ionise the outermost electron of the sodium atom. Calculate the ionisation energy of sodium atom.* ($c = 3 \times 10^8\ m.s^{-1}$, $h = 6.625 \times 10^{-34}\ J.s$) *(Delhi B.Sc. Hons. 1975)*

Solution. Here $c = 3 \times 10^8\ m.s^{-1}$ and $\lambda = 242\ nm = 242 \times 10^{-9}\ m$

$$v = \frac{c}{\lambda} = \frac{3\times10^8}{242\times10^{-9}}\ Hz$$

$\therefore$ Energy (E) of this radiation $= hv$

$$= (6.625\times10^{-34})\times\frac{3\times10^8}{242\times10^{-9}}\ J/atom$$

$$= 8.21 \times 10^{-19}\ J$$

$$= 8.21 \times 10^{-22}\ KJ$$

$$= 8.21 \times 10^{-22} \times (\text{Avogadro's number})\ KJ/mole$$

$$= 8.21 \times 10^{-2} \times (6.023 \times 10^{23})\ KJ/mole$$

$$= 494.48\ KJ/mole.$$

The radiation of energy equal to 494.48 KJ/mole is sufficient to ionise the outermost electron of Na atom. Thus ionisation energy of Na atom = 494.48 KJ/mole.

Problem 4 (In S.I. units). *Calculate the energy of a photon of light of frequency of* $3 \times 10^{15}\ s^{-1}$

Solution. Here $v = 3 \times 10^{-15} s^{-1}$

and $h = 6.624 \times 10\ J.s$

$\therefore$ $E = hv = (6.624 \times 10^{-34} Js) \times (3 \times 10^{15} s^{-1})$

$= 6.624 \times 3 \times 10^{-19}\ J$

$= 19.872 \times 10^{-19}\ J.$

Problem 5 (In S.I. units). *Calculate the energy in KJ/mole associated with a radio wave of wavelength equal to* 3×10^{13} Å.

Solution. We know that :

$$E = hv = h.\frac{c}{\lambda}$$

Now since h is in Js, c is in ms^{-1} and λ is in Å, E cannot be obtained in joules. Thus in order to get E in joules, λ should be converted into m. Thus :

$\lambda = 3 \times 10^{13}$ Å $= 3 \times 10^{13} \times 10^{-10}\ m = 3 \times 10^3\ m$

$c = 3 \times 10^8\ ms^{-1}$

$h = 6.626 \times 10^{-34}\ Js$

$\therefore$ $$E = \frac{(6.626\times10^{-34}\ Js)\times(3\times10^8\ ms^{-1})}{3\times10^3\ m}$$

$= 6.626 \times 10^{-29}\ J/atom$

Now since Avogadro's number $= 6.023 \times 10^{23}$

$\therefore$ $E = 6.626 \times 10^{-29} \times 6.023 \times 10^{23}\ J/mole$

$$= \frac{6.626 \times 10^{-29} \times 6.023 \times 10^{23}}{10^3} \text{ KJ/mole}$$

$$= 6.\ 626 \times 6.023 \times 10^{-9} \text{ KJ/mole}$$

$$= 0.6626 \times 6.023 \times 10^{-8} \text{ KJ/mole}$$

$$= 3.990 \times 10^{-8} \text{ KJ/mole}$$

Photoelectric Effect

What is Photoelectric Effect ?

In some of their experiments Sir J.J. Thomson and P. Lenard showed that *when a beam of light of suitable wavelength or frequency is allowed to fall on the surface of a metal, the electrons are emitted (or ejected) from the surface of the metal* (Fig. 1.25) This phenomenon of emission of electrons is known as **photoelectric effect** or **photoelectric emission** (*photo* means *light*). Although the electrons emitted from the surface are no different from all other electrons, it is customary to call there electrons as **photoelectrons.**

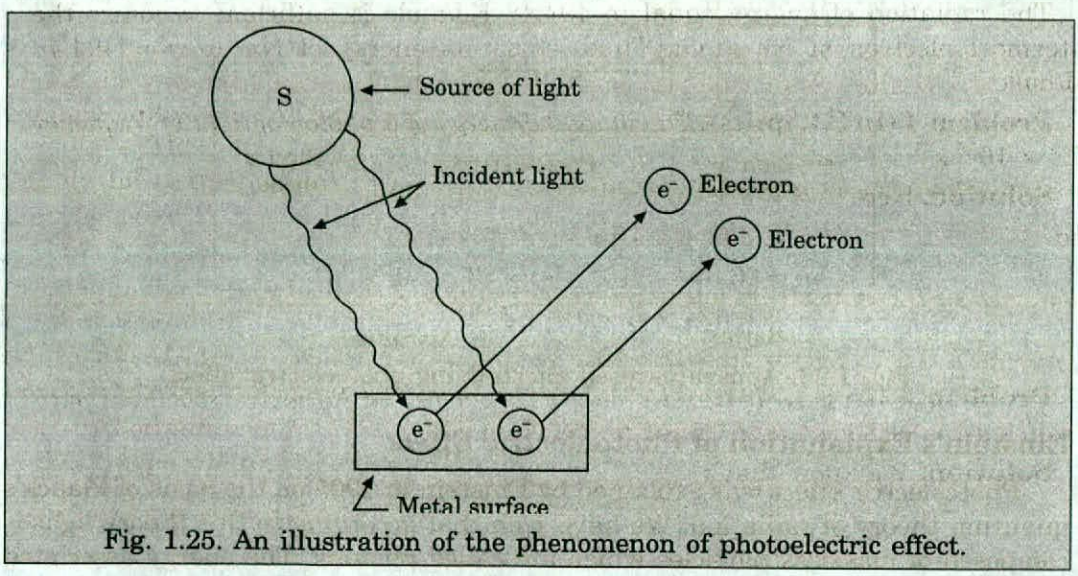


Fig. 1.25. An illustration of the phenomenon of photoelectric effect.

It may be noted that only a few metals can eject electrons when radiations from visible (which has less energy and hence is less energetic) fall on them, but many more metals are very much capable of ejecting electrons when radiations from ultraviolet light (which has more energy and hence is more energetic) fall on them.

Experimental Study of Photoelectric Effect

The phenomenon of photoelectric effect can be studied with the help of a simple apparatus shown in Fig. 1.26. The apparatus consists of two photosensitive plates, E (called *emitter*) and C (called *collector*) enclosed in an evacuated quartz tube which is called photoelectric cell. In the absence of light there is no flow the

current in the circuit and the ammeter, A reads zero. When monochromatic light from source S falls on plate E connected to the negative terminal of the battery, current starts to flow as indicated by the ammeter. The explanation of the flow of the current lies in the fact that when plate E is irradiated with light, the incident photons colloid with the atoms of the plate and eject the electrons (called photoelectrons) from it. These photoelectrons are immediately attracted by the collector plate C and consequently current starts flowing as indicated by the ammeter. Since the effect is produced under the influence of light, it is called photoelectric effect (*photo* means light).

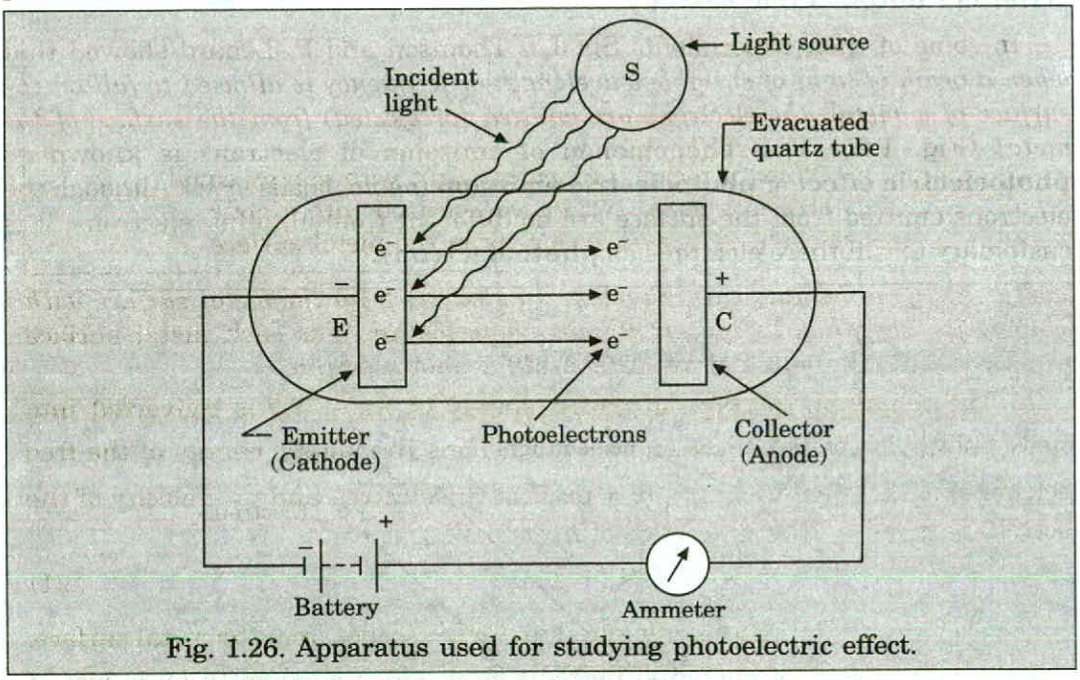


Fig. 1.26. Apparatus used for studying photoelectric effect.

Einstein's Explanation of Photoelectric Effect

Photoelectric effect was explained by Einstein in 1905 on the basis of Planck's quantum theory of radiation. We have seen that according to this theory light is composed of massless particles which are called photons. The energy associated with each photon, E_{photon} is given by Planck's equation :

$$E_{photon} = h\upsilon$$

When a photon of incident light which is associated with an energy equal to $h\upsilon$ strikes a metal surface (Fig. 1.27), the photon is completely absorbed by the surface and transfers its energy ($= h\upsilon$) to an electron on the surface. The energy imparted by the photon is utilised for two purposes :

(*a*) Some portion of the photon energy ($= h\upsilon$) is used up in removing the electrons from the metal surface by overcoming the attraction between the electrons and the nucleus without giving them any velocity. Let the energy used up in this process be represented by W_0 which is called **photoelectric work function** or **threshold energy** of the metal and is defined as *the work to be*

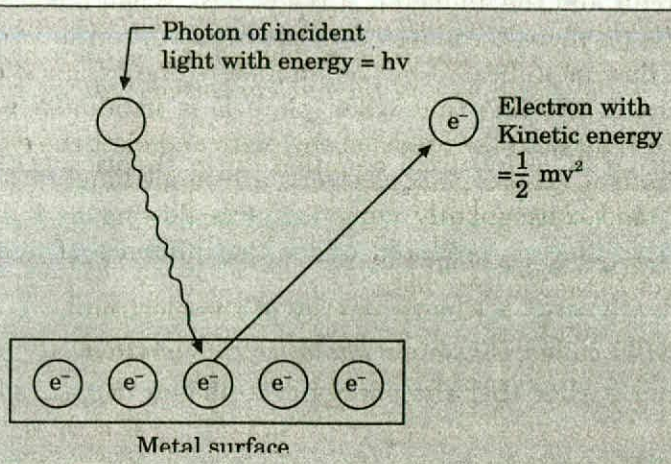


Fig. 1.27. When a photon of incident light with energy equal to $h\upsilon$ strikes a metal surface, an electron with kinetic energy equal to $\frac{1}{2}\ mv^2$ escapes from the metal surface.

done (or energy to be used up) to remove an electron from the metal surface with zero velocity and thus to convert it into photoelectron. For each metal surface there is a minimum value of W_0 to liberate a photoelectron.

(*b*) The remaining portion of photon energy ($= h\upsilon - W_0$) is converted into kinetic energy of the free electron ($= \frac{1}{2}mv^2$). Thus the kinetic energy of the free electron which is equal to $\frac{1}{2}mv^2$ (m = mass of the electron and v = velocity of the electron) is given by the difference of $h\upsilon$ and W_0, *i.e.*

$$h\upsilon - W_0 = \tfrac{1}{2}mv^2 \qquad ...(1)$$

The electron with kinetic energy equal to $\frac{1}{2}mv^2$ escapes from the metal surface.

Now if the energy of photon of incident light which is equal to $h\upsilon$ is just of such an amount that it can remove the electron only from the metal surface, then $h\upsilon$ will give no kinetic energy to the electron (*i.e.*, $\frac{1}{2}mv^2 = 0$) and will be equal to W_0, *i.e.*, in this case :

$$\tfrac{1}{2}mv^2 = 0$$

and hence from equation (1),

$$h\upsilon = W_0$$

Under this condition the incident light is of the minimum frequency which can emit the electrons from the metal surface. This minimum frequency is called **threshold frequency** or **cut-off-frequency** and is represented as υ_0. Hence :

$$h\upsilon_0 = W_0 \qquad ...(2)$$

Incident radiations having frequencies less than υ_0 will not eject the electrons from the metal surface while the incident radiations having frequencies greater than υ_0 can eject the electrons with a definite velocity and hence give kinetic energy to the free electron ($= \frac{1}{2}mv^2$). Quite obviously at the threshold frequency, υ_0 kinetic energy will be equal to zero. Thus υ_0 can be defined as follows :

Threshold frequency is defined as the minimum frequency of the incident radiation that can eject electrons from a given metal surface by overcoming the attraction between the electrons and the nucleus without giving them any velocity or kinetic energy.

On substituting $W_0 = h\upsilon_0$ from equation (2) in equation (1), we get :

$$h\upsilon - h\upsilon_0 = \tfrac{1}{2}mv^2$$

or $$h(\upsilon - \upsilon_0) = \tfrac{1}{2}mv^2$$

or $$h(\upsilon - \upsilon_0) = \text{Kinetic energy of the electron} \quad \text{...(3)}$$

Equation (3) is called *Einstein's photoelectric equation.*

We have said earlier that the energy of a photon (E_{photon}) of frequency υ is given by :

$$E_{photon} = h\upsilon$$

But the energy corresponding to the minimum frequency of photon (*i.e.* corresponding to thershold frequency, υ_0) is the minimum energy of the photon and is given by :

$$E_{photom}\ (\text{minimum energy}) = h\upsilon_0$$

Here υ_0 is the minimum frequency of the photon.

Laws of Photoelectric Emission

From the experimental data collected by Richardson and Compton in 1921, photoelectric emission was found to be governed by the following laws.

1. *Relation between the intensity of incident light and the number of photo electrons.* If the frequency of the incident radiation is kept constant, then the number of electrons emitted from the metal surface in one second is directly proportional to the intensity or brightness of the incident light falling on the metal surface. Thus an increase in the intensity of incident light of a given frequency increases the number of electrons emitted per second from the metal surface, but the volocity and hence the kinetic energy of the emitted electron remains the same.

2. *Relation between the magnitude of frequency of incident light and the emission of electrons.* The emission of electrons from a metal surface depends on the magnitude of frequency of the radiations falling on the metal surface. Radiations of all frequencies can not make the metal surface to eject the electrons. Only those radiations which have a certain *critical* or *limiting minimum* value of frequency which is called *threshold frequency* or *cut-off frequency* (represented as υ_0) can eject the electrons. Below this value of υ_0 no electrons are emitted. From Einstein's photo-electric equation it is evident that if the frequency (υ) of the incident light is less than υ_0, $\frac{1}{2}mv^2$ (*i.e.* kinetic energy of the photoelectron) will be negative. Negative value of $\frac{1}{2}mv^2$ means that the incident radiation having υ less than υ_0 is not able to give kinetic energy to the electron and hence cannot eject electron from the metal surface. Thus an incident radiation having υ less than υ_0, no matter how long the radiation falls on the metal surface and how greater is its intensity, is not able to eject the electrons. On the other hand, since

the incident radiation having υ more than υ_0 is able to give velocity and hence kinetic energy ($= \frac{1}{2}mv^2$) to the ejected electron, it is able to produce the electron emission.

The magnitude of υ_0 depends on the nature of the metal, *e.g.*, υ_0 is quite low (visible light) for alkali metals like K, Na and Cs while it is quite high (ultraviolet light) for many other metals. υ_0 for Pt, Ag and K are $15.1 \times 10^{11}\ s^{-1}$, $11.3 \times 10^{14}\ s^{-1}$ and $4.22 \times 10^{14}\ s^{-1}$ respectively.

The wavlength corresponding to the value of υ_0 is called **threshold wavelength or long wavelength limit** and is represented as λ_0. No photoelectrons are emitted by the incident light having wavelength greater than λ_0.

3. *Relation between frequency of the incident light and kinetic energy of the photoelectron.* Einstein's photoelectric equation shows that since m (mass of the electron) remains constant, an increase in the magnitude of the frequency (υ) of the incident radiation will increase the velocity (v) with which the photoelectrons are ejected. An increase in the velocity will increase the kinetic energy of the photoelectrons and hence maximum kinetic energy of the emitted electron [$(K.E.)_{max}$] is directly proportional to the frequency of the incident radiation. Consequently the magnitude of kinetic energy of the photoelectrons will increase with an increase of the frequency of the incident radiation above the threshold frequency and hence a plot between the kinetic energy of the photoelectrons and the frequency of the incident radiation will be a straight line as shown in Fig. 1. 28.

The intercepts on the energy axis and frequency axis were found to be equal to $-W_0$ and W_0/h respectively. Now since W_0 is equal to $h\upsilon_0$, W_0/h is equal to $h\upsilon_0/h = \upsilon_0$. Thus the intercept on the frequency axis is equal to the threshold

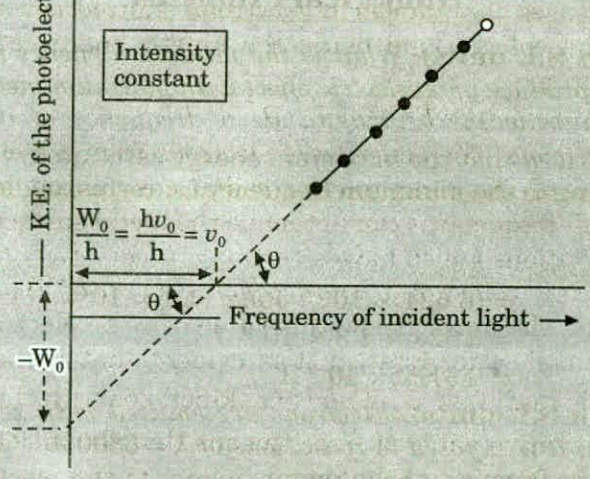


Fig. 1.28. A plot between the kinetic energy (K.E.) of the photoelectrons and the frequency of the incident light.

frequency, υ_0. The slope of the straight line was determined by Millikan who showed that the slope is given by :

$$\tan \theta = \frac{W_0}{W_0/h} = h$$

From a determination of this slope, Millikan found the value of h to be 6.570×10^{-34} J.s. This value is almost equal to that of Planck's constant, h ($h = 6.624 \times 10^{-34}$ Js) as determined experimentally by Planck himself from black-body measurements.

4. *Relation between the intensity of incident light and kinetic energy of photo electrons.* Since Eisten's photoelectric equation does not contain any term related to the intensity of radiation, kinetic energy remains independent of the intensity of radiation.

5. *The velocities of emitted electrons have values between zero and a definite maximum. The proportion of the electrons having a particular velocity is independent of the intensity of the radiation.*

6. *Electrons are emitted almost instantaneously even when the intensity of incident radiations is very low. The time log between the incidence of radiation and emission of first electrons is less than 10^{-8} seconds.*

The points given above could not be explained by the classical Maxwell's wave theory of radiation, since, if radiations are continuous as assumed by wave theory, any radiation should be able to accumulate enough energy to knock out the electrons from the metal surface. But this has not been found true in practice.

Thus we see that Einstein has explained photoelectric effect by assuming that radiations which were considered as waves (*Maxwell's wave theory of radiation*) are also considered as small particles which are called *photons*. (*Planck's quantum theory of radiation*). *Consequently radiation has both wave and particle nature simultaneously* (*wave-particle dualism*).

Numerical Problems

Problem 1 (In S.I. units). *What is the minimum energy that photons must possess in order to produce photoelectric effect with platinum metal ? The threshold frequency of platinum is* $1.3 \times 10^{25}\ s^{-1}$

Solution. We know that the maximum energy associated with a photon is the energy corresponding to the minimum frequency *i.e.* corresponding to the threshold frequency, υ_0.

$$\therefore \quad E_{photon} = h\upsilon_0$$
$$= (6.624 \times 10^{-34}\ \text{Js}) \times (1.3 \times 10^{25}\ \text{s}^{-1})$$
$$= 6.624 \times 1.3 \times 10^{-9}\ \text{J}$$
$$= 8.6112 \times 10^{-9}\ \text{J}$$

Problem 2 (In S.I. units). *Electrons are emitted with zero velocity from a metal surface when it is exposed to radiations of* $\lambda = 6800\ A^0$. Calculate threshold frequency and work function of the metal.

Solution. Since the electrons are emitted with zero velocity from the metal surface, λ is the threshold frequency, *i.e.*

$$\lambda_0 = 6800\ A^0 = 6800 \times 10^{-10}\ \text{m}$$

∴ Threshold frequency,

$$\upsilon_0 = \frac{c}{\lambda_0} = \frac{3\times10^8 \text{ m.s}^{-1}}{6800\times10^{-10} \text{ m}}$$

$$= \frac{3\times10^8}{68\times10^2\times10^{-10}} \text{ s}^{-1}$$

$$= \frac{3\times10^{16}}{68} \text{ s}^{-1} = 0.0441\times10^{16} \text{ s}^{-1}$$

$$= 0.441\times10^{15} \text{ s}^{-1}$$

Work function, $W_0 = h\upsilon_0$

$$= (6.624 \times 10^{-34} \text{ Js}) \times (0.441 \times 10^{15} \text{ s}^{-1})$$

$$= 6.624 \times 0.441 \times 10^{-19} \text{ J}$$

$$= 2.9145 \times 10^{-19} \text{ J}$$

Problem 3 (In C.G.S. units). *Calculate the kinetic energy of an electron emitted from a surface of potassium metal by light of wavelength* 5.5×10^{-8} cm (*work function* = 3.62×10^{-12} *erg*).

Solution. Here $\lambda = 5.5 \times 10^{-8}$ cm

$$\therefore \quad \upsilon = \frac{c}{\lambda} = \frac{3\times10^{10} \text{ cm.s}^{-1}}{5.5\times10^{-8} \text{ cm}} = 0.545\times10^{18} \text{ s}^{-1}$$

Now kinetic energy of the emitted electron

$$= \frac{1}{2} mv^2 = h\upsilon - h\upsilon_0$$

$$= h\upsilon - W_0$$

$$= (6.624\times10^{-27} \text{ erg.s})\times(0.545\times10^{18} \text{ s}^{-1}) - (3.62\times10^{-12} \text{ erg})$$

$$= (3.6100\times10^{-9} - 3.62\times10^{-12}) \text{ erg}$$

$$= \left[3.6100 - \frac{3.62}{10^3}\right]\times10^{-9} \text{ erg}$$

$$= (3.6100 - 0.00362)\times10^{-9} \text{ erg}$$

$$= 3.6063\times10^{-9} \text{ erg.}$$

Problem 4 (In S.I. units). *Photoelectric threshold wavelength of metallic copper is* $\lambda = 3000\ A^0$. *Find out* (*i*) *the maximum kinetic energy of the photoelectrons ejected and* (*ii*) *the work function of the metal, when ultra violet light of* $\lambda = 2536\ A^0$ *falls on the metal surface.*

Solution. Here $\lambda_0 = 3000\ \text{A}^0 = 3000 \times 10^{-10}$ m

$$\lambda = 2536\ \text{A}^0 = 2536 \times 10^{-10} \text{ m}$$

$$\therefore \quad \upsilon_0 = \frac{c}{\lambda_0} = \frac{3\times10^8 \text{ m.s}^{-1}}{3000\times10^{-10} \text{ m}} = 1\times10^{15} \text{ s}^{-1}$$

and $$\upsilon = \frac{3\times10^8 \text{ m.s}^{-1}}{2536\times10^{-10} \text{ m}} = 1.18\times10^{15 \text{ s}^{-1}}$$

Maximum kinetic energy = $E_{max} = \frac{1}{2} mv^2_{max}$

$$= h\upsilon - h\upsilon_0$$
$$= h\ (\upsilon - \upsilon_0)$$
$$= 6.624 \times 10^{-34} \times (1.18 \times 10^{15} - 10^{15})\ \text{J.s.s.}^{-1}$$
$$= 6.624 \times 10^{-34} \times 10^{15} \times 0.18\ \text{J}$$
$$= 1.1923 \times 10^{-19}\ \text{J}.$$

Evidently, work function (W_0) is given by :

$$W_0 = h\upsilon_0$$
$$= (6.624 \times 10^{-34}\ \text{Js}) \times (10^{15}\ \text{s}^{-1})$$
$$= 6.624 \times 10^{-19}\ \text{J}.$$

Scattering of X-rays—Compton Effect

In 1923 during the course of his experiments on the scattering of X-rays by solid matter (called *scattering substance* or *scatterer*), A.H. Compton found that when X-rays of high energy are allowed to fall on solid matter like carbon block or some other light element, an electron is ejected from the carbon block and X-rays are scattered from their original path. In this process a photon from the incident X-rays collides with the loosely-bound electron in the carbon block (scatterer) and, after receiving an impact from the photon, the electron which was initially at rest gains some velocity and hence moves below the direction of the incident X-rays while the photon is deflected above. Thus we see that X-rays are scattered from their original path as a result of the collision between the photon and the electron. The collision between the photon and the electron can be regarded as a collision between two balls—one moving and the other at rest. It has been found that the scattered X-rays have longer wavelength (*i.e.* lower frequency or lower energy) than the incident X-rays. If the wavelengths of the incident X-rays and the scattered X-rays and λ and λ' respectively, then hc/λ and hc/λ' are the energies associated with the photon of the incident and scattered X-rays respectively. Thus the decrease in energy is equal to $\left(\frac{hc}{\lambda} - \frac{hc}{\lambda'}\right)$, since $hc/\lambda > hc/\lambda'$. This energy $\left(= \frac{hc}{\lambda} - \frac{hc}{\lambda'}\right)$ is transferred to the electron at rest and therefore, the electron gains some velocity and moves from its path in this process. *This phenomenon in which there is a change in wavelength of the scattered X-rays is called* **Compton effect.** The angle through which the incident X-rays are deflected from their original path is known as *angle of scattering* and is denoted by θ. Thus θ is the angle between the incident and the scattered X-rays (See Fig. 1.29).

By applying the laws of conservation of energy and of momentum, and by assuming that X-rays are composed of photons each of which has energy equal to $h\upsilon$, Compton showed that the wavelength, λ' of the scattered X-rays and the wavelength, λ of the incident X-rays are related to each other by the relation :

$$\lambda' - \lambda = \frac{h}{mc}(1 - \cos\theta)$$

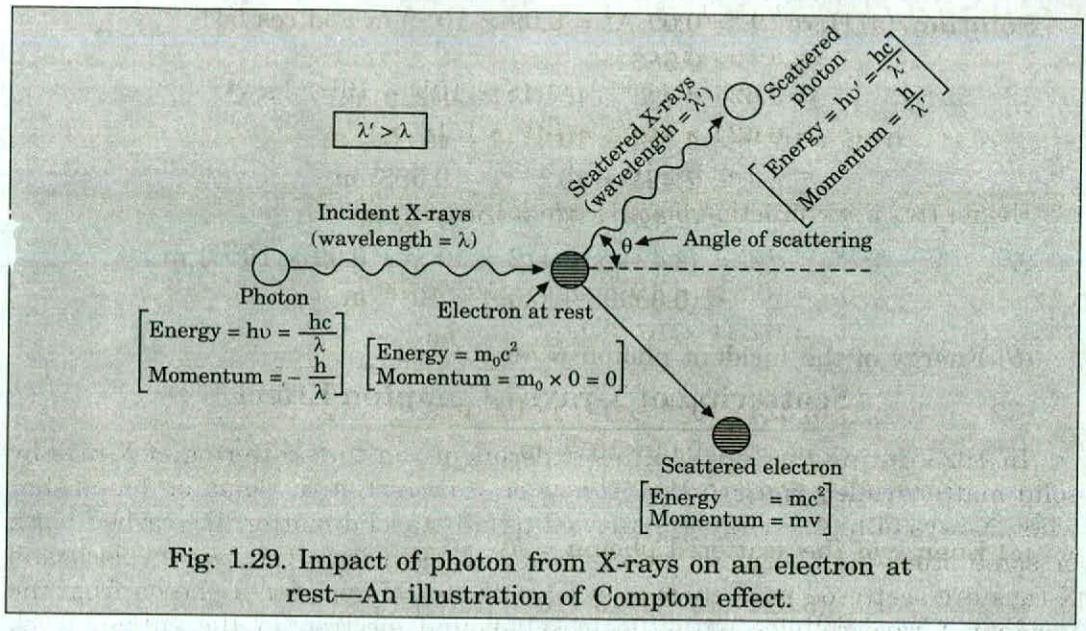


Fig. 1.29. Impact of photon from X-rays on an electron at rest—An illustration of Compton effect.

where h is the Planck's constant, m is the rest mass of the electron and c is the velocity of light. The difference in λ' and λ [*i.e.* $(\lambda' - \lambda)$] is called *Compton wavelength shift* and is denoted by $\Delta\lambda$. Thus :

$$\textit{Increase in wavelength} = \Delta\lambda = \lambda' - \lambda = \frac{h}{mc}(1 - \cos\theta).$$

This equation clearly shows that $\Delta\lambda$ depends on the magnitude of the angle of scattering, θ and is produced as a result of the collision between the photon of incident X-rays and electron at rest (photon-electron collision). This equation also shows that $\Delta\lambda$ is indepedent of the nature of the scattering substance and the wavelength of the incident X-rays. The term *h/mc* is called *Compton wavelength* whose value, in S.I. units, is equal to 2.424×10^{-12} metre as shown below :

$$\frac{h}{mc} = \frac{6.624\times10^{-34}\ \text{Js}}{(9.108\times10^{-31}\ \text{kg})\times(3\times10^{8}\ \text{ms}^{-1})}$$

$$= \frac{6.624\times10^{-11}\ \text{kg.m}^2\text{.s}^{-2}\text{.s}}{9.108\times3\ \text{kg.m.s}^{-1}} \quad (\because \text{J} = \text{kg.m}^2\text{.s}^{-2})$$

$$= 0.2424 - 10^{11}\ \text{m}$$

$$= 2.424\times10^{-12}\ \text{m}$$

Thus :

$$\Delta\lambda = \lambda' - \lambda = 2.424 \times 10^{-12}\ (1 - \cos\theta)\ \text{m}$$

$$= 2.424 \times 10^{-12} \times (2 \sin^2 \theta/2)\ \text{m}$$

$$= 4.848 \times 10^{-12} \sin^2 \theta/2\ \text{m}$$

Numerical problem. *A beam of monochromatic X-rays with* $\lambda = 0.09\ A°$ *is incident on a carbon scatterer. The scattered X-rays are observed at an angle of* 54° *with the direction of the incident beam. Find* (*a*) *the wavelength of the scattered X-rays, and* (*b*) *the energies of the incident and scattered photons.*

Solution. (a) Here $\lambda = 0.09\ A^\circ = 0.09 \times 10^{-10}$ m and $\cos 54^\circ = 0.588$.

$$\therefore \quad \lambda' - \lambda = 2.424 \times 10^{-12} (1 - \cos \theta)\ m$$

$$\lambda' - 0.09 \times 10^{-10} = 2.424 \times 10^{-12} (1 - \cos 54)\ m$$

$$= 2.424 \times 10^{-12} (1 - 0.588)\ m$$

$$= (2.424 \times 10^{-12} \times 0.412)\ m$$

$$\therefore \quad \lambda' = [2.424 \times 0.412 \times 10^{-12} + 0.09 \times 10^{-10}]\ m$$

$$= (0.00998 + 0.09) \times 10^{-10}\ m$$

(*b*) Energy of the incident photon $= h\upsilon = \dfrac{hc}{\lambda}$

$$= \frac{(6.624 \times 10^{-34}\ Js) \times (3 \times 10^8\ m.s^{-1})}{0.09 \times 10^{-10}\ m}$$

$$= 2.208 \times 10^{-14}\ J$$

(*c*) Energy of the scattered photon $= h\upsilon' = \dfrac{hc}{\lambda'}$

$$= \frac{(6.624 \times 10^{-34}) \times (3 \times 10^8)}{0.09998 \times 10^{-10}}\ J$$

$$= 19.875 \times 10^{-16}\ J.$$

Postulates of Bohr's Atomic Model

Bohr's atomic model retains the two essential features of Rutherford's atomic model which are :

(*i*) The atom has a very small positively charged nucleus at its centre. All the protons and neutrons are contained in the nucleus. Thus most of the mass of the atom is concentrated in the nucleus.

(*ii*) Negatively charged electrons are revolving round the nucleus in the same way as planets are revolving round the sun.

However, he applied Planck's quantum theory to the revolving electrons and thus explained why the electrons, while revolving round the nucleus, do not lose energy and consequently do not fall into the nucleus.

While describing his model of atomic structure, Bohr made the following postulates.

1. *Fixed circular orbits.* Bohr assumed that an electron is a material particle which is revolving round the nucles in concentric circular orbits situated at *definite* (*i.e.*, fixed) *distance* from the nucleus and with a *definite velocity.*

2. *Stationary energy levels.* As long as an electron remains in a particular orbit, it neither emits (*i.e.* radiates or loses) nor absorbs (*i.e.*, gains) energy. Thus in a particular orbit the energy of a revolving electron remains constant or stationary. Hence each of the fixed orbits is associated with a definite amount of energy, *i.e.*, with a definite whole number of quanta of energy. The orbits are, therefore, also called *stationary energy levels* or simply *energy levels or energy shells.* This concept of stationary energy levels explains the stability of the atom, since an electron cannot lose energy gradually and fall into the nucleus.

Different energy levels have been represented by n which can have integer (whole number) values like 1, 2, 3, ... ∞, starting from the nucleus. n has been called **principal quantum number** by Bohr. Different values of n are also represented by capital letters K, L, M, N, etc. Thus:

Principal quantum number $(n) \rightarrow$ *1* *2* *3*.....

Letter designation of energy level $\rightarrow$ *K (1st shell)* *L(2nd shell)* *M(3rd shell)*

Thus for K shell (*1st* shell) $n = 1$, for L shell (*2nd* shell) $n = 2$ and so on. K, L, M.....shells are also called $n = 1$ shell, $n = 2$ shell, $n = 3$ shell, etc. respectively. Representation of various orbits is depicted in Fig. 1.30.

The energy associated with a certain energy level increases with the increase of its distance from the nucleus. Thus, if E_1, E_2, E_3, ... , etc. are the energies associated with the energy levels numbered as 1 (*K*-shell), 2 (*L*-shell), 3 (*M*-shell), etc. the order of the energies is as :

$$E_1 < E_2 < E_3 < \text{.....}, \text{ etc.}$$

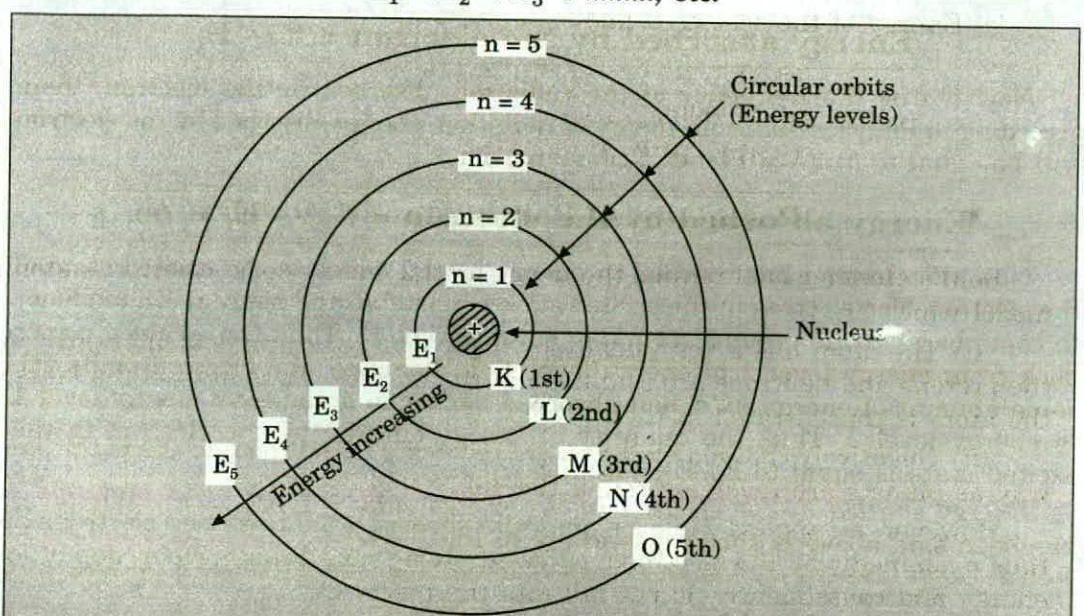


Fig. 1.30. Representation of various orbits (energy levels) round the nucleus. E_1, E_2, E_3....., etc. are the energies associated with orbits having $n = 1$ (K-shell), 2(L-shell)..., etc. Energies of different orbits are in the order : $E_1 < E_2 < E_3 < E_4 < E_5 < ...$

3. *Jumping of an electron from one energy level to the other—Ground state and excited state of an electron.* As long as an electron remains in a particular orbit, it neither emits (*i.e.*, radiates or loses) nor absorbs (*i.e.*, gains) energy. But when the electron is excited from a lower energy level to a higher energy level, it absorbs energy. On the other hand when it comes back from a higher energy level to a lower energy level, it emits energy. According to Planck's quantum theory of radiation, the absorption or emission of energy takes place not continuously but discontinuously (discretely), *i.e.*, the absorption or emission of energy takes place not as continuous waves but as small packets or bundles or

discrete (separate) units of the waves each of which is called a quantum (plural is quanta) or photon. In short we say that the absorption or emission of energy takes place in the form of quanta or photons.

When an electron is present in energy level 1 which is the lowest energy level, the electron is said to be in the *ground state*. Thus energy level 1 is called the ground state of the electron or atom. Since energy level I (*i.e.*, ground state) has the minimum energy, ground state is the most stable state of the atom. Now if energy is supplied to the electron residing in energy level 1, it will absorb the supplied energy in the form of quanta or photons (Planck's quantum theory) and hence will move to one of the higher energy levels 2, 3 ....., etc. depending on the amount of energy absorbed by the electron. The electron present in these energy levels is said to be in the *excited state*.

Suppose an electron moves from energy level 1 to energy level 2. Let the energies associated with the electron present in these levels be E_1 and E_2 respectively. Then the amount of energy absorbed by the electron in coming from energy level 1 to energy level 2 is equal to E_2–E_1, *i.e.*

Energy absorbed by the electron = $E_2 - E_1$.

Now if υ is the frequency of the radiation absorbed by the electron, then, according to Planck's quantum theory of radiation, energy absorbed by the electron will be equal to $h\upsilon$ (h = Planck's constant) Thus :

Energy absorbed by the electron = $E_2 - E_1 = h\upsilon$.

Now the electron has reached in energy level 2 which is the excited state of the electron. The electron in the excited state is unstable and hence has a tendency to come back to the ground state (*i.e.* energy level 1). Thus the electron comes back from energy level 2 to energy level 1. In doing so, the electron emits the same amount of energy as it had absorbed earlier in going from energy level 1 to energy level 2. Thus the quantity of energy emitted by the electron in the excited state is equal to E_2–E_1 = $h\upsilon$, *i.e.*

Energy emitted by the electron in the excited state = E_2–E_1 = $h\upsilon$. Whatever has been said above is shown pictorially in Fig. 1.31.

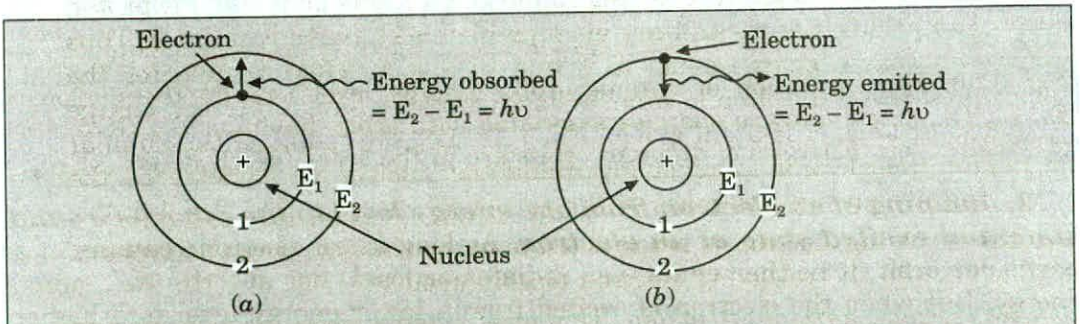


Fig. 1.31. (*a*) When an electron in energy level 1 (ground state) moves to energy level 2 (excited state), it absorbs energy equal to E_2–E_1 = $h\upsilon$. (*b*) When the electron in energy level 2 comes back to energy level 1, it emits the same amount of energy as it had absorbed earlier in going from energy level 1 to energy level 2, *i.e.*, it emits energy equal to $E_2 - E_1 = h\upsilon$.

4. *Principle of quantisation of angular momentum of the moving electron.* Bohr postulated that an electron cannot move in all the orbits. It can move only in that orbit in which the angular momentum of the electron (= mvr) moving round the nucleus is integral whole number multiple of $\frac{h}{2\pi}$ such as $1h/2\pi$, $2h/2\pi$, $3h/2\pi$, ..., $nh/2\pi$. Thus according to this postulate the angular momentum of a moving electron is given by :

$$mvr = n.\frac{h}{2\pi} \qquad ...(1)$$

Thus according to the postulate represented by equation (1), *angular momentum of a moving electron is quantinised.*

In equation (1) m = mass of the electron; v = velocity of the electron; h = Planck's constant = 6.624×10^{-27} erg-s; r = radius of the orbit in which the electron is moving; and n = an integral which has been called principal quantum number by Bohr. n gives the number of the orbit in which the electron is moving. It can have the values 1, 2, 3, ... for the orbit numbered as 1 (K orbit), 2 (L orbit), 3 (M orbit) from the nucleus. Thus for K, L, M, ... orbits n = 1, 2, 3, ... respectively as shown below :

Orbits →	K	L	M	N ...
Principal quantum number (n) →	1	2	3	4 ...

Bohr's Theory As Applied to Hydrogen Atom

By using the postulates of his theory and some classical laws of Physics, Bohr was able to calculate the radius of each orbit of H-atom, energy associated with the electron in each orbit of H-atom, velocity of electron in each orbit of H-atom, and the frequency and wavelength of the spectral lines observed in hydrogen spectrum.

1. Radii of Various Orbits in Hydrogen Atom

(*a*) **In C.G.S. units.** Let us consider a hydrogen atom. Quite obviously this atom contains only one electron revolving round the nucleus and only one proton present in the nucleus. Let the solitary electron have a charge equal to $-e$. Thus the proton will bear a charge equal to $1 \times (+e) = +1e$. Here 1 indicates the number of protons or the atomic number of hydrogen atom. Thus the charge carried by the nucleus of H-atom is equal to $+1e$. Let the radius of the circular orbit in which the electron is revolving round the nucleus be r. Let v be the tangential velocity and m, the mass of the revolving electron (See Fig. 1.32).

Now the revolving electron is being acted upon by the following two types of forces which act on the revolving electron simultaneously.

(*i*) *Electrostatic force of attraction.* This force acts between the nucleus and the revolving electron, and tends to attract the electron towards the nucleus. According to Coulomb's law this force is equal to :

$$\frac{e \times e}{r^2} = \frac{e^2}{r^2}$$

Here e is in electrostatic units (*e.s.u.*) and r is in centimetres (cm).

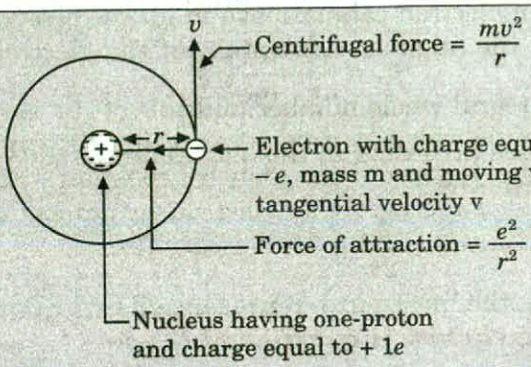


Fig. 1.32. Different types of forces acting on an electron revolving round the nucleus in hydrogen atom.

(*ii*) *Centrifugal or centripetal force.* This force tends to take the electron away from its orbit and is equal to:

$$\frac{mv^2}{r}$$

Here m is in grams.

Both the above forces act in opposite directions. Bohr assumed that in order to keep the electron revolving in its orbit, both these forces must be equal to each other, *i.e.*

$$\frac{e^2}{r^2} = \frac{mv^2}{r}$$

or
$$v^2 = \frac{e^2}{r\,m} \qquad ...(1)$$

Now since the electron is revolving in a circular orbit, according to one of the postulates of Bohr's theory, the angular momentum of the revolving electron ($= mvr$) must be equal to $\frac{nh}{2\pi}$ where n is the number of the orbit in which the electron is revolving, *i.e.*

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

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

Here h is in erg. sec (erg-s)

Eliminating v^2 from equations (1) and (2), we get

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

or
$$r = \frac{n^2h^2}{4\pi^2\ me^2} \qquad ...(3)$$

If r_n is the radius of the nth orbit of hydrogen atom, then r_n will be given by :

$$\boxed{r_n = \frac{n^2h^2}{4\pi^2\, me^2}} \quad ...(4)$$

The value of r_n can be calculated by substituting the experimental values of h, m and e in equation (4) given as h (Planck's constant) = 6.624×10^{-27} *erg. s*; π (*pi*) = 3.14; m (mass of the revolving electron in grams) = 9.108×10^{-28} g; e (charge on electron in *e.s.u*) = 4.8×10^{-10} *e.s.u.* Thus :

$$r_n = \frac{n^2 \times (6.624 \times 10^{-27}\ erg.s)^2}{4 \times (3.14)^2 \times (9.108 \times 10^{-28}\ g) \times (4.8 \times 10^{-10}\ e.s.u.)^2}$$

Now since $erg = g.cm^2 \,.\, s^{-2}$

and $esu = g^{1/2} \,.\, cm^{3/2} .\, s^{-1}$,

$$r_n = \frac{n^2 \times (6.62 \times 10^{-27}\ g.cm^2.s^{-2}.s)^2}{4 \times (3.14)^2 \times (9.108 \times 10^{-28}\ g) \times (4.8 \times 10^{-10}\ g^{1/2}.cm^{3/2}.s^{-1})^2}$$

$$= n^2 \times 0.529 \times 10^{-8}\ cm$$

or $\boxed{r_n = n^2 \times 0.529\ \text{A}^\circ}$ ($\because 10^{-8}\ cm = 1\ A^\circ$) ...(5)

On putting n = 1, 2, 3..., etc. in equation (5), the values of the radii of 1st (n = 1), 2nd (n = 2), 3rd (n = 3), etc. orbits of hydrogen can be calculated as shown below :

Radius of 1*st* orbit (n = 1), $r_1 = 1^2 \times 0.529$ Å = 0.529 Å.

Radius of 2*nd* orbit (n = 2), $r_2 = 2^2 \times 0.529$ Å = 2.11 Å.

Radius of 3*rd* orbit (n = 3), $r_3 = 3^2 \times 0.529$ Å = 4.75 Å.

Radius of 4*th* orbit (n = 4), $r_4 = 4^2 \times 0.529$ Å = 8.45 Å.

Radius of 5*th* orbit (n = 5), $r_5 = 5^2 \times 0.529$ Å = 13.22 Å.

Radius of the 1*st* orbit of hydrogen atom is also represented by other symbols like r_H, a_0 etc. Radius of the 1st orbit of hydrogen atom is called **Bohr radius.** Thus :

$$\boxed{r_1 (\text{or } r_H \text{ or } a_0) = \frac{h^2}{4\pi^2 me^2}} \quad ...(6)$$

In order to find out the values of r_2, r_3, r_4 etc. in terms of r_1, we divide equation (4) by equation (6)

$$\frac{r_n}{r_1} = \frac{n^2h^2}{4\pi^2me^2} \times \frac{4\pi^2me^2}{h^2} = n^2$$

or $\boxed{r_n = r_1 \times n^2}$ ...(7)

The values of the radii of the first five orbits of hydrogen atom, as calculated above, are represented in Fig. 1.33.

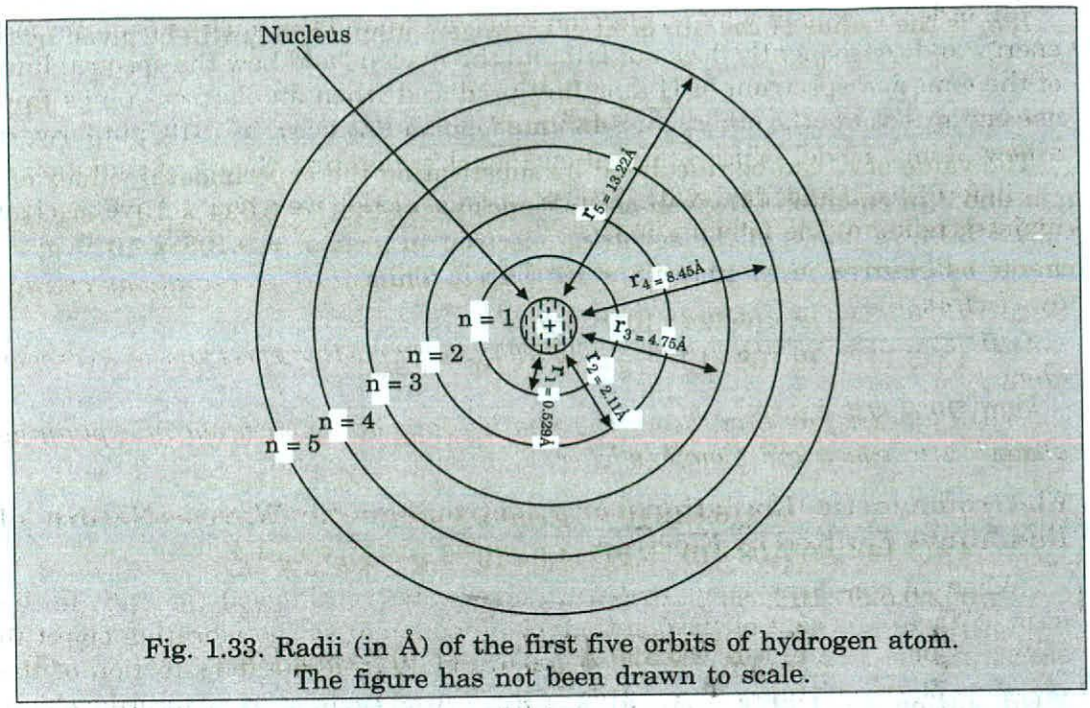


Fig. 1.33. Radii (in Å) of the first five orbits of hydrogen atom. The figure has not been drawn to scale.

(*b*) **In S.I. units.** In S.I. units the electrostatic force of attraction acting on the revolving electron is equal to :

$$\frac{1}{4\pi\epsilon_0} \times \frac{e^2}{r^2}$$

Here e is the electronic charge in coulombs, r is the distance between the nucleus and the revolving electron, expressed in metres and ϵ_0 is a constant which is called absolute *permittivity* of the medium (*viz.* vacuum in this case). The value of ϵ_0 is equal to 8.85×10^{-12}.

Now in order to keep the electron revolving in its orbit, the electrostatic force of attraction $\left(= \frac{1}{4\pi\epsilon_0} \times \frac{e^2}{r^2} \right)$ must be equal to the centrifugal force $\left[= \frac{mv^2}{r} \text{ in which } m \text{ is in kilogram (kg)} \right]$, *i.e.*,

$$\frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{r^2} = \frac{mv^2}{r}$$

or
$$v^2 = \frac{e^2}{4\pi\epsilon_0 \, r\, m} \qquad ...(8)$$

Now,
$$mvr = n.\frac{h}{2\pi}$$

or
$$v^2 = \frac{n^2h^2}{4\pi^2m^2v^2} \qquad ...(9)$$

Here h is in joules-sec (J-s).

Eliminating v^2 from equations (8) and (9), we get

$$r = \frac{\epsilon_0 \, n^2 h^2}{\pi \, me^2}$$

i.e.

$$\boxed{\mathbf{r_n = \frac{\epsilon_0 \, n^2 h^2}{\pi \, me^2}}} \qquad ...(10)$$

Substituting the experimental values of ϵ_0, h, m and e in equation (10) given as $\epsilon_0 = 8.85 \times 10^{-12}$; $h = 6.624 \times 10^{-34}$ J-s; $\pi = 3.14$; $m = 9.108 \times 10^{-31}$ kg; and $e = 1.602 \times 10^{-19}$ C, we get

$$r_n = \frac{(8.85 \times 10^{-12}) \times n^2 \times (6.624 \times 10^{-34} \text{ J-s})^2}{3.14 \times (9.108 \times 10^{-31} \text{ kg}) \times (1.602 \times 10^{-19} \text{ C})^2}$$

$$= \frac{8.85 \times (6.62)^2 \times 10^{-11} \times n^2 \times (\text{kg}.m^2.s^{-2}.s)^2}{3.14 \times 9.108 \times (1.602)^2 \times \text{kg} \times (\text{kg}^{1/2}.m^{3/2}.s^{-1})^2} \qquad \left[\because \begin{array}{l} \text{J} = \text{kg}.m^2.s^{-2} \\ \text{C} = \text{kg}^{1/2}.m^{3/2}.s^{-1} \end{array}\right]$$

$$= \frac{0.885 \times (6.62)^2 \times 10^{-10} \times n^2}{3.14 \times 9.108 \times (1.602)^2} m$$

or

$$\boxed{\mathbf{r_n = n^2 \times 0.529 \times 10^{-10} \text{ m}}} \qquad ...(11)$$

2. Radii of H-like Species

So far we have considered a hydrogen atom which contains one electron and one proton. Now let us consider hydrogen-like species such as He^+ (At. No., $Z = 2$), Li^{2+} ($Z = 3$), etc. in which the number of electrons is equal to 1 but the number of protons is more than 1. The number of protons in He^+ and Li^{3+} ions is 2 and 3 respectively. Thus the charge carried by the nucleus of these ions is equal to + 2e and + 3e respectively where 2 and 3 stand to indicate the atomic number of He and Li atoms. Consequently, in general, the charge carried by the nucleus of a hydrogen-like atom with atomic number, Z will be equal to + Ze. On the basis of the same arguments as used above, we can show that the electrostatic force of attraction acting between the nucleus and the revolving electron will be equal to

$$\frac{Ze \times e}{r^2} = \frac{Ze^2}{r^2} \text{ (\textit{in C.G.S. units})} \text{ or } \frac{Ze^2}{4\pi\epsilon_0 e^2} \text{ (\textit{in S.I. units})}$$

and hence the radius, r_n of the nth orbit of a hydrogen like atom with atomic number Z will be given by :

$$\left.\begin{aligned} r_n &= \frac{n^2 h^2}{4\pi^2 me^2 Z} \\ &= \frac{n^2 \times 0.529 \times 10^{-8}}{Z} \text{ cm} \\ &= \frac{n^2 \times 0.529}{Z} \text{ A}^\circ \end{aligned}\right\} \quad (\textit{In C.G.S. units}) \qquad ...11\,(a)$$

$$\left.\begin{aligned} r_n &= \frac{\epsilon_0\, n^2h^2}{\pi\, me^2Z} \\ &= \frac{n^2 \times 0.529 \times 10^{-10}}{Z}\ \text{m} \end{aligned}\right\} \quad (In\ S.I.\ units) \qquad ...11\ (b)$$

3. Energy of an Electron in Various Orbits in Hydrogen Atom

(a) **In C.G.S. units.** The energy associated with a revolving electron at any instant is equal to the sum of its kinetic energy (K.E.) and potential energy (P.E.). Kinetic energy of a moving electron is due to its motion in the circular orbit while the potential energy arises because the electron lies in the electric field of the positive nucleus. Again we know that since K.E. = $\frac{1}{2}mv^2$ and P.E. = $-\frac{e^2}{r}$, total energy (E) of the electron is given by :

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

$$= \frac{1}{2}mv^2 + \left(-\frac{e^2}{r}\right)$$

or $$\text{E} = \frac{1}{2}mv^2 - \frac{e^2}{r} \qquad ...(12)$$

Putting $mv^2 = \frac{e^2}{r}$ from equation (1) in equation (12), we get :

$$\text{E} = \frac{1}{2} \cdot \frac{e^2}{r} - \frac{e^2}{r}$$

or $$\text{E} = -\frac{e^2}{2r} \qquad ...(13)$$

Putting $r = \frac{n^2h^2}{4\pi^2me^2}$ from equation (3) in equation (13), we get :

$$\text{E} = -\frac{e^2}{2} \times \frac{4\pi^2me^2}{n^2h^2}$$

or $$\text{E} = -\frac{2\pi^2me^4}{n^2h^2}$$

If E_n is the energy associated with an electron revolving in the nth orbit, then E_n is given by :

$$\boxed{\mathbf{E_n = -\frac{2\pi^2me^4}{n^2h^2}}} \qquad ...(14)$$

The value of E_n can be calculated by substituting the experimental values of m (= 9.108×10^{-28} g); e (= 4.8×10^{-10} *esu*) and h (= 6.624×10^{-27} erg.s) in equation (14). Thus :

$$E_n = \frac{2 \times (3.14)^2 \times (9.108 \times 10^{-28}\ g) \times (4.8 \times 10^{-10}\ esu)^4}{n^2 \times (6.624 \times 10^{-27}\ \text{erg-s})^2}$$

$$= \frac{2\times(3.14)^2\times(9.108\times10^{-28})\times(4.8\times10^{-10})^4\ \text{g.}(esu)^4}{n^2\times(6.624\times10^{-27})^2.\text{erg}^2.\text{s}^2}$$

$$= \frac{2\times(3.14)^2\times(9.108)\times(4.8)^4\times10^{-68}\ \text{g.}(esu)^4}{n^2\times(6.624)^2\times10^{-54}.\text{erg}^2.\text{s}^2}$$

$$= \frac{2\times(3.14)^2\times0.009108\times(4.8)^4\times10^{-11}\ \text{g.}(esu)^4}{n^2\times(6.624)^2.\text{erg}^2.\text{s}^2}$$

$$= -\frac{2.179\times10^{-11}\ \text{g.}(\text{g}^{1/2}.\text{cm}^{3/2}.\text{s}^{-1})^4}{n^2\times(\text{g.cm}^2.\text{s}^{-2})^2.\text{s}^2}$$

$$= -\frac{2.179\times10^{-11}\ \text{g.g.}^2.\text{cm}^6.\text{s}^{-4}}{n^2.\text{g}^2.\text{cm}^4.\text{s}^{-4}.\text{s}^2}$$

$$= -\frac{2.179\times10^{-11}\ \text{g.cm.}^2}{n^2.\text{s}^2}$$

$$= -\frac{2.179\times10^{-11}}{n^2}\ (\text{g.cm}^2.\text{s}^{-2})$$

or
$$\boxed{\mathbf{E}_n = -\frac{\mathbf{2.179\times10^{-11}}}{\mathbf{n^2}}\ \mathbf{erg/atom}} \qquad ...(15)$$

Since E_n has a negative sign, it implies that energy increases directly with the square of n.

On putting n = 1, 2, 3, etc. in equation (15), we can get the energies associated with an electron revolving in *1st* (n = 1), *2nd* (n = 2), *3rd* (n = 3) etc. orbits of hydrogen atom as shown below :

Energy of electron in *1st* orbit (n = 1),

$$\text{E}_1 = -\frac{2.179\times10^{-11}}{1^2}\ \text{erg/atom} = -2.179\times10^{-11}\ \text{erg/atom}$$

Energy of electron in *2nd* orbit (n = 2),

$$\text{E}_2 = -\frac{2.179\times10^{-11}}{2^2} = -0.5448\times10^{-11}\ \text{erg/atom}$$

Energy of electron in *3rd* orbit (n = 3),

$$\text{E}_3 = -\frac{2.179\times10^{-11}}{3^2} = -0.2421\times10^{-11}\ \text{erg/atom}$$

Energy of electron in *4th* orbit (n = 4),

$$\text{E}_4 = -\frac{2.179\times10^{-11}}{4^2} = -0.1362\times10^{-11}\ \text{erg/atom}$$

Energy of electron in *5th* orbit (n = 5),

$$\text{E}_5 = -\frac{2.179\times10^{-11}}{5^2} = -0.08716\times10^{-11}\ \text{erg/atom}$$

The values of E_1, E_2, E_3, etc. calculated as above show that these go on increasing (*i.e.*, go on becoming less and less negative) as the electron moves away from the nucleus.

(*b*) **In S.I. units.** Kinetic energy of the electron, as before, is equal to $\frac{1}{2}mv^2$ while the potential energy of the electron moving at a distance of r from the nucleus is equal to $-\frac{e^2}{4\pi\epsilon_0 r}$. Here m, e and h are measured in S.I. units namely kg, coulomb and J.s. respectively. Thus total energy (E) of the electron is given by :

$$E = \frac{1}{2}mv^2 - \frac{e^4}{4\pi\epsilon_0 r} \qquad ...(16)$$

Putting $mv^2 = \frac{e^2}{4\pi\epsilon_0 r}$ from equation (8) in equation (16), we get :

$$E = \frac{1}{2}.\frac{e^2}{4\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 r}$$

$$E = -\frac{e^2}{8\pi\epsilon_0 r} \qquad ...(17)$$

Now put $r = \frac{\epsilon_0 n^2 h^2}{\pi m e^2}$ in equation (17) to get

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

or $$\boxed{\mathbf{E_n = -\frac{me^4}{8\epsilon_0^2 n^2 h^2}}} \qquad ...(18)$$

The value of E_n can be calculated by putting

$m = 9.108 \times 10^{-31}$ kg;

$e = 1.602 \times 10^{-19}$ coulomb;

$\epsilon_0 = 8.85 \times 10^{-12}$;

and $h = 6.62 \times 10^{-34}$ J-s in equation (18). Thus :

$$E_n = -\frac{(9.108\times10^{-31}\ \text{kg})\times(1.602\times10^{-19}\ \text{C})^4}{8\times(8.85\times10^{-12})^2\times n^2\times(6.62\times10^{-34}\ \text{J.s})^2}$$

$$= -\frac{9.108\times(1.602)^4\times10^{-15}\times \text{kg}\times(\text{kg}^{1/2}.\text{m}^{3/2}.\text{s}^{-1})^4}{8\times(8.85)^2\times n^2\times(6.62)^2\times(\text{kg.m}^2.\text{s}^{-2}.\text{s})^2}$$

$$(\text{C} = \text{kg.}^{1/2}\text{m}^{3/2}.\text{s}^{-1};\ \text{J} = \text{kg.m}^2.\text{s}^{-2})$$

$$= -\frac{59.9854\times10^{-15}\times\text{kg.kg}^2.\text{m}^6.\text{s}^{-4}}{27509.29\times n^2\times\text{kg}^2.\text{m}^4.\text{s}^{-2}}$$

$$= -\frac{0.0021805\times10^{-15}}{n^2}\ \text{kg.m}^2.\text{s}^{-2}$$

$$= -\frac{218.05\times10^{-20}}{n^2}\ \text{Joules/atom} \qquad [\because\ \text{J} = \text{kg.m}^2.\text{s}^{-2}]$$

$$= -\frac{218.05\times10^{-20}\times(\text{Avogadro s number})}{n^2}\text{ J/mole}$$

$$= -\frac{218.05\times10^{-20}\times6.023\times10^{23}}{n^2}\text{ J/mole}$$

$$= -\frac{218.05\times10^{-20}\times6.023\times10^{23}}{n^2\times10^3}\text{ KJ/mole}$$

or $$\boxed{\mathbf{E}_n = -\frac{\mathbf{1313.315}}{\boldsymbol{n^2}}\ \mathbf{KJ/mole}} \qquad ...(19)$$

Substituting n = 1, 2, 3, 4, etc. in equation (19) we get the energies associated with an electron revolving in *1st* (n = 1), *2nd* (n = 2), *3rd* (n = 3), etc. orbits of hydrogen atom as shown below :

Energy of electron in *1st* orbit (n = 1),

$$E_1 = -\frac{1313.31}{1^2} = -1313.31 \text{ KJ/mole}$$

Energy of electron in *2nd* orbit (n = 2),

$$E_2 = -\frac{1313.31}{2^2} = -328.32 \text{ KJ/mole}$$

Energy of electron in *3rd* orbit (n = 3),

$$E_3 = -\frac{1313.31}{3^2} = -145.92 \text{ KJ/mole}$$

Energy of electron in *4th* orbit (n = 4),

$$E_4 = -\frac{1313.31}{4^2} = -82.08 \text{ KJ/mole}$$

Energy of electron in *5th* orbit (n = 5),

$$E_5 = -\frac{1313.31}{5^2} = -52.53 \text{ KJ/mole}$$

The energy values in KJ/mole associated with an electron in various orbits in hydrogen atom, calculated as above, are represented in Fig. 1.34.

On the same lines of argument it can be shown that total energy of an electron in *nth* orbit of a hydrogen-like atom with atomic number, Z is given by :

$$E_n = \text{K.E.} + \text{P.E.}$$

$$= \frac{1}{2}mv^2 + \left(-\frac{Ze^2}{r}\right)$$

$$= \frac{1}{2}mv^2 - \frac{Ze^2}{r} \textit{ (in C.G.S. units)}$$

and $$E_n = \frac{1}{2}mv^2 + \left(-\frac{Ze^2}{8\pi\epsilon_0 r}\right)$$

$$= \frac{1}{2}mv^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \textit{ (in S.I. units)} \qquad ...(A)$$

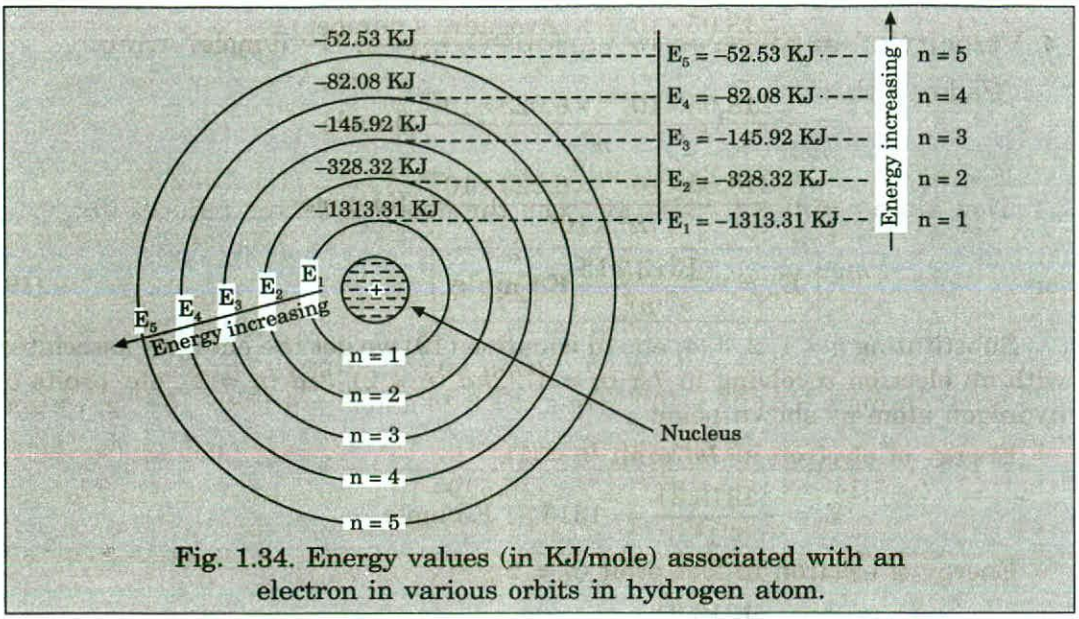


Fig. 1.34. Energy values (in KJ/mole) associated with an electron in various orbits in hydrogen atom.

On utilising the relations :

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

or $$mv^2 = \frac{Ze^2}{r} \text{ (in C.G.S. units)} \quad ...(a)$$

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

or $$mv^2 = \frac{Ze^2}{4\pi \in_0 r} \text{ (in S.I. units)} \quad ...(b)$$

$$r = \frac{n^2h^2}{4\pi^2 me^2 Z} \text{ (in C.G.S. units)} \quad ...(c)$$

$$r = \frac{\in_0 n^2h^2}{\pi me^2 Z} \text{ (in S.I. units)} \quad ...(d),$$

the equation (A) becomes :

$$\left.\begin{aligned} E_n &= -\frac{2\pi^2 me^4 Z^2}{n^2h^2} \\ &= -\frac{2.179\times10^{-11}\times Z^2}{n^2} \text{ erg/atom} \end{aligned}\right\} \text{(In C.G.S. units) ...(20)}$$

and

$$\left.\begin{aligned} E_n &= -\frac{me^4 Z^2}{8 \in_0{}^2 n^2h^2} \\ &= -\frac{218.05\times10^{-20}\times Z^2}{n^2} \text{ J/atom} \\ &= -\frac{1313.315Z^2}{n^2} \text{ KJ/mole} \end{aligned}\right\} \text{(In S.I. units) ...(21)}$$

4. Velocity of an Electron in Various Orbits of Hydrogen Atom.

We know that :

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

Now since $r = n^2 \times 0.529 \times 10^{-8}$ cm, the above equation, reduces to :

$$mv \times n^2 \times 0.529 \times 10^{-8} = n.\frac{h}{2\pi}$$

$$\therefore \qquad v = \frac{h}{2\pi mn \times 0.529 \times 10^{-8}}$$

Substituting $h = 6.624 \times 10^{-27}$ erg-s, $\pi = 3.14$ and $m = 9.108 \times 10^{-28}$ g, we get :

$$v = \frac{6.624 \times 10^{-27} \text{ erg.s.}}{2 \times 3.14 \times (9.108 \times 10^{-28} \text{ g}) \times n \times (0.529 \times 10^{-8} \text{ cm})}$$

$$= \frac{6.624 \times 10^{-27} \text{ g.cm}^2\text{.s}^{-2}\text{.s}}{2 \times 3.14 \times (9.108 \times 10^{-28} \text{ g}) \times n \times (0.529 \times 10^{-8} \text{ cm})} \qquad (\because \text{erg} = \text{g.cm}^2\text{.s}^{-2})$$

$$= \frac{2.188 \times 10^8}{n} \text{ cm/sec}$$

Now if v_n is the velocity of the electron in the *nth* orbit, then v_n is given :

$$\boxed{\mathbf{v_n = \frac{2.188 \times 10^8}{n} \text{ cm/s}}}$$

Numerical Problems

Problem 1. (In C.G.S. units). *Calculate the excitation energy for the electronic transition from state n = 1 to state n = 2 in a hydrogen atom ($h = 6.626 \times 10^{-27}$ erg-s, $e = 4.803 \times 10^{-10}$ esu, $m = 9.109 \times 10^{-28}$ g).* *(Raj. B.Sc. I 1980)*

Solution. Let the energy associated with the orbit having $n = 1$ be E_1 and that associated wth the orbit with $n = 2$ be E_2.

$\therefore$ Excitation energy $= E_2 - E_1$

$$= -\frac{2\pi^2 me^4}{n_2^2 h^2} - \left(-\frac{2\pi^2 me^4}{n_1^2 h^2}\right)$$

$$= -\frac{2\pi^2 me^4}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Substituting $\pi = 3.14$; $m = 9.109 \times 10^{-28}$ g; $e = 4.803 \times 10^{-10}$ esu; $h = 6.626 \times 10^{-27}$ erg-s; $n_1 = 1$ and $n_2 = 2$, we get :

Excitation energy $= 16.3526 \times 10^{-22}$ erg/atom

Problem 2. (In C.G.S. units). *Calculate the radii of first and fourth orbit in hydrogen atom. Given that $h = 6.6238 \times 10^{-27}$ erg-s, $m = 9.1072 \times 10^{-28}$ g, $\pi = 3.1416$, $e = 4.8022 \times 10^{-10}$ esu.* *(Udaipur B.Sc. 1980)*

Solution. We know that :

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

$$\therefore \quad r_1 = \frac{(1)^2 \times h^2}{4\pi^2me^2} \qquad ...(1)$$

and $$r_4 = \frac{(4)^2 \times h^2}{4\pi^2me^2} \qquad ...(2)$$

Substituting $h = 6.6238 \times 10^{-27}$ erg-s, $\pi = 3.1416$, $m = 9.1072 \times 10^{-28}$ g and $e = 4.8022 \times 10^{-10}$ esu, we get :

$$r_1 = (1)^2 \times 0.529 \times 10^{-8} \text{ cm}$$

or $$= 0.529 \times 10^{-8} \text{ cm}$$

and $$r_4 = (4)^2 \times 0.529 \times 10^{-8} \text{ cm}$$

$$= 8.45 \times 10^{-8} \text{ cm.}$$

Problem 3. (In C.G.S. units). *Calculate the velocity of an electron in the 3rd orbit of hydrogen atom ($\pi = 3.14$, $h = 6.6208 \times 10^{-27}$ erg-s, $e = 4.8029 \times 10^{-10}$ esu).* *(Raj. B.Sc. I 1983)*

Solution. v_n is given by :

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

$$\therefore \quad v_3 = \frac{2.188 \times 10^8}{3} \text{ cm.s}^{-1}$$

$$= 0.728 \times 10^8 \text{ cm.s}^{-1}$$

Problem 4. (In S.I. units). *The solitary electron in H-atom revolves in 2nd energy level. Calculate (i) The energy of the electron in this level (ii) Bohr's radius corresponding to this level. Given that $m = 9.109 \times 10^{-31}$ kg, $e = 1.602 \times 10^{-19}$ C, $\in_0 = 8.85 \times 10^{-12}$, $c = 3.0 \times 10^8$ m.s^{-1} and $h = 6.626 \times 10^{-34}$ J.s.*

Solution. We know that :

$$E_n = -\frac{me^4}{8 \in_0^{\,2} n^2h^2}$$

Substituting the values of different quantities

$$E_n = -\frac{9.109 \times 10^{-31} \times (1.602 \times 10^{-19})^4}{8 \times (8.85 \times 10^{-12})^2 \times 2^2 \times (6.626 \times 10^{-34})^2} \text{ J/atom}$$

$$= -5.45 \times 10^{-19} \text{ J/atom}$$

$$= -5.45 \times 10^{-19} \times 6.023 \times 10^{23} \text{ J/mole}$$

$$= -\frac{5.45 \times 10^{-19} \times 6.023 \times 10^{23}}{10^3} \text{ kJ/mole}$$

$$= -338.33 \text{ kJ/mole}$$

Radius of 2*nd* energy level is given by :

$$r_2 = \frac{\epsilon_0 \times (2)^2 \times h^2}{\pi m e^2}$$

$$= \frac{(8.85\times10^{-12})\times4\times(6.626\times10^{-34})^2}{3.14\times(9.109\times10^{-31})\times(1.602\times10^{-19})^2} \text{ m}$$

$$= 2.115\times10^{-10} \text{ m}.$$

Problem 5. (In S.I. units). *The first ionisation energy of hydrogen is* 2.179×10^{-18} *J. Calculate the second ioniastion energy of helium atom.*

(*Delhi. B.Sc. Hons.* 1977)

Solution. Since the first ionisation energy of hydrogen is 2.179×10^{-18} J, energy associated with an electron in the 1st orbit of H atom is equal to 2.179×10^{-18} J; *i.e.*

$$E_1 = \frac{me^4}{8\epsilon_0^2 n^2 h^2} = 2.179\times10^{-18} \text{ J}$$

Now second ionisation energy of He atom corresponds to the removal of one electron from He^+ ion and this electron will be removed from 1st orbit of He atom, since the electronic configuration of He atom is 2.

$\therefore$ Second ionisation energy of He atom ($Z = 2$)

= Energy of the electron in the first orbit of He atom

$$= \frac{me^4Z^2}{8\epsilon_0^2 n^2 h^2}$$

$$= 2.179 \times 10^{-18} \times Z^2 \text{ J}$$

$$= 2.179 \times 10^{-18} \times (2)^2 \text{ J}$$

$$= 8.716 \times 10^{-18} \text{ J}.$$

Origin of Hydrogen Spectrum on the Basis of Bohr's Theory

When an electronic discharge is passed through hydrogen gas filled in a discharge tube at a very low pressure, the molecules of hydrogen break into atoms. These atoms absorb energy from the electric spark and the solitary electron (present in 1st energy level) in different atoms of hydrogen gets *excited*, *i.e.*, the electron shifts from the energy level 1 (lowest energy level—*Ground state*) to different higher energy levels 2, 3, 4 etc. depending on the amount of energy absorbed by the atoms of hydrogen. The shifting of an electron from energy level 1 (*ground state*) to higher energy levels 2, 3, 4, 5, 6, 7, etc. (*Excited states*) has been shown in Fig. 1.35. These transitions are represented as $1\rightarrow2$, $1\rightarrow3$, $1\rightarrow4$, etc. respectively.

Now when the electron reaches in the higher energy levels, it is said to be in the excited state and hence has a tendency to come back to one of the lower energy levels or even to the lowest energy level (ground state) after a short interval of time, i.e. the electron which is unstable in the. excited state comes back to one of the lower energy levels or even to the lowest energy level as shown

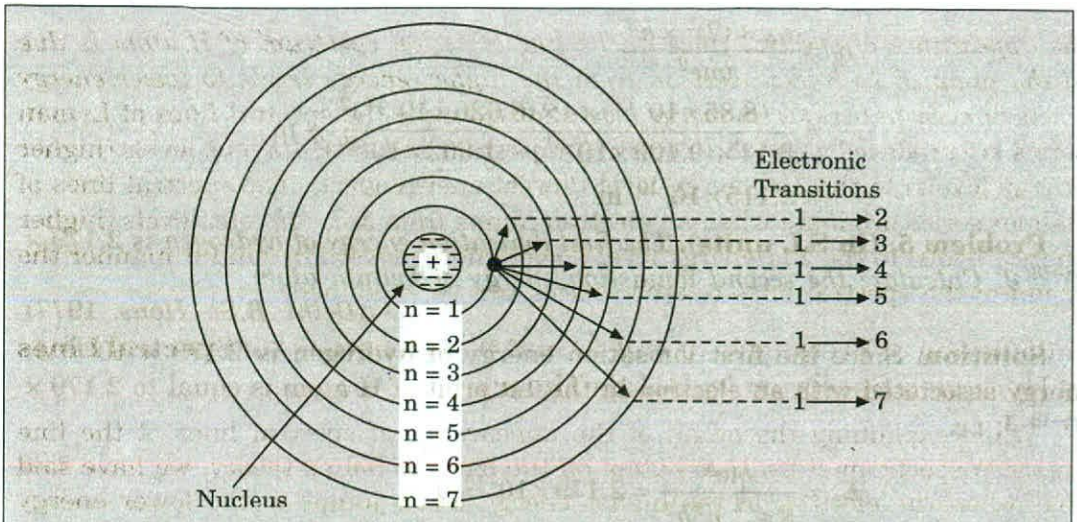


Fig. 1.35. Jump of hydrogen electron (shown by black circle) from the lowest energy level 1 (n = 1, ground state) to higher energy levels 2 (n = 2), 3 (n = 3), 4 (n = 4), 5 (n = 5), 6 (n = 6) and 7 (n = 7), etc.

in Fig. 1.36. When the electron in the excited state comes back to the lower energy levels, it *emits* energy it had absorbed earlier, in the form of photons of light of specific frequency and hence of specific wavelength. Thus spectral lines of different series observed in the emission spectrum of hydrogen are due to the emission of energy photons of different wavelengths when the excited electron in hydrogen atom comes back to lower energy levels. In simple words we say that

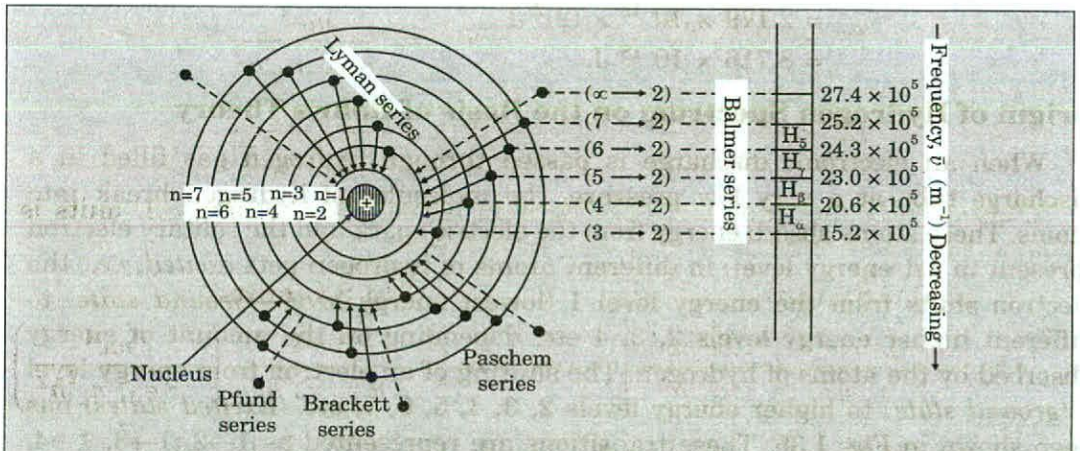


Fig. 1.36. Origin of hydrogen spectrum on the basis of Bohr's theory. This figure shows the jump of hydrogen electron (shown by black circle from higher energy levels to lower energy levels or even to the lowest energy level (n = 1) to produce spectral lines of various series. The jump of the electron from infinity to lower energy levels has been shown by dotted line and gives the limiting spectral line of each series. The frequency of the spectral lines of the Balmer series have also been shown.

the appearance of spectral lines in the line emission spectrum of H-atom is due to the jump of hydrogen electron from the higher energy levels to lower energy levels or even to the lowest energy level. For example the spectral lines of Lyman series are produced when the electron jumps from 2*nd*, 3*rd*, 4*th*, etc. levels (higher energy levels) to the 1*st* energy level (lowest energy level). The spectral lines of Balmer series originate when an electron jumps from 3*rd*, 4*th*, etc. levels (higher energy levels) to the 2*nd* energy level (lower energy level). In similar manner the origin of the spectral lines of other series can be explained.

Calculation of Frequency (υ and $\bar{\upsilon}$) and Wavelength (λ) of Spectral Lines of Hydrogen Spectrum by Bohr's Theory

While explaining the origin of the appearance of spectral lines of the line emission spectrum of hydrogen atom on the basis of Bohr's theory, we have said that when the electron in the higher energy levels jumps to the lower energy levels or to the lowest energy level, energy is liberated by the electron in the form of photon of light of specific frequency and wavelength which appears as spectral line in the spectrum. Frequency and wavelength of a spectral line depends on the quantity of energy liberated by the electron. Now suppose that an electron jumps from a higher energy level n_2 with energy E_{n_2} to a lower energy level n_1 whose energy is E_{n_1}. In this process of jumping the amount of energy liberated by the electron is equal to $E_{n_2} - E_{n_1}$. Now let us calculate the value of $E_{n_2} - E_{n_1}$ in terms of C.G.S. and S.I. units as follows :

In C.G.S. units	**In S.I. units**
$E_{n_1} = -\frac{2\pi^2 me^4}{n_1^2 h^2}$	$E_{n_1} = -\frac{me^4}{8\epsilon_0^2 n_1^2 h^2}$
$E_{n_2} = -\frac{2\pi^2 me^4}{n_2^2 h^2}$	$E_{n_2} = -\frac{me^4}{8\epsilon_0^2 n_2^2 h^2}$

Consequently the value of $\left(E_{n_2} - E_{n_1}\right)$ in terms of C.G.S. and S.I. units is given as :

In C.G.S. units	**In S.I. units**
$E_{n_2} - E_{n_1} = -\frac{2\pi^2 me^4}{n_2^2 h^2} - \left(-\frac{2\pi^2 me^4}{n_1^2 h^2}\right)$	$E_{n_2} - E_{n_1} = -\frac{me^4}{8\epsilon_0 n_2^2 h^2} - \left(-\frac{me^4}{8\epsilon_0^2 n_1^2 h^2}\right)$
$= \frac{2\pi^2 me^4}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$	$= \frac{me^4}{8\epsilon_0^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

(*a*) Calculation of frequency (υ). We know that if υ is the frequency of the emitted spectral line in hydrogen spectrum, then

$$h\upsilon = E_{n_2} - E_{n_1}$$

(*a*) *In C.G.S. units,* $h\upsilon = \frac{2\pi^2 me^4}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

$$\therefore \quad \upsilon = \frac{2\pi^2 me^4}{h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

On substituting $\pi = 3.14$; $m = 9.108 \times 10^{-28}$ g; $e = 4.8 \times 10^{-10}$ *esu* and $h = 6.624 \times 10^{-27}$ erg-s in the above equation, we get the value of $2\pi^2 me^4/h^3$ to be equal to 3.2906×10^{15} cycles/s. Thus the frequency (υ) of the spectral line emitted when the electron falls from energy level n_2 to energy level n_1 is given by :

$$\upsilon_{n_2 \to n_1} = \frac{2\pi^2 me^4}{h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{ cycles/sec}$$

$$\text{or} \quad \upsilon_{n_2 \to n_1} = 3.2906 \times 10^{15}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{ cycles/sec}$$

Any of the above equations can be used to calculate the value of υ in C.G.S. units.

(b) In S.I. units, $$h\upsilon = \frac{me^4}{8\epsilon_0^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\therefore \quad \upsilon = \frac{me^4}{8\epsilon_0^2 h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

On substituting $m = 9.108 \times 10^{-31}$ kg;
$e = 1.602 \times 10^{-19}$ C;
$\epsilon_0 = 8.85 \times 10^{-12}$;
$h = 6.624 \times 10^{-34}$ J-s.

we get the value of $me^4/8\epsilon_0^2 h^3$ to be equal to 3.2906×10^{15} Hz. Thus :

$$\therefore \quad \upsilon_{n_2 \to n_1} = \frac{me^4}{8\epsilon_0^2 h^3}\left(\frac{1}{n_1^1} - \frac{1}{n_2^2}\right) \text{Hz}$$

$$\text{or} \quad \upsilon_{n_2 \to n_1} = 3.2906 \times 10^{15}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{Hz}$$

Any of the above equations can be used to calculate the value of υ in S.I. units. It may be noted that the values of υ obtained in both the units (C.G.S. and S.I. units) are the same.

***(b)* Calculation of frequency in wave number ($\bar{\upsilon}$).** We know that $\bar{\upsilon}$ is given by :

$$\bar{\upsilon} = \frac{\text{Frequency } (\upsilon)}{\text{Velocity of light } (c)}$$

Now $$\upsilon = \frac{2\pi^2 me^4}{h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \textit{(in C.G.S. units).}$$

Dividing both sides of the equation by c, we get :

$$\frac{\upsilon}{c} = \frac{2\pi^2 me^4}{h^3 c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Now since

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

$$\therefore \quad \bar{\upsilon} = \frac{2\pi^2 me^4}{h^3 c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \textit{(in C.G.S. units).}$$

In this equation the expression $2\pi^2 m e^4/h^3c$ is called *Rydberg's constant*, R and hence the equation reduces to :

$$\bar{\upsilon} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \textit{ (in C.G.S. units)} \qquad ...(1)$$

Equation (1) gives the value of $\bar{\upsilon}$ in C.G.S. units. By putting $\pi = 3.14$; $m = 9.108 \times 10^{-28}$ g; $e = 4.8 \times 10^{-10}$ *e.s.u.*; $h = 6.624 \times 10^{-27}$ erg-s; $c = 3 \times 10^{10}$ cm-s^{-1}, the value of R in C.G.S. units has been obtained to be equal to 109.686×10^3 cm^{-1}. Thus :

$$\bar{\upsilon} = \frac{2\pi^2 me^4}{h^3 c}\left(\frac{1}{n_1^1} - \frac{1}{n_2^2}\right) \text{cm}^{-1}$$

$$\text{or} \quad \bar{\upsilon} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{cm}^{-1} \qquad ...(2)$$

$$\text{or} \quad \bar{\upsilon} = 109.686 \times 10^3 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{cm}^{-1}$$

Any of the above equations can be used to calculate the value of $\bar{\upsilon}$ in C.G.S. units.

On similar grounds it can be shown that the value of $\bar{\upsilon}$ in S.I. units is given by :

$$\bar{\upsilon} = \frac{me^4}{8\epsilon_0^2 h^3 c}\left(\frac{1}{n_1^1} - \frac{1}{n_2^2}\right) \textit{ (in S.I. units).}$$

By putting $m = 9.108 \times 10^{-3}$ kg; $e = 1.602 \times 10^{-19}$ *C*; $\epsilon_0 = 8.85 \times 10^{-12}$; $h = 6.624 \times 10^{-34}$ J-s and $c = 3 \times 10^8$ m.s^{-1}, the value of R in S.I. units has been obtained to be equal to 109.686×10^5 m^{-1}. Thus :

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

$$\text{or} \quad \bar{\upsilon} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{m}^{-1} \qquad ...(3)$$

$$\text{or} \quad \bar{\upsilon} = 109.686 \times 10^5 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{m}^{-1}$$

Any of the above equations can be used to calculate the value of $\bar{\upsilon}$ in S.I. units.

(c) Calculation of wavelength (λ). We know that wavelength (λ) of a spectral line in hydrogen spectrum is given by any of the following relations :

$$\lambda = \frac{1}{\text{Frequency in wave number } (\bar{\upsilon})} = \frac{1}{\bar{\upsilon}} \qquad ...(1)$$

$$\lambda = \frac{\text{Velocity of height } (c)}{\text{Frequency } (\upsilon)} = \frac{c}{\upsilon} \qquad ...(2)$$

Any of the above relations can be used to calculate the value of λ. Considering equation (1) we have (in C.G.S. units)

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

$$= \frac{1}{\dfrac{2\pi^2 me^4}{h^3 c}\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right] \text{cm}^{-1}}$$

Now we know that $\dfrac{2\pi^2 me^4}{h^3 c} = R = 109.686 \times 10^3 \text{ cm}^{-1}$

$$\therefore \quad \lambda = \frac{1}{\dfrac{2\pi^2 me^4}{h^3 c}\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]} \text{ cm}$$

$$= \frac{1}{R\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]} \text{ cm}$$

$$= \frac{1}{109.686 \times 10^3 \left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]} \text{ cm}$$

Any of the above three equations can be used to calculate the value of λ in C.G.S. units. Similarly in S.I. units λ can be calculated by any of the following relations :

$$\lambda = \frac{1}{\dfrac{me^4}{8\varepsilon_0^2 h^3 c}\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]} \text{ m}$$

$$= \frac{1}{R\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]} \text{ m}$$

$$= \frac{1}{109.686 \times 10^5 \left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]} \text{ m}$$

Calculation of Frequencies in Terms of Wave-number, $\bar{\upsilon}$ (in m^{-1}) of Different Spectral Lines of Different Series of Hydrogen Spectrum.

We have already shown that the frequency in terms of wave number, $\bar{\upsilon}$ (in m^{-1}) of a spectral line of a given series appearing in the hydrogen spectrum is given by :

$$\bar{\upsilon} = \frac{me^4}{8\varepsilon_0^{\,2}h^3c}\left(\frac{1}{n_1^{\,2}} - \frac{1}{n_2^{\,2}}\right) m^{-1}$$

$$= R\left(\frac{1}{n_1^{\,2}} - \frac{1}{n_2^{\,2}}\right) m^{-1}$$

$$= 10.9686 \times 10^6 \left(\frac{1}{n_1^{\,2}} - \frac{1}{n_2^{\,2}}\right) m^{-1}$$

or
$$\bar{\upsilon} = 109.686 \times 10^5 \left(\frac{1}{n_1^{\,1}} - \frac{1}{n_2^{\,2}}\right) m^{-1} \quad ...(1)$$

Now let us use equation (1) for the calculation of frequencies of spectral lines of various series as follows :

1. Lyman series. The various spectral lines of this series are obtained when an electron jumps from the *2nd, 3rd, 4th* or any other *higher energy level* to the *1st energy level.* Thus the frequencies of various spectral lines of this series can be obtained by putting $n_1 = 1$ and $n_2 = 2, 3, 4 \ldots\ldots \infty$ in equation (1) given above.

(*a*) *First line.* For this line $n_1 = 1$ and $n_2 = 2$, and hence :

$$\bar{\upsilon} = 109.686 \times 10^5 \left(\frac{1}{1^2} - \frac{1}{2^2}\right) m^{-1}$$

$$= 82.26 \times 10^5 \ m^{-1}$$

(*b*) *Second line.* For this line $n_1 = 1$ and $n_2 = 3$, and hence :

$$\bar{\upsilon} = 109.686 \times 10^5 \left(\frac{1}{1^2} - \frac{1}{3^2}\right) m^{-1}$$

$$= 97.49 \times 10^5 \ m^{-1}$$

(*c*) *Limiting line.* For this line $n_1 = 1$ and $n_2 = \infty$, and hence :

$$\bar{\upsilon} = 109.686 \times 10^5 \left(\frac{1}{1^2} - \frac{1}{\infty^2}\right) m^{-1}$$

$$= 109.686 \times 10^5 \ m^{-1}$$

On similar lines of calculations the frequencies of other lines can also be calculated.

2. Balmer series. The various spectral lines of this series are obtained when an electron jumps from *3rd, 4th, 5th etc.*, energy levels to *2nd* energy level. Thus the frequencies of various spectral lines of this series can be obtained by putting $n_1 = 2$ and $n_2 = 3, 4, 5 \ldots\ldots \infty$ in equation (1) given above.

(*a*) *First line* (H_α *line*). For this line $n_1 = 2$ and $n_2 = 3$, and hence :

$$\bar{\upsilon} = 109.686 \times 10^5 \left(\frac{1}{2^2} - \frac{1}{3^2} \right) \text{m}^{-1}$$

$$= 15.234 \times 10^5 \text{ m}^{-1}$$

(*b*) *Second line* (H_β *line*). For this line $n_1 = 2$ and $n_2 = 4$, and hence :

$$\bar{\upsilon} = 109.686 \times 10^5 \left(\frac{1}{2^2} - \frac{1}{4^2} \right) \text{m}^{-1}$$

$$= 20.566 \times 10^5 \text{ m}^{-1}$$

(*c*) *Limiting line.* For this line $n_1 = 2$ and $n_2 = \infty$, and hence :

$$\bar{\upsilon} = 109.686 \times 10^5 \left(\frac{1}{2^2} - \frac{1}{\infty^2} \right) \text{m}^{-1}$$

$$= \frac{109.686 \times 10^5}{4} \text{ m}^{-1}$$

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

On similar lines of calculations the frequencies of other lines can also be calculated.

3. Paschen series. The various spectral lines of this series originate from the electronic jumps from the *4th, 5th, 6th* etc., energy levels to the *3rd* energy level. Thus the frequencies of various spectral lines of this series can be obtained by putting $n_1 = 3$ and $n_2 = 4, 5, 6 \ldots\ldots \infty$ in equation (1) given above.

(*a*) *First line.* For this line $n_1 = 3$ and $n_2 = 4$, and hence :

$$\bar{\upsilon} = 109.686 \times 10^5 \left(\frac{1}{3^2} - \frac{1}{4^2} \right) \text{m}^{-1}$$

$$= 5.331 \times 10^5 \text{ m}^{-1}$$

(*b*) *Second line.* For this line $n_1 = 3$ and $n_2 = 5$, and hence :

$$\bar{\upsilon} = 109.686 \times 10^5 \left(\frac{1}{3^2} - \frac{1}{5^2} \right) \text{m}^{-1}$$

$$= 7.799 \times 10^5 \text{ m}^{-1}$$

(*c*) *Limiting line.* For this line $n_1 = 3$ and $n_2 = \infty$, and hence :

$$\bar{\upsilon} = 109.686 \times 10^5 \left(\frac{1}{3^2} - \frac{1}{\infty^2} \right) \text{m}^{-1}$$

$$= \frac{109.686 \times 10^5}{9} \text{ m}^{-1}$$

$$= 12.187 \times 10^5 \text{ m}^{-1}$$

On similar lines the frequencies of other lines can also be calculated.

4. Brackett series. The various spectral lines of this series originate when an electron jumps from *5th, 6th, 7th* etc. energy levels to *4th* energy level. Thus the

frequency of various spectral lines of this series can be obtained by putting $n_1 = 4$ and $n_2 = 5, 6, ...\infty$ in equation (1).

(*a*) *First line.* For this line $n_1 = 4$ and $n_2 = 5$, and hence :

$$\bar{\upsilon} = 109.686 \times 10^5 \left(\frac{1}{4^2} - \frac{1}{5^2} \right) m^{-1}$$
$$= 2.45 \times 10^5 \ m^{-1}$$

(*b*) *Second line.* For this line $n_1 = 4$ and $n_2 = 6$, and hence :

$$\bar{\upsilon} = 109.686 \times 10^5 \left(\frac{1}{4^2} - \frac{1}{6^2} \right) m^{-1}$$
$$= 3.808 \times 10^5 \ m^{-1}$$

(*c*) *Limiting line.* For this line $n_1 = 4$ and $n_2 = \infty$, and hence :

$$\bar{\upsilon} = 109.686 \times 10^5 \left(\frac{1}{4^2} - \frac{1}{\infty^2} \right) m^{-1}$$
$$= \frac{109.686 \times 10^5}{16} \ m^{-1}$$
$$= 6.855 \times 10^5 \ m^{-1}$$

5. Pfund series. The various spectral lines of this series originate when an electron jumps from *6th, 7th, 8th* etc. energy levels to *5th* energy level. Thus the frequency of various spectral lines of this series can be obtained by putting $n_1 = 5$ and $n_2 = 6, 7, 8..... \infty$ in equation (1).

(*a*) *First line.* For this line $n_1 = 5$ and $n_2 = 6$, and hence :

$$\bar{\upsilon} = 109.686 \times 10^5 \left(\frac{1}{5^2} - \frac{1}{6^2} \right) m^{-1}$$
$$= 1.340 \times 10^5 \ m^{-1}$$

(*b*) *Second line.* For this line $n_1 = 5$ and $n_2 = 7$, and hence :

$$\bar{\upsilon} = 109.686 \times 10^5 \left(\frac{1}{5^2} - \frac{1}{7^2} \right) m^{-1}$$
$$= 2.148 \times 10^5 \ m^{-1}$$

(*c*) *Limiting line.* For this line $n_1 = 5$ and $n_2 = \infty$, and hence :

$$\bar{\upsilon} = 109.686 \times 10^5 \left(\frac{1}{5^2} - \frac{1}{\infty^2} \right) m^{-1}$$
$$= \frac{109.686 \times 10^5}{25} \ m^{-1}$$
$$= 4.387 \times 10^5 \ m^{-1}.$$

The calculated values of the frequencies in terms of wave numbers, $\bar{\upsilon}$ (in m^{-1}) of the various spectral lines of all the five series of hydrogen spectrum and those determined experimentally have been given in Table 1.5. In the same table the values of n_1 and n_2, different types of electronic jumps due to which the various

spectral lines are produced, etc. are also given. It may be seen from this table that there is an excellent agreement between the calculated and experimental values of frequency. *This excellent agreement offers another strong support to Bohr's theory of hydrogen spectrum.*

Table 1.5. Calculated and experimental values of frequency in terms of wave number, $\bar{\upsilon}$ (in m^{-1}) of various spectral lines of different series of hydrogen spectrum.

Spectral series	Frequency (m^{-1}) of various spectral lines		Values of n_1 and n_2 for various spectral lines the		Electronic jumps producing spectral lines
	Calculated (by Bohr)	Experimental	n_1	n_2	
1. Lyman series (Ultraviolet region)	82.26×10^5 97.49×10^5 102.80×10^5 105.20×10^5 106.30×10^5 107.20×10^5	82.20×10^5 97.60×10^5 102.70×10^5 105.20×10^5 106.20×10^5 107.10×10^5	1	2 3 4 5 6 7	$2 \rightarrow 1$ $3 \rightarrow 1$ $4 \rightarrow 1$ $5 \rightarrow 1$ $6 \rightarrow 1$ $7 \rightarrow 1$
2. Balmer series (Visible region)	15.23×10^5 (H_α line) 20.56×10^5 (H_β line) 23.00×10^5 (H_γ line) 24.30×10^5 (H_δ line) 25.20×10^5	15.21×10^5 (H_α line) 20.60×10^5 (H_β line) 23.05×10^5 (H_γ line) 24.35×10^5 (H_δ line) 25.18×10^5	2	3 4 5 6 7	$3 \rightarrow 2$ $4 \rightarrow 2$ $5 \rightarrow 2$ $6 \rightarrow 2$ $7 \rightarrow 2$
3. Paschen series (Infra-red region)	5.33×10^5 7.79×10^5 9.13×10^5 9.95×10^5	5.30×10^5 7.80×10^5 9.12×10^5 9.95×10^5	3	4 5 6 7	$4 \rightarrow 3$ $5 \rightarrow 3$ $6 \rightarrow 3$ $7 \rightarrow 3$
4. Brackett series (Infra-red region)	2.45×10^5 3.80×10^5 4.61×10^5	2.46×10^5 3.80×10^5 4.61×10^5	4	5 6 7	$5 \rightarrow 4$ $6 \rightarrow 4$ $7 \rightarrow 4$
5. Pfund series (Infra-red region)	1.34×10^5 2.14×10^5	1.34×10^5 2.14×10^5	5	6 7	$6 \rightarrow 5$ $7 \rightarrow 5$

Derivation of Rydberg's Equation from Bohr's Theory

We have already seen that, before Bohr's theory came to be known, Rydberg suggested that the wavelength (in terms of wave number, $\bar{\upsilon}$) of various lines in Lyman series, Balmer series etc. of hydrogen spectrum could be calculated with the help of the following empirical equation which is called Rydberg's equation.

$$\bar{\upsilon} = R\left(\frac{1}{x^2} - \frac{1}{y^2}\right) m^{-1} \text{ (Rydberg s equation)} \qquad ...(1)$$

Here R is a constant which is called Rydberg's constant and its experimental value, as determined by Ritz, is 109.678×10^3 cm^{-1} or 109.678×10^5 m^{-1}, and x and y are two simple whole numbers. Later on Bohr obtained the above equation directly with the help of his theory. This is shown below :

We have seen that Bohr, with the help of his theory, deduced the following equations for the calculation of frequency in wave number, $\bar{\upsilon}$ (in cm^{-1} or m^{-1}) of a spectral line of a given series.

$$\left.\begin{aligned}\bar{\upsilon} &= \frac{2\pi^2 me^4}{h^3 c}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) \text{ cm}^{-1} \text{ (in C.G.S. units)} \quad ...(2)\\ \bar{\upsilon} &= \frac{me^4}{8\varepsilon_0^2 h^3 c}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) \text{m}^{-1} \text{ (in S.I. units)} \quad ...(3)\end{aligned}\right\} \text{(Bohr s equations)}$$

It is obvious that Bohr's equations are equivalent to Ritz equation (1), if $x = n_1$, $y = n_2$ and $R = 2\pi^2 me^4/h^3 c$ (in C.G.S. units) or $me^4/8\varepsilon_0^2 h^3 c$ (in S.I. units). Now let us calculate the value of R in both units.

(*a*) *In C.G.S. units.* The value of R is obtained by putting $\pi = 3.14$; $m = 9.108 \times 19^{-28}$ g; $e = 4.8 \times 10^{-19}$ esu; $h = 6.624 \times 10^{-27}$ erg-s; $c = 3 \times 10^{10}$ cm . s^{-1} in

$$R = \frac{2\pi^2 me^4}{h^3 c}$$

$$= \frac{2\times(3.14)^2\times(9.108\times10^{-28})\times(4.8\times10^{-10}\text{ esu})^4}{(6.624\times10^{-27}\text{ erg-s})^3\times(3\times10^{10}\text{ cm.s}^{-1})}$$

$$= 109.686\times10^3 \text{ cm}^{-1}.$$

(*b*) *In S.I. units.* The value of R is obtained by. putting $m = 9.108 \times 10^{-31}$ kg; $e = 1.602 \times 10^{-19}$ C; $\varepsilon_0 = 8.85 \times 10^{-12}$, $h = 6.624 \times 10^{-34}$ J-s; $c = 3 \times 10^8$ m.s^{-1} in

$$R = \frac{me^4}{8\varepsilon_0^2 h^3 c}$$

$$= \frac{(9.108\times10^{-31}\text{ kg})\times(1.602\times10^{-19}\text{ C})^4}{8\times(8.85\times10^{-12})^2\times(6.624\times10^{-34})^3\times(3\times10^3\text{ m.s}^{-1})}$$

$$= 109.686\times10^5 \text{ m}^{-1}.$$

Thus we find that the calculated value of R in both the units is the same and agrees closely with the experimental value (= 109.678 × 10^3 cm or 109.678 × 10^5 m^{-1}) obtained by Ritz. The agreement between the theoretical value of R as calculated by Bohr and that obtained experimentally by Ritz gives a further support to Bohr's theory.

Derivation of Mosley's Equation by Bohr's Theory

We have seen that Mosley, while working on X-rays, showed that the square root of the frequency ($\sqrt{\upsilon}$) of a line of a given series of characteristic X-ray spectrum is related to the atomic number (Z) of the element used as anticathode (target material) by the following equation which is called Mosley's equation :

$$\sqrt{\upsilon} = a(Z - b) \quad ...(1)$$

Here *a* is a proportionality constant and b is another constant which is called *screening constant* and takes into account the screening effect of electrons. The above equation can also be derived by Bohr's theory as follows :

We have seen that according to Bohr's theory, when an electron in an atom with atomic number, Z jumps from an orbit n_2 to the orbit n_1, the frequency (υ) of radiation given out is given by :

$$\upsilon = \frac{2\pi^2 Z^2 me^4}{h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{ cycles/s}$$

$$= \frac{2\pi^2 me^4}{h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right).Z^2 \text{ cycles/s}$$

Thus :

$$\upsilon \alpha Z^2$$

or $$\sqrt{\upsilon} \alpha Z$$

Now if the screening constant, b which takes into account the screening effect of the electrons, is considered, the above relation becomes

$$\sqrt{\upsilon} \alpha (Z - b)$$

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

This equation is the same, as equation (1) given above.

Numerical Problems

Problem 1 (In C.G.S. units). *A spectral line in the Lyman series of hydrogen atom has a frequency of 82, 200 cm^{-1}. What transition is responsible for this radiation? (R = 109,600 cm^{-1})* *(Raj. B.Sc. I 1982)*

Solution. We know that the frequency of various spectral lines of Lyman series of hydrogen spectrum can be obtained by putting $n_1 = 1$ and $n_2 = 2, 3$, etc. in the following equation :

$$\bar{\upsilon} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{cm}^{-1}$$

Substituting $\bar{\upsilon}$ = 82,200, R = 109,600 and $n_1 = 1$ in the above equation we get :

$$82200 = 109600\left(\frac{1}{1^2} - \frac{1}{n_2^2}\right)$$

From this equation $n_2 = 2$ which means that the spectral line having $\bar{\upsilon}$ = 82200 cm^{-1} originates from the jump of the electron from 2*nd* orbit ($n = 2$) to 1*st* orbit ($n = 1$)

Problem 2 (In C.G.S. units). *Calculate the wavelength of light emitted from hydrogen for the electronic transmission for energy level $n = 3$ to $n = 2$ (R = 109,678 cm^{-1})* *(Raj. P.M.T. 1981)*

Solution. We know that wavelength λ is given by :

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

Substituting R = 109678, $n_1 = 2$ and $n_2 = 3$ in the above equation, we get :

$$\lambda = \frac{1}{109678\left[\frac{1}{2^2} - \frac{1}{3^2}\right]} \text{ cm}$$

$$= \frac{36}{109678 \times 5} = \frac{36}{109.678 \times 10^3 \times 5}$$

$$= \frac{36}{548.390 \times 10^3}$$

$$= 0.0656 \times 10^{-3} \text{ cm}$$

Problem 3. *Calculate the frequency of the line in the emission spectrum of hydrogen when the atoms of the gas contain electrons in the 3rd energy level.* (*Delhi B.Sc. Hons. Part I 1974*)

Solution. (*a*) *When the electron falls from 3rd energy to 2nd energy level, i.e.* $n_1 = 2$ *and* $n_2 = 3$.

$$\therefore \quad \upsilon_{3\to2} = 3.290 \times 10^{15}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{Hz}$$

or $$= 3.290 \times 10^{15}\left(\frac{1}{2^2} - \frac{1}{3^2}\right) \text{Hz}$$

$$\therefore \quad = 0.4569 \times 10^{15} \text{ Hz}$$

(*b*) *When the electron falls from 3rd energy level to 1st energy level i.e.* $n_1 = 1$ *and* $n_2 = 3$.

$$\therefore \quad \upsilon_{3\to1} = 3.290 \times 10^{5}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{Hz}$$

$$= 3.290 \times 10^{15}\left(\frac{1}{1^2} - \frac{1}{3^2}\right) \text{Hz}$$

or $$= 2.924 \times 10^{15} \text{ Hz}$$

Problem 4 (In S.I. units). *Calculate the wave number and wavelength of the sepctral line observed in hydrogen spectrum with* $n_1 = 2$ *and* $n_2 = 3$. *The value of Rydberg's constant (R) =* $109.686 \times 10^6\ m^{-1}$.

To which line does this line correspond in the spectral lines of Balmer series?

Solution. Substituting the values of n_1, n_2 and R in

$$\bar{\upsilon} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) m^{-1}$$

$$= 109.686 \times 10^5\left[\frac{1}{2^2} - \frac{1}{3^2}\right] \text{m}^{-1}$$

$$= \frac{109.686 \times 10^5 \times 5}{36}$$

$$= 15.234 \times 10^5 \text{ m}^{-1}$$

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

$$= \frac{1}{109.686 \times 10^5 \left[\frac{1}{2^2} - \frac{1}{3^2}\right]}$$

$$= \frac{36}{109.686 \times 10^5} \times 10^{-5} \text{ m}$$

$$= 0.0656 \times 10^{-5} \text{ m}$$

Quite obviously the spectral line with frequency, $\upsilon = 15.234 \times 10^5$ m^{-1} is Hα line in the Balmer series of hydrogen spectrum.

Problem 5. (In S.I. units). *Calculate the wave number and the energy of the spectral line in the hydrogen spectrum corresponding to $n_1 = 3$ and $n_2 = 5$. The value of Rydberg's constant (R) = 10.97 × 10^6 m^{-1}.*

Solution. Substituting the values of n_1, n_2 and R in

$$\bar{\upsilon} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{m}^{-1}$$

$$= 10.97 \times 10^6 \left[\frac{1}{3^2} - \frac{1}{5^2}\right] \text{m}^{-1}$$

$$= \frac{10.97 \times 10^6 \times 16}{225} \text{ m}^{-1}$$

or $$= 7.80 \times 10^5 \text{ m}^{-1}$$

Now the energy (E) of the spectral line is given by Planck's equation *viz.*

$$E = h\upsilon = h.\frac{c}{\lambda} \qquad \left(\because \frac{1}{\lambda} = \frac{\upsilon}{c}\right)$$

or $$E = h.c\bar{\upsilon} \qquad \left(\because \bar{\upsilon} = \frac{1}{\lambda}\right)$$

Now on substituting h (Planck's constant) = 6.624 × 10^{-34} J-s, c (velocity of light) = 3 × 10^8 m/sec and $\bar{\upsilon}$ (wave number) = 7.8 × 10^5 m^{-1} (obtained as above) in the above equation, we get

$$\text{E} = hc\bar{\upsilon}$$
$$= (6.624 \times 10^{-34} \text{ J-s/} \times (3 \times 10^8 \text{ m.s}^{-1}) \times (7.8 \times 10^5 \text{ m}^{-1})$$
$$= 6.624 \times 3 \times 7.8 \times 10^{-21} \text{ J}$$
$$= 0.0624 \times 3 \times 7.8 \times 10^{-19} \text{ J}$$
$$= 1.55 \times 10^{-19} \text{ J}$$
$$= 1.55 \times 10^{-22} \text{ KJ}$$

Problem 6 (In S.I. units). *Energy in Bohr's orbit is given to be equal to $-A/n^2$, where A = 2.179 × 10^{-18} J. Calculate the frequency of radiation and also*

find out the wave number when the electron moves from the third orbit to the second orbit ($h = 6.62 \times 10^{-34}$ J-s). *(Delhi B.Sc. Hons. 1979)*

Solution. In S.I. units energy of nth Bohr's orbit is given by :

$$E_n = -\frac{me^4}{8\varepsilon_0^{\,2} n^2 h^2}$$

$$= -\frac{me^4}{8\varepsilon_0^{\,2} h^2} \cdot \frac{1}{n^2}$$

According to question,

$$E_n = -\frac{A}{n^2} = -2.179 \times 10^{-18} \times \frac{1}{n^2}$$

$$\therefore \quad \frac{me^4}{8\varepsilon_0^{\,2} h^2} = 2.179 \times 10^{-18}$$

or
$$\frac{me^4}{8\varepsilon_0^{\,2} h^2} \times \frac{1}{h} = \frac{2.179 \times 10^{-18}}{h} = \frac{2.179 \times 10^{-18}}{6.62 \times 10^{-34}}$$

$$= \frac{2.179 \times 10^{16}}{6.62}$$

$$= 3.29 \times 10^{15}$$

Now in S.I. units frequency, υ is given by :

$$\upsilon = \frac{me^4}{8\varepsilon_0^{\,2} h^2}\left[\frac{1}{n_1^{\,2}} - \frac{1}{n_1^{\,2}}\right] \text{Hz}$$

$$= 3.29 \times 10^{15}\left[\frac{1}{2^2} - \frac{1}{n_2^{\,2}}\right] \text{Hz}$$

Substituting $n_1 = 2$ and $n_2 = 3$ in the above equation, we get :

$$\upsilon = 3.29 \times 10^{15}\left[\frac{1}{2^2} - \frac{1}{3^2}\right] \text{Hz}$$

$$\therefore \quad = \frac{3.29 \times 10^{15} \times 5}{36} \text{ Hz} = 0.45 \times 10^{15} \text{ Hz}$$

Now wave number, $\bar{\upsilon}$ is given by :

$$\bar{\upsilon} = \frac{me^4}{8\varepsilon_0^{\,2} h^3 c}\left[\frac{1}{n_1^{\,2}} - \frac{1}{n_2^{\,2}}\right] \text{m}^{-1}$$

$$= \frac{3.29 \times 10^{15}}{3 \times 10^8}\left[\frac{1}{2^2} - \frac{1}{3^2}\right] \text{m}^{-1}$$

$$= \frac{3.29 \times 10^{15} \times 5}{3 \times 36 \times 10^8} \text{ m}^{-1}$$

$$= \frac{3.29 \times 5 \times 10^7}{3 \times 36} \text{ m}^{-1} = 1.52 \times 10^6 \text{ m}^{-1}$$

Problem 7 (In S.I. units). *Calculate the frequencies of lines in the emission spectrum of hydrogen when the atoms of the gas contain the electrons in the 3rd energy level. Calculate the wavelength of any one of these. The energy of hydrogen electron in the ground state is -2.18×10^{-18} J/atom. The value of Planck's constant is 6.625×10^{-34} J-s. Velocity of light is 3×10^8 m.s^{-1}.*

(Delhi B.Sc. Hons. Part I 1974; Mysore 1974)

Solution. Frequency (υ) of a spectral line is given by :

$$\upsilon = \frac{me^4}{8\varepsilon_0{}^2 h^3}\left(\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right) \text{Hz}$$

and energy of the electron in the ground state ($n = 1$) is given by :

$$E_1 = \frac{me^4}{8\varepsilon_0{}^2 \times (1)^2 \times h^2} = -2.18 \times 10^{-18} \text{ J/atom}$$

$$\therefore \quad \frac{me^4}{8\varepsilon_0{}^2 h^3} = \frac{2.18 \times 10^{-18}}{h} = \frac{2.18 \times 10^{-18}}{6.625 \times 10^{-34}} = \frac{2.18 \times 10^{16}}{6.625}$$

$$= \frac{21.8 \times 10^{15}}{6.625} = 3.29 \times 10^{15}$$

$$\therefore \quad \upsilon = 3.29 \times 10^{15}\left[\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right] \text{Hz}$$

Now the following cases are studied.

(a) When the electron falls from 3rd energy level to 2nd energy level, i.e. $n_2 = 3$ *and* $n_1 = 2$,

$$\therefore \quad \upsilon_{3\to2} = 3.29 \times 10^{15}\left(\frac{1}{2^2} - \frac{1}{3^2}\right) \text{Hz}$$

$$= \frac{3.29 \times 10^{15} \times 5}{36} \text{Hz}$$

$$= 0.456 \times 10^{15} \text{ Hz}$$

(b) When the electron falls from 2nd energy level to 1st energy level, i.e. $n_2 = 2$ *and* $n_1 = 1$.

$$\therefore \quad \upsilon_{2\to1} = 3.29 \times 10^{15}\left(\frac{1}{1^2} - \frac{1}{2^2}\right) \text{Hz}$$

$$= 3.29 \times 10^{15} \times 0.75 \text{ Hz}$$

$$= 2.46 \times 10^{15} \text{ Hz}$$

(c) The electron falls directly from 3rd energy level to 1st energy level, i.e., $n_2 = 3$ *and* $n_1 = 1$.

$$\therefore \quad \upsilon_{3\to1} = 3.29 \times 10^{15}\left(\frac{1}{1^2} - \frac{1}{3^2}\right) \text{Hz}$$

$$= \frac{3.29 \times 10^{15} \times 8}{9} \text{Hz}$$

$$= 2.92 \times 10^{15} \text{ Hz}$$

Problem 8 (In C.G.S. units). *Find the wavelength in A° of the line in Balmer series that is associated with drop of the electron from the fourth orbit. The value of Rydberg's constant is 109, 676 cm^{-1}.*

Solution. Here $n_1 = 2$, $n_2 = 3$ and R = 109676 cm^{-1}. The wavelengths (λ) of the lines in Balmer series are given by :

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

$$= \frac{1}{109676\left[\frac{1}{2^2} - \frac{1}{3^2}\right]} \text{ cm} = \frac{1 \times 36}{109676 \times 5} \text{ cm}$$

$$= 0.0000656 \text{ cm} = 6.56 \times 10^{-5} \text{ cm}$$

Defects of Bohr's Atomic Model

1. No explanation of fine structure—Existence of additional quantum numbers. We have seen that Bohr's theory had successfully explained the origin of hydrogen spectrum. But, when the hydrogen spectrum is observed by means of spectroscope of high resolving power, it is found that the individual spectral lines are not really single but consist of several very fine lines lying close together. For example H_α line in the Balmer series of hydrogen spectrum is found to consists of five component lines. Such a spectrum which consists of closely-spaced spectral lines is called **fine structure** or **multiple structure.** This fine structure of spectral lines in the hydrogen spectrum cannot be explained by Bohr's theory. Thus the appearance of the several lines in a single line suggests that only one quantum number *viz.*, principal quantum number (n) suggested by Bohr is not sufficient to explain the origin of various spectral lines. Rather, there are additional quantum numbers for a given principal quantum number. This, in other words, means that in a given orbit (or shell or energy level) there are several orbits (or shells or energy levels), called *sub-orbits* (or *sub-shells* or *sub-energy levels*), which are slightly different in energies.

2. No explanation for the spectra of multi-electron systems. Bohr's theory has successfully explained the origin of the spectrum of hydrogen atom and of hydrogen-like ions (*e.g.*, He^+, Li^{2+}, Be^{3+} etc.) which are *one-electron systems*, but it is not able to explain the origin of the spectrum of *many-electron* (or *multi-electron* or *poly-electron*) *systems*.

3. According to Bohr's theory the electrons move in circular orbits round the nucleus, but the modern researches have shown that the motion of the electron is not limited to a single plane but takes place in *three-dimensional space*. In other words, atomic model is not *flat* as suggested by Bohr, but has a *three-dimensional existence.*

4. No explanation for Zeeman and Stark effects. It has been observed that when an excited atom which gives a line emission spectrum is put in magnetic

field, its spectral lines are further split up into still thinner (*i.e.*, closely-spaced) lines. This type of splitting of spectral lines into a number of closely-spaced lines is called **Zeeman effect.** For example when the source producing sodium spectrum is placed in a weak magnetic field, D_1 and D_2 lines of the spectrum are found to split up into components (Fig. 1.37).

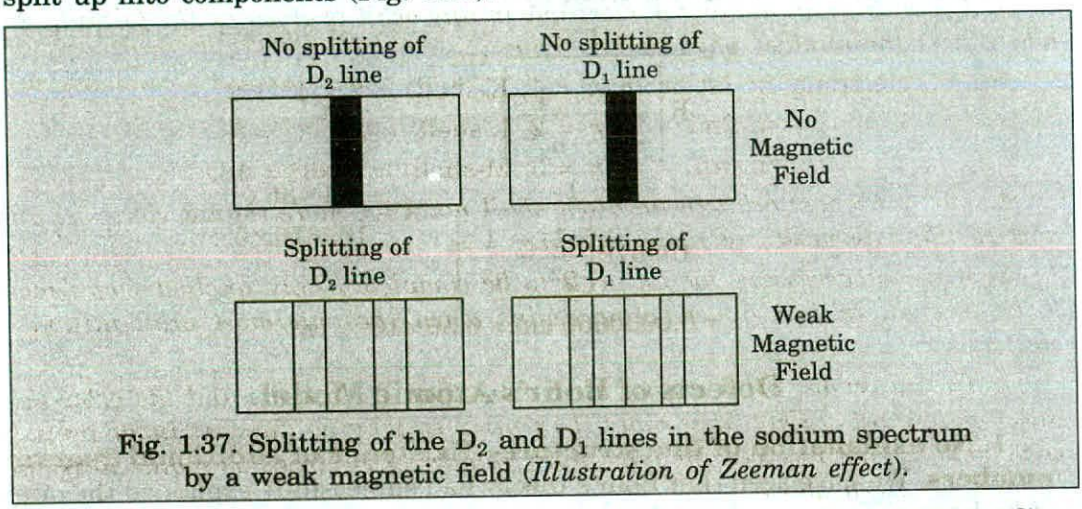


Fig. 1.37. Splitting of the D_2 and D_1 lines in the sodium spectrum by a weak magnetic field (*Illustration of Zeeman effect*).

Another similar splitting of the spectral lines into a number of thinner lines is also observed when the excited atom is placed in an electric field. This type of splitting is called **Stark effect.** Bohr's theory has no explanation for any of these effects.

5. Dual nature of electron and Heisenberg's uncertainty principle. We have seen that Bohr had assumed that an electron behaves as a *material particle* of small mass moving round the nucleus in fixed circular orbits. But de Broglie suggested that *an electron has a dual nature, i.e., an electron, like light, behaves both as a material particle and as a wave.*

We have also seen that Bohr had also assumed that an electron which is a material particle is revolving round the nucleus in circular orbits situated at *definite* (*i.e.*, fixed) distance from the nucleus and with a *definite velocity*. But any exact measurement of the position of an electron which also has a wave-like nature would create some uncertainty in the exact measurement of its velocity and vice-versa *i.e.*, for an electron it is impossible to measure simultaneously its exact position and exact velocity. This is called **Heisenberg's uncertainty principle** which can be stated as follows :

It is impossible to measure simultaneously the exact position and exact velocity of a sub-atomic particle like electron and neutron.

Thus we see that Bohr's assumption that an electron revolving in circular orbits situated at a fixed distance from nucleus and with fixed velocity is against the Heisenberg's uncertainty principle.

Bohr-Bury Scheme of Distribution of Electrons in Orbits

Having known that the number of planatory electrons in an atom is numerically equal to the atomic number of the element and they are revolving about the

nucleus in closed orbits, the question arises as to how these electrons are arranged in these orbits.

In 1912 Bohr and Bury simultaneously put forward two identical schemes for the distribution of electrons in orbits. This scheme is now called **Bohr-Bury scheme.** According to this scheme :

1. *The maximum number of electrons in any orbit is given by the formula* $2n^2$ *where n is the number of the orbit. Thus* :

No. of. electrons in 1st orbit (n = 1, K-shell) = $2 \times 1^2 = 2$
" " in 2nd " (n = 2, L-shell) = $2 \times 2^2 = 8$
" " in 3rd " (n = 3, M-shell) = $2 \times 3^2 = 18$.

2. *The outermost orbit in an atom shall not have more than 8 electrons and next to the outermost not more than 18.*

3. *It is not necessary for an orbit to be complete before another commences to be formed. In fact a new orbit begins when the outermost orbit attains 8 electrons.*

4. *The outermost orbit cannot have more than 2 electrons and the orbit next to the outermost cannot have more than nine, so long as the next inner orbit in each case has not received the maximum number of electrons as required by rule (1) and (2) given above.*

Electronic Configuration of Inert Gases

On the basis of Bohr-Bury scheme the configuration of the atoms of inert gases is given in a tabular form as follows :

Inert gas	Atomic number	Distribution of electrons in various orbits					
		1st (K)	2nd (L)	3rd (M)	4th (N)	5th (O)	6th (P)
Helium (He)	2	2					
Neon (Ne)	10	2	8				
Argon (Ar)	18	2	8	8			
Krypton (Kr)	36	2	8	18	8		
Xenon (Xe)	54	2	8	18	18	8	
Radon (Rn)	86	2	8	18	32	18	8

Sommerfeld's Extension of Bohr's Atomic Model : Bohr-Sommerfeld's Atomic Model

To account for the *fine structure* in the spectrum of hydrogen atom Sommerfeld extended Bohr's theory in 1915 and suggested *that the moving electron might describe, in addition to the circular orbits, elliptical orbits as well, with the nucleus situated at one of the focii of the ellipse.*

It is well known that in a circle, the only coordinate that changes is the angle of revolution, ϕ while the radial coordinate, r (*i.e.*, the radius) remains constant. In an elliptical orbit like that shown in Fig. 1.38, however, both the polar

coordinates *viz.*, radius vector, r (which is the distance of the electron from the nucleus situated at one of the focii, Z) and the vectorial angle, ϕ known as azimuthal angle (which is the angle between the radius vector and the major axis of the ellipse) change.

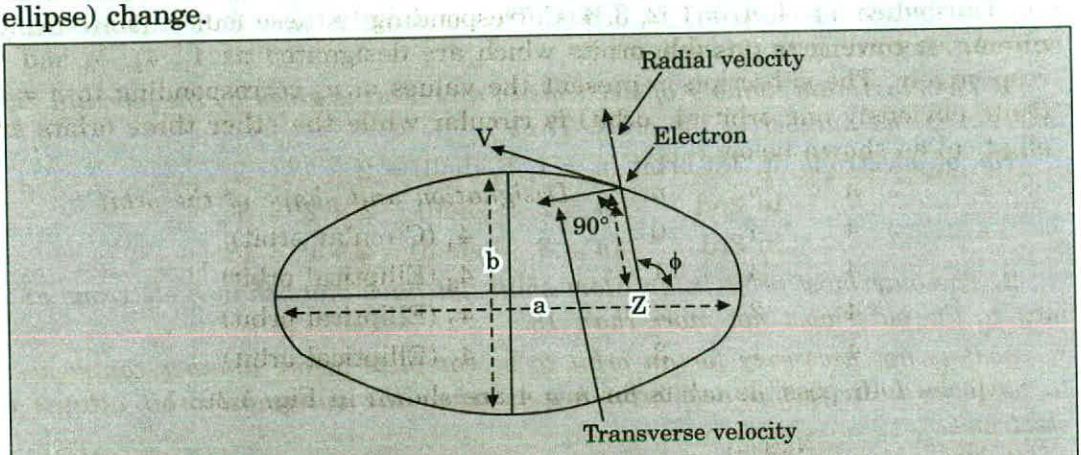


Fig. 1.38. Velocity of an electron in an elliptical orbit. a and b are the lengths of the ellipse. V represents the tangential velocity of the electron at any instant. Z is its the nucleus.

Now the tangential velocity, V of the electron at any instant can be resolved into two components one of which is along the radius vector and is called the *radial velocity* while the other is perpendicular to the radius vactor and is called *transverse* or *angular velocity*. These two velocities give rise to *radial momentum and angular* (or *azimuthal*) *momentum*. Sommerfeld assumed that these momentums must obey the quantum conditions, *i.e.*, these momentums must be integral multiple of $h/2\pi$. Thus :

$$\text{Radial momentum} = n_r \cdot \frac{h}{2\pi}$$

$$\text{Azimuthal momentum} = n_\phi \cdot \frac{h}{2\pi}$$

Here the integrals n_r and n_ϕ are two new quantum numbers which are called **radial quantum number** and **azimuthal quantum number** respectively. n_r and n_ϕ are related to Bohr's quantum number, n as follows :

$$n = n_r + n_\phi$$

n and n_ϕ are related to the geometry of the ellipse as :

$$\frac{n}{n_\varphi} = \frac{n_r + n_\varphi}{n_\varphi} = \frac{\textit{Length of the major axis } (a)}{\textit{Length of the minor axis } (b)} \qquad ...(i)$$

Now let us consider the following possibilities :

1. *When* $n_\phi = 0$. In this case the length of the minor axis (b) of the ellipse will also become equal to zero. In other words the electronic path will be a straight line passing through the nucleus, Z which is impossible. Thus n_ϕ *cannot be equal to zero.*

2. *When* $n_\phi > n$. In this case the length of the minor axis (b) will be greater than the length of the major axis (a). Thus n_ϕ *cannot be greater than* n.

3. *When* $n_\phi = n$. In this case a becomes equal to b and the orbit becomes circular. Thus circular orbit is a special case of elliptical orbit.

4. *When* $n_\phi < n$. In this case the orbit will remain elliptical.

Thus when $n = 4$, $n_\phi = 1, 2, 3, 4$. Corresponding to these four values of n_ϕ for $n = 4$, we have four possible orbits which are designated as 4_1, 4_2, 4_3 and 4_4 respectively. The subscripts represent the values of n_ϕ corresponding to $n = 4$. Quite obviously one orbit (4_4 orbit) is circular while the other three orbits are elliptical as shown below :

n	n_ϕ	n_r	*Designation and shape of the orbit*
4	4	0	4_4 (Circular orbit)
4	3	1	4_3 (Elliptical orbit)
4	2	2	4_2 (Elliptical orbit)
4	1	3	4_1 (Elliptical orbit)

All the four possible orbits for $n = 4$ are shown in Fig. 1.39.

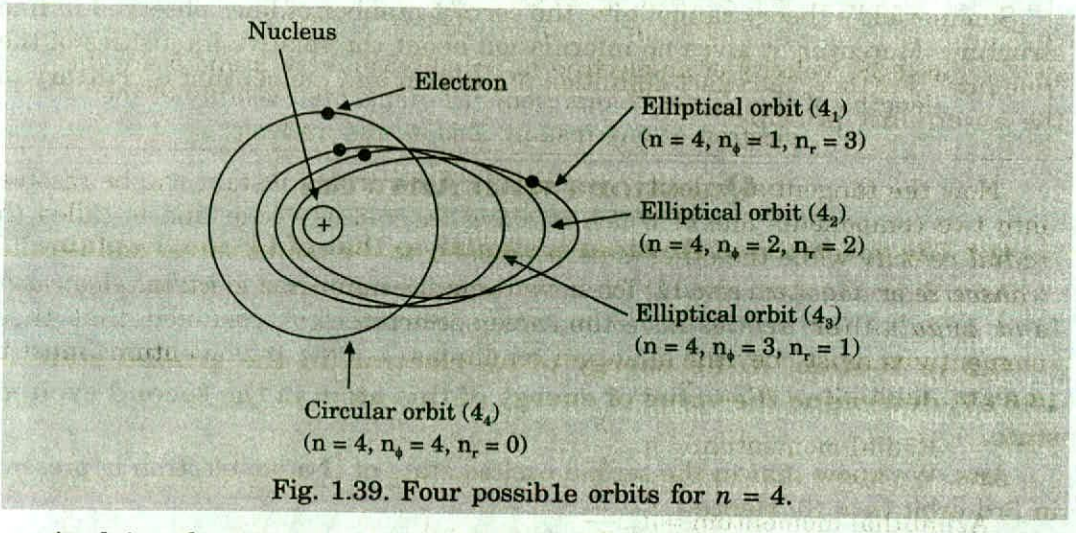


Fig. 1.39. Four possible orbits for $n = 4$.

Applying the principle of quantisation of momentum to the electron moving in an elliptical orbit, Sommerfeld deduced the energy of the electron in the hydrogen atom as :

$$E_n = \frac{2\pi^2 e^4 m}{(n_\phi + n_r)^2 h^2}$$

Thus we find that the energy depends not only on the principal quantum number, n but also to some extent on the azimuthal quantum number, n_ϕ. The frequency of the radiation emitted as a result of transition of an electron from a level of energy E_2 to a level of energy E_1 ($E_2 > E_1$) would, therefore, vary, depending on the various values of n_ϕ and as a result a group of closely-spaced lines would appear instead of a single line in the spectrum of hydrogen atom or hydrogen like atoms.

The concepts advanced by Sommerfeld evidently postulate existence of sub-energy level for electrons in each of the principal energy levels of the atom.

Weakness of Bohr-Sommerfeld's Atomic Model

Experimental observations and theoretical treatment based on wave mechanics show that the different values of azimuthal quantum number are : 0, 1, 2, 3, ..., $(n-2)$, $(n-1)$ (total n values) and not 1, 2, 3, ..., $(n-1)$, n (total n values). The new quantum number beginning with zero and ending at $(n-1)$ has been represented by l in order to avoid the confusion with n_φ. Thus l is related with n_ϕ and n by the following relations :

$$\left.\begin{aligned} l &= n_\phi - 1 \\ \text{or} \quad n_\phi &= l + 1 \end{aligned}\right\} \qquad ...(ii)$$

$$l = 0, 1, 2, ..., (n-2), (n-1)$$

With the help of relation (ii), equation (i) becomes

$$\frac{n}{l+1} = \frac{a}{b}$$

Sommerfeld's theory cannot give the correct number of lines observed in fine structure. Moreover, it gives no information about the relative intensities of the *"fine line"*. Further, the exact definition of position and momentum is contrary to the uncertainty principle.

Questions with Answers

Q.1 The spectrum of He atom is similar to that of Li^+ ion. Explain.

Ans. Since He-atom and Li^+ ion have the same number of electrons (He = $1s^2$, Li^+ = $1s^2 2s^0$), these species have the same spectrum.

Q.2 In H-atom, if the energy of an electron in the ground state is 13.6 eV, determine the value of energy of this atom in the second excited state.

Ans. We know that in the second excited state of H-atom electron is present in 3rd orbit (n = 3). Hence :

$$E_3 = -\frac{13.6}{n^2} \times Z^2 eV = -\frac{13.6}{(3)^2} \times (1)^2 eV = -\frac{13.6}{9} eV = \mathbf{-1.51\ eV}\ \textbf{(Ans.)}$$

Q.3 In Bohr series of lines of H-spectrum which inter orbit jump of the electron gives 3*rd* line from the red end ?

Ans. We know that the lines at the red end of H-spectrum belong to Balmer series. The lines of this series are obtained due to the following electronic jumps : $n_3 \rightarrow n_1$ (*1st* line), $n_4 \rightarrow n_1$ (*2nd* line), $n_5 \rightarrow n_1$ (*3rd* line), etc. Obviously *3rd* line is obtained due to $n_5 \rightarrow n_1$ or $5 \rightarrow 1$ electronic jump.

Q.4 If IP of H-atom is 13.6 eV, find out the IP of He^+ ion.

Ans. Since H-atom and He^+ ion both have one electron, IP of He^+ is given by :

$$(IP)_{He^+} = (IP)_H \times (\text{Atomic number of He})^2\ eV$$

$$= 13.6 \times 2^2\ eV = \mathbf{54.4\ eV}\ \textbf{(Ans.)}$$

Q.5 Find out the value of frequency (υ) of radiation emitted when an electron falls from $n = 4$ to $n = 1$ orbit in H-atom. Given : IE of H-atom = 2.18×10^{-18} J atom^{-1} and $h = 6.625 \times 10$ Js.

Ans. ΔE for $n_4 \rightarrow n_1$ jump $= E_4 - E_1$

$$= -2.18\times10^{-18}\left(\frac{1}{n_4^{\,2}} - \frac{1}{n_1^{\,2}}\right)\text{J atom}^{-1}$$

$$= -2.18\times10^{-18}\left(\frac{1}{4^2} - \frac{1}{1^2}\right)\text{J atom}^{-1}$$

$$= +2.044\times10^{-18}\text{ J atom}^{-1}$$

Now $\Delta E = h\upsilon$

or $$\upsilon = \frac{\Delta E}{h} = \frac{2.044\times10^{-18}\text{ J atom}^{-1}}{6.625\times10^{-34}\text{ Js}}$$

$$= \mathbf{3.085\times10^{15}\,s^{-1}\ (Ans.)}$$

Q.6 Which of the following ions has the same radius as that of the 1st orbit of H-atom ? $He^+(n = 2)$, $Li^{2+}(n = 2)$, $Li^{2+}(n = 3)$ and $Be^{3+}(n = 2)$.

Ans. We know that :

r_1 ($n = 1$) of H-atom = 0.529 Å.

Now let us calculate the radii of the given ions.

Radius of 2nd orbit ($n = 2$) of $He^+(Z = 2)$

$$= \frac{0.529\times n^2}{Z} = \frac{0.529\times2^2}{2} = 0.529\times\text{Å}$$

Radius of 2nd orbit ($n = 2$) of $Li^{2+}(Z = 3)$

$$= \frac{0.529\times2^2}{3} = 0.529\times\frac{4}{3}\text{ Å}$$

Radius of 3rd orbit ($n = 3$) of Li^{2+} ($Z = 3$)

$$= \frac{0.529\times3^2}{3} = 0.529\times3\text{Å}$$

Radius of 2nd orbit ($n = 2$) of Be^{3+} ($Z = 4$)

$$= \frac{0.529\times2^2}{4} = 0.529\text{Å}$$

Obviously 2nd orbit of Be^{3+} in has the same radius as the 1st orbit of H-atom.

Q.7 Calculate the wavelength of the electron emitted when in a H-atom electron falls from infinity to stationary state. Given $R = 1.097 \times 10^7$ m^{-1}.

Ans. Frequency in terms of wave number ($\bar{\upsilon}$) is given by :

$$\bar{\upsilon} = R\left(\frac{1}{n_1^{\,2}} - \frac{1}{n_2^{\,2}}\right)$$

$$= 1.097\times10^7\left(\frac{1}{1^2} - \frac{1}{\infty^2}\right)\text{m}^{-1}$$

$$= 1.097\times10^7\,\text{m}^{-1}$$

$$\therefore \text{ Wavelength } (\lambda) = \frac{1}{\bar{\upsilon}} = \frac{1}{1.097\times10^{7}\,m^{-1}}$$

$$= \mathbf{0.91\times10^{-7}\,m\ (Ans.)}$$

Q.8 Calculate the ratio of the area covered by 2nd orbit to the 1st orbit of H-atom.

Ans. We know that area covered by nth orbit of H-atom = πr_n^2

$$= \pi\times\left(\frac{0.529\times n^2}{Z}\right)^2$$

$$= \frac{\pi\times(0.529)^2\times n^4}{1^2}$$

$$\therefore \qquad A_1 = \frac{\pi(0.529)^2\times1^4}{1^2}$$

and $$A_2 = \frac{\pi\times(0.529)^2\times2^4}{1^2}$$

$$\therefore \quad \frac{A_2}{A_1} = \frac{\pi\times(0.529)^2\times2^2}{1^2}\times\frac{1^2}{\pi\times(0.529)^2\times1^4}$$

$$= \frac{16}{1}\ \textbf{(Ans.)}$$

Q.9 Which of the following one-electron ions has IE = 54.4 eV ? B^{4+}, Li^{2+}, Be^{2+} and He^{2+}

Ans. $(IE)_{B^{4+}}$ $(Z = 5) = 13.6 \times Z^2$ eV $= 13.6 \times 5^2$ eV $= 340$ eV

$(IE)_{Li^{2+}}$ $(Z = 3) = 13.6 \times Z^2$ eV $= 13.6 \times 3^2$ eV $= 122.4$ eV

$(IE)_{Be^{2+}}$ $(Z = 4) = 13.6\ Z^2$ eV $= 13.6 \times 4^2$ eV $= 217.6$ eV

$(IE)_{He^{2+}}$ $(Z = 2) = 13.6\ Z^2$ eV $= 13.6 \times 2^2$ eV $= 54.4$ eV

Obviously He^{2+} ion has IE = 54.4 eV **(Ans.)**

Q.10 Find out the value of most probable radius (in pm) for the electron in He^+ ion.

Ans. We know that the radius of 1st orbit (n = 1) of He^+ ion (Z = 2)

$$= \frac{0.529\times n^2}{Z}\,\text{Å} = \frac{0.529\times n^2}{Z}\times10^2\ \text{pm} \qquad (\because 1\ \text{Å} = 10^2\ \text{pm})$$

$$= \frac{52.9\times n^2}{Z}\,\text{pm} = \frac{52.9\times1^2}{2}\,\text{pm}$$

$$= \mathbf{26.5\ pm\ Ans.}$$

Q.11 Which of the following electronic transitions will have minimum wavelength ? $n_4 \rightarrow n_1$, $n_2 \rightarrow n_1$, $n_4 \rightarrow n_2$ and $n_3 \rightarrow n_1$.

Ans. We know that :

$$\Delta E = h\upsilon = \frac{hc}{\lambda} \qquad \left(\because \upsilon = \frac{c}{\lambda}\right)$$

or $$\frac{hc}{\Delta E} \qquad \ldots(i)$$

In equation (*i*), since *hc* is constant, $\lambda \times \frac{1}{\Delta E}$. Now since $(\Delta E)_{n_4 \to n_1}$ corresponding to $n_4 \to n_1$ transition is maximum, λ for this transition is minimum.

University Questions

1. Describe Millikan's oil drop method for the determination of the charge on an electron. (*North Bengal 81; Poona 81*)
2. How is e/m ratio of the electron determined ? (*Triruchirapalli 1985; Poona 86; Madras 85; Madurat 85*)
3. Describe the characteristics of proton. (*Venkateshwara B.Sc. 1979*)
4. Write a short note on, "Discovery of neutron". (*Garhwal 1988; Kanpur 1982*)
5. How and when was the neutron discovered ? Mention its use. (*Madras 86*)
6. Describe Rutherford's model of the atom. How was it improved by Bohr ? (*Banaras 80; Poona 81*)
7. Describe Mosley's work on X-ray spectra of elements with respect to instrument and equation. Bring out its theoretical importance. (*Poona 86; Madras 85*)
8. Write a note on photoelectric effect. (*Nagpur 81; Baroda 82; Madras 85*)
9. Write a note on "Compton Effect". (*Nagpur 81; Baroda 82*)
10. Write a note on "Planck's quantum theory of radiation". (*Kanpur 1982, 83, 84*)
11. Give a brief account of Bohr's model of hydrogen atom covering the following points: (*a*) postulates (*b*) energy and radius (*c*) short-comings. (*Allahabad 89*)
12. Explain how Bohr's theory accounts for the line spectrum of H-atom. (*Calicut 80; Osmania 81; Himachal 82; Raj 82, 86; Banaras 80*)
13. How did Sommerfeld modify the Bohr's model of atom? (*Raj B.Sc. 1987*)
14. K.E. of an electron is 5.76×10^{-15} J. Calculate the wavelength associated wit the electron. (Mass of electron = 9.1×10^{-31} kg and *h* 6.626×10^{-34} Js) (*Delhi 99*)
15. Deduce the following relation from Bohr's theory.

$$E_n = -\frac{2\pi^2 Z^2 me^4}{n^2 h^2}$$

[*Gauhati (General) 2000*]

16. (*a*) Discuss Bohr's model of the atom. How does it account for the hydrogen spectra? What are its limitations?

    (*b*) Calculate the frequency of spectral line emitted in case of hydrogen atom when the electron jumps from level 2 to level 1. (*Lucknow 2001*)
17. Write the demerits of Bohr's atomic model. (*Nagpur 2002*)

CHAPTER

2 Structure of the Atom (ii)

(*Wave Mechanical Approach*)

Dual Nature of Matter or Electron : Wave-Particle Nature of Matter—de Broglie's Concept of Matter Wave.

According to *Max Planck's quantum theory of radiation* some phenomena like photoelectric effect and black body radiation can be explained, if light radiation is supposed to behave *as a material particle* which is localised at a particular point in space, while according to *Maxwell's wave theory of radiation* certain other phenomena like diffraction, interference and polarisation can be explained, if light radiation is supposed to behave as a wave which is spread out over space. Thus we find that *light shows dual character, i.e. it behaves both as a material particle and as a wave.*

In 1924 a French physicist, Lonius de Broglie extended the idea of dual character of light to matter particles and suggested that *all matter particles in motion* (*e.g.* electrons, protons, neutrons, atoms or molecules etc.) *have a dual character, i.e. all matter particles possess characteristics of both a material particle and a wave.* The wave associated with matter particles is called **de Broglie's matter wave.** The revolutionary idea proposed by de Broglie that a material object possesses both the particle and the wave properties is known as the **wave-particle duality in matter.** The idea of wave -particle duality in matter led de Broglie to a very important conclusion that since an electron is also kind of matter particle, *it also, like matter particle, has a dual character i.e. an electron, like all other matter particles, behaves both as a material particle and as a wave.*

Difference Between de Broglie's Matter Waves and Electromagnetic Waves

Main differences are given below :

(*i*) de Broglie's matter wave are not radiated into empty space or emitted by oscillating particles, *i.e.*, they are never dissociated from the particle but remain attached to the particle. On the other hand the electromagnetic waves (*i.e.*, radiations) can be absorbed or emitted.

(*ii*) de Broglie's matter waves travel with speeds which depend on the nature of the matter particles while electromagnetic waves proceed with the speed of light.

(*iii*) de Broglie's matter waves are not electromagnetic in nature.

de Broglie's Equation

With the help of *Planck's equation,* $E = h\upsilon$ and *Einstein's mass-energy relationship,* $E = mc^2$ (E = energy of photon, h = Planck's constant, υ = frequency

of radiation (photon), m = mass of photon and c = velocity of light), de Broglie derived a mathematical equation which gives the magnitude of wavelength, λ of a moving electron in terms of its mass, m and velocity, v. This equation is :

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

This equation is called **de Broglie's equation** and the wavelength, λ is called **de Broglie's wavelength.**

Since the product of m and v (*i.e., mv*) is called the momentum of the moving electron, the above equation can also be written as :

$$\boxed{\textbf{de Broglie's wavelength } (\lambda) = \frac{\textbf{Planck's constant (h)}}{\textbf{Momentum of the electron (mv)}}}$$

The equation shows that, since h is constant of proportionality, *the momentum of a moving electrons* (= mv) *is inversely proportional to its wavelength* (= λ).

Derivation of de Broglie's Equation

We have seen that energy of a photon, E is related to its frequency, υ by *Planck's equation* as :

$$E = h\upsilon \text{ (Planck s equation)}$$

or $$E = h.\frac{c}{\lambda} \qquad \left(\because \upsilon = \frac{c}{\lambda}\right) \qquad ...(i)$$

Here λ is the wavelength of radiation (photon).

Again the energy of a photon, E with mass, m and velocity, c is also given by *Einstein's mass-energy relationship* as :

$E = mc^2$ (*Einstein's mass-energy relationship*) ...(*ii*)

Equating equations (*i*) and (*ii*), we get

$$h.\frac{c}{\lambda} = mc^2$$

or $$\frac{h}{\lambda} = mc$$

or $$\lambda = \frac{h}{mc}$$

If the above equation is applied to a moving electron of mass m and moving with a velocity v, then the above equation reduces to :

$$\lambda = \frac{h}{mv} \text{ (de Broglie ? s equation)}$$

This is de Broglie's equation which gives the value of wavelength (λ) of a moving electron in terms of its mass (m) and velocity (v).

De Broglie's Equation as Applied to Large and Small Particles in Motion—Limitations of de Broglie's Equation.

Whether de Broglie's equation is applicable to large particles like a stone or small particles such as electrons, neutrons etc. can be known by calculating the

magnitude of de Broglie's wavelengths for these particles and then comparing them.

(*a*) **Wavelength of large particles.** Let us consider a large particle like a stone in motion of mass of 1 g (= 1×10^{-3} kg) moving with a velocity equal to 1 m/sec. Then :

$$\lambda = \frac{h}{mv} = \frac{6.624 \times 10^{-34}}{(1 \times 10^{-3}) \times (1)} \text{ m}$$

$$= 6.624 \times 10^{-31} \text{ m.}$$

This value of λ is shorter than the wavelength of any electron-magnetic radiation (except cosmic rays) and hence cannot be measured by any conceivable method. Thus de Broglie's equation has no significance for large particles.

(*b*) **Wavelength of small particles.** Let us consider an electron in a hydrogen atom with mass = 9.108×10^{-31} kg and moving with a velocity = 2.188×10^{6} m/s. Then :

$$\lambda = \frac{h}{mv} = \frac{6.624 \times 10^{-34}}{(9.108 \times 10^{-31}) \times (2.188 \times 10^{6})} \text{ m}$$

$$= 0.3323 \times 10^{-9} \text{ m}$$

This value of λ is quite large and comparable to the wavelength of X-rays and hence can be measured.

As may be seen from the above calculations, de Broglie's wavelength of large particles in motion is very small and hence cannot be measured while the same for small particles is large enough and hence can be measured. Thus we find *that de Broglie's equation is applicable only for small particles (microscopic particles) like electrons, neutrons etc. and has no significant for large particles (macroscopic particles).*

Numerical Probelms

Problem 1. (In S.I. units). *Calculate the wavelength of a body of mass 1 mg moving with a velocity of 3 ms^{-1}.* *(Delhi B.Sc. Hons. 1975)*

Solution. We know that according to de Broglie's equation :

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

Substituting $h = 6.624 \times 10^{-34}$ Js, $m = 1$ mg $= 1 \times 10^{-6}$ kg, and $v = 3$ ms^{-1} in the above equation, we get

$$\lambda = \frac{6.624 \times 10^{-34} \text{ Js}}{(1 \times 10^{-6} \text{ kg}) \times (3 \text{ ms}^{-1})}$$

$$= \frac{6.624 \times 10^{-34} \text{ Js}}{3 \times 10^{-6} \text{ kg . ms}^{-1}}$$

$$= \frac{2.20 \times 10^{-28} \text{ Js}}{\text{kg.ms}^{-1}} = 2.20 \times 10^{-28}$$

$$= \frac{2.20\times10^{-28}\ \text{kg.m}^2\text{.s}^{-2}\text{.s}}{\text{kg.m.s}^{-1}} \qquad (\because\ \text{J} = \text{kg.m}^2\text{.s}^{-2})$$

$$= 2.20\times10^{-28}\ \text{m}$$

Problem 2. (In S.I. units). *Applying de Broglie's equation, calculate the wavelength associated with the motion of the earth, a stone and an electron. The masses and velocities of these objects are given below :*

Mass	*Velocity*
Earth = 6 × 10^{24} kg	*3 × 10^{4} ms^{-1}*
Stone = 0.1 kg	*1.0 ms^{-1}*
Electron = 10^{-30} kg	*6 × 10^{5} ms^{-1}*

Planck's constant = 6.6 × 10^{-34} Js. Which of these objects will have the measureable wavelength? *(Delhi B.Sc. 1982)*

Solution. (*a*) *For earth :*

$$\lambda = \frac{h}{mv} = \frac{6.6\times10^{-34}}{(6\times10^{24})\times(3\times10^{4})} = 3.68\times10^{-63}\ \text{m}$$

(*b*) *For stone*

$$\lambda = \frac{h}{mv} = \frac{6.6\times10^{-34}}{(0.1)\times(1.0)} = 66\times10^{-34}\ \text{m}$$

(*c*) *For electron :*

$$\lambda = \frac{h}{mv} = \frac{6.6\times10^{-34}}{(10^{-30})\times(6\times10^{5})} = 1.1\times10^{-9}\ \text{m}$$

Quite obviously wavelength of electron is maximum and hence is a measurable quantity.

Problem 3. (In S.I. units). *Calculate the wavelength of an electron moving with a velocity of 2.5 × 10^{7} ms^{-1} (h = 6.63 × 10^{-34} Js, mass of an electron = 9.11 × 10^{-31} kg).* *(Bangalore B.Sc. 1981)*

Solution. Applying de Broglie's equation

$$\lambda = \frac{h}{mv} = \frac{6.63\times10^{-34}}{(9.11\times10^{-31})\times2.5\times10^{7}}\ \text{m}$$

$$= \frac{6.63\times10^{-10}}{9.11\times2.5}\ \text{m}$$

$$= 0.2911\times10^{-10}\ \text{m}.$$

Problem 4. (in C.G.S. units). *Calculate the wavelength of matter-wave associated with an electron moving with a velocity of 1.20 × 10^{7} $cm.s^{-1}$. (Mass of electron = 9.1 × 10^{-28} g; Planck's constant h = 6.626 × 10^{-27} erg.s).*

Solution. Here $v = 1.20\times10^{7}\ \text{cm.s}^{-1}$, $m = 9.1\times10^{-28}$ g and

$h = 6.626\times10^{-27}$ erg.s.

$$\therefore \qquad \lambda = \frac{h}{mv} = \frac{6.626\times10^{-27}\ \text{erg.s}}{(9.1\times10^{-28}\ \text{g})\times(1.20\times10^{7}\ \text{cm.s}^{-1})}$$

$$= \frac{6.626 \times 10^{-6} \text{ g.cm}^2.\text{s}^{-2}.\text{s}}{9.1 \times 1.20 \text{ g.cm.s}^{-1}} = 0.6057 \times 10^{-6} \text{ cm}$$

Davisson and Germer's Experiment to Verify the Wave Nature of Moving Electrons

The first experimental proof of the fact that moving electrons have waves of definite wavelength associated with them was provided in 1927 by two American physicists, Davission and Germer. In their experiment they studied the scattering of slow moving electrons by reflecting them from the surface of nickel crystal.

Experimental procedure. In their experiment electrons were produced from a heated tungsten filament and were accelerated by passing them through charged plates kept at a potential difference of V volts. The accelerated electrons were passed through slits which collimate the accelerated electrons into a fine parallel pencil.

Due to the electrical force equal to Ve (where e = charge on the electron) acting on the electron, the electrons emerge out of the charged plates with a uniform velocity equal to v units. Thus in this case the kinetic energy acquired by an electron due to the electric field would be equal to $\frac{1}{2}mv^2$. This kinetic energy will be equal to the electrical Ve, *i.e.*

$$\frac{1}{2}mv^2 = eV$$

$\therefore$ $$v = \sqrt{\frac{2Ve}{m}}$$

Substituting this value of v in de Broglie's equation, we have :

$$\lambda = \frac{h}{mv} = \frac{h}{m} \times \sqrt{\frac{m}{2Ve}}$$

or $$\lambda = \frac{h}{\sqrt{2Vem}}$$

On putting h = 6.624 × 10^{-34} Js; e = 1.602 × 10^{-19} C; m = 9.108 × 10^{-31} kg; the above equation becomes :

$$\lambda = \frac{6.624 \times 10^{-34}}{\sqrt{2 \times 1.602 \times 10^{-19} \times 9.108 \times 10^{-31} \times \text{V volts}}}$$

$$= \frac{12.26 \times 10^{-10}}{\sqrt{\text{V volts}}} \text{ m}$$

or $$\lambda = \frac{12.26}{\sqrt{\text{V volts}}} \text{ Å} \qquad \textit{(de Broglie s equation)} \qquad ...(i)$$

If a potential difference of 10 volts is applied, the wavelength, λ of the electron-wave emerging out would be equal to 3.877 Å. Similarly, if the potential difference is varied between 10 and 10,000 volts, λ should vary between 3.877 Å. and 0.1226 Å. It is well known that X-rays have the wavelengths in this range. It is also known that the X-rays having the wavelength in the above range can undergo diffraction when they fall on the crystalline solids like nickel crystal, known as *target*.

When the accelerated electrons fall on the nickel crystal as shown in Fig. 2.1, the electrons of a definite wavelength are deflected from the crystal in different directions. The angle of diffraction (θ) can be measured with the help of an electron detector (called *collector*) which is connected with a sensitive galvanometer and can be moved along graduated circular scale. The electron detector has two walls C and D which are insulated from each other. The nickel crystal which is known to be of the face-centered cubic type is cut so as to have a smooth reflecting surface parallel to the lattice plane (1, 1, 1).

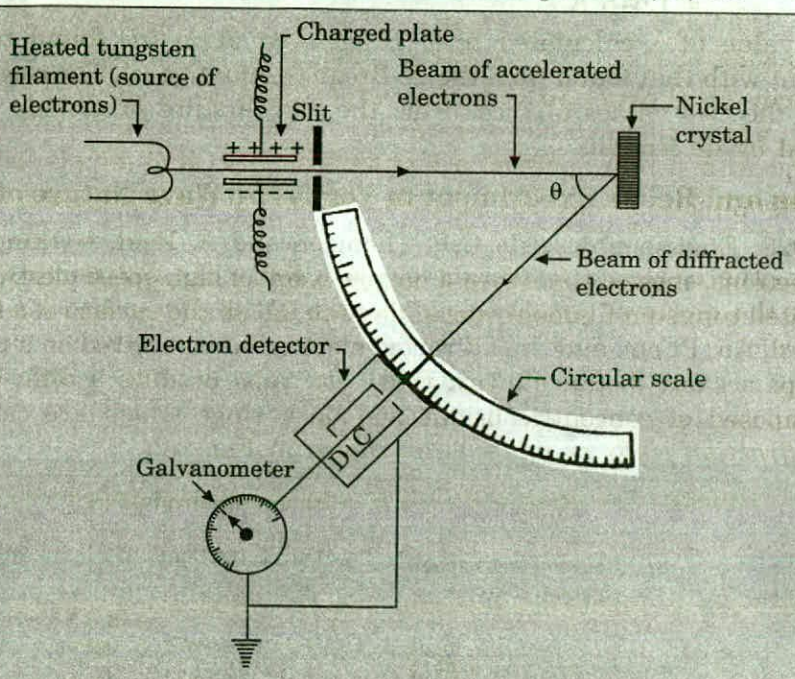


Fig. 2.1. Davisson and Germer's experiment to verify the wave-nature of moving electrons.

The intensities of electron waves scattered by the Ni crystal at different angles were measured and it was found that the most intense reflection took place when the angle of refraction was 50° and the electrons were accelerated through 54 volts. Substituting V = 54 volts in de Broglie's equation (*i*), we get the value of wavelength, λ of the electron-wave equal to 1.668 Å as shown below.

$$\lambda = \frac{12.26}{\sqrt{54 \text{ volts}}} \text{ Å} = \frac{12.26}{7.3484} \text{ Å}$$

or $$\lambda = 1.688 \text{ Å}$$

This wavelength also lies in the X-rays range. Thus there is similarity between electron waves and X-rays. Since λ = 1.668 Å lies in the X-ray range, Bragg's equation viz.

$$n\lambda = 2d \sin \theta \text{ (Bragg's equation)} \qquad ...(ii)$$

which has been derived for X-ray diffraction, can be applied to electron diffraction as well and can be used to calculate the value of λ. In Bragg's equation n is a

whole number (1, 2, 3 etc) of wavelength λ for a reflection of maximum intensity, d is the vertical distance (called *inter planar distance*) between two adjacent lattice planes of the crystal (nickel crystal in the present case) and θ is the angle of diffraction of the waves. By substituting $n = 1$ (first order Bragg's reflection occurs), $a = 50°$ and $d = 1.075$ Å, the value of λ is obtained as follows :

$$1 \times \lambda = 2 \times 1.075 \times \sin 50$$
$$= 2 \times 1.075 \times 0.7660$$
$$= 1.648 \text{ Å}$$

The value of λ calculated from Bragg's equation (*ii*) found to be in full agreement with that found from the de Broglie's equation (*i*). The close agreement between the two values of λ confirms the wave-nature of moving electrons as suggested by de Broglie.

Thomson and Reid's Experiment to Verify the Wave Nature of Electrons.

In 1928, English physicists G.P. Thomson and A. Reid, working with high-speed electrons, showed that when a narrow beam of high-speed electrons produced from heated tungsten filament was allowed to fall on the surface of a thin metallic foil like Al, Au, Pt etc. and the diffracted electrons are received on a photographic plate kept a short distance away, these electrons produce a diffused luminous spot composed of concentric bright and dark rings which are called *electron beam diffraction rings or patterns* as shown in Fig. 2.2.

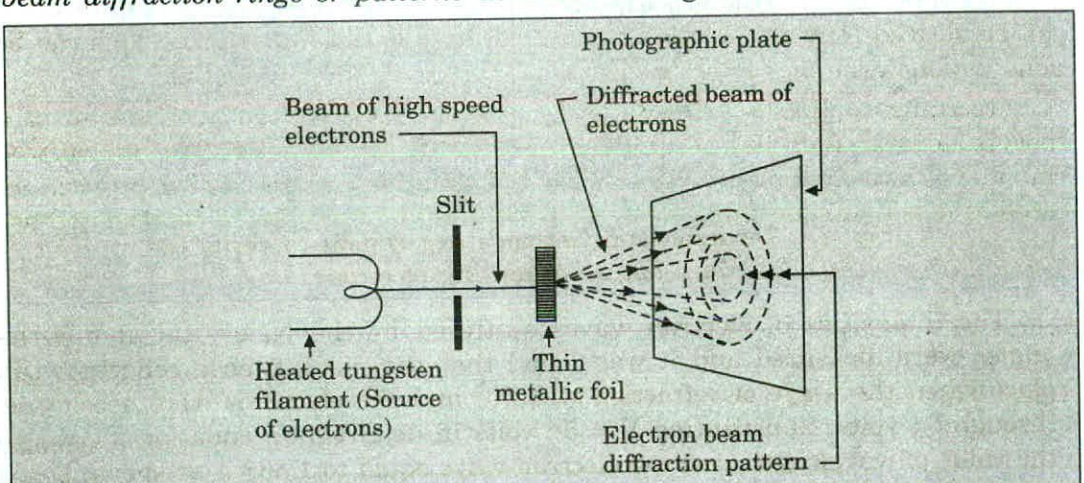
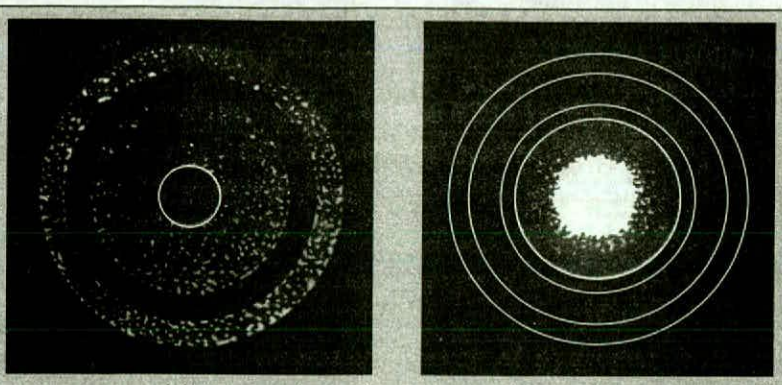


Fig. 2.2. Thomson and Reid's experiment to verify the wave-nature of electrons.

These diffraction patterns are obtained due to the fact that metals consist of many microscopic crystals arranged in random fashion so that some are always at the proper angles to give reflection in accordance with Bragg's equation. These diffraction rings given by electron beam are found to be similar to those given by X-rays (which are waves) when they are diffracted by the same metal foil. (See Fig 2.3). This similarity between the electron beam diffraction rings and those of X-rays rings confirms that electrons are also waves.



(a) (b)

Fig. 2.3. (*a*) Electron beam diffraction rings (*b*) X-rays beam diffraction rings

Applications of Wave Nature of Electrons

(*i*) The wave nature of electrons has been utilised in the construction of electron microscope of high resolving power. This microscope is an important tool in research.

(*ii*) Wave nature of electrons has been used in the study of thin surface films.

Bohr's Theory vs de Broglie's Concept

Bohr's principle of quantisation of angular momentum of a moving electron can be derived from de Broglie's concept of wave nature of electron. This can be done as follows :

According to Bohr's principle of quantisation of angular momentum of a moving electron (Bohr had assumed an electron as a material particle), an electron can move only in that orbit in which the angular momentum (= mvr) is an integral whole number multiple of $h/2\pi$, *i.e.*, the principle can be represented as :

$$mvr = n.\frac{h}{2\pi} \text{ (Bohr s equation)},$$

where m = mass of the electron, v = velocity of the electron, r = radius of the orbit in which the electron is revolving, n = an integral whole number which can have values 1, 2 etc. and h = Planck's constant.

Now according to de Broglie an electron behaves as a standing or stationary wave which extends round the nucleus in a circular orbit (Fig. 2.4). If the two ends of the electron-wave meet to give a regular series of crests and troughs, the electron-wave is said to be in *phase*, *i.e.*, there is constructive interference of electron waves and the electron motion has a character of a standing wave or *non-energy radiating motion*. [Fig. 2.4 (*a*)]. Whatever be the path of the electron-wave round the nucleus, it is a necessary condition to get an electron-wave in phase that the circumference of the Bohr's orbit (= $2\pi r$) is equal to the whole number multiple of the wavelength (λ) of the electron wave, *i.e.*,

$$2\pi r = n.\lambda$$

or

$$\lambda = \frac{2\pi r}{n} \qquad ...(i)$$

Here n is a whole number which denotes the number of wavelengths associated with an electron-wave extending round the nucleus.

An electron-wave associated with five wavelengths (*i.e.*, $n = 5$) is shown in Fig. 2.4 (*a*).

Now according to de Broglie, the wave length (λ) of an electron which behaves as a wave is given by :

$$\lambda = \frac{h}{mv} \quad (de\ Brogli\ s\ equation) \qquad ...(ii)$$

On comparing equations (*i*) and (*ii*) we get

$$\frac{2\pi r}{n} = \frac{h}{mv}$$

or
$$mvr = n.\frac{h}{2\pi} \quad (Bohr\ s\ equation)$$

This equation which is Bohr's equation clearly shows that the angular momentum (= mvr) of an electron moving round the nucleus is a whole number multiple of $h/2\pi$. Thus we see that *Bohr's assumption namely the angular momentum (mvr) of an electron is a whole number multiple of h/2π is also confirmed if an electron is also supposed to behave as a wave as suggested by de Broglie*. In other words de Broglie's and Bohr's concepts are in agreement with each other.

If mvr is not a whole number multiple of $h/2\pi$ or if the circumference of the Bohr's orbit (= $2\pi r$) is bigger or smaller than $n\lambda$, the electron-wave is said to be *out of phase* [Fig. 2.4 (*b*)] and hence the electron-wave will not extend round the nucleus in circular orbit and ultimately will come out of the Bohr's orbit, *i.e.*, the destructive interference of waves will cause radiation of energy.

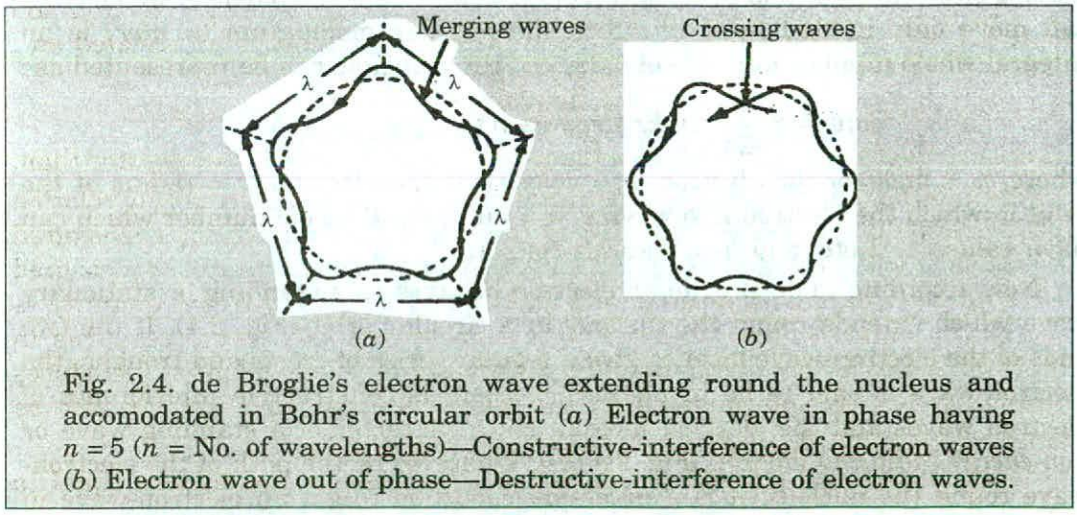


Fig. 2.4. de Broglie's electron wave extending round the nucleus and accomodated in Bohr's circular orbit (*a*) Electron wave in phase having $n = 5$ (n = No. of wavelengths)—Constructive-interference of electron waves (*b*) Electron wave out of phase—Destructive-interference of electron waves.

Heisenberg's Uncertainty Principle

We have seen that Bohr had assumed an electron to be a material particle of small mass revolving round the nucleus in circular orbits situated at definite

(*i.e.* fixed) distance from the nucleus and with a definite velocity (or momentum). Thus according to Bohr's theory which considers an electron as a material particle, the position and momentum of an electron can be determined with great accuracy. But, when an electron is considered as a wave as suggested by de Broglie, it is not possible for us to measure simultaneously its exact position in space at some given instant and its velocity, since the wave is extending throughout a region of space. This means that if an attempt is made to make the exact measurement of the position of an electron, the exact measurement of its velocity becomes uncertain and *vice-versa*. That the measurement of the position and momentum of an electron cannot be made simultaneously was suggested by Werner Heisenberg of Germany in 1927 in his principle which is known after his name as **Heisenberg's uncertainty principle.** This principle states as :

It is impossible to measure simultaneously the exact position and exact velocity (or momentum) of a sub-atomic particle like electron and neutron.

Illustration of the principle. The uncertainty principle can be better understood by considering the relations existing between a hostel suprintendent and a student living in the hostel. Suppose a student is very irresponsible and hence, for most of the time he prefers to keep away from his room. Now if, the superintendent becomes strict, the student stays in his room and hence the relations between the student and the superintendent become uncordial (*i.e.* uncertain). On the other hand if the superintendent becomes linient, the student does not stay in his room and hence the relations between them become cordial (*i.e.* certain). Thus, if the presence of the student in his room becomes certain; the relations between the two become uncertain.

Mathematical expression for the principle. If Δx represents the error (or uncertainty) in the measurement of the position and Δp represents the uncertainty in the measurement of the momentum of a sub-atomic particle like electron and neutron, then according to this principle, these two quantities are related as :

$$\boxed{\Delta x . \Delta p \geq \frac{h}{2\pi} \text{ (Uncertainty relation)}}$$

where h is the Plank's constant and the sign $\geq$ indicates equal to or greater than.

The relation given above is called **uncertainty relation**. From this relation it is evident that, if Δx is small (*i.e.* if the position of a particle is measured accurately or with accuracy), Δp will be large (*i.e.* the momentum will be measured less accurately or with less accuracy) and *vice versa*. Thus, if one quantity is measured accurately, the other quantity is measured less accurately: This in other words means that certainty of the determination of one quantity introduces uncertainty for the determination of the other quantity. This fact can also be shown as follows :

If the position of a particle is measured accurately, Δx should be equal to zero and hence

$$\Delta p = \frac{h}{2\pi \times \Delta\pi} = \frac{h}{2\pi \times 0} = \infty$$

$\Delta p = \infty$ means that error in the determination of the momentum is infinite, *i.e.* the measurement of the momentum of the particle *cannot* be made. In other words the simultaneous measurement of position and momentum (or velocity) with absolute accuracy is impossible.

If m is the rest mass of the particle and is the uncertainty in the measurement of its velocity, then

$$\Delta p = \Delta v.m$$

On putting $\Delta p = \Delta v.m$ in the uncertainty relation, we get another form of the uncertainty relation *viz.*

$$\Delta x.\Delta v.m \geq \frac{h}{2\pi}$$

or $$\boxed{\Delta x.\Delta v \geq \frac{h}{2\pi.m}}$$

Heisenberg's Uncertainty Principle as Applied to Large and Small Particles—Limitations of Heisenberg's Uncertainty Principle.

Whether Heisenberg's uncertainty principle is applicable to large particles like a ball or small particles such as electrons, neutrons etc. can be known be calculating the value of Δx or Δv of these particles from uncertainty relation, $\Delta x.\Delta v \geq \frac{h}{2\pi}$ and then comparing these values with the velocity or size (diameter) of the particle respectively. For example, if the calculated value of Δv for a given particle is very small compared to the velocity of that particle, uncertainty principle is meaningful for that particle. On the other hand if the value of Δv for a given particle is quite large compared to the velocity of that particle, this principle is meaningless for that particle. Similarly the value of Δx can be compared to the size (diameter) of the particle and the applicability of the principle to the particle can be predicted. Let us consider the following examples.

(a) Δv of large particles. Let us consider a large particle like a ball of mass equal to 1g (1×10^{-3} kg) whose uncertainty in position (Δx) is equal to 10^{-10} m. Then :

$$\Delta v = \frac{h}{2\pi.m.\Delta x} = \frac{6.624\times10^{-34}\ \text{J.s.}}{2\times3.14\times(10^{-10}\,\text{m})\times(10^{-3}\ \text{kg})}$$

$$= 1.0547\times10^{-21}\ \text{m.s.}^{-1}$$

This value of uncertainty in velocity (Δv) is very small and hence is negligible to the unusual velocity of the ball. Thus to talk about the trajectory of a large particle like a ball having such a small value of Δv is meaningful. In a similar way, if the value of uncertainty in position (Δx) is calculated for large particles, it is found to be very small and hence is negligible compared. to the size (diameter) of the particle. Consequently in case of large particles we can talk about the position and velocity simultaneously.

(b) Δv of small particles. Let us consider an electron in H-atom with mass $= 9.108 \times 10^{-31}$ kg whose uncertainty in position (Δx) is equal to 10^{-10} m. Then :

$$\Delta v = \frac{h}{2\pi.\Delta x.m} = \frac{6.614\times10^{-34}\ \text{J.s}}{2\times3.14\times(10^{-10}\text{m})\times(9.108\times10^{-31}\ \text{kg})}$$

$$= \frac{6.624\times10^{7}}{6.28\times9.108}\ \text{m.s}^{-1}$$

$$= 0.11580\times10^{7}\ \text{m.s}^{-1}$$

$$= 11.580\times10^{5}\ \text{m.s}^{-1}.$$

This value of uncertainty in velocity (Δv) is quite large compared to the velocity of the electron (velocity of an electron = 1.2×10^5 ms^{-1}). Thus to talk about the tragectory of a small particle like an electron having such a large value of Δv is meaningful. In a similar manner if the value of Δx is determined for small particles, it is found to be very large compared to the size (diameter) of the particle.

The above description clearly shows *that uncertainty principle is applicable only for small particles (microscopic particles) like electrons, neutrons etc and has no significance for large particles (macroscopic particles).*

Compton Effect and Uncertainty Principle

Compton effect provides a good illustration of the uncertainty principle. Let us attempt to determine the position and momentum of an electron moving in a Bohr's orbit. Suppose we wish to determine the position of the electron. We cannot obviously see it with visible light, since its wavelength is perhaps a million times as large as the diameter of the electron. So we try to use the radiation of shorter wavelength, say, X-rays of wavelength, λ. But in any case the uncertainty in the measurement of the position cannot be less than λ; at the best it can only be equal to λ. So the smaller the wave length used, the more accurate will be the measurement of the position.

We have seen in Compton effect that when a photon from X-rays strikes an electron at rest, the momentum of the electron changes from zero to mv where m = moving mass of the electron and v = velocity gained by the electron after an impact from the X-rays photon. Since this momentum change cannot be precisely measured, the measurement of the original momentum of the electron will be quite uncertain. Moreover, since the momentum of the X-rays photon, before impact, is equal to h/λ, the smaller the wavelength of X-rays, the greater is the photon momentum and, consequently, the greater the uncertainty in the measurement of the electron momentum. We thus see, the shorter wavelength we use in order to achieve greater accuracy in locating the position, the greater becomes the uncertainty in momentum and vice versa. It is impossible to determine both the original momentum as well as the position; and this uncertainty of either position or momentum is evidently not a matter of physical imperfections in the measuring apparatus, nor is it one that may be overcome by some improved technique. This uncertainty represents a fundamental limit of nature and sets a fundamental limit to our knowledge.

Bohr's Theory vs Heisenberg's Uncertainty Principle—Probability Concept of Electron

Heisenberg's uncertainty principle tells us that, due to the wave nature of electron, we cannot describe the exact path (*i.e.*, position) followed by an electron in an atom at any time. Thus Bohr's theory according to which the electrons are regarded as having fixed position (orbits) of definite energy is no longer correct. *Then how to describe the position of an electron in an atom*? In order to describe its position in an atom the maximum that we can do is that we can only predict the probability or relative chance of finding or locating an electron with a probable velocity in a particular region of space round the nucleus *i.e.*, we can only predict where an electron is most likely to be found. We have seen that Bohr's theory considers electrons as material particles revolving round the nucleus in circular orbits whereas the concept of probability visualises an electron in terms of probability of its being found in a particular region of space round the nucleus and thus does not define an exact path for the motion of the electron. Thus we see that the concept of probability rules out the possibility of strictly defined orbit for an electron as suggested by Bohr.

The probability of finding an electron at any position is given by the square of the wave function ψ *i.e.* the probability of finding an electron is given by ψ^2.

Numerical Problems

Problem 1 (In S.I. units). *Calculate the uncertainty in the position (Δx) of an electron, if Δv is 0.1 percent. Take velocity of electron = 2.2×10^6 ms^{-1}, mass of electron = 9.1×10^{-31} kg and $h = 6.6 \times 10^{-31}$ J-s. Comment on the result.*

Solution. Here Δv = 0.1% of the velocity of the electron.

$$= \frac{0.1 \times 2.2 \times 10^6}{100} \text{ ms}^{-1}$$

$$= 2.2 \times 10^3 \text{ m.s}^{-1}$$

Now $$\Delta x = \frac{h}{2\pi . m . \Delta v}$$

$$= \frac{6.6 \times 10^{-34} \text{ J.s}}{2 \times 3.14 \times (9.1 \times 10^{-31} \text{ kg}) \times (2.2 \times 10^3 \text{ m s}^{-1})}$$

$$= \frac{6.6 \times 10^{-6}}{2 \times 3.14 \times 9.1 \times 2.2} \text{ m}$$

$$= 0.0524953 \times 10^{-6} \text{ m}$$

$$= 524.953 \times 10^{-10} \text{ m}$$

Since the calculated value of Δx is much longer than the atomic diameter ($\approx 10^{-10}$ m), uncertainty principle is applicable to electron.

Problem 2. (In S.I. units). *Calculate the uncertainty in the position (Δx) of a dust particle, if 0.1% error in the measurement of velocity is allowed. Take velocity of the particle = 10^{-6} ms^{-1}, mass of the particle = 10^{-14} kg, $h = 6.6 \times 10^{-34}$ Js and diameter of the particle = 10^{-6} m. Comment on the result.*

Solution. Here $v = 10^{-6}$ m.s^{-1}, $m = 10^{-14}$ kg, $h = 6.6 \times 10^{-34}$, J-s, $\Delta v = 0.1\%$ of the velocity of the particle

$$= \frac{0.1 \times 10^{-6}}{100} \text{ m.s}^{-1} = 10^{-9} \text{ m.s}^{-1}$$

$$\Delta x = \frac{h}{2\pi \times \Delta v \times m}$$

$$= \frac{6.6 \times 10^{-34} \text{ J.s}}{2 \times 3.14 \times (10^{-9} \text{ m.s}^{-1}) \times (10^{-14} \text{ kg})}$$

$$= \frac{6.6 \times 10^{-11}}{6.28} \text{ m.}$$

$$= 1.05095 \times 10^{-11} \text{ m}$$

$$= \frac{1.05095 \times 10^{-6}}{10^5} \text{ m}$$

$$= 0.0000105 \times 10^{-6} \text{ m}$$

Since this value of Δx is much smaller as compared to the size (diameter) of the particle (= 10^{-6} m as given in the question), uncertainty principle is meaningful for this particle. Thus in case of this particle we can talk about the position and velocity simultaneously.

Problem 3. (In C.G.S. units). *An electron has a speed of 30000 cm/s accurate upto 0.001%. What is the uncertainty in locating its position? (Mass of an electron = 9.1 × 10^{-28} g, h = 6.626 × 10^{-27} erg-s).*

Solution. Here $h = 6.626 \times 10^{-27}$ erg-s, $m = 9.1 \times 10^{-28}$ g and velocity = 30000 cm/s.

$$\therefore \quad \Delta v = \frac{30000 \times 0.001}{100} \text{ cm.s}^{-1} = 0.3 \text{ cm.s}^{-1}$$

Now according to Heisenberg's uncertainty principle :

$$\Delta x.m.\Delta v = \frac{h}{2\pi}$$

or

$$\Delta x = \frac{h}{2\pi \times m \times \Delta v}$$

$$= \frac{6.626 \times 10^{-27} \text{ erg.s}}{2 \times 3.14 \times (9.1 \times 10^{-28} \text{ g}) \times (0.3 \text{ cm.s}^{-1})}$$

$$= 386.48 \text{ cm.}$$

Problem 4. (In S.I. units). *A microscope using suitable photons is employed to locate an electron in an atom within a distance of 0.1 Å. What is the uncertainty involved in the measurement of its velocity. (Mass of electron = 9.1 × 10^{-31} kg, h = 6.626 × 10^{-34} J.s.)*

Solution. Here $\Delta x = 0.1$ Å $= 0.1 \times 10^{-10}$ m,

$m = 9.1 \times 10^{-31}$ kg and $h = 6.626 \times 10^{-34}$ J.s.

Now $\Delta x.m.\Delta v = \frac{h}{2\pi}$

$$\therefore \quad \Delta v = \frac{h}{2\pi \times \Delta x \times m}$$

$$= \frac{6.626 \times 10^{-34} \text{ J.s.}}{2 \times 3.14 \times (0.1 \times 10^{-10} \text{ m}) \times (9.1 \times 10^{-31} \text{ kg})}$$

$$= \frac{6.626 \times 10^{7}}{2 \times 3.14 \times 0.1 \times 9.1} \text{ m.s}^{-1}$$

$$= 1.159 \times 10^{7} \text{ m.s}^{-1}.$$

Wave Mechanical Model of the Atom and Schrodinger's Wave Equation

Although Bohr's concept of strictly defined orbits round the nucleus was abondoned when de Broglie's concept of wave-nature of the electron and Heisenberg's uncertainty principle (idea of the uncertainty of the position of the electron in the atom) came in light, yet Bohr's concept of the existence of the stationary energy states (or energy levels) round the nucleus was retained in order to explain the atomic spectra. Now after the failure of Bohr's atomic model, the scientists were in search of a new model that could combine the following three concepts and explain the movement of an electron in an atom:

(*i*) *Wave-nature of the electron (de Broglie's concept)*

(*ii*) *The idea of the uncertainty of the position of the electron in an atom (Heisenberg's uncertainty principle).*

(*iii*) *The idea of stationary energy levels (fixed energy levels) for the electrons round the nucleus (Bohr's postulate).*

The atomic model that takes into account the wave and particle nature of the electron is refered to as **wave mechanical model of the atom.** In 1926 Erwin Schrodinger, an Austrian physicist developed the wave mechanical model of the atom. In his model he visualised the *atom as a positively charged nucleus surrounded by a standing or stationary electron wave which extends round the nucleus in Bohr's circular orbits.* Thus this model described the electron as a three dimensional wave in the electronic field of a positively charged nucleus.

Schrodinger proposed that if the electron has wave-like nature, it should obey the same equation of motion as all other known types of wave obey. On the basis of this simple idea, he derived an equation which describes the wave motion of an electron-wave along any of the three axes *viz.* x, y and z axes and is called Schrodinger's wave equation. This equation can be written in many forms one of which is given below :

$$\boxed{\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}(E - V)\,\psi = 0,}$$

where ψ [pronounced as sign (साई) or shy (शाई)] is a mathematical function which is called **wave function.** ψ represents the amplitude of the electron-wave at various points surrounding the nucleus, Amplitude is expressed in terms of *x, y, z* space co-ordinates of the electron with respect to the nucleus (0, 0, 0); *m* is the mass of the electron; *h* is Planck's constant and E is the total energy of the electron, *i.e.* E is the sum of kinetic energy and potential energy (V) of the electron.

Schrodinger's wave equation is a differential equation of the second order. The first three terms on the left hand side of the above equation indicate the mathematical operations that we must do on ψ to solve the equation for E. These terms are represented by $\Delta^2\psi$ (pronounced as *del square sigh*). Δ^2 is known as **Laplacian operator.** Thus the above equation can also be written as :

$$\Delta^2\psi + \frac{8\pi^2 m}{h}(E - V)\,\psi = 0,$$

where $$\Delta^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}$$

Derivation of Schrodinger's Wave Equation

The wave motion of a wave of a vibrating string can be described by the equation :

$$\psi = A \sin\frac{2\pi x}{\lambda}, \qquad ...(1)$$

where ψ represents the amplitude of the wave and is called the *wave function*; A is a constant; x is the displacement of the wave in a given direction and λ is the wavelength.

On differentiating equation (1) with respect to x, we get :

$$\frac{d\psi}{dx} = \left(A \cos\frac{2\pi x}{\lambda}\right)\left(\frac{2\pi}{\lambda}\right)$$

or $$\frac{d\psi}{dx} = \frac{2\pi A}{\lambda}.\cos\frac{2\pi x}{\lambda} \qquad ...(2)$$

By differentiating again equation (2), we get :

$$\frac{d^2\psi}{dx^2} = \frac{2\pi A}{\lambda}\left(-\sin\frac{2\pi x}{\lambda}\right)\left(\frac{2\pi}{\lambda}\right)$$

or $$= -\frac{4\pi^2 A}{\lambda^2}.\sin\frac{2\pi x}{\lambda}$$

$$= -\frac{4\pi^2}{\lambda^2}\left(A.\sin\frac{2\pi x}{\lambda}\right)$$

$$= -\frac{4\pi^2}{\lambda^2}.\psi \qquad \left[\because \psi = A \sin\frac{2\pi x}{\lambda}\right]$$

or $$\boxed{\frac{d^2\psi}{dx^2} + \frac{4\pi^2\psi}{\lambda^2} = 0} \qquad ...(3)$$

This is the *classical wave equation* which describes the wave motion of any particle vibrating along x-axis.

With the confirmation of the idea that an electron in an atom is described as a standing wave round the nucleus, the classical wave equation (3) which describes the wave motion of any particle vibrating along x-axis should be applicable to the standing wave of an electron.

We have seen in Bohr's theory that the total energy (E) of an electron is the sum of its kinetic energy (K.E.) and potential energy (V), *i.e.*

$$E = K.E. + V$$

or $$E = \tfrac{1}{2}mv^2 + V \qquad ...(4)$$

In equation (4) m is the mass of the electron and v is the velocity with which the electron is moving.

Now from de Broglie's equation, we have

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

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

or $$m^2v^2 = h^2/\lambda^2$$

or $$\tfrac{1}{2}m^2v^2 = \frac{h^2}{2\lambda^2}$$

or $$\tfrac{1}{2}mv^2 = \frac{h^2}{2\lambda^2 m} \qquad ...(5)$$

Putting the value of $\frac{1}{2}mv^2$ from equation (5) in equation (4), we get :

$$E = \frac{h^2}{2\lambda^2 m} + V$$

or $$\frac{1}{\lambda^2} = \frac{2m}{h^2}(E - V) \qquad ...(6)$$

Putting the value of $1/\lambda^2$ from equation (6) in equation (3), we get :

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2\psi \times 2m}{h^2}(E - V) = 0$$

or $$\boxed{\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - V)\,\psi = 0} \qquad ...(7)$$

Equation (7) is the Schroding's wave equation of a wave moving in one dimension x, *i.e.* the wave is moving in one direction x. If an electron wave is moving in any of the three axes x, y, z, its wave motion can be described by the wave equation :

$$\boxed{\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}(E - V)\,\psi = 0} \qquad ...(8)$$

Equation (8) is called Schrodinger's wave equation.

Eigen-values and Eigen-functions

Being a differential equation of second order, Schrodinger's equation has several solutions for ψ but many of these are imaginary and hence are not valid. Only those values of ψ are valid which satisfy the following conditions :

(*i*) The wave function must be finite and continuous.

(*ii*) The solution must be single valued *i.e.* at a given point there can never be more than one value for the amplitude, ψ.

(*iii*) $\frac{d\psi}{dx}$, $\frac{d\psi}{dy}$, and $\frac{d\psi}{dz}$ must be continuous functions of x, y, and z respectively.

(*iv*) The solutions must be normalised *i.e.* they must satisfy the relation

$$\int_0^{+\infty} \psi^2 dr = 0,$$

where dr is a small volume element.

The above conditions clearly show that the wave function, ψ is always *finite, single-valued* and *continuous*. It has zero value at infinite distance.

Values of E obtained by substituting the values of ψ in Schrodinger's wave equation [equation (8)] satisfying the above conditions are called **eigen-values** while the values of ψ obtained by substituting the proper values of E in equation (8) are called **eigen-functions.** Thus E values are called eigen-values while ψ values are called eigen-functions. The eigen-function for an electron is called an atomic orbital. As the eigen-values (*i.e.* E values) correspond very nearly to the energy levels associated with different Bohr orbits, the occurrence of definite energy levels in an atom follows directly from the wave mechanical concepts.

Physical Significance of ψ and ψ^2

In Schrodinger's wave equation the wave function, ψ represents the amplitude of the wave. From this equation the value of ψ for *1s* electron situated at a distance of r from the proton in the ground state of hydrogen atom is given by :

$$\psi_{1s} = C_1 . e^{-C_2 r}, \qquad ...(1)$$

where C_1 and C_2 are constants.

The energy for the same electron is given by

$$E_{1s} = 2.18 \times 10^{-11} \text{ ergs/atom} \qquad ...(2)$$

The wave function, ψ by itself has no physical meaning and all that we can extract from the wave mechanical approach to the internal structure of the atom is through its square (*i.e.* ψ^2) which measures the probability of finding an electron of given energy in an extremely small volume round the nucleus. The probability or chance of finding an electron in the space round the nucleus is called **electron probability function,** D whose value for an extremely small spherical shell of radius r and thickness, dr round the nucleus is given by :

Electron probability function, D

$$= \text{Volume of the spherical shell of radius } r \text{ and thickness } dr \times \psi^2$$

or $$= 4\pi r^2.dr.\psi^2$$

The above equation clearly shows that the magnitude of electron probability function, D depends on the value of r. In case of 1*s* electron of H-atom the following points may be noted :

(*a*) When $r = 0$ or ∞, D becomes equal to zero, *i.e.* there is no probability of finding an 1*s* electron of H-atom at the nucleus ($r = 0$) or at an infinite distance ($r = \infty$).

(*b*) When $r = 0.529$Å which is the radius of Bohr's first orbit, the probability of finding the electron is maximum ($\approx 95\%$), *i.e.* the radius of maximum probability of finding the 1*s* electron of H-atom is 0.529 Å.

The facts mentioned at (*a*) and (*b*) above will be made more clear when we study *Radial Probability Distribution Curves* discussed in this chapter.

Applications of Schrodinger's Wave Equation

Important applications of Schrodinger's wave equation are given below :

1. To Calculate Energy and Wave Function of a Particle in One-Dimensional Box.

Let us consider a particle (say, an electron) of mass m bounding back and forth from one side of the box to the other as shown in Fig. 2.5. The length of the box is a and height is infinite. Suppose that the particle moves only in one direction, say, along the x-axis, and is confined between $x = 0$ and $x = a$. Inside the box, the potential energy, V of the particle is constant and may be taken, for convenience, equal to zero (V = 0) so that there is no restriction on the movement of the particle within the box. Thus *inside* the box V = 0. Let the value of V be infinite when $x < 0$ (*i.e.* negative value of x) and $x > a$, (*i.e.*, out side the box) the

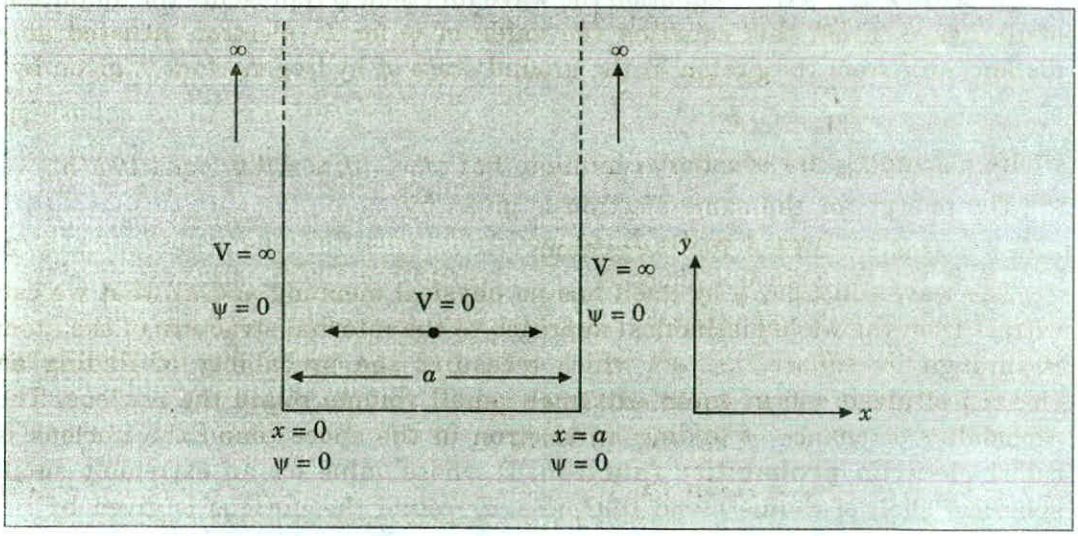


Fig. 2.5. Particle (shown by a dot) in one-dimensional box.

value of V is infinite. ($V = \infty$ at $x < 0$ and $x > a$). Obviously the wave function, ψ and hence the probability of finding the particle, ψ^2 must be zero when $x < 0$ (*i.e.* negative value of x), $x = 0$, $x = a$ and $x > a$. In other words this means that the particle is confined to the box and cannot escape the box, *i.e.* the particle does not exist outside the box.

Now our task is to find out the value of energy (E) and wave function (ψ) of the particle inside the box, *i.e.* between the region $x = 0$ and $x = a$.

We have seen that the equation given below is the Schrodinger's wave equation describing the motion of a wave in one dimension.

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - V)\,\psi = 0 \qquad ...(1)$$

Now since inside the box V = 0, the above equation becomes :

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - 0)\,\psi = 0$$

or $$\boxed{\frac{d^2\psi}{dx^2} + \frac{8\pi^2 mE}{h^2}\psi = 0} \qquad ...(2)$$

Equation (2) has the following solution for the wave function, ψ.

$$\psi = A.\sin bx + B.\cos bx \qquad ...(3)$$

In equation (3) A and B are two parameters.

Differentiating equation (3) twice with respect to x, we get :

$$\frac{d^2\psi}{dx^2} = -b^2(A.\sin bx + B.\cos bx)$$

or $$\boxed{\frac{d^2\psi}{dx^2} = -b^2\psi} \quad \text{[From equation (3)]} \qquad ...(4)$$

Comparing equations (2) and (4), we get

$$\boxed{b^2 = \frac{8\pi^2 mE}{h^2}} \qquad ...(5)$$

Now applying the boundary condition that at $x = 0$, $\psi = 0$ to equation (3), we get :

$$0 = A.\sin b \times 0 + B.\cos b \times 0$$
$$= A.\sin 0 + B.\cos 0$$
$$= A \times 0 + B \times 1$$

or $$B = 0 \qquad ...(6)$$

On putting B = 0 in equation (3) we get :

$$\psi = A.\sin bx + 0 \times \cos bx$$

or $$\boxed{\psi = A.\sin bx} \qquad ...(7)$$

Applying the other boundary condition that at $x = a$, $\psi = 0$ to equation (3), we get :

$$0 = A.\sin ba + B.\cos ba$$

$$= A.\sin ba + 0 \times \cos ba \qquad (\because B = 0)$$

or $$0 = A.\sin ba \qquad ...(8)$$

Now A cannot be equal to zero ($A \neq 0$) because in that case the probability of finding the particle in the box will be zero which is not acceptable.

$$\therefore \quad \sin ba = 0$$

or $$\sin ba = \sin n\pi$$

or $$ba = n\pi$$

or $$\boxed{b = \frac{n\pi}{a}} \qquad ...(9)$$

or $$\boxed{b^2 = \frac{n^2\pi^2}{a^2}} \qquad ...(10)$$

Comparing equations (10) and (5), we get :

$$\frac{n^2\pi^2}{a^2} = \frac{8\pi^2 mE}{h^2},$$

which gives the value of the energy (E_n) of the particle satisfying equation (2) as follows :

$$\boxed{E_n = \frac{n^2h^2}{8ma^2}} \qquad ...(11)$$

In equation (11) n is an integer which is called a quantum number and can have the values 1, 2, 3, ... This quantum number arises as a consequence of the boundary conditions imposed. n cannot be equal to zero, because then ψ and hence ψ^2 would be zero every where within the box. E_n values are usually called **eigen-values.** It is evident from equation (11) that the energy of the particle is quantised and so cannot vary continuously. Permissible values of E_n depend on the magnitude of n. E_n increases as n^2 increases and it cannot be equal to zero, since, as we have shown above, n cannot be equal to zero. E_n remains independent of x.

The values of energy that a particle in the box can possess are 1, 4, 9, 16...n^2 times the unit $h^2/8ma^2$. There are no energy values in between these values Thus an electron cannot have zero energy, since n is never zero. On the other hand, according to classical mechanics, all the energy values including E = 0 are permissible.

Substituting $b = n\pi/a$ from equation (9) in equation (7), we get the value of wave function, ψ_n given by :

$$\boxed{\psi_n = A.\sin\left(\frac{n\pi x}{a}\right)} \qquad ...(12)$$

ψ_n values are called **eigen-functions.**

Fig. 2.6 shows the plots of ψ and ψ^2 against x for the particle in the box. The following points may be noted from the figure :

(*i*) The probability of finding the particle (ψ^2) depends on x and energy, E

(*ii*) For the lowest or ground state one half-wave-length covers the box and hence there is no internal node, *i.e.* there is no point where the probability of finding the particle (ψ^2) is zero. In second energy level the wave function has one node and third has two nodes. Thus, in general, the number of nodes in the nth energy level is always equal to (n—1). Greater the number of nodes, more is the curvature in the wave function and greater is the total energy. This total energy is equal to kinetic energy, since in this case the potential energy has been assumed to be equal to zero inside the box.

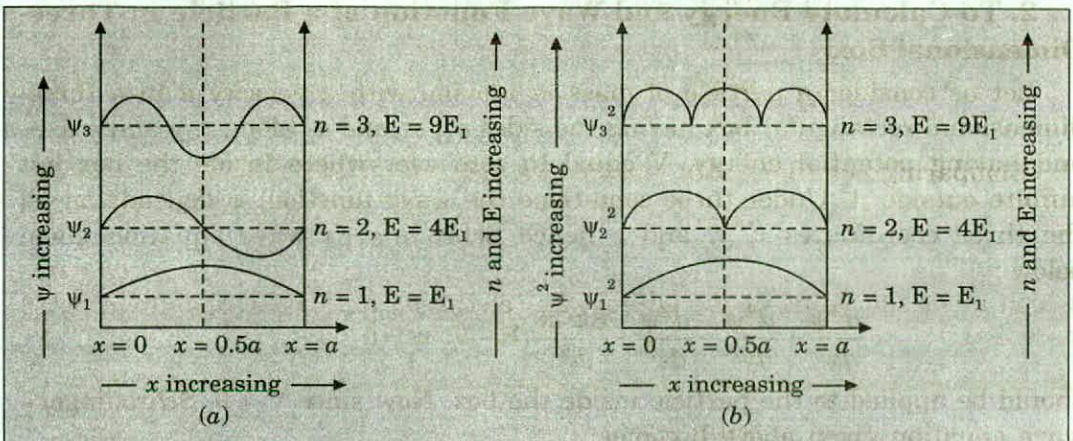


Fig. 2.6. Plot of wave function, ψ and its square, ψ^2 (called probability of finding the particle) of a particle in one-dimensional box against x (*a*) Plot of ψ against x (*b*) Plot of ψ^2 against x.

Determination of the value of A. The value of the constant A can be determined by *normalising* the wave function, ψ. Since the probability (expressed as ψ^2) of finding the particle within the box (*i.e.* between $x = 0$ and $x = a$) is unity, we have :

$$\int_0^a \psi^2 dx = 1 \qquad ...(13)$$

Substituting the value of ψ from equation (12) in this equation, we have :

$$\int_0^a A^2 \sin^2\left(\frac{n\pi x}{a}\right) dx = 1$$

or

$$\frac{1}{A^2} = \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx$$

On solving the above equation we get :

$$A = \sqrt{\frac{2}{a}}$$

This mathematical operation is called **normalisation** and the constant value is called **normalisation factor.** Thus the normalised wave function (Ψ_n) is given by :

$$\boxed{\psi_n = \sqrt{\frac{2}{a}}.\sin\left(\frac{n\pi x}{a}\right)} \quad ...(14)$$

Equation (14) has been obtained by putting $A = \sqrt{\frac{2}{a}}$ in equation (12). In equation (14) the factor, $\sqrt{\frac{2}{a}}$ is called normalisation factor

2. To Calculate Energy and Wave Function of a Particle in Three-Dimensional Box.

Let us consider a particle of mass m moving with a velocity u in a three-dimensional rectangular box having the sides a_x, a_y and a_z along x, y and z axes and having potential energy, V equal to zero everywhere inside the box but infinite outside it. Under these conditions the wave function, ψ depends on all the three coordinates x, y, and z hence Schrodinger's wave equation given below :

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}(E - V)\,\psi = 0$$

should be applied to the particle inside the box. Now since V = 0, Schrodinger's wave equation given above becomes :

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2} E\psi = 0 \quad ...(15)$$

Now, as already mentioned, since the wave function ψ depends on all the three coordinates *viz.* x, y and z, it should be equal to the product of three wave functions namely ψ_x, ψ_y, and ψ_z depending only on one axis *viz.* x, y or z respectively. Thus :

$$\psi = \psi_x.\psi_y.\psi_z \quad ...(16)$$

Now since ψ_x depends on x only,

$$\frac{d\psi}{dx} = \psi_y.\psi_z.\frac{d\psi_x}{dx}$$

or
$$\frac{d^2\psi}{dx^2} = \psi_y.\psi_z.\frac{d^2\psi_x}{dx^2} \quad ...(a)$$

Similarly the following relations can also be obtained :

$$\frac{d^2\psi}{dy^2} = \psi_x.\psi_z.\frac{d^2\psi_y}{dy^2} \quad ...(b)$$

$$\frac{d^2\psi}{dz^2} = \psi_x.\psi_y.\frac{d^2\psi_z}{dz^2} \quad ...(c)$$

Substituting the relations given at (16), (*a*), (*b*) and (*c*) in equation (15), we get :

$$\psi_y.\psi_z.\frac{d^2\psi_x}{dx^2}+\psi_x.\psi_z.\frac{d^2\psi_y}{dy^2}+\psi_x.\psi_y.\frac{d^2\psi_z}{dz^2}+\frac{8\pi^2 m}{h^2}.E\,\psi_x.\psi_y.\psi_z=0$$

On dividing by $\psi_x\ \psi_y\ \psi_z$, we get :

$$\frac{1}{\psi_x}.\frac{d^2\psi_x}{dx^2}+\frac{1}{\psi_y}.\frac{d^2\psi_y}{dy^2}+\frac{1}{\psi_z}.\frac{d^2\psi_z}{dz^2}+\frac{8\pi^2 mE}{h^2}=0$$

Thus we see that the above equation (Schrodinger's wave equation) can be broken into the following three differential equations :

$$\frac{1}{\psi_x}.\frac{d^2\psi_x}{dx^2}+\frac{8\pi^2 mE_x}{h^2}=0 \qquad ...(d)$$

$$\frac{1}{\psi_y}.\frac{d^2\psi_y}{dy^2}+\frac{8\pi^2 mE_y}{h^2}=0 \qquad ...(e)$$

$$\frac{1}{\psi_z}.\frac{d^2\psi_z}{dz^2}+\frac{8\pi^2 mE_z}{h^2}=0 \qquad ...(f)$$

Here E_x, E_y and E_z are the three components of the total energy, E of the particle in the box along the three axes x, y and z.

The solutions of (*d*), (*e*) and (*f*) equations give the following expressions for E_x, E_y, and E_z

$$E_x=\frac{n_x^2h^2}{8ma_x^2}=\frac{h^2}{8m}.\frac{n_x^2}{a_x^2}$$

$$E_y=\frac{n_y^2h^2}{8ma_y^2}=\frac{h^2}{8m}.\frac{n_y^2}{a_y^2}$$

$$E_z=\frac{n_z^2h^2}{8ma_z^2}=\frac{h^2}{8m}.\frac{n_z^2}{a_z^2}$$

In the above equations n_x, n_y and n_z are the quantum numbers in the direction of x, y and z axes respectively. Thus the total energy, E of the particle is given by :

$$E = E_x + E_y + E_z$$

or

$$\boxed{E=\frac{h^2}{8m}\left(\frac{n_x^2}{a_x^2}+\frac{n_y^2}{a_y^2}+\frac{n_z^2}{a_z^2}\right)} \qquad ...(17)$$

It is evident from equation (17) that the energy of a particle in a three-dimensional rectangular box is *quantised*. Such a thing does not happen with the energy of the particle in one-dimensional box.

If the particle is considered to be present in a cubic box, then $a_x = a_y = a_z = a$ (say) and hence the energy, E of such a particle is given by :

$$\boxed{\mathbf{E} = \frac{\mathbf{h}^2}{\mathbf{8ma}^2}(\mathbf{n}_x^{\,2} + \mathbf{n}_y^{\,2} + \mathbf{n}_z^{\,2})} \qquad ...(18)$$

From equation (18) it is evident that the energy of a particle in a cubic box of side 'a' depends on the *sum* of the squares of the three quantum numbers, n_x, n_y, and n_z. It is also evident that it is possible for an energy level to have independent states, each having specified quantum numbers. For example, if the energy of a level is equal to $6h^2/8ma^2$, then this energy level has three independent states having the following values of quantum numbers, n_x, n_y and n_z.

	Quantum numbers		
	n_x	n_y	n_z
Set No. 1	2	1	1
Set No. 2	1	2	1
Set No. 3	1	1	2

These three independent states have the same energy (= $6h^2/8ma^2$) and, since the number of states is three, these states are called *three-fold degenerate* or *triply degenerate states*. In other words the energy level having energy equal to $6h^2/8ma^2$ is triply degenerate. The degenerate states of an energy level having energy equal to $9h^2/8ma^2$, $11h^2/8ma^2$ and $14h^2/8ma^2$ are shown in Fig. 2.7. It may be noted from the figure that the states of energy levels with energy equal to $3h^2/8ma^2$ and $12h^2/8ma^2$ are *non-degenerate*, since there is only one set of quantum numbers for these states.

Since according to equation (14).

$$\psi_x = \sqrt{\frac{2}{a_x}}.\sin\left(\frac{n_x\pi x}{a_x}\right)$$

$$\psi_y = \sqrt{\frac{a}{a_y}}.\sin\left(\frac{n_y\pi y}{a_y}\right)$$

and

$$\psi_z = \sqrt{\frac{2}{a_z}}.\sin\left(\frac{n_z\pi z}{a_z}\right),$$

$$\psi = \psi_x.\psi_y.\psi_z$$

$$= \left[\sqrt{\frac{2}{a_x}}.\sin\left(\frac{n_x\pi x}{a_x}\right)\right]\left[\sqrt{\frac{2}{a_y}}.\sin\left(\frac{n_y\pi y}{a_y}\right)\right]\left[\sqrt{\frac{2}{a_z}}.\sin\left(\frac{n_z\pi z}{a_z}\right)\right]$$

$$= \sqrt{\frac{8}{a_x.a_y.a_z}}.\sin\left(\frac{n_x\pi x}{a_x}\right).\sin\left(\frac{n_y\pi y}{a_y}\right).\sin\left(\frac{n_z\pi z}{a_z}\right)$$

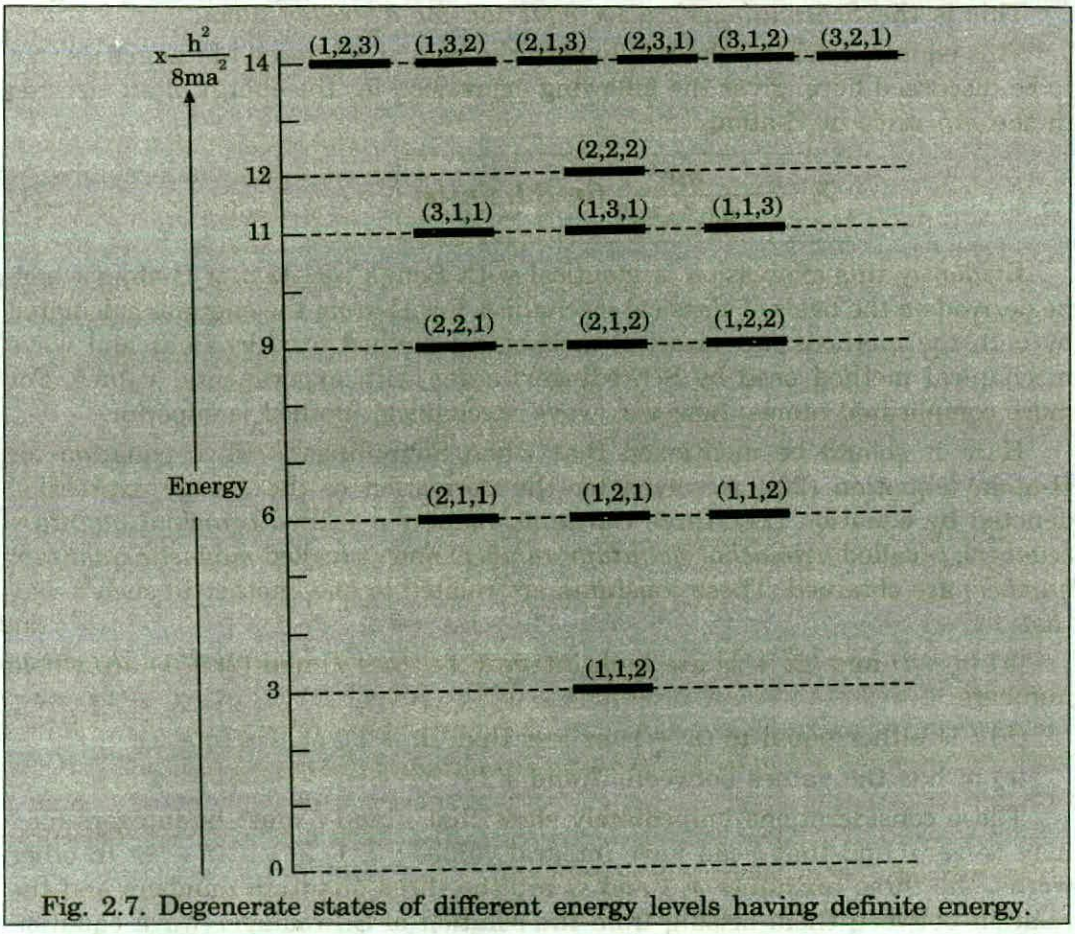


Fig. 2.7. Degenerate states of different energy levels having definite energy.

Now since the volume of the box, $V = a_x.a_y.a_z$, the above equation reduces to :

$$\psi = \sqrt{\frac{8}{V}}.\sin\left(\frac{n_x \pi x}{a_x}\right).\sin\left(\frac{n_y \pi y}{a_y}\right).\sin\left(\frac{n_z \pi z}{a_z}\right) \quad ...(19)$$

Equation (19) gives the value of normalised wave function, ψ. Here the factor, $\sqrt{8/V}$ is the normalisation factor.

3. To Derive an Expression for the Energy of an Electron in H-atom.

We know that H-atom has one proton in its nucleus and one electron revolving round the nucleus in an orbit of radius, say r. Let the charge on the proton be equal to $+e$. The charge on the electron would, therefore, be equal to $-e$. Consequently the potential energy, V of the electron would be equal to $(-e) \times (+e)/r = -e^2/r$. When Schrondinger's wave equation (equation given on page 10.4) is applied to H-atom, we get :

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}\left[E - \left(-\frac{e^2}{r}\right)\right] = 0$$

or

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}\left(E + \frac{e^2}{r}\right) = 0 \quad ...(20)$$

This is the *Schrondinger's wave equation for hydrogen atom.*

This equation, when solved fully with the help of advanced Mathematics (not to be discussed here) gives the following expression for the energy of an electron in the *nth* orbit in H-atom.

$$\boxed{E_n = -\frac{me^4}{8\varepsilon_0{}^2 h^2 n^2} \textbf{(in S.I. units)}} \quad ...(21)$$

Evidently this expression is identical with Bohr's equation of H-atom which he derived on the basis of classical mechanics. For H-atom the energies calculated by both the methods (*i.e.* classical mechanical method used by Bohr and wave mechanical method used by Schrodinger) agree with experimental values. For more complicated atoms, however, wave mechanical method is superior.

Here it should be mentioned that when Sohrodinger's wave equation for H-atom [equation (20)] is solved for the derivation of the energy expression denoted by equation (21), three constants namely n (called *principal quantum number*), l (called *azimuthal quantum number*) and m (called *magnetic quantum number*) are obtained. These constants are related to one another in such a way that;

(*a*) $(n + l)$ and $(2l + 1)$ are both integral, *i.e.* $(n + l)$ and $(2l + 1)$ are whole numbers.

(*b*) l is either equal to $(n - 1)$ or less than $(n - 1)$, *i.e.* $l \leq (n - 1)$.

(*c*) m has the values between $-l$ and $+ l$.

These considerations immediately show that n and l must be integers (or l may be zero) and that l can have integral values : 0, 1, 2, ... $(n - 1)$. In other words, the three constants n, l and m are the three quantum numbers and the relation between them arising from the solution of Schrodinger wave equation is also exactly the same which has been deduced by means of spectroscopic measurements.

Here it should be understood clearly that spin quantum number, s, does not appear in the solution of wave equation. It has, therefore, to be added.

4. Concept of Atomic Orbital.

If a line is drawn enclosing a region where an electron can be found, say 90 to 95% of time, such a region or space is called an **atomic orbital**. Thus :

The three-dimensional region or space (i.e., volume) round the nucleus of an atom where there is maximum probability of finding an electron having a certain energy is called atomic orbital.

OR

An atomic orbital represents the space round the nucleus in an atom where the electron spends most of its time while in constant motion.

OR

The thin, shell-like, region in space surrounding the nucleus for which electron probability has a high value is known as an atomic orbital.

The energy of the electron in an atomic orbital is always the same. The electron is free to be found anywhere in the atomic orbital at any given time. A spherical symmetrical orbital can be pictured as a tennis ball fluffed both inside and outside. For the **excited hydrogen** atom other orbitals of spherical as well as non- spherical shapes also exist and the probability of finding the electron may change not only with distance but also with direction from the nucleus.

Differences between Orbit and Orbital

The points of difference between an orbit and an orbital are given below in a tabular form.

Orbit	*Orbital*
(*i*) As postulated by Bohr, an orbit is a definite circular path at a definite distance from the nucleus in which the electron revolves round the nucleus. Orbits are numbered as 1, 2, 3, 4..... from the nucleus and are designated by the capital letters K, L, M, N.....etc.	(*i*) As postulated by wave nature of an electron, an orbital is defined as a three-dimensional region or space around the nucleus within which the probability of finding an electron with a certain energy is maximum.
(*ii*) An orbit indicates an exact position or location of an electron in an atom. For example, according to Bohr's theory, an electron of hydrogen is found at a distance of 0.53Å from the nucleus.	(*ii*) An orbital does not specify the definite or exact position of an electron in an atom, since the electron, due to its wave-nature, can not be found at a fixed distance from the nucleus.
(*iii*) There is a certainty about the movement of an electron in an orbit.	(*iii*) Due to uncertainty principle, there is no certainty about the movement of an electron in an orbital.
(*iv*) It represents the planar motion of the electron.	(*iv*) It represents the three-dimensional motion of the electron round the nucleus.
(*v*) The maximum number of electrons in an orbit is equal to $2n^2$ where n is the number of the orbit.	(*v*) An orbital cannot accommodate more than two electrons. These two electrons must have opposite spins.
(*vi*) Orbits are circular in shape.	(*vi*) Orbitals have different shapes, *e.g.*, *s*-orbital is spherically symmetrical, *p* orbitals are dumb-bell shaped etc.

Quantum Numbers

The term quantum number is used to identify the various energy levels available with the atom in which the electron of the atom can reside. The word *quantum* is used to signify that all the energy levels which are available to an electron are governed by the laws of quantum mechanics.

Just as a college student is identified by (*i*) *his name* (*ii*) *the name of his college* (*iii*) *class in which he is studying and* (*iv*) *the locality in which his college is situated*, an electron in an atom is completely described by its four quantum numbers. Thus the quantum numbers serve as **identification numbers** or **labels** which completely define the electron in an atom, *i.e.* these numbers

(*i*) specify the position (or location) of an electron in an atom.

(*ii*) predict the direction of spin or self-rotation of the electron.

and, (*iii*) determine the energy and angular momentum of the electron.

Four quantum numbers which are required to completely specify the character of an electron are discussed below. Each quantum number refers to a particular character of an electron in an atom.

We have already seen that when Schrodinger's wave equation for H-atom is solved for the derivation of an expression giving the energy of an electron in H-atom, three constants called *principal quantum number* (*n*), *azimuthal quantum number* (*l*) and *magnetic quantum number* (*m*) are automatically obtained.

1. Principal Quantum Number (*n*).

We have seen that Bohr had assumed that electrons in an atom are revolving round the nucleus in circular orbits or shells which he had also called energy levels. Different energy levels in an atom have been represented by *n* which can have *non-zero positive integer* (whole number) *values upto infinity i.e.*

$$n = 1, 2, 3, \ldots \infty$$

Thus *n* can have infinite values and it has been called principal quantum number by Bohr.

Informations given by *n* values. (*i*) *The value of n represents the shells or energy levels* in which the electron revolves round the nucleus. These shells or energy levels are designated by capital letters K, L, M ... For example the shell for which $n = 1$ is called K shell (*1st* shell), that for which $n = 2$ is called L shell (*2nd* shell) and so on. Thus :

Value of n	→	1	2	3	4	.....
Designation of shells	→	K (*1st shell*)	L (*2nd shell*)	M (*3rd shell*)	N (*4th shell*)	.....

K, L, M etc shells are called $n = 1$ shell (*1st* shell), $n = 2$ shell (*2nd* shell) etc. Thus *n* values tell as to in which shell an electron is residing.

(*ii*) *n also determines the location of the electron in a shell, i.e. n* determines the distance of the electron from the nucleus. More is the value of *n*, more far is the electron from the nucleus, *e.g.*, the electron for which $n = 2$ is more far from the nucleus than that for which $n = 1$. Similarly the electron having $n = 3$ will be more far from the nucleus than an electron with $n = 2$. Thus :

	—*n values increasing*⟶
n-values →	$1 < 2 < 3 < 4 < .....$
r-values →	$r_1 < r_2 < r_3 < r_4 < .....$
	—*r values increasing* ⟶

Thus we see that n represents the size of the electron orbits (*i.e.*, effective volume of the electron cloud). Higher is the value of n, higher is the size of the electron orbit or atom.

(*iii*) *n also determines the energy of the electron in a given orbit.* We know that the energy of an electron of hydrogen-like atoms or ions in an orbit with principal quantum number, n (*i.e.*, *nth* orbit) is given by :

$$E_n = -\frac{2\pi^2 me^4}{n^2h^2},$$

where E_n is the energy of the electron in *nth* orbit and π, m, e and h have their usual meanings. This equation shows that, due to the presence of negative sign, as the value of n increases, the value of energy becomes less negative *i.e.*, with the increase of the value of n, the magnitude of energy also increases. When n becomes equal to infinity, energy becomes zero. Thus the relation between n and E values of an electron in various orbits can be shown as :

	*n*values increasing →
n-values →	$1 < 2 < 3 < 4 < .....$
E-values →	$E_1 < E_2 < E_3 < E_4 < .....$
	E values increasing →

(*iv*) *n also gives the maximum number of electrons that a shell can hold.* A shell with principal quantum number, n can have $2n^2$ electrons. Thus :

Maximum number of electrons in K-shell (1st shell) with n = 1 } $= 2 \times 1^2 = 2$

Maximum number of) electrons in L-shell (2nd shell) with n = 2 } $= 2 \times 2^2 = 8$

Maximum number of) electrons in M-shell (3rd shell) with n = 3 } $= 2 \times 3^2 = 18$

Maximum number of) electrons in N-shell (4th shell) with n = 4 } $= 2 \times 4^2 = 32$

2. Azimuthal or Subsidiary Quantum Number (*l*)

We have seen that when hydrogen spectrum is observed by means of spectroscope of high resolving power, the individual spectral lines are found to consist of several very fine lines lying close together. For example H_α line in the

Balmer series of hydrogen spectrum is found to consist of five component lines. Such a spectrum which consists of closely-spaced spectral lines is called **fine structure**. The appearance of several lines in a single line has been explained by saying that each shell is divided into sub-shells which give closely-spaced lines in the spectrum. In order to represent these sub-shells only one quantum number viz., principal quantum number (n) is not sufficient. Rather, another quantum number which is called **azimuthal** or **subsidiary quantum number** (l) is used to represent the sub-shells of which the shells are composed.

The value of l depends on the value of n. For a given value of n, l can have the values from 0 to $(n - 1)$, *i.e.*,

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

Thus l can have n values.

Informations given by l values. (i) Different values of l represent different sub-shells which are designated by small letters *s, p, d, f*... These letters stand *for sharp, principal, diffuse* and *fundamental* which are the spectral terms used to describe the series of lines observed in atomic spectrum. For example, the sub-shell for which $l = 0$ is called *s* sub-shell, that for which $l = 1$ is called *p* sub-shell and so on. Thus :

Value of l	→	*0*	*1*	*2*	*3* .....
Designation of sub-shell	→	*s*	*p*	*d*	*f* .....

Thus electrons with $l = 0$, 1, 2 and 3 are said to be residing in *s, p, d* and *f* sub-shells respectively. Consequently l value tells us as to in which sub-shell an electron is residing.

s, p, d, and *f* sub-shells are also called $l = 0$ sub-shell, $l = 1$ sub-shell, $l = 2$ sub-shell and $l = 3$ sub-shell respectively.

The energies of the sub-shells belonging to the same shell are in the following order :

$$s < p < d < f$$

Thus the sequence of filling of *s, p, d* and *f* sub-shells belonging to the same shell is as :

$$\xrightarrow[s,\ p,\ d,\ f]{}$$

(ii) *Values of l define the shape of the sub-shell (electron cloud) occupied by the electron, i.e.*, whether the sub-shell is *spherical, dumb-bell or with some other complicated shape.* Each value of l gives a particular shape to the sub-shell. For example the sub-shell (electron cloud) with $l = 0$ has a *spherical shape*, that with $l = 1$ has a *dumb-bell shape with distorted spheres of high probability of the electron density on each side of the nucleus* while that with $l = 2$ has a shape which approximates to four pears with their stems pointing towards the nucleus. Sub-shells with higher l values have *very complex shape.*

(iii) *l values enable us to calculate the total number of sub-shells which a main shell* (K, L, M etc., shells) *has. Total number of sub-shells in a main shell*

with principal quantum number, n is equal to the total number of l values for the given value of n. For example :

(*a*) *K-shell (1st shell) for which n = 1.* When $n = 1$, $l = 0$. Since l has only one value, K-shell (1st shell) has only *one* sub-shell which is designated as *nl* or *1s*. Thus for 1s sub-shell $n = 1$ and $l = 0$. Thus :

$$n \rightarrow 1 \text{ (K-shell)}$$
$$l \rightarrow 0$$
$$\text{Designation of sub-shell } (nl) \rightarrow 1s$$

(*b*) *L-shell (2nd shell) for which n = 2.* When $n = 2$, $l = 0, 1$. Since l has two values, L-shell (2nd shell) has *two* sub-shells which are designated as 2s and 2p. Thus :

$$n \rightarrow 2 \quad 2 \text{ (L-shell)}$$
$$l \rightarrow 0 \quad 1$$
$$\text{Designation of sub-shell } (nl) \rightarrow 2s \quad 2p$$

(*c*) *M-shell (3rd shell) for which n = 3.* When $n = 3$, $l = 0, 1, 2$. Since l has three values, M-shell (3*rd* shell) has *three* sub-shells which are designated as 3*s*, 3*p* and 3*d*. Thus :

$$n \rightarrow 3 \quad 3 \quad 3 \text{ (M-shell)}$$
$$l \rightarrow 0 \quad 1 \quad 2$$
$$\text{Designation of sub-shell } (nl) \rightarrow 3s \quad 3p \quad 3d$$

(*d*) *N-shell (4th shell) for which n = 4.* When $n = 4$, $l = 0, 1, 2$ and 3. Since l has four values. N-shell (4*th* shell) has four sub-shells which are designated as *4s, 4p, 4d* and *4f*. Thus :

$$n \rightarrow 4 \quad 4 \quad 4 \quad 4 \text{ (N-shell)}$$
$$l \rightarrow 0 \quad 1 \quad 2 \quad 3$$
$$\text{Designation of sub-shell } (nl) \rightarrow 4s \quad 4p \quad 4d \quad 4f$$

It is evident from the above discussion that the total number of l values for a given n value is equal to the value of n and hence *the number of sub-shells in a main shell with principal quantum number, n is equal to n.*

Whatever has been said so far can be summarised as follows :

(*a*) K-shell (*1st* energy level) having $n = 1$ contains only *one* sub-shell, called *s* sub-shell ($l = 0$) and designated as 1s ($n = 1$, $l = 0$).

(*b*) L-shell (*2nd* energy level) with $n = 2$ contains two sub-shells which are designated as 2*s* ($n = 2$, $l = 0$) and 2*p* ($n = 2$, $l = 1$)

(*c*) M-shell (*3rd* energy level) with $n = 3$ is composed of *three* sub-shells which are represented as *3s* ($n = 3$, $l = 0$), *3p* ($n = 3$, $l = 1$) and *3d* ($n = 3$, $l = 2$).

(*d*) N-shell (*4th* energy level) with $n = 4$ consists of four sub-shells which are *4s* ($n = 4$, $l = 0$), *4p* ($n = 4$, $l = 1$), *4d* ($n = 4$, $d = 2$) and 4*f* ($n = 4$, $l = 3$).

All the above points have been illustrated in Fig. 2.8.

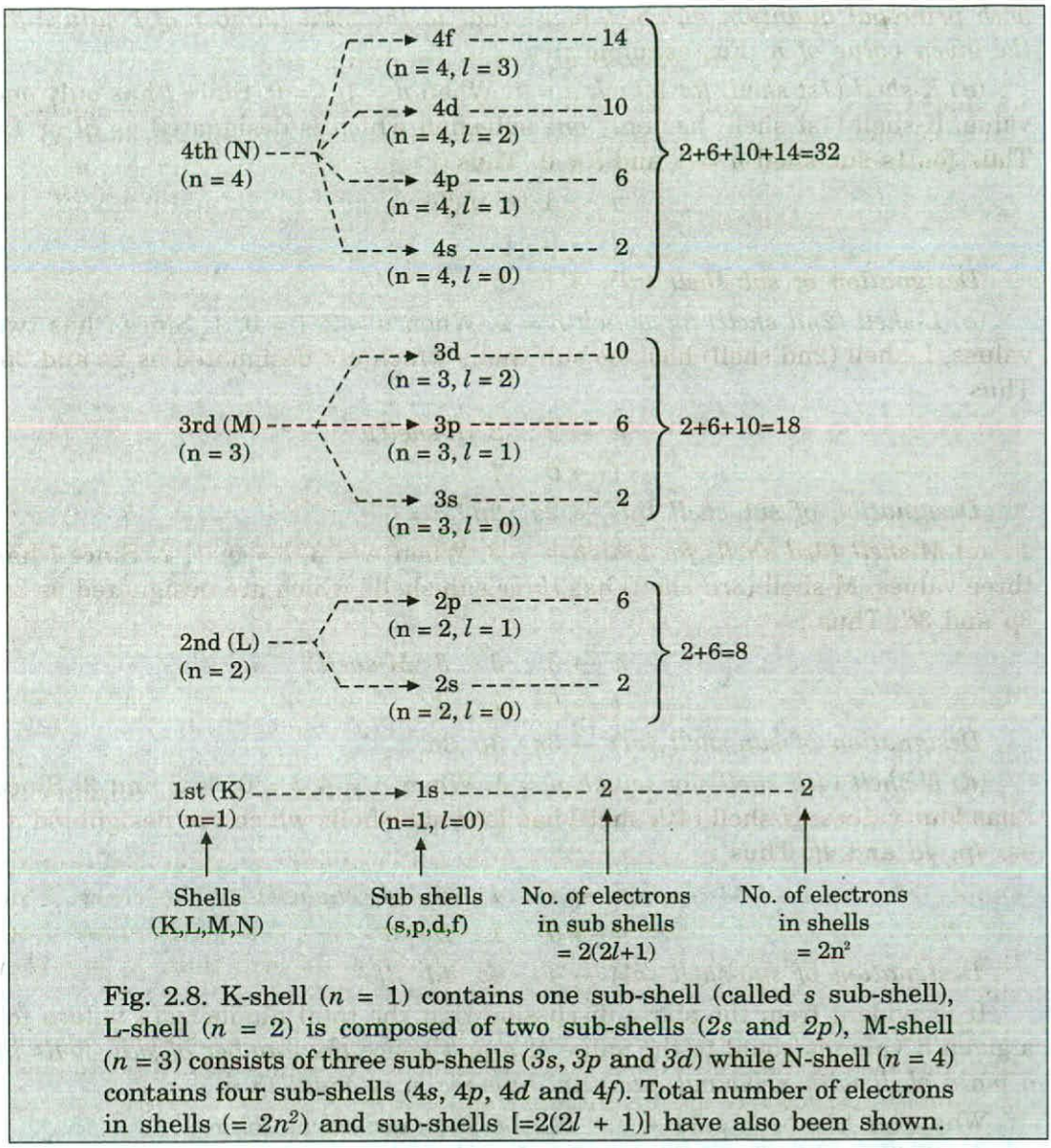


Fig. 2.8. K-shell (n = 1) contains one sub-shell (called s sub-shell), L-shell (n = 2) is composed of two sub-shells ($2s$ and $2p$), M-shell (n = 3) consists of three sub-shells ($3s$, $3p$ and $3d$) while N-shell (n = 4) contains four sub-shells ($4s$, $4p$, $4d$ and $4f$). Total number of electrons in shells ($= 2n^2$) and sub-shells [$=2(2l + 1)$] have also been shown.

(*iv*) *l values also enable us to calculate the total number of electrons in a given sub-shell (s, p, d and f sub-shells).* Total number of electrons in a given sub-shell with a given l value is equal to $2(2l + 1)$. Thus s, p, d and f sub-shells have 2, 6, 10 and 14 electrons respectively as shown below : (Also see Fig. 2.8 and Table 2.1).

Sub-shell	→	*s*	*p*	*d*	*f*
Value of l	→	*0*	*1*	*2*	*3*
No. of electrons in a sub-shell = 2(2l + 1)	→	*2*	*6*	*10*	*14*

Table 2.1. Relation between principal quantum number (n) and azimuthal quantum number (l)

Value of n and the shell designation	Value of l and designation of sub-shell (nl)	No. of sub-shells in main shell = n	No. of electrons in sub-shells = $2(2l+1)$ and their designation [$nl^{2(2l+1)}$]	Total number of electrons in main shell = $2n^2$
1 (K-shell or *1st* shell)	0 (*1s*)	1	$2(2 \times 0 + 1) = 2(1s^2)$	$2 \times 1^2 = 2$
2 (L-shell or *2nd* shell)	0 (*2s*)	1+1 = 2	$2(2 \times 0 + 1) = 2(2s^2)$	$2 \times 2^2 = 1$ *or* $2 + 6 = 8$
	1 (*2p*)		$2(2 \times 1 + 1) = 6(2p^6)$	
3 (M-shell or *3rd* shell)	0 (*3s*)	1+1+1 = 3	$2(2 \times 0 + 1) = 2(3s^2)$	$2 \times 3^2 = 18$ *or* $2 + 6 + 10 = 18$
	1 (*3p*)		$2(2 \times 1 + 1) = 6(3p^6)$	
	2 (*3d*)		$2(2 \times 2 + 1) = 10(3d^{10})$	
4 (N-shell or *4th* shell)	0 (*4s*)	1+1+1+1 = 4	$2(2 \times 0 + 1) = 2(4s^2)$	$2 \times 4^2 = 32$ *or* 2+6+10+14 = 32
	1 (*4p*)		$2(2 \times 1 + 1) = 6(4p^6)$	
	2 (*4d*)		$2(2 \times 2 + 1) = 10(4d^{10})$	
	3 (*4f*)		$2(2 \times 3 + 1) = 14(4f^{14})$	

(*v*) l value is a measure of the *orbital angular momentum* of an electron during its orbital motion about the nucleus. It is for this reason that l is also called **angular momentum quantum number** or **orbital quantum number** and sometimes **subsidiary quantum number.**

(*vi*) Sub-shells having equal l values (but with different n values) have similar shapes but their sizes increase as the corresponding n values increase. Thus, although *1s* and *2s* sub-shells (for both the sub-shells $l = 0$) have the same shape, their sizes are different; *2s* sub-shell being greater in size than *1s* sub-shell; since n for *2s* sub-shell is 2 while n for *1s* sub-shell is equal to 1.

Similarly *2p, 3p, 4p* sub-shells for which $l = 1$ have similar shapes but their sizes increase in the order : $2p < 3p < 4p$, since n values for these sub-shells *viz.* 2, 3 and 4 respectively are also increasing.

3. Magnetic Quantum Number (m)

We have seen that when an excited atom which gives a line emission spectrum is placed in a strong magnetic field, its spectral lines are further resolved into still thinner (*i.e.* closely spaced) lines. This type of splitting of spectral lines into a number of closely spaced lines has been explained by Linde who assumes that under the influence of magnetic field each sub-shell is further sub-divided into sub-shells, called **orbitals** which give the thinner lines in the spectrum.

In order to represent these orbitals the first two quantum numbers *viz.* principal quantum number (n) and azimuthal quantum number (l) are not sufficient. Rather, a third quantum number which is called **magnetic quantum number** (m) is used to represent the orbitals of which a given sub-shell is composed.

Values of *m*. Different values of m depend on the value of l which itself depends on the value of n.

m can have integral values ranging from $-l$ through 0 to $+ l$ *i.e.*

$$m = 0, \pm 1, \pm 2, \pm 3, ..., \pm l$$

Consequently :

When $l = 0$ (s sub-shell), $m = 0$ (only one value)

When $l = 1$ (p sub-shell), $m = 0, \pm 1$ (Three values)

When $l = 2$ (d sub-shell), $m = 0, \pm 1, \pm 2$ (Five values)

When $l = 3$ (f sub-shell), $m = 0, \pm 1, \pm 2, \pm 3$ (Seven values)

It may be seen from the above description that for a given value of l, total number of m values is $(2l + 1)$.

Information given by *m* values. Different values of m for a given value of l (*i.e.*, for a given sub-shell) give us the total number of different ways in which a given *s, p, d, f* sub-shell, in the presence of a magnetic field, can be arranged in space along *x, y* and *z* axes or the total number of orbitals into which a given *s, p, d* etc. sub-shell can be divided. Thus different values of m for a given value of l (a given sub-shell) give us the total number of different space orientations for the given *s, p, d* etc. sub-shells.

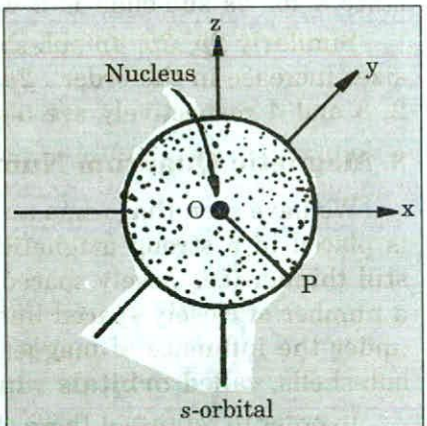
Examples (1) *s* sub-shell. We have seen that for *s* sub-shell $l = 0$. Now when $l = 0$, $m = 0$ (*only one value*). One value of m $(= 0)$ for $l = 0$ (*s* sub-shell) implies that *s* sub-shell of any energy level has only one space orientation and hence can be arranged in space only in one way along *x, y* or *z*-axis (See Fig. 2.9). Consequently *s* sub-shell is *not* sub-divided into any other orbital or *s* sub-shell has no orbital and is present in all the energy levels. Thus :

$$l \rightarrow 0 \text{ (}s \text{ sub-shell)}$$

$$m \rightarrow 0$$

$$\textit{Designation of orbital} \rightarrow s$$

The shape of *s*-orbital has been depicted in Fig. 2.9 which clearly shows that if a straight line is drawn at a certain angle from the origin O (nucleus) to cut the surface at a point P, the length of the line remains the same in all the directions. This means that the probability of finding the electron (*i.e.* electron density) in all the directions from the nucleus is the same in *s*-orbital. Consequently *s*-orbital has a symmetrically spherical shape and hence is usually represented by a circle which, in turn, represents a cut of sphere. (Fig. 2.9).



($l = 0$, $m = 0$)
Fig. 2.9. Space orientation and shape of *s*-orbital.

As the value of the principal quantum number (n) for an energy level increases, the size of the *s*-orbital also increases. For example *2s* orbital $(n = 2)$ is bigger in size than *1s* orbital $(n = 1)$.

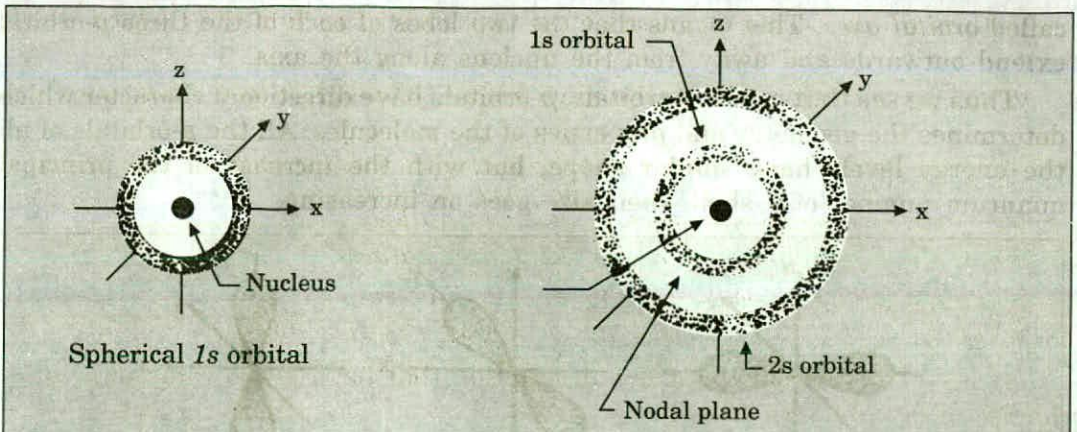


Fig. 2.10. *2s* orbital is bigger in size than *1s* orbital, since the value of principal quantum number (n) for *2s* orbital (= 2) is higher than that for 1*s* orbital (= 1).

An electron in *2s* orbital is farther away from the nucleus and has greater energy than in *1s* orbital. *2s* orbital begins with 2nd energy level (n = 2) which, in addition to *1s* orbital, also contains *2s* orbital. Thus *1s* orbital lies completely within *2s* orbital which, in turn, is surrounded by *3s* orbital (which begins with *3rd* energy level with n = 3) and so on. Thus we see that 2*s* orbital has a spherical shell in between *1s* and *2s* orbitals where the probability of finding the electron (*i.e.*, electron density) is zero. This spherical shell is called *nodal plane* or *nodal surface*. Consequently there are two concentric dense shells in *2s* orbital and hence this orbital is *bigger in size, more diffused* and has *more energy* than *1s* orbital. In general the number of spherical nodal surfaces in *s*-orbital of a given main energy level with principal quantum number, n is equal to $(n-1)$.

(2) *p* sub-shell (*a*) *Space orientation and shape.* For this sub-shell l = 1. Now when l = 1, m = 0, ±1 (Three values). Three values of m (= 0, ±1) for l = 1 (*p* sub-shell) imply that *p* sub-shell of any energy level (*p* sub-shell starts from *2nd* energy level with n = 2) has three space orientations and hence can be arranged in space in three different ways along *x*, *y* and *z* axes (Fig. 2.11). Consequently *p* sub-shell is sub-divided into three orbitals which, on the basis of the orientation of their lobes of maximum electron density with respect to *x*, *y* and *z* axes, are designated as p_x (m = 0), p_y (m = +1) and p_z (m = –l). Thus :

$$l \rightarrow 1 \ (p \text{ sub-shell})$$
$$m \rightarrow 0 \quad +1 \quad -1$$
$$\text{Designation of orbitals} \rightarrow p_x \quad p_y \quad p_z$$

Thus all the three *p*-orbitals have different space orientations. Since the three axes *viz.* *x*, *y* and *z* axes are perpendicular to each other, the three *p*-orbitals are also perpendicular to each other.

All the three *p*-orbitals namely p_x, p_y and p_z have *dumb-bell shape*. Each of the three *p*-orbitals has two *egg-shaped lobes* which touch each other at the origin (*i.e.* nucleus) and are *disposed symmetrically* along one of the three axes,

called *orbital axes*. This means that the two lobes of each of the three *p*-orbital extend outwards and away from the nucleus along the axis.

Thus we see that unlike *s*-orbitals, *p*-orbitals have directional character which determines the geometry and properties of the molecules. All the *p*-orbitals of all the energy levels have similar shape, but with the increase of the principal quantum number of a shell, their size goes on increasing.

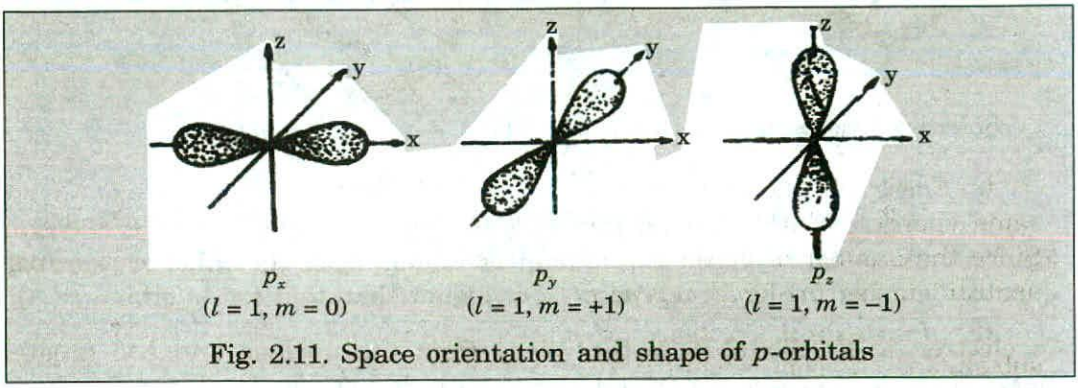


Fig. 2.11. Space orientation and shape of *p*-orbitals

(*b*) *Electron density and nodal plane.* The concept of electron density in *p*-orbitals can be understand by drawing a straight line OP at a certain angle from the origin O (nucleus) to cut the surface at a point P. The length of OP line is proportional to the probability of finding the electron anywhere in that direction. The probability decreases rapidly as the angle between OP and a given axis (*x*-axis, *y*-axis or *z*-axis) increases (Fig. 2.12). *x*, *y* and *z* axes are the directions of the maximum probability of electron density in case of p_x, p_y and p_z orbitals.

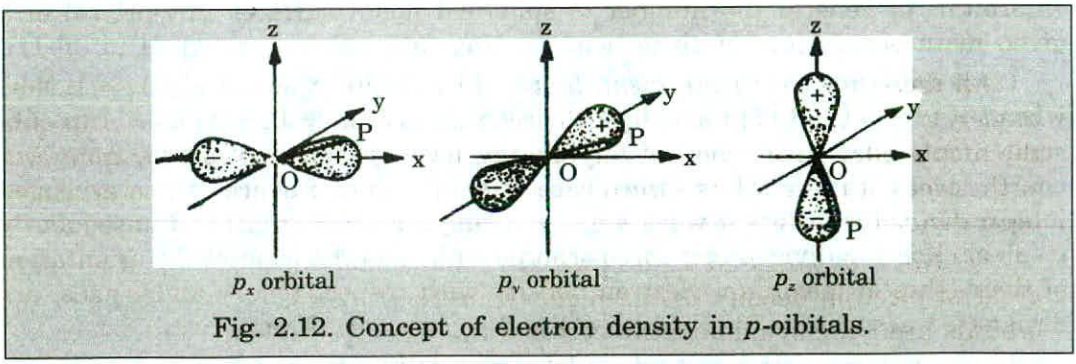


Fig. 2.12. Concept of electron density in *p*-oibitals.

The two lobes of a *p*-orbital can be separated by a plane which contains the nucleus and is perpendicular to the orbital axis. (See Fig. 2.13). The electron density (*i.e.* probability of finding the electron) at the nucleus as well as on the plane is zero. The nucleus at which the electron density is zero is called **node** and the plane passing through the orbital-axis (at this plane as well) the electron density is zero is called **nodal plane**.

It can be seen that each of the three *p*-orbitals has **one** such nodal plane. *e.g.*, for p_x orbital *yz* plane is the nodal plane.

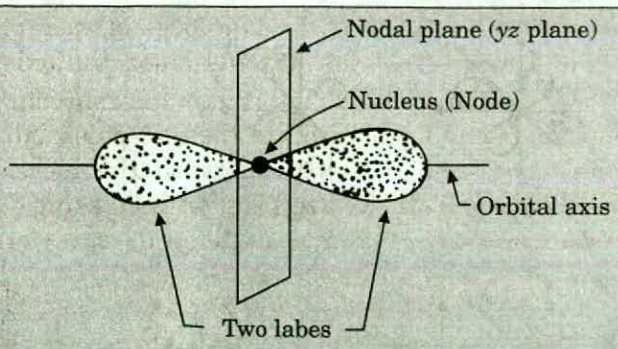


Fig 2.13. A *p*-orbital with two lobes and a nodal plane.

(*c*) *Energy*. In the absence of magnetic field, all the three *p*-orbitals have the same energy. Orbitals having the same energy are called *degenerate orbitals*. Since the number of *p*-orbitals having the same energy is three, these orbitals are said to be *three-fold degenerate or triply degenerate orbitals*.

(3) *d* sub-shell (*a*) *Space orientation, shape and electron density*. For this sub-shell $l = 2$. Now when $l = 2$, $m = 0, \pm 1, \pm 2$ (*Five values*). Five values of m (= 0, ±1, ±2) imply that *d* sub-shell of any energy level (*d* sub-shell starts from *3rd* energy level) has five space orientations and hence can be arranged in space in five different ways along *x, y* and *z* axes (Fig. 2.14). Consequently *d* sub-shell is sub-divided into five orbitals which, on the basis of the orientation of their lobes of maximum electron density with respect to *x, y* and *z* axes, 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} $(m = 0)$. Thus :

$$l \rightarrow 2 \text{ (}d \textit{ sub-shell)}$$

$$m \rightarrow 0 \quad +1 \quad -1 \quad +2 \quad -2$$

$$\textit{Designation of orbitals} \rightarrow d_{z^2} \quad d_{xz} \quad d_{yz} \quad d_{x^2-y^2} \quad d_{xy}$$

All these five *d*-orbitals are not identical in shape. Four of the five *d*-orbitals namely d_{xy}, d_{yz}, d_{zx} and $d_{x^2-y^2}$ for a given energy level contain *four lobes* while the fifth orbital *viz.* d_{z^2} consists of only *two* lobes. On the basis of the orientation of the lobes of these orbitals with respect to *x, y* and *z* axes these *d*-orbitals have been divided into two sets

Set No. 1. d_{xy}, d_{yz} and d_{xz} orbitals are the members of this set and have their greatest electron density in the region *between the axes, i.e.*, the lobes of these orbitals are lying symmetrically between the axes. For example the lobes of d_{xy}, orbital are lying between *x* and *y* axes. Similar is the case with other orbitals. Group theory has called the three orbitals of this set as t_{2g} set where *t* refers to triply degenerate set.

Set No. 2. $d_{x^2-y^2}$ and d_{z^2} orbitals constitute this set and have their greatest electron density in the region *along the axes, i.e.*, the lobes of these orbitals are lying along the axes. For example the four lobes of $d_{x^2-y^2}$ orbital are lying along *x* and *y* axes while the two lobes of d_{z^2} orbital (which has dumb-bell shape) are lying along *z*-axis and contain a ring (also called *torus, collar* or *tyre*) of negative charge (electron density) surrounding the nucleus in *xy* plane. Group theory has called the two orbitals of this set as e_g set wherein *e* refers to doubly degenerate

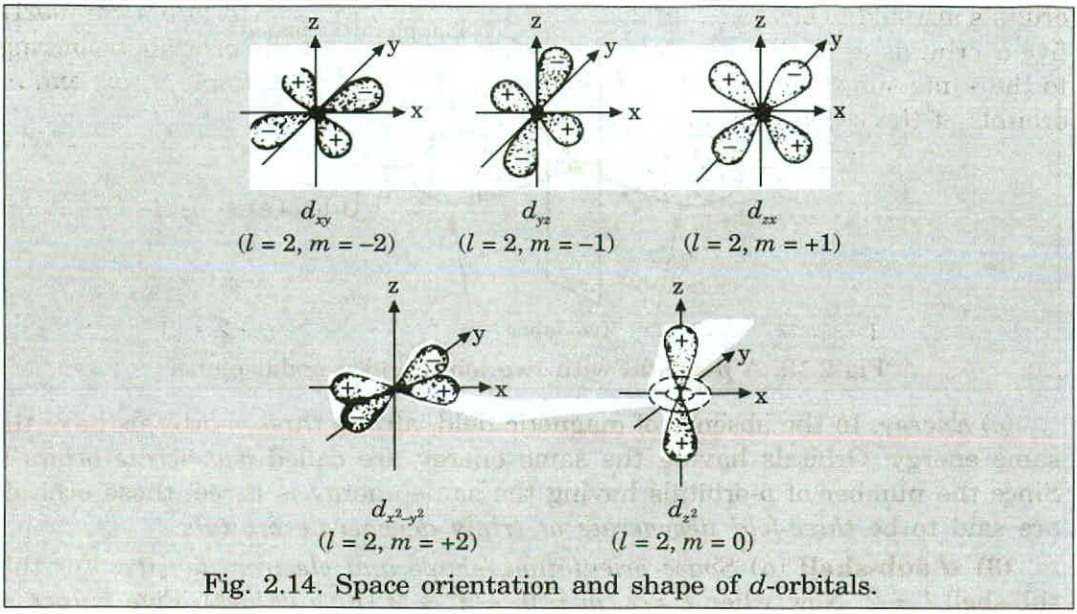


Fig. 2.14. Space orientation and shape of *d*-orbitals.

set. The torus of electron density of d_z^2 orbital in the *xy* plane is also referred to as a *doughnut* or as a *belly band*.

(*b*) *Energy.* In the absence of magnetic field all the five *d* orbitals have the same energy (degenerate orbitals). Since the number of *d*-orbitals having the same energy is five, these orbitals are said to be *five-fold degenerate orbitals.*

(4) *f* sub-shell. For this sub-shell $l = 3$. Now when $l = 3$, $m = 0, \pm1, \pm2, \pm3$ (*seven values*). Since m has *seven* values ($= 0, \pm 1, +2, \pm3$) for $l = 3$ value (*f* sub-shell), *f* sub-shell has *seven* space orientations and hence can be arranged in space in seven different ways with respect to *x, y* and *z* axes. Consequently *f* sub-shell is sub-divided into *seven* orbitals which have complicated shape.

Since magnetic quantum number, as shown above, determines the orientation of the orbitals, it is also called **orbital orientation quantum number.**

Whatever has been said so far can be summarised as follows :

(*i*) *s* sub-shell which is present in all the energy levels contains only one orbital, called *s*-orbital.

(*ii*) *p* sub-shell which starts from *2nd* energy level (L-shell) with $n = 2$ contains *three* orbitals which are designated as p_x, p_y and p_z.

(*iii*) *d* sub-shell, starting from *3rd* energy level (M-shell) with $n = 3$, is composed of five orbitals which are represented as d_{xy}, d_{yz}, d_{zx}, d_z^2, $d_{x^2-y^2}$.

(*iv*) *f* sub-shell which starts from 4th energy level (N-shell) with $n = 4$ is composed of seven orbitals which have complicated shape.

All the above points have been illustrated in Fig. 2.15.

Characteristics of orbitals. (*i*) In the absence of magnetic field all the orbitals of the same sub-shell of an isolated atom have the same energy, *i.e.*, they are degenerate. For example $2p_x$, $2p_y$ and $2p_z$ orbitals of 2*p* sub-shell have the same energy. Since the number of *p*-orbitals having the same energy is three, these

orbitals are said to be *three-fold degenerate or triply degenerate orbitals.* Similarly five *d* orbitals are called *five-fold degenerate orbitals.* All the orbitals belonging to the same sub-shell have the same size and shape. For example p_x, p_y and p_z orbitals of the *p*-sub-shell have the same size and shape.

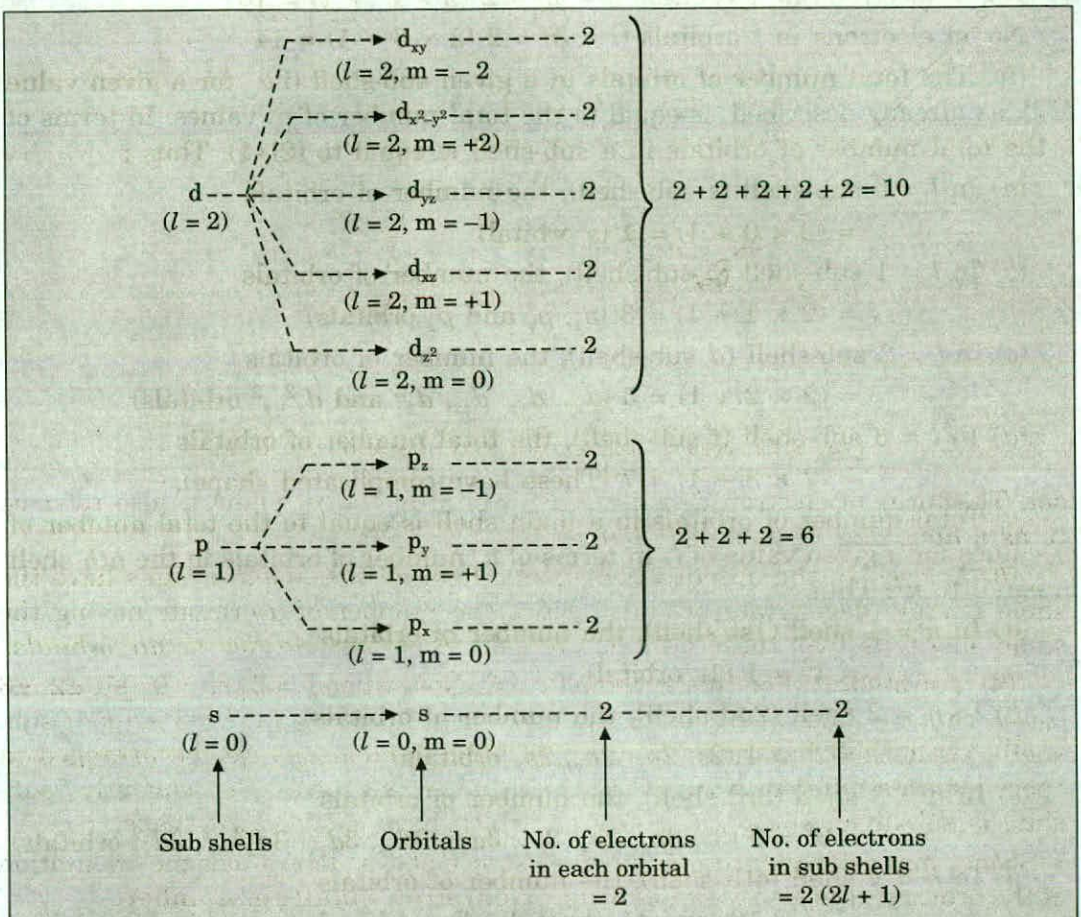


Fig. 2.15. *s* sub-shell ($l = 0$) contains one orbital (called *s*-orbital), *p* sub-shell ($l = 0$) is composed of three orbitals (p_x, p_y, and p_z) while *d* ($l = 2$) sub-shell contains five orbitals (d_{xy}, d_{yz}, d_{zx}, d_z^2, d_{x2-y2}).

(*ii*) All the orbitals of the same sub-sell differ in the direction of their space orientation or disposition. For example $2p_x$, $2p_y$ and $2p_z$ orbitals which belong to the same sub-shell namely 2*p* sub-shell ($n = 2$, $l = 1$) have different space orientations. Similarly $3d_{xy}$, $3d_{yz}$, $3d_{zx}$, $3d_z^2$ and $3d_{x-y}^2$ orbitals of 3*d* sub-shell ($n = 3$, $l = 2$) also have different space orientations.

(*iii*) Since the maximum capacity of an orbital to contain the electrons is two, total number of electrons in *s*, *p*, *d* and *f* sub-shells

$= 2 \times$ *No. of orbitals in a sub-shell*

$= 2 \times (2l+1)$

$= 2\,(2l+1)$

Thus :

No. of electrons in s orbital ($l = 0$) = $2(2 \times 0 + 1) = 2$

No. of electrons in p orbitals ($l = 1$) = $2(2 \times 1 + 1) = 6$

No. of electrons in d orbitals ($l = 2$) = $2(2 \times 2 + 1) = 10$

No. of eleetrons in f orbitals ($l = 3$) = $2(2 \times 3 + 1) = 14$

(*iv*) The total number of orbitals in a given sub-shell (i.e., for a given value of l), as already described, is equal to the total number of m values. In terms of l, the total number of orbitals in a sub-shell is equal to (2l+1). Thus :

(*a*) In $l = 0$ sub-shell (s sub-shell), the number of orbitals
$= (2 \times 0 + 1) = 1$ (s orbital)

(*b*) In $l = 1$ sub-shell (p sub-shell), the number of orbitals
$= (2 \times 1 + 1) = 3$ (p_x, p_y and p_z orbitals)

(*c*) In $l = 2$ sub-shell (d sub-shell), the number of orbitals
$= (2 \times 2 + 1) = 5$ (d_{xy}, d_{yz}, d_{zx}, d_z^2 and $d_{x^2-y^2}$ orbitals)

(*d*) In $l = 3$ sub-shell (f sub-shell), the total number of orbitals
$= (2 \times 3 + 1) = 7$ (These have complicated shape).

(*v*) Total number of orbitals in a main shell is equal to the total number of m values for a given value of l. In terms of n, number of orbitals in the nth shell is equal to n^2. Thus

(*a*) In $n = 1$ shell (1st shell), the number of orbitals
$= 1^2 = 1$ ($1s$ orbital)

(*b*) In $n = 2$ shell (2nd shell), the number of orbitals
$= 2^2 = 4$ ($2s$, $2p_x$, $2p_y$, $2p_z$ orbitals)

(*c*) In $n = 3$ shell (3rd shell), the number of orbitals
$= 3^2 = 9$ ($3s$, $3p_x$, $3p_y$, $3p_z$, $3d_{xy}$, $3d_{yz}$, $3d_{zx}$, $3d_{x^2-y^2}$, $3d_z^2$ orbitals)

(*d*) In $n = 4$ shell (4th shell), the number of orbitals
$= 4^2 = 16$ (one $4s$, three $4p$, five $4d$ and seven $4f$ orbitals).

4. Spin Quantum Number (s).

When the spectral lines of alkali metals are observed by means of spectroscope of high resolving power, each line in the spectrum is found to consist of a pair of lines known as *double* or *doublet-line structure*. These lines are widely separated from each other. Here it should be understood clearly that this double or double-line structure is different from fine spectrum of hydrogen (*See* azimuthal quantum number), since the lines of the double-line structure are widely separated from each other while those of fine structure are closely spaced together.

In order to explain the double or doublet-line structure observed in the spectrum of alkali metals, Goudsmit and Uhlenbeck in 1925 suggested that *an electron, while moving in an orbit round the nucleus, also rotates or spins about its own axis (self-rotation) either in a clockwise direction or in an anti-clockwise*

direction as shown in Fig. 2.16. Since a spinning charge is associated with a magnetic field, an electron which is spinning about its own axis also has a magnetic moment associated with it. The spinning of the electron in clock-wise and anticlock-wise directions produces opposite magnetic fields.

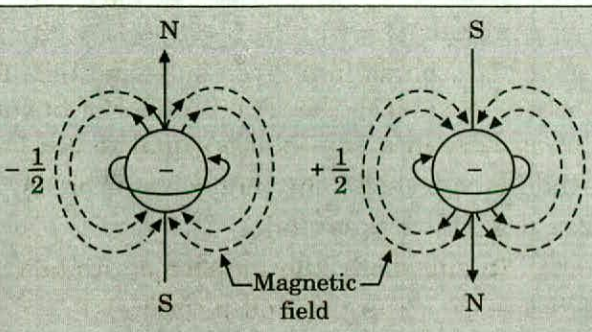


Fig. 2.16. Spinning of an electron about its own axis in clock-wise and anticlock-wise directions. Clock-wise and anticlock-wise spinning of the electron produces opposite magnetic fields.

In order to represent the direction of the spin or self-rotation of an electron about its own axis, Goudsmit and Uhlenbeck introduced another quantum number which they called spin quantum number (s), since it represents the direction of the spin of the electron. We know that since an electron can spin in any of the two directions *viz.* either in clockwise direction or in an anti-clock wise direction, spin quantum number can have two values namely $+\frac{1}{2}$ and $-\frac{1}{2}$ which differ from each other by unity as the values of other quantum numbers do. As a convention $s = +\frac{1}{2}$ is used to indicate the clockwise direction of the spin of the electron while $s = -\frac{1}{2}$ is used to indicate the anti-clockwise direction of the spin of the electron.

An electron spinning in a clockwise direction is represented by an arrow pointing upwards (↑) while that spinning in an anti- clockwise direction is represented by an arrow pointing downwards (↓). According to *Paulie's Exclusion Principle*, when there are two electrons in the same orbital, they have *opposite spins or antiparallel spins* $\left(+\frac{1}{2} \text{ and } -\frac{1}{2}\right)$ which oppose and cancel each other, since the magnetic field produced by one electron is cancelled by that produced by the other electron. Thus an electron pair in an orbital is represented as $\boxed{\uparrow\downarrow}$. Here the two electrons which have opposite spins are said to be *paired up electrons*.

Summary

The study of quantum numbers that we have made so far can be summarised as follows (Also see Table 2.2 and Fig. 2.17).

Table 2.2. Informations given by quantum numbers

n	l	Designation of sub-shell (nl)	m	Designation of orbital (nm)	No. of electrons in each orbital = 2	s for two electrons	No. of sub-shells in a main shell = n	No. of orbitals in a sub-shell = $(2l+1)$	No. of orbitals in a main shell = n^2	No. of electrons in a main shell = $2n^2$	No. of electrons in a sub-shell = $2(2l+1)$
1 (*1st* shell or K-shell)	0	*1s*	0	*1s*	2(↑↓)	+1/2, –1/2	1 (*1s*)	2×0+1 = 1	$1^2 = 1$ (*1s*)	$2\times1^2 = 2$	2×1 = 2
2 (*2nd* shell or L-shell)	0	*2s*	0	*2s*	2(↑↓)	+1/2, –1/2	2 (*2s*, *2p*)	2×0+1 = 1	$2^2 = 4$ or	$2\times2^2 = 8$	2×1 = 2
	1	*2p*	–1	$2p_z$	2(↑↓)	+1/2, –1/2			1+3 = 4(*2s*,		
			+1	$2p_y$	2(↑↓)	+1/2, –1/2			$2p_z$, $2p_y$, $2p_x$		2×3 = 6
			0	$2p_x$	2(↑↓)	+1/2, –1/2		2×1+1 = 3			
3 (*3rd* shell or M-shell)	0	*3s*	0	*3s*	2(↑↓)	+1/2, –1/2	3 (*3s*, *3p*, *3d*)	2×0+1 = 1	$3^2 = 9$ or	$2\times3^2 = 18$	2×1 = 2
	1	*3p*	–1	$3p_z$	2(↑↓)	+1/2, –1/2					
			+1	$3p_y$	2(↑↓)	+1/2, –1/2		2×1+1 = 3	1+3+5 = 9		2×3 = 6
			0	$3p_x$	2(↑↓)	+1/2, –1/2			(*3s*, $3p_z$, $3p_y$,		
	2	*3d*	0	$3d_z^2$	2(↑↓)	+1/2, –1/2			$3p_x$, $3d_z^2$,		
			+1	$3d_{xz}$	2(↑↓)	+1/2, –1/2			$3d_{xz}$, $3d_{yz}$,		
			–1	$3d_{yz}$	2(↑↓)	+1/2, –1/2		2×2+1 = 5	$3d_{x^2-y^2}$,		
			+2	$3d_{x^2-y^2}$	2(↑↓)	+1/2, –1/2			$3d_{xy}$)		2×5 = 10
			–2	$3d_{xy}$	2(↑↓)	+1/2, –1/2					

1. **Shells** (*a*) Electrons in an atom revolve round the nucleus in orbits or shells which are associated with some energy and hence are also called energy levels. These are represented as K, L, M etc. having principal quantum number, n = 1, 2, 3 etc. respectively.

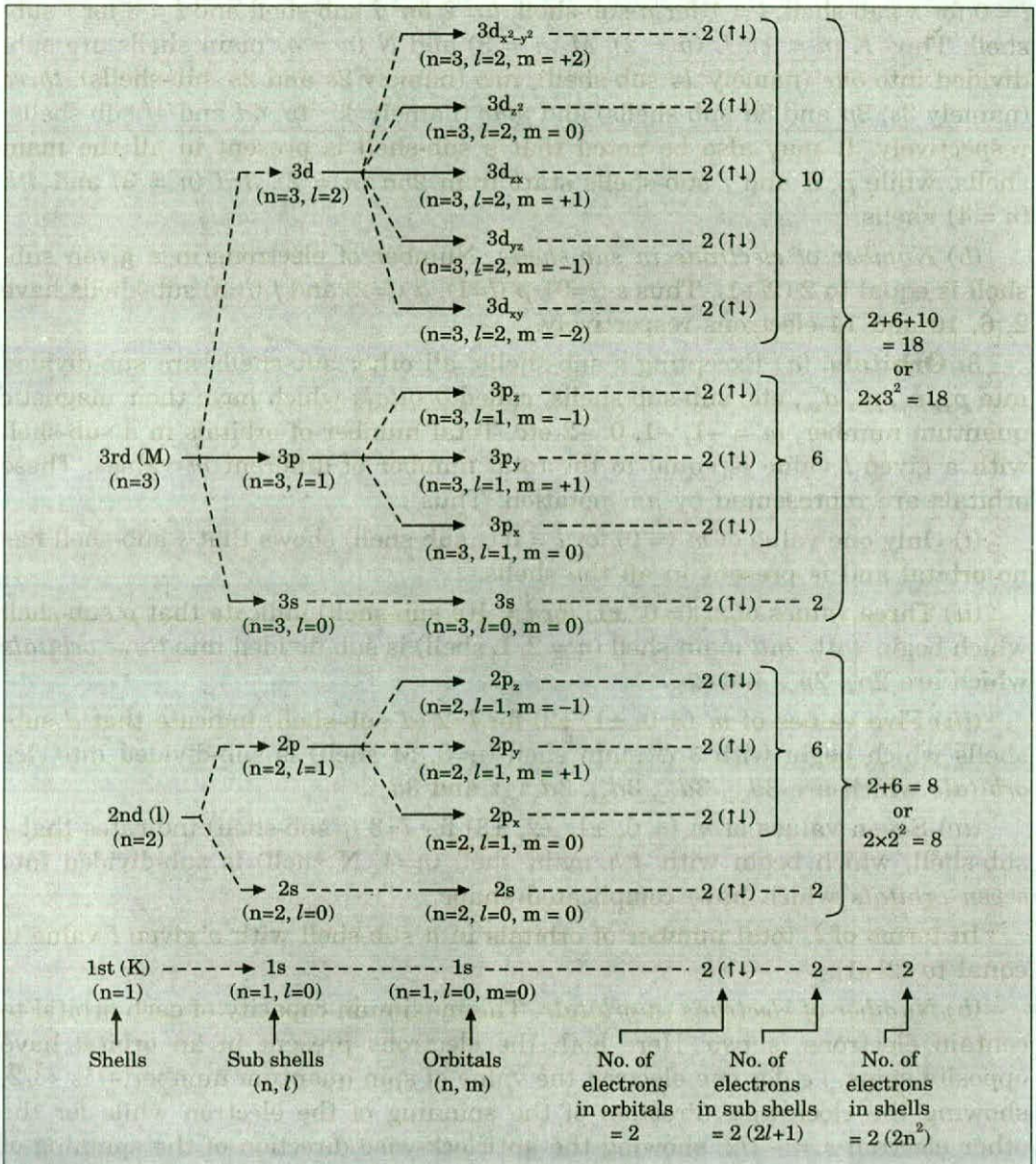


Fig. 2.17. Informations given by quantum numbers. Two electrons shown in each orbital [represented as (↑↓)] have opposite spins. For one electron the value of spin quantum number, s = + 1/2 while for the other s = −1/2.

(*b*) *No. of electrons in shells.* Number of electrons in a shell with a given n value is equal to $2n^2$.

2. **Sub-shells** (*a*) Each of the main shells is sub-divided into *s, p, d, f* sub-shells which have azimuthal quantum, $l = 0, 1, 2$ and 3 respectively. Total number of sub-shells in a main shell with given n value is equal to n value or total number of l values These sub-shells are represented by the notation nl where $l = 0$ for s sub-shell, $l = 1$ for p sub-shell, $l = 2$ for d sub-shell and $l = 3$ for f sub-shell. Thus K ($n = 1$), L ($n = 2$), M ($n = 3$) and N ($n = 4$) main shells are sub-divided into *one* (namely *1s* sub-shell), *two* (namely 2*s* and 2*p* sub-shells), *three* (namely 3*s*, 3*p* and 3*d* sub-shells) and *four* (namely 4*s*, 4*p*, 4*d* and 4*f* sub-shells) respectively. It may also be noted that s sub-shell is present in all the main shells, while *p, d* and *f* sub-shells start from *2nd* ($n = 2$), *3rd* ($n = 3$) and *4th* ($n = 4$) shells.

(*b*) *Number of electrons in sub-shells.* Number of electrons in a given sub-shell is equal to $2(2l+1)$. Thus *s* (l=0), *p* (l=1), *d* (l=2) and *f* (l=3) sub-shells have 2, 6, 10 and 14 electrons respectively.

3. **Orbitals.** (*a*) Excepting *s* sub-shells, all other sub-shells are sub-divided into p_x, p_y, p_z, d_{xy}, etc. sub-sub-shells, called *orbitals* which have their magnetic quantum number, $m = -1, +1, 0, -2$ etc. Total number of orbitals in a sub-shell with a given l value is equal to the total number of different m values. These orbitals are represented by nm notation. Thus :

(*i*) Only one value of m (= 0) for $l = 0$ (*s* sub-shell) shows that *s* sub-shell has no orbital and is present in all the shells.

(*ii*) Three values of m (= 0, ±1) for $l = 1$(*p* sub-shell) indicate that *p* sub-shell which begin with *2nd* main shell ($n = 2$, L shell) is sub-divided into *three orbitals* which are $2p_x$, $2p_y$, and $2p_z$.

(*iii*) Five values of m (= 0, ±1, ±2) for l=2 (*d* sub-shell) indicate that *d* sub-shells which begin with *3rd* main shell (n=3, M shell) is sub-divided into *five orbitals* which are $3d_{xy}$, $3d_{yz}$, $3d_{zx}$, $3d_{x^2-y^2}$ and $3d_{z2}$.

(*iv*) Seven values of m (= 0, ±1, ±2, ±3) for l=3 (*f* sub-shell) indicates that *f* sub-shell, which begin with *4th* main shell (n=4, N shell) is sub-divided into *seven orbitals* which have complicated shape.

In terms of l, total number of orbitals in a sub-shell with a given l value is equal to $(2l+1)$.

(*b*) *Number of electrons in orbitals.* The maximum capacity of each orbital to contain electrons is two. Here both the electrons present in an orbital have opposite spins, *i.e.* for one electron the value of spin quantum number(s) is +1/2, showing the clock-wise direction of the spinning of the electron while for the other electron $s = -1/2$, showing the anticlock-wise direction of the spinning of the electron.

(*c*) *Number of orbitals in a main shell.* The number of orbitals in a main shell with a given n value is equal to n^2. Thus K ($n = 1$), L ($n = 2$) and M ($n = 3$) shells have *one* (namely *1s*), *four* (namely 2*s*, $2p_x$, $2p_y$, $2p_z$) and nine (namely 3*s*, $3p_x$, $3p_y$, $3p_z$, $3d_{xy}$ etc.) orbitals.

Problems Based On Quantum Numbers

Problem 1. *Which of the orbitals namely 1p, 2s, 2p, 3f are not possible ? Give reason for your answer.* *(Delhi B.Sc. 1976)*

Solution. The orbitals which are not possible are 1*p* and 3*f*. The reason for their non-existence is given as follows :

We know that when $n = 1$ (1st shell), $l=0$. $l=0$ value means that *1st* shell has only one sub-shell namely 1*s* for which $l=0$. Thus 1st shell does not contain 1*p* orbital.

It is known to us that when $n=3$, $l=0$, 1, 2. Three values of l mean that *3rd* shell has only three sub-shells namely *3s* (for which $l=0$), 3*p* (for which $l=1$) and 3*d* (for which $l=2$). Thus 3*rd* shell does not contain 3*f* orbital.

Problem 2. *An electron is in 4f orbital. What possible values for the quantum number of n, 1, m and s it can have ?* *(Punjab B.Sc. 1981)*

Solution. We know that for 4*f* orbital $n=4$ and $l=3$. Now when $l=3$, $m=0$, ±1, ±2, ±3 (seven values). Seven values of m imply that the electron may be in any of the seven 4*f* orbitals and for this electron m may have any of the above seven values. For this electron $s = +\frac{1}{2}$ or $-\frac{1}{2}$.

Thus *n, l, m* and s values for an electron residing in 4*f* orbital are :

$n= 4$, $l=3$, m=any of the seven values namely 0, ±1, ±2, ±3 and $s = +\frac{1}{2}$ or $-\frac{1}{2}$.

Problem 3. *What is the maximum number of electrons in (i) all 4d orbitals (ii) all the orbitals with l = 1.* *(Kurukshetra B.Sc. I 1983)*

Solution. We know that the maximum number of electrons in an orbital with a given value of l is equal to 2 (2*l*+l). Thus :

(*i*) Maximum number of electrons in 4*d* orbitals ($l=2$)

$$= 2\ (2 \times 2 + 1) = 10$$

(*ii*) Maximum number of electrons in all the orbitals with $l = 1$

$$= 2\ (2 \times 1 + 1)$$

$$= 6$$

Problem 4. *Write the name of the orbital for which the quantum numbers are : n = 2 and l = 1.* *Jabalpur B.Sc. 1981; Himachal 1982)*

Solution. We know that $n = 2$ indicates *2nd* main shell. Now when $n= 2$, $l= 0$, 1. $l= 0$ stands for s sub-shell while $l=1$ indicates *p* sub-shell. Thus *p* ($l=1$) sub-shell belongs to 2nd shell and hence $n=2$ and $l=1$ stands for 2*p* sub-shell.

Problem 5. *Give the symbols for orbital types when the values of l are 0, 2 and 3.* *(Punjab B.Sc. 1972; Raj. 1972; Delhi 1974; Gorakhpur 1973)*

Solution. Obviously the orbitals having $l=0$, 2 and 3 are *s*, *d* and *f* respectively.

Problem 6. *Write correct orbital notation for each of the following set of quantum numbers :*

(*i*) $n = 1,\ l = 0,\ m = 0$

(*ii*) $n = 2,\ l = 1,\ m = 1$

(*iii*) $n = 3,\ l = 2,\ m = -1$ *(Meerut B.Sc. 1984)*

Solution. With reference to Table 2.2 given on page 131

(*i*) The orbital for which $n = 1$, $l = 0$ and $m = 0$ is $1s$.

(*ii*) The orbital for which $n=2$, $l=1$ and $m=1$ is $2p_y$.

(*iii*) The orbital for which $n=3$, $l=2$ and $m= -1$ is $3d_{yz}$.

Problem 7. *What are n, l and m values for 3s, $3p_x$ and $3d_{xy}$ electrons ?* *(Meerut B.Sc. 1984)*

Solution. With reference to Table 2.2 given on page 131

(*i*) For $3s$ electrons, $n=3$, $l= 0$, $m = 0$

(*ii*) For $3p_x$ electrons, $n= 3$, $l=1$, $m = 0$

(*iii*) For $3d_{xy}$ electrons, $n= 3$, $l=2$, $m= -2$

Problem 8. *What will be the values of other quantum numbers of an electron for which the principal quantum number is 3 ?*

Solution. The values of other quantum numbers namely l, m and s are as follows :

n	l	m	s
3	0	0	+1/2, –1/2
	1	0	+1/2, –1/2
		+1	+1/2, –1/2
		–1	+1/2, –1/2
	2	0	+1/2, –1/2
		+1	+1/2, –1/2
		–1	+1/2, –1/2
		+2	+1/2, –1/2
		–2	+1/2, –1/2

Problem 9. *What are the possible values of s for an electron with m = 0 ?*

Solution. s is always equal to +1/2 or –1/2, regardless of the values of other quantum numbers.

Problem 10. (*i*) *How are the electrons distributed in various sub-shells for n = 3 ? (ii) Give the quantum numbers for the electron in the first sub-shell appearing in n = 3 shell.*

Solution. (*i*) When $n = 3$, the shell is 3rd shell and $l = 0$ ($3s$ sub-shell), 1 ($3p$ sub-shell), 2 ($3d$ sub-shell). Thus 3rd main shell contains three sub-shells which are $3s$, $3p$ and $3d$.

Now we know that the total number of electrons in 3rd main shell = 2×3^2 = 18. These 18 electrons in $3s$, $3p$ and $3d$ sub-shells are distributed as follows :

No. of electrons in $3s$ sub-shell ($l = 0$) = $2(2l+1) = 2(2\times0+1) = 2$.

No. of electrons in $3p$ sub-shell ($l = 1$) = $2(2\times1+1) = 6$.

No. of electrons in $3d$ sub-shell ($l = 2$) = $2(2\times2+1) = 10$.

(*ii*) Quite evidently 1st sub-shell in 3rd main shell is 3*s* sub-shell which contains two electrons as shown above. The four quantum numbers for the two electrons in 3*s* sub-shell are as follows :

		Quantum numbers			
		n	*l*	*m*	*s*
Electron number	1st electron	3	0	0	+1/2
	2nd electron	3	0	0	—1/2

Problem 11. *Find the number of electrons in atoms which have the following levels in the ground state. (a) K shell, L shell, 3s sub-shell and half-filled 3p sub-shell. (b) K, L and M shells, and 4s, 4p and 4d sub-shells. What atoms are these?*

Solution. (*a*) No. of electrons in K-shell (n=1)

$$= 2n^2 = 2 \times 1^2 = 2$$

No. of electrons in L-shell (n=2) = $2 \times 2^2 = 8$

No. of electrons in 3*s* sub-shell (l=0) = $2(2l+1)$

$$= 2\ (2 \times 0 + 1) = 2$$

Half the number of electrons in 3*p* sub-shell (l=1)

$$= \frac{2(2\times1+1)}{2} = 3$$

Total number of electrons = 2 + 8 + 2 + 3 = 15

This number indicates the atomic number of the element. Thus the element is **phosphorus.**

(*b*) No. of electrons in K-shell (n = 1) = $2n^2 = 2 \times 1^2 = 2$

No. of electron in L-shell (n = 2) = $2 \times 2^2 = 8$

No. of electrons in M-shell (n = 3) = $2 \times 3^2 = 18$

No. of electrons in 4*s* sub-shell (l = 0) = $2\ (2l + 1)$

$$= 2\ (2 \times 0 + 1) = 2$$

No. of electrons in 4*p* sub-shell (l = 1) = $2\ (2 \times 1 + 1) = 6$

No. of electrons in 4*d* sub-shell (l = 2) = $2\ (2 \times 2 + 1) = 10$

$\therefore$ Total number of electrons = 2 + 8 + 18 + 2 + 6 + 10 = 46.

Thus the element is **palladium.**

Problem 12. *For n = 4 principal shell, find the following (i) name of the shell (ii) number of sub-shells in it (iii) total number of orbitals in each sub-shell (iv) numbers of orbitals in the principal shell.*

Solution. (*i*) n = 4 is the 4th shell (*i.e.*, N-shell).

(*ii*) No. of sub-shells in a main shell with a given value of n = 4 = n = 4.

(*iii*) We know that for n = 4 shell, l = 0 (4*s* sub-shell), 1(4*p* sub-shell), 2 (4*d* sub-shell), 3 (4*f* sub-shell). Now since total number of orbitals in a sub-shell with a given value of l = $(2l + 1)$,

No. of orbitals in 4*s* sub-shell (l = 0) = $(2 \times 0 + 1) = 1$

No. of orbitals in 4*p* sub-shell (l = 1) = $(2 \times 1 + 1) = 3$

No. of orbitals in $4d$ sub-shell ($l = 2$) = $(2 \times 2 + 1) = 5$

No. of orbitals in $4f$ sub-shell ($l = 3$) = $(2 \times 3 + 1) = 7$.

(*iv*) No. of orbitals in 4th shell ($n = 4$) = $4^2 = 16$

Pauli's Exclusion Principle

In 1925 Wolfgang Pauli put forward a principle which controls the assignment of values to the quantum numbers of an electron in an orbital. It imposes some restrictions on the assignment of the values of quantum numbers of electrons in the same orbital of an atom and hence the name *Exclusion Principle*. This principle can be stated in many ways some of which are given below :

(*i*) *It is imposible for two electrons residing in the same orbital of a given poly-electron atom (same atom) to have the same values of all the four quantum numbers.*

(*ii*) *In an atom no two electrons contained in the same orbital can have the same set of values of all the four quantum numbers.*

(*iii*) *No two electrons residing in the same orbital of an atom can be described by an identical set of four quantum numbers.*

(*iv*) *In the same orbital of an atom two electrons can have three quantum numbers identical at the most, but the fourth quantum number namely spin quantum number (s) will definitely be different for both the electrons, i.e.,* for one electron s will be +1/2 while for the other electron s will be –1/2. s = +1/2 indicates the clock-wise direction of the spinning of one electron while s = –1/2 stands to show the anticlock-wise direction of the other electron. This means that two electrons residing in the same orbital of an atom have opposite spins, since this state of the electrons having opposite spins (↑ ↓) gives lower energy to the orbital while the state with parallel spins (↑ ↑) gives higher energy to the orbital. According to thermodynamics a system with lower energy has greater stability. Thus an orbital having two electrons with opposite spins (↑ ↓) has lower energy and hence is more stable than that containing the two electrons with parallel or paired spins (↑ ↑).

(*v*) *The maximum number of identical quantum numbers which two electrons in an orbital can have is only three but never four.*

Illustration of the principle. In order to illustrate the principle let us consider helium atom which has two electrons (Atomic number = 2) in 1*s* orbital for which $n = 1$, $l = 0$ and $m = 0$. The four quantum numbers for the two electrons in 1*s* orbital are as follows :

Electron number	*Quantum numbers* n	l	m	s	*Set of values of quantum numbers* (n, l, m, s)
1st electron (↑)	1	0	0	+1/2	(1, 0, 0, +1/2)
2nd electron (↓)	1	0	0	–1/2	(1, 0, 0, –1/2)

Thus we see that for one electron shown as (↑) the set of values of quantum numbers is (1, 0, 0, +1/2) while for the electron shown as (↓) this set is (1, 0, 0, −1/2). As is evident, the two electrons have different sets of four quantum numbers which is in accordance with Pauli's exclusion principle.

Applications of Pauli's Exclusion Principle.

With the help of this principle, the maximum number of electrons that can be accommodated in an orbital, sub-shell and main shell can be calculated as shown below :

(*i*) **1st shell** (*K-shell with n = 1*). For this shell $n = 1$. The values of l and m for $n = 1$ are $l = 0$ and $m = 0$. Hence s can have a value either equal to +1/2 or —1/2. Thus these different values of n, l and m give the following **two** sets of the values of four quantum numbers, keeping in view Pauli's exclusion principle.

Set number	n	l	m	s	*Set*
1	1	0(1*s*)	0	+1/2	(1, 0, 0, + 1/2)
2	1	0(1*s*)	0	−1/2	(1, 0, 0, − 1/2)

Since the number of permitted sets of four quantum numbers is two for 1st shell ($n = 1$), this shell contains at the maximum two electrons which are contained in 1*s* orbital.

(*ii*) **2nd shell** (*L-shell with n = 2*). For this shell $n = 2$. For $n = 2$, the different values of l, m and s give the following **eight** sets of quantum numbers which indicate that 2*nd* shell contains eight electrons of which two are contained by 2*s* sub-shell while the remaining six are contained in 2p sub-shell. Six electrons in 2*p* sub-shell are distributed in $2p_x$, $2p_y$, and $2p_z$ orbitals as $2p_x^2$, $2p_y^2$, $2p_z^2$ in which the superscript indicates the number of electrons contained in the orbital.

Set number	n	l	m	s	*Set*
1	*2*	*0 (2s)*	*0 (2s)*	*+1/2*	*(2, 0, 0, + 1/2)*
2	*2*	*0 (2s)*	*0 (2s)*	*−1/2*	*(2, 0, 0, − 1/2)*
3	*2*	*1 (2p)*	*0 ($2p_x$)*	*+1/2*	*(2, 1, 0, + 1/2)*
4	*2*	*1 (2p)*	*0 ($2p_x$)*	*−1/2*	*(2, 1, 0, − 1/2)*
5	*2*	*1 (2p)*	*+1 ($2p_y$)*	*+1/2*	*(2, 1, + 1, + 1/2)*
6	*2*	*1 (2p)*	*+1 ($2p_y$)*	*−1/2*	*(2, 1, + 1, − 1/2)*
7	*2*	*1 (2p)*	*−1 ($2p_z$)*	*+1/2*	*(2, 1, − 1, + 1/2)*
8	*2*	*1 (2p)*	*−1 ($2p_z$)*	*−1/2*	*(2, 1, − 1, − 1/2)*

(*iii*) **3rd and 4th shells** (*M and N shells*). On the same lines of arguement it can be shown that 3*rd* shell ($n = 3$) can contain at the maximum 18 electrons (2 in 3*s* sub-shell, 6 in 3*p* sub-shell and 10 in 3*d* sub-shell) and 4*th* shell ($n = 4$) can have 32 electrons (2 in 4*s* sub-shell, 6 in 4*p* sub-shell, 10 in 4*d* sub-shell and 14 in 4*f* sub-shell).

Whatever has been said above has been shown in Table 2.3.

Table 2.3 Determination of the number of electrons present in orbitals, sub-shells and main shells by Pauli's exclusion principle.

n and shell designation	*l* and sub-shell designation (*nl*)	*m* and orbital designation	Value of *s*	No. of electrons in orbitals and sub-shells	No. of electrons present in main shells
1 (1*st* shell or K-shell)	0 (1*s*)	0 (1*s*)	+1/2, −1/2	2	2 or $2n^2 = 2\times1^2 = 2$
2 (2*nd* shell or L-shell)	0 (2*s*)	0 (2*s*)	+1/2, −1/2	2	2+6 = 8 or $2n^2 = 2\times2^2 = 8$
	1 (2*p*)	0 ($2p_x$)	+1/2, −1/2	2	
		+1 ($2p_y$)	+1/2, −1/2	2 } 6	
		−1 ($2p_z$)	+1/2, −1/2	2	
3 (3*rd* shell or M-shell)	0 (3*s*)	0 (3*s*)	+1/2, −1/2	2	2+6+10 = 18 or $2n^2 = 2\times3^2 = 18$
	1 (3*p*)	0 ($3p_x$)	+1/2, −1/2	2	
		+1 ($3p_y$)	+1/2, −1/2	2 } 6	
		−1 ($3p_z$)	+1/2, −1/2	2	
	2 (3*d*)	0 ($3d_z^2$)	+1/2, −1/2	2	
		+1 ($3d_{xz}$)	+1/2, −1/2	2	
		−1 ($3d_{yz}$)	+1/2, −1/2	2 } 10	
		+2 ($3d_{x^2-y^2}$)	+1/2, −1/2	2	
		−2 ($3d_{xy}$)	+1/2, −1/2	2	

Table 2.3 makes the following two rules evident :

(*a*) *An orbital like s, p_x, p_y, p_x, d_{xy}, d_{yz} etc., can have at the most two electrons and these two electrons must have opposite spins, i.e.,* one electron should have the value of spin quantum number (*s*) equal to +1/2 and the other equal to −1/2 so that both the electrons residing in the same orbital may have different sets of four quantum numbers in accordance with Pauli's exclusion principle.

(*b*) *Maximum number of electrons that can be accommodated by a shell with principal quantum number, n is equal to $2n^2$.*

These two rules have been used in the determination of the electronic configuration of the atoms of the elements.

Energy Level Diagrams

We have seen that the energy of an electron is determined by *n* and *l* quantum numbers. When we discuss the energy of orbitals, the following two cases may arise :

1. Energy Level Diagram of One-Electron Atoms (Hydrogen and Hydrogen Like-Atoms)

Hydrogen has only one electron which is present in the lowest energy level which is 1*st* energy level (*i.e.* 1*s* orbital) with $n = 1$. When hydrogen atom absorbs energy, its 1*s* electron may jump to higher energy levels with $n = 2$, (L-level), 3 (M-level) etc., or to higher sub-shells represented by their l values (*e.g.*, 2*s*, 2*p* etc., sub-shells). The spectral study of hydrogen atom has shown that its spectral lines correspond to the major energy levels only. Thus the energy of an electron present in a given principal energy level is the same irrespective of the orbitals of the same principal energy to which it belongs.

In other words this means that *the energies of all s, p, d, f orbitals of the same principal energy level are identical.* For example 3*s*, 3*p* and 3*d* orbitals which belong to 3*rd* energy level ($n = 3$) have the same energy (Fig. 2.18)

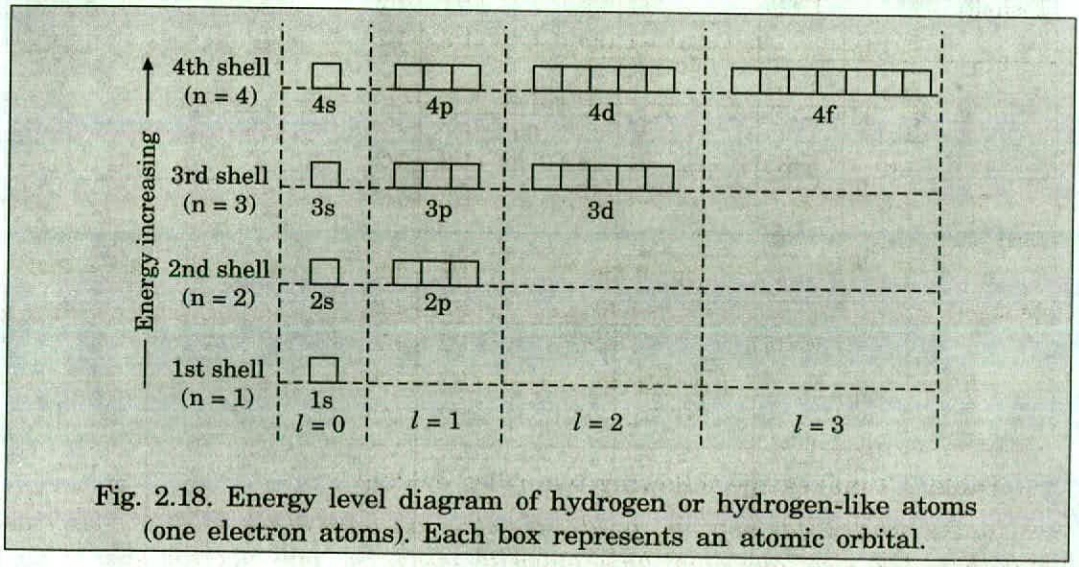


Fig. 2.18. Energy level diagram of hydrogen or hydrogen-like atoms (one electron atoms). Each box represents an atomic orbital.

Thus the order of energy of various orbitals in hydrogen atom, as shown in Fig. 2.18 is as follows :

$$1s\ (n = 1) < 2s = 2p\ (n = 2) < 3s = 3p = 3d\ (n = 3)$$
$$< 4s = 4p = 4d = 4f\ (n = 4)$$

Fig. 2.18, in which the above order has been shown is called *energy level diagram of hydrogen* or *hydrogen-like atoms.*

2. Energy Level Diagram of Poly-Electron Atoms.

For poly-electron atom the situation is, however, different. The relative order of energy values of different orbitals based on spectral data of these atoms is shown in Fig. 2.19 which is called *energy level diagram of poly-electron atoms.* From this diagram the following points may be noted :

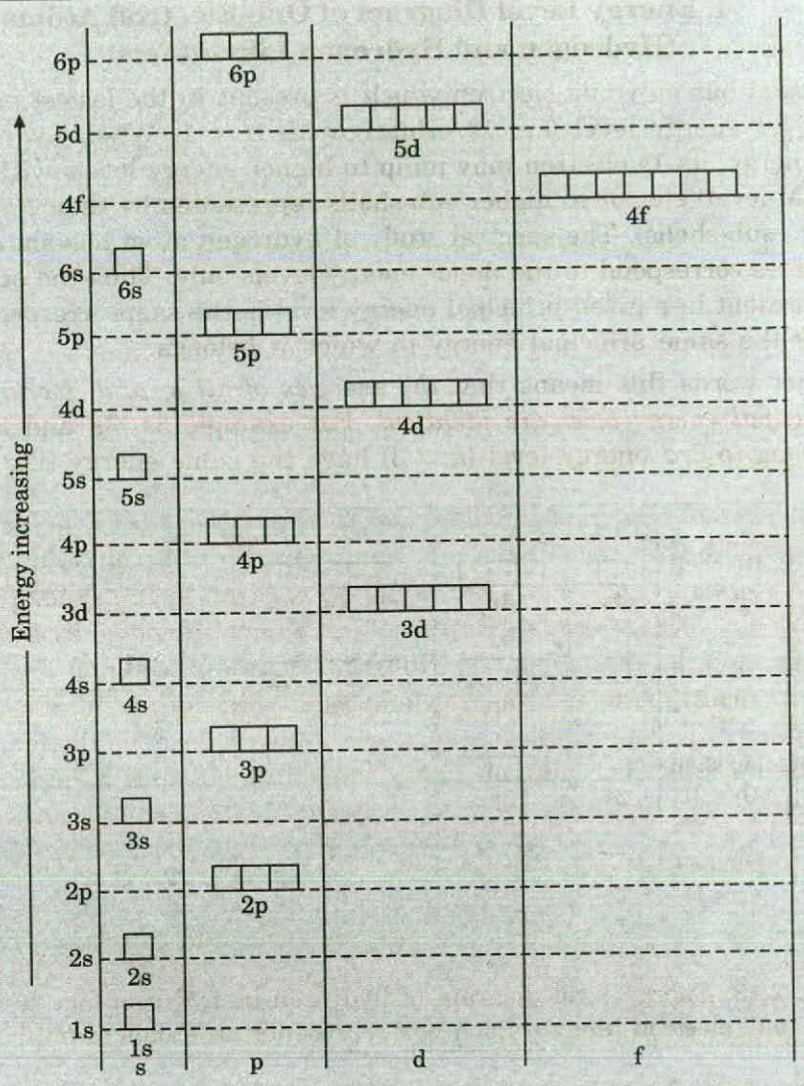


Fig. 2.19. Energy level diagram of poly-electron atoms. Each box represents an atomic orbital.

(*i*) The relative order of energy of various orbitals is as follows :

Energy Increasing ⟶

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6d$$
$$4f < 5d < 6p < .....$$

(*ii*) Orbitals of the same principal energy level have different energy values, *i.e.*, the orbitals with the same value of n but with different l values have different

energy values. Thus the energy of *ns*, *np*, *nd* and *nf* orbitals which belong to the same energy level is in the order :

$$ns\ (l = 0) < np\ (l = 1) < nd\ (l = 2) < nf\ (l = 3)$$

The above order shows that with the increase of l value the energy of the orbital also increases.

Probability Distribution Curves

The probability of finding an electron in a given volume element can be represented by two types of probability distribution curves which are (1) *Radial probability distribution curves, and* (2) *Angular probability distribution curves.*

Now let us discuss these curves, one by one, as follows :

1. Radial Probability Distribution Curves.

These curves tell how the probability of finding an electron varies with its radial distance from the nucleus without any reference to its direction from the nucleus. The probability or chance of finding an electron in the space round the nucleus is called **electron probability function** which is denoted by D and gives an idea of the electron probability distribution in the space round the nucleus. Suppose that the space round the nucleus is divided into a number of thin concentric spherical shells of thickness dr and radius r, *i.e.*, the distance of this shell from the nucleus is r. Quite obviously the volume of such a spherical shell is equal to $4\pi r^2 dr$ and hence the value of electron probability function D is given by the product of $4\pi r^2 dr$ and ψ^2, *i.e.*,

Electron probability function, $\mathbf{D = 4\pi r^2 dr\psi^2}$

The curves obtained by plotting the electron probability function; D ($= 4\pi r^2 dr \cdot \psi^2$) of the electron against its distance, r from the nucleus are called **radial probability distribution curves**. These curves for 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, and 3*d* orbitals are given in Fig. 2.20.

From these curves the following points may be noted :

(*i*) In each case the probability of finding the electron at the origin (which is the nucleus) is zero. This means that the electron will never be found at the nucleus.

(*ii*) The distance for the maximum probability of finding an electron in an orbital increases with the value of its principal quantum number, n. For example this distance for 1*s*, 2*s* and 3*s* orbitals is in the order $1s < 2s < 3s$ as is evident from the curves of these orbitals.

(*iii*) The total number of peaks appearing in the curves for *s*, *p* and *d* orbitals is equal to n, $(n-1)$ and $(n-2)$ respectively (n the principal quantum number). For example the number of peaks for 1*s*, 2*s*, 3*s*, 2*p*, 3*p* and 3*d* orbitals is equal to 1, 2, 3, 1, 2 and 1 respectively as is evident from the curves.

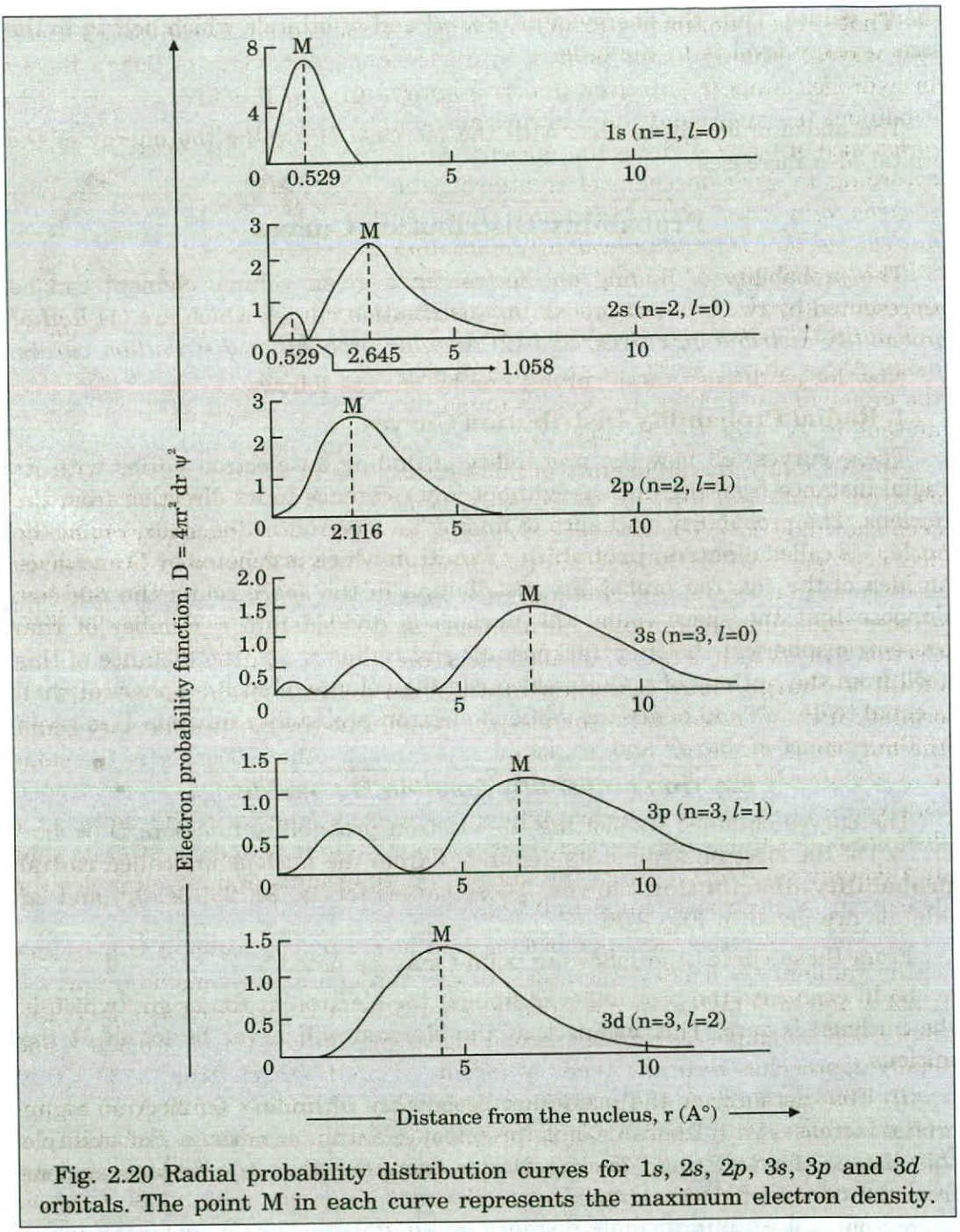


Fig. 2.20 Radial probability distribution curves for 1*s*, 2*s*, 2*p*, 3*s*, 3*p* and 3*d* orbitals. The point M in each curve represents the maximum electron density.

(*iv*) From the curve for 1*s*-electron it is evident that the value of D is zero at the nucleus where $r = 0$. D increases as r increases from zero, passes through a maximum (*i.e.* peak) at $r = 0.529$ A° which is equal to the radius of Bohr's first orbit, and finally falls to zero as r tends to infinity. Thus for 1*s*-electron D = 0 at $r = 0$ and ∞, and D = maximum at $r = 0.529$ A° (radius of Bohr's first orbit).

That D is maximum at $r = 0.529$ A° makes a difference between Bohr's theory and wave mechanical treatment of hydrogen atom. According to Bohr's theory, in hydrogen atom the electron under ordinary conditions (*i.e.* in ground state) always stays at a distance of 0.529 A° from the nucleus, while according to wave mechanical treatment, the *electron may exist at any distance from the nucleus but the maximum probability of locating it lies at a distance of 0.529 A° from the nucleus. In other words the radius of maximum probability* (≈ 95%) *of 1s electrons in H-atom is 0.529* A° as shown in Fig. 2.21 which depicts the probability of finding an electron round the nucleus in 1*s* orbital of H-atom.

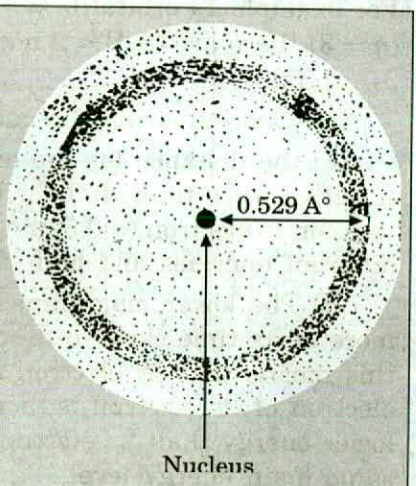


Fig. 2.21. Probability of finding the electron round the nucleus of 1*s* orbital of H-atom and the radius of maximum probability (= 0.529 A°).

In this figure the probability of finding the electron round the nucleus in 1*s* orbital has been shown by dots. The intensity of shading of dots is proportional to the probability of finding electron at that location. Such a representation of the probability of finding the electron (or electron density as it is called) is called **electron cloud** or **charge cloud representation of an orbital.** (Here the orbital is 1*s* orbital). It may be seen from the electron cloud that the electron density round the nucleus is denser at certain points and rarer at others. Denser is the cloud at a certain small volume, greater is the probability of finding the electron is that volume. The maximum blackening of the cloud shown in the figure at a distance of 0.529 A° indicates that 1*s* electron of H-atom spends most of its time at a distance of 0.529 A° from the nucleus *i.e.* the radius of maximum electron density in 1*s* electron is equal to 0.529 A°.

(*v*) For 2*s* electron the value of D is zero at $r = 0$. The value of D increases as the value of $r = 0.529$ Å increases, passes through a lower maximum at $r = 0.529$ Å and falls to zero at $r = 1.058$ Å. The value of D increases as r increases from 1.058 Å and passes through second higher maximum at $r = 5 \times 0.529$ Å and finally approaches zero as r tends to infinity. Thus for 2*s*-electron (*a*) D = 0 at $r = 0$, 1.058 Å, 0.529 Å and ∞ (*b*) lower maximum lies at $r = 0.529$ Å (*c*) higher maximum lies at $r = 2.645$ Å. Thus the distance for the maximum probability of 2*s* electron is equal to 2.645 Å (higher maximum) while the distance for the probability of 2*s* electron *very close* to the nucleus is equal to 0.529 Å (lower maximum). At an intermediate distance (= 1.058 Å) there is a surface at which the probability of finding the electron is zero. This implies that within the spherical orbital of a 2*s* electron, there is a spherical shell in which the probability of finding the electron is almost zero. This is called a **node** or **nodal plane** or **nodal surface.** Thus the surfaces at which the probability of finding the electron is zero

are called **nodes**. *For any orbital having principal quantum number, n there are always (n–1) nodes or nodal planes* (neglecting the node of infinity). For example 1*s* orbital (n = 1) has *no* (1–1 = 0) nodal plane while in 3*s* orbital (n = 3) there are (3–1) = 2 nodal planes as is evident from the curves for 1*s* and 3*s* orbitals.

(*vi*) On comparing the curves for 2*s* and 2*p* electrons, we find that :

(*a*) the distance for the maximum probability for 2*s* electron (= 2.645 Å) is *slightly larger* than that for the 2*p* electron (= 2.116 Å) but much larger than that for 1*s* electron (= 0.529 Å). Thus 2*s* and 2*p* electrons or orbitals have slightly different energies and both these orbitals have greater energy than 1*s* orbital.

(*b*) The lower maximum lying at 0.529 Å indicates that 2*s* electron spends more of its time close to the nucleus than does the 2*p* electron. In other words this means that 2*s* electron is bound more tightly to the nucleus than the 2*p* electron or 2*s* electron is more stable than the 2*p* electron, *i.e.* 2*s* electron has lower energy than 2*p*-electron (2*s* < 2*p*), although both the electrons are of the same main energy level.

2. Angular Probability Distribution Curves—Space Orientations and Shapes or Boundary Surfaces of Orbitals.

These curves tell how the probability of finding the electron varies with its direction from the nucleus without any reference to its distance from the nucleus. These curves show how the various orbitals of a given sub-shell are disposed along *x*, *y* and *z* axes. The shapes, pace orientation, electron density etc. of orbitals have already been discussed under the study of *Magnetic Quantum Number*.

Questions with Answers

Q.1 Arrange the orbitals with the following quantum numbers in the increasing order of their energy.

(*a*) $n = 3, l = 0, m = 0, s = +\frac{1}{2}$

(*b*) $n = 3, l = 1, m = 1, s = +\frac{1}{2}$

(*c*) $n = 3, l = 2, m = 1, s = +\frac{1}{2}$

(*d*) $n = 4, l = 0, m = 0, s = +\frac{1}{2}$

Ans. Oribtals represented by the given quantum numbers are : (*a*) 3*s* (*b*) 3*p* (*c*) 3*d* (*d*) 4*s*. According to Aufban principle the energy of 3*s*, 3*p*, 3*d* and 4*s* orbitals increases as :

$$3s < 3p < 4s < 3d$$ **(Ans.)**

Q.2 Write the expression representing the electron probability function (D).

Ans. Electron probability function (D) = $4\pi r^2 dr\psi^2$

Q.3 Determine the number of orbitals in the subshell having $n = 4$ and $l = 3$.

Ans. Sub-shell having $n = 4$ and $l = 3$ is $4f$ sub-shell. Obviously $4f$ sub-shell has seven orbitals, since when $l = 3$, $m = 0, \pm 1, \pm 2, \pm 3$ (seven values).

Q.4 Explain why the following sets of quantum numbers are not possible.

	n	l	m	s
(*a*)	2	2	1	+ 1/2
(*b*)	1	0	–1	– 1/2
(*c*)	3	2	3	+ 1/2

Ans. (*a*) $n = 2$ (2*nd* shell) and $l = 2$ (d-sub shell) represents $2d$ sub-shell. Since 2*nd* shell does not contain d sub-shell, $2d$ sub-shell does not exist. Consequently this set of quantum numbers is not possible.

(*b*) $n = 1$ and $l = 0$ represents $1s$ sub-shell. Since for this sub-shell m should have zero ($m = 0$) value and not –1 as given in question, the given set of quantum numbers is not possible.

(*c*) $n = 3$ and $l = 2$ represents $3d$ sub-shell. Since d sub-shell should have any of the five values of m *viz.* $\pm 2, \pm 1, 0$ and not 3 as given in the question, the given set of quantum numbers is not possible.

Q.5 The set of quantum numbers : $n = 3$, $l = 2$, $m \pm 2$ for an electron in the ground state of an atom (X) with Z = 19 is not possible. Explain.

Ans. $n = 3$ and $l = 2$ represents $3d$ sub shell. Complete E.C. of X atom with Z = 19 is $1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^1$. Since this E.C. does not contain d sub-shell, the given set of quantum numbers is not possible.

Q.6 Find out the number of orbitals for which the following set of quantum numbers is possible. $n = 3$, $l = 2$ and $m = +2$.

Ans. $n = 3$ and $l = 2$ represents $3d$ sub shell. Since this sub shell has five values of m namely +2, –2, +1, –1 and 0, this sub shell has five $3d$ orbitals namely $3d_{xy}$, $3d_{yz}$, $3d_{zx}$, $3d_{x^2-y^2}$ and $3d_{z^2}$. $m = +2$ represents one of the five orbitals given above. Thus there is one orbital ($3d$ orbital) for which $n = 3$, $l = 2$ and $m = +2$.

Q.7 Find out the maximum number of electrons in an atom having quantum numbers as $n = 4$ and $m = +1$.

Ans. $n = 4$ represents $4th$ shell. This shell contains $4s$, $4p$, $4d$ and $4f$ sub shells. The values of m for these sub-shells are: for $4s$, $m = 0$ (one $4s$ orbital), for $4p$, $m = 0, +1, -1$ (three $4p$ orbitals), for $4d$, $m + 2, -2, +1, -1, 0$ (five $4d$ orbitals) and for $4f$, $m = +3, -3, +2, -2, +1, -1, 0$ (seven $4f$ orbitals). Thus the orbitals for which $m = +1$ may be $4p_x$, $4d_{xy}$, $4f_z 3$. Since each of these orbitals contains two electrons, maximum number of electrons in the atom = 2 + 2 + 2 = **6** (**Ans.**)

Q.8 There are three orbitals having quantum number values as $n = 5$, $l = 0$; $n = 4$, $l = 1$ and $n = 3$, $l = 2$. In which orbital will the electron enter first ?

Ans. The orbitals represented by the given values of quantum numbers are as : $5s$ ($n = 5$, $l = 0$), $4p$ ($n = 4$, $l = 1$) and $3d$ ($n = 3$, $l = 2$) respectively. The energy of these orbitals is in the order : $3d < 4p < 5s$. Since $3d$ orbital has the lowest energy, the electron will enter $3d$ orbital for whicn $n = 3$ and $l = 2$.

Q.9 Which of the orbitals having the following set of quantum numbers have the same energy? (*a*) $n = 2, l = 1, m = +1$ (*b*) $n = 2, l = 1, m = -1$ (*c*) $n = 2, l = 1, m = 0$ and (*d*) $n = 2, l = 0, m = 0$.

Ans. Orbitals represented by the given sets of quantum numbers are $2p_x$ ($n = 2, l = 1, m = +1$), $2p_y$ ($n = 2, l = 1, m = -1$), $2p_z$ ($n = 2, l = 1, m = 0$), and $2s$ ($n = 2, l = 0, m = 0$). All the three $2p$ orbitals are degenerate. Hence these orbitals have the same energy but $2s$ orbital has different energy.

Q.10 Find out the number of radial nodes in 3*s* and 2*p* orbitals.

Ans. Number of radial nodes in a given orbital = $n - l - 1$. Hence :

No. of radial nodes in $3s$ orbital = $3 - 0 - 1 = 2$

No. of radial nodes in $2p$ orbital = $2 - 1 - 1 = 0$

Q.11 Arrange *ns, np,* (*n*–1)*d* and (*n*–1)*f* orbitals in the increasing order of their energy.

Ans. The energy of orbitals increases with the increase of their $(n + l)$ value. If two orbitals have the same value of $(n + l)$, the orbital with higher value of n has higher energy. $(n + l)$ values for the given orbitals are given below :

Orbitals :	ns	np	$(n - 1)d$	$(n - 1)f$
$(n + l)$ values :	$n + 0$	$n + 1$	$n-1 + 2$	$n-1 + 3$
	$= n$	$= n + 1$	$= n + 1$	$= n + 2$

It may be seen that np and $(n - 1)d$ orbitals have the some value of $(n + l)$. Now since np orbital has higher value of $n(= n)$ than $(n - 1)d$ orbital ($= n - 1$), np orbital has higher energy than $(n - 1)d$ orbital. Thus the increasing order of energy is as $ns < (n - 1)d < np < (n - 1)f$.

Q.12 What is the atomic number (Z) of an atom having quantum numbers as $n = 3$, $l = 0$ and $m = 0$?

Ans. $n = 3$, $l = 0$ and $m = 0$ represents $3s$ orbital. E.C. of the atom having $3s$ orbital is $1s^2, 2s^2 2p^6, 3s^1$ (Z = 11) or $1s^2, 2s^2 2p^6, 3s^2$ (Z = 12). The atom having $n = 3$, $l = 0$ and $m = 0$ can have 11 or 12 as its atomic number.

University Questions

1. (*a*) Derive Schrodinger wave equation in three dimensions and what is the justification for this equation.
   (*b*) Draw the shape of *d*-orbitals.
   (*c*) Place the electrons identified by quantum numbers n and l (*i*) $n = 4, l = 1$ (*ii*) $n = 4, l = 0$ (*iii*) $n = 3, l = 2$ (*iv*) $n = 3, l = 1$ in the order of their decreasing energy. *(Himachal Pradesh 2000)*
2. (*a*) Derive Schrodinger wave equation. How does it help in determining position of electron in an atom?
   (*b*) Write a note on Hamiltonian operator. *(Kanpur 2000)*
3. Write a note on "Magnetic quantum number". *(Kumaon 2000)*
4. (*a*) What are quantum numbers? Explain them clearly.

(*b*) Mention number of unpaired electrons in a subshell of the element whose atomic number is 29.

(*c*) Give all the four quantum numbers of 15th electron of the atom with atomic number 19.

(*d*) Designate the orbital for which : (*i*) $n = 3$, $l = 1$, $m = 0$ (*ii*) $n = 2$, $l = 1$, $m = 0$.

(*e*) Write down the general form of Schrodinger's wave equation and define each of its term.

(*f*) Explain Heisenberg uncertainty principle. How does its influence the concept of the electron?

(*g*) A moving cricket ball, weighing 200g, is to be located within 0.2 Å. What is the uncertainty in its velocity ? Comment on your result. Given : $h = 6.626 \times 10^{-34}$ Js. (*Lucknow 2001*)

5. (*a*) Write a note on significance of Ψ.

(*b*) What is the significance of four quantum numbers ? (*Delhi 2002*)

6. (*a*) Define orbital.

(*b*) What are n, l and m values for $2p_x$ and $3p_y$ electrons ?

(*c*) Explain briefly time independent Schrodinger wave equation. (*Delhi 2003*)

7. (*a*) Calculate screening constant for the elements with atomic numbers 11 and 17.

(*b*) State Paulies' exclusion principle. (*Nagpur 2003*)

8. *1st, 2nd, 3rd* and *4th* shells of an atom may certain maximum 2, 8, 18 and 32 electrons respectively. Explain this arrangement in terms of quantum numbers. (*Rohilkhand 2003*)

9. (*a*) Which of the following orbitals are not possible ? 1*p*, 2*s*, 2*p*, 2*d* and 3*f*.

(*b*) What are the values of question number of 10th electron of K-atom ?

(*c*) What are n, l and m values for $3p_x$ electron ? (*Meerut 2006*)

10. (*a*) Which of the following orbitals is nearest to the nucleus ? 4*f*, 5*d*, 6*s* and 6*p* ?

(*b*) Name the rule according to which the V.S.E.C. of C-atom is $2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$ and not $2s^2\ 2p_x^2\ 2p_y^0\ 2p_z^0$. (*H.N. Bahuguna 2006*)

11. What we the values of n, m and l for $2p_x^1$ electron ? (*Meerut 2007*)

12. (*a*) Arrange the following orbitals in the increasing order of their energy : 5*p*, 3*s*, 4*d*, 6*s*.

(*b*) What are the values of n and l for 5*d* orbital ? (*Purvanchal 2007*)

13. (*a*) Write a note on Heisenberg's uncertainty principle.

(*b*) What are quantum numbers ? Explain their significance. (*H.N. Bahuguna 2007*)

14. (*a*) What is Schrödinger wave equation ? Give its derivation and significance of ψ and ψ^2.

(*b*) Give a brief account of wave nature of electron. Derive de Broglie equation.

(*c*) Write short notes on : (*i*) Heisenber's incerainty principle (*ii*) Paulie's exclusion principle. (*Meerut 2008*)

15. Discuss Heisenberg's uncertainty principle in detail alongwith its experimental verification. (*Agra 2008*)

16. (*a*) Explain Paulie's exclusion principle.

(*b*) Derive de-Broglie's equation for a particle of mass m and moving with a velocity of v. (*H.N. Bahuguna 2008*)

17. (*a*) Explain the concept of atomic orbital and explain the differences between orbit and orbital with suitable examples.

(*b*) What are quantum numbers ? Explain Hind's rule of maximum multiplicity. (*Gurukul Kangri 2008*)

18. (*a*) Explain quantum numbers and their significance in characterising an electron in an atom.

(*b*) What is Heisenberg's uncertainty principle ? (*Meerut 2009*)

CHAPTER

3 Modern Periodic Table and Electronic Configuration of Atoms

Periodic Table

Mendeleef's Periodic Law and Mendeleef's Periodic Table

Attempts were made to classify the elements in a number of ways. Most noteworthy of these is that made by Russian chemist, Mendeleef (*men-de-h-lay-eff*) who gave a law known as *Mendeleef's Periodic Law* which states as :

The properties of elements are a periodic function of their atomic weights, i.e., if the elements are arranged in the increasing order of their atomic weights, the properties of the elements (i.e., similar elements) are repeated after definite regular intervals or periods.

Working on this law, Mendeleef arranged the elements in the increasing order of their atomic weights in the form of a table which is known as *Mendeleef's Periodic Table* after his name.

In this table the elements are arranged in *groups* (*or columns*) and *periods* (*or rows*).

Defects of Mendeleef's Periodic Table

Mendeleef's periodic table suffers from the following defects :

1. Position of hydrogen. Hydrogen resembles both the alkali metals and the halogens. Its position in the periodic table is, therefore, anomalous.

2. Position of lanthanides and actinides. A group of 15 elements (At. No. 57 to 71) which is called rare earths or lanthanides does not find its proper place in the table and has been placed at one place in group III and period 6. Similarly, another group of 15 elements (At. No. 89 to 103) called actinides does not find its proper place and has been put at one place in group III and period 6.

3. Similar elements are separated while dissimilar elements are placed in the same group. Certain elements which possess similar properties are separated in the periodic table, as, for example, copper and mercury; silver and thalium; and barium and lead; while many dissimilar elements have been grouped together. For example Cu, Ag, and Au are grouped along with the alkali metals though there is little resemblance between them. Similarly manganese is grouped with the halogens.

4. Existence of four anomalous pairs of elements. The order of increasing atomic weight has been ignored in case of four pairs of elements in order to place

them in a position justified by their properties. *Thus elements of higher atomic weights precede those of lower atomic weight at four places as shown below* :

(*a*) Ar (Z = 18, at. wt. = 40) precedes K (Z = 19, at. wt. = 39.0)

(*b*) Co (Z = 27, at. wt. = 59.9) precedes Ni (Z = 28, at. wt. = 58.6)

(*c*) Te (Z = 52, at. wt. = 127.6) precedes I (Z = 53, at. wt. = 126.9)

(*d*) Th (Z = 90, at. wt. = 232.12) precedes Pa (Z = 91, at. wt. = 231)

5. Position of isotopes. If the elements are arranged in the order of their increasing atomic weights, it is not possible to accommodate large number of *isotopes* in the periodic table.

6. Group does not represent valency. Excepting osmium, elements placed in group eight do not show a valency of 8. Also the elements lying in the middle of long periods show two or more valencies *e.g.* Cr, Mn etc.

Mosley's Modern Periodic Law

Mosley showed in 1911 that, since the physical and chemical properties of an element depend on the number of electrons and their arrangement in different orbitals of the atom, the classification of the elements should be based on the number of these electrons (*i.e.* atomic number) and their arrangement in different orbitals. This idea led Mosley to predict that most of the defects 0f Mendeleef's periodic table disappear, if the basis of classification of elements is changed to atomic number in place of atomic weight. Accordingly, Mosley put forward Modern Periodic Law which states as follows :

The properties of elements are a periodic function of their atomic numbers, i.e. if the elements are arranged in the increasing order of their atomic numbers, the properties of the elements (i.e. similar elements) are repeated after definite regular intervals or periods.

With the replacement of atomic weight by atomic number as the basis of classification of elements, many of the irregularities in the Mendeleef's table disappear as shown below

1. Position of hydrogen. The dual role of hydrogen is explained by the fact that it has one electron in its outer orbit. It has equal tendency of gaining or losing one electron for assuming a stable configuration. When it loses one electron to give H^+, it resembles alkali metals (which give Li^+, Na^+, K^+, etc. ions) while when it gains one electron to give H^-, it resembles halogens (which give Cl^-. Br^- etc.).

2. Anomalous pairs of elements. This anomally disappears altogether and the pairs Ar—K, Co—Ni, Te—I and Th—Pa are found arranged in the table in the order in increasing atomic numbers as shown below :

Pairs of elements →	*Ar*	*K*	*Co*	*Ni*	*Th*	*I*	*Ta*	*Pa*
Atomic numbers →	*18*	*19*	*27*	*28*	*52*	*53*	*90*	*91*
Atomic weights →	*40*	*39*	*59.9*	*58.6*	*127.6*	*126.9*	*232.12*	*231*

3. Position of rare earths. The arrangement of extranuclear electrons in all the rare earth elements can be represented as 2, 8, 18 (18 + x), 9, 2, where x

varies from 0 (for La) to 14 (for Lu). With this general arrangement of electrons, all of them possess the same valency and similar chemical properties. This justifies their grouping at the same place.

4. Position of isotopes. Since isotopes of the same element possess the same atomic number, all of them should occupy one and the same place in the periodic table.

5. Justification for dissimilar elements being placed together. The length of the periods is determined by arrangement of electrons in different orbits. The end of every period results from the completion of the last orbit (last number is always an inert gas). Different periods carry 2, 8, 18 and 32 elements.

When 18 elements are to be distributed among 8 groups; groups 1—7 get two elements each while group 0 gets only one. The three elements which cannot be arranged elsewhere are placed in a special group VIII. This lack of space is enough *justification for group VIII.*

Out of the two elements which every long period adds to a group, one resembles the typical element, the other does not. This gives rise to the formation of sub-groups. This explains *why dissimilar elements have been grouped together.*

Extended or Long Form of Periodic Table : Modern Periodic Table

In order to remove the defects of Mendeleef's periodic table, a number of tables have been suggested from time to time by various workers for classifying the elements in the increasing order of their atomic numbers. Out of the various tables the *Extended Long Form of Periodic Table* is the most simple and is widely accepted.

This table is shown on the next page and is also called *Bohr's Periodic Table*, since it is based on Bohr's scheme of the classification of the elements into four types depending on the number of incomplete shells of electrons in the atom. This table was proposed by Rang (1893) and then modified by Werner (1905) and extended by Bury (1921).

Groups

The vertical columns shown in the periodic table are called *groups* or *families* or simply *columns.*

(*a*) There are *nine groups* in all including VIII group consisting of three triads (Fe, Co, Ni; Ru, Rh, Pd; Os, Ir, Pt.) and zero group of inert gases. Groups I to VII are sub-divided into sub-groups A and B. Thus there are 18 vertical columns which are: IA, IIA, III A, IVA, VA, VIA, VII A, zero, IB, II B, III B, IV B, VB, VI B, VII B and three columns of group VIII.

(*b*) Elements of groups IA, IIA, IIIA, IVA, VA, VIA and VII A have their *outermost shells incomplete while each of their inner shells is complete.* These elements are called *normal or representative elements.* These elements consist of some metals, all non-metals and metalloids.

(*c*) Elements of groups I B, II B, III B (only Sc, Y, La and Ac) IVB, VB, VIB, VIIB and VIII have their *two outermost shells incomplete.* These are called *transition elements.* These elements are placed in the middle of the table. All these elements are *metals.*

Table: Extended or Long Form of Periodic Table (Modern or Bohr's Periodic Table). The number given below the symbol indicates the atomic number of the elements.

Periods and No of Elements	IA	IIA	Metals (Active metals and Transition metals)										Non-metals Metalloids and Noble gases					Zero
													IIIA	IVA	VA	VIA	VIIA	
1 (2) (H_1 — He_2)	H 1	Active metals																He 2
2 (8) (Li_3 — Ne_{10})	Li 3	Be 4	Transition metals										B 5	C 6	N 7	O 8	F 9	Ne 10
3 (8) (No_{11} — Ar_{18})	Na 11	Mg 12	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
4 (18) (K_{19} — Kr_{36})	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
5 (18) (Rb_{37} — Xe_{54})	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
6 (32) (Cs_{55} — Rn_{86})	Cs 55	Sr 56	La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
7 (19) (Fr_{87} — Lw_{103})	Fr 87	Ra 88	Ac 89	Ku 104	Ha 105													

Inner-transition Elements (Group III B, Period 6 and 7)

Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71	Lanthanides
Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lw 103	Actinides

(*d*) Elements of group zero have *all their shells completely filled.* These elements are called *noble gases.* These are placed at the extreme right of the table.

(*e*) Two groups of 14 elements lying in group III B [Ce(Z = 58) to Lu (Z = 71) and Th (Z = 90) to Lw (Z = 103)] have their *three outermost shells incomplete.* These are called *lanthanides* and *actinides* respectively and have been placed at the bottom of the table.

Periods

The horizontal rows shown in the periodic table are called *periods* or simply *rows.* There are *seven periods* in the table.

(*a*) *1st* period consists of 2 elements which are H (Z = 1) and He (Z = 2).

(*b*) *2nd* and *3rd* periods have 8 elements each.

2nd period → Li (Z = 3) to Ne (Z = 10)

3rd period → Na (Z = 11) to Ar (Z = 18)

Both these periods are called *short periods.* The elements of *2nd* and *3rd* short periods were called *typical elements* by Mendeleef as these elements were considered to be the true representatives of their respective groups. But, now since it has been found that the elements of *2nd* period resemble more with the elements diagonally related to them than with the elements of their own groups, the elements of *2nd* period are not considered as true representatives of their respective groups. Now a days the elements of only *3rd period namely Na, Mg, Al, Si, P, S, Cl are called typical elements.* These elements have the following characteristics :

(*i*) They show their group characteristics as valency, chemical behaviour etc.

(*ii*) They form a connecting link between the first member of their respective groups and with the elements of B sub-groups. Hence these elements serve as a bridge between the two sub-groups. However, they show very little resemblance with elements of B sub-groups. For example Na and Cl which are the typical elements of I and VII groups respectively, resemble more closely with the elements of their own sub-groups and show a very little resemblance with the elements of B sub-groups.

(*c*) *4th* and *5th* periods have 18 elements each while *6th* period has 32 elements as shown below :

4th period → K (Z=19) to Kr (Z=36)

5th period → Rb (Z=37) to Xe(Z=54)

6th period → Cs (Z=55) to Rn (Z=86)

All these three periods are called *long periods. 6th* period also includes 14 rare earths or lanthanides [Ce (Z=58) to Lu (Z=71)].

(*d*) *7th* period is an incomplete period and at present it consists of 19 elements which are Fr (Z=87) to Ha (Z= 105). All the elements of this period are radioactive. This period also includes 14 actinides [Th (Z=90) to Lw (Z = 103)]. The elements after U (Z=92) are called *transuranic elements.* These elements are the result of atomic research and hence are synthetic elements.

Thus we see that in this table the long periods have keen extended and short periods have been broken so as to accommodate the transitional elements in the long periods at their proper places between groups II A and III A.

General Characteristics of Groups

1. Number of valency electrons. On moving down a given group the number of valency electrons does not change, *i.e.* remains the same.

2. Valency. The valencies of all the elements of the same group are the same. The valency of an element with respect to oxygen is equal to its group number.

3. Properties of elements. All the elements of a given group possess very similar physical and chemical properties. There is a regular gradation in their properties when we move from top to bottom in a group. For example :

(*a*) The alkali metals (group IA) resemble each other and their base-forming tendency increases from Li to Cs.

(*b*) The reactivity of halogens (group VII A) decreases as we pass from F to I.

4. Size of atoms. *Size of atoms increases on descending a group.* For example in group IA, atomic size increases from Li to Cs. Thus :

$$Li < Na < K < Rb < Cs$$

5. Metallic character. *The metallic character of the elements increases in moving from top to bottom in a group.* This is particularly apparent in groups IVA, VA and VIA, which begin with non-metals (namely C, N and O respectively), and end with metals (namely Pb, Bi and Po respectively). For example, in group VA, N and P are non-metals, As and Sb are metalloids and Bi is a typical metal. Thus the metallic character of these elements increases from N to Bi as shown below :

Elements of group VA : $\underbrace{N, P,}_{\text{Non-metals}}$ $\underbrace{As, Sb,}_{\text{Metalloids}}$ $\underbrace{Bi}_{\text{Metal}}$

Metallic character : *—Metallic character increasing→*

It is because of a gradual increase of the metallic character of the elements from top to bottom that the *oxides of the elements become more and more basic in the same direction.* For example :

Oxides of the elements of group VA : $\underbrace{N_2O_3, P_2O_5,}_{\text{Acidic}}$ $\underbrace{As_2O_3, Sb_2O_3,}_{\text{Amphoteric}}$ $\underbrace{Bi_2O_3}_{\text{Basic}}$

Basic character : *—Basic character increasing→*

6. Number of electron shells. *In going down a group the number of electron shells increases by one at each step and ultimately becomes equal to the number of the period to which the element belongs* as shown below for the elements of Group IA.

Elements	*Electronic configuration*	*No. of shells*
Li	*2, 1*	*2*
Na	*2, 8, 1*	*3*

K	*2, 8, 8, 1*	*4*
Rb	*2, 8, 18, 8, 1*	*5*
Cs	*2, 8, 18, 18, 8, 1*	*6*
Fr	*2, 8, 18, 32, 18, 8, 1*	*7*

General Characteristics of Periods

1. Number of valency electrons. Number of valency electrons increases from 1 to 8 when we proceed from left to right in a period.

2. Valency. The valency of the elements with respect to (w.r.t.) hydrogen in each short period increases from 1 to 4 and then falls to one while the same with respect to oxygen increases from 1 to 7 as shown below for the elements of *2nd* and *3rd* period :

Elements of 2nd period :	*Li*	*Be*	*B*	*C*	*N*	*O*	*F*
Hydrides of the elements :	*LiH*	*BeH_2*	*BH_3*	*CH_4*	*NH_3*	*H_2O*	*HF*
Valency of the elements w.r.t hydrogen :	*1*	*2*	*3*	*4*	*3*	*2*	*1*
Elements of 3rd period :	*Na*	*Mg*	*Al*	*Si*	*P*	*S*	*Cl*
Oxides of the elements :	*Na_2O*	*MgO*	*Al_2O_3*	*SiO_2*	*P_2O_5*	*SO_3*	*Cl_2O_7*
Valency of the elements w.r.t. oxygen :	*1*	*2*	*3*	*4*	*5*	*6*	*7*

3. Size of atoms. *Size of atoms decreases from left to right in a period.* Thus alkali metals have the largest size while the halogens have the smallest size.

4. Properties of elements. The properties of the elements of a given period differ considerably but the elements in the two adjacent periods show marked similarity between them. For example, when we consider the elements of *2nd* and *3rd* periods, we find that Na resembles Li, Mg resembles Be, Al resembles B, Si resembles C, P resembles N, S resembles O, Cl resembles F and Ar resembles Ne.

5. Metallic character. On moving from left to right in a period the metallic character of the elements decreases. For example in *3rd* period, Na, Mg and Al are *metals* while Si, P, S and Cl are *non-metals* as shown below :

Elements of 3rd period : Na, Mg, Al (*Metals*) Si, P, S, Cl (*Non-metals*)

Metallic character : *—Metallic character decreasing→*

It is because of the gradual decrease of the metallic character from left to right that the oxides of the elements become less and less basic in the same direction. For example :

Oxides of the elements of 3rd period :	*Na_2O*	*MgO*	*Al_2O_3*	*SiO_2*	*P_2O_5*	*SO_3*	*Cl_2O_7*
Basic character :	*Strongly basic*	*Basic*	*Amphoteric*	*Feebly acidic*	*Acidic*	*More acidic*	*Most acidic*

—Basic character decreasing→

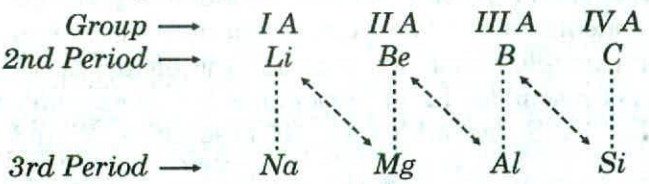
6. Number of shells. *In going from left to right in a period the number of electron shells remains the same and the number of a period corresponds to the number of the shells found in the elements of that period, e.g.* all the elements of *2nd* period have the electrons only in first *two shells* as shown below :

Elements of 2nd period	:	*Li*	*Be*	*B*	*C*	*N*	*O*	*F*	*Ne*
Atomic number	:	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
Electronic configuration	:	*2, 1*	*2, 2*	*2, 3*	*2, 4*	*2, 5*	*2, 6*	*2, 7*	*2, 8*
No. of shells	:	*2*	*2*	*2*	*2*	*2*	*2*	*2*	*2*

7. Diagonal relationship. It is one of the important features of the earlier elements of *2nd* period of the long form of the periodic table (*e.g.* Li, Be and B) that they resemble more with the elements lying at their right hand side in the *3rd* period (*i.e.* diagonally opposite elements) than with other members of their own sub-groups. Thus Li resembles more in its properties with Mg which lies at its lower right in the *3rd* period than with other members of its own sub-group IA. Similarly Be shows similarities with Al and B resembles Si. The two elements showing similarities in properties are called *diagonal neighbours* or *diagonal pair* and the *across-the-street* similarity in properties existing between the two elements of a diagonal pair is known as *diagonal relationship.* Thus :

Diagonal relationship is the resemblance of the properties of the elements of 2nd period with their diagonally opposite members lying in 3rd period.

Three diagonal pairs *viz.* Li—Mg, Be—Al and B—Si are shown below :



The two elements of a diagonal pair are also called *bridge elements*, since each diagonal pair forms a sort of bridge between the periods to which the members of a given diagonal pair belong.

The following are the important examples of diagonal relationship found in the periodic table.

(*i*) *Li—Mg diagonal relationship.* It will be discussed in Chapter No. 20

(*ii*) *Be—Al diagonal relationship.* It will be discussed in Chapter No. 22

(*iii*) *B—Si diagonal relationship.* It will be discussed in Chapter No. 25

Cause of diagonal relationship. Why the two members of a given diagonal pair show diagonal relationship (*i.e.* similarities in properties) has been explained on the basis of the following :

(*a*) *Applications of electronegativity.* For this see chapter 4 namely "*Periodic Properties*"

(*b*) *Application of polarisation of ions.* For this see chapter 7 namely "*Chemical Bonding (Lewis Theory)*"

Merits of Long Form of Periodic Table over Mendeleef's Periodic Table.

The long form of periodic table has a number of merits over the Mendeleef's periodic table in the following respects :

(1) The classification of the elements is based on a more fundamental property *viz.*, atomic number.

(2) It relates the position of an element to its electronic configuration. Thus each group contains elements with similar electronic configuration and hence similar properties. For example, all the alkali metals have similar valence-shell electronic configuration *viz.* ns^1 configuration and hence have similar properties.

Alkali metals	*Atomic number*	*Complete electronic configuration*	*Valence-shell configuration*
Li	*3*	*2, 1*	$2s^1$
Na	*11*	*2, 8, 1*	$3s^1$
K	*19*	*2, 8, 8, 1*	$4s^1$
Rb	*37*	*2, 8, 18, 8, 1*	$5s^1$
Cs	*55*	*2, 8, 18, 18, 8, 1*	$6s^1$
Fr	*87*	*2, 8, 18, 32, 18, 8, 1*	$7s^1$

(3) It explains the similarities and variations in the properties of the elements in terms of their electronic configurations and brings out clearly the trends in chemical properties across the long periods.

(4) The inert gases having completely filled electron shells have been placed at the end of each period. Such a location of the inert gases represents a logical completion of each period.

(5) In this form of the periodic table, the elements of the two sub-groups have been placed separately and thus dissimilar elements do not fall together.

(6) It provides a clear demarcation of different types of the elements like active metals, transition metals, non-metals, metalloids, inert gases, lanthanides and actinides. The elements of group IA and IIA are active metals and are located at the extreme left of the table. The transition metals are found in the middle of the table. The elements lying to the right of a dark line shown in the long form of periodic table in the form of ladder (i.e. steps) are noble gases, metalloids and non-metals while those lying to the left of the line are metals (*active metals and transition metals*).

(7) It is easier to remember, understand and reproduce.

Defects of Long Form of Periodic Table

Although the long form of the periodic table is superior to Mandeleef's periodic table in many respects, it retains some of the defects as such. For example :

(*i*) The problem of the position of hydrogen still remains unsolved.

(*ii*) Like the Mendeleef's table, it fails to accommodate the lathanides and actinides in the main body of the table.

(*iii*) The arrangement is unable to reflect the electronic configuration of many elements.

Electronic Configuration of Atoms

What is Electronic Configuration ?

The distribution of electrons in various shells, sub-shells and orbitals of an atom is called its *complete electronic configuration* or simply *electronic configuration.*

What is Valence-shell Configuration ?

The distribution of electrons in various sub-shells and orbitals of the valence-shell (or outermost shell) is called *valence-shell configuration.*

Representation of Electronic Configuration

The electronic configuration of an atom is written in terms of nl^x notation where l indicates the sub-shell as given below :

Value of l	:	0	1	2	3	.....
Sub-shell	:	*s*	*p*	*d*	*f*	.....

In the notation nl^x, super-script x written at the top of l indicates the number of electrons present in the sub-shell given by l, while n written to the left of l^x indicates the number of the shell to which the sub-shell denoted by l belongs. For example $3p^2$ in which $n = 3$, $x = 2$ and $l = 1$ (p sub-shell) indicates that two electrons ($x = 2$) are present in p sub-shell ($l = 1$) which belongs to *3rd* main shell ($n = 3$). (Fig. 3.1).

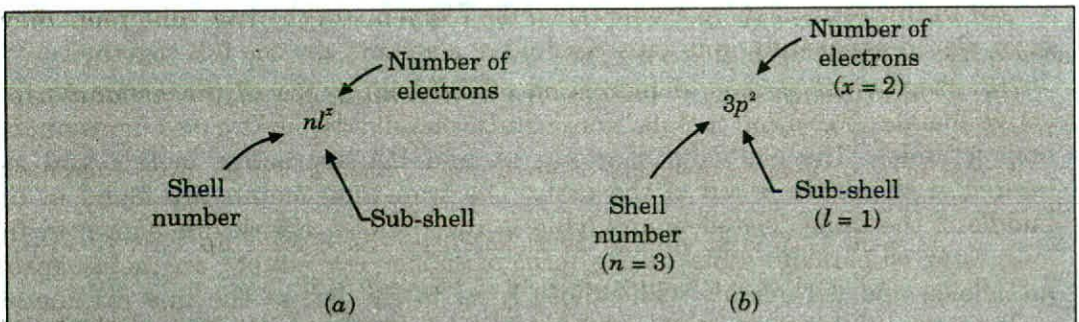


Fig. 3.1. (*a*) Representation of electronic configuration of an atom. (*b*) Representation of electronic configuration of an atom containing two electrons ($x = 2$) in p sub-sell ($l = 1$) belonging to *3rd* shell ($n = 3$).

Rules for Writing Electronic Configuration of a Given Atom

The rules used for writing the electronic configurations of the atoms of the elements in the ground state are :

1. **Maximum number of electrons in a shell.** According to *Bohr-Bury scheme* the maximum number of electrons that a shell can hold is equal to $2n^2$ where n is the number of the shell (*i.e.*, principal quantum number). Thus :

The maximum number of electrons in 1st shell (n = 1) = 2 × 1^2 = 2

The maximum number of electrons in 2nd shell (n = 2) = 2 × 2^2 = 8

The maximum number of electrons in 3rd shell (n = 3) = 2 × 3^2 = 18

The maximum number of electrons in 4th shell (n = 4) = 2 × 4^2 = 32

2. **Maximum number of electrons in a sub-shell.** We have seen during the study of azimuthal quantum number that the maximum number of electrons in a sub-shell is equal to 2(2*l* + 1) where *l* = 0, 1, 2 or 3 for *s*, *p*, *d* or *f* sub-shells respectively. Thus :

Value of l	:	*0*	*1*	*2*	*3*
Sub-shell	:	*s*	*p*	*d*	*f*
Max. number of electrons = 2(2l + 1)	:	*2*	*6*	*10*	*14*

3. **Aufbau principle.** Aufbau is a German word which means *build up* or *construction*. It is for this reason that the principle is also often called *building up principle* or *construction principle*. It is pronounced as *of bow*. This principle gives us a sequence in which various orbitals are filled with electrons. This principle states as follows :

The orbitals are filled up with electrons in the increasing order of their energy.

The principle can also be restated in any of the following forms :

(i) The orbitals of minimum energy are filled up first with electrons and then the orbitals of higher energy start to fill.

(ii) Electrons occupy the orbitals of minimum energy first and then they occupy the orbitals of higher enegry.

(iii) Orbitals with lowest energy are better seats for electrons and are, therefore, occupied first.

The energy of various orbitals of an atom *a multi-electron atom* increases as :

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p < 8s \ .....$$

Thus the sequence in which various orbitals are filled up with electrons is the same as the relative order of the energy of orbitals. Thus the orbitals will be filled up with electrons in the following sequence :

Orbitals being filled →

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, ...

The sequence given above is represented diagramatically in Fig. 3.2.

Limitations (Deviations) of Aufbau principle. There are some elements in which the extra electron, while entering the orbital, does not obey Aufbau principle as shown by the following examples :

(i) Configuration of La (Z = 57) atom. We know that, according to Afbau principle, the configuration of Ba (Z = 56) atom is $[Xe]_{54}\ 6s^2$ where $[Xe]_{54}$ indicates the configuration of Xe (Z = 54) atom which is 2, 8, 18. 18, 8.

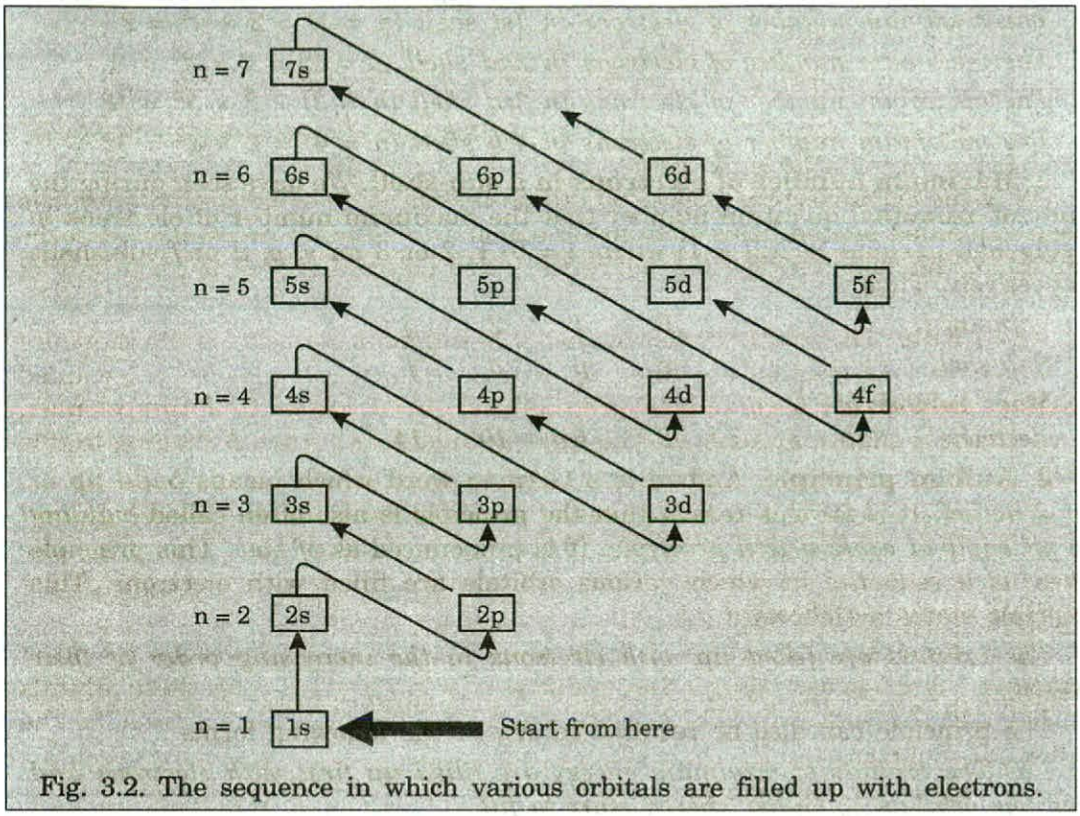


Fig. 3.2. The sequence in which various orbitals are filled up with electrons.

Now after 6s orbital has been completely filled at Ba, the next electron, according to Aufbau principle, must enter 4*f* orbital in La atom to give $[Xe]_{54}4f^{1}5d^{\circ}6s^{2}$ configuration to La atom; but it has been observed that the extra electron enters 5*d* orbital (instead of 4*f* orbital) to give $[Xe]_{54}4f^{\circ}5d^{1}6s^{2}$ configuration to La atom as shown below :

La (Z = 57) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 5d^1$.

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^2p^6d^1, 6s^2$

$\rightarrow$ 2, 8, 18, 18, 9, 2

$\rightarrow$ $[Xe]_{54}\ 4f^{\circ}5d^{1}6s^{2}$

Why the extra electron goes to 5*d* orbital, instead of 4*f* orbital in La atom has been explained on the basis that at La, 5*d* and 4*f* orbitals are supposed to have almost the same energy and hence the extra electron is free to occupy any of these two orbitals.

(ii) Configuration of Ac (Z = 89) atom. We know that, according to Aufbau principle, the configuration of Ra (Z = 88) atom is $[Rn]_{86}\ 7s^2$ where $[Rn]_{86}$ is the configuration of Rn (Z = 86) atom which is 2, 8, 18, 32, 18, 8.

Now after 7*s* orbital has been completely filled at Ra, the next electron, according to Aufbau principle, must enter 5*f* orbital in Ac atom; but it has been observed that the extra electron enters 6d orbital (instead of 5*f* orbital) to give $[Rn]_{86}\ 5f^{\circ}.6d^{1}.7s^{2}$ configuration to Ac atom as shown below :

Ac (Z = 89) → $1s$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^{10}$, $4p^6$
$5s^2$, $4d^{10}$, $5p^6$, $6s^2$, $4f^{14}$, $5d^{10}$, $6p^6$, $7s^2$, $6d^1$
→ $1s^2$, $2s^2p^6$, $3s^2p^6d^{10}$, $4s^2p^6d^{10}f^{14}$, $5s^2p^6d^{10}$, $6s^2p^6d^1$, $7s^2$
→ 2, 8, 18, 32, 18, 9, 2
→ $[Rn]_{86}$ $5f^{\circ}.6d^1.7s^2$

Why the extra electron goes to $6d$ orbital instead of $5f$ orbital in Ac atom has been explained on the basis that in Ac, $6d$ and $5f$ orbitals are supposed to be almost of the same energy and hence the extra electron is free to go to any of these two orbitals.

(n+l) Rule. The relative order of energy of different orbitals (or the sequence in which various orbitals are filled up with electrons) can also be determined with the help of $(n + l)$ value for a given orbital (n = principal quantum number, l = azimuthal quantum number). This rule is called $(n + l)$ rule. According to this rule :

The orbital having the lowest value of $(n + l)$ has the lowest energy and hence is filled up first with electrons. When two or more orbitals have the same value of $(n + l)$, the orbital with lower value of n is lower in energy and hence is filled up first with electrons.

Thus the order of energies of, for example, $3d$, $4p$ and $5s$ orbitals for all of which $(n + l) = 5$ is as : $3d$ ($n = 3$) < 4p (n=4) < 5s (n=5), since n for these orbitals is 3, 4 and 5 respectively. Thus orbitals will be filled up with electrons in the following sequence :

Table 3.1. Determination of the relative order of energy of different orbitals on the basis of (n + l) rule.

Orbitals	n	l	$(n + l)$	Relative order of energy of different orbitals (Sequence of filling of orbitals)
$1s$	1	0	1	$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d 6p < 7s < 5f < 6d < 7p.$
$2s$	2	0	2	
$2p$	2	1	3	
$3s$	3	0	3	
$3p$	3	1	4	
$3d$	3	2	5	
$4s$	4	0	4	
$4p$	4	1	5	
$4d$	4	2	6	
$4f$	4	3	7	
$5s$	5	0	5	
$5p$	5	1	6	
$5d$	5	2	7	
$5f$	5	3	8	
$6s$	6	0	6	
$6p$	6	1	7	
$6d$	6	2	8	
$7s$	7	0	7	
$7p$	7	1	8	

——— *Orbitals being filled* ———→

$3d$ (n = 3), $4p$ (n = 4), $5s$ (n = 5)

The determination of relative order of energy of different orbitals, on the basis of $(n + l)$ rule, has been shown in Table 3.1.

4. Pauli's exclusion principle. While filling up the various orbitals with electrons, we should obey Pauli's exclusion principle which imposes some restrictions on the assignment of the values of quantum numbers of electrons residing in an orbital of an atom. This principle, as we have already seen in the chapter: *Structure of the Atom Wave : Mechanical Approach* (Chapter 2), can be stated as :

In the same orbital of an atom, two electrons can have three quantum numbers identical at the most, but the fourth quantum number, namely spin quantum number (s), will definitely be different for both the electron, i.e., for one electron s will be + 1/2 while for the other electron it will be — 1/2. In other words, this means that two electrons residing in the same orbital of an atom have opposite spins, since this state with opposite spins (↑↓)gives lower energy to the system, while the state with parallel spins (↑↑) gives higher energy to the system. According to thermodynamics, a system with lower energy has greater stability. Thus an orbital having two electrons with opposite spins (↑↓) has lower energy and hence is more stable than that containing the two electrons with paired spins (↑↑). s = + 1/2 indicates the clock-wise direction of the spinning of one electron while s = –1/2 stands to indicate the anticlock-wise direction of the spinning of other electron.

Pauli's exclusion principle, as mentioned above, clearly makes the following rules evident. These rules are used in the determination of the electronic configuration of the atoms of the elements.

(*i*) *An orbital like s, p_x, p_y, p_z, d_{xy}, d_{yz} etc can have at the most two electrons and these two electrons must have opposite spins i.e. one electron should have the value of s equal to +1/2 and the other equal to –1/2, so that both the electrons residing in the same orbital may have different sets of four quantum numbers, which is in accordance with Pauli's exclusion principle.*

(*ii*) *Maximum number of electrons that can be accommodated by a shell with principal quantum number, n is equal to $2n^2$.*

5. Hund's rule of maximum multiplicity. On the basis of magnetic measurements, Hund postulated an important empirical rule, popularly known after his name as Hund's rule of maximum multiplicity. This rule states as :

The distribution of electrons in a set of degenerate orbitals like p_x, p_y, p_z set, d_{xy}, d_{yz}, d_{zx}, d_z^2, $d_{x^2-y^2}$ set etc., of a given sub-shell takes place in such a way as to give the maximum number of unpaired electrons and these electrons must have the same direction of their spins.

This rule is based on the fact that electrons, being of the same charge, repel each other and hence try to keep farther apart from each other as much as possible. This they do by entering the degenerate orbitals as far as possible.

Their entering the orbitals in this manner minimises the inter-electronic repulsion energy of the system and hence we get a stable system. Thus we can also call this rule as a **rule of minimum energy.**

This rule can also be restated in any of the following forms :

(*i*) *When electrons enter a set of orbitals of a given sub-shell, electrons will pair up only when all the available orbitals have had at least one electron each.*

(*ii*) *The orbitals of a given sub-shell are first filled singly and then the pairing of electrons in each orbital begins.*

(*iii*) *When several orbitals of equal energy (degenerate orbitals) are available, electrons prefer to occupy separate orbitals, rather than getting paired in the same orbital.* Such electrons tend to have the same spins. This principle means that pairing of electrons begins with the introduction of *2nd* electron in *s*-orbital, the *4th* electron in *p*-orbitals, *6th* electron in *d*-orbitals and *8th* electron in *f*-orbitals.

(*iv*) *If the number of electrons is equal to or smaller than the number of available degenerate orbitals, the electrons prefer to occupy the orbitals singly. But when the number of electrons is greater than the number of available degenerate orbitals, the pairing of etectrons takes place.*

(*v*) *None of degenerate orbitals like* p_x, p_y, p_z *or* d_{xy}, d_{yz} *etc., will have two electrons as long as any other orbital is vacant or as long as each one of them has attained at least one electron.*

Illustration of the principle. In order to illustrate the principle, let us consider the electronic configuration of oxygen atom, whose atomic number is 8. Let the eight electrons in this atom be numbered as 1, 2, 3, ... 7, 8. Quite evidently the electron numbered as 1 will enter 1s-orbital (which is the lowest energy orbital), and the electron 2 will also enter 1s-orbital to fill it completely (See Fig. 3.3). These two electrons in 1*s*-orbital will have opposite spins, in accordance with Pauli's exclusion principle (For electron 1, $n = 1$, $l = 0$, $m = 0$

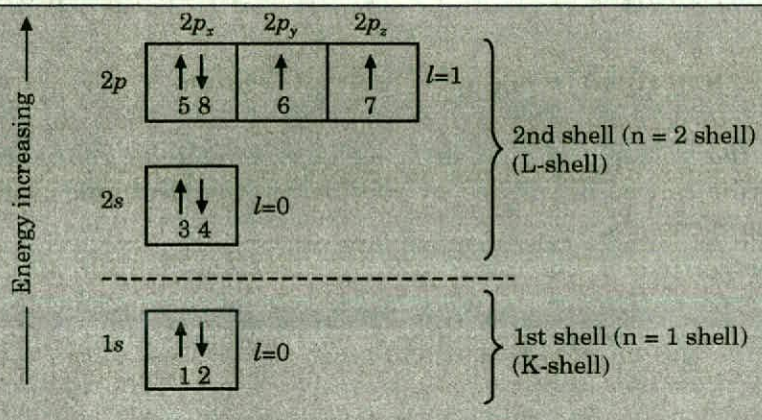


Fig. 3.3. Electronic configuration of oxygen atom (atomic number = 8). The boxes represent orbitals, The arrows indicate the electrons while the numbers shown below the arrows represent the electron number.

and $s = +1/2$ and for electron 2, $n = 1$, $l = 0$, $m = 0$ and $s = -1/2$). Electrons 3 and 4 will occupy 2*s*-orbital to make it completely filled. These electrons will also have opposite spins to obey Pauli's exclusion principle. Now, according to Hund's rule of maximum multiplicity, the degenerate $2p_x$, $2p_y$, and $2p_z$ orbitals will first be filled *singly* with electrons numbered as 5, 6 and 7 and all these three electrons will have the same spins. Electron number 8, which is the last electron will pair with the electron number 5 in $2p_x$ orbital. Thus the complete electronic configuration of oxygen atom, in its ground state, will be as given below :

$1s^{1,2}$, $2s^{3,4}$, $2p_x^{5,8}$ $2p_y^{6}$ $2p_z^{7}$ (Here the numbers used as super-scripts indicate the electron number).

or $1s^2$, $2s^2$, $2p_x^2$ $2p_y^1$ $2p_z^1$ (Here the numbers used as super-scripts indicate the number of electrons present in a given orbital).

The values of the four quantum numbers *viz., n, l, m* and *s* for each electron are given below :

Shell	Orbital	Electron number	*n*	*l*	*m*	*s*
1st	*1s*	*1*	*1*	*0*	*0*	*+1/2*
		2	*1*	*0*	*0*	*−1/2*
2nd	*2s*	*3*	*2*	*0*	*0*	*+1/2*
		4	*2*	*0*	*0*	*−1/2*
	$2p_x$	*5*	*2*	*1*	*0*	*+1/2*
		8	*2*	*1*	*0*	*−1/2*
	$2p_y$	*6*	*2*	*1*	*+1*	*+1/2*
	$2p_z$	*7*	*2*	*1*	*−1*	*+1/2*

These values clearly show that *no two electrons in the same orbital have the same values of all the four quantum numbers and hence obey Pauli's exclusion principle.*

6. Rule of half-filled or completely-filled orbitals. This rule states *that the orbitals tend to become half-filled or completely-filled, since such orbitals are more stable than other orbitals and hence give more stable configuration to the atom.* This rule can be illustrated by considering the electronic configuration of the following elements.

(i) Electronic configuration of Cr (Z = 24), Cu (Z = 29), Mo (Z = 42), Pd (Z = 46), Ag (Z = 47) and Au (Z = 79). In case of these elements one or both the electrons from *ns* orbital get shifted to $(n-1)d$ orbitals to make $(n-1)d$ orbitals half-filled or completely- filled, since such half-filled or completely-filled orbitals are more stable than any other $(n-1)d$ orbitals and hence give more stable configuration to the atom.

Element (Z = Atomic number)	Expected configuration	Actual (observed) configuration	Explanation of observed configuration
Cr (Z = 24)	$[Ar]_{18}\ 4s^2.3d^4$	$[Ar]_{18}\ 4s^1.3d^5$	One electron from 4*s* orbital gets shifted to 3*d* orbital to make 3*d* orbital half-filled ($3d^5$) which is more stable than $3d^4$ orbital.
Cu (Z = 29)	$[Ar]_{18}\ 4s^2.3d^9$	$[Ar]_{18}\ 4s^1.3d^{10}$	One electron from 4*s* orbital gets shifted to 3*d* orbital to make 3*d* orbital completely-filled ($3d^{10}$) which is more stable than $3d^9$ orbital.
Mo (Z = 42)	$[Kr]_{36}\ 5s^2.4d^4$	$[Kr]_{36}\ 5s^1.4d^5$	One electron from 5*s* orbital gets shifted to 4*d* orbital to make 4*d* orbital half-filled ($4d^5$) which is more stable than $4d^4$ orbital.
Pd (Z = 46)	$[Kr]_{36}\ 5s^2.4d^8$	$[Kr]_{36}\ 5s^0.4d^{10}$	Both the electrons from 5*s* orbital get shifted to 4*d* orbital to make 4*d* orbital completely-filled ($4d^{10}$) which is more stable than $4d^8$ orbital.
Ag (Z = 47)	$[Kr]_{36}\ 5s^2.4d^9$	$[Kr]_{36}\ 5s^1.4d^{10}$	One electron from 5*s* orbital gets shifted to 4*d* orbital to make 4*d* orbital completely-filled ($4d^{10}$) which is more stable than $4d^9$ orbital.
Au (Z = 79)	$[Xe]_{54}\ 6s^2.4f^{14}.5d^9$	$[Xe]_{54}\ 6s^1.4f^{14}.5d^{10}$	One electron from 6*s* orbital gets shifted to 5*d* orbital to make 5*d* orbital completely-filled ($5d^{10}$) which is more stable than $5d^9$ orbital.

(ii) Electronic configuration of Nb (Z = 41), Ru (Z = 44), Rh (Z = 45) and Pt (Z = 78). In case of these elements one of the two electrons from *ns* orbital gets shifted to $(n-1)d$ orbital to make *ns* orbital half-filled, *since half-filled ns orbitals probably seem to be more stable than* ns^2 *orbitals in these cases.*

Element	Expected configuration	Actual (observed) configuration	Explanation of observed configuration
Nb (Z = 41)	$[Kr]_{36}\ 5s^2.4d^3$	$[Kr]_{36}\ 5s^1.4d^4$	One electron from 5*s* orbital gets shifted to 4*d* orbital so that 5*s* orbital becomes half-filled
Ru (Z = 44)	$[Kr]_{36}\ 5s^2.4d^6$	$[Kr]_{36}\ 5s^1.4d^7$	One electron from 5*s* orbital gets shifted to 4*d* orbital so that more stable $5s^1$ configuration is obtained.
Rh (Z = 45)	$[Kr]_{36}\ 5s^2.4d^7$	$[Kr]_{36}\ 5s^1.4d^8$	One electron from 5*s* orbital gets shifted to 4*d* orbital so that more stable $5s^1$ orbital is achieved.
Pt (Z = 78)	$[Xe]_{54}\ 6s^2.4f^{14}.5d^8$	$[Xe]_{54}\ 6s^1.4f^{14}.5d^9$	One electron from 6*s* orbital comes to 5*d* orbital to make 6*s* orbital half-filled ($6s^1$) and hence more stable

(iii) Electronic configuration of Gd (Z = 64) and Cm (Z = 96). In case of these elements one electron from *nf* orbital gets shifted to $(n + 1)d$ orbital to make *nf* orbital half-filled and hence more stable.

Element	Expected configuration	Actual (observed) configuration	Explanation of observed configuration
Gd (Z = 64)	$[Xe]_{54}\ 6s^2.4f^8.5d^0$	$[Xe]_{54}\ 6s^2.4f^7.5d^1$	One electron from 4*f* orbital gets shifted to 5*d* obrital so that 4*f* orbital becomes half-filled
Cm (Z = 96)	$[Rn]_{86}\ 7s^2.5f^8.6d^0$	$[Rn]_{86}\ 7s^2.5f^7.6d^1$	One electron from 5*f* orbital goes to 6*d* orbital to make 5*f* orbital half-filled.

Determination of the Electronic Configuration of the Elements According to their Position in a Period of the Periodic Table

Every element in a period has its atomic number (= No. of electrons) one unit more than its preceding element, *i.e.* an additional electron enters, as we move to the right in period. Thus the electronic configuration of the next higher element is obtained by adding one electron to the orbital, which is higher in energy than that which has already been filled up (*Aufbau principle*).

Total number of elements present in a period is equal the total number of electrons to be added in the whole of the period. Thus the orbitals that are filled up with electrons in each period can be shown as :

Period number	No. of elements (Z = atomic number)	Orbitals beings filled	Total number of electrons to be added in a period
1	2 [H(Z = 1) and He(Z = 2)]	1s	2
2	8 [Li(Z = 3) to Ne (Z = 10)]	2s, 2p	2 + 6 = 8
3	8 [Na(Z = 11) to Ar(Z = 18)]	3s, 3p	2 + 6 = 8
4	18[K(Z = 19) to Kr(Z = 36)]	4s, 3d, 4p	2 + 10 + 6 = 18
5	18[Rb(Z = 37) to Xe(Z = 54)]	5s, 4d, 5p	2 + 10 + 6 = 18
6	32[Cs(Z = 55) to Rn(Z = 86)]	6s, 4f, 5d, 6p	2 + 14 + 10 + 6 = 32
7	19[Fr(Z = 87) to Ha(Z = 105)]	7s, 5f, $6d^3$	2 + 14 + 3 = 19

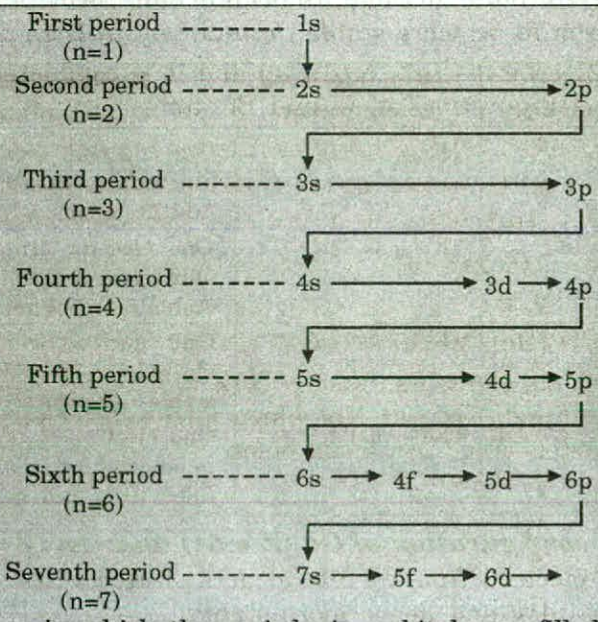


Fig. 3.4. Sequence in which the period-wise orbitals are filled with electrons.

It is obvious from the table given above that the sequence in which the period-wise orbitals are filled with electrons, can be shown as given in Fig. 3.4. This figure makes it evident that at the beginning of each period a new electron enters the *ns* orbital where *n* is the number of the period. For example at the beginning of *7th* period (*i.e.* at Fr with atomic number, Z = 87) a new electron enters 7*s* orbital, which belongs to *7th* energy level (*n* = 7). Consequently *each period in the periodic table begins with a new principal energy level.*

On the basis of the table given above and the sequence in which the period-wise orbitals are filled with electrons (Fig. 3.4), let us now proceed to determine the electronic configuration of each of the elements given in the periodic table. (Z is the atomic number of the element)

1st period (*1s*). Since this period has two elements *viz.* H(Z = 1) and He(Z = 2), only two electrons are added upto the end of this period and it is 1*s* orbital which is completely filled at the end of this period. One electron goes to 1*s* orbital giving 1*s* configuration to H atom while *2nd* electron also goes to 1*s* orbital giving $1s^2$ configuration to He atom. $1s^2$ configuration is also represented as 2 or $[He]_2$. Thus the configurations of H and He can be written as.

H (Z = 1) → $1s^1$
→ 1
He (Z = 2) → $1s^2$
→ 2
→ $[He]_2$

Here $[He]_2$ indicates the configuration of He atom (Z = 2) which is $1s^2$ or 2.

Thus we see that at the end of this period 1s orbital (or K-shell) is *completely filled.*

2nd period (2*s*, 2*p*). Since this period has 8 elements *viz.* Li (Z = 3) to Ne (Z = 10), only 8 electrons are added upto the end of this period and these electrons enter 2*s* and 2*p* orbitals which are filled completely at the end of the period.

At Li (Z = 3) 2*s* orbital starts to fill up and it is completely filled up at Be (Z = 4). Thus the configurations of Li and Be atoms are :

Li (Z = 3) → $1s^2, 2s^1$
→ 2, 1
→ $[He]_2\ 2s^1$
Be (Z = 4) → $1s^2, 2s^2$
→ 2, 2
→ $[He]_2\ 2s^2$

Now in the next six elements, namely B (Z = 5) to Ne (Z = 10) 2*p* orbital is being progressively filled. Thus at Ne, which is the last element of this period 2*p* orbital is completely filled as shown below :

B (Z = 5) → $1s^2\ 2s^2, 2p^1$
→ $1s^2, 2s^2p^1$
→ 2, 3
→ $[He]_2\ 2s^2p^1$

C (Z = 6) → $1s^2, 2s^2, 2p^2$
→ $1s^2, 2s^2p^2$
→ 2, 4
→ $[He]_2\ 2s^2p^2$
N (Z = 7) → $1s^2, 2s^2, 2p^3$
→ $1s^2, 2s^2p^3$
→ 2, 5
→ $[He]_2\ 2s^2p^3$
O (Z = 8) → $1s^2, 2s^2, 2p^4$
→ $1s^2, 2s^2p^4$
→ 2, 6
→ $[He]_2\ 2s^2p^4$
F (Z = 9) → $1s^2, 2s^2, 2p^5$
→ $1s^2, 2s^2p^5$
→ 2, 7
→ $[He]_2\ 2s^2p^5$
Ne (Z = 10) → $1s^2, 2s^2, 2p^6$
→ $1s^2, 2s^2p^6$
→ 2, 8
→ $[He]_2\ 2s^2p^6$
→ $[Ne]_{10}$

Here $[Ne]_{10}$ indicates the configuration of Ne atom (Z = 10) which, as shown above, is 2, 8. It may be seen from the configurations of the elements of *2nd* period that at the end of this period 1*s* (*i.e.* K- shell) and, 2*s* and 2*p* orbitals (*i.e.* L-shell) are completely filled.

3rd period (3*s*, 3*p*). Since this period has 8 elements *viz.* Na (Z = 11) to Ar (Z = 18), only 8 electrons are added upto the end of this period and these electrons enter 3*s* and 3*p* orbitals which are completely filled at the end of this period.

At Na (Z = 11) 3*s* orbital starts to fill up and it is completely filled at Mg (Z = 12). Thus the configurations of Na and Mg are as :

Na (Z = 11) → $1s^2, 2s^2, 2p^6, 3s^1$
→ $1s^2, 2s^2p^6, 3s^1$
→ 2, 8, 1
→ $[Ne]_{10}\ 3s^1$
Mg (Z = 12) → $1s^2, 2s^2, 2p^6, 3s^2$
→ $1s^2, 2s^2p^6, 3s^2$
→ 2, 8, 2
→ $[Ne]_{10}\ 3s^2$

Now in the next six elements, namely Al (Z = 13) to Ar (Z = 18) 3*p* orbital is being progressively filled. Thus at Ar winch is the last element of this period, 3*p* orbital is completely filled as shown below :

Al (Z = 13) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^1$
→ $1s^2, 2s^2p^6, 3s^2p^1$
→ 2, 8, 3
→ $[Ne]_{10}\ 3s^2p^1$

Si (Z = 14) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^2$
→ $1s^2, 2s^2p^6, 3s^2p^2$
→ 2, 8, 4
→ $[Ne]_{10}\ 3s^2p^2$

P (Z = 15) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^3$
→ $1s^2, 2s^2p^6, 3s^2p^3$
→ 2, 8, 5
→ $[Ne]_{10}\ 3s^2p^3$

S (Z = 16) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^4$
→ $1s^2, 2s^2p^6, 3s^2p^4$
→ 2, 8, 6
→ $[Ne]_{10}\ 3s^2p^4$

Cl (Z = 17) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^5$
→ $1s^2, 2s^2p^6, 3s^2p^5$
→ 2, 8, 7
→ $[Ne]_{10}\ 3s^2p^5$

Ar (Z = 18) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$
→ $1s^2, 2s^2p^6, 3s^2p^6$
→ 2, 8, 8
→ $[Ne]_{10}\ 3s^2p^6$
→ $[Ar]_{18}$

Here $[Ar]_{18}$ indicates the configuration of Ar atom (Z = 18) which is 2,8, 8.

We see that at the end of this period M-shell (3*rd* shell) whose maximum capacity to contain the electrons is 18 is *not completely filled*, since 3*d* orbitals of this shell are still vacant. K (1*st* shell) and L (2*nd* shell) shells are, however, completely filled at the end of this period, since 1s, 2s and 2p orbitals are completely filled.

4th period (4*s*, 3*d*, 4*p*). Since this period has 18 elements *viz.* K (Z = 19) to Kr (Z = 36), only 18 electrons are added upto the end of this period and these electrons enter 4*s*, 3*d* and 4*p* orbitals which are completely filled at the end of this period.

At K (Z = 19) 4*s* orbital starts to fill up and is completely filled at Ca (Z = 20). Thus the configurations of these two elements are as :

K (Z = 19) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$
→ $1s^2, 2s^22p^6, 3s^2p^6, 4s^1$
→ 2, 8, 8, 1
→ $[Ar]_{18}\ 4s^1$

Ca (Z = 20) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$
→ $1s^2, 2s^2p^6, 3s^2p^6, 4s^2$
→ 2, 8, 8, 2
→ $[Ar]_{18}\ 4s^2$

Now after the completion of 4*s* orbital at Ca [Ca → $[Ar]_{18}4s^2$], as shown above, the next electron, according to Aufbau principle, enters 3*d* orbital in the next ten elements namely Sc (Z = 21) to Zn (Z = 30) (*first transition series*). 3*d* orbital is thus completely filled at Zn, which is the last member of the first transition series. Thus the configurations of the members of first transition series can be given as shown below :

Sc (Z = 21) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^1$
→ $1s^2, 2s^2p^6, 3s^2p^6d^1, 4s^2$
→ 2, 8, 9, 2
→ $[Ar]_{18}\ 3d^1.4s^2$

Ti (Z = 22) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^2$
→ $1s^2, 2s^2p^6, 3s^2p^6d^2, 4s^2$
→ 2, 8, 10, 2
→ $[Ar]_{18}\ 3d^2.4s^2$

V (Z = 23) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^3$
→ $1s^2, 2s^2p^6, 3s^2p^6d^3, 4s^2$
→ 2, 8, 11, 2
→ $[Ar]_{18}\ 3d^3.4s^2$

The configurations of the elements from Sc(Z = 21) to V(Z = 23), as given above, show that in all these elements 3*d* orbital is being progressively filled and hence the expected configuration of Cr (Z = 24) should be $[Ar]_{18}\ 3d^4.4s^2$, but it has been observed that the actual (or observed) configuration of Cr is $[Ar]_{18}3d^5.4s^1$ which is obtained by shifting one of the electrons from 4*s* orbital to 3*d* orbital. This type of electronic shifting makes 3*d* orbital half-filled ($3d^5$) and hence more stable than $3d^4$ configuration, as suggested by the rule of half-filled orbitals. Thus :

Cr (Z = 24) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$
→ $1s^2, 2s^2p^6, 3s^2p^6d^5, 4s^1$
→ 2, 8, 13, 1
→ $[Ar]_{18}\ 3d^5.4s^1$

Mn(Z = 25) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^5$
→ $1s^2, 2s^2p^6, 3s^2p^6d^5, 4s^2$
→ 2, 8, 13, 2
→ $[Ar]_{18}\ 3d^5.4s^2$

Fe(Z = 26) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$
→ $1s^2, 2s^2p^6, 3s^2p^6d^6, 4s^2$

$\rightarrow$ 2, 8, 14, 2

$\rightarrow$ $[Ar]_{18}$ $3d^6.4s^2$

Co (Z = 27) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^7$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^7, 4s^2$

$\rightarrow$ 2, 8, 15, 2

$\rightarrow$ $[Ar]_{18}$ $3d^7.4s^2$

Ni (Z = 28) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^8$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^8, 4s^2$

$\rightarrow$ 2, 8, 16, 2

$\rightarrow$ $[Ar]_{18}$ $3d^8.4s^2$

In case of Cu (Z = 29) (as in case of Cr) one of the electrons from 4*s* orbital gets shifted to $3d^9$ orbital so that 3*d* orbital becomes completely-filled ($3d^{10}$) and hence more stable than $3d^9$ configuration, as suggested by the rule of completely-filled orbitals. Thus :

Cu(Z = 29) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}$

$\rightarrow$ $1s^2, 3s^2p^6, 3s^2p^6d^{10}, 4s^1$

$\rightarrow$ 2, 8, 18, 1

$\rightarrow$ $[Ar]_{18}$ $3d^{10}.4s^1$

Zn(Z = 30) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2$

$\rightarrow$ 2, 8, 18, 2

$\rightarrow$ $[Ar]_{18}$ $3d^{10}.4s^2$

Now in the next six elements *viz.* Ga (Z = 31) to Kr (Z = 36) 4*p* orbital is being progressively filled. Thus at Kr, which is the last element of this period, 4*p* orbital is completely filled.

Ga (Z = 31) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^1$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^1$

$\rightarrow$ 2, 8, 18, 3

$\rightarrow$ $[Ar]_{18}$ $3d^{10}4s^2p^1$

Ge (Z = 32) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^2$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^2$

$\rightarrow$ 2, 8, 18, 4

$\rightarrow$ $[Ar]_{18}$ $3d^{10}4s^2p^2$

As (Z = 33) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^3$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^3$

$\rightarrow$ 2, 8, 18, 5

$\rightarrow$ $[Ar]_{18}$ $3d^{10}4s^2p^3$

Se (Z = 34) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^4$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^4$

$\rightarrow$ 2, 8, 18, 6

$\rightarrow$ $[Ar]_{18}\ 3d^{10}4s^2p^4$

Br (Z = 35) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^5$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^5$

$\rightarrow$ 2, 8, 18, 7

$\rightarrow$ $[Ar]_{18}\ 3d^{10}4s^2p^5$

Kr (Z = 36) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6$

$\rightarrow$ 2, 8, 18, 8

$\rightarrow$ $[Ar]_{18}\ 3d^{10}4s^2p^6$

$\rightarrow$ $[Kr]_{36}$

Here $[Kr]_{36}$ indicates the configuration of Kr atom (Z = 36), which is 2, 8, 18, 8. It may be noted from the configuration of Kr that at the end of *4th* period, *1st*, *2nd* and *3rd* shells are completely filled, while the *4th* shell is not, since it has only 8 electrons. Note that the maximum capacity of *4th* shell to contain the electrons is 32.

5th period (5*s*, 4*d*, 5*p*). Since this period has 18 elements *viz.*, Rb (Z = 37) to Xe (Z = 54), only 18 electrons are added upto the end of this period and these electrons enter 5*s*, 4*d* and 5*p* orbitals which are completely filled at the end of this period.

At Rb (Z = 37), 5*s* orbital starts to fill up and is completely filled at Sr (Z = 38). Thus the configurations of these two elements are as given below :

Rb (Z = 37) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^1$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6, 5s^1$

$\rightarrow$ 2, 8, 18, 8, 1

$\rightarrow$ $[Kr]_{36}\ 5s^1$

Sr (Z = 38) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6, 5s^2$

$\rightarrow$ 2, 8, 18, 8, 2

$\rightarrow$ $[Kr]_{36}\ 5s^2$

Now, after the completion of 5*s* orbital at Sr [Sr $\rightarrow$ $[Kr]_{36}\ 5s^2$], as shown above, the next electron, according to Aufbau principle, enters 4*d* orbital in the next ten elements namely Y (Z = 39) to Cd (Z = 48) (*second transition series*). 4*d* orbital is thus completely filled at Cd which is the last member of second transition series. Thus the configurations of the members of the second transition series can be given as shown below :

Y (Z = 39) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^1$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^1, 5s^2$

$\rightarrow$ 2, 8, 18, 9, 2

$\rightarrow$ $[Kr]_{36}\ 4d^1.5s^2$

Zr (Z = 40) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^2$
→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^2, 5s^2$
→ 2, 8, 18, 10, 2
→ $[Kr]_{36}\ 4d^2.5s^2$

In case of Nb (Z = 41), Mo (Z = 42), Ru (Z = 44) and Rh (Z = 45) one of the electrons from 5*s* orbital gets shifted to 4*d* orbital to make 5*s* and 4*d* orbitals half-filled which, in accordance with the rule of half-filled orbitals are more stable. Thus :

Nb (Z = 41) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^1, 4d^4$
→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^4, 5s^1$
→ 2, 8, 18, 12, 1
→ $[Kr]_{36}\ 4d^4.5s^1$

Mo (Z = 42) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^1, 4d^5$
→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^5, 5s^1$
→ 2, 8, 18, 13, 1
→ $[Kr]_{36}\ 4d^5.5s^1$

Tc (Z = 43) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^5$
→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^5, 5s^2$
→ 2, 8, 18, 13, 2
→ $[Kr]_{36}\ 4d^5.5s^2$

Ru (Z = 44) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^1, 4d^7$
→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^7, 5s^1$
→ 2, 8, 18, 15, 1
→ $[Kr]_{36}\ 4d^7.5s^1$

Rh (Z = 45) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^1, 4d^8$
→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^8, 5s^1$
→ 2, 8, 18, 16, 1
→ $[Kr]_{36}\ 4d^8.5s^1$

In case of Pd (Z= 46) both the electrons from 5*s* orbital move to $4d^8$ orbital to make 4*d* orbital completely-filled ($4d^{10}$) and hence more stable than $4d^8$ configuration. Thus :

Pd (Z = 46) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^0, 4d^{10}$
→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^0$
→ 2, 8, 18, 18, 0
→ $[Kr]_{36}\ 4d^{10}.5s^0$

In case of Ag (Z = 47) one of the electrons from 5*s* orbital is shifted to $4d^9$ orbital so that 4*d* orbital becomes completely-filled ($4d^{10}$) and hence more stable. Thus :

Ag (Z = 47) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^1, 4d^{10}$
→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^1$

$\rightarrow$ 2, 8, 18, 18, 1

$\rightarrow$ $[Kr]_{36}\ 4d^{10}.5s^1$

Cd (Z = 48) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^2$

$\rightarrow$ 2, 8, 18, 18, 2

$\rightarrow$ $[Kr]_{36}\ 4d^{10}.5s^2$

Now in the next six elements namely in (Z = 49) to Xe (Z = 54) $5p$ orbital is being progressively filled. Thus at Xe which is the last element of this period, $5p$ orbital is completely filled as shown below :

In (Z = 49) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^1$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^2p^1$

$\rightarrow$ 2, 8, 18, 18, 3

$\rightarrow$ $[Kr]_{36}\ 4d^{10}5s^2p^1$

Sn (Z = 50) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^2$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^2p^2$

$\rightarrow$ 2, 8, 18, 18, 4

$\rightarrow$ $[Kr]_{36}\ 4d^{10}5s^2p^2$

Sb (Z = 51) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^3$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^2p^3$

$\rightarrow$ 2, 8, 18, 18, 5

$\rightarrow$ $[Kr]_{36}\ 4d^{10}5s^2p^3$

Te (Z = 52) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^4$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^2p^4$

$\rightarrow$ 2, 8, 18, 18, 6

$\rightarrow$ $[Kr]_{36}\ 4d^{10}5s^2p^4$

I (Z = 53) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^5$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^2p^5$

$\rightarrow$ 2, 8, 18, 18, 7

$\rightarrow$ $[Kr]_{36}\ 4d^{10}5s^2p^5$

Xe (Z = 54) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^2p^6$

$\rightarrow$ 2, 8, 18, 18, 8

$\rightarrow$ $[Kr]_{36}\ 4d^{10}5s^2p^6$

$\rightarrow$ $[Xe]_{54}$

Here $[Xe]_{54}$ indicates the configuration of Xe atom (Z = 54) which is 2, 8, 18, 18, 8.

6th period ($6s$, $4f$, $5d$, $6p$). Since this period contains 32 elements viz Cs (Z = 55) to Rn (Z = 86), 32 electrons are added upto the end of this period and these electrons enter $6s$, $4f$, $5d$ and $6p$ orbitals which are completely filled at the end of this period.

At Cs (Z = 55), 6s orbital starts to fill up and is completely filled at Ba (Z = 56). Thus the configurations of these two elements are as given below :

Cs (Z = 55) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^1$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^2p^6, 6s^1$

→ 2, 8, 18, 18, 8, 1

→ $[Xe]_{54}\ 6s^1$

Ba (Z = 56) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^2p^6, 6s^2$

→ 2, 8, 18, 18, 8, 2

→ $[Xe]_{54}\ 6s^2$

Now after the completion of 6s orbital at Ba[Ba→$[Xe]_{54}\ 6s^2$], the next electron, according to Aufbau principle, must enter 4*f* orbital to give $[Xe]_{54}\ 4f^1.5d^0.6s^2$ configuration to La (Z = 57); but it has been observed that the extra electron enters 5*d* orbital (instead of 4*f* orbital) to give $[Xe]_{54}\ 4f^0.5d^1.6s^2$ configuration to La atom as shown below :

La (Z = 57) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 5d^1$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^2p^6d^1, 6s^2$

→ 2, 8, 18, 18, 9, 2

→ $[Xe]_{54}\ 4f^0\ .\ 5d^1\ .\ 6s^2$

Why the extra electron goes to 5*d* orbital, instead of 4*f* orbital, in La atom has been explained on the basis that at La, 5*d* and 4*f* orbitals are supposed to have almost the same energy and hence the extra electron is free to occupy any of these two orbitals.

In the next fourteen elements [Ce(Z = 58) to Lu (Z = 71)] called *lanthanides*, 4*f* orbital is being progressively filled. While filling 4*f* orbital with electrons we should keep the following rule in mind.

It is only in Ce (Z = 58), Gd (Z = 64) and Lu(Z = 71) that 5d orbital has one electron while in all the remaining lanthanides 5d orbital remains vacant.

Keeping in mind the above rule the configurations of the lanthanides can be written as shown below :

Ce (Z = 58) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^1, 5d^1$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^1, 5s^2p^6d^1, 6s^2$

→ 2, 8, 18, 19, 9, 2

→ $[Xe]_{54}\ 4f^1\ .\ 5d^1\ .\ 6s^2$

Some authors suggest that the configuration of Ce is $[Xe]_{54}\ 4f^2\ 5d^0\ .\ 6s^2$.

Pr (Z = 59) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^3, 5d^0$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^3, 5s^2p^6d^0, 6s^2$

→ 2, 8, 18, 21, 8, 2

→ $[Xe]_{54}\ 4f^3\ .\ 5d^0\ .\ 6s^2$

Nd (Z = 60) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^4, 5d^0$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^4, 5s^2p^6d^0, 6s^2$

→ 2, 8, 18, 22, 8, 2

→ $[Xe]_{54}\ 4f^4 . 5d^0 . 6s^2$

Pm (Z = 61) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^5, 5d^0$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^5, 5s^2p^6d^0, 6s^2$

→ 2, 8, 18, 23, 8, 2

→ $[Xe]_{54}\ 4f^5 . 5d^0 . 6s^2$

Sm (Z = 62) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^6, 5d^0$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^6, 5s^2p^6d^0, 6s^2$

→ 2, 8, 18, 24, 8, 2

→ $[Xe]_{54}\ 4f^6 . 5d^0 . 6s^2$

Eu (Z = 63) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^7, 5d^0$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^7, 5s^2p^6d^0, 6s^2$

→ 2, 8, 18, 25, 8, 2

→ $[Xe]_{54}\ 4f^7 . 5d^0 . 6s^2$

The configurations of the elements from Ce (Z = 58) to Eu (Z = 63) as given above, show that in all these elements 4*f* orbital is being progressively filled and hence the expected configuration of Gd (Z = 64) should be $[Xe]_{54}\ 4f^8 . 5d^0 . 6s^2$, but it has been observed that the actual configuration of Gd is $[Xe]_{54}\ 4f^7 . 5d^1 . 6s^2$ which is obtained by shifting one of the electrons from 4*f* orbital to the vacant 5*d* orbital. This type of electronic shifting makes 4*f* orbital half-filled ($4f^7$) and hence more stable than $4f^8$ configuration as suggested by the rule of half-filled orbitals. Thus :

Gd (Z = 64) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^7, 5d^1$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^7, 5s^2p^6d^1, 6s^2$

→ 2, 8, 18, 25, 9, 2

→ $[Xe]_{54}\ 4f^7 . 5d^1 . 6s^2$

Tb (Z = 65) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^9, 5d^0$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^9, 5s^2p^6d^0, 6s^2$

→ 2, 8, 18, 27, 9, 2

→ $[Xe]_{54}\ 4f^9 . 5d^0 . 6s^2$

Dy (Z = 66) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{10}, 5d^0$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{10}, 5s^2p^6d^0, 6s^2$

→ 2, 8, 18, 28, 8, 2

→ $[Xe]_{54}\ 4f^{10} . 5d^0 . 6s^2$

Ho (Z = 67) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{11}, 5d^0$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{11}, 5s^2p^6d^0, 6s^2$

→ 2, 8, 18, 29, 8, 2

→ $[Xe]_{54}\ 4f^{11} . 5d^0 . 6s^2$

Er (Z = 68) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{12}, 5d^0$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{12}, 5s^2p^6d^0, 6s^2$

→ 2, 8, 18, 30, 8, 2

→ $[Xe]_{54}\ 4f^{12} . 5d^0 . 6s^2$

Tm (Z = 69) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{13}, 5d^0$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{13}, 5s^2p^6d^0, 6s^2$

→ 2, 8, 18, 31, 8, 2

→ $[Xe]_{54}\ 4f^{13} . 5d^0 . 6s^2$

Yb (Z = 70) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^0$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^0, 6s^2$

→ 2, 8, 18, 32, 8, 2

→ $[Xe]_{54}\ 4f^{14} . 5d^0 . 6s^2$

Lu (Z = 71) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^1$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^1, 6s^2$

→ 2, 8, 18, 32, 9, 2

→ $[Xe]_{54}\ 4f^{14} . 5d^1 . 6s^2$

Now the extra electron in the next *nine* elements namely Hf (Z = 72) to Hg (Z = 80) goes to 5*d* orbital which is already singly-filled at Lu, the last member of lanthanide series. 5*d* orbital is thus completely filled at Hg.

Hf (Z = 72) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^2$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^2, 6s^2$

→ 2, 8, 18, 32, 10, 2

→ $[Xe]_{54}\ 4f^{14}.5d^2.6s^2$

Ta (Z = 73) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^3$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^3, 6s^2$

→ 2, 8, 18, 32, 11, 2

→ $[Xe]_{54}\ 4f^{14}.5d^3.6s^2$

W (Z = 74) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^4$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^3, 6s^2$

→ 2, 8, 18, 32, 12, 2

→ $[Xe]_{54}\ 4f^{14}.5d^4.6s^2$

Re (Z = 75) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^5$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^5, 6s^2$

→ 2, 8, 18, 32, 13, 2

→ $[Xe]_{54}\ 4f^{14}.5d^5.6s^2$

Os (Z = 76) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^6$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^6, 6s^2$

→ 2, 8, 18, 32, 14, 2

→ $[Xe]_{54}\ 4f^{14}.5d^6.6s^2$

Ir (Z = 77) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^7$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^7, 6s^2$

→ 2, 8, 18, 32, 15, 2

→ $[Xe]_{54}\ 4f^{14}.5d^7.6s^2$

Now the expected configuration of Pt (Z = 78) should be $[Xe]_{54}\ 4f^{14}.5d^8.6s^2$, but the actual configuration is $[Xe]_{54}\ 4f^{14}.5d^9.6s^1$ which is obtained by shifting one of the two electrons from 6s orbital to $5d^8$ orbital. Thus :

Pt (Z = 78) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^1, 4f^{14}, 5d^9$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^9, 6s^1$

→ 2, 8, 18, 32, 17, 1

→ $[Xe]_{54}\ 4f^{14}.5d^9.6s^1$

Now the expected configuration of Au (Z = 79) is $[Xe]_{54}4f^{14}.5d^9.6s^2$, but the actual configuration is $[Xe]_{54}4f^{14}.5d^{10}.6s^1$ which is obtained by shifting one of the two electrons from 6s orbital to $5d^9$ orbital to make 5d orbital completely-filled ($5d^{10}$) which, according to the *rule of completely-filled orbitals*, is more stable than $5d^9$ orbital. Thus :

Au (Z = 79) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^1, 4f^{14}, 5d^{10}$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}, 6s^1$

→ 2, 8, 18, 32, 18, 1

→ $[Xe]_{54}\ 4f^{14}.5d^{10}.6s^1$

Hg (Z = 80) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}, 6s^2$

→ 2, 8, 18, 32, 18, 2

→ $[Xe]_{54}\ 4f^{14}.5d^{10}.6s^2$

Now in the next six elements namely Tl (Z = 81) to Rn (Z = 86) $6p$ orbital is being progressively filled. Thus at Rn which is the last element of this period $6p$ orbital is completely filled as shown below :

Tl (Z = 81) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^1$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}, 6s^2p^1$

→ 2, 8, 18, 32, 18, 3

→ $[Xe]_{54}\ 4f^{14}.5d^{10}.6s^2p^1$

Pb (Z = 82) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^2$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}, 6s^2p^2$

→ 2, 8, 18, 32, 18, 4

→ $[Xe]_{54}\ 4f^{14}.5d^{10}.6s^2p^2$

Bi (Z = 83) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^3$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}, 6s^2p^3$

→ 2, 8, 18, 32, 18, 5

→ $[Xe]_{54}\ 4f^{14}.5d^{10}.6s^2p^3$

Po (Z = 84) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^4$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}, 6s^2p^4$

→ 2, 8, 18, 32, 18, 6

→ $[Xe]_{54}\ 4f^{14}.5d^{10}.6s^2p^4$

At (Z = 85) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^5$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}, 6s^2p^5$

→ 2, 8, 18, 32, 18, 7

→ $[Xe]_{54}\ 4f^{14}.5d^{10}.6s^2p^5$

Rn (Z = 86) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}, 6s^2p^6$

→ 2, 8, 18, 32, 18, 8

→ $[Xe]_{54}\ 4f^{14}.5d^{10}.6s^2p^6$

→ $[Rn]_{86}$

Here $[Rn]_{86}$ indicates the configuration of Rn atom (Z = 86) which is 2, 8, 18, 32, 18, 8.

7th period (7*s*, 5*f*, 6*d*). At present, since this period has only 19 elements *viz.* Fr (Z = 87) to Ha (Z = 105), 19 electrons are added upto Ha and these electrons in 7*s*, 5*f* and 6*d* orbitals are distributed as : $7s^2$, $5f^{14}$, $6d^3$.

At Fr (Z = 87), 7*s* orbital starts to fill and is completely filled at Ra (Z = 88). Thus the configurations of these two elements can be written as :

Fr (Z = 87) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^1$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}, 6s^2p^6, 7s^1$

→ 2, 8, 18, 32, 18, 8, 1

→ $[Rn]_{86}\ 7s^1$

Ra (Z = 88) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}, 6s^2p^6, 7s^2$

→ 2, 8, 18, 32, 18, 8, 2

→ $[Rn]_{86}\ 7s^2$

Now after the completion of 7*s* orbital at Ra [Ra → $[Rn]_{86}\ 7s^2$], the next electron, according to Aufbau principle, must enter 5*f* orbital to give $[Rn]_{86}\ 5f^1.6d^0.7s^2$ configuration to Ac (Z = 89), but it has been observed that the extra electron enters 6*d* orbital (instead of 5*f* orbital) to give $[Rn]_{86}\ 5f^0.\ 6d^1\ .\ 7s^2$ configuration to Ac as shown below :

Ac (Z = 89) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 6d^1$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}, 6s^2p^6d^1, 7s^2$

→ 2, 8, 18, 32, 18, 9, 2

→ $[Rn]_{86}\ 5f^0\ .\ 6d^1\ .\ 7s^2$

Why the extra electron goes to 6*d* orbital instead of 5*f* orbital in Ac has been explained on the basis that in Ac, 6*d* and 5*f* orbitals are supposed to be almost of the same energy and hence the extra electron is free to go to any of these two orbitals.

In the next fourteen elements, [Th (Z = 90) to Lw (Z = 103)], called *actinides*, 5*f* orbital is being progressively filled. While filling 5*f* orbital with electrons we should keep the following rule in mind.

It is only in Th (Z = 90), Pa (Z = 91), U (Z = 92), Cm (Z = 96) and Lw (Z = 103) that 6d orbital has one electron while in all the remaining actinides 6d orbital remains vacant.

Keeping in mind the above rule the configurations of the actinides can be written as shown below :

Th (Z = 90) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^1, 6d^1$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}f^1, 6s^2p^6d^1, 7s^2$

→ 2, 8, 18, 32, 19, 9, 2

→ $[Rn]_{86}\ 5f^1\ .\ 6d^1\ .\ 7s^2$

Some authors suggest that the configuration of Th is $[Rn]_{86}\ 5f^0\ .\ 6d^2\ .\ 7s^2$.

Pa (Z = 91) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^2, 6d^1$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}f^2, 6s^2p^6d^1, 7s^2$

→ 2, 8, 18, 32, 20, 9, 2

→ $[Rn]_{86}\ 5f^2\ .\ 6d^1\ .\ 7s^2$

Some authors suggest that the configuration of Pa is $[Rn]\ 5f^1\ .\ 6d^2\ .\ 7s^2$.

U (Z = 92) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^3, 6d^1$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}f^3, 6s^2p^6d^1, 7s^2$

→ 2, 8, 18, 32, 21, 9, 2

→ $[Rn]_{86}\ 5f^3\ .\ 6d^1\ .\ 7s^2$

Np (Z = 93) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^5, 6d^0$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}f^5, 6s^2p^6d^0, 7s^2$

→ 2, 8, 18, 32, 23, 8, 2

→ $[Rn]_{86}\ 5f^5\ .\ 6d^0\ .\ 7s^2$

Some authors suggest that the configuration of Np is $[Rn]_{86}\ 5f^4\ .\ 6d^1\ .\ 7s^2$.

Pu (Z = 94) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^6, 6d^0$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}f^6, 6s^2p^6d^0, 7s^2$

→ 2, 8, 18, 32, 24, 8, 2

→ $[Rn]_{86}\ 5f^6\ .\ 6d^0\ .\ 7s^2$

Some authors have suggested that the configuration of Pu is $[Rn]_{86}\ 5f^5\ .\ 6d^1\ .\ 7s^2$.

Am (Z = 95) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^7, 6d^0$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}f^7, 6s^2p^6d^0, 7s^2$

→ 2, 8, 18, 32, 25, 8, 2

→ $[Rn]_{86}\ 5f^7\ .\ 6d^0\ .\ 7s^2$

The configurations of the elements from Th to Am, as given above, show that in all these elements $5f$ orbital is being progressively filled and hence the expected configuration of Cm (Z = 96) should be $[Rn]_{86}\ 5f^8.\ 6d^0\ .\ 7s^2$, but it been observed that the actual configuration of Cm is $[Rn]_{86}\ 5f^7.\ 6d^1.\ 7s^2$ which is obtained by shifting one of the electrons from $5f$ orbital to the vacant $6d$ orbital. This type of electronic shifting makes $5f$ orbital half-filled and hence more stable than $5f^8$ configuration as suggested by the rule of half-filled orbitals. Thus :

Cm (Z = 96) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^7, 6d^1$.

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}f^7, 6s^2p^6d^1, 7s^2$

→ 2, 8, 18, 32, 25, 9, 2

→ $[Rn]_{86}\ 5f^7 \cdot 6d^1 \cdot 7s^2$

Bk (Z = 97) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^9, 6d^0.$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}f^9, 6s^2p^6d^0, 7s^2$

→ 2, 8, 18, 32, 27, 8, 2

→ $[Rn]_{86}\ 5f^9 \cdot 6d^0 \cdot 7s^2$

Some authors say that the configuration of Bk is $[Rn]_{86}\ 5f^7 \cdot 6d^2 \cdot 7s^2$.

Cf (Z = 98) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{10}, 6d^0$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}f^{10}, 6s^2p^6d^0, 7s^2$

→ 2, 8, 18, 32, 28, 8, 2

→ $[Rn]_{86}\ 5f^{10} \cdot 6d^0 \cdot 7s^2$

Some authors are of the opinion that the configuration of Cf is $[Rn]_{86}\ 5f^9 \cdot 6d^1 \cdot 7s^2$.

Es (Z = 99) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{11}, 6d^0.$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}f^{11}, 6s^2p^6d^0, 7s^2$

→ 2, 8, 18, 32, 29, 8, 2

→ $[Rn]_{86}\ 5f^{11} \cdot 6d^0 \cdot 7s^2$

Fm(Z = 100)→ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{12}, 6d^0.$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}f^{12}, 6s^2p^6d^0, 7s^2$

→ 2, 8, 18, 32, 30, 8, 2

→ $[Rn]_{86}\ 5f^{12} \cdot 6d^0 \cdot 7s^2$

Md(Z = 101)→ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{13}, 6d^0.$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}f^{13}, 6s^2p^6d^0, 7s^2$

→ 2, 8, 18, 32, 31, 8, 2

→ $[Rn]_{86}\ 5f^{13} \cdot 6d^0 \cdot 7s^2$

No(Z = 102) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{14}, 6d^0$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}f^{14}, 6s^2p^6d^0, 7s^2$

→ 2, 8, 18, 32, 32, 8, 2

→ $[Rn]_{86}\ 5f^{14} \cdot 6d^0 \cdot 7s^2$

Lw(Z = 103)→ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{14}, 6d^1$

→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}f^{14}, 6s^2p^6d^1, 7s^2$

$\rightarrow$ 2, 8, 18, 32, 32, 9, 2

$\rightarrow$ $[Rn]_{86}\ 5f^{14}\ .\ 6d^{1}\ .\ 7s^{2}$

Now the extra electron in the next two elements *viz.* Ku (Z = 104) and Ha (Z = 105) goes to 6*d* orbital which is already singly-filled at Lw, the last member of actinide series.

Ku(Z = 104) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{14}, 6d^2$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}f^{14}, 6s^2p^6d^2, 7s^2$

$\rightarrow$ 2, 8, 18, 32, 32, 10, 2

$\rightarrow$ $[Rn]_{86}\ 5f^{14}\ .\ 6d^{2}\ .\ 7s^{2}$

Ha(Z = 105) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{14}, 6d^3$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}f^{14}, 6s^2p^6d^3, 7s^2$

$\rightarrow$ 2, 8, 18, 32, 32, 11, 2

$\rightarrow$ $[Rn]_{86}\ 5f^{14}\ .\ 6d^{3}\ .\ 7s^{2}$

Problems Based on the Determination of the Electronic Configuration of a Given Element

Here we will consider some examples, showing how the rules given above can be used to determine the electronic configuration of a given element.

Problem 1. *Write the electronic configuration of the elements whose atomic numbers are 24, 29, 46, 56, 57, 58, 64 and 78.*

Solution. *Element with at. no. = 24.* Using Aufbau principle and the rule of half-filled 3*d* orbital, one of the 4*s* electrons is shifted to 3*d* orbital and the configuration of the element with at. no. 24 becomes :

24 $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^5, 4s^1$

$\rightarrow$ 2, 8, 13, 1

Element with at. no. = 29. Using Aufbau principle and the rule of completely-filled 3*d* and half-filled 4*s* orbital, one of the 4*s* electrons is shifted to 3*d* orbital and the configuration of the element with at. no. 29 becomes :

29 $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^1$

$\rightarrow$ 2, 8, 18, 1

Element with at. no. = 46. Using Aufbau principle and the rule of completely-filled 4*d* orbitals, both the 5*s* electrons are shifted to 4*d* orbital and the configuration of the element with at. no. 46 becomes :

46 $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^0, 4d^{10}$

$\rightarrow$ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^0$

$\rightarrow$ 2, 8, 18, 18, 0

Element with at. no. = 56. Using Aufbau principle the configuration of the element having at. no. 56 is :

$$56 \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2$$
$$\rightarrow 1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^2p^6, 6s^2$$
$$\rightarrow 2, \quad 8, \quad 18, \quad 18, \quad 8, \quad 2$$

Element with at. no. = 57. Keeping in view the deviation of Aufbau principle the last electron in this element enters $5d$ orbital instead of $4f$ orbital and hence the configuration of this element becomes :

$$57 \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 5d^1$$
$$\rightarrow 1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^2p^6d^1, 6s^2$$
$$\rightarrow 2, \quad 8, \quad 18, \quad 18, \quad 9, \quad 2$$

Element with at. no. = 58. The configuration of this element is built up in accordance with Aufbau principle as shown below :

$$58 \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^1, 5d^2$$
$$\rightarrow 1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^1, 5s^2p^6d^1, 6s^2$$
$$\rightarrow 2, \quad 8, \quad 18, \quad 19, \quad 9, \quad 2$$

Element with at. no. = 64. Using Aufbau principle and the rule of half-filled $4f$ orbital, one of the $4f$ electrons is shifted to $5d$ orbitals and the configuration of the element with at. no. 64 becomes :

$$64 \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^7, 5d^1$$
$$\rightarrow 1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^7, 5s^2p^6d^1, 6s^2$$
$$\rightarrow 2, \quad 8, \quad 18, \quad 25, \quad 9, \quad 2$$

Element with at. no. = 78. In the configuration of this element one of the $6s$ electrons gets shifted to $5d$ orbitals and the configuration of the element with at. no. 78 becomes :

$$78 \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^1, 4f^{14}, 5d^9$$
$$\rightarrow 1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^9, 6s^1$$
$$\rightarrow 2, \quad 8, \quad 18, \quad 32, \quad 17, \quad 1$$

Problem 2. *A neutral atom of an element has two K, eight L and five M electron.. Give the following information : (i) Atomic number (ii) Total number of s-orbitals (iii) Total number of p-electrons (iv) Total number of d-electrons (v) Total number of f-electrons.* *(Raj. B. Sc. I. 1977)*

Solution. As given, the electronic configuration of the neutral atom is :

K	L	M
2	8	5
$1s^2$	$2s^2.2p^6$	$3s^2.3p^3.3d^0$

Thus : (*i*) Atomic number of the element = 2 + 8 + 5 = 15

(*ii*) Total number of *s*-orbitals = one 1*s* orbital + one 2*s* orbital + one 3*s* orbital
= Three *s*-orbitals

(*iii*) Total number of *p*-electrons = 6 + 3 = 9

(*iv*) Total number of *d*-electrons = 0

(*v*) Total number of *f*-electrons = 0

Problem 3. *Write the electronic configuration (with electron spins) of the following :*

(*i*) *Elements with atomic number 4, 7, 21 and 42*

(*ii*) *Ions : V^{3+}, Fe^{2+}, Br^-, S^{2-}*

Solution. (*i*) Using Aufbau principle and Hund's rule of maximum multiplicity, the configuration of the elements with at no. 4, 7 and 21 are given below :

At No. = 4 → $1s^2$, $2s^2$ or $\underset{1s^2}{\boxed{\uparrow\downarrow}}$ $\underset{2s^2}{\boxed{\uparrow\downarrow}}$

At No. = 7 → $1s^2$, $2s^2$, $2p^3$ or $\underset{1s^2}{\boxed{\uparrow\downarrow}}$ $\underset{2s^2}{\boxed{\uparrow\downarrow}}$ $\underset{2p^3}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}$

At No. = 21 → $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^1$

→ $1s^2$, $2s^2p^6$, $3s^2p^6d^1$, $4s^2$

$3s^2$ $3p^3$ $3d^1$ $4s^2$

→ 2, 8, $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}\boxed{\ }\boxed{\ }\boxed{\ }\boxed{\ }$ $\boxed{\uparrow\downarrow}$

At. No. 42. In case of this element one of the 5*s* electrons is shifted to 4*d* orbital to make it half-filled and hence the configuration of this element becomes :

$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^{10}$, $4p^6$, $5s^1$, $4d^5$

or $1s^2$, $2s^2p^6$, $3s^2p^6d^{10}$, $4s^2p^6d^5$, $5s^1$

$4s^2$ $4p^6$ $4d^5$ $5s^1$

or 2, 8, 18, $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ $\boxed{\uparrow}$

(*ii*) The electronic configuration of the cations are obtained by removing the electrons from the configuration of their parent atom. The number of electrons removed is equal to the number of positive charges on the cation. On the other hand the electronic configuration of the anions are obtained by adding the electrons to the configuration of their parent atom. The number of electrons added is equal to the number of negative charges carried by the anion. Now :

$\because$ V (at. no. = 23) → $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^3$

→ $1s^2$, $2s^2p^6$, $3s^2p^6d^3$, $4s^2$

$\therefore$ V^{3+} → $1s^2$, $2s^2p^6$, $3s^2p^6d^2$

$3s^2$ $3p^6$ $3d^2$

→ 2, 8, $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\ }\boxed{\ }\boxed{\ }$

$\because$ Fe (at. no. = 26) → $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^6$

→ $1s^2$, $2s^2p^6$, $3s^2p^6d^6$, $4s^2$,

$\therefore$ Fe^{2+} → $1s^2$, $2s^2p^6$, $3s^2p^6d^6$.

$$\rightarrow 2, 8, \underset{\boxed{\uparrow\downarrow}}{3s^2} \quad \underset{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}}{3p^6} \quad \underset{\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}{3d^6}$$

$\because$ Br (at. no. = 35) $\rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^5$

$\therefore Br^- \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6$

$\rightarrow 1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6$

$$\rightarrow 2, 8, 18, \underset{\boxed{\uparrow\downarrow}}{4s^2} \quad \underset{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}}{4p^6}$$

$\because$ S (at. no. = 16) $\rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^4$

$\therefore S^{2-} \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6$

$\rightarrow 1s^2, 2s^2p^6, 3s^2p^6$

$$\rightarrow 2, 8, \underset{\boxed{\uparrow\downarrow}}{3s^2} \quad \underset{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}}{3p^6}$$

Problem 4. *How many orbits, orbitals and electrons are there in an atom having atomic weight 23 and atomic number 11?*

Solution. At wt. = No. of protons + No. of neutrons = 23

At. no. = No. of protons = No. of electrons = 11

$\therefore$ No. of neutrons = 23 − 11 = 12

Electronic configuration = $1s^2, 2s^2p^6, 3s^1$

No. of orbits = 3 which are K, L and M

No. of orbitals = 14 (one 1*s* + one 2*s* + three 2*p* + one 3*s* + three 3*p* + five 3*d*)

No. of electrons = 11.

Problem 5. *There are two elements having atomic number 7 and 9.*

(i) Write their electronic configuration

(ii) Which has maximum number of unpaired electrons?

(iii) What is the valency of each?

Solution. (*i*) Electronic configuration of the element with at. no. 7 is :

$$1s^2, 2s^2 . 2p_x^1 . 2p_y^1 . 2p_z^1$$

Electronic configuration of the element with at. no. 9 is :

$$1s^2, 2s^2 . 2p_x^2 . 2p_y^2 . 2p_z^1$$

(*ii*) The element with at. no. 7 has 3 unpaired electrons while the element with at. no. 9 has 1 unpaired electron (See the electronic configurations given above).

(*iii*) Since the element having at. no. 7 has three unpaired electrons in its valence-shell, its valency is 3. Similarly the valency of the other element is 1.

Problem 6. *An atom has 2K, 8L and 2M electrons. Find the total number of:*

(i) protons

(ii) principal quantum number

(iii) sub-levels

(*iv*) *orbits*

(*v*) *p-electrons*

(*vi*) *paired electrons*

(*vii*) *unpaired electrons*

(*viii*) *valency of the atom.*

Solution. Electronic configuration of the atom is

$$\underbrace{1s^2}_{\text{K}} \qquad \underbrace{2s^2.2p^6}_{\text{L}} \qquad \underbrace{3s^2}_{\text{M}}$$

Total number of electrons = 2 + 8 + 2 = 12

(*i*) Total no. of protons = 12

(*ii*) Principal quantum number = 3

(*iii*) Sub-levels = 6 (one 1*s* + one 2*s* + three 2*p* + one 3*s*)

(*iv*) Orbits = 3(K, L, M)

(*v*) *p*-electrons = 6

(*vi*) Paired electrons = 12

(*vii*) Unpaired electrons = 0

(*viii*) Valency of the atom = 0

Problem 7. *The electronic configuration of carbon is* $1s^2, 2s^2.2p_x^1.2p_y^1.2p_z^0$ *and not* $1s^2, 2s^2.2p_x^2.2p_y^0.2p_z^0$. *Explain.* *(Lucknow B.Sc. 1981)*

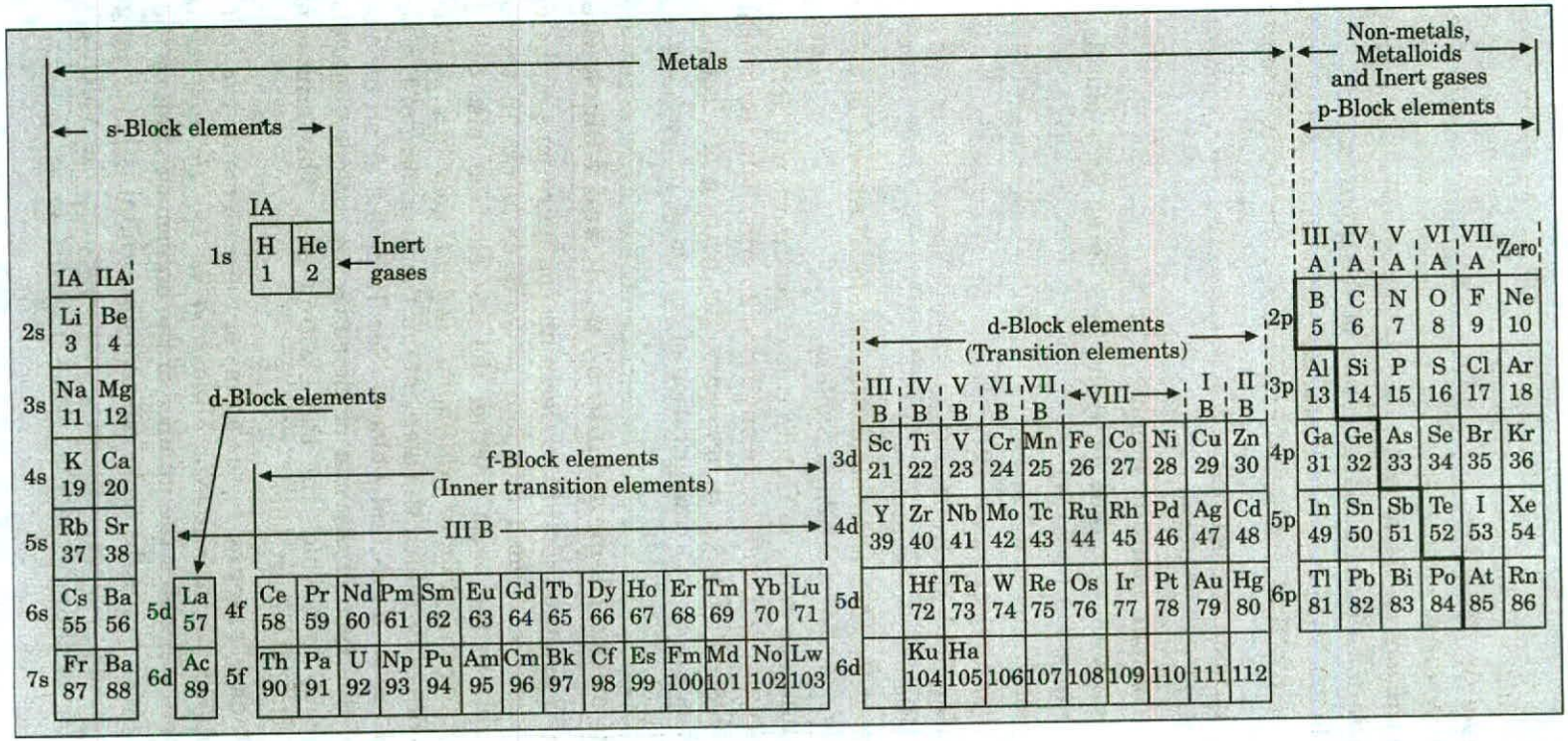
Solution. According to Hund's rule of maximum multiplicity, when applied to the orbitals $2p_x$, $2p_y$, and $2p_z$ belonging to 2*p* sub-shell, these orbitals should first be filled singly and then, if necessary, the pairing of electrons in each orbital begins. Thus the correct configuration of carbon is $1s^2, 2s^2, 2p_x^1.2p_y^1.2p_z^0$ and not $1s^2, 2s^2.2p_x^2.2p_y^0.2p_z^0$.

Division of the Elements into s-, p-, d- and f-Block Elements

A careful examination of the electronic configurations of the elements reveals that they may be divided into four *sections* or *blocks* in the long form of the periodic table on the basis whether the last electron (also called *differentiating electron or extra electron or additional electron*) goes to *s, p, d* or *f* orbital. Thus the four blocks into which the elements in the long form of the periodic table can be divided are *s-, p-, d-* and *f*-blocks (See Table 3.2 given on page 190). For the purpose of this type of division of elements we consider only the orbital of the highest energy into which the last electron goes. This orbital may not always belong to the outermost shell.

1. s-Block Elements. In the atoms of these elements *the last electron enters the s-orbital of the ultimate (outermost) shell, i.e., the last electron goes to ns-orbital* where *n* denotes the number of the outermost shell or the number of the period. In other words, in these elements *ns*-orbital is being progressively filled. Hence the name *s-block elements*. Consequently, the valence shell electronic configuration of these elements varies from ns^1 to ns^2.

Table 3.2. Division of the elements into s, p, d, and f block elements. Thick line shown in the form of ladder (i.e. steps) separates the metals from non-metals, metalloids and inert gases



The elements of group IA (H to Fr : *Alkali metals*), group II A (Be to Ra : *Alkaline earth metals*) and He (zero group) belong to this block, since their valence-shell configuration is ns^1 and ns^2 respectively where n is the number of the period or the principal quantum number. The elements of this block are collectively known as *normal elements or representative elements.*

The valence-shell electronic configurations of *s*-block elements are given in Table 3.3.

Table 3.3. Valence-shell electronic configuration of s-block elements. The number given above the symbol of each element indicates the atomic number of the element.

Period number (n) and the orbital being filled	IA ns^1	IIA ns^2	Zero
n = 1, 1*s*	1 H $1s^1$		2 He $1s^2$
n = 2, 2*s*	3 Li $2s^1$	4 Be $2s^2$	
n = 3, 3*s*	11 Na $3s^1$	12 Mg $3s^2$	
n = 4, 4*s*	19 K $4s^1$	20 Ca $4s^2$	
n = 5, 5*s*	37 Rb $5s^1$	38 Sr $5s^2$	
n = 6, 6*s*	55 Cs $6s^1$	56 Ba $6s^2$	
n = 7, 7*s*	87 Fr $7s^1$	88 Rn $7s^2$	

It may be seen from these configurations (Table 3.3) that the last electron goes into 1*s* orbital in H and He (*1st period, n = 1*) into 2*s* orbital in Li and Be (*2nd period, n = 2*), into 3*s* orbital in Na and Mg (*3rd period, n* = 3), into 4*s* orbital in K and Ca (*4th period, n* = 4), into 5*s* orbital in Rb and Sr (*5th period, n* = 5), into 6*s* orbital in Cs and Ba (*6th period, n* = 6) and into 7*s* orbital in Fr and Ra (*7th period, n* = 7). Thus we see that *s*-block elements are located at the extreme left of the periodic table and consist of active metals. It may also be seen

from the electronic configurations of *s*-block elements that the principal quantum number (n) of the differentiating electron for these elements is equal to the period number in which these elements are present. The properties of *s*-block elements depend on the number of electrons present in *ns* orbital.

2. p-Block Elements. In the atoms of these elements *the last etectron enters the p-orbital of the ultimate (outermost) shell, i.e. the last electron goes to np orbital.* (n = number of the outermost shell or period). In other words, in these elements *np*-orbital is being progressively filled. Hence the name *p-block elements*. In the atoms of these elements the *ns*-orbital is completely filled and hence the valence-shell configuration of these elements varies from ns^2p^1 to ns^2p^6. The elements of groups III A (B to TI), IVA (C to Pb), VA (N to Bi), VIA (O to Po), VII A (F to At) and zero (Ne to Rn) belong to this block, since the valence-shell configurations are ns^2p^1, ns^2p^2, ns^2p^3, ns^2p^4, ns^2p^5 and ns^2p^6 respectively. The elements of this block, like *s*-block elements, are also called *normal elements or representative elements.*

The valence-shell electronic configurations of p-block elements are given in Table 3.4.

Table 3.4. Valence-shell electronic configuration of p-block elements. The number given above the symbol of each element indicates the atomic number of the element.

Period number (n) and the orbital being filled	III A ns^2p^1	IV A ns^2p^2	VA ns^2p^3	VI A ns^2p^4	VII A ns^2p^5	Zero ns^2p^6
n = 2, 2p	5 B $2s^2p^1$	6 C $2s^2p^2$	7 N $2s^2p^3$	8 O $2s^2p^4$	9 F $2s^2p^5$	10 Ne $2s^2p^6$
n = 3, 3p	13 Al $3s^2p^1$	14 Si $3s^2p^2$	15 P $3s^2p^3$	16 S $3s^2p^4$	17 Cl $3s^2p^5$	18 Ar $3s^2p^6$
n = 4, 4p	31 Ga $3d^{10}4s^2p^1$	32 Ge $3d^{10}4s^2p^2$	33 As $3d^{10}4s^2p^3$	34 Se $3d^{10}4s^2p^4$	35 Br $3d^{10}4s^2p^5$	36 Kr $3d^{10}4s^2p^6$
n = 5, 5p	49 In $4d^{10}5s^2p^1$	50 Sn $4d^{10}5s^2p^2$	51 Sb $4d^{10}5s^2p^3$	52 Te $4d^{10}5s^2p^4$	53 I $4d^{10}5s^2p^5$	54 Xe $4d^{10}5s^2p^6$
n = 6, 6p	81 TI $4f^{14}.5d^{10}6s^2p^1$	82 Pb $4f^{14}.5d^{10}6s^2p^2$	83 Bi $4f^{14}.5d^{10}6s^2p^3$	84 Po $4f^{14}.5d^{10}6s^2p^4$	85 At $4f^{14}.5d^{10}6s^2p^5$	86 Rn $4f^{14}.5d^{10}6s^2p^6$

It may be seen from these configurations that the last electron goes into 2p orbital in B to Ne (2*nd* period, n = 2), into 3p orbital in Al to Ar (3*rd* period,

$n = 3$), into $4p$ orbital in Ga to Kr (*4th* period, $n = 4$), into $5p$ orbital in In to Xe (*5th* period, $n = 5$) and into $6p$ orbital in Tl to Rn (*6th* period, $n = 6$). Thus the principal quantum number for these elements is equal to the period number in which these elements are present.

It may also be seen that *p*-block elements are located at the extreme right of the periodic table and consist of *metals, non-metals, metalloids* and *inert gases*.

The properties of p-block elements are determined by the number of electrons present in *np* orbitals. These elements have a general electronic configuration of the outermost shell as $ns^2.np^{1...6}$ where n stands for the number of the period.

3. d-Block Elements (Transition Elements). In these elements, either in their atomic state or in any of their common oxidation state, *the last electron enters the d-orbital of the penultimate (inner to ultimate) shell, i.e. the last electron goes to (n–1)d orbital.* In other words, in these elements $(n - 1)d$ orbitals are being progressively filled. Hence the name *d-block elements*. With the exceptions of Cr, Cu, Nb, Mo, Ru, Rh, Pd, Ag, Pt and Au, in the atoms of these elements the *ns*-orbital is completely filled (ns^2 configuration). Consequently, the valence-shell configuration of most of these elements varies from $(n - 1)d^1.ns^2$ (Group III B) to $(n - 1)d^{10}.ns^2$ (Group II B) configuration. The elements of groups III B. IV B, VB, VI B. VII B, VIII, I B and II B belong to this block as is evident from their valence-shell configurations given in Table 3.5.

These elements are located in the middle of the periodic table [*i.e.* between *s* (electropositive elements) and p-block (electronegative elements) elements] and consist of metals only. *d*-block elements are also called *transition elements*, since their properties are intermediate between those of *s* and *p*-block elements.

These elements are classified into *four series viz.* 3*d*, 4*d*, 5*d*, and 6*d* series corresponding to the filling of 3*d*, 4*d*, 5*d*, and 6*d* orbitals of 3rd (M-shell, $n = 3$), 4th (N-shell, $n = 4$), 5th (O-shell, $n = 5$) and 6th (P-shell, $n = 6$) shells respectively.

(*a*) **3d-series** (*1st transition series*). In the elements of this series 3*d* orbitals are being progressively filled up with electrons. This series has *ten* elements, beginning with Sc (Z = 21) and ending at Zn (Z = 30). The elements of this series lie in 4th period ($n = 4$).

(*b*) **4d-series** (*2nd transition series*). In the elements of this series 4*d* orbitals are being progressively filled up with electrons. This series also has ten elements, beginning with Y (Z = 39) and ending at Cd (Z = 48). The elements of this series lie in 5th period ($n = 4$).

(*c*) **5d-series** (*3rd transition series*). In the elements of this series 5*d* orbitals are being filled up with electrons. This series also has ten elements *viz.* La (Z = 57), Hf (Z = 72) to Hg (Z = 80). The elements of this series lie in 6th period ($n = 6$).

(*d*) **6d-series** (*4th transition series*). In the elements of this series 5*d* orbitals are being filled up with electrons At present this series has three elements viz.

Table 3.5. Valence-shell electronic configuration of d-block elements (Transition elements). The number given above the symbol of each element indicates the atomic number of the element.

Period number (n), orbital being filled and the name of the series	III B	IV B	V B	VI B	VII B	VIII			I B	II B
n = 4, 3d, 3d series	21 Sc $3d^1.4s^2$	22 Ti $3d^2.4s^2$	23 V $3d^3.4s^2$	24 Cr $3d^5.4s^1$	25 Mn $3d^5.4s^2$	26 Fe $3d^6.4s^2$	27 Co $3d^7.4s^2$	28 Ni $3d^8.4s^2$	29 Cu $3d^{10}.4s^1$	30 Zn $3d^{10}.4s^2$
n = 5, 4d, 4d series	39 Y $4d^1.5s^2$	40 Zr $4d^2.5s^2$	41 Nb $4d^4.5s^1$	42 No $4d^5.5s^1$	43 Tc $4d^5.5s^2$	44 Ru $4d^7.5s^1$	45 Rh $4d^8.5s^1$	46 Pd $4d^{10}.5s^0$	47 Ag $4d^{10}.5s^1$	48 Cd $4d^{10}.5s^2$
n = 6, 5d, 5d series	57 La $4f^0.5d^1.6s^2$	72 Hf $4f^{14}.5d^2.6s^2$	73 Ta $4f^{14}.5d^3.6s^2$	74 W $4f^{14}.5d^4.6s^2$	75 Re $4f^{14}.5d^5.6s^2$	76 Os $4f^{14}.5d^6.6s^2$,	77 Ir $4f^{14}.5d^7.6s^2$,	78 Pt $4f^{14}.5d^9.6s^1$	79 Au $4f^{14}.5d^{10}.6s^1$	80 Hg $4f^{14}.5d^{10}.6s^2$
n = 7, 6d 6d series	89 Ac $5f^0.6d^1.7s^2$	104 Ku $5f^{14}.6d^2.7s^2$	105 Ha $5f^{14}.6d^3.7s^2$	106	107	108	109	110	111	112

Ac (Z = 89), Ku (Z = 104) and Ha (Z = 105). The elements of this series lie in 7th period (n = 7) which is an incomplete period. It is expected that the elements with atomic number 106, 107, 108, 109, 110, 111 and 112 which are still to be discovered will be the members of 6*d* series, *i.e.* in these unknown elements the additional electron will enter 6*d* orbital.

All the transition elements are metals, since the number of electrons in the outer-most shell is very small, being equal to 2. They are hard, malleable and ductile and possess high tensile strength. They exhibit all the three types of structures *viz. face centred cubic (fcc), hexagonal close packed (hcp)* and *body centrered cubic (bcc).*

4. *f*-Block Elements (Inner-transition Elements). In these elements, either in their atomic state or in any of their common oxidation state, *the last electron enters the f-orbital of ante-penultimate (inner to the penultimate) shell i.e. the last electron goes to (n–2) f-orbital.* In other words, in these elements (*n*–2)*f*-orbitals are being progressively filled. Hence the name *f-block elements.* The valence shell electronic configuration of the atoms of these elements is represented as :

$$(n-2)\, f^{1...7,\ 9...14} \,.\, (n-1)d^{0,\ 1} \,.\, ns^2 \text{ as shown in Table 3.6.}$$

These elements are located in group III B and have been given a separate place at the bottom of the periodic table. *f*-block elements are also called *inner-transition elements* and are classified into two series *viz.* 4*f* and 5*f* corresponding to the filling of 4*f* and 5*f* orbitals of 4th (N-shell, *n* = 4) and 5th (O-shell, *n* = 5) shells respectively. (See Table 3.6).

(*a*) **4f-series.** (*1st inner transition series*). In the elements of this series, the extra electron enters 4*f* orbital, *i.e.* 4*f* orbitals are being progressively filled with electrons. This series has 14 elements beginning with Ce (Z = 58) and ending at Lu (Z = 71). The elements of this series lie in 6th period (*n* = 6) and are called *rare-earths or lanthanides or lanthanones.*

(*b*) **5f-series.** (*2nd inner transition series*). In the elements of this series, 5*f* orbitals are being progressively filled, *i.e.*, the extra electron goes to 5*f* orbital. This series, like 4*f* series, also has 14 elements beginning with Th (Z = 90) and ending at Lu (Z = 103). The elements of this series lie in *7th* period (incomplete period with *n* = 7) and are called *actinides or actinones.* The elements after U(Z = 92) are called *trans-uranic elements* which have been obtained as a result of atomic research. Thus *trans-uranic elements* are synthetic (man-made) elements.

Classification of Elements on the Basis of their Complete and Incomplete Electron Shells

There are four types of elements based on the presence of the complete and incomplete electron shells in them.

1. Noble Gases. *In the atoms of these elements the outermost shell which has ns^2p^6 configuration* (He which has $1s^2$ configuration is an exception) *is completely filled* (See Table 3.4). ns^2p^6 configuration is stable and hence these elements generally do not enter into ordinary chemical reactions. These elements are present in zero group of the periodic table.

Table 3.6. Valence-shell electronic configuration of f-block elements (Lanthanides and Actinides). The number given above the symbol of each element indicates the atomic number of the element. All these elements belong to Group III B

Period number (n), orbital being filled and the name of the series	Elements with their atomic numbers and valence-shell electronic configurations.						
n = 6, 4f, 4f series (Lanthanides)	58 Ce $4f^1.5d^1.6s^2$ or $4f^2.5d^0.6s^2$	59 Pr $4f^3.5d^0.6s^2$	60 Nd $4f^4.5d^0.6s^2$	61 Pm $4f^5.5d^0.6s^2$	62 Sm $4f^6.5d^0.6s^2$	63 Eu $4f^7.5d^0.7s^2$	64 Gd $4f^7.5d^1.7s^2$
	65 Tb $4f^9.5d^0.6s^2$	66 Dy $4f^{10}.5d^0.6s^2$	67 Ho $4f^{11}.5d^0.6s^2$	68 Er $4f^{12}.5d^0.6s^2$	69 Tm $4f^{13}.5d^0.6s^2$	70 Yb $4f^{14}.5d^0.6s^2$	71 Lu $4f^{14}.5d^1.6s^2$
n = 7, 5f, 5f series (Actinides)	90 Th $5f^1.6d^1.7s^2$ or $5f^0.6d^2.7s^2$	91 Pa $5f^2.6d^1.7s^2$ or $5f^1.6d^2.7s^2$	92 U $5f^3.6d^1.7s^2$	93 Np $5f^5.6d^0.7s^2$ or $5f^4.6d^1.7s^2$	94 Pu $5f^6.6d^0.7s^2$ or $5f^5.6d^1.7s^2$	95 Am $5f^7.6d^0.7s^2$	96 Cm $5f^7.6d^1.7s^2$
	97 Bk $5f^9.6d^0.7s^2$ or $5f^7.6d^2.7s^2$	98 Cf $5f^{10}.6d^0.7s^2$ or $5f^9.6d^1.7s^2$	99 Es $5f^{11}.6d^0.7s^2$	100 Fm $5f^{12}.6d^0.7s^2$	101 Md $5f^{13}.6d^0.7s^2$	102 No $5f^{14}.6d^0.7s^2$	103 Lw $5f^{14}.6d^1.7s^2$

2. Representative or Normal Elements. *In the atoms of these elements the outermost shell (i.e. nth shell) is partly filled while the inner shells (i.e., 1st, 2nd,.....(n–1)th shells) are completely filled* (Table 3.3 and 3.4). The electronic configuration of the outermost shell of the atoms of these elements varies from ns^1 to ns^2p^5. The elements of IA, IIA, IIIA, IVA, VA, VIA and VIIA groups belong to this type. The configurations of the outermost shell of these elements are given below :

Group IA (Li—Fr) → ns^1
Group IIA (Be—Ra) → ns^2
Group IIIA (B—TI) → ns^2p^1
Group IVA (C—Pb) → ns^2p^2
Group VA (N—Bi) → ns^2p^3
Group VIA (O—Po) → ns^2p^4
Group VIIA (F—At) → ns^2p^5

The configurations given above show that *s* and *p* block elements constitute representative or normal elements. The groups containing these elements are also known as main groups of the periodic table. Metals, non-metals and metalloids are present in these groups.

3. Transition Elements. *In the atoms of these elements two outermost shells [i.e. nth and (n–1)th] are partly filled while the remaining inner shells [i.e. 1st, 2nd), ... (n–2)th shells] are completely filled.* (Table 3.5). These elements lie in *4th, 5th, 6th* and *7th* periods of the long form of periodic table. The complete electronic configurations of these elements can be represented as follows :

Period number	Elements	Electronic configurations	Remarks
4	Sc (Z = 21) to Zn (Z = 30)	2, 8, $3s^2p^6d^x$, 2 (x = 1, 2, 3, ..., 10)	Last shell of Cr (Z = 24) and Zn (Z = 30) contains only one electron and hence in these elements x = 5 and 10 respectively.
5	Y (Z = 39) to Cd (Z = 48)	2, 8, 18, $4s^2p^6d^x$, 2 (x = 1, 2, ...10)	Last shell of Nb (Z = 41), Mo (Z = 42), Ru (Z = 44), Rh (Z = 45) and Ag (Z = 47) contains one electron while that of Pd (Z = 46) is empty. Thus for these elements x = 4, 5, 7, 8, 10 and 10 respectively.
6	La (Z = 57)	2, 8, 18, 18, $5s^2p^6d^x$, 2 (x = 1)	—
	Hf (Z = 72) to Hg (Z = 80)	2, 8, 18, 32, $5s^2p^6d^x$, 2 (x = 2, 3, 4, ..., 10)	Last shell of Pt (Z = 78) and Au (Z = 79) contains one electron only and hence for these elements x = 9 and 10 respectively.
7	Ac (Z = 89)	2, 8, 18, 32, 18, $6s^2p^6d^x$, 2 (x = 1)	—
	Ku (Z = 104) and Ha (Z = 105)	2, 8, 18, 32, 32, $6x^2p^6d^x$, 2 (x = 2, 3)	—

The configurations given above clearly show that these elements *generally* contain two electrons in their *ns* orbital while the differentiating electron enters an available $(n—1)d$ orbital and hence the electronic configuration of the outermost shell of these elements varies from $(n—1)d^1.\ ns^2$ to $(n—1)\ d^{10}.\ ns^2$. The elements of IIIB, IVB, VB, VIB, VIIB, VIII, IB and IIB groups belong to this type. Thus we see that these elements are located between electropositive elements of groups IA and IIA (*s*-block elements) and electronegative elements of groups IIIA to VIIA (*p*-block elements).

4. Inner-transition Elements. *In the atoms of these elements three outermost shells [i.e. nth, (n—l)th and (n—2)th shells] are partly filled while the remaining inner shells [i.e. 1st, 2nd,...(n—3)th shells] are completely filled.* (Table 3.6) Lanthanides [Ac (Z = 58) to Lu (Z = 71)—fourteen elements] and actinides [Th (Z = 90) to Lw (Z = 104)—fourteen elements] belong to this type. These elements lie in *6th* and *7th* periods respectively. The complete electronic configuration of these elements can be represented as follows :

Lanthanides : 2, 8, 18, $4s^2p^6d^{10}f^x$, $5s^2p^6d^y$, 2 *(Six shells)*

Actinides : 2, 8, 18, 32, $5s^2p^6d^{10}f^x$, $6s^2p^6d^y$, 2 *(Seven shells)*

The values of x and y for these elements are as follows :

Lanthanides	x	y	Actinides	x	y
Ce (Z = 58)	1 or 2	1 or 0	Th (Z = 90)	1 or 0	1 or 2
Pr (Z = 59)	3	0	Pa (Z = 91)	2 or 1	1 or 2
Nd (Z = 60)	4	0	U (Z = 92)	3	1
Pm (Z = 6l)	5	0	Np (Z = 93)	5 or 4	0 or 1
Sm (Z = 62)	6	0	Pu (Z = 94)	6 or 5	0 or 1
Eu (Z = 63)	7	0	Am (Z = 95)	7	0
Gd (Z = 64)	7	1	Cm (Z = 96)	7	1
Tb (Z = 65)	9	0	Bk (Z = 97)	9 or 7	0 or 2
Dy (Z = 66)	10	0	Cf (Z = 98)	10 or 9	0 or 1
Ho (Z = 67)	11	0	Es (Z = 99)	11	0
Er (Z = 68)	12	0	Fm (Z = 100)	12	0
Tm (Z = 69)	13	0	Md (Z = 101)	13	0
Yb (Z = 70)	14	0	No (Z = 102)	14	0
Lu (Z = 71)	14	1	Lw (Z = 103)	14	1

The configurations given above clearly show that these elements have not only partially filled $(n—1)d$ orbitals but also underlying partially filled $(n—2)f$ orbitals. *ns* orbital is completely filled (ns^2 configuration). Thus the antepenultimate shell [*i.e.* $(n—2)th$ shell] is being expanded from 18 to 32 by the addition of electrons to $(n—2)$ *f* orbital. In case of lanthanides $(n—2)f$ orbitals are $4f$ orbitals while in case of actinides $(n—2)f$ orbitals are $5f$ orbitals. Thus in case of lanthanides $4f$ orbital while in case of actinides $5f$ orbital is being progressively filled. Elements within each of these series are very similar in chemical properties.

These elements are located in group IIIB and have been given a separate place at the bottom of the periodic table.

Characteristic of *s*-Block Elements

1. Size of atoms and ions. Size of an atom is expressed in terms of atomic radius, van der Waals radius or covalent radius. For comparative purposes any of the above radii can be used to express the size of an atom.

Size of an atom of *s*-block elements decreases on moving horizontally from group I A to group II A while the same increases on moving down the group as is evident from the values of covalent radii of these elements given in Table 3.7. The size of an ion is given by ionic radius. Ionic radii also show the same variation in the periodic table as covalent radii (See Table 3.8).

Table 3.7. Cavalent radii (in Å) of s-block elements

Group I A	Group II A
Li	Be
1.23	0.90
Na	Mg
1.54	1.36
K	Ca
2.03	1.74
Rb	Sr
2.16	1.91
Cs	Ba
2.35	1.98

Table 3.8. Ionic radii (in Å) of s-block elements

Group I A (M^+ ions)	Group II A (M^{2+} ions)
Li^+	Be^{2+}
0.60	0.31
Na^+	Mg^{2+}
0.95	0.65
K^+	Ca^{2+}
1.33	0.99
Rb^+	Sr^{2+}
1.48	1.13
Cs^+	Ba^{2+}
1.69	1.35

2. Atomic volumes. Since atomic radius decreases when we move from group I A to II A, atomic volume also decreases in the same direction. Similarly with the increase of atomic radius on moving down the group, the atomic volume also increases considerably in the same direction.

Group I A elements :	Li	Na	K	Rb	Cs
Atomic volume (c.c.) :	13.1	23.7	45.3	55.9	70.0
Group II A elements :	Be	Mg	Ca	Sr	Ba
Atomic volume (c.c.) :	5.0	14.0	29.9	33.7	39.0

3. Binding energies. The binding energies of *s*-block elements are low, since there are one (Group IA) or two (Group II A) *s*-electrons per atom available for bond formation in the crystal lattice of the metal. Binding energy decreases with the increase of the atomic radius. Thus binding energy decreases on going down a group while the same increases on moving horizontally from group I A to group II A.

The binding energies of these elements are lower than those of transitional elements lying to their right in the periodic table. This is due to the fact that the

one or two *s*-electrons in the atoms of these elements are present outside a noble gas core and are shielded from direct attraction of the nucleus.

4. Melting and boiling points. Since the binding energies of *s*-block elements decrease on going down a group while the same increases on moving horizontally from group I A to group II A, the melting and boiling points of these elements invariably show the same trend. (See Table 3.9)

Table 3.9. Melting and boiling points (°C) of *s*-block elements.

Group IA elements	Group IIA elements
Li	Be
180.5; 1330	1277; 2770
Na	Mg
97.8; 892	650; 1107
K	Ca
63.7; 760	838; 1440
Rb	Sr
38.9; 688;	768; 1380
Cs	Ba
28.7; 690	714; 1640

5. Specific heats. Specific heats of *s*-block elements show the same pattern as the melting and boiling points of these elements.

6. Ionisation energies. Ionisation energy of an element is defined as the amount of energy required to remove the most loosely bound electron (*i.e.* outermost shell electron) from the isolated neutral gaseous atom in its lowest energy state (*i.e.* ground state) to convert it into a gaseous cation. Thus ionisation energy of an atom, M (*g*) can be defined by the following process.

$$\underset{\text{Isolated gaseous atom}}{M\ (g)} \longrightarrow e^-(g) + \textit{Energy supplied (called ionization energy)} \rightarrow \underset{\text{Gaseous cation}}{M^+\ (g)}$$

Ionisation energy defined as above is strictly called *first ionisation energy*, since it corresponds to the removal of *one* electron only.

Ionisation energy increases on moving horizontally from group I A to group II A and decreases on moving down a group as shown below.

Group I A elements :	Li	Na	K	Rb	Cs
First ionisation energy (K.J./mole) :	520.3	495.8	418.9	403.0	375.7
Group II A elements :	Be	Mg	Ca	Sr	Ba
First ionization energy (KJ/mole) :	899.5	737.7	589.8	549.5	502.9

The values of first ionisation energies of *s*-block elements as given above are comparatively lower than those of *p*-block elements. Their lower values are due

to their lower binding energies. Due to low ionisation energies, these elements have a great tendency to lose their *s*-electrons easily in aqueous solution and can thus form M^+ (Group I A) and M^{2+} (Group II A) ions.

$$M\ (s) — e^- \rightarrow M^+\ (aq)\ \text{(Group I A)}$$

$$M\ (s) — 2e^- \rightarrow M^{2+}\ (aq)\ \text{(Group II A)}$$

7. Electropositive or metallic character. Metallic character of an element is defined as its tendency to lose one or more electrons to form a cation.

$$M - ne^- \rightarrow M^{n+}$$

Thus greater is the tendency of an element to lose the electron to form the cation, greater is its metallic or electropositive character. Electropositive character of an element depends on the magnitude of its ionisation energy. With the increase of ionisation energy, the metallic character of the element decreases. Thus since all the *s*-block elements have low values of ionisation energy, these elements have strongly electropositive character, *i.e.* all the *s*-block elements are metals. In other words these elements have a great tendency to lose one or two *s*-electrons to form M^+ or M^{2+} cations.

$$M — e^- \rightarrow M^+\ \text{(Group I A)}$$

$$M — 2e^- \rightarrow M^{2+}\ \text{(Group II A)}$$

Since the ionisation energy increases on moving horizontally from group IA to group IIA and decreases on moving down a group, the metallic or electropositive character of the *s*-block elements and hence the basic character of their oxides decreases as we move from group IA to group II A and increases on moving down a group. For example, Na_2O is more basic than MgO.

8. Electronegativity. When two *different* atoms in a molecule are bonded together by a covalent bond, the electron pair forming the covalent bond is not shared equally by both the atoms. The electron pair lies nearer to one atom than the other atom. *The relative tendency (or ability or power) of a bonded atom in a molecule to attract the shared electron pair towards itself is termed as its electronegativity.*

Since the electropositive character of *s*-block elements, as we have seen above, increases down the group and decreases on moving in a period, electronegativity which is opposite of electropositive character, will show opposite periodic variation, *i.e.*, the electronegativity of *s*-block elements decreases down the group and increases in a period as shown below :

Elements of group IA :	H	Li	Na	K	Rb	Cs	Fr
Electronegativity :	2.2	0.98	0.93	0.82	0.82	0.79	0.70
Elements group II A :		Be	Mg	Ca	Sr	Ba	Ra
Electronegativity :		1.57	1.31	1.00	0.95	0.89	0.90

The values of electronegativity as given above are Pauling's electronegativity values. The values show that s-block elements have low values of electronegativity.

9. Oxidation states. Since the first ionisation potential of the elements of group IA is very low, these elements can lose their single ns^1 electron easily to form M^+ cation and hence show an oxidation state of +1. On the other hand, since

the 2*nd* ionisation potential of these elements is very high, they cannot lose the second electron residing in the (n—1)*th* shell to form M^{2+} cation and hence cannot show +2 oxidation state.

Since the first and second ionisation potentials of the elements of group II A both are low, these elements can easily lose both ns^2 electrons to form M^+ and M^2+ cations and hence show +2 oxidation state. Thus the elements of group I A are *monovalent* (+1 oxidation state) and those of II A are *divalent* (+2 oxidation state).

10. Density. In general, these metals have high density which is because of the fact that the atoms in metallic crystal are closely packed together. However, Li, Be and Mg have low densities which are due to low atomic weights of these elements.

Density increases on moving down the group as well as on moving from group I A to group II A , since the atomic weights of the atoms also increases in the same direction.

11. Electron affinity. *Electron affinity* (abbreviated as EA) *of an element is defined as the amount of energy released in adding an extra electron from outside to an isolated neutral gaseous atom in its lowest energy state (i.e. ground state) to convert it into gaseous anion.* Thus electron affinity of an atom, M(*g*) can be defined by the following process :

$$\underset{\text{Isolated gaseous atom}}{M(g)} + e^-(g) \rightarrow \underset{\text{Gaseous anion}}{M^-(g)} + \textit{Energy released } (= -EA_1)$$

Electron affinity defined above is strictly called *first electron affinity*, since it corresponds to the addition of one electron only. Hence it is represented as $-EA_1$ where negative (minus) sign represents the release of energy.

The above process which depicts the addition of an electron to a gaseous atom is an *exothermic process*, since in the addition of an electron energy is also released.

Electron affinity is also called *electron affinity energy*. It is measured in electron volts, kilocalories or kilojoules. The values of electron affinity are shown by a negative (minus) sign which is placed before them. Negative sign represents the release of energy in the addition of an electron to M(g) atom.

Values of first electron affinity (in KJ/mole) of *s*-block elements are given below. Here minus sign indicates the release of energy (exothermic reaction) when an electron is added to an atom to convert it into an anion.

Group I A	*Group II A*
$H \xrightarrow[-72.9]{+e^-} H^-$	
$Li \xrightarrow[-59.8]{+e^-} Li^-$	$Be \xrightarrow[\approx 0]{+e^-} Be^-$

$Na \xrightarrow{+e^-} Na^-$	$Mg \xrightarrow{+e^-} Mg^-$
-52.9	≈ 0
$K \xrightarrow{+e^+} K^-$	$Ca \xrightarrow{+e^+} Ca^-$
-48.9	≈ 0
$Rb \xrightarrow{+e^-} Rb^-$	$Sr \xrightarrow{+e^-} Sr^-$
-46.9	≈ 0

It may be seen that EA values of alkali metals are decreasing when we move from Li to Rb. It may also be seen that the EA values of the elements of group II A are practically zero. This is because of the fact that *ns* orbitals of the valence shell of these elements are completely-filled and hence the addition of an extra electron from outside to these atoms is not possible.

12. Heats of atomisation. Heats of atomisation of the elements of group IA and group II A (in KJ/mole) are given below :

Group I A	*Group II A*
Li	Be
163.6	327
Na	Mg
104.2	147
K	Ca
83.2	178
Rb	Sr
79.5	164
Cs	Ba
75.7	177

In case of the elements of group IA the values fall when we pass from Li to Cs. Thus the metallic bond in Li has maximum strength while the same in Cs has minimum strength.

The heat of atomisation of Be is much higher than that of other elements of group II A which have almost similar values. This shows that metallic bond strength in Be atom is maximum.

It may also be seen that the heats of atomisation increase when we pass from group IA to group IIA. Thus the metallic bond strength in case of the elements of group IIA is greater than that of the elements of group IA. This also explains why the elements of group II A are harder than those of group IA.

13. Hardness. Elements of group IA (alkali metals) are soft and hence can be cut with a knife while those of group II A (alkaine earth metals) are harder. The greater hardness of akaline earth metals is due to the fact that the metallic bonding in alkaline earth metals is stronger than that in the alkali metals, because the alkali metals have one s-electron per atom while alkaline earth

metals have two *s*-electrons per atom. The greater hardness of the elements of group II A can also be explained on the basis of the fact that the elements of group II A have higher values of heat of automisation than those of the elements of group IA.

14. Reducting property. The reducing property of an element depends on the magnitude of its ionisation energy. An element with lower value of ionisation energy can easily lose electron(s) and hence can act as a good reducing agent. Thus an element with lower value of ionisation energy will be a stronger reducing agent than the element with higher ionisation energy. Now since all the *s*-block elements have low ionisation energy values, all these elements are good reducing agents. Again since the ionisation energies of these elements decrease down the group and increase along the period, the reducing property of these elements increases on going down the group and decreases as we move along the period from group IA to group II A.

The reducing property of these elements in solution is measured by the magnitude of their standard reduction potential value (E° value) of the system:

$$M^+ + e^- \rightarrow M \text{ (Group IA)}$$

$$M^{2+} + 2e^- \rightarrow M \text{ (Group II A)}$$

If we make an observation of the electrochemical series, we find that the species having negative E° value, *i.e.*, the species lying below hydrogen in the electrochemical series, show a strong tendency to lose electron(s) to undergo oxdiation and hence these are strong reducing agents. E° values of s-block elements as given below :

Group IA (Alkali metals)	*Group IIA (Alkaline earth metals)*
$Li^+ + e^- \rightarrow Li$, $E° = -3.04$ V	$Be^{2+} + 2e^- \rightarrow Be$, $E° = -1.85$ V
$Na^+ + e^- \rightarrow Na$, $E° = -2.71$ V	$Mg^{2+} + 2e^- \rightarrow Mg$, $E° = -2.37$ V
$K^+ + e^- \rightarrow K$, $E° = -2.92$ V	$Ca^{2+} + 2e^- \rightarrow Ca$, $E° = -2.87$ V
$Rb^+ + e^- \rightarrow Rb$, $E° = -2.92$ V	$Sr^{2+} + 2e^- \rightarrow Sr$, $E° = -2.89$ V
$Cs^+ + e^- \rightarrow Cs$, $E° = -2.9$ V	$Ba^{2+} + 2e^- \rightarrow Ba$, $E° = -2.90$ V

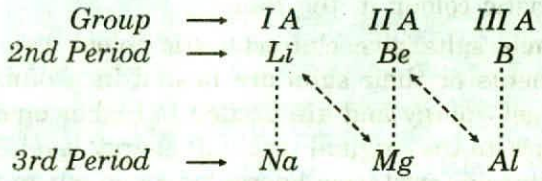
show that these values are negative and quite high, and, therefore, *s*-block elements are strong reducing agents. Again it is known that with the decrease of E° values (*i.e.* as E° values becomes more negative), the tendency of species to lose electrons to undergo oxidation increases and hence the reducing power of the species also increases.

Now among the alkali metals since Li has the minimum E° value (*i.e.* Li has maximum negative E° value), it is the strongest reducing agent among all the alkali metals.

Among alkaline earth metals, since E° values are decreasing (*i.e.* E° values are becoming more and more negative) from Be to Ba, the reducing power of these metals is also increasing in the same direction, *i.e.*, Be with maximum E° value (*i.e.* with minimum negative E° value) is the weakest reducing agent, while Ba which has minimum E° value (*i.e.* maximum negative E° value) is the strongest reducing agent.

When we compare the E° values of alkali metals with those of alkaline earth metals, we find that E° values increase on moving from group IA to group IIA (*i.e.* E° values becomes less negative). Due to this increase in E° values, alkaline earth metals are weaker reducing agents than alkali metals.

15. Diagonal relationship. The *s*-block elements of *2nd* period show similarities in properties with the elements which are situated diagonally opposite to them in *3rd* period. For example Li (Group IA, Period = *2nd*) shows similar properties with Mg (Group IIA, Period = *3rd*) and Be (Group IIA, Period = *2nd*) shows similarities with Al (Group IIIA, Period = *3rd*)



The two elements like Li and Mg or Be and Al showing similarities in properties are called diagonal neighbour or diagonal pair. The across-the-street similarity in properties existing between the two elements of a diagonal pair is known as diagonal relationship. Both the elements of each diagonal pair differ significantly in many properties from the other members of their own sub-groups. Rather they show many pronounced similarities with the elements situated diagonally opposite to them. Why the two elements of a given diagonal pair show diagonal relationship has been explained on the basis of the concept of eleotronegativity and polarisation of ions.

16. Hydration of ions. Ions of *s*-block elements are extensively hydrated in aqueous solutions. The degree of hydration of an ion depends on its size. The smaller the size of an ion, the greater is the degree of its hydration. Thus since the size of the ions increases from top to bottom in a group of *s*-block elements, the degree of hydration decreases down the group from Li^+ to Cs^+ (Group I A) and from Be^{2+} to Ba^{2+} (Group IIA) as shown below :

$$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+ \text{ (Group IA)}$$

$$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} \text{ (Group IIA)}$$

The decrease in the degree of hydration from Li^+ to Cs^+ and from Be^{2+} to Ba^{2+} as shown above is also confirmed by the fact that the heats of hydration ($-\Delta H_{hyd}$) of these ions also decrease in the same order :

M^+ ions :	Li^+	Na^+	K^+	Rb^+	Cs^+
Heat of hydration (ΔH_{hyd}) (*KJ/mole*) :	514.7	405.9	322.2	292.9	54.4
M^{2+} ions :	Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Heat of hydration (ΔH_{hyd}) (*KJ/mole*)	2406	1929	1632	1485	1276

It is because of the decrease of degree of hydration from Li^+ to Cs^+ and from Be^{2+} to Ba^{2+} that :

(*i*) The radii of these ions in water decrease in the order :

$Li^+(aq) > Na^+(aq) > K^+(aq) > Rb^+(aq) > Cs^+(aq)$ (Group IA)

$Be^{2+}(aq) > Mg^{2+}(aq) > Ca^{2+}(aq) > Sr^{2+}(aq) > Ba^{2+}(aq)$ (Group IIA)

(*ii*) The mobility of these ions in an electric field increases in the order :

$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ (Group IA)

$Be^{2+} < Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$ (Group IIA)

The above order of mobility explains why the electrical conductance of Cs^+ salts is the highest while that of Li^+ salts is the lowest.

17. Flame colouration. When *s*-block elements or their salts are heated in a bunsen flame, they give characteristic colour in the flame.

Why the *s*-block elements or their salts give characteristic colour can be explained as follows. When the elements or their salts are heated in a bunsen flame, the electrons of the elements get energy and are excited to higher energy levels. When these electrons come back to the original (ground) energy level, the energy absorbed by them during excitation (excitation energy) is given out in the form of light which appears in the visible region of the spectrum. Thus the following characteristic colours are given :

Li	Na		K	Rb Cs	
Crimson	Yellow		Violet	Violet	
Be	Mg	Ca	Sr	Ba	Ru
—	—	Brick red	Crimson	Apple green	Crimson

Since Be and Mg are smaller atoms, the electrons in these atoms are more strongly bound to the nucleus and hence are not excited by the energy of the flame to higher energy levels. Thus these elements do not give any colour in bunsen flame.

18. Action of air—Formation of oxides. These elements have a strong affinity for oxygen and tarnish quickly in air because they form a film of their oxide on their surface. The reactivity of the elements increases on moving down the group and decreases in a period from group IA to group II A. Thus the reactivity of alkaline earth metals (Group II A) towards O_2 is less than that of alkali metals (Group I A).

19. Action of water—Formation of hydroxides. These elements vigorously decompose H_2O with the formation of metallic hydroxide and liberation of H_2. The reaction with water increases on moving down the group and decreases as we move from group I A to group II A.

20. Action of hydrogen—Formation of hydrides. The elements combine with H_2 to form hydrides. The ease of formation of hydrides decreases on proceeding down the group as well as on moving from group I A to group II A.

21. Action of halogen—Formation of halides. All the metals combine directly with halogens at appropriate temperatures forming halides of MX (Group I A) and MX_2 (Group II A) type. Metals of group II A combine at higher temperatures.

Characteristics of p-Block Elements

1. Size of atoms or ions. Size of an atom of *p*-block elements decreases on moving from left to right in a period while the same increases on descending a group (see Table 3.10). As already said, the size of an ion is expressed as ionic radius. Ionic radii, like atomic radii, also decrease on moving from left to right in a period and increase on moving down the group (See Table 3.10).

Table 3.10. Covalent radii (in Å) of p-block elements. The values shown for the positive or negative oxidation states given in parentheses are ionic radii.

Group→ / Period↓	III A	IV A	V A	VI A	VII A	Zero
2	B 0.82 0.20 (+3) —	C 0.77 0.15 (+4) 2.60 (–4)	N 0.75 0.11 (+5) 1.71 (–3)	O 0.73 0.09 (+6) 1.40 (–2)	F 0.72 0.07 (+7) 1.36 (–1)	Ne 0.71 — —
3	Al 1.18 0.50 (+3) —	Si 1.11 0.41 (+4) 2.71 (–1)	P 1.06 0.34 (+5) 2.12 (–3)	S 1.02 0.29 (+6) 1.84 (–2)	Cl 0.99 0.26 (+7) 1.81 (–1)	Ar 0.98 — —
4	Ga 1.26 0.62 (+3) 1.13 (+1)	Ge 1.22 0.53 (+4) 0.93 (+2)	As 1.20 0.47 (+5) 2.22 (–3)	Se 1.16 0.42 (+6) 1.98 (–2)	Br 1.14 0.39 (+7) 1.95 (–1)	Kr 1.12 — —
5	In 1.44 0.81 (+3) 1.32 (+1)	Sr 1.41 0.71 (+4) 1.12 (+2)	Sb 1.40 0.62 (+5) 2.45 (–3)	Te 1.36 0.56 (+6) 2.21 (–2)	I 1.33 0.50 (+7) 2.16 (–1)	Xe 1.31 — —
6	Tl 1.48 0.95 (+3) 1.40 (+1)	Pb 1.47 0.84 (+4) 1.20 (+2)	Bi 1.46 0.74 (+5) 1.20 (+3)	Po 1.46 — —	At 1.45 — —	Rn — — —

2. Ionisation energies. First ionisation energy of *p*-block elements are given in Table 3.11 from which it can be seen that these values generally increase on moving from left to right in a period and decrease on descending the group.

The increase in the period is not uniform *i.e.* there are certain elements which show irregular trends. For example, in *2nd* period Be and N have higher ionisation energy values than their next neighbours namely B and O. Similarly in *3rd* period Mg and P have higher values than Al and S A detailed explanation

Table 3.11. First ionisation energies (in KJ/mole) of p-block elements.

Group→ / Period ↓	III A	IV A	V A	VI A	VII A	Zero
2	B 800.6	C 1086.4	N 1402.3	O 1314.0	F 1681.0	Ne 2080.7
3	Al 577.6	Si 786.5	P 1011.8	S 999.6	Cl 1251.1	Ar 1520.5
4	Ga 578.8	Ge 762.2	As 944.0	Se 940.9	Br 1139.9	Kr 1350.7
5	In 558.3	Sn 708.6	Sb 831.6	Te 869.3	I 1008.4	Xe 1170.4
6	Tl 589.3	Pb 715.5	Bi 703.3	Po 812.0	At —	Rn 1037.0

for this abnormal behaviour shown by Be, N, Mg and P has been given in the chapter on *Periodic Properties*. (Chapter No 4.)

3. Electropositive (or metallic or basic) character of the elements and the nature of their oxides. Electropositive character of an element depends on the magnitude of its ionisation energy. With the increase of ionisation energy, the metallic character of the elements decreases. Thus :

(*i*) Since the ionisation energy of *p*-block elements increases on moving from left to right in a period, the metallic character of the elements decreases. For example the elements lying at the extreme right of each period (*i.e.* halogens) show minimum electropositive character and hence are non-metals.

(*ii*) Since the ionisation energy of *p*-block elements decreases on descending a group, the metallic character of these elements increases in the same direction. The successive increase of metallic character of the elements on descending a group is particularly apparent in groups IV A, V A and VI A which begin with non-metals namely C, N and O and end with metals namely Pb, Bi and Po respectively.

The metallic elements of *p*-block give basic oxides (*e.g.* PbO_2, Bi_2O_3), metalloids give amphoteric oxides (*e.g.* GeO_2, As_2O_3, Sb_2O_3) while non metallic elements give acidic oxides (*e.g.* CO_2, P_4O_{10}, SO_3, Cl_2O_7). The variation of acidic/basic nature of these oxides in the periodic table depends on the metallic (electropositive) character of the element forming the oxide. With the decrease of the metallic character of the elements on moving across a period, the oxides of the elements of the same period become more and more acidic in the same direction. For example the oxides of the elements of 3*rd* period become more and more acidic when we proceed from Al_2O_3 to Cl_2O_7.

Group :	III A	IVA	V A	VI A	VII A
Oxides :	Al_2O_3 Amphoteric	SiO_2 Acidic	P_4O_{10} More acidic	SO_3 More acidic	$C1_2O_7$ Most acidic
Asidic nature :		*—Acidic nature increasing →*			

With the increase of the metallic character of the elements, on descending a group, the oxides of the elements of the same group become more and more basic (*i.e.* less and less acidic) in the same direction. For example the oxides of MO_2 type of the elements of group IV A become more and more basic (*i.e.* less and less acidic) from CO_2 to PbO_2 as shown below :

$\underbrace{CO_2,\ SiO_2,}_{\text{Acidic}}$ $\underbrace{GeO_2,\ SnO_2,}_{\text{Amphoteric}}$ $\underset{\text{Basic}}{PbO_2}$

—Basic character increasing →

Similarly the oxides of M_2O_3 type of the elements of group VA become more and more basic (*i.e.* less and less acidic) from N_2O_3 to Bi_2O_3 as shown below :

$\underbrace{N_2O_3,\ P_2O_3,}_{\text{Acidic}}$ $\underbrace{As_2O_3,\ Sb_2O_3,}_{\text{Amphoteric}}$ $\underset{\text{Basic}}{Bi_2O_3}$

—Basic character increasing →

4. Electronegativity. Since the electropositive character of *p*-block elements, as we have seen above, decreases on moving in a period and increases down the group, electronegativity which is opposite of electropositive character will show opposite periodic variation, *i.e.* the electronegativity of *p*-block elements decreases down the group and increases in a period as is evident from the values given in Table 3.12.

Table 3.12. Electronegativity values (Pauling's values) of p-block elements.

Group→ / Period↓	III A	IV A	V A	VI A	VII A	Zero
2	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne –
3	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar –
4	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 2.9
5	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 2.6
6	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn –

5. Oxidation states and inert electron pair effect. The lighter elements of *p*-block like those of *2nd* and *3rd* period show a variety of oxidation states, both positive and negative, as shown below :

Group	III A	IV A	V A	VI A	VII A
Elements of 2nd period :	B	C	N	O	F
Positive oxidation states :	+3	+4	+5	–	–
Negative oxidation states :	–	–4	–3	–2	–1
Elements of 3rd period :	Al	Si	P	S	Cl
Positive oxidation states :	+3	+4	+5	+6	+7
Negative oxidation states :	–	–4	–3	–2	–1

It may be seen that on moving from left to right in each period the positive oxidation states increase while the negative oxidation states decrease.

Some of the heavier elements of *p*-block like those of groups III A (Ga, In, Tl), IV A (Ge, Sn, Pb), V A (As, Sb, Bi) and VI A (Te, Po) show two oxidation states. These oxidation states differ from each other by two units. The higher oxidation state for most of the elements is equal to their group number, G while the lower one is equal to (G–2) as shown below :

III A (ns^2p^1) *G = 3*	*IV A* (ns^2p^2) *G = 4*	*V A* (ns^2p^3) *G = 5*	*VI A* (ns^2p^4) *G = 6*
–	–	–	
–	–	–	
Ga	Ge	As	
+1, +3	+2, +4	+3, +5	
In	Sn	Sb	Te
+1, +3	+2, +4	+3, +5	+4. +6
Tl	Pb	Bi	Po
+1, + 3	+2, +4	+3, +5	+2, +4

Group number oxidation state, G (*i.e.* higher oxidation state) is obtained when all the *ns* and *np* electrons from ns^2p^x configuration of *p*-block elements (x = 1, 2, 3 and 4 for the elements of groups IIIA, IVA, VA and VIA respectively) are lost, while the lower oxidation state equal to (G—2) is obtained when only *np*-electrons are lost and the *ns*-electron pair, due to its extra stability, remains inert, *i.e.*, it is not lost. Such a pair of *ns*-electrons is called **inert electron pair** and the effect caused by it is known as **inert pair effect**.

How the concept of inert electron pair can be used to explain the two oxidation states (*i.e.* electrovalencies) of the elements given above can be shown by considering the following examples :

(a) Electrovalencies of Ga = + 1 and + 3. In chemical combinations Ga (Z = 31) atom which has $4s^2p^1$ as its valence-shell configuration initially loses its $4p^1$ electron, forming Ga^+ ion and thus shows an electrovalency of +1. In Ga^+ ion $4s^2$ electron pair remains inert due to its extra stability and hence does not participate in bonding. This $4s^2$ electron pair is called *inert electron pair*. If the $4s^2$ electron pair participates in bonding, both the electrons of $4s^2$ pair are lost

by Ga^+ ion and Ga^{3+} ion is formed. Thus the variable electrovalencies of +1 and +3 of Ga atom are explained.

$$\underset{(2,\,8,\,18,\,4s^2.4p^1)}{Ga^\circ} \xrightarrow[(-1e^-)]{4p^1 \text{ electron lost}} \underset{(2,\,8,\,18,\,4s^2)}{Ga^{1+}} \xrightarrow[(-2e^-)]{4s^2 \text{ electrons lost}} \underset{(2,\,8,\,18)}{Ga^{3+}}$$

$$\underset{(O.S. = 0)}{} \qquad \underset{(O.S. = +1)}{} \qquad \underset{(O.S. = +3)}{}$$

Here O.S. indicates the oxidation state of the atom or ion as the case may be.

(b) *Electrovalencies of Tl = + 1 and +3.* These are explained as follows :

$$\underset{(2,\,8,\,18,\,32,\,18,\,6s^2.6p^1)}{Tl^\circ} \xrightarrow[(-1e^-)]{6p^1 \text{ eletron lost}} \underset{(2,\,8,\,18,\,32,\,18,\,6s^2)}{Tl^{1+}} \xrightarrow[(-2e^-)]{6s^2 \text{ electrons lost}} \underset{(2,\,8,\,18,\,32,\,18)}{Tl^{3+}}$$

$$\underset{(O.S. = 0)}{} \qquad \underset{(O.S. = +1)}{} \qquad \underset{(O.S. = +3)}{}$$

(c) *Electrovalencies of Sn = +2 and +4.* These are explained as follows :

$$\underset{(2,\,8,\,18,\,18,\,5s^2.5p^2)}{Sn^\circ} \xrightarrow[(-2e^-)]{5p^2 \text{ electrons lost}} \underset{(2,\,8,\,18,\,18,\,5s^2)}{Sn^{2+}} \xrightarrow[(-2e^-)]{5s^2 \text{ electrons lost}} \underset{(2,\,8,\,18,\,18)}{Sn^{4+}}$$

$$\underset{(O.S. = 0)}{} \qquad \underset{(O.S. = +2)}{} \qquad \underset{(O.S. = +4)}{}$$

(d) *Electrovalencies of As = +3 and +5.* These are explained as follows :

$$\underset{(2,\,8,\,18,\,4s^2.4p^3)}{As^\circ} \xrightarrow[(-3e^-)]{4p^3 \text{ electrons lost}} \underset{(2,\,8,\,18,\,4s^2)}{As^{3+}} \xrightarrow[(-2e^-)]{4s^2 \text{ electrons lost}} \underset{(2,\,8,\,18)}{As^{5+}}$$

$$\underset{(O.S. = 0)}{} \qquad \underset{(O.S. = +3)}{} \qquad \underset{(O.S. = +5)}{}$$

In general the variable electrovalency in these elements is due to the presence of ns^2 inert electron pair. The inertness of ns^2 electrons is found only (*i*) when the ns^2-electrons are in *4th* or higher principal quantum number, and (*ii*) when their loss does not give a species with a noble gas configuration.

A partial explanation of the inert electron pair effect is given by the fact that the outer ns^2 electrons penetrate to some extent the 18-electron shell immediately below them [*i.e.* $(n-1)s^2p^6d^{10}$ electrons]. ns^2-electrons are, thus, less effectively screened from the attractive power of the nucleus and so are nearer to the nucleus and hence are more strongly held to the atom. As a consequence the energy required to remove these ns^2-electrons is very high and cannot be compensated by the energy released even on additional bond formation.

The inert electron pair effect increases as we move down a group. For example this effect increases as we move from Ge to Pb through Sn (Group IV A) (Ge < Sn < Pb), indicating that this effect is not much marked in Ge compounds. In order to show how this effect changes the properties of the elements we can consider the elements of group IV A. In this group the first two elements namely C and Si uniformly show +4 oxidation state while the remaining three elements *viz.* Ge, Sn and Pb show both +2 and +4 oxidation states. Now since the inert electron pair effect in Ge, Sn and Pb is in the order : Ge <Sn < Pb, stability of M^{2+} (divalent ions) and M^{4+} (tetravalent ions) ions is in the order :

$$\boxed{\begin{array}{l} \mathbf{Ge^{2+} < Sn^{2+} < Pb^{2+}} \\ \mathbf{Ge^{4+} > Sn^{4+} > Pb^{4}}, \end{array}}$$

while that of M^{2+} and M^{4+} ions of the same element is in the order :

$$Ge^{2+} < Ge^{4+}$$
$$Sn^{2+} < Sn^{4+}$$
$$Pb^{2+} >> Pb^{4+}$$

The above order clearly shows that Ge^{2+} compounds are *unstable* and hence can easily be oxidised to Ge^{4+} compounds. In other words Ge^{2+} compounds are *strong reducing agents* while Ge^{4+} compounds are *stable*.

$$\underset{\text{Unstable (Reduced form, } i.e. \text{ reducing agent)}}{Ge^{2+}} - 2e^- \xrightarrow{\text{Oxidation}} \underset{\text{Stable (Oxidised form, } i.e. \text{ oxidising agent)}}{Ge^{4+}}$$

Similarly Sn^{2+} compounds are also *unstable* and hence can easily be oxidised to Sn^{4+} compounds. In other words Sn^{2+} compounds (*e.g.* SnO, $SnCl_2$) are *reducing agents* while Sn^{4+} compounds are *stable* and *covalent*.

$$\underset{\text{Unstable (Reduced form } i.e. \text{ reducing agent)}}{Sn^{2+}} - 2e^- \xrightarrow{\text{Oxidation}} \underset{\text{Stable covalent (Oxidised form, } i.e. \text{ oxidising agent)}}{Sn^{4+}}$$

Now since Pb shows the maximum inert electron pair effect, Pb^{2+} ion is much more stable than Pb^{4+} ion as shown above *i.e.* Pb^{4+} compounds are unstable and hence can easily be reduced to Pb^{2+} compounds. In other words Pb^{4+} compounds (*e.g.* PbO_2, $PbCl_4$) are *powerful oxidising agents* while Pb^{2+} compounds are *stable* and *ionic*.

$$\underset{\text{Unstable (Oxidised form } i.e. \text{ oxidising agent)}}{Pb^{4+}} + 2e^- \xrightarrow{\text{Reduction}} \underset{\text{Stable and ionic (Reduced form } i.e. \text{ reducing agent)}}{Pb^{2+}}$$

6. Electron affinity. Electron affinity values (EA values) of *p*-block elements are given in Table 3.13. Minus sign indicates the release of energy while plus sign indicates the absorption of energy.

From these values the following points may be noted :

(*i*) On moving from left to right in a period, EA values increase. However, there are certain elements in each period which have abnormal values. For example in 2*nd* period N and Ne have abnormal values. Similarly in 3*rd* period P and Ar have abnormal values. The abnormal values of N (2*nd* period) and P (3*rd* period) have been explained on the basis of the extra stability associated with their half-filled 2*p* (in N) and 3*p* (in P) orbitals. Being extraordinarily stable these orbitals are not able to accept the extra electron. Hence these elements have comparatively smaller EA values. On the basis of extra stability of ns^2p^6 configuration of Ne and Ar, their zero values can be explained.

Table 3.13. Electron affinity values (in KJ/mole) of p-block elements

Group→ / Period↓	III A	IV A	V A	VI A	VII A	Zero
1						$He \xrightarrow{+e^-} He^-$ ~ 0
2	$B \xrightarrow{+e^-} B^-$ −23	$C \xrightarrow{+e^-} C^-$ −122	$N \xrightarrow{+e^-} N^-$ −20.1	$O \xrightarrow{+e^-} O^-$ −141; $O \xrightarrow{+2e^-} O^{2-}$ +780	$F \xrightarrow{+e^-} F^-$ −322	
3	$Al \xrightarrow{+e^-} Al^-$ −44	$Si \xrightarrow{+e^-} Si^-$ −120	$P \xrightarrow{+e^-} P^-$ −74	$S \xrightarrow{+e^-} S^-$ −200.4; $S \xrightarrow{+2e^-} S^{2-}$ +590	$Cl \xrightarrow{+e^-} Cl^-$ −348.7	$Ar \xrightarrow{+e^-} Ar^-$ ~ 0
4	$Ga \xrightarrow{+e^-} Ga^-$ −36	$Ge \xrightarrow{+e^-} Ge^-$ −116	$As \xrightarrow{+e^-} As^-$ −77	$Se \xrightarrow{+e^-} Se^-$ −195; $Se \xrightarrow{+2e^-} Se^{2-}$ +420	$Br \xrightarrow{+e^-} Br^-$ −324.5	$Kr \xrightarrow{+e^-} Kr^-$ ~ 0
5	$In \xrightarrow{+e^-} In^-$ −34	$Sn \xrightarrow{+e^-} Sn^-$ −121	$Sb \xrightarrow{+e^-} Sb^-$ −101	$Te \xrightarrow{+e^-} Te^-$ −190.1	$I \xrightarrow{+e^-} I^-$ −295	$Xe \xrightarrow{+e^-} Xe^-$ ~ 0

(*ii*) On moving down the group, EA values go on decreasing as is evident from these values for (*a*) C, Si and Ge (Group IV A) (*b*) S, Se and Te (Group VI A) (*c*) O, S and Se for two electrons (Group VI A) and (*d*) Cl, Br and I (Group VII A). However, EA values of some of the elements of 2*nd* period are lower than the EA values of the elements lying just below them in 3*rd* period. For example B < Al, N < P, < O < S and F < Cl. The lower values of the elements of 2*nd* period are explained by saying that, due to the smaller size of the atoms of the elements of 2*nd* period, the addition of an extra electron to these atoms produces high electron density round the resulted anions. This high electron density increases the repulsion between the electrons (called electron—electron repulsion) already present in the relatively compact 2*p* orbital of the 2*nd* shell of these atoms and the electron being added. Due to this electron—elctron repulsion, the atoms of the elements of 2*nd* period show lesser tendency to attract the extra electron from outside and hence lower value of electron affinity for these elements.

7. Oxidising and reducing property. The oxidising property of an element depends on the magnitude of its electron affinity. An element with higher value of electron affinity can easily accept electron(s) and hence can act as a good oxidising agent. Thus an element with higher value of electron affinity will be a stronger oxidising agent than the element with lower value of electron affinity. Now since electron affinity decreases on descending a group and increases along

the period, the oxidising property of p-block elements decreases on descending the group and increases from left to right across the period. Thus the halogens which lie at the extreme right of the periodic table and have high values of electron affinity are strong oxidising agents.

The reducing property of an element depends on the magnitude of its ionisation energy. An element with lower value of ionisation energy can easily lose electron(s) and hence can act as a good reducing agent. Thus an element with lower value of ionisation energy will be a stronger reducing agent than the element with higher ionisation energy. Now since some of the *p*-block elements have low values of ionisation energy, they are good reducing agents. Again since the ionisation energies of these elements decrease down the group and increase along the period, the reducing property of *p*-block elements increases on going down the group and increases as we move along the period from group III A to group VII A.

The oxidising and reducing property of these elements in solution is measured by the magnitude of their standard reduction potential (E° values).

If we make an observation of electrochemical series, we find that some of the elements have positive E° values while others have negative E° values. The elements with positive E° values, *i.e.*, the elements lying above hydrogen in the series have a strong tendency to gain electrons to undergo reduction and hence they are strong oxidising agents. For example the non-metals like F_2, Cl_2, Br_2, I_2 and O_2 which have positive E° values are all strong oxidising agents. With the decrease of E value of a given element the tendency of that element to gain electrons to undergo the reduction decreases and hence the oxidising power of that element also decreases. For example among the non-metals mentioned above, F_2, which has the maximum E° value is the strongest oxidising agent while O_2 which has the lowest E° value is the weakest oxidising agent. Thus the oxidising power of these non-metals is in the order :

$$F_2 > Cl_2 > Br_2 > I_2 > O_2,$$

since E° values are also decreasing in the same order as shown below :

$F_2 + 2e^- \rightarrow 2F^-$,	$E° = +2.85V$	E° values decreasing ↓
$Cl_2 + 2e^- \rightarrow 2Cl^-$,	$E° = +1.36V$	
$Br_2 + 2e^- \rightarrow 2Br^-$,	$E° = +1.06V$	
$I_2 + 2e^- \rightarrow 2I^-$,	$E° = +0.53V$	
$O_2 + 2H^+ + 2e^- \rightarrow 2OH^-$,	$E° = +0.40V$	Oxidising power decreasing ↓

The elements with negative E° values *i.e.* the elements lying below hydrogen in the electrochemical series, have a strong tendency to lose electrons to undergo oxidation and hence they are strong reducing agents. For example both Al and Sn have negative E° values and hence are strong reducing agents.

$$Al^{3+} + 3e^- \rightarrow Al, \quad E° = -1.67V$$

$$Sn^{2+} + 2e^- \rightarrow Sn, \quad E° = -0.14V$$

With the decrease of E° value of a given element (*i.e.* as E° value becomes more negative), the tendency of that element to lose electrons to undergo oxidation increases and hence the reducing property of that element also increases. For example Al whose E° value is lower (*i.e.* E° value of Al is more negative) than

that of Sn (*i.e.* E° value for Sn is less negative), Al is a stronger reducing agent as compared to Sn.

8. Diogonal relationship. Boron which is a *p*-block element and is present in the *2nd* period of the periodic table shows similarities in properties with silicon which is situated diagonally opposite to it in 3rd period. This type of across-the-street similarity in properties existing between B and Si is called diagonal relationship. This relationship can be explained on the basis of the concept of electronegativity and polarisation of ions.

9. Flame colouration. None of the *p*-block elements or its salt gives characteristic colour in the bunsen flame, when it is heated in it. The reason is that excitation energy given out by the electrons, when they come back to the original (ground) energy level, does not appear in the vissible region of the spectrum.

10. Formation of hydrides. Many of the elements of *p*-block form hydrides. The stability of the hydrides of the elements of a given group decreases as we descend the group. For example the stability of the hydrides of group VA decreases from NH_3 to BiH_3.

$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$

—Stability decreases →

Again we know that, since the groups IV A, V A and VI A begin with non-metals (C, N and O) and end with metals (Pb, Bi and Po), the hydrides of non-metals are more stable than those of metals.

The aqueous solution of these hydrides show acidic character which increases from top to bottom in a group. For example the acidic nature of the hydrides *viz.*, HF, HCl, HBr and HI in aqueous solution increases from HF to HI.

$$HF < HCl < HBr < HI$$

—Acidic character increases →

11. Formation of halides. *p*-block elements also form halides. The covalent character of the halides containing different cations belonging to the *same period* of the periodic table but same halide ion increases from left to right in the period. For example in *2nd* period BCl_3 is partially ionic while CCl_4 is covalent. Similarly in *5th* period $SbCl_3$ is partly ionic whereas $TeCl_4$ is essentially covalent. The increase in covalent character from left to right in a period is due to the increase of the polarising power of the cation to polarise the anion due to the decrease of the size of the cations from left to right in a period (*One of the Fajans's rules*).

The covalent character of the halides containing the same cation but different anions belonging to the same group increases from top to bottom in a group. For example AlF_3 has essentially ionic character. $AlCl_3$ has intermediate character while $AlBr_3$ and AlI_3 have essentially covalent character.

AlF_3	$AlCl_3$	$AlBr_3$, AlI_3
Essentially ionic character	Intermediate character	Essentially covalent character

—Covalent character increasing →

The increase in covalent character from top to bottom is due to the increase of the polarisability of the anions or due to the increase of the size of the anions from top to bottom in a group (*One of the Fajans's rules*).

Characteristics of d-Block Elements

1. Metallic character. All the transition elements are metals, since the number of electrons in the outermost shell is very small; being equal to 2. They are hard, malleable and ductile and possess high tensile strength. They exhibit all the three types of structures : face centred cubic (*fcc*), hexagonal close packed (*hcp*), and body centered cubic (*bcc*). Metals of VIII and IB groups are softer and more ductile than other metals.

It appears that covalent and metallic bonding both exist in the atoms of transition metals. *The presence of unfilled d-orbitals favours covalent bonding.*

These metals are good conductors of heat and electricity.

2. Melting and boiling points. These are very heavy metals and have high melting and boiling points. The last member of each series, *i.e.*, Zn, Cd, and Hg have comparatively lower values. This is because these metals have *completely filled d-orbitals with no unpaired electrons* (n) as is evident from their valence-shell electronic configurations given below :

$$Zn \rightarrow 3d^{10}\ 4s^2 \text{ with } n = 0$$

$$Cd \rightarrow 4d^{10}\ 4s^2 \text{ with } n = 0$$

and

$$Hg \rightarrow 5d^{10}\ 6s^2 \text{ with } n = 0$$

3. Atomic volumes and densities. The atomic volumes of the metals are much lower than those of alkaline earth metals. As the inner orbitals get filled, the increased nuclear charge pulls the electronic cloud inward. The atomic volume, therefore, decreases. The decrease in atomic volume increases the density. Accordingly, the densities of transition elements are very high as compared to those of the metals of groups I A and II A.

4. Ionisation potentials. The ionisation potential values of most of the *d*-block elements lie between those of *s* and *p*-block elements. *Thus d-block elements are less electropositive than the s-block elements and more so than p-block elements.* Consequently, these elements *do not form ionic compounds so readily as s-block elements* (alkali and alkaline earth metals). In general, compounds with metals in lower valency state are ionic and others are covalent. The tendency to form ionic compounds decreases as the size of the atom increases.

5. Low reactivity. These elements have low reactivity and this tendency is most pronounced in Au and Pt which are, therefore, called noble metals. Their low reactivity is due to the high values of their melting and boiling points, heats of sublimation and ionisation potential.

6. Colour. The transition metals usually form coloured compounds. If an ion is coloured, it means that it absorbs light of a particular colour whose wavelength is in the visible region *viz.* λ = 400–7000 Å and reflects (*i.e.* transmits) the light which has the colour complementary to that of the absorbed light. This complementary colour which is actually the colour of the reflected light is the colour of the substance.

The colour is due to the promotion of unpaired *d*-electrons from one energy level to the other in *d* level. In general the atoms, ions or molecules which have

unpaired electrons in *d*-orbitals (*i.e.* partially filled *d*-orbitals) are coloured because it is only in case of such orbitals that the promotion of unpaired *d*-electrons to higher energy level within the same sub-shell is possible. On the other hand, the atoms. ions or molecules having all the electrons paired in *d*-orbitals (*i.e.* completely filled *d*-orbitals) or no electrons (*i.e.* empty *d*-orbitals) are colourless, since in case of such *d*-orbitals there are no vacant *d*-orbitals to accept the electrons promoted to them. Thus, if n is the number of unpaired electrons, then the atoms, ions or molecules having $n = 0$ are *colourless* while those having $n = 1, 2, \ldots$ are *coloured* as shown below :

Ion	*Configuration*	*n*	*Colour*
Sc^{3+}	$3d^0$	0	Colourless
Ti^{4+}	$3d^0$	0	Colourless
Cu^{+}	$3d^{10}$	0	Colourless
Zn^{2+}	$3d^{10}$	0	Colourless
Ti^{3+}	$3d^1$	1	Purple
V^{3+}	$3d^2$	2	Green
Cr^{3+}	$3d^3$	3	Green
Fe^{2+}	$3d^6$	4	Pale green or faintly green
Fe^{3+}	$3d^5$	5	Yellow

7. Variable valency. Transition elements show variable valency. This is because in their case the core or kernel left after their atom loses valency electron is unstable and tends to lose one or more electrons further. For example, in case of iron we can represent the two valencies as below :

Fe 26 = 2, 8, 14, 2

Fe^{2+} 24 = 2, 8, 14, (Core)

The core being unstable loses one more electron to give Fe^{3+} ion

Fe^{3+} 23 = 2, 8, 13

8. Catalytic properties. Most of transition metals, their alloys and compounds are used as catalysts. Some common examples are: Pt, Ni, Fe, Cr, V_2O_5 etc. Catalytic power of these metals is due to either the use of their *d*-orbitals or due to the formation of interstitial compounds which absorb and activate the reacting substances.

9. Magnetic properties. Most of the transition metals are paramagnetic. *i.e.*, they tend to set themselves with their lengths parallel to the field, when they are placed between the magnetic poles. Thus these are attracted into magnetic field. This property is due to *the presence of unpaired electrons in d-orbitals.* Thus, the transition elements having all the electrons paired are diamagnetic. Fe and Co are ferromagnetic and can be magnetised.

10. Tendency to form complexes. The cations of transition elements have a great tendency to form complexes with several ligands. This tendency is due to the following reasons :

(*a*) The cations are relatively very small in size and hence have high positive density which makes it easy for the cations to accept the lone pairs of electrons from the ligands.

(*b*) The cations have *vacant* $(n-1)d$ orbitals which are of appropriate energy to accept lone pairs of electrons from the ligands for bonding with them.

11. Formation of interstitial compounds. Small non-metallic atoms (*e.g.* H, B, C, N, etc.) are able to fit into the interstitial sites of transition metal lattices to form the compounds which are called **interstitial compounds.** These have variable composition and cannot, therefore, be expressed by simple formulae, *i.e.* these are *non-stoichiometric.*

Characteristics of f-Block Elements

The characteristics of *f*-block elements have been discussed in chapter 50.

Questions with Answers

Q.1 Give different steps used for writing the valence-shell electronic configuration of a given element.

Ans. The technique used for writing the valence-shell configuration of an element consists of the following steps :

(*i*) Find out the difference between the atomic number of the given element and that of the noble gas present in the previous period. For example the difference between Pb_{82} (6*th* period) and Xe_{54} (5*th* period) = 82 – 54 = 28. Let this difference be denoted by x. This difference denotes the number of electrons present in the valence-shell of the given element.

(*ii*) Now find out the sub-shells which are to be filled up with x electrons.

(*iii*) Then fill up these sub-shells with x electrons. This gives the valence-shell configuration of the given element.

Example. *Find out the valence-shell configuration of the atom of the following elements : Te_{52}, La_{57}, Pr_{59}, Pt_{78}, Pb_{82}, Ac_{89}, U_{92} and Ha_{105}.*

Solution : (*i*) **Te_{52} :** This element is present in 5*th* period and $x = Te_{52} - Kr_{36} = 16$.

Hence valence-shell configuration of Te_{52} (5*th* period) = $5s^2\ 4d^{10}\ 5p^4 = 4d^{10}\ 5s^2\ 5p^4$

(*ii*) **La_{57} :** Here $x = La_{57} - Xe_{54} = 3$

Hence valence-shell configuration of Li_{57} (6*th* period) = $6s^2 5d^1 = 5d^1 6s^2$

(*iii*) **Pr_{59} :** Here $x = Pr_{59} - Xe_{54} = 5$

$\therefore$ Expected valence-shell configuration of Pr_{59} (6*th* period) = $6s^2 5d^1 4f^2$

The actual valence-shell configuration is $6s^2 5d^0 4f^3 = 4f^3 5d^0 6s^2$

(*iv*) **Pt_{78} :** Here $x = Pt_{78} - Xe_{54} = 24$

Expected valence-shell configuration of Pt_{78} (6*th* period) = $6s^2 5d^1 4f^{14} 5d^7 = 6s^2 5d^8 4f^{14}$

But the actual valence-shell configuration = $6s^1 5d^9 4f^{14} = 4f^{14} 5d^9 6s^1$

(*v*) **Pb_{82} :** Here $x = Pb_{82} - Xe_{54} = 28$

$\therefore$ Valence-shell configuration of Pb_{82} (*6th* period) = $6s^2 5d^1 4f^{14} 5d^9 6p^2 = 6s^2 5d^{10} 4f^{14} 6p^2 = 4f^{14} 5d^{10} 6s^2 6p^2$

(*vi*) **Ac_{89} :** Here $x = Ac_{89} - Rn_{86} = 3$

$\therefore$ Valence-shell configuration of Ac_{89} (*7th* period) = $7s^2 6d^1 = 6d^1 7s^2$

(*vii*) **U_{92} :** Here $x = U_{92} - Rn_{86} = 6$

$\therefore$ Valence-shell configuration of U_{92} (*7th* period) = $7s^2 6d^1 5f^3 = 5f^3 6d^1 7s^2$

(*viii*) **Ha_{105} :** Here $x = Ha_{105} - Rn_{86} = 19$

$\therefore$ Valence-shell configuration of Ha_{105} (*7th* period) = $7s^2 6d^1 5f^{14} 6d^2 = 7s^2 6d^3 5f^{14} = 5f^{14} 6d^3 7s^2$

Q.2 What are different steps for writing the electronic configuration of an ion.

Ans. In order to write the electronic configuration of a given ion proceed as follows :

(*i*) Write the complete or valence-shell configuration of the element from which the ion has been derived.

(*ii*) (*a*) In case of a cation, remove the electron(*s*), equal to the number of positive charges on the cation from the outer-most shell of the parental atom. This gives the electronic configuration of the cation.

(*b*) In case of an anion, add electron(*s*), equal to the number of negative charges on the anion to the outer-most shell of the parental atom. This gives the configuration of the anion.

Examples. *(i) Write the complete and valence-shell configuration of Pb^{2+} ion (Z = 82)*

Solution : Configuration of Pb-atom (Z = 82) = $[Xe]_{54}\ 6s^2 5d^{10} 4f^{14} 6p^2 = [Xe]_{54}\ 4f^{14} 5d^{10} 6s^2 6p^2$

$\therefore$ Configuration of Pb^{2+} ion = $[Xe]_{54}\ 4f^{14} 5d^{10} 6s^2$

Valence-shell configuration of Pb-atom = $4f^{14} 5d^{10} 6s^2 6p^2$

$\therefore$ Valence-shell configuration of Pb^{2+} ion = $4f^{14} 5d^{10} 6s^2$

(ii) Write down complete and valence-shell configuration of O^{2-} ion (Z = 8)

Solution : Configuration of O-atom (Z = 8) = $[He]_2\ 2s^2 2p^4$

$\therefore$ Configuration of O^{2-} ion = $[He]_2 2s^2 2p^6$

Valence-shell configuration of O-atom (Z = 8) = $2s^2 2p^4$

$\therefore$ Valence-shell configuration of O^{2-} ion = $2s^2 2p^6$

Q.3 Give IUPAC nomenclature of the elements having Z > 100 (Superheavy elements).

Ans. Superheavy elements are trans-fermium elements, *i.e.*, superheavy elements are those which are placed after fermium, Fm (Z = 100) in the long form of periodic table. In other words these are the elements whose atomic number is greater than 100. For IUPAC nomenclature of these elements the following rules have been proposed.

(*i*) **Roots.** The names have three roots which indicate the three digits of the atomic number of the elements. In the last root-*ium* is added. The roots and symbols for the digit are given below :

Digit :	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Root :	**nil**	**un**	**bi**	**tri**	**quad**	**pent**	**hex**	**sept**	**oct**	**enn**
Symbol :	**n**	**u**	**b**	**t**	**q**	**p**	**h**	**s**	**o**	**e**

(*ii*) **Symbol.** The symbol for the element has three letters derived from the roots.

(*iii*) **Name.** The name of the element starts with a small letter but the symbol of the element starts with a capital letter. The names are written as a complete word.

The above rules are clear from the following examples. In the IUPAC name column, a hyphen (-) has been put between each part of the names to make them more understandable. Present names and symbols of the elements with atomic number 101 to 109 have also been given. Present names of other elements have not been fixed as yet.

Atomic number	*IUPAC name*	*Symbol*	*Present name*	*Symbol*
101	un-nil-unium	Unu	Mendelevium	Md
102	un-nil-bium	Unb	Nobelium	No
103	un-nil-trium	Unt	Lawrencium	Lr
104	un-nil-quadium	Unq	Rutherfordium	Rf
105	un-nil-pentium	Unp	Dubnium	Db
106	un-nil-hexium	Unh	Seaborgium	Sg
107	un-nil-septium	Uns	Bohrium	Bh
108	un-nil-octium	Uno	Hassium	Hs
109	un-nil-ennium	Une	Meitnerium	Mt
110	un-un-nilium	Uun	—	—
111	un-un-unium	Uuu	—	—
112	un-un-bium	Uub	Eka mercury	—
113	un-un-trium	Uut	—	—
114	un-un-quadium	Uuq	—	—
115	un-un-pentium	Uup	—	—
116	un-un-hexium	Uuh	—	—
117	un-un-septium	Uus	—	—
118	un-un-octium	Uuo	—	—
119	un-un-ennium	Uue	—	—
120	un-bi-nilium	Ubn	—	—
130	un-tri-nilium	Utn	—	—
140	un-quad-nilium	Uqn	—	—
150	un-pent-nilium	Upn	—	—

Q.4 Give the electronic configuration of elements according to their position in different periods of long form of periodic table.

Ans. The electronic configurations of the elements based on their position in the long form of periodic table are given below :

1st period (n = 1)		
Orbitals being filled	**Atomic number and symbol**	**Electronic configuration**
↑ 1s ↓	1 (H)	$1s^1$
	2 (He)	$1s^2$ or $[He]_2$
2nd period (n = 2)		
Orbitals being filled	**Atomic number and symbol**	**Electronic configuration**
↑ 2s ↓	3 (Li)	$[He]_2\ 2s^1$
	4 (Be)	$[He]_2\ 2s^2$
↑ 2p ↓	5 (B)	$[He]_2\ 2s^2p^1$
	6 (C)	$[He]_2\ 2s^2p^2$
	7 (N)	$[He]_2\ 2s^2p^3$
	8 (O)	$[He]_2\ 2s^2p^4$
	9 (F)	$[He]_2\ 2s^2p^5$
	10 (Ne)	$[He]_2\ 2s^2p^6$ or $1s^2$, $2s^2p^6$ or $[Ne]_{10}$
3rd period (n = 3)		
Orbitals being filled	**Atomic number and symbol**	**Electronic configuration**
↑ 3s ↓	11 (Na)	$[Ne]_{10}\ 3s^1$
	12 (Mg)	$[Ne]_{10}\ 3s^2$
↑ 3p ↓	13 (Al)	$[Ne]_{10}\ 3s^2p^1$
	14 (Si)	$[Ne]_{10}\ 3s^2p^2$
	15 (P)	$[Ne]_{10}\ 3s^2p^3$
	16 (S)	$[Ne]_{10}\ 3s^2p^4$
	17 (Cl)	$[Ne]_{10}\ 3s^2p^5$
	18 (Ar)	$[Ne]_{10}\ 3s^2p^6$ or $1s^2$, $2s^22p^6$, $3s^23p^6$ or $[Ar]_{18}$

4th period (n = 4)		
Orbitals being filled	**Atomic number and symbol**	**Electronic configuration**
↑ 4s ↓	19 (K)	$[Ar]_{18}\ 4s^1$
	20 (Ca)	$[Ar]_{18}\ 4s^2$
↑ 3d ↓	21 (Sc)	$[Ar]_{18}\ 4s^2 3d^1$ or $[Ar]_{18}\ 3d^1 4s^2$
	22 (Ti)	$[Ar]_{18}\ 4s^2 3d^2$ or $[Ar]_{18}\ 3d^2 4s^2$
	23 (V)	$[Ar]_{18}\ 4s^2 3d^3$ or $[Ar]_{18}\ 3d^3 4s^2$
	24 (Cr)	$[Ar]_{18}\ 4s^1 3d^5$ or $[Ar]_{18}\ 3d^5 4s^1$
	25 (Mn)	$[Ar]_{18}\ 4s^2 3d^5$ or $[Ar]_{18}\ 3d^5 4s^2$
	26 (Fe)	$[Ar]_{18}\ 4s^2 3d^6$ or $[Ar]_{18}\ 3d^6 4s^2$
	27 (Co)	$[Ar]_{18}\ 4s^2 3d^7$ or $[Ar]_{18}\ 3d^7 4s^2$
	28 (Ni)	$[Ar]_{18}\ 4s^2 3d^8$ or $[Ar]_{18}\ 3d^8 4s^2$
	29 (Cu)	$[Ar]_{18}\ 4s^1 3d^{10}$ or $[Ar]_{18}\ 3d^{10} 4s^1$
	30 (Zn)	$[Ar]_{18}\ 4s^2 3d^{10}$ or $[Ar]_{18}\ 3d^{10} 4s^2$
↑ 4p ↓	31 (Ga)	$[Ar]_{18}\ 4s^2 3d^{10} 4p^1$ or $[Ar]_{18}\ 3d^{10} 4s^2 4p^1$
	32 (Ge)	$[Ar]_{18}\ 4s^2 3d^{10} 4p^2$ or $[Ar]_{18}\ 3d^{10} 4s^2 4p^2$
	33 (As)	$[Ar]_{18}\ 4s^2 3d^{10} 4p^3$ or $[Ar]_{18}\ 3d^{10} 4s^2 4p^3$
	34 (Se)	$[Ar]_{18}\ 4s^2 3d^{10} 4p^4$ or $[Ar]_{18}\ 3d^{10} 4s^2 4p^4$
	35 (Br)	$[Ar]_{18}\ 4s^2 3d^{10} 4p^5$ or $[Ar]_{18}\ 3d^{10} 4s^2 4p^5$
	36 (Kr)	$[Ar]_{18}\ 4s^2 3d^{10} 4p^6$ or $[Ar]_{18}\ 3d^{10} 4s^2 4p^6$ or $1s^2$, $2s^2 2p^6$, $3s^2 3p^6 3d^{10}$, $4s^2 4p^6$ or $[Kr]_{36}$
5th period (n = 5)		
Orbitals being filled	**Atomic number and symbol**	**Electronic configuration**
↑ 5s ↓	37 (Rb)	$[Kr]_{36}\ 5s^1$
	38 (Sr)	$[Kr]_{36}\ 5s^2$
↑ 4d ↓	39 (Y)	$[Kr]_{36}\ 5s^2 4d^1$ or $[Kr]_{36}\ 4d^1 5s^2$
	40 (Zr)	$[Kr]_{36}\ 5s^2 4d^2$ or $[Kr]_{36}\ 4d^2 5s^2$
	41 (Nb)	$[Kr]_{36}\ 5s^1 4d^4$ or $[Kr]_{36}\ 4d^4 5s^1$
	42 (Mo)	$[Kr]_{36}\ 5s^1 4d^5$ or $[Kr]_{36}\ 4d^5 5s^1$
	43 (Tc)	$[Kr]_{36}\ 5s^2 4d^5$ or $[Kr]_{36}\ 4d^5 5s^2$
	44 (Ru)	$[Kr]_{36}\ 5s^1 4d^7$ or $[Kr]_{36}\ 4d^7 5s^1$
	45 (Rh)	$[Kr]_{36}\ 5s^1 4d^8$ or $[Kr]_{36}\ 4d^8 5s^1$
	46 (Pd)	$[Kr]_{36}\ 5s^0 4d^{10}$ or $[Kr]_{36}\ 4d^{10} 5s^0$
	47 (Ag)	$[Kr]_{36}\ 5s^1 4d^{10}$ or $[Kr]_{36}\ 4d^{10} 5s^1$
	48 (Cd)	$[Kr]_{36}\ 5s^2 4d^{10}$ or $[Kr]_{36}\ 4d^{10} 5s^2$

↑ 5p ↓	49 (In)	$[Kr]_{36}\ 5s^2 4d^{10} 5p^1$ or $[Kr]_{36}\ 4d^{10} 5s^2 5p^1$
	50 (Sn)	$[Kr]_{36}\ 5s^2 4d^{10} 5p^2$ or $[Kr]_{36}\ 4d^{10} 5s^2 5p^2$
	51 (Sb)	$[Kr]_{36}\ 5s^2 4d^{10} 5p^3$ or $[Kr]_{36}\ 4d^{10} 5s^2 5p^3$
	52 (Te)	$[Kr]_{36}\ 5s^2 4d^{10} 5p^4$ or $[Kr]_{36}\ 4d^{10} 5s^2 5p^4$
	53 (I)	$[Kr]_{36}\ 5s^2 4d^{10} 5p^5$ or $[Kr]_{36}\ 4d^{10} 5s^2 5p^5$
	54 (Xe)	$[Kr]_{36}\ 5s^2 4d^{10} 5p^6$ or $[Kr]_{36}\ 4d^{10} 5s^2 5p^6$ or $1s^2$, $2s^2 2p^6$, $3s^2 3p^6\ 3d^{10}$, $4s^2 4p^6 4d^{10}$, $5s^2\ 5p^6$ or $[Xe]_{54}$
6th period (n = 6)		
Orbitals being filled	**Atomic number and symbol**	**Electronic configuration**
↑ 6s ↓	55 (Cs)	$[Xe]_{54}\ 6s^1$
	56 (Ba)	$[Xe]_{54}\ 6s^2$
5d	57 (La)	$[Xe]_{54}\ 6s^2 5d^1$ or $[Xe]_{54}\ 5d^1 6s^2$
↑ 4f or 5d ↓	58 (Ce)	$[Xe]_{54}\ 6s^2 5d^1 4f^1$ or $[Xe]_{54}\ 4f^1 5d^1 6s^2$
	59 (Pr)	$[Xe]_{54}\ 6s^2 4f^3$ or $[Xe]_{54}\ 4f^3 6s^2$
	60 (Nd)	$[Xe]_{54}\ 6s^2 4f^4$ or $[Xe]_{54}\ 4f^4 6s^2$
	61 (Pm)	$[Xe]_{54}\ 6s^2 4f^5$ or $[Xe]_{54}\ 4f^5 6s^2$
	62 (Sm)	$[Xe]_{54}\ 6s^2 4f^6$ or $[Xe]_{54}\ 4f^6 6s^2$
	63 (Eu)	$[Xe]_{54}\ 6s^2 4f^7$ or $[Xe]_{54}\ 4f^7 6s^2$
	64 (Gd)	$[Xe]_{54}\ 6s^2 4f^7 5d^1$ or $[Xe]_{54}\ 4f^7 5d^1 6s^2$
	65 (Tb)	$[Xe]_{54}\ 6s^2 4f^9$ or $[Xe]_{54}\ 4f^9 6s^2$
	66 (Dy)	$[Xe]_{54}\ 6s^2 4f^{10}$ or $[Xe]_{54}\ 4f^{10} 6s^2$
	67 (Ho)	$[Xe]_{54}\ 6s^2 4f^{11}$ or $[Xe]_{54}\ 4f^{11} 6s^2$
	68 (Er)	$[Xe]_{54}\ 6s^2 4f^{12}$ or $[Xe]_{54}\ 4f^{12} 6s^2$
	69 (Tm)	$[Xe]_{54}\ 6s^2 4f^{13}$ or $[Xe]_{54}\ 4f^{13} 6s^2$
	70 (Yb)	$[Xe]_{54}\ 6s^2 4f^{14}$ or $[Xe]_{54}\ 4f^{14} 6s^2$
	71 (Lu)	$[Xe]_{54}\ 6s^2 4f^{14} 5d^1$ or $[Xe]_{54}\ 4f^{14} 5d^1 6s^2$
↑ 5d ↓	72 (Hf)	$[Xe]_{54}\ 6s^2 4f^{14} 5d^2$ or $[Xe]_{54}\ 4f^{14} 5d^2 6s^2$
	73 (Ta)	$[Xe]_{54}\ 6s^2 4f^{14} 5d^3$ or $[Xe]_{54}\ 4f^{14} 5d^3 6s^2$
	74 (W)	$[Xe]_{54}\ 6s^2 4f^{14} 5d^4$ or $[Xe]_{54}\ 4f^{14} 5d^4 6s^2$
	75 (Re)	$[Xe]_{54}\ 6s^2 4f^{14} 5d^5$ or $[Xe]_{54}\ 4f^{14} 5d^5 6s^2$
	76 (Os)	$[Xe]_{54}\ 6s^2 4f^{14} 5d^6$ or $[Xe]_{54}\ 4f^{14} 5d^6 6s^2$
	77 (Ir)	$[Xe]_{54}\ 6s^2 4f^{14} 5d^7$ or $[Xe]_{54}\ 4f^{14} 5d^7 6s^2$
	78 (Pt)	$[Xe]_{54}\ 6s^1 4f^{14} 5d^9$ or $[Xe]_{54}\ 4f^{14} 5d^9 6s^1$
	79 (Au)	$[Xe]_{54}\ 6s^1 4f^{14} 5d^{10}$ or $[Xe]_{54}\ 4f^{14} 5d^{10} 6s^1$
	80 (Hg)	$[Xe]_{54}\ 6s^2 4f^{14} 5d^{10}$ or $[Xe]_{54}\ 4f^{14} 5d^{10} 6s^2$

↑ 6*p* ↓	81 (Tl)	$[Xe]_{54}\ 6s^2 4f^{14} 5d^{10} 6p^1$ or $[Xe]_{54}\ 4f^{14} 5d^{10} 6s^2 6p^1$
	82 (Pb)	$[Xe]_{54}\ 6s^2 4f^{14} 5d^{10} 6p^2$ or $[Xe]_{54}\ 4f^{14} 5d^{10} 6s^2 6p^2$
	83 (Bi)	$[Xe]_{54}\ 6s^2 4f^{14} 5d^{10} 6p^3$ or $[Xe]_{54}\ 4f^{14} 5d^{10} 6s^2 6p^3$
	84 (Po)	$[Xe]_{54}\ 6s^2 4f^{14} 5d^{10} 6p^4$ or $[Xe]_{54}\ 4f^{14} 5d^{10} 6s^2 6p^4$
	85 (At)	$[Xe]_{54}\ 6s^2 4f^{14} 5d^{10} 6p^5$ or $[Xe]_{54}\ 4f^{14} 5d^{10} 6s^2 6p^5$
	86 (Rn)	$[Xe]_{54}\ 6s^2 4f^{14} 5d^{10} 6p^6$ or $[Xe]_{54}\ 4f^{14} 5d^{10} 6s^2 6p^6$ or $1s^2$, $2s^2 2p^6$, $3s^2 3p^6 3d^{10}$, $4s^2\ 4p^6\ 4d^{10}\ 4f^{14}$, $5s^2\ 5p^6\ 5d^{10}$, $6s^2 6p^6$ or $[Rn]_{86}$
7th period (n = 7)		
Orbitals being filled	**Atomic number and symbol**	**Electronic configuration**
↑ 7*s* ↓	87 (Fr)	$[Rn]_{86}\ 7s^1$
	88 (Ra)	$[Rn]_{86}\ 7s^2$
↑ 5*f* or 6*d* ↓	89 (Ac)	$[Rn]_{86}\ 7s^2 6d^1$ or $[Rn]_{86}\ 6d^1 7s^2$
	90 (Th)	$[Rn]_{86}\ 7s^2 6d^1 5f^1$ or $[Rn]_{86}\ 5f^1 6d^1 7s^2$
	91 (Pa)	$[Rn]_{86}\ 7s^2 6d^1 5f^2$ or $[Rn]_{86}\ 5f^2 6d^1 7s^2$
	92 (U)	$[Rn]_{86}\ 7s^2 6d^1 5f^3$ or $[Rn]_{86}\ 5f^3 6d^1 7s^2$
	93 (Np)	$[Rn]_{86}\ 7s^2 6d^1 5f^4$ or $[Rn]_{86}\ 5f^4 6d^1 7s^2$
	94 (Pu)	$[Rn]_{86}\ 7s^2 5f^6$ or $[Rn]_{86}\ 5f^6 7s^2$
	95 (Am)	$[Rn]_{86}\ 7s^2 5f^7$ or $[Rn]_{86}\ 5f^7 7s^2$
	96 (Cm)	$[Rn]_{86}\ 7s^2 5f^7 6d^1$ or $[Rn]_{86}\ 5f^7 6d^1 7s^2$
	97 (Bk)	$[Rn]_{86}\ 7s^2 5f^9$ or $[Rn]_{86}\ 5f^9 7s^2$
	98 (Cf)	$[Rn]_{86}\ 7s^2 5f^{10}$ or $[Rn]_{86}\ 5f^{10} 7s^2$
	99 (Es)	$[Rn]_{86}\ 7s^2 5f^{11}$ or $[Rn]_{86}\ 5f^{11} 7s^2$
	100 (Fm)	$[Rn]_{86}\ 7s^2 5f^{12}$ or $[Rn]_{86}\ 5f^{12} 7s^2$
	101 (Md)	$[Rn]_{86}\ 7s^2 5f^{13}$ or $[Rn]_{86}\ 5f^{13} 7s^2$
	102 (No)	$[Rn]_{86}\ 7s^2 5f^{14}$ or $[Rn]_{86}\ 5f^{14} 7s^2$
	103 (Lw)	$[Rn]_{86}\ 7s^2 5f^{14} 6d^1$ or $[Rn]_{86}\ 5f^{14} 6d^1 7s^2$
↑ 6*d* ↓	104 [Rf or Ku or Unq Rutherfordium or Kurchatovium (Unnilquadium)]	$[Rn]_{86}\ 7s^2 5f^{14} 6d^2$ or $[Rn]_{86}\ 5f^{14} 6d^2 7s^2$
	105 [Ha or Db or Unp, Hahnium or Dubnium (Unnilpentium)]	$[Rn]_{86}\ 7s^2 5f^{14} 6d^3$ or $[Rn]_{86}\ 5f^{14} 6d^3 7s^2$
	106 [Sg or Unh Seaborgium (Unnihexium)]	$[Rn]_{86}\ 7s^2 5f^{14} 6d^4$ or $[Rn]_{86}\ 5f^{14} 6d^4 7s^2$

6d	107 [Ns or Bh or Uns Neilsbohrium or Bohrium (Unnilseptium]	$[Rn]_{86}\ 7s^2 5f^{14} 6d^5$ or $[Rn]_{86}\ 5f^{14} 6d^5 7s^2$
	108 [Hs or Uno Hassnium (Unniloctium)]	$[Rn]_{86}\ 7s^2 5f^{14} 6d^6$ or $[Rn]_{86}\ 5f^{14} 6d^6 7s^2$
	109 [Mt or Une Meitnerium (Unnilennium)]	$[Rn]_{86}\ 7s^2 5f^{14} 6d^7$ or $[Rn]_{86}\ 5f^{14} 6d^7 7s^2$
	110 [Uun (Ununnilium) or Ekaplatinum]	$[Rn]_{86}\ 7s^2 5f^{14} 6d^8$ or $[Rn]_{86}\ 5f^{14} 6d^8 7s^2$
	111 [Uuu (Unununium) or Ekagold]	$[Rn]_{86}\ 7s^1 5f^{14} 6d^{10}$ or $[Rn]_{86}\ 5f^{14} 6d^{10} 7s^1$
	112 [Uub (Ununbium) or Ekamercury]	$[Rn]_{86}\ 7s^2 5f^{14} 6d^{10}$ or $[Rn]_{86}\ 5f^{14} 6d^{10} 7s^2$
7p	113 [Uut (Ununtrium)]	$[Rn]_{86}\ 7s^2 5f^{14} 6d^{10} 7p^1$ or $[Rn]_{86}\ 5f^{14} 6d^{10} 7s^2 7p^1$
	114 [Uuq (Ununquadium)]	$[Rn]_{86}\ 7s^2 5f^{14} 6d^{10} 7p^2$ or $[Rn]_{86}\ 5f^{14} 6d^{10} 7s^2 7p^2$
	115 [Uup (Ununpentium)]	$[Rn]_{86}\ 7s^2 5f^{14} 6d^{10} 7p^3$ or $[Rn]_{86}\ 5f^{14} 6d^{10} 7s^2 7p^3$

Q.5 Discuss the possibility of the atom for existing in the following electronic configurations :

(*i*) $1s^2\ 2s^2\ 2p_x^1$ **(*ii*) $1s^2\ 2s^1\ 2p_x^2\ 2p_y^1\ 2p_z^1$**

(*iii*) $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1$ **(*iv*) $1s^2\ 2s^2\ 3s^2$**

Solution. (*i*) This electronic configuration is correct since it is in accordance with the rules for filling up of various orbitals.

(*ii*) This electronic configuration is wrong because it violates aufbau principle which states that an orbital with lower energy, *i.e.* 2*s* sub-shell in the present case should be completely filled before the electrons go to higher energy sub-shell, *i.e.* 2*p* in the present case.

(*iii*) This electronic configuration is not correct since it violates Hund's rule. According to this rule all the three 2*p* orbitals must have one electron each before the pairing occurs. But in the present case $2p_x$ orbital has two electrons while $2p_z$ orbital is empty.

(*iv*) This electronic configuration is wrong since after filling 2*s*-orbital, the electrons should go to 2*p*-orbital rather than 3*s*-orbital.

Q.6 Find the number of unpaired electrons present in phosphorus (atomic No. 15), chromium (atomic No. 24) and copper (atomic No. 29) after writing their orbital electronic configuration.

Solution.

Element	At. No.	Electronic configuration	No. of unpaired electrons
P	15	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$	3
Cr	24	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^5, 4s^1$	5 + 1 = 6
Cu	29	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^1$	1

Q.7 Neutral atom of an element has 2K, 8L and 5M electrons. Find out the following from the data : (a) Atomic No. (b) Total No. of s electrons (c) Total No. of p-electrons (d) No. of protons in the nucleus and (e) Valency of the element.

Solution. The electronic configuration of the element with 2K, 8L and 5M electrons will be

$$\underbrace{1s^2}_{2K} \quad \underbrace{2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2}_{8L} \quad \underbrace{3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1}_{5M}$$

(*a*)Total No. of electrons = 2 + 8 + 5 = 15

$\therefore$ Atomic No. of the element = 15

(*b*) Total no. of s-electrons = 2 + 2 + 2 = 6

(*c*) Total no. of p-electrons = 6 + 3 = 9

(*d*) Since the atom is neutral,

$\therefore$ No. of protons = No. of electrons = Atomic No. = 15

(*e*) Since the element has only three half-filled atomic orbitals, therefore, valency of the element = 3.

Q.8 Write the electronic configurations of the elements with the following atomic numbers :

3, 8, 10, 14, 17, 25, 29, and 38.

Also mention the groups of the periodic table to which they belong.

Solution.

Atomic No.	Electronic configuration	Group of periodic table
3	$1s^2\ 2s^1$	1
8	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$	16
10	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$	18
14	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^1\ 3p_y^1$	14
17	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1$	17
25	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$	7
29	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$	11
38	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 5s^2$	2

Q.9 An atom of an element contains 29 electrons and 35 neutrons. Deduce (*i*) the number of protons and (*ii*) the electronic configuration of the element.

Solution. (*i*) For neutral atom, number of protons = number of electrons = 29

(*ii*) Atomic number of the element = 29

Electronic configuration of element with Z = 29 will be $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$ or $[Ar]_{18}\ 3d^{10}\ 4s^1$

Note. No. of neutrons are needed only to find mass number.

Mass number = No. of protons + No. of neutrons

= 29 + 35 = 64

Q.10 Give the electronic configuration of the following ions :

(*i*) Cu^{2+} (*ii*) Cr^{3+} (*iii*) Fe^{2+} and Fe^{3+} (*iv*) H^- (*v*) S^{2-}

Solution. During the formation of cations, electrons are lost while in the formation of anions, electrons are added to the valence shell. The number of electrons added or lost is equal to the numerical value of the charge present on the ion. Following this general concept, we can write the electronic configurations of all the ions given in the question.

(*i*) $Cu^{2+} = {}_{29}Cu - 2e^-$

$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1 - 2e^-$

$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$

(*ii*) $Cr^{3+} = {}_{24}Cr - 3e^-$

$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1 - 3e^-$

$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

(*iii*) $Fe^{2+} = {}_{26}Fe - 2e^-$

$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2 - 2e^-$

$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$

$Fe^{3+} = {}_{26}Fe - 3e^-$

$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$

(*iv*) $H^- = {}_1H + 1e^- = 1s^1 + 1e^1 = 1s^2$

(*v*) $S^{2-} = {}_{16}S + 2e^-$

$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^1\ 3p_z^1 + 2e^-$

$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^2$

Q.11 What atoms are indicated by the following electronic configurations ?

(*i*) $1s^2\ 2s^2\ 2p^1$ (*ii*) $[Ar]\ 4s^2\ 3d^1$

Solution. (*i*) Total number of electrons in $1s^2\ 2s^2\ 2p^1 = 2 + 2 + 1 = 5$

$\therefore$ Atomic number of the element = 5

Hence the element is *Boron* (B)

(*ii*) Total number of electrons in $[Ar]\ 4s^2\ 3d^1 = 18 + 2 + 1 = 21$

$\therefore$ Atomic number of the element = 21

Hence the element is *Scandium* (Sc)

Q.12 What are the rules for finding group number of a given element ?

Ans. Following are the rules for finding out the group number of an element whose electronic configuration is given.

(*i*) If the last shell contains 1 or 2 electrons, then the group number is 1 and 2 respectively.

(*ii*) If the last shell contains more than 2 electrons, then the group number is the total number of electrons in the last shell plus 10.

(*iii*) If electrons are present in $(n-1)$ *d* orbitals in addition to those in the *ns* orbital, then the group number is equal to the total number of electrons present in the $(n-1)$ *d* orbital and *ns* orbital.

Q.13 (*a*) Find out the E.C. of P-atom in H_3PO_4.

(*b*) Which of the following two ions have the same V.S.E.C. ? Cr^{3+}, Fe^{3+}, Mn^{2+} and Co^{3+}.

(*c*) Which of the following ions have $3d^2$ as their V.S.E.C. ? Ti^{2+}, Ti^{3+}, V^{3+}, V^{4+}, Cr^{4+}, Cr^{3+}, Mn^{5+} and Mn^{2+}.

Ans. (*a*) In H_3PO_4, P-atom is present as P^{5+}.

E.C. of P^{5+} ion = E.C. of P-atom $-5e^-$

$= 1s^2, 2s^2 2p^6, 3s^2 3p^3 - 5e^-$

$= 1s^2, 2s^2 2p^6$ **(Ans.)**

(*b*) V.S.E.Cs of the given ions are : $Cr^{3+} = 3d^3$, $Fe^{3+} = 3d^5$, $Mn^{2+} = 3d^5$ and $Co^{2+} = 3d^7$. Obviously Fe^{3+} and Mn^{2+} ions have the same V.S.E.C. $(= 3d^5)$

(*c*) V.S.E.Cs of the given ions are $Ti^{2+} = 3d^2$, $Ti^{3+} = 3d^1$, $V^{3+} = 3d^2$, $V^{4+} = 3d^1$, $Cr^{4+} = 3d^2$, $Cr^{3+} = 3d^3$, $Mn^{5+} = 3d^2$ and $Mn^{2+} = 3d^5$. Obviously Ti^{2+}, V^{3+}, Cr^{4+} and Mn^{5+} ions have $3d^2$ configuration.

University Questions

1. Write a note on "Aufbau principle." *(Kanpur 2000)*
2. Explain the trends of the following properties of *p*-block elements of the periodic table : (*i*) Atomic radii (*ii*) ionisation potential (*iii*) Electronegativity (*iv*) Oxidation states. *(Kumaon 2000)*
3. (*a*) Give an account of the modern periodic table. Dicuss its advantages.
   (*b*) Write notes on (*i*) Heisenberg's uncertainty principle (*ii*) Pauli's exclusion principle. *(Kumaon 2000)*
4. Write a note on Heisenberg's uncertainty principle. *[Gauhati (General) 2000]*
5. Give in brief the general characteristics of *s*-block elements. How do the elements of ns^1 block differ from the elements of ns^2 block? *(Lucknow 2000)*
6. (*a*) Which has the lowest number of unpaired electrons? B, C, N.
   (*b*) Elements A, B and C have atomic number Z, Z +3 and Z + 6 respectively. The element A is an alkali metal. Answer the following :

(*i*) which group and block of P.T. the elements A, B and C are associated.

(*ii*) Decide the nature of the bond in the compound formed by combination of atoms of elements B and C.

(*iii*) Explain the shape of molecule formed by the combination of atoms of elements B and C.

(*iv*) Name the elements A, B and C when Z = 11, and write down their electronic configurations.

(*v*) Write down the reaction of water with compound formed by the combination of atoms of B and C. (*Avadh 2000*)

7. (*i*) Write a note on "Diagonal relationship".

(*ii*) What are *s*-block elements ? How do these elements differ *p*-block elements? Give their main characteristics. (*Lucknow 2001*)

8. Give an account of the modern periodic table. State how it is more useful than Mendeleef's periodic table ? (*Lucknow 2002*)

9. Write a note on Aufbau principle. (*Lucknow 2002*)

10. Give electronic configuration of group IA and IIA elements.(*Nagpur 2002*)

11. Write electronic configuration of Cr (24) and Cu (29). (*Nagpur 2002*)

12. (*a*) Write the electronic configuration of La(Z = 57) and Ce(Z = 58).

(*b*) What are the advantages of classifying the elements into *s, p, d* and *f* blocks in the periodic table? (*Delhi 2002*)

13. Correct the electronic configurations given below and give reasons for your answer :

(*a*) $1s^2, 2s^2\ 2p_x^2\ 2p_y^0\ 2p_z^0$ (*b*) $1s^2, 2s^2\ 2p^6, 3s^2\ 3p^4, 4p^1$

(*VBS Purvanchal 2003*)

14. On the basis of electronic configuration, which of the following ions has maximum number of unpaired electrons?

(*a*) Mg^{2+} (*b*) Ti^{3+} (*c*) V^{3+} (*d*) Fe^{2+} (*VBS Purvanchal 2003*)

15. (*a*) What is A U F B A U principle? Use this principle to explain the filling of electrons in 4s-orbital before 3d-orbitals.

(*b*) Write the most stable electronic configuration using *s, p, d* notation of atoms with atomic number 21 and 31 and decide the position of each in periodic table, indicating (*i*) The block (*ii*) The number of unpaired electrons for each. (*Rohilkhand 2003*)

16. (*a*) Elements A, B and C have atomic numbers 11, 29 and 35 respectively. Write their electronic configuration and classify them as *s, p* and *d* blocks.

(*b*) How many unpaired electrons are there in Cr^{2+} and Fe^{2+} ions? (*Rohilkhand 2003*)

17. (*a*) What is Aufbau principle? Give the sequence in which energy levels are filled. Write the electronic configuration of elements having atomic numbers 24 and 29.

(*b*) State Hund's rule of maximum multiplicity. Give suitable example.

(*c*) Write the general valence shell electronic configuration of IA and IIA group elements.

18. (*a*) Write the electronic configuration of F^-, Al^{3+}, Mn, Cu
(Given : Z of F = 9, Al = 13, Mn = 25, Cu= 29).

(*b*) What are s-block elements? Write electronic configuration of IA group elements. *(Nagpur 2003)*

(*c*) Write the general electronic configuration of IA and IIA group elements. *(Nagpur 2003)*

19. Name the element whose electronic configuration is $[Xe]_{54}\ 4f^{14}5d^{1}6s^{2}$. *(H.N. Bahuguna 2004)*

20. (*a*) Name the orbital occupied by 19*th* electron of Cr atom (Z = 21).

(*b*) If the E.C. of V(Z = 23) is [Ar] $3d^{3}4s^{2}$, write the E.C. of the next element.

(*c*) Write the E.C. of the most electronegative element. *(H.N. Bahuguna 2004)*

21. Using Aufbau principle write down the E.C. of Cr(Z = 24) atom. *(H.N. Bahuguna 2005)*

22. Write a note on Aufbau principle. *(H.N. Bahuguna 2006)*

23. Find out the outer electronic configuration of Cu(Z = 29). *(Agra 2007)*

24. How many unpaired electrons are there in Cr atom (Z = 24)? *(Purvanchal 2007)*

25. (*a*) Write the number of electrons that can be accomodated by a *p*-orbital.

(*b*) Write the number of unpaired electrons in Fe^{3+} ion. *(H.N. Bahuguna 2007)*

26. Find out the number of unpaired electrons in Mn^{2+} ion. *(Agra 2008)*

CHAPTER

4 Periodic Properties

Periodicity of Properties and Magic Number

The term periodicity of properties indicates that the elements with similar properties reappear at certain regular intervals of atomic number in the periodic table. In order to understand the concept of periodicity of properties we may consider the properties of the elements of groups I A (*Alkali metals*), zero (*Inert gases*) and VII A (*Halogens*) given below :

Periodic number	Group I A	Group zero	Group VII A
1	*H(1)*	*H(2)*	
2	*Li (3)*	*Ne (10)*	*F (9)*
3	*Na (11)*	*Ar (18)*	*Cl (17)*
4	*K (19)*	*Kr (36)*	*Br (35)*
5	*Rb (37)*	*Xe (54)*	*I (53)*
6	*Cs (55)*	*Rn (86)*	*At (85)*
7	*Fr (87)*		

The examination of the properties of these elements will show that the elements belonging to the same group have similar properties, In other words we can say that the atomic number intervals at which the elements with similar properties reappear are 2, 8, 8, 18, 18, 32 and 32, *i.e.* we have to pass 2, 8, 8, 18, 18, 32, and 32 elements before we come across an element with similar properties. *The repetition of the elements with similar properties is the order of increasing atomic number as in the periodic table is called* **periodicity of properties** and the numbers 2, 8, 8 and 32 are called **magic numbers.**

Cause of Periodicity of Properties

What is the cause of periodicity of properties, *i.e.*, why do the elements placed in the same group have similar properties ?

In order to answer this question we may consider the valence- shell electronic configurations, for example, of the elements of groups I A, zero and VII A as given on the next page.

An examination of the valence-shell electronic configurations of the elements given in the table shows that the elements showing periodicity of properties *i.e.* the elements belonging to the same group have the same valence-shell electronic configuration. Thus we see that in any group similar valence-shell electronic configurations of the elements reoccur after certain regular intervals of atomic number and it is this reoccurrence of similar valance-shell electronic configurations

of the elements at certain regular intervals of atomic number which becomes the cause of periodicity of properties.

Group I A	Group zero	Group VII A
H (1) $1s^1$	He (2) $1s^2$	
Li (3) $2s^1$	Ne (10) $2s^2p^6$	F (9) $2s^2p^5$
Na (11) $3s^1$	Ar (18) $3s^2p^6$	Cl (17) $3s^2p^5$
K (19) $4s^1$	Kr (36) $4s^2p^6$	Br (35) $4s^2p^5$
Rb (37) $5s^1$	Xe (54) $5s^2p^6$	I (53) $5s^2p^5$
Cs (55) $6s^1$	Rn (86) $6s^2p^6$	At (85) $6s^2p^5$
Fr (87) $7s^1$		

We have already said that, according to modern periodic law, the properties of the elements (i.e. atomic properties) like atomic volume, atomic and ionic radii, ionisation potential, electron affinity electronegativity etc. are periodic functions of their atomic number. Here the word *periodic* means *with the rise of atomic number of the elements in the same period or group, there is a gradual variation (i.e. increase or decrease) in a particular property of the element.* These properties depend on the electronic configuration (particularly valence-shell configuration) of the atoms of the elements. Some of such properties which are more useful to the students are: *(1) Atomic volume (2) Size of the atoms and ions (atomic and ionic radii) (3) Ionisation potential (4) Electron affinity (5) Electronegativity (6) Bond energy or bond strength (7) Polarisation of ions.*

Some Important Concepts

Before discussing the periodic properties we shall discuss some important concepts which are very useful in having a clear understanding of periodic properties. These concepts are (1) *Shielding or screening effect of the inner-shell electrons on the valence shell electron* and (2) *Effective nuclear charge*. These are discussed below.

I. Shielding or Screening Effect of Inner-shell Electrons on the Valence-shell Electron.

In a multi-electron atom the valence-shell electrons are attracted by the nucleus and also at the same time repelled by the electrons present between the nucleus and the valence-shell electrons (*i.e.* inner shell electrons) (See Fig. 4.1). Thus the nucleus exerts an attractive force on the valence-shell electrons while the inner-shell electrons exert a repulsive force on the valence-shell electron. The combined

effect of these two forces is that the actual force exerted by the nucleus on the valence-shell electron is partially decreased or weakened by the presence of repulsive force exerted by the inner-shell electrons on the valence-shell electrons. Thus the valence-shell electrons experience less attraction or pull towards tile nucleus. *The decrease in the attractive force exerted by the nucleus on the valence-shell electron, which is obviously due to the presence of the electrons lying between the nucleus and valence-shell electrons,* (called intervening electrons) *is called* **shielding effect** or **screening effect.** In other words, the intervening electrons screen or shield the valence-shell electrons from the nucleus.

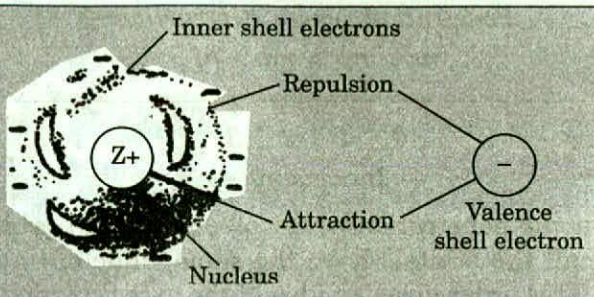


Fig. 4.1. The valence-shell electrons experience less attraction from the nucleus due to the presence of inner-shell electrons–called shielding or screening effect of inner shell electrons.

Factors Affecting the Magnitude of Shielding Effect

Following are the important factors on which the magnitude of shielding effect caused by the inner-shell electrons on the valence-shell electron depends.

***(i)* No. of inner-shell electrons or inner shells.** Greater is the number of inner-shell electrons or inner shells, greater is the magnitude of shielding effect caused by the inner electrons on the valence- shell electron. Thus as we move down a group, the number of inner-shells or inner shell electrons increases and hence the shielding effect also increases. For example in the elements of group IA, with the increase of the number of inner shells and electrons in them, the shielding effect caused by these electrons on the valence-shell electron also increases from Li to Cs as shown below :

Elements of group I A	Electronic configuration	No. of electrons in the inner shells	No. of inner shells	Order of shielding effect
Li	2, 1	2		↓
Na	2, 8, 1	2+8 = 10	2	Increasing
K	2, 8, 8, 1	2+8+8 = 18	3	↓
Rb	2, 8, 18, 8, 1	2+8+18+8 = 36	4	
Cs	2, 8, 18, 18, 8, 1	2+8+18+18+8 = 54	5	

***(ii)* Type of the orbital occupied by the electrons.** From the shapes of electron charge clouds of orbitals we find that s-electrons spend most of their time nearer the nucleus while *p*-electrons belonging to the same shell spend most

of their time farther away from the nucleus. This, in other words means that an electron in an *s*-orbital of a given shell penetrates the nucleus more strongly than that in a *p*-orbital of the same shell. Thus for a given shell the penetration power (or penetration effect) of an *ns* electron is greater than that of an *np* electron (*ns* > *np*). The penetration power of an *np* electron is greater than that of an *nd* electron (*np* > *nd*) which has higher penetration power than an *nf* electron (*nd* > *nf*). Thus the penetration power of an electron in ns, np, nd and *nf* orbitals of a given *nth* shell is in the following order : (The values of *l* for all the orbitals are also given)

$$\text{— Penetration power decreasing} \rightarrow$$

$$ns > np > nd > nf$$

Value of n :	*—same—*
Value of l :	*0 1 2 3*

$$\text{— Increasing} \rightarrow$$

Thus we see that the penetration power of *s, p, d* and *f* orbitals belonging to the same shell (*i.e.*, all the orbitals have the same value of *n*) decreases, as the value of *l* increases. This order gives an idea of the extent of binding the electrons of various orbitals to the nucleus. The above order indicates that s-electrons are more tightly bound with the nucleus than *p*-electrons which, in turn, are bound more tightly than *d*-electrons and so on. Due to greater penetration power of s-electron, it screens the nucleus more effectively than a *p*-electron and a p-electron screens the nucleus more effectively than a d-electron and so on. Thus the order in which an electron in the intervening *ns, np, nd* and *nf* orbitals screens the nucleus (*i.e. nuclear charge*) is as :

$$\text{— Screening power decreasing} \rightarrow$$

$$ns > np > nd > nf$$

This order shows that for the same shell, the *s*-electrons are more effective in shielding the nuclear charge than *p*-electrons, the *p* electrons are more effective than *d* electrons and *d* electrons are more effective than *f* electrons. This order also means that the electrons present in *d* or *f* orbitals are more effectively shielded than those in *s* or *p*-orbitals by the inner shell electrons. Thus an electron in *np* orbital is more effectively screened than the *ns* electron by the inner-shell electrons. This becomes evident when we consider Be and B atoms. 2*p* electron of B atom ($1s^2$, $2s^2$, $2p^1$) is more effectively shielded by 1*s* and 2*s* electrons while the 2*s* electron of Be atom ($1s^2$, $2s^2$) is not effectively shielded by the 1*s* electrons and the second 2*s* electron.

An electron present in *nth* orbital is more effectively screened by the electrons in the (*n*–1)*th* orbital while the same electron is *more effectively* shielded by the other electron present in the same orbital. For example in Li atom ($1s^2$, $2s^1$) $2s^1$ electron is *more effectively* screened by the two electrons present is 1*s* orbital while in He atom ($1s^2$) one of the two electrons in 1*s* orbital in not effectively screened by the other electron present in the same orbital *i.e.* 1*s* orbital.

Applications of Shielding Effect

(*i*) The concept of shielding effect has been used to explain why the ionisation potential values of the elements of a given group decrease on descending the group.

(*ii*) This concept has also been used to explain that when we proceed from an inert gas to an alkali metal, a large decrease in the value of ionisation potential is observed.

II. Effective Nuclear Charge (Z_{eff}) : Consequence of Shielding Effect

It is due to the shielding effect of the inner electrons on the outer-electrons that the valence electron experiences less attractive pull from the nucleus. The decrease in the attractive force reduces the nuclear charge, Z represented by the atomic number of the element. This decreased nuclear charge is called **effective nuclear charge** and is represented by Z_{eff}. It is given by the relation :

$$\boxed{Z_{eff} = Z - \sigma} \quad ...(i)$$

Here σ is a constant which is called **screening constant.** This constant is a measure of the extent to which the other electrons in an atom are able to screen the nucleus from the chosen electron. Thus :

Effective nuclear charge, Z_{eff} is defined as the actual nuclear charge, Z minus the screening effect caused by the electrons intervening between the nucleus and the outer electrons.

Greater is the number of electrons intervening between the nucleus and the outer electrons, more will be the magnitude of σ and hence the magnitude of effective nuclear charge, Z_{eff} will decrease.

By putting the value of σ in relation (*i*) the value of Z_{eff} for an element can be calculated. The value of σ can be calculated from *Slater's rules*. Thus we see that as a result of shielding effect, the effective nuclear charge, Z_{eff} that a valence shell electron experiences is not exactly the nuclear charge, Z.

Calculation of σ and Z_{eff} by Slater's Rules.

The value of σ and hence that of Z_{eff} can be calculated by using slater's rules. According to these rules the value of σ for a given electron is estimated as follows:

(1) Write down the complete electronic configuration of the element and divide the electrons into the following orbital groups starting from the inside of the atom. (1*s*); (2*s*, 2*p*); (3*s*, 3*p*); (3*d*); (4*s*, 4*p*); (4*d*); (4*f*); (5*s*, 5*p*); (6*s*, 6*p*) etc.

(2) Now select the electron for which the value of σ is to be calculated. For this calculation add up the contributions to σ for the other electrons according to the following rules :

Type of electron	Contribution to σ for each electron of this type
(*a*) All electrons in groups outside the electron chosen	0
(*b*) All other electrons in the same group as chosen one	0.35 (or 0.30 for 1*s* electron)

(*c*) All electrons in shell immediately inside 0.85

(*d*) All electrons further inside 1.00

In order to understand the above rules let us consider the following examples.

Example 1. *Calculate the effective nuclear charge experienced by the 4s electron in potassium atom.*

Solution. The electronic configuration of K atom (Z = 19) is $1s^2$, $2s^2p^6$, $3s^2p^6$, $4s^1$ and this atom has 4 shells in all. Evidently the magnitude of Z_{eff} experienced by 4*s* electron is given by :

$Z_{eff} = Z - \sigma$

= 19–[(0.85 × No. of electrons in 3*rd* shell) + (1.00 × Total number of electrons in the inner shells)]

= 19 – [0.85 × 8 + 1.00 × (2 + 8)]

or $Z_{eff} = 2.20$

This is the effective nuclear charge experienced by 4*s* electron in potassium atom.

Example 2. *Calculate the effective nuclear charge of the last electron in an atom whose configuration is $1s^2$, $2s^2p^6$, $3s^2p^5$.*

Solution. Evidently the atomic number, Z of the element having this configuration is 17 and it has three shells in all

$\therefore Z_{eff} = Z - \sigma$

= 17 – [(0.35 × No. of electrons left in 3*rd* shell) + (0.85 × No. of electrons in 2*nd* shell) + (1.00 × Total number of electrons in the inner shell)]

= 17 – [(0.35 × 6) + (0.85 × 8) + (1 × 2)

= 17 – 10.2 = 6.8

Variation of Screening Effect or σ in the Periodic Table.

The magnitude of screening constant is a measure of the extent to which the electrons intervening between the nucleus and the valance-shell shield valence-shell electron from the nucleus. Thus *greater is the magnitude of σ, greater is the amount of shielding effect caused by the intervening electrons on the valence-shell electron.*

Since σ increases on descending a group and on proceeding from left to right in a period of the periodic table, *the magnitude of screening effect also increases in the same direction on proceeding from top to bottom of a group and from left to right in a period.* This has been shown for the elements of group IA and 2*nd* period (Z = atomic number).

Elements of group IA	:	Li	Na	K	Rb	Cs			
Value of Z	:	3	11	19	37	55			
Value of σ	:	1.7	8.8	16.80	34.80	52.80			
Elements of 2nd period	:	Li	Be	B	C	N	O	F	Ne
Value of Z	:	3	4	5	6	7	8	9	10
Value of σ	:	1.70	2.05	2.40	2.75	3.10	3.45	3.80	4.15

Thus the variation of screening effect or σ in a period and a group can be shown as depicted in Fig. 4.2.

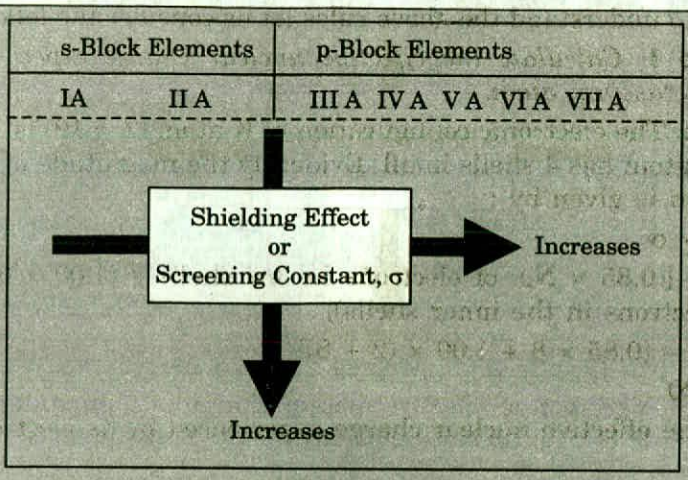


Fig. 4.2. Variation of shielding effect or screening constant, σ in the periodic table.

Variation of Effective Nuclear Charge in the Periodic Table.

(*a*) **In period.** The values of effective nuclear charge of different elements, a calculated by Slater's rules, show that *they increase when we proceed from left to right in a period of the periodic table.*

When we proceed from loft to right across a period, the atomic number (*i.e.* nuclear charge) increases by one at each next element and the next element has one more valence electron with its effective repulsion equal to 0.35 and therefore the effective nuclear charge increases by 1–0.35 = 0.65 from member to member. Consequently the effective nuclear charge of each next atom is greater by 0.65 than the previous atom. For example

Elements of 2nd period	: Li	Be	B	C	N	O	F	Ne
Effective nuclear charge	: 1.30	1.95	2.60	3.25	3.90	4.55	5.20	5.85
Elements of 3rd period	: Na	Mg	Al	Si	P	S	Cl	Ar
Effective nuclear charge	: 2.20	2.85	3.50	4.15	4.80	5.45	6.10	6.75

(*b*) **In group.** *When we descend a group, the values of effective nuclear charge remain almost the same* as is evident from these values for the elements of group IA and IIA. Li = 1.30, Na = 2.20, K = 2.20, Rb 2.20, Cs = 2.20, Fr = 2.20 (Group IA – Li is a typical case); Be = 1.95, Mg = 2.85, Ca = 2.85 and so on (Group IIA).

The variation of effective nuclear charge in the periodic table has been shown in Fig. 4.3.

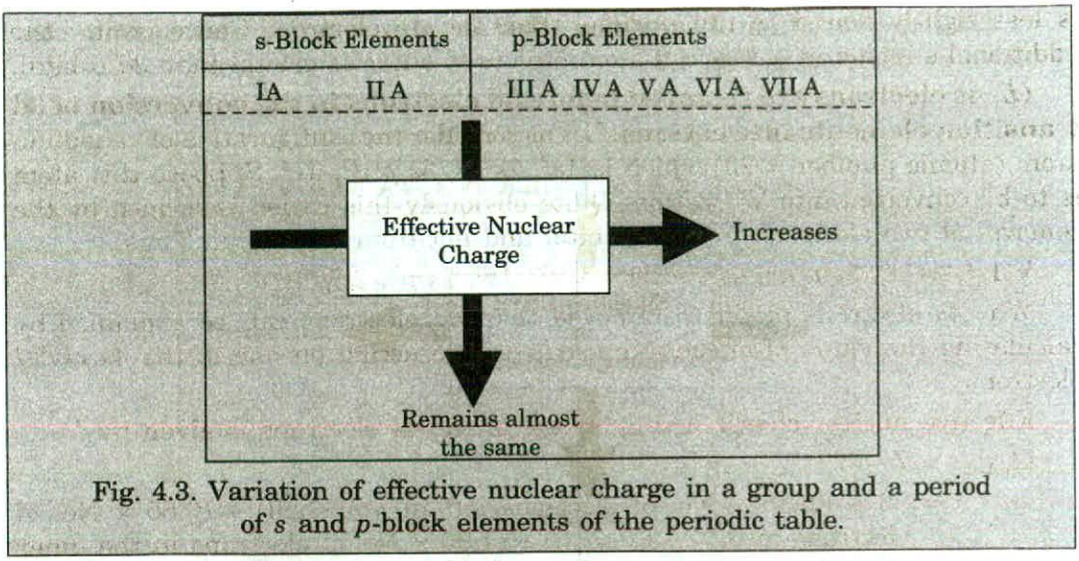


Fig. 4.3. Variation of effective nuclear charge in a group and a period of *s* and *p*-block elements of the periodic table.

Applications of Effective Nuclear Charge

A number of facts can be explained on the basis of the concept of effective nuclear charge. Some examples are given below :

(*i*) 4*s* orbital is filled before 3*d* orbitals. We know that the configuration of argon (atomic number, Z = 18) is $1s^2$, $2s^2p^6$, $3s^2p^6$ while the configuration of potassium (Z = 19) is obtained by adding the extra electron to 4*s* orbital and not to 3*d* orbitals, giving $1s^2$, $2s^2p^6$, $3s^2p^6$, $4s^1$ configuration to this atom. Why 4*s* orbital is filled before 3*d* orbitals can be explained as follows on the basis of the concept of effective nuclear charge.

Suppose potassium can have any of the following two configurations :

(*a*) $1s^2$, $2s^2p^6$, $3s^2p^6d^0$, $4s^1$ (4*s* orbital is filled before 3*d* orbitals)

(*b*) $1s^2$, $2s^2p^6$, $3s^2p^6d^1$. $4s^0$ (3*d* orbitals are filled before 4*s* orbital)

Now let us calculate the effective nuclear charge acting on 4*s* electron [configuration (*a*)]

$[Z_{eff}]_{4s}$ = 19 –[(0.85 × No. of electrons in (*n* –1)th shell) + (1.00 × Total number of electrons in the inner shells)]

= 19–[(0.85 × 8) + (1.00 × 10)]

= 2.20

Now let us calculate the effective nuclear charge acting on 3*d* electron [configuration (*b*)]

$[Z_{eff}]_{3d}$ = 19 – 1.00 × Total number of inner electrons (*i.e.* $1s^2$, $2s^2p^6$, $3s^2p^6$ electrons)

= 19 – 1 × 18

= 1

Lower value of effective nuclear charge acting on 3d electron as compared to that acting on 4s electron makes it evident that in potassium atom 3d electron

is less tightly bound to the nucleus than the 4*s* electron. Consequently the additional electron in potassium atom prefers to enter 4*s* orbital than 3*d* orbital.

***(ii)* 4s electrons are removed before 3d electrons in the conversion of 3d transition elements into cations.** Let us consider the configuration of vanadium atom (atomic number = 23) which is $1s^2$, $2s^2p^6$, $3s^2p^6d^3$, $4s^2$. Suppose this atom is to be converted into V^{2+} cation. Quite obviously this cation is formed by the removal of two electrons from 4*s* orbital and not from 3*d* orbital. Thus :

$$V(1s^2, 2s^2p^6, 3s^2p^6d^3, 4s^2) - 2e^- \rightarrow V^{2+}(1s^2, 2s^2p^6, 3s^2p^6d^3)$$

Why 4*s* electrons prefer to removed than 3*d* electrons can be explained by calculating the value of effective nuclear charge acting on one of the 4*s* or 3*d* electrons.

Effective nuclear charge acting on one of the 4*s* electrons is given by :

$$[Z_{eff}]_{4s} = Z - \sigma$$

= 23 − [(0.35 × No. of electrons left in *nth* shell) + (0.85 × No. of electrons in $(n-1)th$ shell) + (1.00 × No. of electrons in the inner shells)]

$$= 23 - [0.35 \times 1 + 0.85 \times 11 + 1 \times 10]$$

$$= 23 - 19.70$$

$$= 3.30$$

Effective nuclear charge acting on one of the 3*d* electrons is given by :

$$[Z_{eff}]_{3d} = Z - \sigma$$

= 23 − [(0.35 × No. of electrons left in 3*d* orbitals) + (1.00 × Total number of electrons in the inner orbitals *i.e.* in 1*s*, 2*s*, 2*p*, 3*s* and 3*p* orbials)]

$$= 23 - (0.35 \times 2 + 1 \times 18)$$

$$= 23 - 18.70$$

$$= 4.30$$

Greater value of effective nuclear charge acting on one of the 3*d* electrons as compared to that acting on one of the 4*s* electrons in vanadium atom makes it evident that in this atom 3*d* electrons are more tightly bound to the nucleus than the 4*s* electrons. Consequently in the conversion of vanadium atom into V^{2+} cation the electrons to be removed are 4*s* electrons and not 3*d* electrons.

***(iii)* The successive ionisation potentials I_1, I_2, I_3, etc. of an atom are in the following order :**

$$I_1 < I_2 < I_3 < .....$$

This order can well be explained on the basis of effective nuclear charge concept.

***(iv)* In going from left to right in a period of s-and p-block elements atomic and ionic radii decrease with the increase of atomic number.** This can be explained on the basis of effective nuclear charge.

***(v)* A cation is smaller in size than its parent atom.** It has been explained on the basis of the concept of effective nuclear charge (see subsequent page).

(vi) An anion is bigger in size than its parent atom. It has been explained on subsequent pages.

Atomic Volume

Atomic volume is defined as the volume in c.c. occupied by one gram atom of the element in the solid state and hence is commonly called gram atomic volume. It is obtained by dividing the atomic weight of the element by its density; *i.e.*

$$\textit{Atomic volume} = \frac{\textit{Atomic weight}}{\textit{Density}}$$

In other words atomic volume is the volume in c.c. occupied by 6.023×10^{23} atoms of an element (Avogadro's number). Thus the atomic volumes of the elements should be the volumes occupied by the same number of the atoms. The volume occupied by a single atom may be obtained by dividing gram atomic volume with Avogadro's number of atoms. However, this conclusion is not very accurate due to certain variable factors which, in turn, depend on the manner in which the atoms are packed in various elements. It is a common practice to use the term gram atomic volume for volume per atom for assignment of sizes of atoms.

Lothar Meyer plotted the atomic volumes (in c.c.) of different elements against their atomic numbers and obtained a graph shown n Fig. 4.4. An inspection of this graph shows that the curve has five complete well-defined loops and a fraction of the sixth, it may be seen that the maxima of the curve are occupied by the alkali metals (most electropositive elements) while the minima are occupied by C (At. number, Z = 6), Al (Z = 13), Ni (Z = 28), Rh (Z = 45) and Os (Z = 76). It may also be seen that when we proceed further from alkali metals, the atomic volumes on each occasion first decrease and then increase again till a sharp maximum is reached at the next alkali metal. Not only alkali metals but all the elements belonging to the same group lie at corresponding positions on the curve.

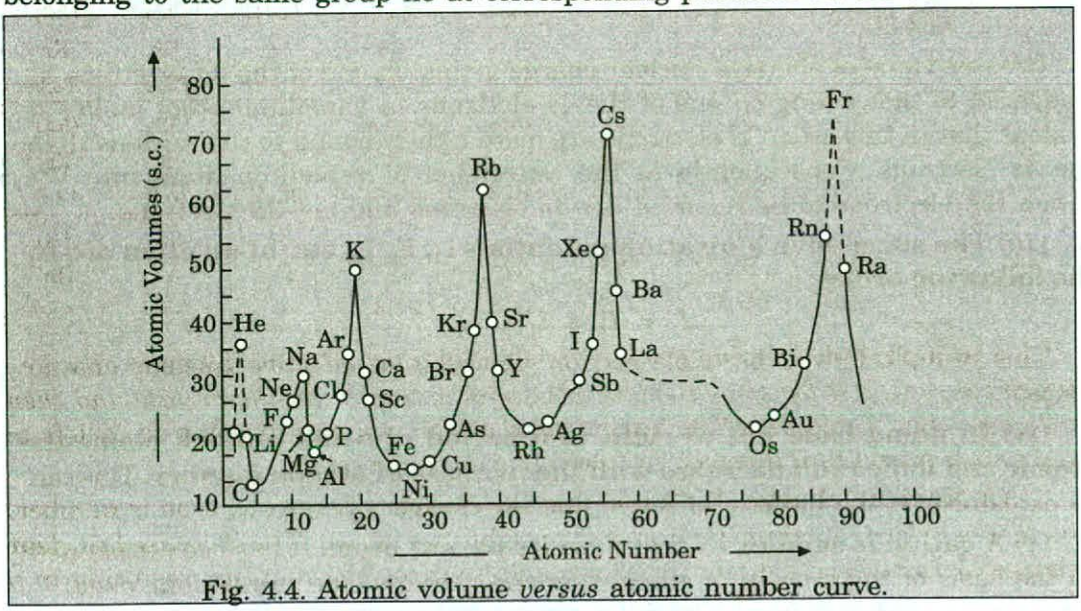


Fig. 4.4. Atomic volume *versus* atomic number curve.

The position of lanthanides [Ce (Z = 58) to Lu (Z = 78)] is to be noted. The expected increase in their atomic volumes is not observed in the curve because as the atomic number increases, the additional electrons enter into the inner $(n-2)th$ shell. This causes a contraction in the atomic volumes of lanthanides. The decrease in atomic volumes on proceeding from Ce to Lu is called *Lanthanide Contraction.*

Variation of Atomic Volume in a Period and a Group.

(*a*) **In a group.** *Atomic volume increases more or less regularly in going down a group* (*See* Table 4.1). The increase in atomic volume in going down a group is due to the increase in the number of shells. The larger the number of shells, the bigger is the volume of the atom.

Table 4.1. Atomic volumes (in c.c.) of *s*-and *p*-block elements. The numbers given in parentheses indicate the atomic numbers.

Group → / Period ↓	*s*-block elements		*p*-block elements					
	I A	*II A*	*III A*	*IV A*	*V A*	*VI A*	*VII A*	*Zero*
1	(1) H 14.1							(2) He 31.8
2	(3) Li 13.1	(4) Be 5.0	(5) B 4.6	(6) C 5.3	(7) N 17.3	(8) O 14.0	(9) F 17.1	(10) Ne 16.8
3	(11) Na 23.7	(12) Mg 14.0	(13) Al 10.0	(14) Si 12.1	(15) P 17.0	(16) S 15.5	(17) Cl 18.7	(18) Ar 24.4
4	(19) K 45.3	(20) Ca 29.9	(31) Ga 11.8	(32) Ge 13.6	(33) As 13.1	(34) Se 16.5	(35) Br 23.5	(36) Kr 32.2
5	(37) Rb 55.9	(38) Sr 33.7	(49) In 15.7	(50) Sn 16.3	(51) Sb 18.4	(52) Te 20.5	(53) I 25.7	(54) Xe 42.9
6	(55) Cs 70.0	(56) Ba 39.0	(81) Tl 17.2	(82) Pb 18.3	(83) Bi 21.3	(84) Po —	(85) At —	(86) Rn —

(*b*) **In a period.** *In going from left to right in a period, it varies cyclically, i.e., it decreases at first for some elements, becomes minimum in the middle and then increases* (*See* Table 4.1). The variation of atomic volume in going from left to right in a period is influenced by the following two factors :

(*i*) Nuclear charge. We know that the nuclear charge (*i.e.* atomic number) increases by one, as we move from left to right in a period. The increased nuclear charge attracts each electron more strongly towards the nucleus, resulting in a decrease in the volume of the atom.

(*ii*) No. of valence electrons. Towards the close of a period, due to an increase in the number of valence-electrons (*i.e.* electrons in the valence shell) the volume of the atom increases, so that it may accommodate all the electrons.

These two factors, one causing an increase and the other causing a decrease, combine to result that in a period atomic volume decreases at first for some elements, becomes minimum in the middle and then increase.

Size of Atoms and Ions
(*Atomic and Ionic Radii*)

An atom is composed of a compact nucleus surrounded by electron cloud which does not have a sharply defined boundary because of its diffused nature (*Wave mechanical picture of atom*). The diffused nature of the electron cloud makes it difficult for us to give an exact definition of atomic size or atomic radius. Thus the atomic radius is an arbitrary concept and is influenced by the nature of neighbouring atoms. However, *it is usually considered as the distance from the centre of the nucleus to the point where the electron density is effectively zero (i.e. negligible).*

Types of Radii

Because of the vagueness of the concept of atomic radius, a number of radii have been defined for an atom which pertain to different types of bonding between the atoms. Some of these radii are : *Covalent radius, Crystal radius (Atomic or metallic radius), van der Waal's radius (Collision radius) and Ionic radius.*

Covalent (Atomic) Radius and Bond Length

The term covalent radius is used for non-metals. Before understanding the concept of covalent radius we should know the meaning of bond length. *The distance between the nuclei of two bonded atoms of a homonuclear diatomic molecule of A_2 type or heteronuclear diatomic molecule of AB type is called bond length (or bond distance or inter-nuclear distance).* In these molecules it is represented as d (A–A) and d (A–B) respectively.

Calculation of covalent radius.

In case of *homonuclear diatomic molecules* of A_2 type (*e.g.* F_2, Cl_2, Br_2 I, etc.), the bond length, d(A–A) is given by :

$$d\ (\text{A–A}) = r\ (\text{A}) + r\ (\text{A})$$

or $$d(\text{A–A}) = 2 \times r\ (\text{A})$$

or $$\text{r}\ (\text{A}) = \frac{d(A-A)}{2} \qquad ...(i)$$

Equation (i) shows that *in case of homonuclear diatomic molecule of A_2 type, the covalent radius of an atom A, r (A) is equal to one-half of the inter-nuclear distance, d(A–A) i.e. the covalent radius of an atom in a homonuclear diatomic molecule can be obtained by dividing the inter-nuclear distance by two.*

In case of *heteronuclear diatomic molecule* of AB type, bond length, d(A–B) is given by :

$$d(\text{A–B}) = r(\text{A}) + r(\text{B}) \quad ...(ii)$$

Here r (A) and r (B) are the covalent radii of A and B atoms. Equation (*ii*) shows that *in case of heteronuclear diatomic molecules of AB type, the bond length, d(A–B) is equal to the sum of the covalent radii of A and B atoms.* It is also obvious from equation (*ii*) that the magnitude of r(A) can be calculated if d(A–B) and r (B) are known.

The covalent radii obtained by equation (*i*) and (*ii*) are called **single bond covalent radii.** Equations (*i*) and (*ii*) reveal that the *single bond covalent radii are additive in nature, i.e.,* when the covalent radii of atoms in A_2 or AB molecules are added, we get the bond length, d (A–A) or d (A–B). This principle is called the ***principle of additivity of covalent radii.*** This principle has been used to calculate the covalent radii of the elements as shown by the following examples :

(i) Cl_2 molecule. The value of Cl–Cl bond distance as found experimentally is 1.98 A°. Thus :

$$r\ (\text{Cl}) = \frac{d\ (\text{Cl} - \text{Cl})}{2} = \frac{1.98}{2} = 0.99\ \text{A}^\circ$$

(ii) Diamond (C_2). The value of d(C – C) distance as found experimentally in a variety of saturated hydrocarbons is 1.54 A°. Thus :

$$r\ (\text{C}) = \frac{d\ (\text{C} - \text{C})}{2} = \frac{1.54}{2} = 0.77\ \text{A}^\circ$$

(iii) Carborundum, *SiC*. In case of this molecule the experimental value of d (Si–C) is 1.93. Thus :

$$d\ (\text{Si–C}) = r\ (\text{Si}) + r\ (\text{C})$$

or
$$r\ (\text{Si}) = d\ (\text{Si–C}) - r\ (\text{C})$$
$$= 1.93 - r\ (\text{C})$$

Thus the covalent radius of silicon atom is obtained by substracting the covalent radius of carbon atom from Si–C bond distance, d (Si–C). Covalent radius of carbon atom, r (C) can also be calculated in a similar way, if that of Si atom, r (Si) is known.

(iv) CCl_4 molecule. In case of this molecule the experimental value of d (C–Cl) is 1.76 A°. Thus :

$$d\ (\text{C–Cl}) = r\ (\text{C}) + r(\text{Cl})$$

or
$$r(\text{C}) = d\ (\text{C} - \text{Cl}) - r\ (\text{Cl})$$
$$= 1.76 - r\ (\text{Cl})$$

Thus the covalent radius of carbon atom can be obtained by substracting the covalent radius of Cl atom from d(C– Cl) bond length. The covalent radius of Cl atom can also be obtained, provided that the covalent radius of C atom is known.

The values of single bond covalent radii of *s*- and *p*-block elements, as determined experimentally, are given below in Table 4.2.

Table 4.2. Single bond covalent radii (in A°) of *s*- and *p*-block elements. The numbers given in parentheses indicate the atomic numbers.

Group → / Period ↓	*s*-block elements		*p*-block elements					
	IA	IIA	IIIA	IVA	VA	VIA	VIIA	Zero
1	(1) H 0.32							(2) He 0.93
2	(3) Li 1.23	(4) Be 0.90	(5) B 0.82	(6) C 0.77	(7) N 0.75	(8) O 0.73	(9) F 0.72	(10) Ne 0.71
3	(11) Na 1.54	(12) Mg 1.36	(13) Al 1.18	(14) Si 1.11	(15) P 1.06	(16) S 1.02	(17) Cl 0.99	(18) Ar 0.98
4	(19) K 2.03	(20) Ca 1.74	(31) Ga 1.26	(32) Ge 1.22	(33) As 1.20	(34) Be 1.16	(35) Br 1.14	(36) Kr 1.12
5	(37) Rb 2.16	(38) Sr 1.91	(49) In 1.44	(50) Sn 1.41	(51) Sb 1.40	(52) Te 1.30	(53) I 1.33	(54) Xe 1.31
6	(55) Cs 2.35	(56) Ba 1.98	(81) Ti 1.48	(82) Pb 1.47	(83) Bi 1.46	(84) Po 1.46	(85) At (1.45)	(86) Rn –

Characteristics of Covalent Radii

(*i*) *As already said, single bond covalent radii are additive in nature. The additive nature of covalent radii is called principle of additvity of covalent radii.*

(*ii*) *The values of covalent radii change with the multiplicity of the bonds between the atoms.* In case of atoms joined by double or triple covalent bonds, the covalent radius is called double bond covalent radius and triple bond covalent radius respectively. These radii are smaller than the single bond covalent radii due to greater overlapping of orbitals in the formation of double and triple covalent bonds.

Double and triple bond covalent radii (in A°) of some common elements are given on the next page.

(*iii*) *Covalent radius of an element is less than its van der Waals radius,* as the formation of a covalent bond involves the overlapping of the electron clouds of the two atoms.

(*iv*) *The magnitude of covalent radius undergoes a change depending on the nature of the space model of the atoms linked such as tetrahedral, square planar, octahedral etc.*

IIIA	IVA	VA	VIA
B = B 0.76 B≡B 0.68	C = C 0.67 C≡C 0.60	N = N 0.60 N≡N 0.55	O = O 0.57
	Si = Si 1.07 Si ≡ Si 1.00	P = P 1.00 P≡P 0.93	S = S 0.97 S≡S 0.94
	Ge = Ge 1.12	As = As 1.11	Se = Se 1.07
	Sn = Sn 1.30	Sb = Sb 1.30	Te = Te 1.27

More About Bond Length

As already said *bond length is defined as the distance between the nuclei of two bonded atoms*. For a homonuclear diatomic molecule of A_2 type it is calculated by :

$$\boxed{d(\text{A–A}) = 2 \times r\,(\text{A})} \qquad ...(i)$$

while in case of heterodiatomic molecule of AB type it is calculated by :

$$\boxed{d(\text{A–B}) = r(\text{A}) + r(\text{B})} \qquad ...(ii)$$

The experimental values of covalent bond lengths for some common homonuclear diatomic molecules are given below. These values are in full agreement with those calculated from equation (*i*).

Homonuclear diatomic molecule	*Bond*	*Bond length (A°)*
H_2	H–H	0.74
F_2	F–F	1.44
Cl_2	Cl–Cl	1.98
Br_2	Br–Br	2.28
$H_3C–CH_3$ (Ethane)	C–C	1.54

Although the values of d (A–B) calculated from equation (*ii*) for diatomic molecules of AB type have been found to the same as found experimentally, yet there are many AB molecules which show deviations, *i.e.* in these molecules d (A–B) is not equal to the sum of r (A) and r (B) as is evident from Table 4.3.

The deviation can also be seen when we consider the N–H bond length [calculated value of d(N–H) = r(N) = r(H) = 0.75 + 0.37 = 1.12 A°] in the following species.

d (N–H) in NH_3 = 1.008 Å

d (N–H) in $[NH_4]^+$ = 1.034 Å

d (N–H) in $[N_3H_6]^{2+}$ = 1.70 Å

d (N–H) in HN_3 = 1.020 Å

Factors Affecting the Magnitude of Bond Length

1. Electronegativity of the bonded atoms, A and B. The increase in the amount of ionic character in A–B bond decreases the bond length, d (A–B). Again we know that since the amount of ionic character in A–B bond depends on the difference in electronegativity of the elements A and B, the decrease in bond length ultimately is due to the difference in electronegativity of the bonded atoms A and B.

Taking into account the ionic character in A–B bond, Schomaker and Stevenson (1941) gave the following empirical equation by which the bond distance, d (A–B) can be calculated.

$$\boxed{d\,(\text{A–B}) = r(\text{A}) + r(\text{B}) - 0.09\,(x_A - x_B)} \qquad ...(iii)$$

Here x_A and x_B are the electronegativities of the elements A and B.

The validity of the above equation can be shown by calculating the N–C distance in $(CH_3)_3N$ molecule by equations (*ii*) and (*iii*).

Table 4.3. Calculated and experimental values of some bond lengths (A°) of A–B bonds in AB molecules.

Bond	Calculated value of d(A–B) = r(A) + r(B)	Experimental value of d(A–B)
S—H	1.02 + 0.37 = 1.39	1.34
S—F	1.02 + 0.70 = 1.72	1.56
S—Cl	1.02 + 0.99 = 2.01	1.99
S—Br	1.02 + 1.14 = 2.16	2.27
B—F	0.82 + 0.70 = 1.52	1.30
B—Cl	0.82 + 0.99 = 1.81	1.72
B—Br	0.82 + 1.14 = 1.96	1.88
C—H	0.77 + 0.37 = 1.14	1.12
C—F	0.77 + 0.70 = 1.47	1.42
C—Br	0.77 + 1.14 = 1.91	1.94
C—I	0.77 + 1.33 = 2.10	2.14
Si—F	1.17 + 0.70 = 1.87	1.54 (in SiF_4)
Si—Cl	1.17 + 0.99 = 2.16	2.02
Si—Br	1.17 + 1.14 = 2.31	2.16
Si—I	1.17 + 1.33 = 2.50	2.44
N—H	0.75 + 0.37 = 1.12	1.00
O—H	0.73 + 0.37 = 1.10	0.96
B—F	0.90 + 0.72 = 1.62	1.42 (in $[BF_4]^-$ ion) 1.29 (in BF_3)

From equation (*ii*), d (N–C) = r(N) + r(C)

= (0.75 + 0.77) Å

= 1.52 Å

This calculated value (= 1.52 A°) obtained as above is not in agreement with the experimental value (=1.47 Å) seen in $(CH_3)_3N$ molecule. But the value calculated from equation (*iii*) has been found in good agreement with the experimental value as shown below :

From equation (*iii*), $d(N–C) = r(N) + r(C) – 0.09\ (x_N - x_C)$

$= 0.75 + 0.77 - 0.09\ (3.0 - 2.5)$

$= 1.475$ Å

2. **Bond order or bond multiplicity.** Bond order or bond multiplicity is defined as the number of covalent bonds between the two bonded atoms. *The bond length between the two atoms decreases with the increase of multiplicity of the bond between the atoms.* For example *d* (C–C) bond length found in ethane ($H_3C–CH_3$) is equal to 1.54 Å while *d* (C–C) bond length found in ethylene ($H_2C = CH_2$) is 1.34 Å and that found in acetylene (HC ≡ CH) is 1.20 Å. Thus we see that *d* (C–C) bond length decreases with the increase of the multiplicity of the bond between two carbon atoms. The decrease in bond length with the increase of the multiplicity of the bond is also evident from the following examples. Bond order is given in bracket.

B—B (1) 1.64 Å B = B (2) 1.52 Å B ≡ B (3) 1.36 Å	C—C (1) 1.54 Å C = C (2) 1.34 Å C ≡ C (3) 1.20 Å	N—N (1) 1.50 Å N = N (2) 1.20 Å N ≡ N (3) 1.12 Å	O—O (1) 1.46 Å O = O (2) 1.14 Å	C—N (1) 1.47 Å C = N (2) 1.29 Å C ≡ N (3) 1.16 Å
	Si—Si (1) 2.34 Å Si = Si (2) 2.14 Å Si ≡ Si (3) 2.00 Å	P—P (1) 2.12 Å P = P (2) 2.0 Å P ≡ P (3) 1.86 Å	S—S (1) 2.04 Å S = S (2) 1.94 Å S ≡ S (3) 1.88 Å	C—O (1) 1.43 Å C = O (2) 1.22 Å
	Ge—Ge (1) 2.44 Å Ge = Ge (2) 2.24 Å	As—As (1) 2.40 Å As = As (2) 2.22 Å	Se—Se (1) 2.32 Å Se = Se (2) 2.14 Å	
	Sn—Sn (1) 2.82 Å Sn = Sn (2) 2.60 Å	Sb—Sb (1) 2.80 Å Sb = Sb (2) 2.62 Å	Te—Te (1) 2.72 Å Te = Te (2) 3.54 Å	

Sometimes bond order increases due to resonance and bond shortening is observed. For example, in benzene molecule the bond distance between two carbon atoms is 1.39 A which is intermediate between the C–C and C=C bond lengths (C–C=154 Å, C=C= 1.34 Å). In other words the bond order between the two carbon atoms is more than 1 and less than 2.

3. Hybridisation. The change in hybridisation affects the shape of the molecule and hence the bond length is also changed in turn. *With the increase of the percentage of s-character in a hybrid orbital, the bond length decreases.* For example with the increase of the percentage of *s*-character from ethane to acetylene via ethylene, C–H and C–C bond lengths decrease in the same direction as shown below :

Molecule	Type of hybridisation	Percentage of s-character	C—H bond length (Å)	C—C bond length (Å)
Ethane ($H_3C—CH_3$)	sp^3	25	1.093	1.54
Ethylene ($H_2C = CH_2$)	sp^2	33.3	1.087	1.34
Acetylene ($HC \equiv CH$)	sp	50	1.057	1.20

Utility of Bond Length Determination

1. Stability of a molecule. The length of a given bond is a measure of its stability. A molecule with small bond length is more stable than that with large bond length.

2. Bond order. A molecule with smaller bond length has higher bond order. Thus the bond length can be used to infer the presence of π-bonding in a molecule. For example in $[BF_4]^-$ ion, the B–F bond length has been found to be equal to 1.42 Å, while B–F bond distance found in BF_3 molecule is 1.29 Å. We know that in $[BF_4]^-$ ion four F atoms are linked with B atom by four σ bonds. Thus the shortening of B–F bond distance in BF_3 molecule is due to the presence of π character in B–.F bonds. This character is produced by the donation of lone pair of electrons from the F atoms into the vacant $2p_z$ orbital of B atom ($p\pi$–$p\pi$ bonding).

Crystal Radius (*Atomic or Metallic Radius*)

The atomic radius as obtained from the metallic crystalline structure of a metal is referred to the crystal or metallic radius. Thus it is used for metal atoms which are assumed to be closely packed spheres in the metallic crystal. The metal atoms are supposed to touch one another in the crystals and *the crystal radius is defined as one-half of the distance between the nuclei of two adjacent metal atoms in the metallic close-packed crystal lattice in which metal exhibits a co-ordination number of 12.* For example the internuclear distance between two adjacent Na atoms in a crystal of sodium metal is 3.80 Å and hence the atomic radius of Na metal = 3.80/2 = 1.90 Å.

It may be noted that *the metallic radii are quite different from other types of radii viz. covalent, ionic or van der Walls radii.*

Since there are weak bonding forces between the metal atoms, the metallic radii are higher (10 to 15%) *than single bond covalent radii. The metallic radii are smaller than the van der Walls radii,* since the bonding forces in the metallic crystal lattice are much stronger than the van der Walls forces.

Metallic radii of *s*-and *p*-block elements are given in Table 4.4. These values are for coordination number of 12.

Table 4.4. Metallic (or atomic) radii of some common elements (in A°). These values are for co-ordination number of 12. The numbers given in parentheses indicate the atomic numbers

	s-block elements		*p*-block elements			
Group → / Period ↓	IA	IIA	IIIA	IVA	VA	VIA
2	(3) Li 1.55	(4) Be 1.12	(5) B 0.98	(6) C 0.91	(7) N 0.92	(8) O —
3	(11) Na 1.90	(12) Mg 1.60	(13) Al 1.43	(14) Si 1.32	(15) P 1.28	(16) S 1.27
4	(19) K 2.35	(20) Ca 1.97	(31) Ga 1.41	(32) Ge 1.37	(33) As 1.39	(34) Se 1.40
5	(37) Rb 2.48	(38) Sr 2.15	(49) In 1.66	(50) Sn 1.62	(51) Sb 1.59	(52) Te 1.60
6	(55) Cs 2.67	(56) Ba 2.22	(81) Tl 1.71	(82) Pb 1.75	(83) Bi 1.70	(84) Po 1.76

The values of the metallic radii depend to some extent on the crystal structure. For example the crystal radius of Ti in body-centred cubic lattice is 1.43 A° while in hexagonal close-packed lattice it is 1.49 A°.

van der Waals Radius (*Collision Radius*)

When two non-bonded isolated atoms or two non-bonded atoms belonging to two adjacent molecules of an element in the solid state approach each other without overlapping their electron clouds to form a bond between them, they cannot come closer than a minimum distance without forming a bond. This minimum distance is called *van der Waals distance* and half of this distance is called van der Waals radius. Thus :

The distance between the nuclei of two non-bonded isolated atoms or the distance between two non-bonded atoms belonging to two adjacent molecules of an element in the solid state is called **van der Waals distance** *while the half of this distance is called* **van der Waals radius.**

Illustration

(*i*) van der Waals radius of an atom in two non-bonded isolated atoms. In Fig. 4.5 two Cl atoms with their nuclei P and Q have been shown. When these

two atoms are just in contact with each other (*No bond formation condition*), the distance between their nuclei P and Q is called van der Waals distance and half of this distance is called van der Waals radius (See Fig. 4.5).

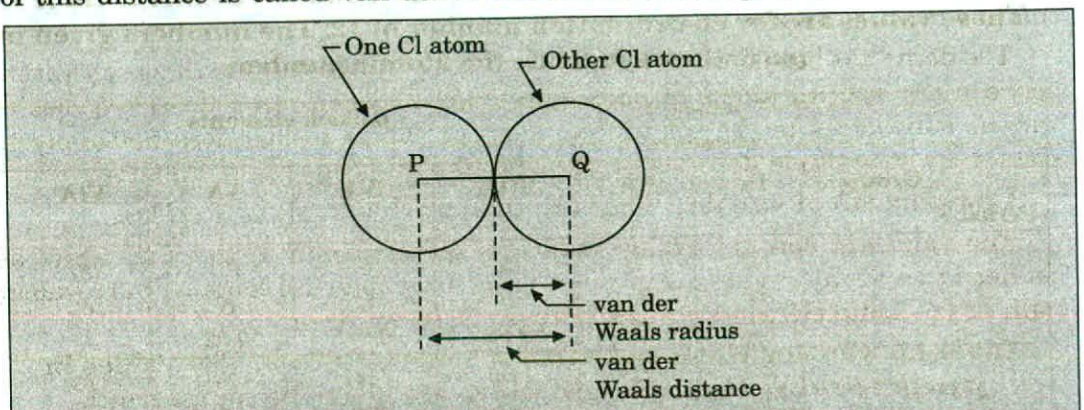


Fig. 4.5. Illustration of van der Waals radius of Cl atom in two non-bonded Cl atoms.

(*ii*) van der Waals radius of an atom in two non- bonded adjacent molecules. In Fig. 4.6 two Cl_2 molecules have been shown. These molecules have resulted by the overlap of the electron clouds of two Cl atoms. Let these molecules be brought in close contact with each other (*No bond formation*). Let P and Q be the nuclei of one Cl_2 molecule and R and S of the other Cl_2 molecule. The distance between the nuclei Q and R is called van der Waals distance while half of this distance is called van der Waals radius. Thus :

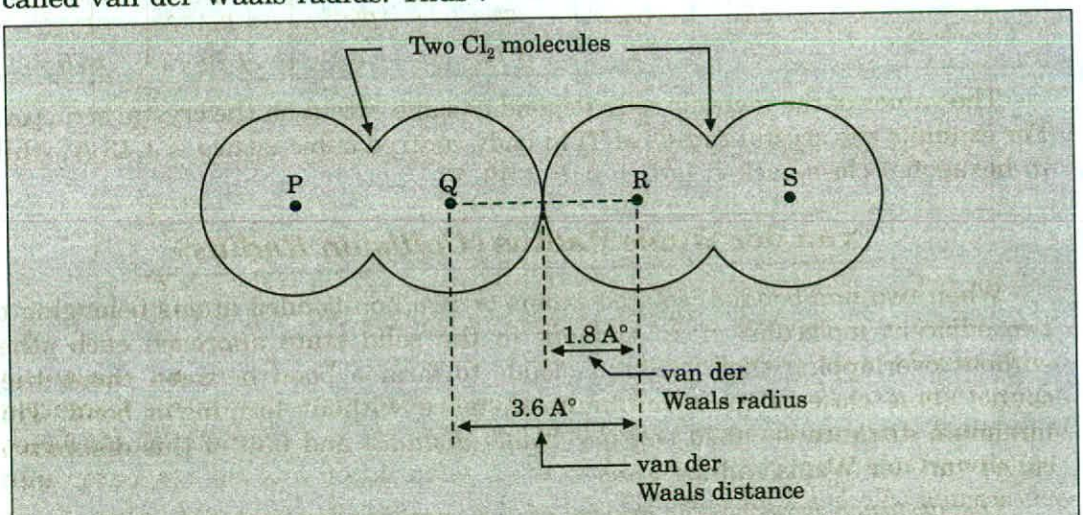


Fig 4.6. Illustration of van der Waals radius of Cl atom in two non-bonded adjacent Cl_2 molecules.

$\because$ van der Waals distance = QR = 3.6 A°

$\therefore$ van der Waals radius = QR/2 = 3.6/2 A° = 1.8 A°

The statement that the van der Waals radius of hydrogen is 1.2 A° means that nuclei of two H-atoms in two different H_2 molecules cannot approach each other

nearer than 2 × 1.2 A° from each other without overlapping of their electron clouds to form a bond. Similarly since two Cl-atoms in two different Cl_2 molecules cannot approach each other nearer than 3.6 A°, the van der Waals radius of chlorine atom is 3.6/2 = 1.8 A°.

The name has been derived from the van der Waals forces which are operating between the neutral atoms of noble gases and between non-polar molecules of various substances in the solid state. van der Waals radius does not apply to metals. Its magnitude depends on the effective packing size of the atom.

Comparison of van der Waals Radius with Covalent Radius.

The values of van der Waals radii of some elements in the solid state as obtained from X-ray studies are given in Table 4.5 which also contains the covalent radii of the same elements for the purpose of comparison.

Table 4.5. van der Waals radii (A°) of some elements. The values in parentheses are covalent radii which are given for comparison.

Group→ / Period ↓	VA	VIA	VIIA	Zero
1			H 1.2 (0.32)	He 1.20 (0.93)
2	N 1.5 (0.75)	O 1.40 (0.73)	F 1.36 (0.72)	Ne 1.60 (0.71)
3	P 1.9 (1.06)	S 1.85 (1.02)	Cl 1.80 (0.99)	Ar 1.91 (0.98)
4	As 2.0 (1.20)	Se 2.0 (1.16)	Br 1.95 (1.14)	Kr 2.0 (1.12)
5	Sb 2.2 (1.40)	Te 2.20 (1.36)	I 2.15 (1.33)	Xe 2.20 (1.31)

It may be seen from the table that *van der Waals radius of an element is higher than its covalent radius*. This is because of the fact that in the formation of covalent bond, atoms have to overlap each other while in van der Waals forces the atoms/molecules simply come closer to each other and do not enter into overlapping (*No bond formation*).

The comparison between van der Waals and covalent radii can be explained by considering the following examples :

(*i*) In Fig. 4.7 there are two Cl atoms with their nuclei P and Q. When these two atoms are just in contact with each other [Fig. 4.7 (*a*)] (*No bond formation condition*), the distance between their nuclei is called van der Waals distance and half of this distance is called van der Waals radius.

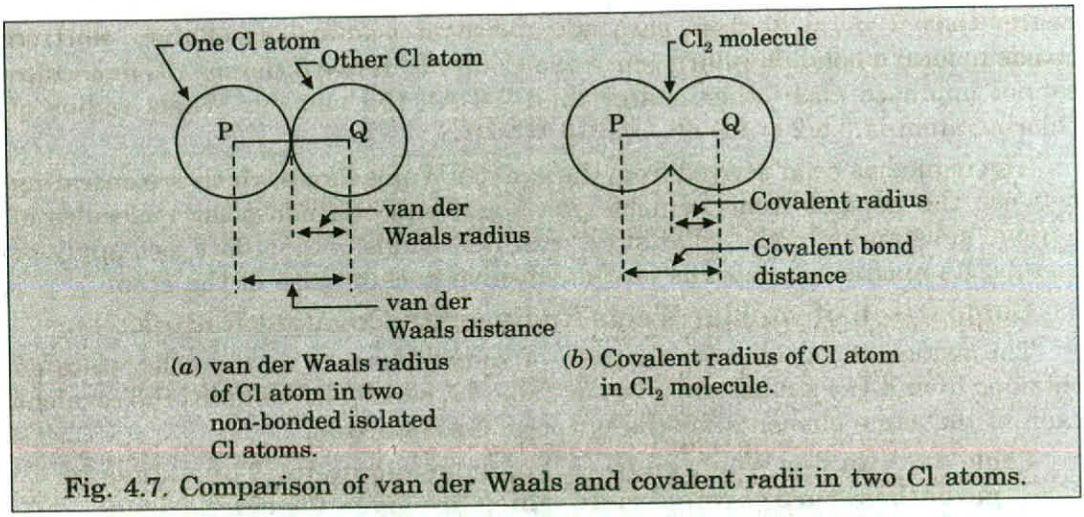


Fig. 4.7. Comparison of van der Waals and covalent radii in two Cl atoms.

On the other hand when the electron clouds of the two Cl atoms merge with each other to form Cl_2 molecule [Fig. 4.7 (*b*)], the distance between the nuclei of Cl_2 molecule is called covalent bond distance and half of it is called covalent radius.

(*ii*) Suppose two Cl_2 molecules formed by the overlapping of electron clouds of two Cl atoms are brought in close contact with each other (*No bond formation*). Let P and Q be the nuclei of one Cl_2 molecule, and R and S of the other Cl_2 molecule (Fig. 4.8). It may be seen from the figure that half of the distance between the nuclei Q and R (called van der Waals distance) of the two non-bonded neighbouring Cl atoms belonging to two adjacent Cl_2 molecules is the van der Waals radius of Cl atom while half of the distance between the two nuclei P and Q (called covalent bond distance) of the same Cl_2 molecule is covalent radius of Cl atom. Thus :

van der Waals distance QR = 3.60 A°

$\therefore$ van der Waals radius = QR/2 = 3.60/2 = 1.80 A°

Covalent bond distance = PQ = 1.98 A°

$\therefore$ Covalent radius = PQ/2 = 1.98/2 = 0.99 A°

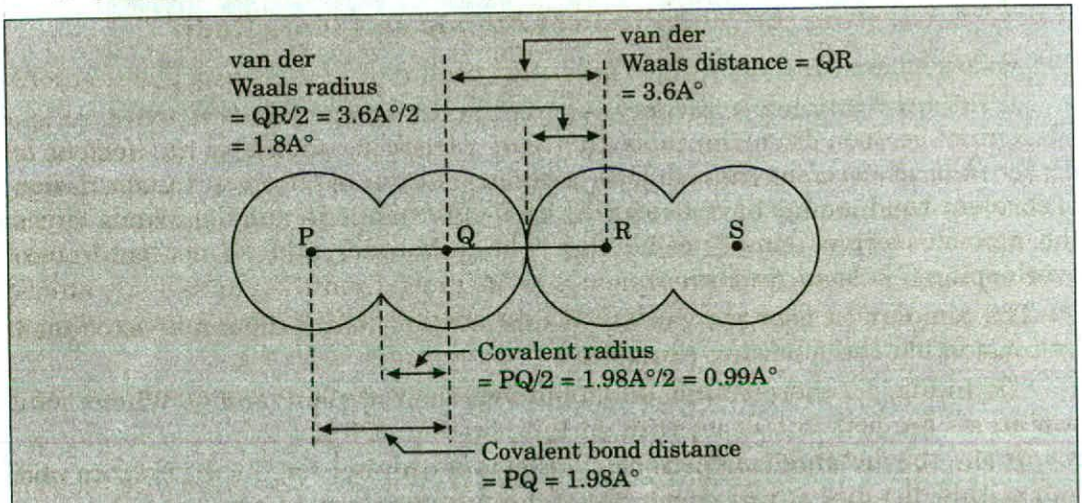


Fig. 4.8. Comparison of van der waals and covalent radii in two Cl_2 molecules.

For noble gases in the solid state the crystal radii (*i.e.* atomic radii) are actually van der Waals radii.

Ionic Radius

The ionic radius is defined as the distance between the nucleus of an ion and the point where the nucleus exerts its influence on the electron cloud.

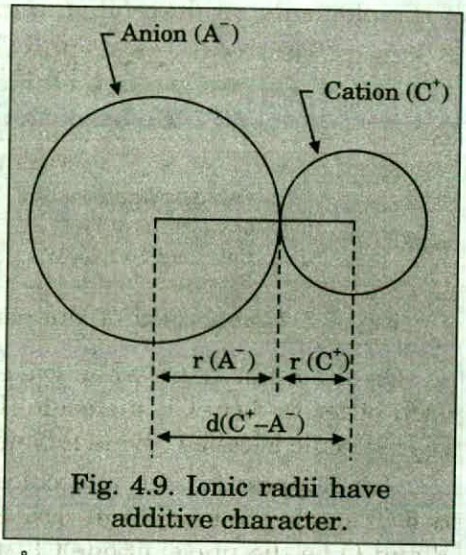


Fig. 4.9. Ionic radii have additive character.

Characteristics of Ionic Radii.

(*i*) The ionic radius of a particular ion is of more or less constant magnitude.

(*ii*) Ionic radii have an additive character. This means that if the ions of an ionic crystal are assumed to be spheres, the inter-nuclear distance between the two ions is equal to the sum of the radii of the ions of which the ionic crystal is composed. Thus in C^+A^- ionic crystal shown in Fig. 4.9.

$$r(C^+) + r(A^-) = d(C^+ - A^-)$$

Problem. *Ionic radius of Na^+ ion is 0.95 Å and the inter-nuclear distance between the ion-pairs in NaCl ionic crystal is equal to 2.76 Å. Calculate the radius of Cl^- ion.*

Solution. $d(Na^+ - Cl^-) = r(Na^+) + r(Cl^-)$

$\therefore \quad 2.76 = 0.95 + r(Cl^-)$

$\therefore \quad r(Cl^-) = 2.76 - 0.95 = 1.81$ Å

Ionic radii of s- and p-block elements are given in Table 4.6.

While describing the sizes of various atoms or ions any of the radii described above can be used.

Factors Affecting the Magnitude of Atomic and Ionic Radii

Following are the factors which affect the magnitude of the size of atoms or ions.

1. Effective nuclear charge. We know that the magnitude of effective nuclear charge determines the magnitude of force of attraction exerted by the nucleus on the outermost electron cloud. Greater is the magnitude of effective nuclear charge, greater is the amount of the force which binds the outermost electrons to the nucleus and hence the electron cloud of the outermost shell is pulled inward nearer to the nucleus and consequently its distance from the nucleus (*i.e.* atomic and ionic radius) is reduced. Thus *with the increase of effective nuclear charge, the size of the atom or ion (i.e. atomic or ionic radii) decrease.*

This factor has been used in explaining the variation of atomic and ionic radius of the elements in a period of the periodic table.

2. Number of shells or principal quantum number (n). As the total number of shells or the magnitude of principal quantum number (n) increases, the outer

electrons get farther and farther away from the nucleus and hence the atomic and ionic radii increase. *Thus with the increase of the number of shells or the principal quantum number, the atomic and ionic radii increase.*

This factor has been used to explain the increase of atomic and ionic radius of the elements on descending a group.

Table 4.6. Ionic radii (in Å) of representative elements (*s*- and *p*-block elements). In parentheses are given the oxidation states of the elements

Group → / Period ↓	*s*-block elements		*p*-block elements				
	IA	IIA	IIIA	IVA	VA	VIA	VIIA
1	H 2.08 (–1) 0.29 (+1)						
2	Li 0.60 (+1)	Be 0.31 (+2)	B 0.20 (+3)	C 2.60 (–4) 0.15 (+4)	N 1.71 (–3) 0.11 (+5)	O 1.40 (–2) 0.09 (+6)	F 1.36 (–1) 0.07 (+7)
3	Na 0.95 (+1)	Mg 0.65 (+2)	Al 0.50 (+3)	Si 2.71 (–1) 0.41 (+4)	P 2.12 (–3) 0.34 (+5)	S 1.84 (–2) 0.29 (+6)	Cl 1.81 (–1) 0.26 (+7)
4	K 1.33 (+1)	Ca 0.99 (+2)	Ga 1.13 (+1) 0.62 (+3)	Ge 0.93 (+2) 0.53 (+4)	As 2.22 (–3) 0.47 (+5)	Be 1.98 (–2) 0.42 (+6)	Br 1.95 (–1) 0.39 (+7)
5	Rb 1.48 (+1)	Sr 1.13 (+2)	In 1.32 (+1) 0.81 (+3)	Sn 1.12 (+2) 0.71 (+4)	Sb 0.45 (–3) 0.62 (+5)	Te 2.21 (–2) 0.56 (+6)	I 2.16 (–1) 0.50 (+7)
6	Cs 1.69 (+1)	Ba 1.35 (+2)	Ti 1.40 (+1) 0.95 (+3)	Pb 1.20 (+2) 0.84 (+4)	Bi 1.20 (+3) 0.74 (+5)	Po — —	At — —
7	Fr 1.76 (+1)	Ra 1.40 (+2)					

Variation of Atomic and Ionic Radii in a Period and a Group of Representative Elements. (*Periodic Trends of Atomic and ionic Radii*)

(*a*) **In a period.** We know that the number of shells in all the elements of a given period remains the same but the value of effective nuclear charge, as calculated by Slater's rules, *increases from left to right*. The increased effective nuclear charge pulls the electron cloud of the atom nearer to the nucleus and thus the size of the atoms and ions goes on decreasing from left to right. *Thus in going from left to right in a period of s-and p-block elements atomic and ionic radii decrease with the increase of atomic number.* This fact can be illustrated by considering the atomic (covalent) and ionic radii of the elements of 2*nd* period as shown below :

Elements of 2nd period:	Li	Be	B	C	N	O	F	Ne
Effective nuclear charge:	1.30	1.95	2.60	3.25	3.90	4.55	5.20	5.85
			—— *Increasing* ⟶					
Atomic (covalent) radius (Å):	1.23	0.90	0.82	0.77	0.75	0.73	0.72	0.71
			—— *Decreasing* ⟶					
Ionic radius (Å):	0.60 (Li^+)	0.31 (Be^{2+})	0.20 (B^{3+})	0.15 (C^{4+})	0.11 (N^{5+})	0.09 (O^{6+})	0.07 (F^{7+})	–
			—— *Decreasing* ⟶					

Thus in any period the alkali metals (that are present at the extreme left of the periodic table) have the largest size while the halogens (that are present at the extreme right, excluding zero group elements) have the smallest size. However, the size of the atoms of inert gases is larger than that of the preceeding halogen.

(*b*) **In a group.** *In going down a group of s-and p-block elements the atomic and ionic radii both increase with the increase of atomic number.* For example the atomic (covalent) and ionic radii of alkali metals increase on proceeding from Li to Cs as shown below :

Alkali metal (atomic numbers given in parentheses)	Effective nuclear charge	Electronic configuration	No. of shells or principal quantum number (n)	Atomic (covalent) radius (Å)	Ionic radius (M^+ ions) (Å)
Li (3)	1.30	2, 1	2	1.23	0.60
Na (11)	2.20	2, 8, 1	3	1.54	0.95
K (19)	2.20	2, 8, 8, 1	4	2.03	1.33
Rb (37)	2.20	2, 8, 18, 8, 1	5	2.16	1.48
Cs (55)	2.20	2, 8, 18, 18, 8, 1	6	2.35	1.60

We have seen that on descending a group the magnitude of effective nuclear charge acting on the valence-shell electron of the elements remains the same (The first element is a typical case). Thus the concept of effective nuclear charge cannot be used to explain the successive increase in the atomic or ionic radii of the elements of a given group. However, the other factor namely *the number of shells or principal quantum number* (n) can be used to explain the increase in radii. As the number of shells or principal quantum number (n) increases from 2 (in case of Li) to 6 (in case of Cs), the outer-most shell electrons get farther and farther away from the nucleus and hence atomic and ionic radii increase. Thus it is due to the progressive addition of a new shell (or the increase in the number of shells) that the atomic or ionic radii increase when we proceed from top to bottom in a group.

The variation of atomic and ionic radii of representative elements (*s*-and *p*-block elements) in a period and a group of the periodic table can be shown as given in Fig. 4.10.

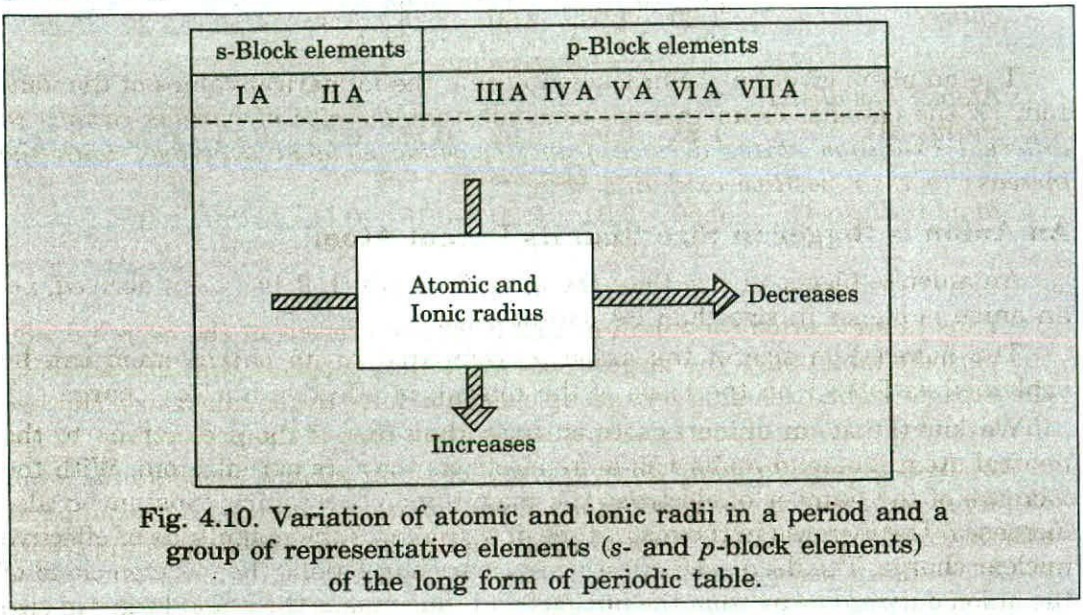


Fig. 4.10. Variation of atomic and ionic radii in a period and a group of representative elements (*s*- and *p*-block elements) of the long form of periodic table.

A Cation is Smaller in Size than its Parent Atom

A cation is smaller in size than the atom from which it has been derived, *i.e.* a cation is smaller in size than its parent atom.

The decrease in size of the cation as compared to its parent atom can be explained as follows on the basis of the concept of effective nuclear charge.

We know that a cation is formed by the removal of one or more electrons from the atom. Thus a cation has lesser number of electrons than its parent atom. With the decrease of the number of electrons the magnitude of screening constant, σ also decreases. The decrease in the magnitude of σ increases the magnitude of effective nuclear charge. The increased effective nuclear charge pulls the electron cloud of the cation inward nearer to the nucleus and thus makes the cation smaller in size than its parent neutral atom.

Thus alkali metal cations are smaller in size than the alkali metal atoms from which they have been derived as shown below :

Alkali metal (Atomic number, Z given in bracket)	σ	$Z_{eff} = Z-\sigma$	Atomic (covalent) radius (Å)	Cation (No. of electrons given in bracket)	σ	$Z_{eff} = Z-\sigma$	Radius of cation (Å)
Li (3)	1.70	1.30	1.22	Li^+ (2)	0.35	1.65	0.60
Na (11)	8.80	2.20	1.54	Na^+ (10)	4.15	6.85	0.95
K (19)	16.80	2.20	2.03	K^+ (18)	11.25	7.75	1.33
Rb (37)	34.80	2.20	2.16	Rb^+ (36)	27.75	9.25	1.48
Ce (55)	52.80	2.20	2.35	Cs^+ (54)	45.75	9.25	1.69

On similar lines of argument it can also be explained that *di, tri, tetra, valent* positive ions would possess successively smaller sizes. For example:

$$Fe^{2+}\ (0.76\ Å) > Fe^{3+}\ (0.64\ Å)$$

$$Pb^{2+}\ (1.20\ Å) > Pb^{4+}\ (0.84\ Å)$$

The numbers given in the brackets indicate the numerical values of the ionic radii of the cations. From this we conclude that *the size of various cations in different oxidation states derived from the same element decreases with the increase in their positive oxidation state.*

An Anion is Bigger in Size than its Parent Atom

An anion is bigger in size than the atom from which it has been derived, *i.e.* an anion is bigger in size than its parent atom.

The increase in size of the anion as compared to its parent atom can be explained as follows on the basis of the concept of effective nuclear charge.

We know that an anion is formed by adding one or more electrons to the neutral atom. Thus an anion has more electrons than its parent atom. With the increase of the number of electrons the magnitude of screening constant, σ also increases. The increase in the magnitude of σ decreases the magnitude of effective nuclear charge. The decreased effective nuclear charge pulls the electron cloud of the anion outward away from the nucleus and thus makes the anion larger in size than its parent atom.

Thus halide ions are bigger in size than the halogen atoms from which they have been derived as shown below :

Halogens (Atomic number, Z given in bracket)	σ	$Z_{eff} = Z-\sigma$	Atomic (covalent) radius (Å)	Halide ions (No. of electrons given in bracket)	σ	$Z_{eff} = Z-\sigma$	Radius of halide ion (Å)
F (9)	3.80	5.20	0.72	F^- (10)	4.15	4.85	1.36
Cl (17)	10.90	6.10	0.99	Cl^- (18)	11.25	5.75	1.81
Br (35)	27.40	7.60	1.14	Br^- (36)	27.75	7.25	1.95
I (53)	45.40	7.60	1.33	I^- (54)	45.75	7.25	2.16

Radii of Iso-Electronic Species

Iso-electronic species are the atoms or ions which have the same number of electrons and same electronic configuration but different magnitude of nuclear charge. For example C^{4-}, N^{3-}, O^{2-}. F^-, Ne^0, Na^+ etc. are iso-electronic species, since these have the same number of electrons (namely 10 electrons) and same configuration *viz.* Ne-type configuration ($1s^2$, $2s^2p^6$). *The size of iso-electronic species decreases with the increase of their atomic number* (Z) as shown below for the iso-electronic species given above.

Iso-electronic species (Atomic number, Z given in bracket)	$Z_{eff} = Z - \sigma$ $= Z - 4.15$	Atomic or ionic radius (Å)
C^{4-} (6)	6 – 4.15 = 1.85	2.60
N^{3-} (7)	7 – 4.15 = 2.85	1.71
O^{2-} (8)	8 – 4.15 = 3.85	1.40
F^{-} (9)	9 – 4.15 = 4.85	1.36
Ne^{0} (10)	10 – 4.15 = 5.85	1.12
Na^{+} (11)	11 – 4.15 = 6.85	0.95
Mg^{2+} (12)	12 – 4.15 = 7.85	0.65
Al^{3+} (13)	13 – 4.15 = 8.85	0.50
Si^{4+} (14)	14 – 4.15 = 9.85	0.41
P^{5+} (15)	15 – 4.15 = 10.85	0.34
S^{6+} (16)	16 – 4.15 = 11.85	0.29
Cl^{7+} (17)	17 – 4.15 = 12.85	0.26

The decrease in size with the increase of atomic number can be explained as follows on the basis of effective nuclear charge.

All the species shown above have $1s^2$, $2s^2p^6$ configuration and hence the value of screening constant, σ in all these cases is equal to 4.15 as shown below :

σ = 0.35 × No. of electrons left in *2nd* shell + 0.85 × No. of electrons in *1st* shell

= 035 × 7 + 0.85 × 2

= 2.45 + 1.70

= 4.15

With the increase of atomic number from C^{4-} to Cl^{7+}, the magnitude of effective nuclear charge, $Z_{eff} = Z - \sigma = Z - 4.15$ also increases. The increased effective nuclear charge pulls the electron cloud of the isoelectronic species inward nearer to the nucleus and thus makes their size decrease successively.

Evaluation of Ionic Radii

The following are the important methods for the evaluation of ionic radii.

1. Lande's Method. Lande (1920) determined the radius of anions by assuming that in an ionic crystal having very small cation and very large anion, the anions touch one another. For example in Li^+I^- ionic crystal which has very small Li^+ cation and very large I^- ion (the radius of I^- ion is 3.6 times that of Li^+ ion), large-sized ions touch each other (Fig. 4.11). Li^+ ions which are very small as compared to I^- ions are accommodated in octahedral holes without disturbing the close packing.

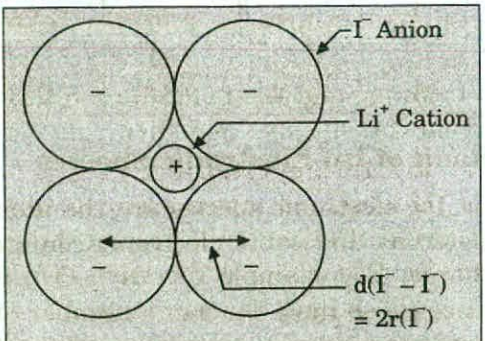


Fig. 4.11. Li^+I^- ionic crystal which has very small Li^+ cations and very large I^- anions (the radius of I^- ion is 3.6 times that of Li^+ ion) and hence I^- ions touch each other, but Li^+ cation does not touch I^- anions.

Since I^- ions touch each other, the anion–anion distance [*i.e.* $I^- - I^-$ inter-ionic distance), $d(I^- - I^-)$ in $Li^+ I^-$ ionic crystal can be assumed to be equal to double the radius of I^- ions, $r(I^-)$, *i.e.*

$$d(I^- - I^-) = 2r\ (I^-)$$

$$\text{or}\quad r(I^-) = \frac{d(I^- - I^-)}{2} \qquad ...(i)$$

The value of $d(I^- - I^-)$ has been found to be equal to 4.32 Å by diffraction technique. Thus from equation (*i*), $r(I^-)$ is given by :

$$r(I^-) = \frac{4.32}{2} = 2.16 \text{ Å}$$

Thus we see that half of the anion–anion distance is equal to the radius of I^- ion. But in case of ionic crystals like K^+I^- having the cations and anions of comparable size, the anions do not touch each other and hence half of the anion–anion distance is not equal to the radius of the anion (Fig. 4.12). In such crystals the cation touches the anions and hence the cation–anion distance is equal to the sum of the radii of the cation and anion. Thus for K^+I^- ionic crystal,

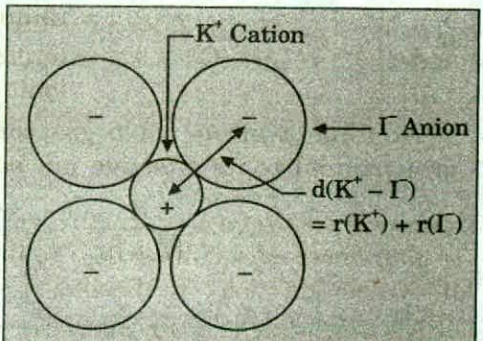


Fig. 4.12. K+I⁻ Ionic crystal which has K^+ and I^- ions of comparable size and hence K^+ cation touches I^- anions, but I^- anions do not touch each other.

$$d(K^+ - I^-) = r(K^+) + r(I^-)$$

$$\text{or}\quad r(K^+) = d\ (K^+ - I^-) - r(I^-) \qquad (ii)$$

Thus the ionic radius of K^+ ion may be obtained by subtracting the known radius of I^- ion (as calculated from Li^+I^- crystal) from the cation–anion distance. For example in KI ionic crystal $d(K^+ - I^-)$ has been found to be equal to 3.49 Å and hence

$$r(K^+) = d(K^+ - I^-) - r(I^-)$$
$$= 3.49 - 2.16$$
$$= 1.33 \text{ Å}.$$

Bragg and West (1926) used this method to obtain the radius for the oxide ion from the silicates and then calculated the ionic radii of over 80 ions.

2. Pauling's Method. Pauling has calculated the radii of the ions on the basis of the observed internuclear distances in four crystals namely NaF, KCl, RbBr and CsI. In each ionic crystal the cations and anions are isoelectronic (*i.e.* have the same number of electrons) with inert gas configuration as shown below :

NaF crystal : $Na^+ \rightarrow 2, 8$; $F^- \rightarrow 2, 8$ } Ne (Z = 10) type configuration

KCl crystal : $K^+ \rightarrow 2, 8, 8$; $Cl^- \rightarrow 2, 8, 8$ } Ar (Z = 18) type configuration

RbBr crystal : $Rb^+ \rightarrow 2, 8, 18, 8$; $Br^- \rightarrow 2, 8, 18, 8$ } Kr (Z = 36) type configuration

CsF crystal : $Cs^+ \rightarrow 2, 8, 18, 18, 8$
$F^- \rightarrow 2, 8, 18, 18, 8$ } Xe (Z = 54) type configuration

Further the following two assumptions are made to assign the ionic radii :

(*i*) The cations and anions of an ionic crystal are assumed to be in contact with each other and hence the sum of their radii will be equal to the inter-nuclear (inter-ionic) distance between them, *i.e.*

$$r(C^+) + r(A^-) = d(C^+ - A^-) \quad ...(i)$$

where $r(C^+)$ = radius of cation, C^+

$r(A^-)$ = radius of anion, A^-

and $d(C^+ - A^-)$ = internuclear distance between C^+ and A^- ions in C^+A^- ionic crystal

(*ii*) For a given noble gas configuration, the radius of an ion is inversely proportional to its effective nuclear charge, *i.e.*

$$r(C^+) \propto \frac{1}{[Z_{eff}]_{C^+}} \quad ...(ii)$$

and $$r(A^-) \propto \frac{1}{[Z_{eff}]_{A^-}} \quad ...(iii)$$

Here $[Z_{eff}]_{C^+}$ and $[Z_{eff}]_{A^-}$ are the effective nuclear charges on cation (C^+) and anion (A^-) respectively.

On combining relations (*ii*) and (*iii*) we get.

$$\frac{r(C^+)}{r(A^-)} = \frac{[Z_{eff}]_{A^-}}{[Z_{eff}]_{C^+}} \quad ...(iv)$$

Equations (*i*) and (*iv*) can be used to evaluate the values of $r(C^+)$ and $r(A^-)$ provided that the values of $d(C^+ - A^-)$, $[Z_{eff}]_{C^+}$ and $[Z_{eff}]_{A^-}$ are known.

Illustration. The method can be illustrated by calculating the radii of K^+ and Cl^- ions in KCl ionic crystal. The internuclear distance between K^+ and Cl^- ions in KCl ionic crystal has been found to be equal to 3.14 Å, *i.e.*

$$r(K^+) + r(Cl^-) = d(K^+ - Cl^-)\ 3.14\ Å \quad ...(v)$$

Now since K^+ and Cl^- ions have Ar(Z = 18) type configuration ($1s^2$, $2s^2p^6$, $3s^2p^6$), $[Z_{eff}]_{K^+}$ and $[Z_{eff}]_{Cl^-}$ can be calculated as follows :

$$[Z_{eff}]_{K^+} = Z - \sigma$$
$$= 19 - [(0.35 \times \text{No. of electrons left in } nth \text{ shell}) + (0.85 \times \text{No. of electrons in } (n-1)th \text{ shell}) + (1.00 \times \text{No. of electrons in the inner shell})]$$
$$= 19 - [0.35 \times 7 + 0.85 \times 8 + 1 \times 2]$$
$$= 19 - 11.25$$
$$= 7.75$$
$$[Z_{eff}]_{Cl^-} = 17 - 11.25$$
$$= 5.75$$

$$\therefore \frac{r(K^+)}{r(Cl^-)} = \frac{[Z_{eff}]_{Cl^-}}{[Z_{eff}]_{K^+}} = \frac{5.75}{7.75} \quad ...(vi)$$

With the help of equations (*v*) and (*vi*) we find that

$$r\ (K^+) = 1.33\ Å$$

and $$r\ (Cl^-) = 18.1\ Å.$$

The values of ionic radii for univalent ions as found by Pauling have been found to be in good agreement with the observed inter-ionic distances.

Bond Energy or Bond Strength

In case of a diatomic molecule bond energy is defined as *the energy released when two neutral atoms A and B get bonded together to form A–B molecule. Thus* :

$$\underbrace{A + B}_{\text{Neutral atoms}} \longrightarrow \underset{\text{AB molecule}}{A - B} + \textit{Energy released}\ (\text{called } \textit{bond energy})$$

When a bond is formed, energy is evolved and hence energy is written with a negative sign.

Bond energy can also be defined as the energy required to break A–B molecule into its neutral atoms, A and B. Thus :

$$\underset{\text{AB molecule}}{A–B} + \textit{Energy required}\ (\text{called } \textit{bond energy}) \longrightarrow \underbrace{A + B}_{\text{Neutral atoms}}$$

When a bond is broken, energy is required and hence bond energy is written with a positive sign. When we consider the dissociation of a molecule into atoms, bond energy is called **dissociation energy** *of the molecule.*

For a poly-atomic molecule two kinds of bond energies are considered. These are (*i*) *Bond dissociation energy*, D and (*ii*) *Average bond energy*, E.

Bond dissociation energy is defined as the energy required to break a particular bond in a polyatomic molecule, while the average bond energy is equal to the energy required to break the molecule into atoms divided by the number of bonds present in the polyatomic molecule. Thus :

$$\textbf{\textit{Average bond energy}} = \frac{\textbf{\textit{Energy required to break the molecule into its atoms}}}{\textbf{\textit{No. of bonds}}}$$

Since the energy required to break the molecule into its atoms is equal to the energy of its formation,

$$\textbf{\textit{Average bond energy}} = \frac{\textbf{\textit{Heat of formation of the molecule}}}{\textbf{\textit{No. of bonds}}}$$

For a polyatomic molecule AB_n having all identical A–B bonds, there are n dissociation energies but this molecule has only one average bond energy. For example there are two dissociation energies for H_2O, three for NH_3 and four for

CH_4 molecules, but there is only one average bond energy in each case. Two successive bond dissociation energies ΔH_1 and ΔH_2 for H_2O molecule are shown below :

$$H\text{–}O\text{–}H \rightarrow H + O\text{–}H; \quad \Delta H_1 = 501.7 \text{ KJ/mole}$$
$$O\text{–}H \rightarrow H + O; \quad \Delta H_2 = 423.5 \text{ KJ/mole}$$

Thus the energy required to break both O–H bonds simultaneously in one molecule of water

$$= 501.7 + 423.5 = 925.2 \text{ KJ/mole}$$

or $$\begin{matrix} H \\ H \end{matrix}\!\!> O \longrightarrow O + H + H; \quad \Delta H = 925.2 \text{ KJ/mole}$$

and hence the average O—H bond energy $= \frac{925.2}{2}$ KJ/mole

$$= 462.2 \text{ KJ/mole}$$

Here we see that the two successive bond dissociation energies for H_2O molecule are different from each other and from the average O–H bond energy. It is also clear that the bond energy of O–H bond is one-half of the energy required to break H_2O molecule (H–O–H) into elements. For NH_3 molecule the three successive bond dissociation energies ΔH_1, ΔH_3 and ΔH_3 are given below :

$$\begin{matrix} H \\ | \\ N\text{–}H \end{matrix} \rightarrow H + \begin{matrix} H \\ | \\ N\text{–}H \end{matrix}; \quad \Delta H_1 = 435.1 \text{ KJ/mole}$$
$$\begin{matrix} | \\ H \end{matrix}$$

$$\begin{matrix} H \\ | \\ N\text{–}H \end{matrix} \rightarrow H + N\text{–}H; \quad \Delta H_2 = 397.5 \text{ KJ/mole}$$

$$N\text{–}H \rightarrow H + N; \quad \Delta H_3 = 338.9 \text{ KJ/mole}$$

Thus the energy required to break all the, three N–H bonds simultaneously in one molecule of ammonia

$$= 435.1 + 397.5 + 338.9 = 1171.5 \text{ KJ/mole}$$

and hence the average N–H bond energy $= \frac{1171.5}{3}$

$$= 390.5 \text{ KJ/mole.}$$

Thus the bond energy of N–H bond is one-third of the energy required to break NH_3 ($\begin{matrix} H \\ | \\ H\text{–}N\text{–}H \end{matrix}$) molecule into elements.

Bond dissociation energies can be determined by calorimetric method, electronic absorption or absorption spectroscopic analysis, mass spectroscopic analysis, magnetic susceptibility measurements, magnetic resonance spectroscopy, molar refraction etc. The bond dissociation energies of some common bonds are given in Table 4.7.

Table 4.7. Bond dissociation energies of some common bonds (KJ/mole)

Bond	Bond dissociation energy	Bond	Bond dissociation energy
H–H	431.0	H–F	560.7
C–C	347.3	H–Cl	426.8
C=C	606.7	H–Br	364.0
C≡C	803.3	H–I	297.1
N–N	163.2	C–H (average in CH_4)	414.2
N=N	418.4	C–N	284.5
N≡N	945.6	C=N	615.1
O–O	146.4	C≡N	866.1
O=O	497.9	C–O	334.7
S–S	225.9	C=O	694.5
F–F	150.6	C≡O	1071.3
Cl–Cl	242.7	C–S	272.0
Br–Br	188.3	C–F	447.7
I–I	150.6	C–Cl	326.4
H–N (average in NH_3)	390.5	C–Br	284.5
H–O (average in H_2O)	462.6	C–I	213.4

Standard ΔH° Values for Atoms

Bond energy, ΔH for H_2 molecule has been experimentally found to be equal to 435.4 KJ/mole. Half of this (217.7 KJ/mole) is called standard ΔH° value for H atom. Similarly, since ΔH for I_2 molecule has been found equal to 150.6 KJ/mole, standard ΔH° value for I atom is half of 150.6 KJ/mole (= 75.3 KJ/mole). Standard ΔH° values for some common atoms (in KJ/mole) in gaseous state are given below :

H(*g*) = 217.7	C(*g*) = 718.3
O(*g*) = 247.5	Cl(*g*) = 121.3
N(*g*) = 473.3	Br(*g*) = 96.42

Calculation of Bond Energy

Standard ΔH° values of atoms can be used to calculate the bond energy of a given bond. For example, since, as we have seen, the standard ΔH° values of H and I atoms are 217.7 KJ/mole and 75.3 KJ/mole, respectively bond energy of H–I bond

= ΔH° value for H atom + ΔH° value for I atom
= 217.7 KJ/mole + 75.3 KJ/mole
= 293.0 KJ/mole

This calculated value (= 293.0 KJ/mole) has been found in close agreement with the experimental value (= 297.1 KJ/mole)

Problem. *From $\Delta H°$ values of the elements as given above, calculate the bond energies of (a) O–H (b) H–N (c) H–Cl (d) H–Br (e) C–Cl (f) C–Br (g) C–O, and (h) C–N bonds.*

Solution. (*a*) Bond energy of O–H bond

= $\Delta H°$ value for O atom + $\Delta H°$ value for H atom

= 247.5 KJ/mole + 217.7 KJ/mole

= 465.2 KJ/mole

On similar lines other bond energies can be calculated.

The average bond energy can also be calculated with the help of Hesse's law. For example average bond energy of C–H bond in CH_4 molecule can be calculated as follows :

For this purpose we need the heat change in the reaction :

$$C(g) + 4H(g) \rightarrow CH_4(g)$$

The magnitude of heat change for the above reaction can be obtained by the following reactions :

$C(s) + 2H_2(g) \rightarrow CH_4(g)$; $\Delta H_1 = -74.4$ KJ/mole

$C(g) \rightarrow C(s)$; $\Delta H_2 = -713.1$ KJ/mole

$4H(g) \rightarrow 2H_2(g)$; $\Delta H_3 = -872.1$ KJ/mole

On adding all these equations we get

$C(g) + 4H(g) \rightarrow CH_4(g)$; $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

$= -74.4 + (-713.1) + (-872.1)$

$= -1659.6$ KJ/mole

Here minus sign indicates the release of energy and 1659.6 KJ/mole represents the bond energy of four C–H bonds in CH_4 molecule. Now since all the four C–H bonds in CH_4 molecule are identical, the average bond energy of C–H bond in this molecule is equal to $\frac{1}{4} \times 1659.6 = 414.9$ KJ/mole.

Bond energy of A–B bond can also be calculated by using Pauling's relationship which is given below :

$$E(A-B) = \frac{D(A-A) + D(B-B)}{2} + 23(x_A - x_B)^2,$$

where E(A–B) = Bond energy of A–B bond

D(A–A) and D(B–B) = Dissociation energies of A–A and B–B bonds

x_A and x_B = Electronegativities of A and B atoms.

Multiple Bond Energies

A double bond in a diatomic molecule has a higher bond energy than a single bond, and a triple bond has a higher bond energy than a double bond. Thus the bond energies of various types of bonds are in the order :

Bond Energy of a triple bond > Bond energy of a double bond > Bond energy of a single bond

Thus we see that *for diatomic molecules bond dissociation energy is directly proportional to the bond order or bond multiplicity.* (Bond order is the number of covalent bonds by which the two atoms in a diatomic molecule are joined together). This fact is evident from the following values of bond energies (KJ/mole) of some single, double and triple bonds.

Bond	Bond order	Bond energy (KJ/mole)	Bond	Bond order	Bond energy (KJ/mole)
C–C	1	347.3	C–O	1	334.7
C=C	2	606.7	C=O	2	694.5
C≡C	3	803.3	C≡O	3	1071.3
N–N	1	163.2	N–O	1	200.8
N=N	2	418.5	N=O	2	611.0
N≡N	3	945.6			
C–N	1	284.5	O–O	1	146.4
C=N	2	615.1	O=O	2	497.9
C≡N	3	866.1			

The strength of a given bond depends on its bond energy. The strength of a bond is proportional to its bond energy value. Thus, the strength of various types of bonds will be in the following order :

Strength of a triple bond > Strength of a double bond > Strength of a single bond

Factors Affecting the Magnitude of Bond Energy

The factors that affect the magnitude of bond energy are :

(*i*) The extent to which the orbitals overlap with each other to form the bond.

(*ii*) The type of hybrid orbital formed.

(*iii*) The resonance energy of the molecule, if resonance is involved.

(*iv*) The type of bonding orbitals involved.

(*v*) Size of the atoms forming the bond.

(*vi*) The repulsion due to the presence of non-bonding electron pairs.

(*vii*) The amount of ionic character in the bond i.e., polarity of the bond.

Ionisation Energy or Ionisation Potential (IE or I or $\Delta_i H$)

Ionisation energy or ionisation potential is an atomic property which is shown by the atoms of all the elements. This property gives us an idea of the tendency of the elements to lose the outer-most shell electron to form a cation. With the help of this property a number of other properties of the elements like reducing power, metallic (or electropositive) character etc. can be explained.

What is Ionisation Potential ?

Ionisation energy of an element is defined as the amount of energy required to remove the most loosely bound electron (i.e. outermost shell electron) from isolated neutral gaseous atom in its lowest energy state (i.e. ground state) to convert it into a unipositive gaseous cation. Thus the ionisation energy of an atom, M(g) can be defined by a process represented by the following equation :

$$\underset{\text{Isolated gaseous atom}}{M(g)} + \textit{Energy supplied } (+ I_1) - e^- \rightarrow \underset{\text{Gaseous cation}}{M^+(g)} + e^-$$

Ionisation energy defined as above is strictly called **first ionisation energy,** since it corresponds to the removal of *one* electron only. Hence it is represented as I_1 or $+I_1$, where positive (plus) sign represents the absorption of energy by atom, M(*g*). It is also represented as $\Delta_i H$

The process represented by the above equation which depicts the removal of an electron from a gaseous atom is an *endothermic process*, since the removal of the electron requires energy.

Ionisation energy is also called **ionisation potential,** since it represents the amount of potential (or voltage) required to remove the most loosely bound electron from the gaseous atom of an element to get a gaseous cation.

Ionisation energy is measured in electron volts per atom (eV/atom), kilo calories per mole (Kcal/mole) or kilo joules per mole (KJ/mole). These quantities are related as :

1 *e*V/atom = 96.4705 KJ/mole = 23.06 Kcal/mole
1 Kcal/mole = 4.185 KJ/mole.

The values of ionisation potential are shown by a positive (plus) sign which is placed before them. *Positive sign represents the absorption of energy by the atom, M(g).*

Values of first ionisation potentials (in KJ/mole) of representative element (*s*-and *p*-block elements) are given Table 4.8. Positive sign has not been shown before the values.

Successive (Higher) Ionisation Potentials (I_1, I_2, I_3 ...)

In addition to first ionisation potential (I_1) defined above, second, third. etc ionisation potentials are also known. **Second ionisation potential (I_2)** *is the energy required to remove one more electron from the gaseous cation, $M^+(g)$ to get the doubly positively charged gaseous cation, $M^{2+}(g)$, i.e,*

$$M^+(g) + I_2 \xrightarrow{-e^-} M^{2+}(g) + e^-$$

Similarly, **third ionisation potential (I_3)** is the energy required to remove still one more electron from $M^{2+}(g)$ cation to get $M^{3+}(g)$ cation, *i.e.*

$$M^{2+}(g) + I_3 \xrightarrow{-e^-} M^{3+}(g) + e^-$$

Similarly ionisation potentials of higher and higher grades are also known. These are obtained by removing the electrons one by one. The values of eight successive ionisation potentials of the first ten elements are given in Table 4.9

Table 4.8. First ionization potentials (in KJ/mole) of representative elements (s-and p-block elements) (Positive sign has not been shown before the values).

Group → / Period ↓	*s*-block elements		*p*-block elements					
	IA	IIA	IIIA	IVA	VA	VIA	VIIA	Zero
1	1 H 1312.0							2 He 2372.3
2	3 Li 520.2	4 Be 899.5	5 B 800.6	6 C 1086.4	7 N 1402.3	8 O 1314.0	9 F 1681.0	10 Ne 2080.7
3	11 Na 495.8	12 Mg 737.7	13 Al 577.6	14 Si 786.5	15 P 1011.8	16 S 999.6	17 Cl 1251.1	18 Ar 1520.5
4	19 K 418.9	20 Ca 589.8	31 Ga 578.8	32 Ge 762.2	33 As 944.0	34 Se 940.9	35 Br 1139.9	36 Kr 1350.7
5	37 Rb 403.0	38 Sr 549.5	49 In 558.3	50 Sn 708.6	51 Sb 831.6	52 Te 869.3	53 I 1008.4	54 Xe 1170.4
6	55 Cs 375.7	56 Ba 502.9	81 Tl 589.3	82 Pb 715.5	83 Bi 703.3	84 Po 812.0	85 At –	86 Rn 1037.0

It may be seen from Table 4.9 that for a given element the magnitudes of its successive ionisation potentials are in the order :

$$\boxed{I_1 < I_2 < I_3 < I_4 \text{... and so on.}}$$

The successive increase in the values of successive ionisation potentials can be explained as follows on the basis of the concept of effective nuclear charge.

We know that the cations are formed by removing the electrons from the atom/cation one by one.

$$M(g) \xrightarrow{-e^-} M^+(g) \xrightarrow{-e^-} M^{2+}(g) \ldots \xrightarrow{-e^-} M^{n+}(g)$$

Thus a given cation has lesser number of electrons than its parent atom or cation. With the decrease of the number of electrons, the magnitude of the effective nuclear charge increases from $M(g)$ to $M^{n+}(g)$. With the increase of effective nuclear charge, the magnitude of the force of attraction between the nucleus and the outer-most shell electron cloud also increases as shown below :

Atom / cation : $M(g)$ $M^+(g)$ $M^{2+}(g)$.....$M^{n+}(g)$

Effective nuclear charge : — *Increasing* →

Force of attraction : — *Increasing* →

With the increase of force of attraction, the magnitude of energy to remove the outer-most shell electron (*i.e.* ionisation potential) also goes on increasing from M(g) to $M^{n+}(g)$ and hence :

$$I_1 < I_2 < I_3 < \text{..... and so on.sss}$$

Table 4.9. Values of I_1 ... I_2 I_s (in kJ/mole) of the ten elements

Elements with atomic number and electronic configuration	Values of successive ionisation potentials							
	I_1	I_2	I_3	I_4	I_5	I_6	I_7	I_8
H (1) ($1s^1$)	1312.0							
He (2) ($1s^2$)	2372.3	5250.4						
Li (3) ($1s^2$, $2s^1$)	520.3	7298.1	11814.9					
Be (4) ($1s^2$, $2s^2$)	899.5	1757.1	14848.7	21006.5				
B (5) ($1s^2$, $2s^2p^1$)	800.6	2427.0	3659.8	25025.7	32826.6			
C (6) ($1s^2$, $2s^2p^2$)	1086.4	2352.6	4620.5	6222.6	37830.4	47276.9		
N (7) ($1s^2$, $2s^2p^3$)	1402.3	2856.1	4578.1	7475.1	9444.9	53266.4	64359.8	
O (8) ($1s^2$, $2s^2p^4$)	1314.0	3388.2	5300.4	7469.3	10989.5	13326.4	71334.5	84077.4
F (9) ($1s^2$, $2s^2p^5$)	1681.0	3374.2	6050.4	8407.7	11022.7	15164.0	17867.7	92037.8
Ne (10) ($1s^2$, $2s^2p^6$)	2080.7	3952.3	6122.0	9370.0	12178.0	15238.0	19999.0	23069.0

When the term ionisation potential is not qualified, it is taken as first ionisation potential.

The total energy required to remove two electrons from a gaseous M(g) atom to get $M^{2+}(g)$ cation is the sum of first (I_1) and second (I_2) ionisation potentials, *i.e.*

$$M(g) + (I_1 + I_2) \xrightarrow{-2e^-} M^{2+}(g) + 2\,e^-$$

Factors Affecting the Magnitude of Ionisation Potential

Following are the factors which influence the magnitude of ionisation potential of atoms of elements.

1. Effective nuclear charge. Greater is the magnitude of effective nuclear charge, greater is the electrostatic force of attraction exerted by the nucleus on

the outer electrons. Thus it would be more difficult to remove the outermost shell electron from an atom with higher effective nuclear charge. This means that *greater the magnitude of effective nuclear charge, higher is the amount of energy* (*i.e.* ionisation potential) *needed to remove the outermost shell electron.* Thus with the *increase of the magnitude of effective nuclear charge, the magnitude of ionisation potential also increases.*

This factor has been used to explain the variation of ionisation potential values of the elements of a period of the representative elements of the periodic table as shown below :

We know that on passing from left to right in a period, the effective nuclear charge increases by 0.65 at each next element. The increase in effective nuclear charge increases the magnitude of ionisation potential as shown below for the elements of *2nd* period (Note the abnormal values of Be and N as compared with those of B and O).

Elements of 2nd period :

Li	Be	B	C	N	O	F	Ne
Effective nuclear charge :							
1.30	1.95	2.60	3.25	3.55	4.55	5.20	5.85

Increasing →

Ionisation potential (KJ/mole) :

520.3	899.5	800.6	1086.4	1402.3	1314.0	1681.0	2080.7

The abnormal values of Be and N as compared to those of B and 0 have been explained on subsequent pages.

2. Size of the atom (*r*). Greater is the magnitude of r of an atom, more far is the outer-most shell electron from the nucleus and hence lesser will be the force of attraction exerted by the nucleus on the outer most shell electron. Thus with the increase of *r*, it would be more and more easy to remove an electron from the outermost shell, *i.e. higher is the value of r of an atom, lower will be its ionisation energy.*

This fact has been used to explain the variation of ionisation potential values of the elements of a group and a period of the periodic table as shown below :

(*a*) *Variation of ionisation potential of the elements in a group.* We know that on proceeding from top to bottom in a group, *the value of r increases and hence the magnitude of ionisation potential decreases* as shown below for the elements of group IA.

Elements of group IA	Atomic (covalent) radius (A)	Ionisation potential (KJ/mole)
H (1)	0.32 ↓ *Increasing*	1312.0 ↓ *Decreasing*
Li (3)	1.23	520.3
Na (11)	1.54	495.8
K (19)	2.03	418.9
Rb (37)	2.16	403.4
Cs (55)	2.35	375.7

(*b*) ***Variation of ionisation potential of the elements in a period.*** We know that on proceeding from left to right in a period *the value of r decreases and hence the magnitude of ionisation potential increases* as shown below for the elements of 3*rd* period. The abnormal values of Mg and P can be noted. These have been explained in subsequent pages.

Elements of 3rd period :

Na	*Mg*	*Al*	*Si*	*P*	*S*	*Cl*	*Ar*
Atomic (covalent) radius (Å) :							
1.54	*1.36*	*1.18*	*1.11*	*1.06*	*1.02*	*0.99*	*0.98*
Ionisation potential (KJ/mole) :							
495.8	*737.7*	*577.6*	*786.5*	*1011.8*	*999.6*	*1251.1*	*1520.5*

3. Principal quantum number (*n*). Greater is the value of *n* for the valence-shell electron of an atom, farther away this electron will be from the nucleus and hence lesser will be the force of attraction exerted by the nucleus on it. This means that lesser amount of energy will be required to remove the valence-shell electron. Thus with the increase of the value of *n* of the valence-shell electron, ionisation potential decreases and vice versa. In simple words the energy required (*i.e.* ionisation potential) to remove an electron from an orbital with higher *n* value (*i.e.* belonging to a higher shell) will be less than that required to remove an electron from an orbital with a lower *n* value (*i.e.* belonging to a lower shell.) *Thus with the increase of the principal quantum number (n) of the orbital from which the electron is to be removed, the magnitude of ionisation potential decreases.*

This factor has been used to explain the following :

(*a*) ***Variation of ionisation potential of elements in a group.*** On moving down a group the value of the principal quantum number (*n*) of the orbital from which the electron is to be removed increases and hence the magnitude of the ionisation potential decreases as shown below for the elements of group II A.

Elements of group II A	Valence shell electronic configuration	*n*	Ionisation potential (KJ/mole)
Be	$2s^2$	2	899.5
Mg	$3s^2$	3	737.7
Ca	$4s^2$	4	589.8
Sr	$5s^2$	5	549.5
Ba	$6s^2$	6	502.9

(*b*) ***Successive ionization potentials of an element.*** (*i*) Values of I_1 and I_2 of Li atom ($1s^2$, $2s^1$) which are 520.3 KJ/mole and 7298.1 KJ/mole respectively can be represented by the following equations :

$$\text{Li}\ (1s^2, 2s^1) \xrightarrow[I_1 = 520.3\ \text{KJ/mole}]{-e^-\ (\text{From } 2s \text{ orbital with } n = 2)} \text{Li}^+(1s^2)$$

$$\xrightarrow[I_2 = 7298.1\ \text{KJ/mole}]{-e^-\ (\text{From } 1s \text{ orbital with } n = 1)} \text{Li}^{2+}(1s^1)$$

Why I_2 is greater than I_1 can be explained by saying that in case of I_1 the electron is removed from 2*s* orbital which has higher value of $n(=2)$ while in case of I_2 the electron is removed from 1*s* orbital which has lower value of $n(=1)$.

(*ii*) I_3 of Mg is very high as compared to I_1 and I_2 (I_1 = 737.7 KJ/mole, I_2 = 1450.7 KJ/mole, I_3 = 7732.8 KJ/mole). This can be explained by considering I_1, I_2 and I_3 as represented by the following equations :

$$Mg\ (1s^2, 2s^2p^6, 3s^2) \xrightarrow[I_1 = 737.7\ KJ/mole]{-e^-\ (From\ 3s\ orbital\ with\ n = 3)} Mg^+(1s^2, 2s^2p^6, 3s^1)$$

$$\xrightarrow[I_2 = 1450.7\ KJ/mole]{-e^-\ (From\ 3s\ orbital\ with\ n = 3)} Mg^{2+}(1s^2, 2s^2p^6)$$

$$\xrightarrow[I_3 = 7732.8\ KJ/mole]{-e^-\ (From\ 2p\ orbital\ with\ n = 2)} Mg^{3+}(1s^2, 2s^2p^5)$$

In case of I_1 and I_2 the electron is removed from an orbital with n = 3 while in case of I_3 the electron is removed from an orbital having a lower value of n (=2). Hence I_3 is very high as compared to I_1 and I_2.

(*iii*) The values of I_1, I_2 and I_3 (in KJ/mole) of Be and B are given below :

	I_1	I_2	I_3
Be	899.5	1757.1	14848.7
B	800.6	2427.0	3659.8

It may be seen from these values that there is a big jump in ionisation potentials of Be from I_2 (= 1757.1 KJ/mole) to I_3 (= 14848.7 KJ/mole) as compared with I_2 (= 2427.0 KJ/mole) to I_3 (= 3659.8 KJ/mole) of B. How to explain this big jump? It has been explained as follows :

$$Be\ (1s^2, 2s^2) \xrightarrow[I_1 = 899.5\ KJ/mole]{-e^-\ (From\ 2s\ orbital\ with\ n = 2)} Be^+(1s^2, 2s^1)$$

$$\xrightarrow[I_2 = 1757.1\ KJ/mole]{-e^-\ (From\ 2s\ orbital\ with\ n = 2)} Be^{2+}(1s^2)$$

$$\xrightarrow[I_3 = 14848.7\ KJ/mole]{-e^-\ (From\ 1s\ orbital\ with\ n = 1)} Be^{3+}(1s^1)$$

$$B\ (1s^2, 2s^2\ 2p^1) \xrightarrow[I_1 = 800.6\ KJ/mole]{-e^-\ (From\ 2p\ orbital\ with\ n = 2)} B^+(1s^2, 2s^2)$$

$$\xrightarrow[I_2 = 2427.0\ KJ/mole]{-e^-\ (From\ 2s\ orbital\ with\ n = 2)} B^{2+}(1s^2, 2s^1)$$

$$\xrightarrow[I_3 = 3659.7\ KJ/mole]{-e^-\ (From\ 2s\ orbital\ with\ n = 2)} B^{3+}(1s^2)$$

It may be seen that in case of I_3 of Be atom the electron is removed from 1*s* orbital having lower value of $n(= 1)$ while in case of I_3 of B atom the electron is removed from 2*s* orbital having higher value of n (= 2).

(c) Ionisation potentials of inert gases as compared to those of alkali metals. When we proceed from an inert gas (*zero group*) to an alkali metal (*IA group*), there is a large decrease in the value of ionisation potential as shown below :

Inert gas (Zero group)	Alkali metal (IA group)
He ($Z = 2$) = 2372.3 KJ/mole $1s^2$	Li ($Z = 3$) = 520.3 KJ/mole $1s^2, 2s^1$
Ne($Z = 10$) = 2080.7 KJ/mole $1s^2, 2s^2p^6$	Na($Z = 11$) = 495.8 KJ/mole $1s^2, 2s^2p^6, 3s^1$
Ar($Z = 18$) = 1520.7 KJ/mole $1s^2, 2s^2p^6, 3s^2p^6$	K($Z = 19$) = 418.9 KJ/mole $1s^2, 2s^2p^6, 3s^2p^6, 4s^1$
Kr($Z = 36$) = 1350.7 KJ/mole $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6$	Rb($Z = 37$) = 403.0 KJ/mole $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6, 5s^1$
Xe($Z = 54$) = 1170 KJ/mole $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^2p^6$	Cs($Z = 35$) = 375.7 KJ/mole $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^2p^6, 6s^1$

The large decrease is explained on the basis of the fact that in case of an alkali metal it is easier to remove an electron from an orbital belonging to a higher shell while in case of an inert gas it is more difficult to remove the same from the orbital belonging to the lower shell.

4. Shielding effect. We have already said that in a multi- electron atom the electrons lying between the nucleus and the valence-shell (called intervening electrons) shield the outermost shell electron from the nucleus. The effect of shielding the valence-shell electron from the nucleus which is caused by the intervening electrons is called *shielding* or *screening effect*. The magnitude of shielding effect determines the magnitude of the force of attraction between the nucleus and the valence-shell electron. Greater is the magnitude of shielding effect working on the valence-shell electron, smaller is the magnitude of the force of attraction between the nucleus and the valence-shell electron and hence lower is the amount of energy (*i.e.* ionisation potential) to remove the valence-shell electron. *Thus with the increase of shielding effect, ionisation potential decreases.*

The magnitude of shielding effect is determined by the magnitude of shelding constant, σ. Greater the value of σ, greater is the amount of shielding effect caused by the intervening electrons on the valence-shell electron and hence lower is the value of ionisation potential. Thus *with the increase of* σ, *the magnitude of ionisation potential decreases.*

This factor can be used to explain the variation of ionisation potential of the elements of a given group of the periodic table. As we move down a group, the number of inner-shell electrons (*i.e.* intervening electrons) increases and hence the magnitude of shielding effect (or the magnitude of σ) caused by these electrons on the valence-shell electron increases. With the increase of the magnitude of shielding effect or σ, the ionisation potential decreases. This can be shown by considering the ionisation potential values of the elements of group IA as given below :

Elements of group IA	Electronic configuration	No. of inner shell electrons	Value of σ	Ionisation potential (KJ/mole)
Li (3)	2, 1	2	1.70	520.3
Na (11)	2, 8, 1	10	8.80	495.8
K (19)	2, 8, 8, 1	18	16.80	418.9
Rb (37)	2, 8, 18, 8, 1	36	34.80	403.0
Cs (55)	2, 8, 18, 18, 8, 1	54	52.80	375.7
		←Increasing	←Increasing	←Decreasing

This factor has also been used to explain the large decrease in the value of ionisation potential when we pass from an inert gas (*zero group*) to an alkali metal (*IA group*). For example when we pass from He to Li, there is large decrease in the value of ionisation potential (He = 2372.3 KJ/mole, Li 520.3 KJ/mole). This large decrease has been explained as follows :

In Li atom ($1s^2$, $2s^1$) the electron to be removed from 2*s*-orbital is *effectively screened* or *shielded* by the two electrons in 1*s*-orbital while in He atom ($1s^2$) the electron to be removed from the 1*s*-orbital is *not effectively* screened by the other electron in 1*s*-orbital, since both the electrons in He atom reside in the same orbital *viz* 1*s* orbital.

On similar grounds a large decrease in the ionisation potential on proceeding from Ne (Z = 10) to Na (Z = 11), from Ar(Z = 18) to K(Z = 19), from Kr(Z = 36) to Rb(Z = 37) and from Xe(Z = 54) to Cs(Z = 55) can also be explained.

5. Half-filled and completely filled orbitals. According to Hund's rule, *half-filled* (ns^1, np^3, nd^5) or *completely-filled* (ns^2, np^6, nd^{10}) *orbitals* are comparatively more stable and hence more energy is needed to remove an electron from such orbitals. This means that *the ionisation potential of an atom having half-filled or completely-filled orbitals in its electronic configuration is relatively higher than that expected normally from its position in the periodic table.*

This factor has been used to explain the higher value of ionisation potential of some of the elements as compared to that of their left-hand neighbour in a period of the periodic table. For example as we proceed from left to right in a period of the long form of periodic table, usually the ionisation potential increases due to the successive increase in nuclear charge (*i.e.* atomic number) and decrease in atomic size. However, there are certain elements which show irregular trends. For example :

(*i*) In 2*nd* period Be (Z = 4) has higher ionisation potential than B (Z = 5). Similarly N (Z = 7) has higher value of ionisation potential than O (Z = 8).

(*ii*) In 3*rd* period Mg (Z = 12) has higher value of ionisation potential than Al (Z = 13). Similarly P (Z = 15) has higher ionisation potential than S (Z = 16).

These irregularities can be explained as follows on the basis of the concept of extra stability associated with completely-filled and half-filled orbitals.

(*a*) *Ionisation potential of Be compared to that of B, and of Mg compared to that of Al.* The equations representing the ionisation potential of Be and B can be written as :

$$Be\ (1s^2, 2s^2) \xrightarrow[I_1 = 899.5\ KJ/mole^{-1}]{-e^-\ (From\ completely\text{-}filled\ 2s\ orbital)} Be^+(1s^2, 2s^1)$$

$$B\ (1s^2, 2s^2, 2p^1) \xrightarrow[I_1 = 800.6\ KJ/mole^{-1}]{-e^-\ (From\ partially\ filled\ 2p\ orbital)} B^+(1s^2, 2s^2)$$

In case of Be it is more difficult to remove an electron from the completely-filled 2*s*-orbital while in case of B it is easier to remove the same from a *partially-filled* 2*p*-orbital. Thus the ionisation potential of Be is higher than that of B. Note that Be and B both have the same value of principal quantum number ($n = 2$).

Similarly the higher value of ionisation potential of Mg as compared to that of Al is because of the fact that in case of Mg the electron is to be removed from the *completely-filled* 3*s*-orbital while in case of Al the same is removed from the *partially-filled* 3*p*-orbital.

$$Mg\ (1s^2, 2s^2p^6, 3s^2) \xrightarrow[I_1 = 737.7\ KJ/mole^{-1}]{-e^-\ (From\ completely\text{-}filled\ 3s\ orbital)} Mg^+(1s^2, 2s^2p^6, 3s^1)$$

$$Al\ (1s^2, 2s^2p^6, 3s^2p^1) \xrightarrow[I_1 = 577.6\ KJ/mole^{-1}]{-e^-\ (From\ partially\text{-}filled\ 3p\ orbital)} Al^+(1s^2, 2s^2p^6, 3s^2)$$

(b) Ionisation potential of N compared to that of O, and of P compared to that of S. The equations representing the ionisation potential of N and O can be written as :

$$N(1s^2, 2s^2 2p^3) \xrightarrow[I_1 = 1402.3\ KJ/mole]{-e^-\ (From\ half\text{-}filled\ 2p\ orbital)} N^+(1s^2, 2s^2.2p^2)$$

$$O(1s^2, 2s^2 2p^4) \xrightarrow[I_1 = 1314.0\ KJ/mole]{-e^-\ (From\ partially\text{-}filled\ 2p\ orbital)} O^+(1s^2, 2s^2.2p^3)$$

In case of N it is more difficult to remove an electron from the *half -filled 2p-orbital* while in case of O it is easier to remove the same from a *partially filled* 2*p*-orbital. Thus the ionisation potential of N is higher than that of O.

On similar grounds. the higher ionisation potential of P as compared to S can be explained.

$$P\ (2, 8, 3s^2 3p^3) \xrightarrow[I_1 = 1011.8\ KJ/mole^{-1}]{-e^-\ (From\ half\text{-}filled\ 3p\ orbital)} P^+(2, 8, 3s^2.3p^2)$$

$$S\ (2, 8, 3s^2 3p^4) \xrightarrow[I_1 = 999.6\ KJ/mole]{-e^-\ (From\ partially\text{-}filled\ 3p\ orbital)} S^+(2, 8, 3s^2.3p^3)$$

Noble gases (ns^2p^6), Zn ($3d^{10}.4s^2$), Cd ($4d^{10}.5s^2$) and Hg ($4f^{10}.5d^{10}.6s^2$) which have completely-filled orbitals possess very high ionisation potentials.

6. Nature of orbitals. The nature of the orbitais of the valence-shell from which the electron is to be removed also influences the magnitude of ionisation potential. The relative order of energy of *s*, *p*, *d* and *f* orbitals of a given nth shell is as :

$$ns < np < nd < nf$$

The above order means that the relative order of ease with which the electron residing in these orbitals can be removed will be as :

$$\text{—Order of ease of removing electron increasing} \rightarrow$$

$$ns < np < nd < nf$$

This order clearly indicates that to remove an electron from *f*-orbital will be the easiest while to remove the same from s-orbital will be the most difficult, *i.e.* the amount of energy required to remove an electron from *f*-orbital is minimum while that required to remove an electron from *s*-orbital is maximum. In other words, other factors remaining the same, the ionisation potentials of an electron in *s*, *p*, *d* and *f*-orbitals are as the following order :

$$ns > np > nd > nf$$

This factor can be used to explain the successive ionisation potentials of an element and higher values of ionisation potential of Be and Mg as compared to that of B and Al respectively.

(*a*) *Successive ionisation potentials of an element.* *1st* (I_1) and *2nd* (I_2) ionisation potentials of B atom ($1s^2, 2s^2\ 2p^1$) are : $I_1 = 800.6$ KJ/mole^{-1}, $I_2 = 2427.0$ KJ/mole^{-1} and can be represented by the following equations :

$$B\ (1s^2, 2s^2 2p^1) \xrightarrow[I_1 = 800.6\ KJ.mole^{-1}]{-e^-\ (2p^1)} B^+(1s^2, 2s^2)$$

$$B^+(1s^2, 2s^2) \xrightarrow[I_2 = 2427.0\ KJ.mole^{-1}]{-e^-\ (2s^1)} B^{2+}(1s^2, 2s^1)$$

Why I_1 is lower than I_2 is explained by saying that since it is easier to remove an electron from $2p$ orbital than to remove the same from $2s$ orbital, I_1 which corresponds to the removal of a $2p$ electron is lower than I_2 which corresponds to the removal of $2s$ electron. Here it may be noted that both the orbitals *viz.* $2p$ and $2s$ belong to the same shell i.e. the value of principal quantum number (n) of $2p$ and $2s$ orbitals is the same *viz.* $n = 2$.

(*b*) *1st ionisation potentials of two different elements of the same period.* In general when we proceed from left to right in a period, ionisation potentials increase. But some of the elements show irregular trends. For example first ionisation potential of Be = 899.5 KJ. mole^{-1} is higher (instead of lower) than that of B = 800.6 KJ. mole^{-1}. These ionisation potentials can be represented as follows :

$$Be\ (1s^2, 2s^2) \xrightarrow[I_1 = 899.5\ KJ.mole^{-1}]{-e^-\ (2s^1)} Be^+(1s^2, 2s^1)$$

$$B\ (1s^2, 2s^2 2p^1) \xrightarrow[I_2 = 800.6\ KJ.mole^{-1}]{-e^-\ (2p^1)} B^+(1s^2, 2s^2)$$

Ionisation potential of Be is higher than that of B, since to remove an electron from a $2s$-orbital of Be requires more energy than to remove the same from a $2p$-orbital of B.

On similar lines of reasoning it can also be explained why ionisation potential of Mg is higher than that of Al (Mg = 737.7 KJ. mole^{-1}, Al = 577.6 KJ. mole^{-1}).

$$\text{Mg}\ (2, 8, 3s^2) \xrightarrow[I_1 = 737.7\ \text{KJ.mole}^{-1}]{-e^-\ (3s^1)} \text{Mg}^+(2, 8, 3s^1)$$

$$\text{Al}\ (2, 8, 3s^2 3p^1) \xrightarrow[I_2 = 577.6\ \text{KJ.mole}^{-1}]{-e^-\ (3p^1)} \text{Al}^+(2, 8, 3s^2)$$

All the factors mentioned above are independent of each other and hence it becomes impossible to predict the exact extent of each to which they can affect the magnitude of ionisation potential.

Variation of Ionisation Potential in a Period and a Group of Representative Elements :

(*a*) **In a period.** *In general, as we move from left to right in a period, the ionisation. potential of the elements increases due to the successive increase in the nuclear charge (i.e. atomic number) and decrease in atomic size.* However there are certain elements which show irregular trends.

1st period. When we pass from H to He, there is a large increase in the value of ionisation potential (H = 1320.0 KJ.mole^{-1}, He = 2372.3 KJ. mole^{-1}). This large increase in case of He atom is explained on the basis of the fact that, since in case of He both the electrons are present in the same orbital namely 1*s* orbital, the first electron is not able to shield the second. This increases the ionisation potential value of He atom.

$$\text{H}\ (1s^1) \xrightarrow[I_1 = 1320.0\ \text{KJ.mole}^{-1}]{-e^-\ (1s^1)} \text{H}^+(1s^0)$$

$$\text{He}\ (1s^2) \xrightarrow[I_1 = 2372.3\ \text{KJ.mole}^{-1}]{-e^-\ (1s^1)} \text{He}^+(1s^1)$$

2nd period. Now when we proceed from He to Li, there is a large decrease in the value of ionisation potential (He = 2372.3 KJ.mole^{-1}, Li = 520.3 KJ.mole^{-1}). This large decrease has been explained by the following two arguments.

(*i*) In case of Li atom ($1s^2$, $2s^1$) it is easier to remove an electron from the 2nd shell (n = 2) while in case of He atom ($1s^2$) it is comparatively more difficult to remove the same from the 1st shell (n = 1). This means that the removal of an electron from 2*s* orbital of Li atom requires less energy while the removal of the same from 1*s* orbital of He atom requires more energy. Hence the ionisation potential of He is much higher than that of Li.

$$\text{He}\ (1s^2) \xrightarrow[I_1 = 2372.0\ \text{KJ.mole}^{-1}]{-e^-\ (1s^1)} \text{He}^+(1s^1)$$

$$\text{Li}\ (1s^2, 2s^1) \xrightarrow[I_1 = 520.3\ \text{KJ.mole}^{-1}]{-e^-\ (2s^1)} \text{Li}^+(1s^2)$$

(*ii*) In Li atom ($1s^2$, $2s^1$) the electron to be removed from 2*s*-orbital is *effectively screened or shielded* by the two electrons in 1*s* orbital while in He atom ($1s^2$) the electron to be removed from the 1*s*-orbital is not effectively screened by the other electron in 1*s*-orbital, since both the electrons in He atom reside in the same orbital *viz*. 1*s*-orbital.

On passing from Li to Ne via Be, B etc. generally the ionisation potential increases with the increase of effective nuclear charge and decrease of atomic size. However Be and N show irregular trends as is evident from the fact that, although Be and N have smaller effective nuclear charges than their next elements namely B and O respectively (Be = 1.95. B = 2.60, N = 3.90, O = 4.55), these elements have higher ionization potential values than B and O respectively. These higher values can be explained as follows.

In case of Be ($1s^2$, $2s^2$) it is more difficult to remove an electron from the *completely filled 2s-orbital* while in case of B ($1s^2$, $2s^22p^1$) it easier to remove the same from a *partially-filled* 2*p*-orbital. Since to remove an electron from a 2*s*-orbital of Be atom requires more energy than to remove the same from a 2*p*-orbital of B atom, ionisation potential of Be is higher than that of B.

In case of N ($1s^2$, $2s^2$, $2p^3$) it is more difficult to remove an electron from the *half-filled 2p.orbital* while in case of O ($1s^2$. $2s^22p^4$) it is easier to remove the same from a *partially-filled 2p-orbital*. Thus the ionization potential of N is higher than that O.

Now when pass from Ne (Z = 10) to Na (Z = 11), there is a large decrease in the value of ionization potential of Na as compared to that of Ne (Ne = 2080.7 KJ.mole^{-1}, Na = 495.8 KJ.mole^{-1}). This large decrease has been explained by the following two arguments :

(*i*) In case of Na atom ($1s^2$, $2s^2p^6$, $3s^1$) it is easier to remove an electron from 3*rd* shell (n = 3) while in case of Ne atom ($1s^2$, $2s^2p^6$) it is comparatively more difficult to remove the same from the 2*nd* shell (n = 2). This means that the removal of an electron from 3*s*-orbital of Na atom requires less energy while the removal of the same from 2*p*-orbital of Ne atom requires more energy. Hence the ionization potential of Ne is much higher than that of Na.

$$\text{Ne}\,(1s^2, 2s^2p^6) \xrightarrow[I_1 = 2080.7\ \text{KJ.mole}^{-1}]{-e^-\,(2p^1)} \text{Ne}^+(1s^2, 2s^2p^5)$$

$$\text{Na}\,(1s^2, 2s^2p^6, 3s^1) \xrightarrow[I_1 = 495.8\ \text{KJ.mole}^{-1}]{-e^-\,(3s^1)} \text{Na}^+(1s^2, 2s^2p^6)$$

(*ii*) In case of Na atom the electron to be removed from 3*s*-orbital is *effectively* screened by the two electrons in 1*st* shell and eight electrons in 2*nd* shell while in case of Ne atom the electron to be removed from 2*p*-oribital is not *effectively* screened by the other five electrons of 2*p*-orbital.

3rd period. The elements of this period also show a general increase in their ionisation potential value with a few exceptions. For example ionisation potentials of Mg and P are higher than those of Al and S.

Higher value of ionisation potential of Mg as compared to Al is explained on the same lines of argument as used in explaining the higher value of Be compared to B in 2*nd* period. Similarly higher value of P as compared to S has been explained on the same lines of argument as used in explaining the higher value of N compared to O in 2*nd* period.

(*b*) **In a group.** *When we proceed from top to bottom in a group of representative elements, the ionisation potential values of the elements go on decreasing.* This

decrease in the ionisation potential values on descending a group can be accounted for as follows.

We have already said that on descending a group, the magnitude of effective nuclear charge acting on the valence-shell electron remains the same (First element is a typical case). Thus the concept of effective nuclear charge cannot be used to explain the decrease in ionisation potential values. However, the decrease has been explained on the basis of the concept of atomic size, the value of principal quantum number (n) of the orbital from which the electron is to be removed and shielding effect (or the magnitude of screening constant, σ) caused by the intervening electrons on the valence-shell electron. It is already known that all these quantities increase on descending a group and *their increase on proceeding from top to botton in a group decreases* the ionisation potential values as shown below for the elements of group IA.

Etements of group IA (Atomic number) given in bracket)	Electronic configuration	Atomic (covalent radius (Å)	(n)	σ	Ionisation potential KJ/mole
Li (3)	2, 1	1.23	2	1.70	520.3
N (11)	2, 8, 1	1.54	3	8.80	495.8
K (19)	2, 8, 8, 1	2.03	4	16.80	418.9
Rb (37)	2, 8, 18, 8, 1	2.16	5	34.80	403.4
Cs (55)	2, 8, 18, 18, 8, 1	2.35	6	52.80	375.7

The variation of ionisation potential in a period and a group of representative elements (s and p block elements) of the long form of periodic table can be shown as given in Fig. 4.13.

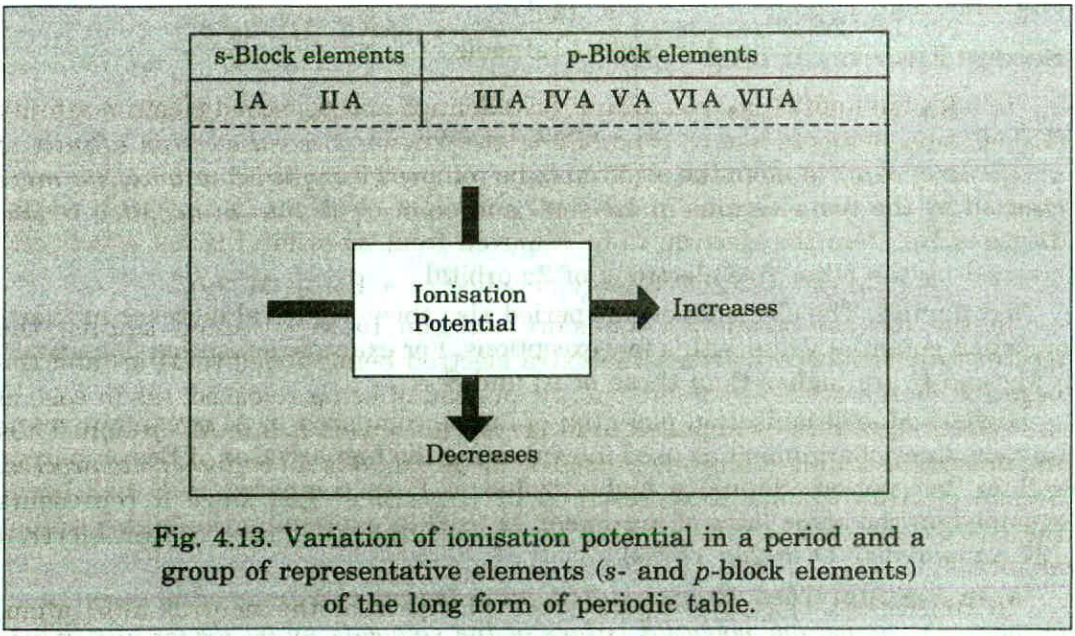


Fig. 4.13. Variation of ionisation potential in a period and a group of representative elements (s- and p-block elements) of the long form of periodic table.

Electron Affinity (EA or $\Delta_{eg}H$)

Electron affinity (abbreviated as EA) is an atomic property which gives us an idea of the tendency of the element to accept the electron to form an anion. With the help of this property a number of properties of the elements like oxidising power and non-metallic (or electronegative) character can well be explained.

What is Electron Affinity ?

Electron affinity of an element is defined as the amount of energy released in adding an extra electron from outside to an isolated neutral gaseous atom in its lowest energy state (i.e. ground state) to convert it into a gaseous anion. Thus electron affinity of an atom, M(g) can be defined by the following process:

$$\underset{\text{Isolated gaseous atom}}{M(g)} + e^-(g) \rightarrow \underset{\text{Gaseous anion}}{M^-(g)} + \textit{Energy released } (= -EA_1)$$

Electron affinity defined above is strictly called **first electron affinity,** since it corresponds to the addition of *one* electron only. Hence it is represented as $-EA_1$ where negative (minus) sign represents the release of energy. It is also represented as E or $\Delta_{eg}H$.

The above process which depicts the addition of an electron to a gaseous atom is an *exothermic process*, since in the addition of an electron energy is released.

Electron affinity is also called **electron affinity energy.** It is measured in electron volts, kilocalories or kilojoules. The values of electron affinity are shown by a negative (minus) sign which is placed before them. Negative sign represents the release of energy in the addition of an electron to M(*g*) atom.

Values of first electron affinity (in KJ/mole) of *s*-and *p*-block elements are given in Table 4.10.

Second Electron Affinity

In addition to first electron affinity (E_1) defined above, second electron affinity (E_2) of some elements like O, S and Se is also known. *Second electron affinity of an element, M(g) is defined as the amount of energy required to add one more electron to its mono-negative anion, $M^-(g)$ to convert it into di-negative anion, $M^{2-}(g)$. Thus.*

$$M^-(g) + e\ (g) + \text{Energy supplied } (= +E_2) \rightarrow M^{2-}(g)$$

In the process of adding one more electron to $M^-(g)$ anion against the electrostatic repulsion between the extra electron being added to $M^-(g)$ and the negative charge on M^- (*g*) anion, energy, instead of being released, (as in case of first electron affinity) is supplied to $M^-(g)$ ion to convert it into $M^{2-}(g)$ ion. Thus the process of adding a second electron to $M^-(g)$ anion is an *endothermic process*. Second electron affinity is represented by a positive sign, since it represents the energy absorbed (*i.e.* supplied) and not released as in case of first electron affinity.

In the formation of a dinegative ion, $M^{2-}(g)$ from the neutral M(*g*) atom, electrons are added one by one. Energy equal to first electron affinity (E_1) is

Table 4.10. Electron affinities of *s*- and *p*-block elements in KJ/mole. Negative sign indicates the release of energy (exothermic reaction) when an electron is added to an atom to convert it into an anion while the positive sign indicates the absorption of energy (endothermic reaction) for the same process

Group → / Period ↓	IA	IIA	IIIA	IVA	VA	VIA	VIIA	Zero
1	$H \xrightarrow{+e^-} H^-$ −72.9							$He \xrightarrow{+e^-} He^-$ ~ 0
2	$Li \xrightarrow{+e^-} Li^-$ −59.8	$Be \xrightarrow{+e^-} Be^-$ ~ 0	$B \xrightarrow{+e^-} B^-$ −23	$C \xrightarrow{+e^-} C^-$ −122	$N \xrightarrow{+e^-} N^-$ +20.1	$O \xrightarrow{+e^-} O^-$ −141 $O \xrightarrow{+2e^-} O^{2-}$ + 780	$F \xrightarrow{+e^-} F^-$ −322	$Ne \xrightarrow{+e^-} Ne^-$ ~ 0
3	$Na \xrightarrow{+e^-} Na^-$ −52.9	$Mg \xrightarrow{+e^-} Mg^-$ ~ 0	$Al \xrightarrow{+e^-} Al^-$ −44	$Si \xrightarrow{+e^-} Si^-$ −120	$P \xrightarrow{+e^-} P^-$ −74	$S \xrightarrow{+e^-} S^-$ −200.4 $S \xrightarrow{+2e^-} S^{2-}$ + 590	$Cl \xrightarrow{+e^-} Cl^-$ −348.7	$Ar \xrightarrow{+e^-} Ar^-$ ~ 0
4	$K \xrightarrow{+e^-} K^-$ −48.9	$Ca \xrightarrow{+e^-} Ca^-$ ~ 0	$Ga \xrightarrow{+e^-} Ga^-$ −36	$Ge \xrightarrow{+e^-} Ge^-$ −116	$As \xrightarrow{+e^-} As^-$ −77	$Se \xrightarrow{+e^-} Se^-$ −195 $Se \xrightarrow{+2e^-} Se^{-2}$ + 420	$Br \xrightarrow{+e^-} Br^-$ −324.5	$Kr \xrightarrow{+e^-} Kr^-$ ~ 0
5	$Rb \xrightarrow{+e^-} Rb^-$ −46.9	$Sr \xrightarrow{+e^-} Sr^-$ ~ 0	$In \xrightarrow{+e^-} In^-$ −34	$Sn \xrightarrow{+e^-} Sn^-$ −121	$Sb \xrightarrow{+e^-} Sb^-$ −101	$Te \xrightarrow{+e^-} Te^-$ −190.1	$I \xrightarrow{+e^-} I^-$ −295	$Xe \xrightarrow{+e^-} Xe^-$ ~ 0

liberated in the addition of one electron to M(*g*) atom to convert it into $M^-(g)$ anion and the process is *exothermic*

$M(g) + e^-(g) \rightarrow M^-(g)$ + *Energy liberated* $(= -E_1)$.....*Exothermic process* ...(*i*)

Negative sign placed before E_1 indicates the *liberation* of energy.

Energy equal to second electron affinity (E_2) is to be supplied in the addition of one more electron to $M^-(g)$ to convert it into $M^{2-}(g)$and the process is *endothermic*.

$M^-(g) + e^-$ + *Energy supplied* $(= + E_2) \rightarrow M^{2-}(g)$...*Endothermic process* ...(*ii*)

Plus sign placed before E indicates the *absorption* of energy.

Now since $E_2 > E_1$, there is net absorption of energy in the formation of a dinegative ion, $M^{2-}(g)$ from the neutral M(*g*) atom and the amount of energy absorbed in this process is equal $E_2–E_1$ which is obtained by adding equations (*i*) and (*ii*) given above. Thus :

$M(g) + 2e^-(g)$ + *Energy absorbed* $(= E_2 - E_1) \rightarrow M^{2-}(g)$

Examples to Illustrate the Concept of Second Electron Affinity

The following examples may be used for the illustration of the concept of second electron affinity.

***(i)* Formation of $O^{2-}(g)$ from O(g).** The formation of $O^{2-}(g)$ from O(*g*) can be shown by the following equations :

$O(g) + e^-(g) \rightarrow O^-(g) + E_1(= -141$ KJ/mole) ...*Exothermic process*

$O^-(g) + e^-(g) + E_2(= + 921$ KJ/mole) $\rightarrow O^{2-}(g)$ ...*Endothermic process*

On adding :

$O(g) + 2e^-(g)$ + Energy $(= + 921 - 141 = + 780$ KJ/mole) $\rightarrow O^{2-}(g)$

Thus the total electron affinity for two electrons for oxygen atom = + 780 KJ/mole.

***(ii)* Formation of $S^{2-}(g)$ from S(g).**

$S(g) + e^-(g) \rightarrow S^-(g) + E_1(= -200.4$ KJ/mole) ...*Exothermic process*

$S^-(g) + e^-(g) + E_2(= + 790.4$ KJ/mole) $\rightarrow S^{2-}(g)$ ...*Endothermic process*

On adding :

$S(g) + 2e^-(g)$ + Energy $(= + 790.4 - 200.4 = + 590$ KJ/mole) $\rightarrow S^{2-}(g)$

Thus the total electron affinity for two electrons for sulphur atom = + 590 KJ/mole.

***(iii)* Formation of $Se^{2-}(g)$ from Se(g)**

$Se^-(g) + e^-(g) \rightarrow Se^-(g) + E_1(= -195$ KJ/mole) ...*Exothermic process*

$Se^-(g) + e^-(g) + E_2(= + 615$ KJ/mole) $\rightarrow Se^{2-}(g)$ ...*Endothermic process*

On adding :

$Se(g) + 2e^-(g)$ + Energy $(= + 615 - 195 = + 420$ KJ/mole) $\rightarrow Se^{2-}(g)$

Thus the total electron affinity for two electrons for Se atom = + 420 KJ/mole.

Factors Affecting the Magnitude of Electron Affinity

The factors on which the magnitude and sign of electron affinities depend are, in general, similar to those which determine the ionisation energies but in the reverse order. These factors are :

1. Atomic radius. Larger the atomic radius, lesser the tendency of the atom to attract the additional electron towards itself, lesser the force of attraction exerted by the nucleus on the extra electron being added to the outer-shell of the atom and hence lesser the amount of energy released when the extra electron is added to the atom to form an anion. Thus *smaller atoms have higher electron affinities.*

2. Effective nuclear charge. Higher the effective nuclear charge, greater the tendency of the atom to attract the additional electron towards itself, greater the force of attraction exerted by the nucleus on the extra electron being added to the outer-shell of the atom and hence higher the amount of energy released when the extra electron is added to the atom. *Thus the atoms with higher effective nuclear charge have higher electron affinities.*

3. Electronic configuration. The effect of this factor on the magnitude of electron affinity of an element can be explained by the following examples :

(*a*) Electron affinity values of the elements of group IIA. *ns* orbital of the valence-shell of the atoms of these elements is completely filled and hence the addition of any extra electron from outside to this *ns* orbital is not possible. *Consequently the elements of group IIA have practically zero electron affinity.*

(*b*) Electron affinity values of N and P. The valence-shell electronic configuration of N and P are :

$$N \rightarrow 2s^2p^3 \; ; \quad P \rightarrow 3s^2p^3$$

$2p$ and $3p$ orbitals in N and P respectively are half-filled and hence are extra ordinarily stable. Thus the addition of any extra electron from outside to these orbitals is not possible. *Consequently N and P have very low electron affinity values* (N = + 20.1 KJ/mole, P = –74 KJ/mole).

(*c*) Electron affinity values of halogens. The valence-shell configuration of halogen atoms (ns^2p^5) has an appetite for one electron to stabilise its configuration by attaining the noble gas configuration (ns^2p^6) which is very stable. Thus halogen atoms have a strong tendency to accept an extra electron from outside and the addition an extra electron makes the configuration of the resulted halide ion similar to that of the noble gas and hence very stable. *Consequently the halogen atoms have very high values of electron affinity.*

(*d*) Electron affinity values of noble gases. The noble gases which have extra-ordinarily stable configuration namely ns^2p^6 show no tendency to accept the additional electron from outside. *Hence the electron affinity values of inert gases are practically zero.*

Variation of Electron Affinity in a Period and a Group : *Periodic Trends of Electron Affinity*

It is difficult to make general views about the periodic variation of electron affinity of various elements for the following reasons

(*i*) The electron affinities of only a very few atoms are known with certainty.

(*ii*) The elements like Be, Mg and noble gases have practically zero electron affinity values, and N and P have very small values.

(*iii*) The elements of 2nd period of the periodic table do not follow the general trend of decrease of electron affinity values on moving from top to bottom in a group.

However, the general trend of variations of electron affinity of various elements can be discussed as follows :

(*a*) **In a period.** On moving from left to right in a period, the size of the atoms decreases and the effective nuclear charge increases. Both these factors favour an increase in the force of attraction exerted by the nucleus on the electron. Consequently the atom has a greater tendency to attract an extra electron from outside towards itself and hence its *electron affinity increases from left to right.* Thus the metals (*e.g.* alkali metals) which lie at the left hand portion of the periodic table have low values of electron affinity while the non-metals (*e.g.* halogens) which lie at the right hand portion of the periodic table have high values of electron affinity.

Exceptions. There are certain elements in each period which have abnormal values. For example in 2*nd* period Li, Be, N and Ne have abnormal values. Similarly in 3*rd* period Na, Mg, P and Ar have abnormal values. The abnormal values of Li and Na cannot be explained by simple mechanism while those of Be, N, Mg, P, Ne and Ar have already been explained.

(*b*) **In a group.** On moving down a group both the size of the atom and the effective nuclear charge increase. The increase in atomic size tends to decrease the electron affinity values while the increase in nuclear charge tends to increase the electron affinity values. The net result is that the effect produced by the progressive increase of the atomic size outweighs the effect produced by the progressive increase in nuclear charge and *consequently the electron affinity goes on decreasing as we move from top to bottom in a group* as is evident from EA values of (*i*) alkali metals (Group IA) (*ii*) C, Si and Ge (Group IVA) (*iii*) S, Se and Te (Group VIA) (*iv*) O, S and Se for two electrons (Group VI A) and (*v*) Cl, Br and I (Group VII A).

Exceptions. Although the elements of 2*nd* period of the periodic table have smaller size than the elements of 3*rd* period, the EA values of some of the elements of 2*nd* period are lower than the EA values of the elements lying just below them in 3*rd* period. For example B<Al, N<P, O<S and F<Cl. The lower values for the elements of 2*nd* period are explained by saying that, due to the smaller size of the atoms of the elements of 2*nd* period, the addition of an extra electron to these atoms produces high electron density round the resulted anions. This high electron density increases the repulsion between the electrons (called electron–electron repulsion) already present in the relatively compact 2*p* orbital of the 2*nd* shell of these atoms and the electron being added. Due to this electron–electron repulsion, the atoms of the elements of 2*nd* period show lesser tendency to attract the extra electron from outside and hence lower values of electron affinity for these elements.

The variation of electron affinity of *s*- and *p*- block elements in a group and a period is shown in Fig. 4.14.

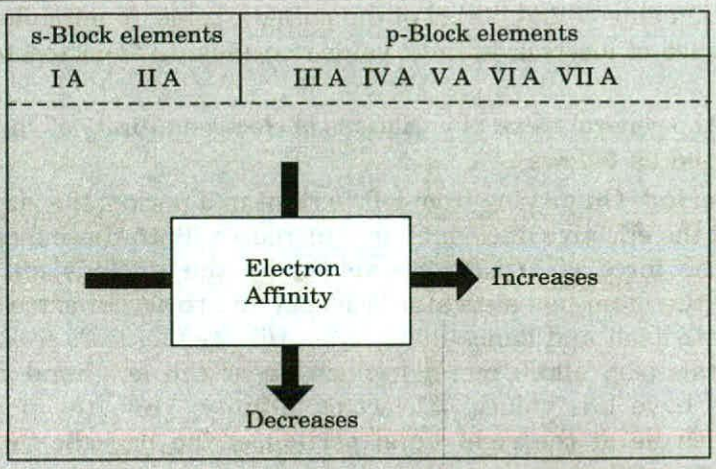


Fig. 4.14. Variation of electron affinity of *s*- and *p*-block elements in the periodic table.

Applications of Ionisation Potential and Electron Affinity

1. Tendency of elements to form cations and anions. We have seen that the magnitude of ionisation potential of an element gives us an idea of the tendency of the element to lose an electron and hence to form a cation. Greater the value of ionisation potential of an element, lower its tendency to lose the electron and hence to form cation. Thus the elements with low values of ionisation potential (*e.g.* alkali metals and alkaline earth metals) have a strong tendency to lose their outermost shell electron and hence form cations quite easily while those having high values (*e.g.* halogens) are not able to lose the electron and hence have no tendency to form cations. Rather, such elements, due to their high electron affinity values, show a strong tendency to accept the electrons and thus form anions.

Again we have seen that the magnitude of electron affinity of an element gives us an idea of the tendency of the elements to accept an electron and hence to form an anion. Greater the value of electron affinity of an element, greater its tendency to accept the electrons and hence to form anions. Thus the elements with high electron affinity values (*e.g.* halogens) have a strong tendency to accept an electron and hence form an anion quite easily while the elements with low electron affinity values (*e.g.* alkali metals and alkaline earth metals) are not able to accept an electron and hence have no tendency to form an anion. Rather, such elements, due to low ionisation potential values, show a strong tendency to lose the electrons and thus form cations.

The above description can be summarised by saying that *with the increase of ionisation potential values of the elements from left to right in a period, the tendency of the elements to lose the electrons and thus to form the cations decreases while with the decrease of ionisation potential values from top to bottom in a group, this tendency increases.* (Fig. 4.15).

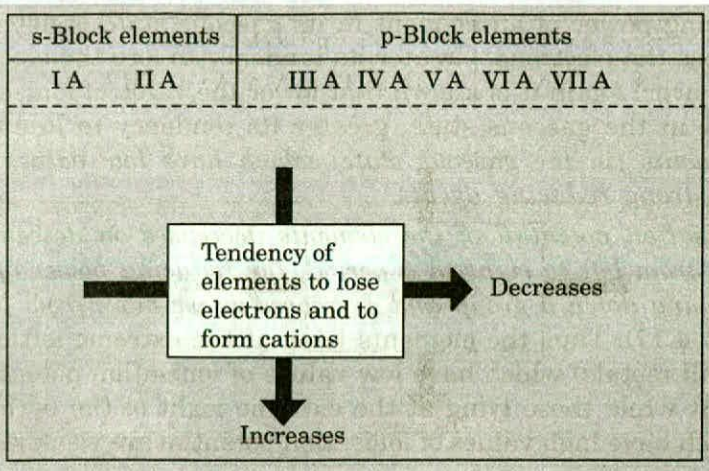


Fig. 4.15. Variation of the tendency of *s*- and *p*-block elements to lose electrons and to form cations in the periodic table.

Similary *with the increase of electron affinity values of the elements from left to right in a period, the tendency of the elements to accept the electrons and thus to form the anions increases while with the decrease of electron affinity values from top to bottom in a group, this tendency decreases* (Fig. 4.16).

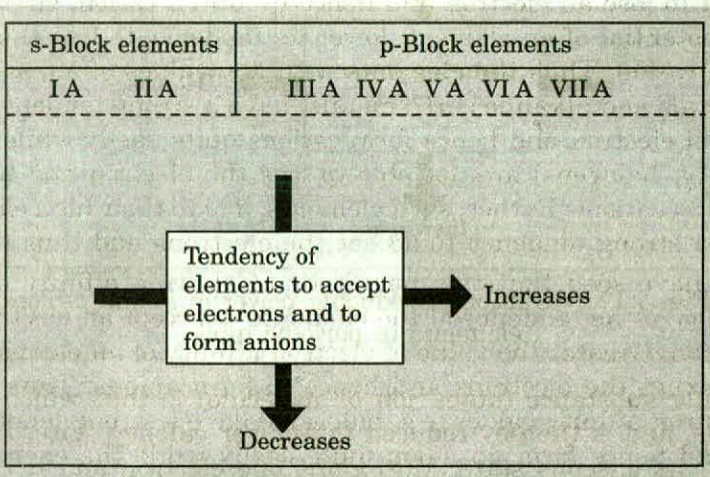


Fig. 4.16. Variation of the tendency of *s*- and *p*-block elements to accept electrons and to form anions in the periodic table.

2. Reducing and oxidising power of elements. A reducing substance (atom, ion or molecule) is that which loses one or more electrons and is thereby oxidised to a higher valency state. For example if an element in its gaseous state, M(*g*) loses one electron and is converted into $M(g)^+$ cation, the element M(*g*) is said to be acting as a reducing agent.

$$\underset{\substack{\text{Reducing agent}\\(\text{Lower valency}\\\text{state} = 0)}}{M(g)} - e^- \longrightarrow \underset{\substack{(\text{Higher valency}\\\text{state} = +1)}}{M^+(g)}$$

The reducing power of an element in its gaseous state is determined by its tendency to lose the electrons. Greater its tendency to lose the electrons, greater its reducing power. Again it is known that lower the value of ionisation potential of an element in the gaseous state, greater its tendency to lose the electrons. *Thus the elements (in the gaseous state) which have low values of ionisation potential are strong reducing agents.*

Since ionisation potential of the elements decreases on descending a group and increases from left to right in a period, the reducing power of the elements increases in going down a group and decreases as we move from left to right in a period. (Fig. 4.17). Thus the elements lying at the extreme left of the periodic table (*i.e.* alkali metals) which have low values of ionisation potential are strong reducing agent while those lying at the extreme right of the periodic table (*i.e.* halogens) which have high values of ionisation potential are weak reducing agents (Fig. 4.17).

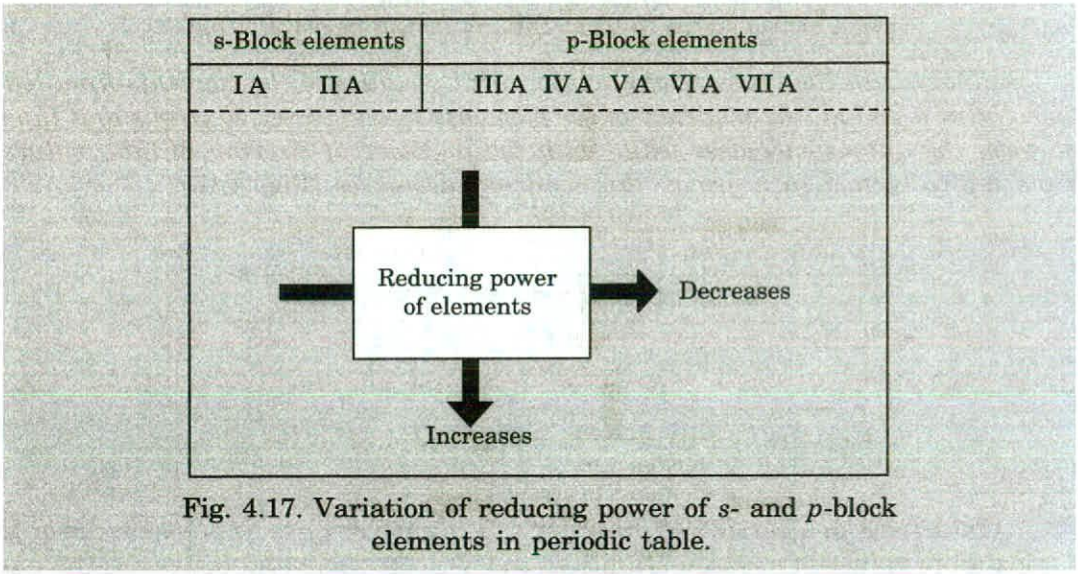


Fig. 4.17. Variation of reducing power of *s*- and *p*-block elements in periodic table.

An oxidising substance (atom, ion or molecule) is that which gains one or more electrons, and is thereby reduced to a lower valency state. For example if an element in its gaseous state, M(g) gains one electron and is converted into $M^-(g)$ anion, the element M(g) is said to be acting as an oxidising agent.

$$\underset{\substack{\text{Oxidising agent}\\(\text{Higher valency}\\ \text{state} = 0)}}{M(g)} + e^- \longrightarrow \underset{\substack{(\text{Lower valency}\\ \text{state} = -1)}}{M^-(g)}$$

The oxidising power of an element in its gaseous state is determined by its tendency to accept the electrons. Greater its tendency to accept the electrons, greater its oxidising power. Again it is known that higher the value of electron affinity of an element in the gaseous state, greater its tendency to accept the electrons. *Thus the elements (in the gaseous state) which have high electron affinity values are strong oxidising agents.*

Since electron affinity of the elements decreases on descending a group and increases from Left to right in a period, the oxidising power of the elements decreases on descending a group and increases from left to right in a period. (Fig. 4.18). Thus the elements lying at the extreme left of the periodic table (*i.e.* alkali metals) which have low values of electron affinity are poor oxidising agents while those lying at the extreme right of the pariodic table (*i.e.* halogens) which have high values of electron affinity are strong oxidising agents.

Here it may be noted that we have considered the reducing and oxidising powers of the elements *only in their gaseous state*. If the chemical reaction is carried out in solution using water as the main solvent, reducing and oxidising powers are better understood in terms of standard oxidation potential value of the elements.

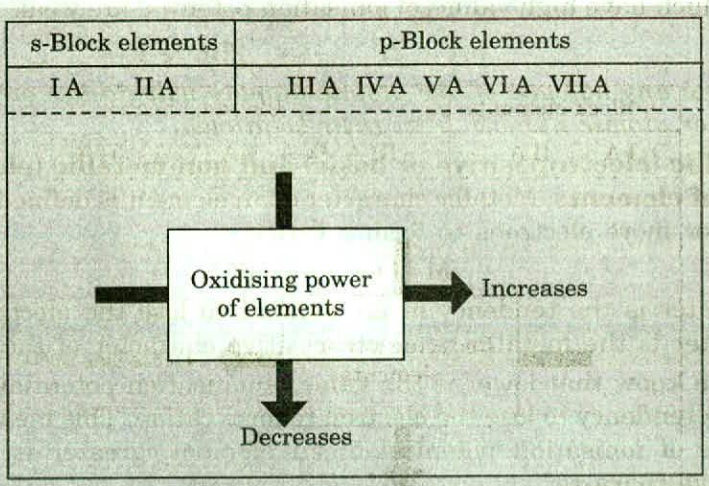


Fig. 4.18. Variation of oxidising power of *s*- and *p*-block elements in periodic table.

Oxidising properties of halogens. We have seen that halogens have the maximum values of electron affinity in the periodic table and hence are the most powerful oxidising agents, *i.e.* they have maximum tendency to accept the electrons.

Again we have also seen that the oxidising power of elements increases with the increase of their electron affinity values. Thus the oxidising power of halogens must be in the following order : (Electron affinity values in KJ. $mole^{-1}$ are also given in parenthesis)

$$Cl(-\ 348.7) > Br(-\ 324.5) > F(322.0) > I(-295.0)$$

In fact, F has been found to be the most powerful oxidising agent and the oxidising power of halogens decreases from F to I as shown below:

$$F > Cl > Br > I$$

The unexpected order of oxidising power of halogens shown above is due to the fact their electron affinity alone does not control the oxidising power of elements but there are many other energy terms like *heat of fusion, heat of evaporation, heat of dissociation and heat of hydration* and their sum on which the oxidising power of a given halogen depends. When all these energy terms for different

halogens are summed up with the help of Born-Haber cycle, the sum is found in the following order :

$$F > Cl > Br > I$$

The order given above is actually the order of the oxidising power of halogens.

That F is the most powerful oxidising agent among all the halogens is evident from the fact that F_2 will *oxidise* or *displace* any of the other halide ions (X^-) *both in solution and dry state*

$$F_2 + 2X^- \longrightarrow 2F^- + X_2$$
$$(X^- = Cl^-, Br^-, I^-)$$

Similarly Cl_2 gas will displace Br^- and I^- ions from their solutions and Br_2 will displace only I^- ions.

$$Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2$$
$$(X^- = Br^-, I^-)$$
$$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$$

In general *any halogen of low atomic number will oxidise or displace halide ions of higher atomic number from their solutions.*

3. Metallic (electropositive or basic) and non-metallic (electronegative) character of elements. Metallic character of an element is defined as its tendency to lose one or more electrons to form a cation

$$M - ne^- \longrightarrow M^{n+}$$

The greater is the tendency of an element to lose the electron to form the cation, greater is the metallic or electropositive character of the element.

Again we know that lower is the value of ionisation potential of an element, greater is its tendency to lose the electron to form cation. This means that smaller is the value of ionisation potential of an element, greater is its metallic or electropositive character.

Now since ionisation potential decreases from top to bottom in a group, metallic character (i.e. basic character) of the elements increases in the same direction. Similarly *with the increase of ionisation potential from left to right in a period, metallic character of the elements decreases in the same direction.* Fig. (4.19.)

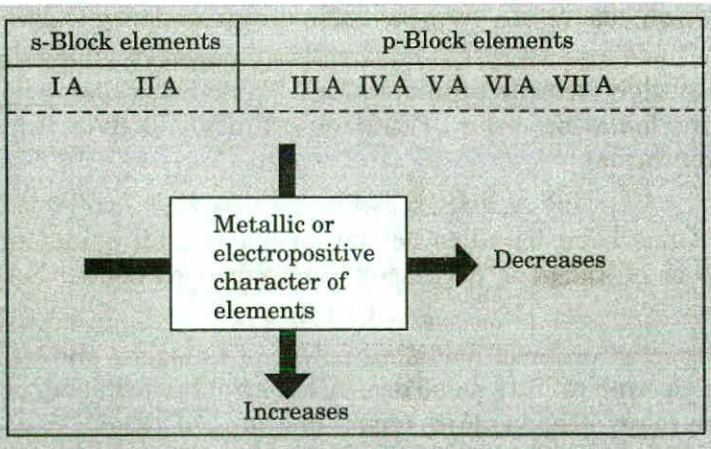


Fig. 4.19. Variation of metallic or electropositive (*i.e.* basic) character of representative elements (*s*- and *p*-block elements) of the periodic table.

The successive increase of metallic character of the elements on descending a group is particularly apparent in groups IVA, VA and VIA which begin with non-metals namely C, N and O and end with metals namely Pb, Bi and Po respectively. The general increase of metallic character in going down a group is also confirmed by the fact that the oxides of the elements of a group become more and more basic when we proceed from top to bottom in a group. For example the oxides of M_2O_3 type of the elements of group VA become more and more basic (*i.e.* less and less acidic) from N_2O_3 to Bi_2O_3 as shown below :

$$\underbrace{N_2O_3,\ P_2O_3,}_{\text{Acidic}}\quad \underbrace{As_2O_3,\ Sb_2O_3,}_{\text{Amphoteric}}\quad \underset{\text{Basic}}{Bi_2O_3}$$

—— *Basic character increasing* ⟶

The general decrease of metallic character of the elements in going from left to right in a period is also confirmed by the fact that the oxides of the elements of a given period become *less and less basic* or *more and more acidic* as we proceed from left to right. For example the oxides of the elements of 3rd period show this type of behaviour as shown below :

Na_2O,	MgO,	Al_2O_3,	SiO_2,	P_2O_5,	SO_3,	Cl_2O_7
Strongly basic	Basic	Amphoteric	Feebly acidic	Acidic	More acidic	Most acidic

—— *Basic character decreasing* ⟶

Non-metallic character of an element is defined as its tendency to accept one or more electrons to form an anion.

$$M + ne^- \rightarrow M^{n-}$$

The greater is the tendency of an element to accept the electron to form the anion, greater is its non-metallic character.

Again we know that greater is the value of electron affinity of an element, greater is its tendency to accept the electron to give the anion. This means *that greater is the value of electron affinity of an element, greater is its non metallic or electronegative character.*

Now since electron affinity values decrease from top to bottom in a group, non-metallic character of the elements also decreases in the same direction. Similarly with the increase of electron affinity values from left to right in a period non-metallic character of the elements also increases. (Fig. 4.20).

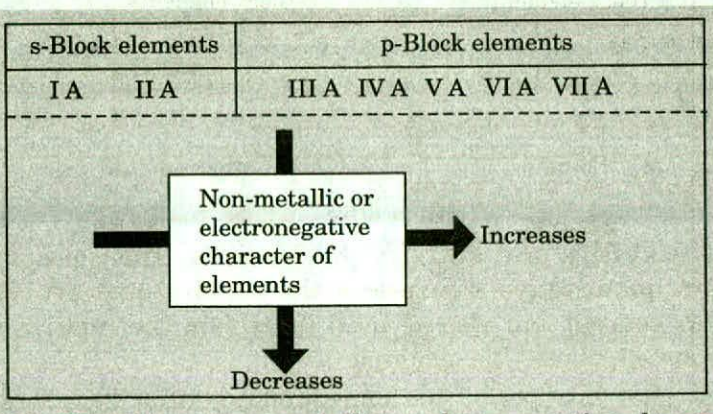


Fig. 4.20. Variation of non-metallic or electronegative character of *s*- and *p*-block elements in the periodic table.

The variation of non-metallic or electronegative character of *s*- and *p*-block elements as described above makes it clear that the elements lying at the extreme right of the periodic table (*i.e.* halogens) show maximum electronegative character and hence are non-metals, while the elements located at the extreme left of the periodic table (*i.e.* alkali metals) show minimum electronegative character and hence are metals.

Metals, non-metals and metalloids. The trend of variation in metallic and non-metallic character of the elements as described above has been used to classify *s*- and *p*-block elements into metals, non-metals and metalloids. The trend of variation shows that *s*- and *p*-block elements lying at the lower left hand side of the periodic table show maximum electropositive character and hence are **metals** while the elements lying at the upper right hand side show minimum electropositive character and hence are **non-metals.** The elements lying in between metals and non-metals (*i.e.* the elements lying in a diagonal strip) show characteristics of both metals and non-metals and hence are called **metalloids.**

The divisions of *s*- and *p*-block elements into metals, non- metals and metalloids is shown in Fig. 4.21.

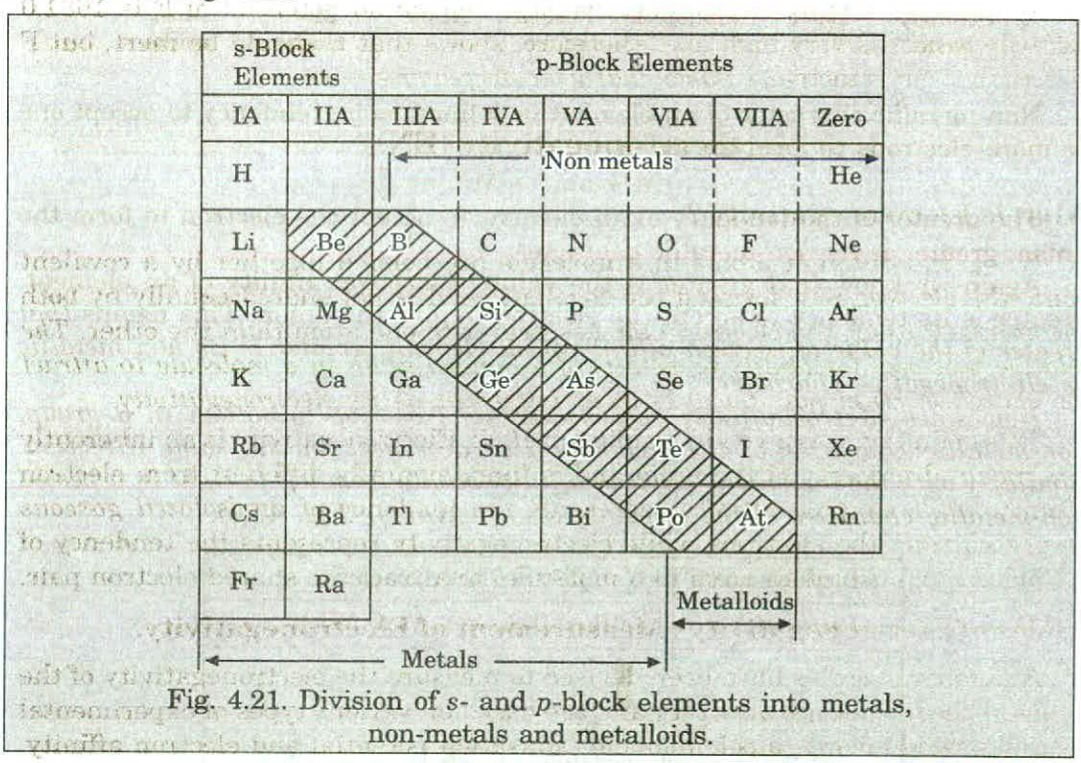


Fig. 4.21. Division of *s*- and *p*-block elements into metals, non-metals and metalloids.

4. Relative stability and activity of elements. The concept of ionisation potential gives a quantitative measure of the stability and activity of various elements *i.e.* this concept can also be used to explain the relative stability and activity of various elements. For example :

(*a*) We know that in a period the ionisation potential increases from left to right, *i.e.* as we move from left to right in a period, more and more energy is

required to remove an electron which means that *stability of the elements goes on increasing or their activity goes on decreasing.* Thus in the 3rd period the relative activity of Na, Mg and Al are in the following order :

$$Na > Mg > Al$$

(*b*) In going down a group the ionisation energy decreases from top to bottom, *i.e.* as the group is descended, less and less energy is required to remove an electron which means that *the stability of the elements goes on decreasing or their activity goes on increasing.* Thus in the 1*st* group the relative activity of Na, K and Rb is in the following order :

$$Na < K < Rb.$$

The relation between the ionisation potential and the activity of the elements studied as above shows that the elements having high values of ionisation potential are less reactive (*e.g.* inert gases), while those having low values are very reactive (*e.g.* alkali metals and alkaline earth metals).

Exceptions. This rule is applicable only to those elements which have dominant electro-positive character (*i.e.* alkali metals and alkaline earth metals) and not to those which are highly electro-negative, *e.g.*, ionisation potential of F is 1681.0 KJ/mole, which is very high and, therefore, shows that F should be inert, but F is actually very reactive.

Electronegativity (EN)

What is Electronegativity ?

When two different atoms in a molecule are bonded together by a covalent bond, the electron pair forming the covalent bond is not shared equally by both the atoms. Rather, the electron pair lies nearer to one atom than the other. *The relative tendency (or ability or power) of a bonded atom in a molecule to attract the shared electron pair towards itself is termed as its electronegativity.*

This definition was given by Pauling in 1932. Electronegativity is an inherently fundamental property of the atom and is fundamentally different from electron affinity, since electron affinity represents the tendency of an *isolated gaseous atom* to attract the electrons while electronegativity represents the tendency of a bonded atom (*i.e.* of an atom in a molecule) to attract the shared electron pair.

Scales of Electronegativity : Measurement of Electronegativity.

A number of scales have been devised to measure the electronegativity of the atoms. These scales are arbitrary and are based on various types of experimental data like bond energy, dipole moment, ionisation potential and electron affinity. More commonly used scales are described below :

1. Pauling's Scale (1932). This scale is based on an empirical relation between the energy of a bond (called *bond energy*) and the electronegativities of the bonded atoms. Let us consider a A–B bond between two dissimilar atoms, A and B of a molecule AB. Let the bond energies of A–A, B–B and A–B bonds be represented as E_{A-A}, E_{B-B} and E_{A-B} respectively.

It has been seen that the energy of A–B bond (E_{A-B}) is almost always greater than the geometric mean of the energies of A–A (E_{A-A}) and B–B (E_{B-B}) bonds, *i.e.*

$$E_{A-B} > \sqrt{E_{A-A} \times E_{B-B}}$$

The difference between E_{A-B} and $\sqrt{E_{A-A} \times E_{B-B}}$ is called **ionic-resonance energy** of A–B bond and is denoted by Δ_{A-B}. It is thus given by :

$$\boxed{\Delta_{A-B} = E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}} \quad ...(i)$$

Δ_{A-B} values do not possess additive property, *i.e.* if we consider three covalent bonds *viz.* A–B, B–C and C–A, then the sum of Δ_{A-B} and Δ_{B-C} is not equal to Δ_{C-A} which means that :

$$\boxed{\Delta_{A-B} + \Delta_{B-C} \neq \Delta_{C-A}} \quad ...(ii)$$

The relation (*i*) is true when the electronegativities of A, B and C are in the order : $x_A > x_B > x_C$.

The validity of relation (*i*) given above can be verified by calculating the values of Δ_{F-O}, Δ_{O-Si} and Δ_{F-Si} for F–O, O–Si and F–Si covalent bonds (electronegativities of F, O and Si are in the order : $x_F > x_O > x_{Si}$) by using the given bond energy values of F–O, O–Si, F–Si, F–F, O–O and Si–Si bonds as :

E_{F-O} = 184.14 KJ. mole^{-1}; E_{O-Si} = 372.46 KJ. mole^{-1}

E_{F-Si} = 535.58 KJ. mole^{-1}; E_{F-F} = 154.84 KJ. mole^{-1}

E_{O-O} = 138.10 KJ. mole^{-1}; E_{Si-Si} = 179.95 KJ. mole^{-1}

Thus by using relation (*i*), we can calculate the values of Δ_{F-O}, Δ_{O-Si} and Δ_{F-Si} for F–O, O–Si and F–Si bonds as shown below :

$$\Delta_{F-O} = E_{F-O} - \sqrt{E_{F-F} \times E_{O-O}}$$
$$= 184.14 - \sqrt{154.84 \times 138.10}$$
$$= 184.14 - 146.23 = 37.91 \text{ kJ.mole}^{-1}$$

$$\Delta_{O-Si} = E_{O-Si} - \sqrt{E_{O-O} \times E_{Si-Si}}$$
$$= 372.46 - \sqrt{138.10 \times 179.95}$$
$$= 372.46 - 157.64 = 214.82 \text{ kJ.mole}^{-1}$$

$$\Delta_{F-Si} = E_{F-Si} - \sqrt{E_{F-F} \times E_{Si-Si}}$$
$$= 535.58 - \sqrt{154.84 \times 179.95}$$
$$= 535.58 - 166.92 = 368.66 \text{ kJ.mole}^{-1}.$$

With the help of the values of Δ_{F-O}, Δ_{O-Si} and Δ_{F-Si} as calculated above it can be shown that

$$\Delta_{F-O} + \Delta_{O-Si} \neq \Delta_{F-Si}$$

or $$37.91 + 214.82 \neq 368.66$$

or $$252.73 \neq 368.66$$

We have already mentioned that the values of ionic-resonance energy (*i.e.* Δ_{A-B} values) do not show additive property. However it has been found that the square roots of these values do show nearly the additive property, *i.e.* if we again

consider the bonds *viz.* A–B, B–C and C–A, then the sum of $\sqrt{\Delta_{A-B}}$ and $\sqrt{\Delta_{B-C}}$ is nearly equal to $\sqrt{\Delta_{C-A}}$, *i.e.*

$$\boxed{\sqrt{\Delta_{A-B}} + \sqrt{\Delta_{B-C}} \approx \sqrt{\Delta_{C-A}}} \quad ...(iii)$$

The validity of relation (*iii*) can be verified by the fact that for F–O, O–Si and F–Si bonds the sum of $\sqrt{\Delta_{F-O}}$ and $\sqrt{\Delta_{O-Si}}$ is almost equal $\sqrt{\Delta_{F-Si}}$ to as shown below :

$$\sqrt{\Delta_{F-O}} + \sqrt{\Delta_{O-Si}} \approx \sqrt{\Delta_{F-Si}}$$

or $\sqrt{37.91} + \sqrt{214.82} \approx \sqrt{368.66}$

or $6.15 + 14.65 \approx 19.20$

or $20.80 \approx 19.20$

The square root of ionic-resonance energy (*i.e.* $\sqrt{\Delta_{A-B}}$) is a measure of the partial ionic character of an A–B covalent bond. With the increase of ionic character of A–B covalent bond, the magnitude of $\sqrt{\Delta_{A-B}}$ also increases. The difference in electronegativity between the bonded atoms (A and B), $x_A - x_B$ ($x_A > x_B$) also increases with the increase of partial ionic character of A–B bond. Thus :

$\sqrt{\Delta_{A-B}} \propto$ *Amount of ionic character in A–B bond*

and

$x_A - x_B \propto$ *Amount of ionic character in A–B bond*

Consequently, $\boxed{x_A - x_B \propto \sqrt{\Delta_{A-B}}}$

or $\boxed{x_A - x_B = K\sqrt{\Delta_{A-B}}}$

Now on putting the value of Δ_{A-B} from equation (*i*) we get

$$\boxed{x_A - x_B = K\left[E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}\right]^{1/2}}$$

The value of the constant, K has been found to be equal to 0.208 which comes from the conversion of experimental values of E_{A-B} measured in Kcals/mole into e*V*. Thus :

$$\boxed{x_A - x_B = 0.208\left[E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}\right]^{1/2}}$$

This equation gives only the differences in electronegativity values. This equation can be used to calculate x value of an atom provided that x value of the other element is known. Pauling assigned an arbitrary value of 4.0 for the electronegativity of fluorine and calculated that of other elements with the help of this equation. It must be remembered that in the calculation of electronegativity values Pauling has expressed ionic-resonance energies not in kcal, but in electron-volts (1 *eV* per bond = 23 kcal per gram bond).

The values of electronegativities of the atoms of elements which Pauling has calculated are given in Table 4.11. These values are arbitrary and only relative.

The disadvantage of Pauling's scale is that bond energies are not known with any degree of accuracy for many solid elements.

Table 4.11. Electronegativity values of elements as estimated by Pauling (Scale used : F = 4.0)

Group→ / Period↓	IA	IIA	IIIB	IVB	VB	VIB	VIIB	←VIII→			IB	IIB	IIIA	IVA	VA	VIA	VIIA	Zero
1	1 H 2.1																	2 He –
2	3 Li 1.0	4 Be 1.5											5 B 2.0	6 C 2.5	7 N 3.0	8 O 3.5	9 F 4.0	10 Ne –
3	11 Na 0.9	12 Mg 1.2											13 Al 1.5	14 Si 1.8	16 P 2.1	16 S 2.5	17 Cl 3.0	18 Ar –
4	19 K 0.8	20 Ca 1.0	21 Sc 1.3	22 Ti 1.5	23 V 1.6	24 Cr 1.6	25 Mn 1.5	26 Fe 1.	27 Co 1.8	28 Ni 1.8	29 Cu 1.9	30 Zn 1.6	31 Ga 1.6	32 Ge 1.8	33 As 2.0	34 Se 2.4	35 Br 2.8	36 Kr –
5	37 Rb 0.8	38 Sr 1.0	39 Y 1.2	40 Zr 1.4	41 Nb 1.6	42 Mo 1.8	43 Tc 1.9	44 Ru 2.2	45 Rh 2.2	46 Pd 2.2	47 Ag 1.9	48 Cd 1.7	49 In 1.7	50 Sn 1.8	51 Sb 1.9	52 Te 2.1	53 I 2.5	54 Xe –
6	55 Cs 0.7	56 Ba 0.9	57 71 La–Lu 1.1 1.2	72 Hf 1.3	73 Ta 1.5	74 W 1.7	75 Re 1.6	76 Os 2.2	77 Ir 2.2	78 Pt 2.2	79 Au 2.4	80 Hg 1.9	81 Tl 1.8	82 Pb 1.8	83 Bi 1.9	84 Po 2.0	85 At 2.2	86 Rn –
7	87 Fr 0.7	88 Ra 0.9	89 – 95 Ac–Am 1.1 1.3															

2. Mulliken's Scale (1934), R.S. Mulliken has suggested that the electronegativity is related to its ionisation potential and its electron affinity, since these properties of an element measure its tendency to lose its valence shell electron and to attract an extra electron respectively. Therefore an atom having a high value of ionisation potential (*i.e.* small tendency to lose its valence-shell electron) and a high value of electron affinity (*i.e.* having a great tendency to attract an electron) has a high value of electronegativity.

Mulliken considers the formation of a covalent bond between two atoms A and B as follows. Suppose :

x_A and x_B = Electronegativities of atoms A and B

$(IP)_A$ and $(IP)_B$ = Ionisation potentials of atoms A and B

and $(EA)_A$ and $(EA)_B$ = Electron affinities of atoms A and B

According to Mulliken :

(*i*) If $x_A > x_B$, then A^-B^+ structure will be obtained and its formation can be regarded as taking place through the following steps;

Step (*i*) $B + \textit{Energy supplied}\ [= (IP)_B] \xrightarrow{-e^-} B^+$

Step (*ii*) $A \xrightarrow{+e^-} A^- + \textit{Energy released}\ [= (EA)_A]$

On adding :

$$B + A + (IP)_B \rightarrow B^+A^- + (EA)_A$$

or $$B + A + (IP)_B - (EA)_A \rightarrow B^+A^-$$

$\therefore$ *Energy change in the formation of* B^+A^- *structure*

$$= (IP)_B - (EA)_A$$

(*ii*) If $x_B > x_A$, the A^+B^- structure will be obtained and the change in energy in its formation = $(IP)_A - (EA)_B$.

Quite obviously in the formation of a covalent bond between A and B (*i.e.* in the formation of A–B structure) x_A will be equal to x_B and the energy changes shown above for B^+A^- and A^+B^- structures must be equal, *i.e.*,

$$(IP)_B - (EA)_A = (IP)_A - (EA)_B$$

or $$(IP)_A + (EA)_A = (IP)_B + (EA)_B \quad ...(i)$$

On the basis of relation (*i*) Mulliken proposed that *the electronegativity of an atom can be taken to be equal to the average of its IP and EA values, i.e.,*

$$\boxed{x_A = \frac{(IP)_A + (EA)_A}{2}} \quad ...(ii)$$

Relation (*ii*) holds good when IP and EA of the element are given in electron volts. If these quantities are given in kilo calories, then the value of x_A is obtained by dividing the right hand side of equation (*ii*) by 62.5. Thus :

$$\boxed{x_A = \frac{(IP)_A + (EA)_A}{2 \times 62.5}}$$

Mulliken's values of electronegativity are about 2.8 times as large as Pauling's values. Hence to make the Mulliken's values approximately equal to the Pauling's values, right hand side of equation (*ii*) is divided by 2.8. Thus :

$$x_A = \frac{(IP)_A + (EA)_A}{2 \times 2.8} = \frac{(IP)_A + (EA)_A}{5.6}$$

The constant 1/5.6 is called **scale adjustment factor.** This factor is used when IP and EA are expressed in electron volts.

Example. *Calculate the electronegativity values of fluorine aid chlorine on Mulliken's scale, given that* $(IP)_F$ *= 17.4 eV/atom,* $(EA)_F$ *=3.62 eV/atom,* $(IP)_{Cl}$ *= 13.0 eV/atom and* $(EA)_{Cl}$ *= 4.0 eV*

Solution. The electronegativities of F and Cl denoted by x_F and x_{Cl} are given by :

$$x_F = \frac{(IP)_F + (EA)_F}{5.6} = \frac{17.4 + 3.62}{5.6} = \frac{21.02}{5.6} = 3.75$$

and

$$x_{Cl} = \frac{(IP)_{Cl} + (EA)_{Cl}}{5.6} = \frac{13.0 + 4.0}{5.6} = \frac{17}{5.6} = 3.03$$

Disadvantages of Mulliken's Scale. (*i*) Although Mullikan's scale is less empirical than Pauling's scale, yet it suffers from a serious disadvantage that electron affinities, with the exception of a few elements, are not reliably known.

(*ii*) The values of ionisation potential and electron affinity refer to the transfer of electrons between the atomic orbitals. However, the exact constitution of such atomic orbitals is not always known. Further ionisation potential and electron affinity values will vary with the nature of valence state. Thus, if the valence electrons in nitrogen atom in its valence state are s^2p^3 (two electrons in *s*-orbital and three electrons in *p* orbitals of valency energy level), the electronegatvity value comes to 2.33 while if the electrons are in sp^4 state which represents the excited state of nitrogen atom one electron in *s*-orbital and four in *p*-orbitals), the electronegativity value becomes 2.55.

3. Sanderson's Scale (1955). Sanderson's electronegativity scale is based on a new quantity called *stability ratio*, SR for an atom which is defined *as the ratio of the average electron density, ED* (electron density differs from point to point as electrons are not evenly spaced round the nucleus) *round the nucleus and its hypothetical electron density,* ED_h which the atom would have, if it were an inert gas atom. Thus :

$$SR = \frac{ED}{ED_h}$$

According to Sanderson the *stability ratio (SR) of an atom, A is a measure of its electronegativity,* x_A, *i.e.*

$$(x_A)_{Sanderson} = SR = \frac{ED}{ED_h} \qquad ...(i)$$

Equation (*i*) is called ***Sanderson's equation***

According to Sanderson ED is a measure of comparative compactness of the atom and it is obtained by dividing the number of electrons (*i.e.* nuclear charge, Z) round the nucleus by $\frac{4}{3}\pi r^3$ where *r* is the non-polar covalent radius of the atom. Thus :

$$ED = \frac{Z}{\frac{4}{3}pr^3} = \frac{3Z}{4pr^3} = \frac{Z}{4.19\ r^3}$$

The value of ED_i for a particular atomic number is found from interpolation obtained by plotting electron densities of inert gas atoms against atomic numbers.

Sanderson's electronegativity values obtained by the above equation can be converted empirically to Pauling's values by using the relation :

$$x_{Pauling} = 0.21\ x_{Sanderson} + 0.77$$

4. Allred and Rochow's Scale (1958). In 1958 Allred and Rochow suggested another scale of electronegativity which is based on covalent radii. According to this scale *electronegativity of an atom is the force of attraction between the nucleus of one atom and an electron of an adjacent atom bonded to it and separated from the nucleus by the covalent radius.*

Thus, if Z_{eff} is the effective nuclear charge, the effective nuclear charge felt by the electron under the influence of the nucleus is Z_{eff} e and the force of attraction between the nucleus and the electron is, therefore, equal to $(Z_{eff}\, e) \times e/r^2$ where r is the distance (in cms) between the nucleus and the electron. This force of attraction is equal to the electronegativity, x_A of an atom A. Thus :

$$x_A = \frac{(Z_{eff}e) \times e}{r^2} = \frac{Z_{eff}e^2}{r^2}$$

In order to correlate Allred and Rochow's electronegativity values (which are absolute values) given by the above equation with Pauling's values (which are arbitrary and only relative), Allred and Rochow's values are plotted against Pauling's values and the best straight line is drawn through the points. From the slope and the intercept of this line they obtained the following relation for the electronegativity values [Allred and Rochow's values denoted by $(x_A)_{AR}$]

$$(x_A)_{AR} = 0.359\frac{Z_{eff}}{r^2} + 0.744$$

In this equation r is in angstrom units (Å units). The value of Z_{eff} can be determined by *Slatter's rules* according to which $Z_{eff} = Z - \sigma$ where σ is the screening constant. Thus the above equation becomes :

$$(x_A)_{AR} = 0.359\frac{Z - \sigma}{r^2} + 0.744$$

Example. *Find out the electronegativity of lead with the help of the given values : screening constant (σ) of Pb = 76.70, atomic number of Pb(Z) = 82 and covalent radius of Pb(r) = 5.3 Å.*

Solution. On substituting the values of σ, Z and r in the equation :

$$(x_{Pb})_{AR} = 0.359\frac{Z - \sigma}{r^2} + 0.744,$$

we get :

$$(x_{Pb})_{AR} = 0.359\frac{82 - 76.70}{(5.3)^2} + 0.744 = 1.55$$

This scale has gained wide acceptance, as it has the advantage that Z_{eff} can be estimated by Slatter's rules and r can be determined experimentally for most elements. It does not depend on the quantities like electron affinities and bond dissociation energies which are known for comparatively few elements.

The most serious disadvantage of this scale is that the values of covalent radii are unreliable.

None of the electronegativity scales discussed above has a distinct advantage over the others. Drago (1960), who has critically examined various proposed scales, is of the view that Pauling's scale with all its limitations is the best one.

Factors Affecting the Magnitude of Electronegativity

Following are the important factors on which the magnitude of electronegativity depends

1. Size of the atom. The smaller the size of an atom, greater is its tendency to attract towards itself the shared pair electrons.

Thus the smaller atoms have greater electronegativity values than the larger atoms. For example :

(*a*) Electronegativity values of the elements of group IA decrease from H(Z = 1) to Cs(Z = 55), since the atomic (covalent) radii of these elements increase in the same order as shown below :

Elements of group IA	Atomic (covalent) radius (Å)		Electronegativity	
H (1)	0.32	Increasing ↓	2.1	Decreasing ↓
Li(3)	1.23		1.0	
Na (11)	1.54		0.9	
K (19)	2.03		0.8	
Rb (37)	2.16		0.8	
Cs (55)	2.35		0.7	

(*b*) Electronegativity values of the elements of 2*nd* period increase from Li (Z = 3) to F(Z = 9), since the atomic (covalent) radii of these elements decrease in the same order as shown below :

Elements of 2nd period :	*Li*	*Be*	*B*	*C*	*N*	*O*	*F*
Atomic (covalent) radius (Å) :	*1.23*	*0.90*	*0.82*	*0.77*	*0.75*	*0.73*	*0.72*
	←			*Decreasing*			→
Electronegativity :	*1.0*	*1.5*	*2.0*	*2.5*	*3.0*	*3.5*	*4.0*
	←			*Increasing*			→

2. Number of inner shells. *The atom with greater number of inner shells (i.e. the shells between the nucleus and the outer-most shell) has less value of electronegativity than the atom with smaller number of inner shells.* For example the electronegativity values of halogens decrease from F(Z = 9) to At(Z = 85), since the number of inner shells increases in the same order as shown below :

Halogens (Elements of VII A group)	No. of inner shells (Complete electronic configurations are given in parenthesis)	Electronegativity
F(9)	1(2, 7)	4.0
Cl (17)	2 (2, 8, 7)	3.0
Br (35)	3(2, 8, 18. 7)	2.8
I (53)	4(2, 8, 18, 18, 7)	2.5
At (85)	5(2, 8, 18, 32, 18, 7)	2.2

← *Increasing* — ← *Decreasing*

3. Charge on the ion (*Type of the ion*). A cation attracts the electron pair more readily towards itself than the atom from which it has been derived. This is due to the smaller size of the cation as compared to its parent atom ($M^+ < M$). *Thus a cation, M^+ has higher electronegativity than its parent atom, M ($M^+ > M$). (See Table 4.12).*

If an element shows many positive oxidation states, *the element in higher oxidation state has more value of electronegativity than that in the lower oxidation state* (Table 4.12). This is due to the fact that the atom in a higher positive oxidation state is smaller in size and hence has greater attraction for electrons. Thus we can say that an increase in the positive oxidation state increases the tendency of that element to attract electron pair towards itself and hence *electronegativity increases with the increase in positive oxidation state* as shown in Table 4.12 (Atoms from which cation has been derived have also been included in the table).

Table 4.12. Electronegativity values of some cations as compared to their parent atoms.

Atom/cation	Atomic (covalent) radius (Å)	Oxidation state of atom/cation	Electro-negativity
Li	1.23	0	1.0
Li^+	0.60	+1	2.5
Mo	1.30	0	1.8
Mo^{4+}	0.68	+4	2.24
Mo^{6+}	0.62	+6	2.35
Fe	1.17	0	1.8
Fe^{2+}	0.76	+2	1.83
Fe^{3+}	0.64	+3	1.96
Sn	1.41	0	1.80
Sn^{2+}	1.12	+2	1.81
Sn^{4+}	0.71	+4	1.96
Pb	1.47	0	1.80
Pb^{2+}	1.20	+2	1.87
Pb^{4+}	0.84	+4	2.33

Table 4.12 makes it evident that, in general, the electronegativity values of M, M^+ and M^{2+} species are in the order :

$$M^{2+} > M^+ > M,$$

while the size of these species is in the reverse order as shown below :

$$M^{2+} < M^+ < M$$

An anion attracts the electron pair less readily than its parent atom. This is also due to the fact that an anion is larger in size than its parent atom ($X^- > X$). *Thus an anion, X^- has less electronegativity than its parent atom, X, i.e.*

Order of electronegativity : $X^- < X$

Order of size : $X^- > X$

The above point is clear from the fact that F^- ion has less electronegativity value than F atom (F^- = 0.8. F = 4.0).

4. Number and nature of atoms to which the atom is bonded. We have seen that, since electronegativity of an atom is not the property of this atom in its isolated state, it depends on the number and nature of the atoms to which the atom is bonded. For this reason the electronegativity value of an atom is not constant. For example electronegativity value of P atom in PCl_3 molecule is different from that in PF_5 molecule in which the number and nature of the atoms both to which P atom is bonded change.

5. Ionisation energy and electron affinity. The numerical value of electronegativity of the atom of an element also depends both on the magnitude of ionisation energy and electron affinity. Higher ionisation energy of an atom means that it is difficult to remove the most loosely bonded electron from the atom which leads us to expect that the electron affinity of that atom will also be greater. *Thus the atoms of the elements which have higher values of ionisation energy and electron affinity also have higher values of electronegativity.* For example, the elements of group VII A (halogens) which have the highest ionisation energies and electron affinities also have the highest values of electronegativity. Similarly, the elements of group IA (alkali metals) which have the lowest ionisation energies and electron affinities have the lowest values of electronegativity.

6. Type of hybridisation. The magnitude of electronegativity of an atom also depends on the type of hybridisation which the atom undergoes in the formation of different bonds in the molecule. *The magnitude of electronegativity increases as the s-character in hybrid orbitals increases.*

Example : The electronegativity of carbon atom in methane (sp^3 hybridisation with 25% *s*-character), ethylene (sp^2 hybridisation with 33% *s*-character) and acetylene (*sp* hybridisation with 50% *s*-character) is in the increasing order as shown below :

Hydrocarbon	:	*Methane* (CH_4)	*Ethylene* ($H_2C = CH_2$)	*Acetylene* ($CH \equiv CH$)
Type of hybridisation	:	sp^3	sp^2	*sp*
Amount of s-character in hybrid orbitals	:	*25%*	*33%*	*50%*
Order of electronegativity of carbon atom	:	——— *Increasing* ——→		

The increasing order of the magnitude of the electronegativity of carbon atom in the above hydrocarbons shows that methane is unreactive, ethylene is *more reactive* while acetylene is *highly reactive*. The highest value of electronegativity of carbon atom in acetylene also accounts for its highly acidic hydrogen atom (*i.e.* acidic properties of acetylene).

Variation of Electronegativity in a Period and a Group of Representative Elements : *Periodic Trends of Electronegativity*

(*a*) **In a period.** *In going from left to right in a period of s- and p-block elements, the electronegativity values increase.* This increase can be explained on the basis of any of the following facts.

(*i*) On moving from left to right in a period, there is a decrease in the size of the atoms. Smaller atoms have greater tendency to attract the electrons towards themselves *i.e. smaller atoms have higher electronegativity values.*

(*ii*) On moving from left to right in a period there is an increase of ionisation energy and electron affinity of the elements. The atoms of the elements which have higher value of ionisation energies and electron affinities also have higher electronegativities.

(*b*) **In a group.** *In going down a group of s- and p-block elements, the electronegativity values decrease.* This decrease can also be explained on the basis of any of the following facts.

(*i*) As we move down a group, there is an increase in the size of the atoms. With the increase in size of the atoms, their electronegativity values decrease.

(*ii*) Ionisation energy and electron affinity on which electronegativity depends decrease as the group is descended. With the decrease of these quantities the electronegativity values also decrease.

The heavier elements of group III A (*i.e.* Ga, In and Tl) show *reverse trend* due to the intervening transition series.

The variation of electronegativity values discussed above reveals that the *halogens* (VII A group elements) which lie on the extreme right of the periodic table are the *most electronegative* (*i.e. least electropositive*) *elements and the alkali metals* (IA group elements) which lie on the extreme left of the periodic table are the *least electronegative* (*i.e. most electropositive*) *elements*. Thus we see that the *most electronegative element is flourine* which occurs at the top right hand corner and the *least electronegative* element is *cesium* which occurs at the bottom left hand corner of the periodic table. Being the most electronegative, F does not show any basic character, *i.e.*, it has no tendency to form positive ions in any of its known compounds. On the other hand, there is, however, evidence to show that Cl, Br and I have a tendency to form positive ions.

The variation of electronegativity in a period and a group of (*s*- and *p*-block elements) is shown in Fig. 4.22.

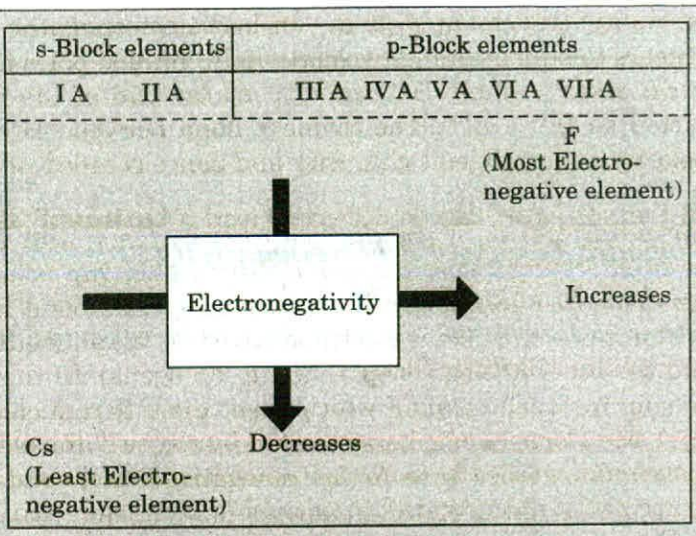


Fig. 4.22 Periodic variation of electronegativity in *s*- and *p*-block elements.

Applications of Electronegativity

1. Nature of bond. The concept of electronegativity can be used to predict the nature of bond formed between two similar or dissimilar atoms, i.e. the concept of electronegativity can predict whether the bond between two similar or dissimilar atoms is *non-polar covalent bond, polar covalent bond* or *ionic bond* as discussed below :

(*i*) **Non-polar covalent bond.** The bonding electron pair constituting the covalent bond between two similar atoms which have the same electronegativity or zero electronegativity difference *is equally shared by both the linked atoms i.e.* the shared electron pair is placed at the centre of the distance between the nuclei of the linked atoms. The equal sharing of the electron pair is because of the fact that both the linked atoms, due to their same electronegativity or zero electronegativity difference, have the same tendency to attract the shared electron pair towards them. It is because of the equal sharing of the electron pair that the resulted covalent bond has no polarity or ionic character, *i.e.* the bond is *non-polar* or *non-ionised*. This bond is therefore, called **non-polar covalent bond** or simply **covalent bond.**

(*ii*) **Polar covalent bond.** The bonding electron pair constituting the covalent bond between two dissimilar atoms like H and Cl which have different electronegativity values (H = 2.1, Cl = 3.0) *is not equally shared by the linked atoms i.e.*, the electron pair is not placed at the centre of the distance between the nuclei of the two atoms *viz.* H and Cl. Rather it is partially displaced (*i.e.* attracted) towards the more electronegative Cl atom owing to its greater affinity for electron pair. This type of partial displacement of the shared electron pair towards the more electronegative Cl atom develops a small (fractional) negative charge (represented as $\delta-$) on more electronegative Cl atom and an equal amount

of small positive charge (represented as δ+) on less electronegative H atom and HCl molecule appears to be containing two oppositely charged poles (called *charge-centres* or *electrical poles*) namely $H^{\delta+}$ and $Cl^{\delta-}$ at the end of the bond and the molecule is depicted as $H^{\delta+} - Cl^{\delta-}$. The covalent bond between H and Cl atoms develops some polarity or partial ionic character and hence is called **polar covalent bond.**

(*iii*) **Ionic or polar bond.** *When the two linked atoms have very different electronegativity or have large electronegativity difference, the bond established between the atoms is called* **ionic bond.** Consequently this bond is established between the two atoms one of which is electropositive (*e.g.* alkali metals or alkaline earth metals) and the other is electronegative (*e.g.* halogens). In the formation of this bond between, for instance Li and F which have very different electronegatives (Li = 1.1, F = 4.01), the electron pair being shared by the two atoms is completely displaced or transferred towards the more electronegative F atom and consequently less electronegative Li atom gains positive (+) charge while the more electronegative F atom aquires equal negative (–) charge and the bond is represented as $Li^+ F^-$. Ionic bond is totally free from covalent character. Thus it is a purely ionic bond.

Whatever has been said above in (*i*), (*ii*) and (*iii*) can be summarised as follows (x_A and x_B are the electronegativity values of atoms A and B in AB molecule) :

(*a*) When $x_A = x_B$, *i.e.* $x_A - x_B = 0$, then A–B bond is non-polar covalent bond or simply *covalent bond* and is represented as A–B. For example H–H bond in H_2 molecule is a covalent bond and is represented as H–H bond.

(*b*) When $x_A > x_B$, *i.e.* $x_A - x_B$ is *small*, then A–B bond is *polar covalent bond* and is represented as $A^{\delta-} + B^{\delta+}$, since $x_A > x_B$. For example both O–H covalent bonds in H_2O molecule are polar covalent bonds and are represented as $O^{\delta-} - H^{\delta+}$, since $x_O > x_H$ and $x_O - x_H$ is small.

(*c*) When $x_A \gg x_B$, *i.e.*, $x_A - x_B$ is *very large*, A–B bond is an *ionic or polar bond* and is represented as $A^- - B^+$, since $x_A \gg x_B$. For example Na–Cl bond in NaCl molecule is an ionic bond and is represented as Na^+Cl^- (Here Cl = A and Na = B).

2. Percentage of ionic character in a polar covalent bond. The concept of electronegativity can also be used to calculate the percentage of ionic character in a polar covalent bond. If two atoms A and B are linked by a polar covalent bond ($A^{\delta-} - B^{\delta+}$ or simply A–B), the amount of ionic character in this bond depends on the difference of electronegativity values of A and B. *Greater is the difference ($x_A - x_B$), greater is the percentage of ionic character in A–B bond.* Here the electronegativity of atom A (x_A) has been assumed to be higher than that of B (x_B). Pauling has estimated the percentage of ionic character in various $A^{\delta-} - B^{\delta+}$ polar covalent bonds from known ($x_A - x_B$) values and has derived the following conclusions :

(*i*) When $(x_A - x_B) = 1.9$, the amount of ionic character in $A^{\delta-} - B^{\delta+}$ bond is 50% and that of covalent character is also 50%. Thus A–B bond is 50% ionic and 50% covalent.

(*ii*) When $(x_A - x_B) < 1.9$, the amount of ionic character in $A^{\delta-} - B^{\delta+}$ bond is less than 50% and that of covalent character is more than 50%. Thus $A^{\delta-} - B^{\delta+}$ bond is *predominantly* covalent and hence is represented as A–B.

(*iii*) When $(x_A - x_B) > 1.9$, the amount of ionic character in $A^{\delta-} - B^{\delta+}$ bond is more than 50% and that of covalent character is less than 50%. Hence $A^{\delta-} - B^{\delta+}$ bond is predominantly ionic and hence is represented as A^-B^+.

Above discussion shows that if $(x_A - x_B)$ increases from 1.9, percent of ionic character in A – B bond also increases as shown below :

$(x_A - x_B)$ *value* :	0.6	0.8	1.2	1.9	2.2	2.8	3.2
	——— *Increases* ——→						
Percent ionic character in A – B bond	10	15	30	50	70	86	92
	——— *Increases* ——→						

3. Acidic and basic character of XOH molecule in aqueous solution. With the help of the concept of electronegativity we can predict whether a given compound of XOH type (X = Metal or non-metal) will behave as an acid or a base in aqueous solution. This prediction can be made by considering the ionisation of XOH molecule in aqueous solution as follows :

(*a*) If $x_O - x_H > x_O - x_X$, O–H bond will be more polar than O–X bond and hence the ionisation of XOH molecule in aqueous solution will take place at O–H bond and H_3O^+ ions will be produced as shown below :

$$\begin{aligned} X\text{–}O\text{–}H &\longrightarrow XO^- + H^+ \\ H^+ + H_2O &\longrightarrow H_3O^+ \\ \hline X\text{–}O\text{–}H + H_2O &\longrightarrow XO^- + H_3O^+ \end{aligned}$$

The production of H_3O^+ ions confirms that XOH molecule will behave as an acid in its aqueous solution.

(*b*) If $x_O - x_H < x_O - x_X$, X–O bond will be more polar than O–H bond and hence the ionisation of XOH molcule in aqueous solution will take place at X–O bond and OH^- ions will be produced as shown below :

$$\begin{aligned} X\text{–}O\text{–}H &\longrightarrow X^+ + OH^- \\ X^+ + H_2O &\longrightarrow [X \leftarrow OH_2]^+ \\ \hline X\text{–}O\text{–}H + H_2O &\longrightarrow [X \leftarrow OH_2]^+ + OH^- \end{aligned}$$

The production of OH^- ions confirms the fact that XOH molecule will behave as a base in its aqueous solution.

Example. *Predict which of the following hydroxy compounds is acidic and which is basic in aqueous solution*? CsOH, IOH

Solution. The electronegativity values of different elements present in CsOH and IOH compounds and those of $x_O - x_H$ and $x_O - x_X$ (X = Cs or I) as given below :

$$\underset{0.7}{Cs}\text{—}\underset{3.5}{O}\text{—}\underset{2.1}{H} \quad (2.8,\ 1.4) \qquad ; \qquad \underset{2.5}{I}\text{—}\underset{3.5}{O}\text{—}\underset{2.1}{H} \quad (1.0,\ 1.4)$$

show that CsOH will give OH^- ions while IOH will give H^+ ions (or $H + H_2O \rightarrow H_3O^+$). Consequently CsOH behaves as a base while IOH behaves as an acid.

The above description clearly shows that the *hydroxy compounds of metals like alkali metals and alkaline earth metals behave as bases in aqueous solution while those of non-metals like halogens behave as acids.*

4. Cause of diagonal relationship. It is one of the important properties of the earlier elements of 2*nd* period of the long form of periodic table (*e.g.* Li, Be and B) that they resemble more with the elements lying at their right hand side in the 3*rd* period (*i.e.* diagonally opposite elements) than with the other members of their own sub-groups. Thus Li resembles in its properties more with Mg which lies to its lower right in the 3*rd* period than with other members of its own sub-group IA. Similarly Be resembles Al, and B resembles Si. This type of similarity in properties in the two diagonally opposite elements is called diagonal relationship. Why the two elements show diagonal relationship has been explained on the basis of the concept of electronegativity as below

We know that the electronegativity of elements increases from left to right in a period and decreases on descending a group. Thus, Be is more electronegative than Li (Be>Li) and Mg is slightly less electronegative than Be (Be>Mg). *Li and Mg, being slightly less electronegative than Be, can be regarded as having almost the same value of electronegativity* and hence have many similar properties, *i.e.* they show diagonal relationship with each other.

4. Bond angle. The concept of electronegativity has been found to be very useful to explain the variation of bond angle. Here we shall consider the following two cases :

(*i*) First of all we shall see how the B–A–B bond angle in the molecule of AB_x type (A is the central atom, B are the atoms attached with atom A and x is the number of B atoms) is changed with the change of eleotronegativity of the central atom. It has been observed that *with the decrease of the electronegativity of the central atom, the B–A –B bond angle also decreases.* For example the bond angle H–A–H (A = N, P, As, Sb) in NH_3, PH_3, AsH_3 and SbH_3 hydrides (hydrides of VA group) decreases from ∠H–N–H to ∠H–Sb–H as the electronegativity of the central atom (*i.e.* N, P, As or Sb) decreases from N to Sb.

Hydrides, AH_3 (A = N, P, As, Sb)	***Electronegativity of the central atom, A***	***H–A–H bond angle***
NH_3	3.0	107.5°
PH_3	2.1	93.3°
AsH_3	2.0	91.8°
SbH_3	1.9	91.3°

With the decrease of electronegativity from N (3.0) to Sb (1.9), the A–H bonding electron pairs in AH_3 molecules are drawn farther away from the central atom (A) but nearer to H-atom. The effect of this shifting of the bonding electron pairs towards H-atom is that the repulsion between the bonding electron pair (*bp*) and lone pair (*lp*) on the central atom [(*bp–lp*) repulsion] *increases*. The increase in (*bp–lp*) repulsion results in that bonding electron pairs come still close to each other and hence the bond angle progressively decreases from NH_3 to SbH_3.

On similar grounds the decrease in the bond angle in the hydrides H_2O, H_2S, H_2Se and H_2Te can also be explained.

Hydrides, AH_2 (A = O, S, Se, Te)	*Electronegativity of the central atom, A*	*H–A–H bond angle*
H_2O	3.5	104.5°
H_2S	2.5	92.3°
H_2Se	2.4	91°
H_2Te	2.1	90°

(*ii*) Now let us see how the B–A–B bond angle in AB_x type molecules is changed with the change of the electronegativity of the atom B. It has been observed that *B–A–B bond angle increases with the decrease of the electronegativity of atom B*. This is evident from the following examples :

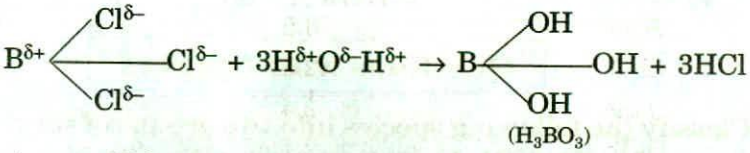
AB_x molecules	Electronegativity of B atom	B–A–B bond angle
PCl_3	3.0	100°
PBr_3	2.8	101.5°
PI_3	2.5	102
$AsCl_3$	3.0	98.4°
$AsBr_3$	2.8	100.5°
AsI_3	2.5	101.5°
NF_3	4.0	102°
NH_3	2.1	107°
OF_2	4.0	103°
OH_2	2.1	104.5°

The increase in bond angle with the decrease of electronegativity of atom B is due to the fact that with the decrease of the electronegativity of atom B, the bonding electron pair forming A–B bond is drawn farther away from B atom but nearer to the central atom, A. The net effect of this type of shifting of A–B bonding electron pair towards the central atom A is that the repulsion between the bonding electron pair and the lone pair on the central atom decreases. The decrease in (*bp–lp*) repulsion results in that the bonding electron pairs get farther away from each other, *i.e.* the B–A–B bond angle increases.

6. Mechanism of hydrolysis. Consider the hydrolysis of Cl_2O and BCl_3 molecules. In Cl_2O molecule O atom has a small negative charge ($-\delta$) on it and each of the two Cl atoms has a small positive charge ($+\delta$), because O atom has higher electronegativity than Cl. When H_2O attacks Cl_2O, the positively charged H atom ($H^{\delta+}$) of H_2O attacks at $O^{\delta-}$ atom of Cl_2O and the product of hydrolysis is hypochlorous acid (HOCl)

$$O^{\delta+}\begin{matrix}\diagup Cl^{\delta-}\\ \diagdown Cl^{\delta-}\end{matrix} + H^{\delta+}O^{\delta-}H^{\delta+} \rightarrow 2HOCl$$

In BCl_3, B atom has a small positive charge on it while each of the three Cl atoms bears a negative charge because B atom has less electronegativity than Cl atom. When H_2O attacks BCl_3, the negatively charged O atom ($O^{\delta-}$) of H_2O attacks at $B^{\delta+}$ atom of BCl_3 and the products of hydrolysis are boric acid, $B(OH)_3$ or H_3BO_3 and HCl.



7. Nomenclature of binary compounds. Generally binary compounds are regarded as derivatives of more electronegative elements. For example :

(*i*) The binary compound of iodine and chlorine is called iodine chloride and not chlorine iodide and hence is represented as ICl and not ClI, since electronegativity of Cl is higher than that of I (Cl = 3.2, I = 2.7).

(*ii*) The binary compound of oxygen and fluorine is called oxygen difluoride rather than fluorine monoxide and hence is represented as OF_2, and not as F_2O, since electronegativity of F is higher than that of O (F = 4.0, O = 3.5). Note that Cl_2O is called chlorine monoxide and not oxygen dichloride since O has higher electronegativity than Cl (O = 3.5, Cl = 3.0).

Exceptions. Names of some binary compounds have been retained for historical reasons. For example ammonia is written as NH_3 and not as H_3N, although the electronegativity of first element namely N is higher than that of H (N = 3.0, H = 2.1).

8. Calculation of bond length. Generally in case of heterodiatomic molecules of AB type, bond length, d(A – B) is equal to the sum of covalent radii of A and B atoms, *i.e.*

$$\boxed{d\,(\text{A–B}) = r\,(\text{A}) + r\,(\text{B})} \qquad ...(i)$$

Although equation (*i*) holds good in most of the heterodiatomic molecules, yet the experimental value of d (A–B) in case of many AB type molecules is slightly less than the sum of r (A) and r (B). The decrease in the bond length is due to the ionic character in A–B bond. The increase in the amount of ionic character in A–B bond decreases the bond length, d (A–B).

Taking the electronegativity difference, $(x_A - x_B)$ into consideration Schomakar and Stevenson (1941) proposed the following empirical equation for the calculation of bond length.

$$\boxed{d\,(\text{A–B}) = r\,(\text{A}) + r\,(\text{B}) - 0.09\,(x_A - x_B)} \qquad ...(ii)$$

Here x_A and x_B are the electronegativities A and B elements.

The validity of equation (*ii*) can be shown by calculating the N–C distance in $(CH_3)_3N$ molecule by equations (*i*) and (*ii*) as shown below :

From equation (*i*), d (N–C) = r (N) + r (C)

= (0.75 + 0.77) Å

= 1.52 Å

The calculated value (= 1.52 Å) obtained as above is not in agreement with the experimental value (= 1.47 Å) seen in $(CH_3)_3N$ molecule. But the value

calculated from equation (*ii*) has been found in good agreement with the experimental value as shown below :

From equation (*ii*), d (N–C) $= r$ (N) $+ r$ (C) $- 0.09\ (x_N - x_C)$

$= 0.75 + 0.77 - 0.09\ (3.0 - 2.5)$

$= 1.475$ Å

Questions with Answers

Q.1 Classify the following species into two groups of species which should be isoelectronic. K^+, NO^+, Ca^{2+}, C_2^{2-}, Sc^{3+}, CN^-, Cl^-, N_2.

Ans. Find out the number of electrons in the given species. $K^+ = 19 - 1 = 18$, $NO^+ = 7 + 8 - 1 = 14$, $Ca^{2+} = 20 - 2 = 18$, $C_2^{2-} = 6 \times 2 + 2 = 14$, $Sc^{3+} = 21 - 3 = 18$, $CN^- = 6 + 7 + 1 = 14$, $Cl^- = 17 + 1 = 18$, $N_2 = 2 \times 7 = 14$. The given species can be classified into the following two groups :

(*i*) K^+, Ca^{2+}, Sc^{3+}, Cl^- (*All contain 18 electrons*)

(*ii*) NO^+, C_2^{2-}, CN^-, N_2 (*All contain 14 electrons*)

Q.2 Arrange the following atoms/ions in the increasing order their size.

(*i*) F^-, Al, Na^+, Mg^{2+}

(*ii*) Ca^{2+}, Ar, K^+, Cl^-, S^{2-}

Ans. (*i*) Since F^-, Na^+ and Mg^{2+} ions are isoelectronic ($F^- = 9 + 1 = 10$, $Na^+ = 11 - 1 = 10$, $Mg^{2+} = 12 - 2 = 10$), their size increases with the decrease of their atomic number. Thus :

$$Mg^{2+}\ (Z = 12) < Na^+\ (Z = 11) < F^-\ (Z = 9)$$

Now since $F^- <$ Al, the overall increasing order is :

$Mg^{2+} < Na^+ < F^- <$ Al (Ans.)

(*ii*) Since all the given species are isoelectronic ($Ca^{2+} = 20 - 2 = 18$, Ar = 18, $K^+ = 19 - 1 = 18$, $Cl^- = 17 + 1 = 18$, $S^{2-} = 16 + 2 = 18$), their size increases with the decrease of their atomic number. Thus :

$$\left.\begin{array}{lccccccc} & Ca^{2+} & < & K^+ & < & Ar & < & Cl^- < S^{2-} \\ Z = & 20 & & 19 & & 18 & & 17 \quad 16 \end{array}\right\} \text{(Ans.)}$$

Q.3 Arrange the elements with E.Cs [He] $2s^1$, [Ne] $3s^1$ and [Ar] $4s^1$ in the decreasing order of their IE_1 values.

Ans. E.Cs show that the given elements belong to group 1. Since IE_1 values decrease on moving down the group, IE_1 values of the given elements decrease as :

[He] $2s^1$ > [Ne] $3s^1$ > [Ar] $4s^1$ (Ans.)

Q.4 Find out the number of valence electrons in an atom whose successive IE values (in $KJmol^{-1}$) are as : $IE_1 = 410$, $IE_2 = 820$, $IE_3 = 1100$, $IE_4 = 1500$ and $IE_5 = 3200$.

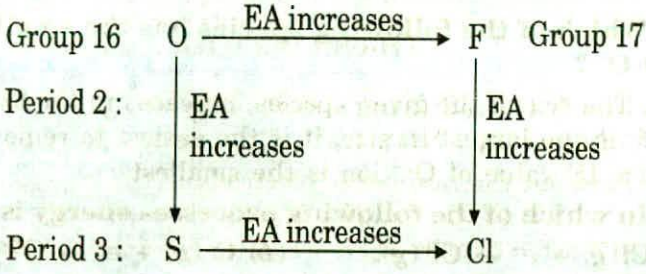
Ans. IE values show that since the magnitude of energy required for removing 5*th* electron from the atom is more than the double the magnitude of energy needed for removing 4*th* electron, the number of valence electrons in the atom is 4.

Q.5 Arrange F, Cl, O and S in the increasing order of their EA values.

Ans. EA values of the given elements are in the following increasing order :

$$O < S < F < Cl$$

Explanation. On the basis of the position of the given elements in the long form of periodic table the variation of their EA values can be shown as :



Hence the increasing order of EA values is O < S < F < Cl.

Q.6 The electronic configurations for four elements A, B, C and D are as : A = $1s^2, 2s^22p^6, 3s^1$; B = $1s^2, 2s^22p^6, 3s^2$; C = $1s^2, 2s^22p^1$; D = $1s^2, 2s^22p^6, 3s^23p^1$. Predict which of these elements has maximum value of ($IE_2 - IE_1$).

Ans. IE_1 and IE_2 values for the given elements correspond to the following ionisation processes.

$$\underset{(A)}{1s^2, 2s^22p^6, 3s^1} \xrightarrow[IE_1]{-3s^1(n=3)} 1s^2, 2s^22p^6 \xrightarrow[IE_2]{-2p^1(n=2)} 1s^2, 2s^22p^5$$

$$\underset{(B)}{1s^2, 2s^22p^6, 3s^2} \xrightarrow[IE_1]{-3s^1(n=3)} 1s^2, 2s^22p^6, 3s^1 \xrightarrow[IE_2]{-3s^1(n=3)} 1s^2, 2s^22p^6$$

$$\underset{(C)}{1s^2, 2s^22p^1} \xrightarrow[IE_1]{-2p^1(n=2)} 1s^2, 2s^2 \xrightarrow[IE_2]{-2s^1(n=2)} 1s^2, 2s^1$$

$$\underset{(D)}{1s^2, 2s^22p^6, 3s^23p^1} \xrightarrow[IE_1]{-3p^1(n=3)} 1s^2, 2s^22p^6, 3s^2 \xrightarrow[IE_2]{-3s^1(n=3)} 1s^2, 2s^22p^6, 3s^1$$

In case of A 1*st* electron is removed from 3*s* orbital (n = 3) and 2*nd* electron is removed from 2*p* orbital (n = 2). Since 3*s* orbital belongs to outer orbit (n = 3) and 2*p* orbital belongs to inner orbit (n = 2), ($IE_2 - IE_1$) for this element is maximum. In case of other elements the orbitals from which electron(s) is (are) removed belong to the same shell.

Q.7 Arrange C, N, O and F in the decreasing order of their IE_2 values.

Ans. The decreasing order of IE_2 values is : O > F > N > C.

Explanatin. IE_2 value of an element A is the energy required to remove an electron from A^+ cation. V.S.E.Cs of $\overset{+}{C}$, $\overset{+}{N}$, $\overset{+}{O}$ and $\overset{+}{F}$ cations are as : $\overset{+}{C} = 2s^22p^1$,

$\overset{+}{N} = 2s^2 2p^2$, $\overset{+}{O} = 2s^2 2p^3$ and $\overset{+}{F} = 2s^2 2p^4$. Since $\overset{+}{O}$ cation has half-filled $2p$ orbitals, $2s^2 2p^3$ configuration is stable. Hence IE_2 of O-atom would be higher than that of F(O > F). Now since C-atom is larger in size than N-atom, IE_2 of C would be lower than that of N(N > C). Thus the overall decreasing order is : O > F > N > C.

Q.8 Which of the following species has the smallest value of IE. O, O^-, O^{2-} and O^+ ?

Ans. The size of the given species increases in the order : $O^+ < O < O^- < O^{2-}$. Since O^{2-} is the largest in size, it is the easiest to remove an electron from this ion. Hence IE value of O^{2-} ion is the smallest.

Q.9 In which of the following processes energy is absorbed ?

(*a*) $Cl(g) + e^- \rightarrow Cl^-(g)$, (*b*) $O^-(g) + e^- \rightarrow O^{2-}(g)$

(*c*) $O(g) + e^- \rightarrow O^-(g)$, (*d*) $S(g) + e^- \rightarrow S^-(g)$

Ans. When an electron is added to a neutral gaseous atom (A), energy is released. Thus in the processes (*a*), (*c*) and (*d*), energy is released. On the other hand, when an electron is added to a given A^- ion, energy is absorbed (required). Thus in process (*b*) energy will be absorbed. In process (*b*) energy is absorbed to overcome the repulsions between the incoming electron and negative charge on $O^-(g)$ ion.

University Questions

1. (*a*) Give Slater's rules for calculating shielding constant or Z_{eff}.

(*b*) Give Pauling's method to determine the electronegativity of an atom.

(*c*) On the basis of Slater's rule, calculate the value of Z_{eff} for (*i*) a 4*s* electron (*ii*) a 3*d* electron. in chromium *(Himachal Pradesh 2000)*

2. Explain why metallic character increases as we move down the group. *(Himachal Pradesh, 2000)*

3. (*a*) Define ionisation potential of an atom. Which factors influence the ionisation potential ? What is effective nuclear charge?

(*b*) I.P. of H is 13.6 eV. Calculate the energy required to produce H hoot 0.5 g of hydrogen. *(Kanpur, 2000)*

4. Write notes on : (*i*) Ionisation potential (*ii*) Electron affinity (*iii*) Electronegativity. *(Kumaon, 2000)*

5. Explain the following :

(*i*) Electron affinities of Be, Mg and noble gases are zero while those nitrogen (= 0.20 eV) and phosphorus (= 0.80 eV) are very low.

(*ii*) The formation of F^- (*g*) ion from F(*g*) atom is exothermic whereas that of O^2 (*g*) ion from O(*g*) is endothermic.

(*iii*) In a period ionisation energy increases from left to right.

(*iv*) In a group electronegativity decreases from top to bottom.

(*v*) Group IA alkali metals form ionic compounds with group VII A halogens. [*Gauhati, 2000 (General)*]

6. What do you understand by the term, "Periodic Properties"? Distinguish between electron affinity and electronegativity. Flourine is more electronegative than chlorine, although its electron affinity is less than that of chlorine. Explain. *(Lucknow, 2000)*

7. (*i*) Arrange the following in the order of their increasing radii : O, F, Ne.

(*ii*) First ionisation potential of nitrogen is more than that of oxygen but 2*nd* ionisation potential of oxygen is more than that of nitrogen. Explain.

(*iii*) Which of the following has the highest electron affinity? F, Cl, Br

(*iv*) The electronic configuration of some elements are given as : (*a*) $1s^2$, $2s^2$ $2p^6$, $3s^2$ (*b*) $1s^2$, $2s^2$ $2p^6$ (*c*) $1s^2$, $2s^2$ $2p^4$ (*d*) $1s^2$, $2s^2$, $2p^6$, $3s^2$ $3p^6$. Which of these elements has the lowest ionisation potential?

(*v*) Arrange the bond angle in the decreasing order of the following hydrides: NH_3, AsH_3 and PH_3.

(*vi*) Arrange the following in the order of increasing covalent character : C – Cl, B –Cl, Be – Cl, Be – F, Cl – Cl.

(*vii*) What is meant by electronegativity ? How does it depend on I.P. and E.A.?

(*viii*) How is electronegativity related with the polarity of a covalent bond? *(Avadh 2000)*

8. (*a*) What is ionization potential ? Discuss the factors on which ionization potential depends. Arrange the following according to decreasing ionization potential: Mg, Ra, Ba, Ca, Be.

(*b*) Atomic radii of the element in a series in the periodic table decrease with increasing atomic number upto VIIth group, but increase in inert gases. Explain giving reasons. *(Avadh 2000)*

9. Explain ionisation potential and electronegativity. *(Lucknow 2001)*

10. What is ionisation potential of an element. Explain why IE of N is higher than that of O ? *(Nagpur 2002)*

11. Write a note on Electron Affinity. *(Lucknow 2002)*

12. Explain why alkali metal cations are generally smaller in size than their corresponding atoms ? *(Delhi 2003)*

13. (*a*) Define electronegativity.

(*b*) Give reasons for the following :

(*i*) The second ionisation energy of sodium is very high as compared to its first ionisation energy.

(*ii*) First ionisation energy of nitrogen is higher than tht of oxygen.

(*c*) Define the followng and explain their trends across the period and down the group in periodic table : (*i*) Atomic radius and (*ii*) Electron affinity. *(Nagpur 2003)*

14. (*a*) Differentiate between covalent reactions and Van der Waal's radius.

(*b*) What are iso-electronic ions ? Arrange the given ions in order of their decreasing size : F^-, O^{2-}, Mg^{2+} and Na^+.

(*c*) What is screening effect ? How does it govern the ionisation energy of an atom ? (*GND Amritsar 2004*)

15. Explain why EA values of N and P atoms are low. (*Meerut 2005, 2008*)

16. (*a*) Which of the following ions has the smallest size ? O^{2-}, F^-, Na^+ and Mg^{2+}.

(*b*) Define EA and state how if changes in a period. (*H.N. Bahuguna 2005*)

17. Explain the following :

(*i*) $(IP)_3$ of Mg is very high.

(*ii*) EA values of N and P atoms are low. (*Meerut 2006*)

18. (*a*) Arrange N, O, Cl and F in the increasing order of their EA values.

(*b*) In a covalent molecule AB, EN values of A and B are 2.1 and 3.5 respectively. Calculate % ionic character in A – B bond. (*H.N. Bahuguna 2006*)

19. Explain why Cl-atom is smaller in size than Cl^- ion. (*Meerut 2007*)

20. (*a*) First IP of N is higher than that of O. Explain.

(*b*) What is the trend in size of N^{3-}, O^{2-} and F^- ?

(*c*) EA of Cl is higher than that of F. Explain. (*Purvanchal 2007*)

21. Define and discuss electronegativity in detail along with the factors affecting it ? (*Meerut 2008*)

22. (*a*) Which of the following elements has the highest IP value ? Li, Na, K and Rb.

(*b*) Which of the following elements is the most electronegative ? F, Cl, Br and I. (*Agra 2008*)

CHAPTER

5 Radioactivity, Isotopes, Isobars and Isotones

Radioactivity

What is Radioactivity? (Discovery of Radioactivity)

Shortly after the discovery of X-rays, French physicist, *Henri Bacquerel*, in 1895, while trying to establish a possible relationship between the fluorescence of the glass walls of an X-ray tube and the phosphorescence of certain fluorescent salts caused by sunlight, left *accidently* a little pile of a uranium mineral on a photographic plate wrapped in a thick black paper lying in the dark room. On developing the plate he found a dark spot on it right below the position of the pile of the mineral. The black spot was a silhourette of the pile of the mineral. Bacquerel concluded that uranium emitted certain rays which penetrated paper wrapper and affected the photographic plate. These rays are invisible to naked eye and are given off by metallic uranium and also by uranium salts. These rays pass through thin sheets of glass or metal, produce ionisation in the gases through which they pass and rapidly discharge the charged leaves of a well-insulated electroscope. Bacquered called these rays as *radioactive rays* (*or radioactive emanations or radioactive radiations*) and the property or phenomenon of giving out these rays is called *radioactivity*. The substances which emit these radioactive rays are called *radioactive substances*. The term radioactivity was first used by *Marie Curie*.

Radioactivity is essentially a nuclear phenomenon and is a drastic process because the element changes in kind. It is spontaneous and an irreversible self-disintegrating activity because the element breaks itself up for good.

Discovery of Polonium and Radium

A year later, in 1896, *Marie Curie* undertook a systemetic study of the substances emitting radioactive rays for his doctorate thesis. During the study she found that pitchblende, a mineral of uranium, was far more radioactive than it could be due to its uranium content. She suggested that the greater activity shown by the mineral might be due to the presence of some new element in it. She and her husband, *Pierre Curie* worked together day and night, hardly stopping to eat or sleep, for the separation of this new hypothetical element. They took a ton of pitchblende and separated it into its constituents and found the radioactivity of each constituent. From the fraction containing bismuth they isolated a new radioactive element which they named **polonium** in honour of Marie Curies' native land of Poland. After a long and tedious process of extraction and fractional crystallisation of barium fraction, wife-husband team obtained, in 1898, a few

milligrams of another radioactive element which they named **radium** after the Latin word for ray. This new element was found to be three million times more radioactive than uranium. As the news of the discovery of the new radioactive elements spread, scientists in different parts of the world discovered many other radioactive elements, *e.g.*, in 1900 *Debierne* reported the discovery of another radioactive element which he called **actinium.**

Types of Radioactive Rays

Rutherford and his co-workers, in 1904, passed the radiations emitted by radioactive elements through a strong electric field between parallel plates and thus separated them into *three* quite different kinds which are : (*See* Fig. 5.1).

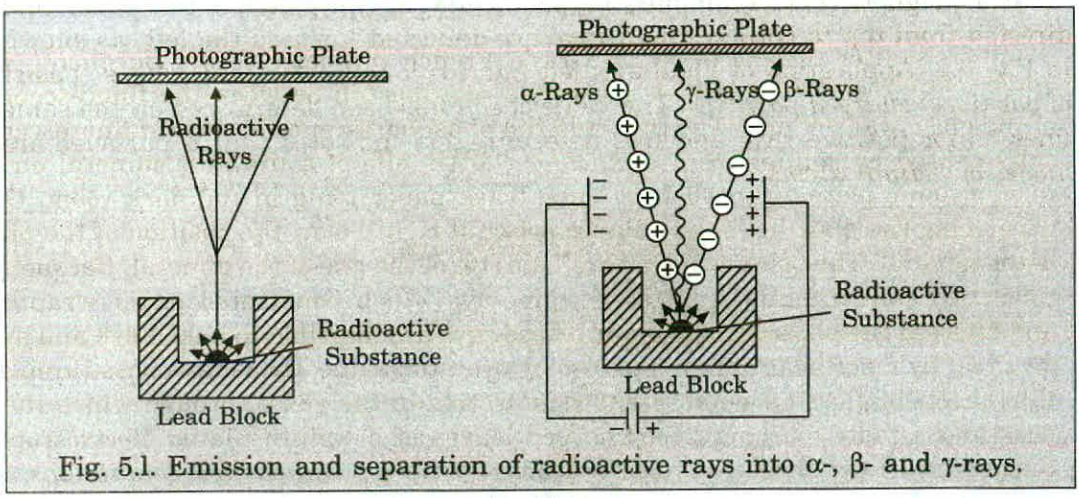


Fig. 5.1. Emission and separation of radioactive rays into α-, β- and γ-rays.

(*i*) **Alpha (α) rays.** The rays which are deflected towards the negative plate are *positively charged* and are called *alpha* (α) *rays or alpha particles*. These rays consist merely of *helium nuclei*.

(*ii*) **Beta (β) rays.** The rays which are deflected towards the positive plate are *negatively charged* and are called *beta* (β) *rays* or *beta particles*. These rays merely consist of electrons.

(*iii*) **Gamma (γ) rays.** These rays which are *not* deflected at all are neutral and are called *gamma* (γ) rays.

General Properties of Radioactive Radiations

(*i*) These radiations are highly penetrating, they affect photographic plates, ionize gases, cause scientillations on fluorescent screen, develop heat and produce chemical changes.

(*ii*) As radiations are given out, new elements are formed in an irreversible process—the new elements themselves being usually radioactive.

(*iii*) The emission of radiations is spontaneous and is not affected by external agents.

(*iv*) The emission is not instantaneous but is prolonged i.e., it is extended over a period of time, otherwise it would not have been discovered at all.

(*v*) Except for radioactivity, there is nothing abnormal about the radioactive elements as regards their physical and chemical properties.

(*vi*) *Effect of electric and magnetic fields—Electrical nature.* (*a*) *α-rays.* If a narrow beam of radioactive radiations proceeding from a deep cavity in a block of lead is subjected to an electric field between parallel plates, the α-particles are deflected towards the negative plate. This shows that α-rays consist of *positively charged particles* which have two units of positive charge and a mass four times the mass of a hydrogen atom. In other words, α-particles are *double charged helium ions*, each consisting of two neutrons and two protons but having no electrons.

If a magnetic field is applied perpendicular to the plane of the paper and directed from top to bottom, the α-rays are deflected towards the left, as shown in Fig. 5.2. Application of Fleming's left hand rule indicates that α-rays consist of *positively charged particles*. The value of *e/m* has been determined on the same lines as for positive rays and this determination indicates that α-particles are *nuclei of helium atoms*.

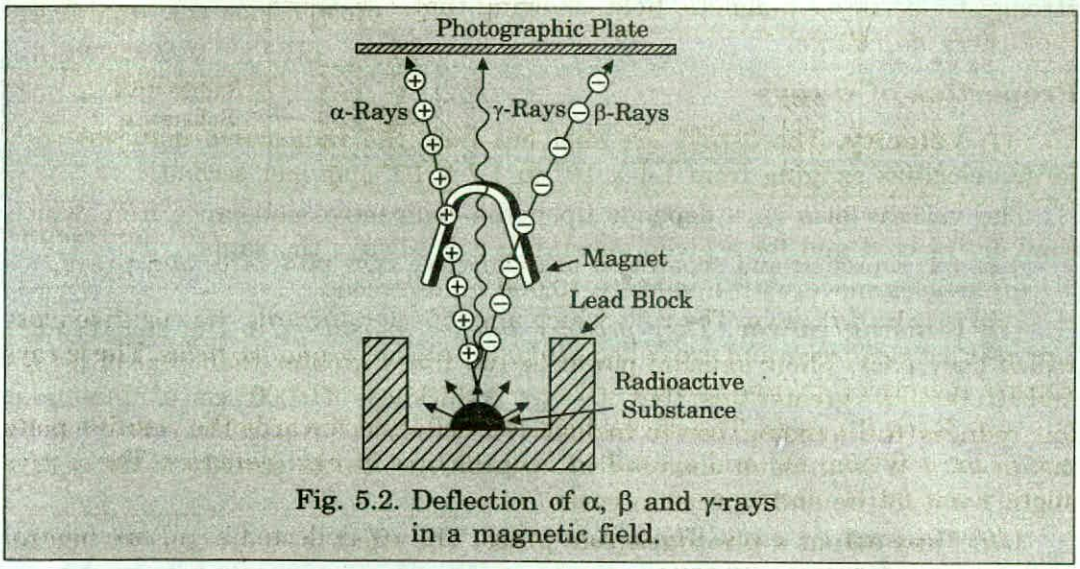


Fig. 5.2. Deflection of α, β and γ-rays in a magnetic field.

It was conclusively proved for the first time by Rutherford and Royds in England in 1909 that α-particles are nothing else *but doubly ionized helium nuclei*. A special discharge tube made of glass (Fig. 5.3) was used for this purpose. A thin-walled glass tube A containing radon gas was sealed inside a thick-walled tube B containing mercury. At the top was a glass capillary tube C with two metal electrodes sealed through glass as shown. Tubes B and C were evacuated through the side tube D after which mercury was raised to the level shown in the figure.

After some time, a few α-particles from radon gas pass through thin walls of A and enter B where they acquire electrons and become neutral atoms of helium. After standing for a few days, mercury level is raised up to L, thereby forcing the helium gas into the discharge tube C. A high-voltage is applied to the electrodes of C and the light from the discharge is observed with a spectroscope. The line

spectrum so obtained is found to be identical with that obtained by passing a discharge through another tube containing regular helium gas.

(*b*) β-*rays*. β-rays are also deflected by electric and magnetic fields. Their direction of deflection has shown that they are *negatively charged particles*. The *e/m* value has been found on the same lines as for cathode rays and this determination shows that β-rays are identical with cathode rays, *i.e.*, these are fast-moving *electrons*.

(*c*) γ-*rays*. γ-rays are similar to X-rays and are short-wave electromagnetic radiations similar to light. They have extremely small wavelengths of the order of 10^{-8} to 10^{-11} cm. They have no mass, hence they cannot be thought to be material particles. They *cannot* be deflected even in the strongest electric or magnetic field, showing that they *carry no charge*.

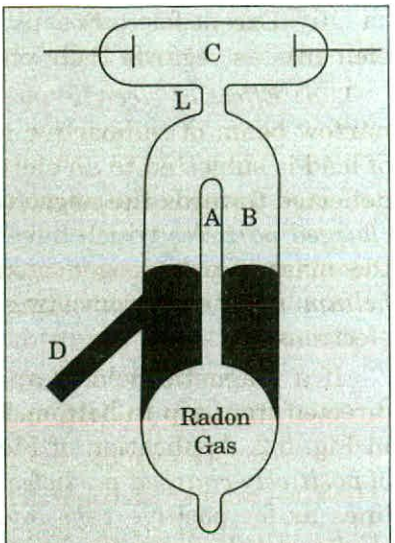


Fig. 5.3. An experimental proof to show that α-particles are doubly charged helium nuclei.

Properties of α-rays

(*i*) **Velocity.** The α-rays are shot out from the radioactive material with large velocities ranging from 1.4×10^9 to 1.7×10^9 cms. per second.

The velocity of α-rays depends upon the radioactive substance from which they are ejected and for a given substance it is always the same.

α-particles move with a velocity 10,000 miles/second.

(*ii*) **Ionising power.** *They produce intense ionisation* in the gas through which they pass. Their ionising power is 100 times greater than that of β-rays and 10,000 times greater than that of γ-rays. A thickness of 0.0005 cm. of aluminium foil reduces the ionising power to half. The tracks of α-particles observed by means of a Wilson cloud chamber are continuous, thick, straight lines with a slight bend in the end in certain cases.

(*iii*) **They affect a photographic plate.** The effect is, of course, very feeble.

(*iv*) **Penetrating power.** Out of the three radioactive radiations, they have the shortest penetrating power. It is so because α-particles produce the greatest number of ions in a given path, hence they penetrate the shortest distance. In *fact, their penetrating power is inversely proportional to their ionizing power.*

(*v*) **Fluorescence.** α-rays emitted by a radioactive material (*e.g.* radium salt) produce fluorescence (*i.e.* lumiscence) when they strike a fluorescent screen like zinc sulphide or barium platinocyanide. In other words, when α-particle strikes a fluorescent screen, a tiny flash of light which is called **scintillation** is produced. Each individual scintillation can be observed with the help of an apparatus called **spin thariscope** which is a low-power microscope. On observing the fluorescence through spin thariscope, it is found to consist of successive *scintillations*, produced by the impact of an individual α-particle. The impact of

a single α-particle can thus be observed and the number of such particles given out per second by a radioactive substance can be found out. The fact that these scientillations are due to α-particles and not due to β or γ-rays can be proved by interposing a thin sheet of mica between the radium salt and the fluorescent screen. Since α-rays are absorbed by mica sheet, the scientillations disappear.

***(vi)* Range of α-particles.** Scintillations from α-particle cease abruptly after it has traversed a certain distance through matter. *The distance that an α-particle can travel in air, at atmospheric pressure, is called its range in air.* It varies from 2.70 cms. for α-particles given by uranium to 8.62 cms. for those of polonium. The range of an α-particle depends upon

(*a*) the radioactive substance from which the rays are given out.

(*b*) the nature of the medium through which the rays travel.

(*c*) velocity of emission. The range is proportional to V^3.

The number of α-particles in a beam remains constant upto the end of the range, but their energy goes on decreasing. Ultimately the α-particles do not have sufficient energy to produce either scientillations or ionisation.

The ionisation first increases slightly, reaches a maximum and then suddenly drops almost to zero value. The distance at which the ionisation drops almost to zero gives the range of α-particles.

When the radioactive sample, say, polonium (P) is moved farther and farther away by pulling the rod (R) back, a point is reached when scientillations are no longer observed through the low-power microscope (M). The distance *d* where the α-particles just fail to reach the screen and hence produce no scientillation gives the range of the α-particles. (*See* Fig. 5.4).

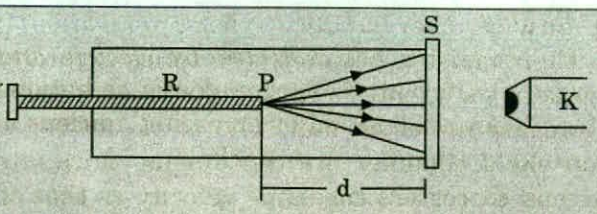


Fig. 5.4. Measurement of the range of an α-particle by scientillations produced on a fluorescent screen. R = Rod; P = Radioactive sample (polonium); S = fluorescent screen; M = Low-power microscope; *d* = Range of α-particles.

***(vii)* The α-rays are scattered when they pass through thin sheets of mica, gold foil, etc.** The divergence of α-particle from its straight line path is 2 to 3 degrees. Geiger and Marsden found that a few particles, sometimes, were deflected by more than 90°. This was explained by Rutherford to be due to the repulsion between the α-particle and the nucleus of the atom scattering it.

***(viii)* The rays are deflected by electric and magnetic fields showing that they are charged particles.**

***(ix)* They produce a heating effect.** A quantity of radium always maintains itself at a temperature higher than that of the surroundings. The evolution of heat is due to the stoppage of α, β and γ-rays by the radioactive substance.

(*x*) When exposed to α-rays the body suffers incurable burns.

Properties of β-rays

(*i*) Velocity and range of β-rays. β-particles do not emerge out of the nucleus with the same range and velocity; rather they have a wide band of velocity ranging from 1 per cent to 99 per cent of the velocity of light.

(*ii*) Ionisation in air. β-rays produce ionisation in air but the number of ions produced is hardly $\frac{1}{1000}$th of those produced by α-rays. Although their velocity is very large, they possess a comparatively small mass and hence have small kinetic energy. As β-particles change their path, their tracks in a Wilson cloud chamber are scattered not continuous as are for the α-particles.

(*iii*) Penetration. β-rays can penetrate through large thickness of matter, *e.g.* they can easily pass through 1 cm. thickness of aluminium sheet.

(*iv*) Deflection. *β-rays are deflected, by electric and magnetic fields.* Their direction of deflection shows that they are *negatively charged* particles. The *e/m* value has been found on the same lines as for cathode rays and this determination shows that β-rays are fast-moving electrons which are of *nuclear* origin although they do not revolve in orbits as do the extra-nuclear electrons.

(*v*) They are readily scattered when passing through matter because of their extremely small mass. Generally, they undergo multiple scattering although single scattering also takes place by impact both with electrons and with nuclei.

(*vi*) They affect photographic plates more strongly than a-particles.

(*vii*) They produce fluorescence in barium platinocyanide, calcium tungstate, Willemite etc.

Properties of γ-rays

(*i*) Deflection. *γ-rays are not deflected by electric and magnetic fields.* This property shows that they are electromagnetic radiations which consist of very energetic photons. They are emitted by an excited nucleus and have extremely short wave-length ranging from 0.5 Å to 0.005 Å.

(*ii*) Velocity. γ-rays prossess the same velocity as that of light, *i.e.* 3×10^{10} cms/sec.

(*iii*) Diffraction. They are diffracted by crystals in the same way as X-rays.

(*iv*) Ionisation in gas and genetrating power. They ionize the gas through which they pass, although the ionization produced by them is comparatively small. Consequently, their penetrating power is very high as compared to that of β-rays, *e.g.* they can pass easily through 30 cms. thickness of iron.

(*v*) They are capable of producing fluorescence and affecting photographic plates more intensely than β-rays.

Applications of Radioactive Radiations

(*i*) Many radiation sources such as cobalt—60 (γ-ray emitter) have been used for industrial radiography *i.e.* for investigating the interiors of metallic castings for detecting any flaws or defects.

(*ii*) Radioactive nuclides emitting α- or β-particles have been used for the production of electric power by thermo-electric conversion. When α- or β-particles are absorbed in matter, the energy of the radiation is converted into heat which can be utilized for production of electric power. Such radio nuclide power generators are particularly suitable for space vehicles because of their light weight, long life and absolute reliability.

(*iii*) Radio nuclides have been used as compact sources of heat energy because of which they find many space-related applications. Radio nuclides of promethium—147, polonium—210 and plutonium—238 have been used to heat the propellant gas (hydrogen) in low-thrust rockets.

(*iv*) Chemical changes initiated by radiations from radioactive substances is the basis of a newly developed subject called *radiation chemistry* which has been applied in the production and modification of plastics and in the production of irradiated wood-plastic combinations.

(*v*) Nuclear radiations like γ-rays have been utilized for the preservation of food. The irradiation of food-stuff mainly meat, poultry, fish and fruits is achieved by exposure to γ-rays from cobalt—60 or calcium—137. A dose of 2 to 5 million rads, is sufficient to destroy almost all bacteria in food. This increases the shelf-life of these articles without refrigeration. Radiations have also been employed for insect disinfestation of wheat and flour.

(*vi*) Gamma radiations from cobalt—60 are used in hospitals for sterilization of materials like dressings, hypodermic syringes and surgical sutures.

(*vii*) Population of insects which causes considerable damage to both plant crops and livestock can be controlled by irradiating the male members of these insects so that they become sterile.

(*viii*) Radiation mutations in plants have been practised to produce new varieties of these plants.

(*ix*) Self-luminous paints for use on instruments and watch dails have been made by adding a natural α-emitting radioactive substance to phosphur.

(*x*) The ionization produced by β-particles has been widely used for the elimination of static electricity which constitutes a serious fire and explosion hazard in the paper, textile, rubber and plastic industries.

Types of Radioactivity

Radioactivity is of two types :

1. Natural radioactivity. We have seen that the naturally occurring elements like uranium, polonium, radium etc. are constantly undergoing a spontaneous change (*i.e.* change by itself) and as a result of this they are emitting α-, β- and γ-rays and thus change into other elements. *This spontaneous change is called natural radioactivity.* In natural radioactivity only a single nucleus is involved It is always found in heavier elements in the periodic table.

2. Artificial or induced radioactivity. Artificial or induced radioactivity *is a process by which an element is converted into a new radioactive isotope of a known element by artificial means.*

Detection and Measurement of Radioactivity

The detection and measurement of radioactivity of a substance can be made by a number of methods some of which are described below :

1. Electroscope Method. The electroscope used for the purpose consists of an ionisation chamber and electroscope box (Fig. 5.5). The ionisation chamber is made of lead and consists of two metallic plates P and P′ separated by the gas which is exposed to the rays. The lower plate is connected with the wall of the chamber and earthed. The upper plate which is insulated by a block of sulphur and connected with the gold leaf system, G is initially charged to a high potential. The radioactive material is then placed in the cavity of the plate P′. The air between the two plates gets ionised and the charge leakes away between P and P′. The gold leaf falls and its rate of fall is proportional to the rate of leakge and thus to the intensity of the rays. The rate of leakage so found is compared with that of a substance of known radioactivity under exactly similar conditions and thus the total radioactivity of the substance under examination is determined.

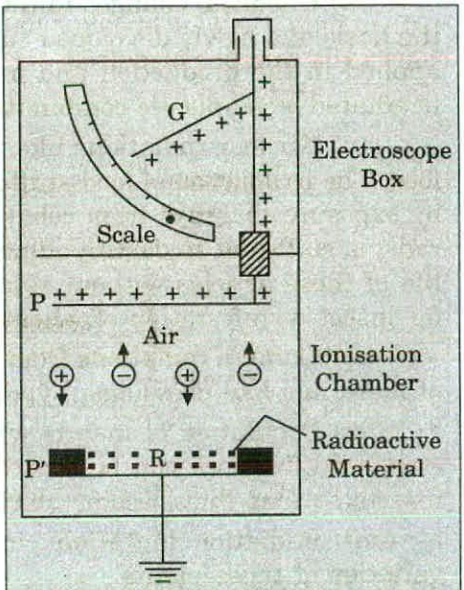


Fig. 5.5. Electroscope used for the measurement of radioactivity of a substance.

2. Wilson's Cloud Chamber Method. The apparatus used in this method was devised by Wilson (1912) and is known as *Wilson's Cloud Chamber* (Fig. 5.6). This is a new technique which is based on the production of ions by radioactive emissions. Such ions when produced in a chamber supersaturated with vapours (say of water) act as nuclei for the condensation of vapours. Since ions are produced along the path of radioactive emission, the track of fog formed indicates the path followed by particle. This path can be photographed.

In actual practice, a gas or dust-free air saturated with water (or alcohol) vapour is enclosed in the chamber. The piston is rapidly moved up to bring about cooling by sudden expansion. Thus the air contained in the chamber becomes supersaturated with water vapour. At this stage the radioactive emissions are led into chamber. A fog track is at once formed along the path transversed by the radioactive emission. This is immediately

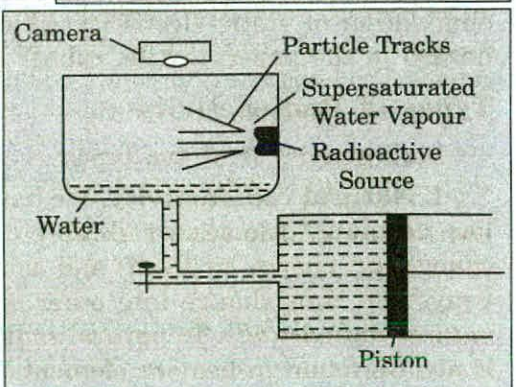


Fig. 5.6. Wilson cloud chamber used for the measurement of radioactivity of a substance.

photographed by the camera. In more recent sophisticated devices, the cloud chamber operates automatically.

3. Geiger-Muller Counter Method. The apparatus used in this method has been shown in Fig. 5.7. This apparatus consists of a hollow cylinderical tube fitted with a thin metal rod along its axis and insulated from the tube. The tube is filled with a gas like oxygen or argon at a low pressure (say, 0.1 atm). A high potential upto 1000 volts is applied at the rod (acting as anode) and the outer tube (acting as cathode). When α and β particles of high energy are allowed to enter the metallic tube through the quartz window, they produce enough ions which cause a pulse of a current to flow between the rod and the tube. This pulse can be amplified and recorded on a loud-speaker as a sharp click. In the more sophisticated instruments, the loud speaker has been replaced by an automatic recorder which counts the number of pulses.

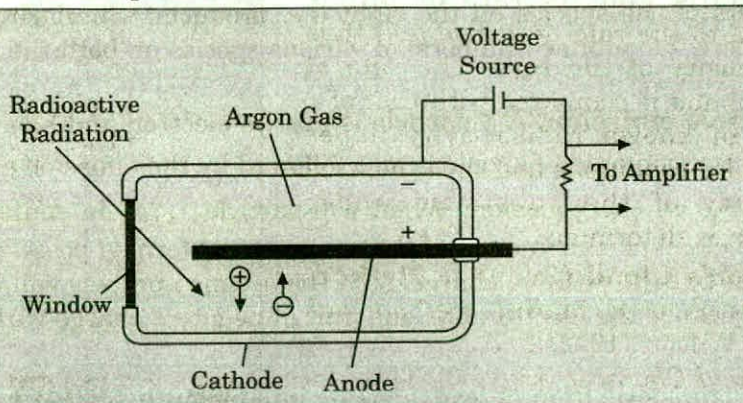


Fig. 5.7. Geiger-Muller counter used for the detection and measurement of radioactivity of a substance.

What is Radioactive Disintegration ?

Atoms of heavy elements like uranium, thorium, polonium and radium etc. are constantly breaking up into fresh radioactive atoms with the emission of α-, β- and γ-rays from their nuclei. In this process, the original (or parent) atom disappears and gives rise to new (daughter) atom. These new atoms are also, in general, radioactive and hence spontaneously break up in their turn, thereby leading to a long chain of different radioactive elements in the form of a series until an inactive element (usually lead) is reached. This *spontaneous breaking up of the nucleus is known as radioactive disintegration or radioactive decay.*

Examples of Modes of Decay

The disintegration process may proceed in one of the following first two ways :

1. α-particle emission. When an α-particle (^4_2He) is emitted from the nucleus of an atom (*called parent element*), the nucleus of the new element formed (*called daughter element*) possesses atomic weight or atomic mass number less by four units and nuclear charge (*i.e.* atomic number) less by two units because α-particle has an atomic mass of four units and nuclear charge of two units. Thus an atom

of radium ($^{226}_{88}Ra$) changes on emission of an α-particle into an atom of radon ($^{222}_{86}Rn$). Here the subscript to the bottom left gives the *atomic number* (*i.e.* the number of protons or positive charges on the nucleus) and the superscript on the top right gives the *atomic weight* (*i.e.* weight of the protons and neutrons put together) or *atomic mass number*.

Thus the disintegration of $^{226}_{88}Ra$ into $^{222}_{86}Rn$ can be represented by the following equation which is called *nuclear equation* (*or transmutation equation*).

$$^{226}_{88}Ra \xrightarrow{-\alpha} {}^{222}_{86}Rn + \alpha$$

or

$$^{226}_{88}Ra \longrightarrow {}^{222}_{86}Rn + {}^{4}_{2}He$$

In a balanced nuclear equation the sum of the mass numbers (*i.e.* atomic mass numbers) of various species on the left (*i.e.* reactants) is equal to the sum of the mass numbers of the species on the right (*i.e.* products). Similarly, the sum of charge numbers (*i.e.* atomic numbers) of various species on both the sides should be equal.

2. β-particle emission. A β-particle is just an electron and hence its symbol is $^{0}_{-1}e$. Since ejection of a β-particle is also followed by the emission of γ-ray, γ-ray is also included in the equation. When a β-particle ($^{0}_{-1}e$) is emitted from the nucleus of an element, the nucleus of the new element formed possesses the same atomic weight but the positive charge, (*i.e.*, the atomic number) will be increased by one unit because the electron has one unit of negative charge with practically no mass.

Thus the transformation of lead ($^{210}_{82}Pb$) into bismuth ($^{210}_{83}Bi$) can be shown as :

$$^{210}_{82}Pb \xrightarrow{-\beta} {}^{210}_{83}Bi + {}^{0}_{-1}e + \gamma\text{-ray}$$

However, it is now believed that in a β-particle emission, a neutron ($^{1}_{0}n$) is converted into a proton ($^{0}_{+1}p$), an electron ($^{0}_{-1}e$) and a neutrino ($^{0}_{0}v$). The neutrino has zero mass and zero charge and is postulated to balance the spins. Thus :

$$\textit{Neutron} \rightarrow \textit{Proton} + \textit{Electron} + \textit{Neutrino}$$

or

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

The electron produced escapes as β-particle leaving the proton behind in the nucleus. The increase in the atomic number of the necleus by one unit is due to this proton left in the nucleus.

3. γ-ray emission. We have already seen that γ-rays are short wave electro magnetic radiations with *no charge* and *no mass*. Thus the emission of γ-rays from a radio-active element will not produce a new element. The emission of γ-rays only results in decrease in energy of the nucleus. When α or β-particle is ejected from the nucleus, it is left in an excited state and emits γ-rays.

Laws of Radioactive Disintegration

Radioactive disintegration is found to obey the following two laws :

1. *Atoms of all radioactive elements are undergoing spontaneous disintegration i.e., are constantly breaking to form fresh rodioactive products with the emission of* α, β- *and* γ-*rays.*

2. *The rate of breaking is not affected by external factors like temperature, pressure, chemical combination, etc. but depends entirely on the law of chance, i.e., the number of atoms breaking per second at any instant is proportional to the number present. In other words, the quantity of a radioactive element which disintegrates in unit time is directly proportional to the amount of the radioactive element present.*

Rate of Disintegration

Suppose an element A disintegrates into another element B. Let the number of atoms of A in the beginning (*i.e.*, at $t = 0$) be N_0. Now as the time passes, the element A undergoes continuous disintegration into B and hence the number of atoms of A goes on decreasing. Let the number of atoms of A left undisintegrated in time t be N. Thus :

$$\begin{array}{lll} & A \rightarrow B \\ \text{At } t = 0 & N_0 \\ \text{At } t = t & N \end{array}$$

If dN atoms of A disintegrates in a small time dt, then the *rate of disintegration* (*i.e., rate of decrease*) of A into B which is also called *activity* is equal to $-\frac{dN}{dt}$ which is proportional to N, *i.e.*

$$-dN/dt \propto N$$

or
$$\frac{-dN}{dt} = \lambda N \qquad ...(i)$$

Here λ is a constant of proportionality which has been called by Rutherford and Soddy as *radioactive* (or *decay* or *disintegration*) *constant.*

Since the intensity and the number of atoms of A decrease with time, the rate of disintegration has been indicated by negative sign.

The differential equation (*i*) can be put in the form

$$\frac{dN}{N} = -\lambda dt$$

Integrating we have

$$\int \frac{dN}{N} = -\int \lambda dt + \text{constant of integration, } C$$

$$\log_e N = -\lambda t + C \qquad ...(ii)$$

Now when $t = 0, N = N_0$

$\because$ $\log_e N_0 = C$

Substituting in (*ii*), we get

$$\log_e \frac{N}{N_0} = -\lambda t$$

or $$\frac{N}{N_0} = e^{-\lambda t}$$

$\therefore$ $$\boxed{N = N_0 e^{-\lambda t}} \quad ...(iii)$$

This decay equation may be used to find the number of the atoms of the original kind present at any time t.

If M_0 is the original mass of the material and M its present mass, then

$$\boxed{M = M_0 e^{-\lambda t}}$$

Definition of Radioactive Constant (λ).

(*a*) Eq. (*i*) given above may be put as

$$\lambda = \frac{-dN/dt}{N}$$

Hence, radioactive constant may be defined as *the ratio of the amount of the substance which disintegrates in a unit time to the amount of the substance present.*

(*b*) Suppose, we put $t = 1/\lambda$ in Eq. (*iii*) above. Then the number of the original atoms present after this tune is

$$N = N_0 e^{-\lambda \times 1/\lambda} = N_0 e^{-1}$$

$$= \frac{N_0}{e} = \frac{N_0}{2.718}$$

$$\boxed{N = 0.368\ N_0 \approx 0.37\ N_0}$$

Hence, radioactive constant may also be defined as the *reciprocal of the time during which the number of atoms of a radioactive substance falls to 37 per cent of its original value.*

Definition of Half-life Period ($t_{1/2}$ or T).

Suppose after time T (or $t_{1/2}$) half of the atoms of the radioactive element has disintegrated, *i.e.*

when $t = T$, $N = N_0/2$

Thus on putting $t = T$ and $N = N_0/2$ in equation (*iii*), we get

$$\frac{N_0}{2} = N_0 . e^{-\lambda T}$$

or $$\frac{1}{2} = e^{-\lambda T}$$

or $$2 = e^{+\lambda T}$$

or $$\lambda T = \log_e 2$$

or $$T = \frac{\log_e 2}{\lambda}$$

Hence $\boxed{t_{1/2} \text{ or } T = \frac{0.6931}{\lambda}}$ ...(*iv*)

As is evident from equation (*iv*), *half-life period* (T or $t_{1/2}$) *of a radioactive substance is the time required to disintegrate one-half of the original amount of the substance.* In other words, *the half-life period of a radioactive substance is the time in which half of the radioactive substance will disintegrate.*

As seen from eqn. (*iv*), T is inversely proportional to the radioactive constant and hence is a characteristic constant which can be employed to differentiate radio elements. For example, it takes nearly 1620 years for one-half of a given quantity of radium to change into radon. In another 1620 years, 1/2 of the remainder would have disintegrated leaving 1/4 of the original amount behind. Accordingly, we say that half-life period of radium is 1620 years. However, radon has a half-life of only 38 days.

In general, it may be said that at the end of time T, only 50% of the radioactive atoms remain unchanged, at the end of $2T$ only 25%, after $3T$ only 12.5%, after $4T$ only 6.25% and at the end of $10T$ only 0.1%. Hence, the life time of a radioactive element, though theoretically infinite, is finite for all practical purposes.

As already seen, λN represents the rate at which particles are emitted by N radioactive atoms.

$$\therefore \textbf{ Rate of emission of particles or activity } = \lambda N = \frac{0.693N}{T}$$

If T is expressed in seconds, then the above equation gives the emission rate in terms of the number of particles expelled per second from N atoms of the given nuclide.

Evidently, half-life period of a given substance is independent of the amount of the substance present initially. It depends only on the disintegration constant (λ) of the element.

Half-life period of a radioactive substance is a measure of the radioactivity of the element, since shorter the half-life period of a radio-active element, larger the number of its atoms that are disintegrating in a unit time.

Determination of half-life period.

To find the half-life period, of a radioactive substance the value of radioactive constant λ is determined and the half-life period is calculated from relation (*iv*).

The radioactive constant λ can be determined experimentally by measuring the activity of a radioactive substance at two instances having an interval of time t. The apparatus used is the same as for measuring the ionisation current with a quadrant electrometer. The radioactive substance is placed in a thin layer on the lower plate and the ionisation current is measured at various intervals of time. A graph is then plotted between log I_t taken along the Y-axis and the time t along the X-axis. Now

$$I_t = I_0 e^{-\lambda t}$$

$$\therefore \quad \log_e I_t = \log_e I_0 - \lambda t$$

or $$y = a - \lambda t$$

where $$\log_e I_t = y \text{ and } \log I_0 = a \text{ (constant)} \quad ...(v)$$

The graph is a straight line. Differentiating equation (v), we have

$$\frac{dy}{dt} = -\lambda$$

Hence the slope of the graph gives the radioactive constant.

Average Life Period (l)

Since atoms of a radioactive element are constantly disintegrating one after another, the life of every atom is different. The atoms which disintegrate earlier have very short life whereas others which disintegrate at the end have a long life. Hence, the process of disintegration will continue indefinitely. Total decay period of any radioactive element is, therefore, infinity. Use of total decay periods or total life periods for radio-elements are thus meaningless.

Instead of total decay period, another term which is generally used is **average life period.** This is also called **mean life period** or **life expectancy** and is defined as follows :

Average life period of a radioactive element is the reciprocal of the disintegration constant (λ). Thus :

$$\boxed{l = \frac{1}{\lambda}}$$

We have already seen that

$$t_{1/2} = \frac{0.693}{\lambda}$$

or $$\frac{1}{\lambda} = \frac{t_{1/2}}{0.693} \quad ...(a)$$

and $$l = \frac{1}{\lambda} \quad ...(b)$$

Hence, from equation, (a) and (b), we get

$$l = \frac{t_{1/2}}{0.693} = 1.34 \times t_{1/2}$$

Thus :

$$\boxed{\textit{Average life period } (l) = 1.44 \times \textit{Half-life period } (t_{1/2})}$$

Radioactive Equilibrium : Law of Successive Disintegration

Consider a long-lived radioactive element *A*. This element, on standing, disintegrates successively into a decay series of radioactive atoms B, C, D etc.

$$A \rightarrow B \rightarrow C \rightarrow D \rightarrow .....$$

In the successive disintegration of radioactive substances *A, B, C, D* etc., any two adjacent elements may be considered as *parent* and *daughter*, the former being that which by its own decay produces the later, *e.g.*, A which produces B,

is the parent with respect to A, the daughter. Evidently in a series, the parent of the following element will be daughter of the preceding one. The law governing successive disintegrations deals with the quantity of the daughter present at any instant and determines the condition of equilibrium between the daughter and the parent.

After some time the rate at which the element B is formed from A becomes equal to the rate of its decay into C. *Thus a stage will be reached when the number of atoms of B formed (from A) per second will become equal to the number of atoms which disintegrate into C per second.* The element B is then said to be in a **radioactive equilibrium** with the given amount of A. In the same way, the element C and the element D will also reach the state of radioactive equilibrium with the preceding number of the decay series. Some authors prefer to call the equilibrium state as **steady state** because equilibrium, as used in a chemical reaction, implies existence of a reversible reaction whereas radioactive disintegrations are *irreversible.*

If N_1, N_2, N_3 etc. are the number of atoms of various members of the decay series at the steady state and λ_1, λ_2, λ_3 etc. are their disintegration constants,

Decay series : $A \rightarrow B \rightarrow C \rightarrow D \rightarrow .....$

No. of atoms : : $N_1 \quad N_2 \quad N_3$

Disintegration constants : $\lambda_1 \quad \lambda_2 \quad \lambda_3$

then $\lambda_1 N_1 = \lambda_2 N_2 = \lambda_3 N_3$ etc.

Now if we consider the elements A and B, then

$$\frac{N_1}{N_2} = \frac{\lambda_2}{\lambda_1} \qquad ...(vi)$$

Now since average life periods are reciprocal of disintegration constants,

$$\frac{\lambda_2}{\lambda_1} = \frac{l_1}{l_2} \qquad ...(vii)$$

With the help of equation (*vii*), equation (*vi*) reduces to :

$$\frac{N_1}{N_2} = \frac{\lambda_2}{\lambda_1} = \frac{l_1}{l_2} \qquad ...(viii)$$

where l_1 and l_2 are the average life periods of the elements A and B. Similar equations can be found by considering the elements B and C, C and D etc.

Relation (*viii*) shows that *at the steady state, the radioactive elements, A, B, C etc. are present in the direct ratio of their average-life periods.* Thus, at the steady state, the element having the highest average life period is present in the largest amount.

Radioactive equilibrium can be had only when the average life-period of the parent element is greater than that of the daughter element.

Numerical Problems

Example 1. *1 gram of radium is reduced by 2.1 mg in 5 years by α decay. Calculate the half-life period of radium.*

Solution. Initial mass of radium (N_0) = 1 gram

Mass of radium left behind (N) = 1 – 0.0021

= 0.9979 gram

$$\frac{N}{N_0} = e^{-\lambda t}$$

Here $$\frac{N}{N_0} = \frac{0.9979}{1}$$

and $$t = 5 \text{ years}$$

Hence $$0.9979 = e^{-5\lambda}$$

or $$e^{5\lambda} = \frac{1}{0.9979}$$

$$5\lambda = 2.3026 \log_{10}\left[\frac{1}{0.9979}\right]$$

$$\lambda = \frac{2.3026 \times 0.0009}{5}$$

or $$\lambda = 41.4468 \times 10^{-45} \text{ per year}$$

$$T = \frac{0.693}{\lambda} = \frac{0.693}{41.4468 \times 10^{-5}} = \mathbf{1672 \text{ years}}$$

Example 2. *A radioactive substance has a half-life period of 30 days. Calculate (i) the radioactive disintegration constant (ii) the average life period (iii) the time taken by $\frac{3}{4}$ of the original number of atoms to disintegrate and (iv) the time taken by $\frac{1}{8}$ of the original number of atoms to remain unchanged.*

Solution. Here T = 30 days

(*i*) $$\lambda = \frac{0.693}{T}$$

or $$\lambda = \frac{0.693}{30} = \mathbf{0.0231} \text{ per day}$$

(*ii*) Average life-period, $l = \frac{1}{\lambda}$

$$l = \frac{1}{0.0231} = \mathbf{43.29 \text{ days}}$$

(*iii*) Number of atoms disintegrated $= \frac{3}{4} N_0$

Number of atoms left behind $(N) = N_0 - \frac{3}{4} N_0 = \frac{1}{4} N_0$

$$N = N_0 e^{-\lambda t}$$

$$\frac{N}{N_0} = e^{-\lambda t}$$

Here $$\frac{N}{N_0} = \frac{N_0/4}{N_0} = \frac{1}{4}$$

$\therefore$ $$\frac{1}{4} = e^{-\lambda t}$$

$$\lambda t = \log_e 4$$

$$t = \frac{2.3026 \log_{10} 4}{0.0231}$$

$$= \frac{23.026 \times 0.6021}{0.0231}$$

$$= \mathbf{60\ days}$$

(*iv*) Here $$\frac{N}{N_0} = \frac{1}{8}$$

$$\frac{N}{N_0} = e^{-\lambda t}$$

$$\frac{1}{8} = e^{-\lambda t}$$

$$\lambda t = \log_e 8 = 2.3026 \log_{10} 8$$

or $$t = \frac{2.3026 \times 0.9031}{0.0231} = \mathbf{90\ days}$$

Example 3. *Calculate the time in which the activity of a sample of thorium reduces to 90% of its original value. Assume the half-life of thorium to be 1.4 × 10^{10} years.*

Solution. Here T = 1.4 × 10^{10} years

$$T = \frac{0.693}{\lambda}$$

$\therefore$ $$\lambda = \frac{0.693}{T}$$

$$\lambda = \frac{0.693}{1.4 \times 10^{10}} \text{ per year}$$

$$N = N_0 e^{-\lambda t}$$

$$\frac{N}{N_0} = e^{-\lambda t}$$

$$\frac{9}{10} = e^{-\lambda t}$$

$$\lambda t = \log_e 1.11$$

$$t = \frac{2.3026\ [\log_{10} 1.11] \times 1.4 \times 10^{10}}{0.693}$$

$$t = \mathbf{2.108 \times 10^9\ years}$$

Theory of Radioactive Disintegration : Stability of the Nucleus and Ratio of Neutrons and Protons.

The stability of a nucleus depends qualitatively on the ratio of the number of neutrons (N) and protons (P) present in it. In case of elements with atomic numbers equal to 20, the ratio N/P is quite close to *unity*, *i.e.* for such elements the number of neutrons is equal to that of protons. For the elements with higher atomic number ratio N/P increases progressively to about 1.6. In such elements the repulsion between them increases.

By plotting a graph between N and P for the nuclei of various elements it has been found that most of the stable nuclei (*i.e. non-radioactive nuclei*) lie in a well-defined belt which is known as the **zone** or **belt of stability** because it contains the stable nuclei. (See Fig. 5.8). *Nuclei whose N/P ratio lies above or below this belt are unstable and, therefore, undergo spontaneous radioactive disintegration from one atom to another, giving α- or β-particles. This process of disintegration continues until a stable nucleus is obtained.* For example, a radium nucleus changes successively into nine other nuclei emitting in all 5α and 4β particles and a stable nucleus of lead, Pb^{206} is obtained.

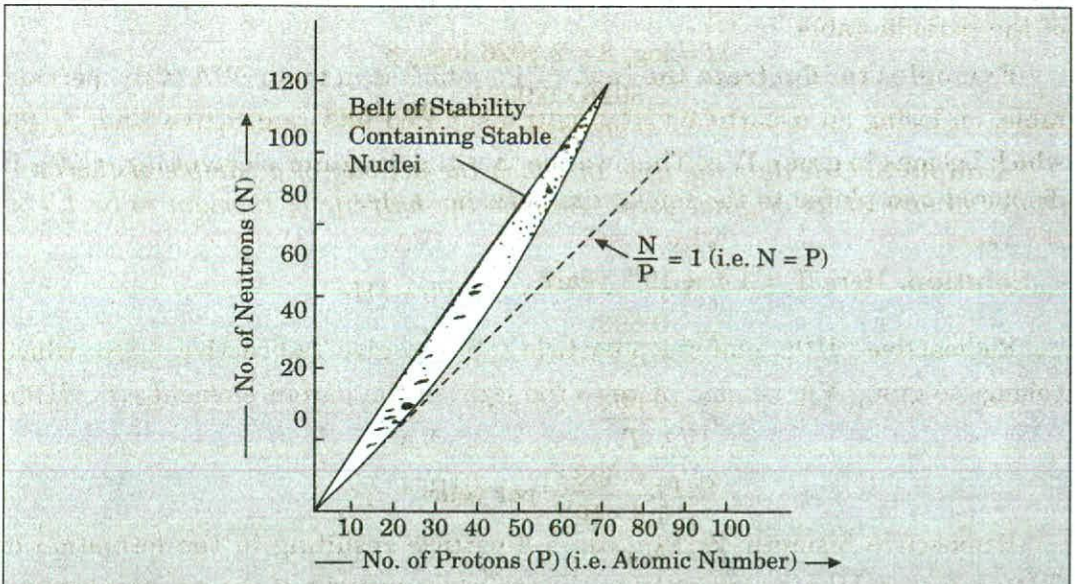


Fig. 5.8. A graph between the number of protons (P) and neutrons (N) having the belt of stability which contains stable nuclei. Nuclei whose N/P ratio lies above or below this belt are unstable and hence undergo spontaneous disintegration.

Group Displacement Law

The changes that occur when an α-particle or a β-particle is emitted from a radioactive element have been stated by *Fajan, Russel* and *Soddy* in 1913 in the form of a law which is known as **Group Displacement Law.** This law states as follows :

When an α-particle is emitted from a radioactive element (i.e. parent element), the new element (i.e. daughter element) formed has atomic number two units less

and mass number four units less than the parent element. The element is consequently displaced two places (i.e. two groups) to the left of the periodic table. Similarly, when a β-particle is emitted, the new element has atomic number one unit more but its mass number remains the same as that of the parent element. Consequently the new element is displaced one place (i.e. one group) to the right of the periodic table.

Explanation of the law. Since α-particle is a helium nucleus of mass number 4 (2 protons and 2 neutrons), the emission of an α-particle from a radioactive element causes the *mass number to decrease by four units*. Further, since two protons have been lost, *the atomic number falls by two units*. Consequently, the new element formed moves two places (*i.e. two groups*) to the left of the periodic table.

The β-particle is an electron and is emitted from the nucleus. But, as there are no electrons in the nucleus, its origin is uncertain. It is, therefore, postulated that a neutron changes into a proton and an electron. The electron is emitted as a β-particle leaving a proton behind. The number of protons in the nucleus increases by one unit, *i.e.* the positive charge (*i.e.* atomic number) increases by one unit. Consequently the daughter element moves one place (*i.e. one group*) to the right of the periodic table.

Examples to illustrate the law. $^{215}_{84}Po$ which is in group VIA of the periodic table, on losing an α-particle ($^{4}_{2}He$) is transformed into radioactive lead, $^{211}_{82}Pb$ which belongs to group IVA. Thus we see that the daughter element *viz.* $^{211}_{82}Pb$ is displaced two places to the left of the periodic table.

VIA IVA

$$^{215}_{84}Po \xrightarrow{-\alpha} {}^{211}_{82}Pb + {}^{4}_{2}He$$

Radioactive $^{211}_{82}Pb$ emits a β-particle ($^{0}_{-1}e$) to give radioactive $^{211}_{83}Bi$ which belongs to group VA, *i.e.* one place to the right of the parent element *viz.* $^{211}_{82}Pb$.

IVA VA

$$^{211}_{82}Pb \xrightarrow{-\beta} {}^{211}_{83}Bi + {}^{0}_{-1}e$$

Radioactive bismuth, $^{211}_{83}Bi$ loses a β-particle resulting in the formation of $^{211}_{84}Po$ which belongs to group VIA, *i.e.*, one place to right of the parent element, $^{211}_{83}Bi$.

VA VIA

$$^{211}_{83}Bi \xrightarrow{-\beta} {}^{211}_{84}Po + {}^{0}_{-1}e$$

The transformations shown above can be summarised as follows :

$$\underset{\text{(VIA)}}{^{215}_{84}Po} \xrightarrow{-{}^{4}_{2}He} \underset{\text{(IVA)}}{^{211}_{82}Pb} \xrightarrow{-{}^{0}_{-1}e} \underset{\text{(VA)}}{^{211}_{83}Bi} \xrightarrow{-{}^{0}_{-1}e} \underset{\text{(VIA)}}{^{211}_{84}Po}$$

In the above example $^{215}_{84}Po$ and $^{211}_{84}Po$ are isotopes while $^{211}_{82}Pb$, $^{211}_{83}Bi$ and $^{211}_{84}Po$ are isobars. Thus we conclude that a β-particle emission gives isobar while the combined emission of one α- and two β-particles results in the formation of an isotope.

Numerical problem. *Calculate the number of α- and β-particle, emitted when $^{238}_{92}U$ changes into $^{206}_{82}Pb$.*

Solution. Let the element formed between $^{238}_{92}U$ and $^{206}_{82}Pb$ be X. The mass number of X should be the same as that of Pb because there is no loss in the mass number of the daughter element formed as a result of β-emission. Now let the number of α- and β-particles emitted be x and y respectively. The disintegration sequence will be as follows :

$$^{238}_{92}U \xrightarrow{-x\alpha} {}^{206}X \xrightarrow{-y\beta} {}^{206}_{82}Pb$$

Thus :

$$238 - 4x = 206$$

$$\therefore \quad x = 32/4 = 8$$

The atomic number of

$$X = 92 - 2 \times 8 = 92 - 16 = 76$$

Consequently

$$y = 82 - 76 = 6$$

Thus the number of various particles emitted is :

α-particles = 8

β-particles = 6

Radioactive Series

Atoms of heavy elements like uranium, thorium, polonium and radium etc. are constantly breaking up into fresh radioactive atoms with the emission of α-, β- and γ-rays from their nuclei. In the process, the original (or parent) atom disappears and gives rise to new (daughter) atom. These new atoms are also, in general, radioactive and hence spontaneously break up in their turn, thereby leading to a long chain of different radioactive elements in the form of a series until an inactive element (usually lead) is reached. *The series of elements thus obtained by the successive disintegration of the new atoms is known as* **radioactive disintegration series** and the *spontaneous breaking up of the nucleus is known as* **radioactive disintegration.**

All the *naturally occurring radioactive elements* belong to one of the following three series : *(1) Uranium series [(4n + 2) series]. (2) Thorium series [4n series], (3) Actinium series [(4n + 3) series].*

These series have been named after the name of the element at or near the head of the respective series. All these three series which are also called **natural radioactive series** end with a stable isotope of lead.

Some elements of each series emit α-particles whereas some other elements emit β-particles. Although no one atom can go both ways, some atoms go either

of the two ways and cause branches in the series. No matter which way the parent goes, the daughter the goes other way so that even though the series branch, they always come together again.

1. Uranium series [$(4n + 2)$ *series*]. This series is also called $(4n + 2)$ series because the mass number of the elements of this series are given by this expression in which n is an integer whose value necreases by unity when we go from one radioactive element to the next one below it. The mass numbers of the members of this series give a remainder of 2 when divided by 4. In this series $^{238}_{92}U$ is the parent element and through the successive disintegrations it is finally transformed into a stable isotope of lead, $^{206}_{82}Pb$ (*See* Fig. 5.9).

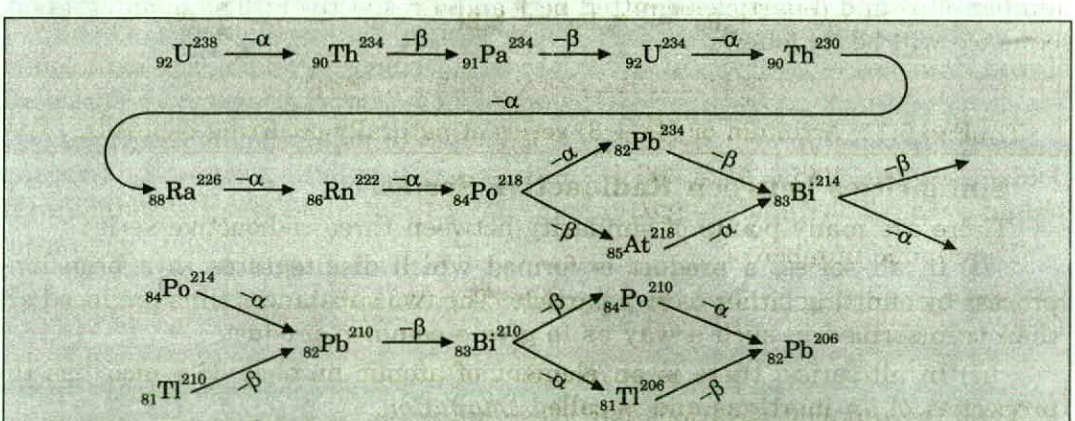


Fig. 5.9. Uranium or $(4n + 2)$ series for naturally occurring elements.

2. Thorium series (*4n series*). This series is also known as $4n$ series because mass numbers of the members of this series are divisible by 4. This series starts with $^{232}_{90}Th$. As shown in Fig. 5.10 by a successive transmutation or disintegration it ends up in a stable isotope of lead, $^{208}_{82}Pb$.

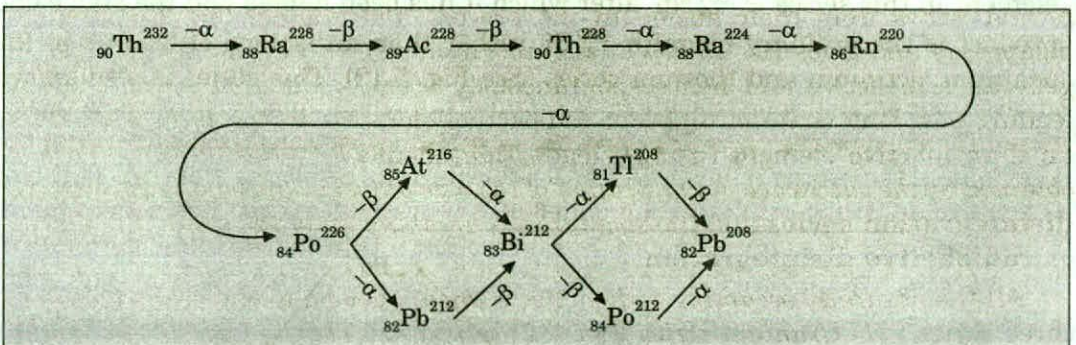


Fig. 5.10. Thorium or $4n$ series for naturally occurring elements.

3. Actinium series [$(4n + 3)$ *series*]. This series is also known as $(4n + 3)$ series because the mass numbers of the members of this series give a remainder of 3 when divided by 4. Actinium was one time thought to be the starting element of this series, but now it is known that the true starting element is $^{235}_{92}U$ which

by successive transformations ends up in a stable isotope of lead, $^{207}_{82}Pb$. The whole chain of elements is shown in Fig. 5.11.

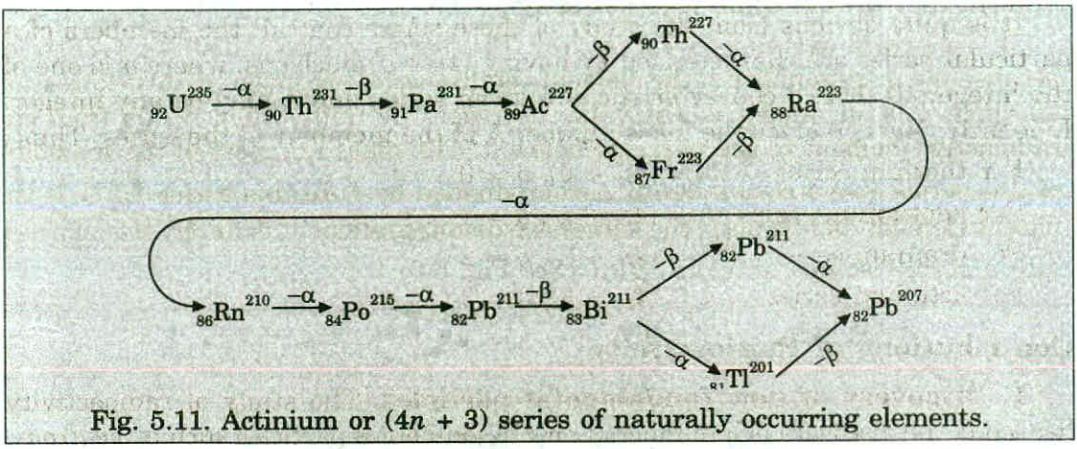


Fig. 5.11. Actinium or ($4n$ + 3) series of naturally occurring elements.

Similarities between Radioactive Series.

There are many points of similarity between three radioactive series :

(*i*) In all series, a product is formed which disintegrates in a branching process by emitting either α- or β-particle. The two substances thus produced are then transformed in such a way as to give a common product.

(*ii*) In all series, there is an element of atomic number 86 which has the properties of an inert gas and is called *emanation.*

(*iii*) The stable end-product in all the three series having an atomic number of 82, is an isotope of lead *i.e.* Pb^{206}, Pb^{207} and Pb^{208}.

Neptunium Series [($4n$ + 1) *series*).

In addition to the three series described above, there is a fourth series which has been obtained from an *artificially-produced* radioactive material. The first element in this series is $^{237}_{93}Np$ after which it has been named and the stable end product is the ordinary bismuth $^{209}_{83}Bi$ rather than an isotope of lead as in the uranium, actinium and thorium series (*See* Fig. 5.12). This series is also known

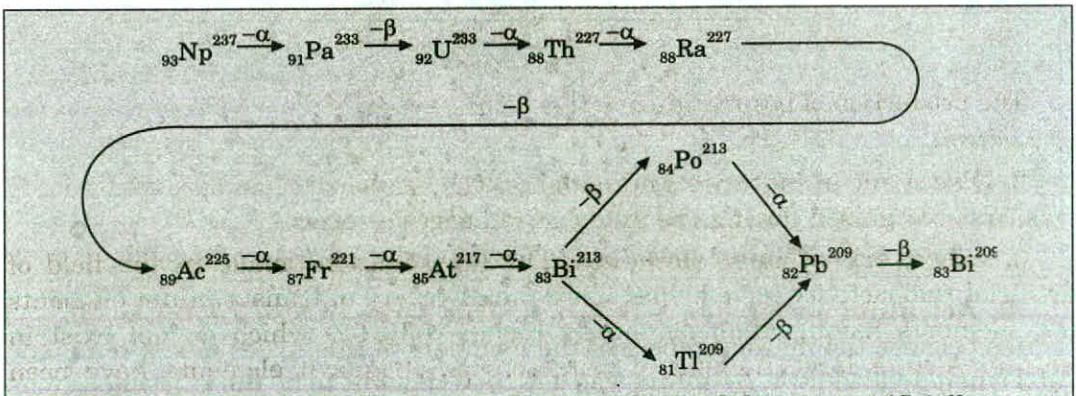


Fig. 5.12. Neptunium or ($4n$ + 1) series obtained from an artificially produced radioactive material.

as $(4n + 1)$ series. All the members of this series are either unknown or extremely rare in nature.

It is quite obvious from the study of these series that all the members of a particular series are characterised by having $(4n + q)$ nucleons, where q is one of the integers 0, 1, 2, 3 characteristic of a given series and n may be any integer. Evidently, $(4n + q)$ gives the mass number A of the members of the series. Thus :

For thorium series $A = (4n + 0), q = 0$

For neptunium series $A = (4n + 1), q = 1$

For uranium series $A = (4n + 2), q = 2$

For actinium series $A = (4n + 3), q = 3$

Contributions of Radioactivity

1. Discovery of new fundamental particles. The study of radioactivity has led to the discovery of a number of new fundamental particles such as *neutrons, positrons, deuterons,* α-, β-, and *γ-particles etc.* These particles have been used as bombarding particles (*projectiles*) in the artificial transmutation of elements and have added to our knowledge of atomic structure. For example :

(*a*) The scattering of α-particles proved that the *nucleus is positively charged.*

(*b*) The extent of the deflection of α-particles indicates that the *atomic number is numerically equal to nuclear charge.*

(*c*) The production of protons $({}_1^1H)$ in the bombardment of lighter elements like ${}_3^6Li$ by deutrons $({}_1^2D)$ shows *the presence of protons in the nucleus.*

$$ {}_3^6Li + {}_1^2D \rightarrow {}_3^7Li + {}_1^1H $$

(*d*) The bombardment of ${}_{12}^{24}Mg$ by ${}_2^4He$ gives ${}_{14}^{27}Si$ which is radioactive and hence disintegrates spontaneously to give stable isotope ${}_{13}^{27}Al$ and positrons $({}_{+1}^0e)$.

$$ {}_{12}^{24}Mg + {}_2^4He \rightarrow \underset{\text{Radioactive}}{{}_{14}^{27}Si} + {}_0^1n $$

$$ {}_{14}^{27}Si \rightarrow \underset{\substack{\text{Non-radio-}\\\text{active isotope}\\(i.e.\ \text{stable})}}{{}_{13}^{27}Al} + \underset{\substack{\text{Posi-}\\\text{tron}}}{{}_{+1}^0e} $$

The production of positron during the disintegration of ${}_{14}^{27}Si$ shows the *presence of positron.*

2. Discovery of isotopes and isobars. The existence of isotopes and isobars was first recognised during the study of radioactive series.

3. Discovery of new elements. The investigations made in the field of artificial radioactivity have helped us in the discovery of transuranium elements (*i.e.* elements having atomic numbers higher than 92) which do not exist in nature. Also, a large number of radioisotopes of known elements have been discovered by transmutation reactions.

4. Release of nuclear energy. The processes involving nuclear fission and nuclear fussion release a huge amount of energy which can be used both in peace and war.

5. Production of radioisotopes. Artificial radioactivity has been used in producing radioisotopes of many elements which are used for various purposes such as :

(*i*) Use of radioisotopes as radioactive tracers.

(*ii*) Use of radioisotopes in the treatment of diseases (*Radiotherapy*).

(*iii*) Determination of the age of the earth by rock dating method.

(*iv*) Determination of the age of the recent objects by radiocarbon dating method.

All the above uses of radioisotopes are described under "*Uses of Radioisotopes*".

Isotopes

What are Isotopes ?

Different kinds of atoms of the same element which have the same atomic number but different mass numbers or atomic masses (or atomic weights) are called isotopes of that element. Since isotopes have the same atomic number, these can also be defined as *different atoms of the same element which have the same number of protons but different number of neutrons in their respective nuclei.*

The name isotope was first introduced by Soddy. The word *isotopes* has been derived form the Greek word meaning *same position* (*isos* = same; *topes* = position), since the isotopes occupy the same position in the periodic table. Isotopes have identical chemical properties and differ slightly only in respect of such properties as depend on their mass numbers.

Symbolic Representation of Isotopes

It is a common practice to represent each isotope of a given element by an appropriate symbol which is internationally adopted. In the representation of an isotope of a given element, the mass number (A) is shown as superscript at the head of the symbol of the element while the atomic number (Z) is shown as subscript at its bottom. The superscripts and subscripts may be shown at the left or right of the symbol of the element. The superscript (*i.e.* mass number) gives the sum of the number of protons and neutrons present in the nucleus while the subscript (*i.e.* atomic number) gives the number of protons or electrons. The symbolic representation of an isotope of an element, X has been shown in Fig. 5.13.

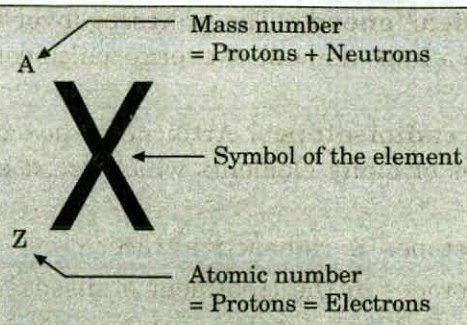


Fig. 5.13. Symbolic representation of an isotope of an element, X

As an example three isotopes of carbon (at no = 6) having mass numbers equal to 12, 13 and 14 can be shown as :

(*i*) ${}^{12}_{6}C$ or ${}^{12}C$ (*ii*) ${}^{13}_{6}C$ or ${}^{13}C$ (*iii*) ${}^{14}_{6}C$ or ${}^{14}C$.

Alternatively the above three isotopes of carbon can also be shown as C–12, C–13 and C–14 which are read as *carbon-twelve*, *carbon-thirteen* and *carbon-fourteen* respectively.

Structure of Isotopes

Since isotopes of an element have the same atomic number, each of these isotopes contains equal numbers of protons in the nucleus and equal number of electrons revolving in different orbits around the nucleus. Now since they have different mass numbers, they have different number of neutrons in their respective nuclei. Thus the number of protons (p), neutrons (n) and electrons (e) in an isotope with atomic number, Z and mass number, $A\left(\begin{matrix}A\\Z\end{matrix}X \text{ isotope}\right)$ is given by the following relations :

(*i*) No. of protons, $p = Z$

(*ii*) No. of neutrons, $n = A–Z$ $\quad (\because A = n + p = n + Z)$

(*iii*) No. of electrons, $e = Z$

Now let us consider the structure of the isotopes of some elements in terms of the number of electrons, protons and neutrons in them.

1. Isotopes of hydrogen. There are three isotopes of hydrogen (At No. Z = 1) with mass number (A) 1, 2 and 3. These are : (*i*) *Ordinary hydrogen or protium,* ${}^{1}_{1}H$ (*ii*) *Heavy hydrogen or deuterium,* ${}^{2}_{1}H$ or D, and (*iii*) *Tritium,* ${}^{3}_{1}H$ or T. As is evident, each of these isotopes has one electron. The nucleus of protium has one proton only; that of deuterium has one proton and one neutron while that of tritium has one proton and two neutrons. The number of electrons, protons and neutrons in each of these three isotopes in given below :

Isotope	Atomic number (Z)	Mass number (A)	Electrons (e) = Z	Protons (p) = Z	Neutrons (n) = (A–Z)
${}^{1}_{1}H$	1	1	1	1	1–1 = 0
${}^{2}_{1}H$ or D	1	2	1	1	2–1 = 1
${}^{3}_{1}H$ or T	1	3	1	1	3–1 = 2

The structure of the three isotopes of hydrogen in terms of the number of electrons, protons and neutrons is shown pictorially in Fig. 5.14.

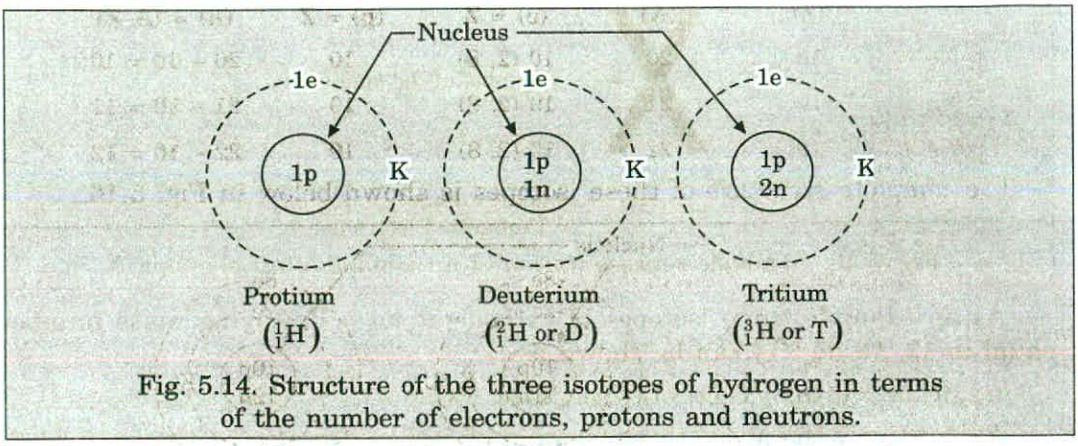


Fig. 5.14. Structure of the three isotopes of hydrogen in terms of the number of electrons, protons and neutrons.

2. Isotopes of oxygen. Oxygen has three isotopes with atomic number, Z = 8 and mass number, A equal to 16, 17 and 18. These are thus represented as $^{16}_{8}O$, $^{17}_{8}O$ and $^{18}_{8}O$ respectively. The number of electrons, protons and neutrons in each of them is given below :

Isotope	Atomic number (Z)	Mass number (A)	Electrons (e) = Z	Protons (p) = Z	Neutrons (n) = (A–Z)
$^{16}_{8}O$	8	16	8(2, 6)	8	16 – 8 = 8
$^{17}_{8}O$	8	17	8(2, 6)	8	17 – 8 = 9
$^{18}_{8}O$	8	18	8(2, 6)	8	18 – 8 = 10

The structure of the three isotopes is shown in Fig. 5.15.

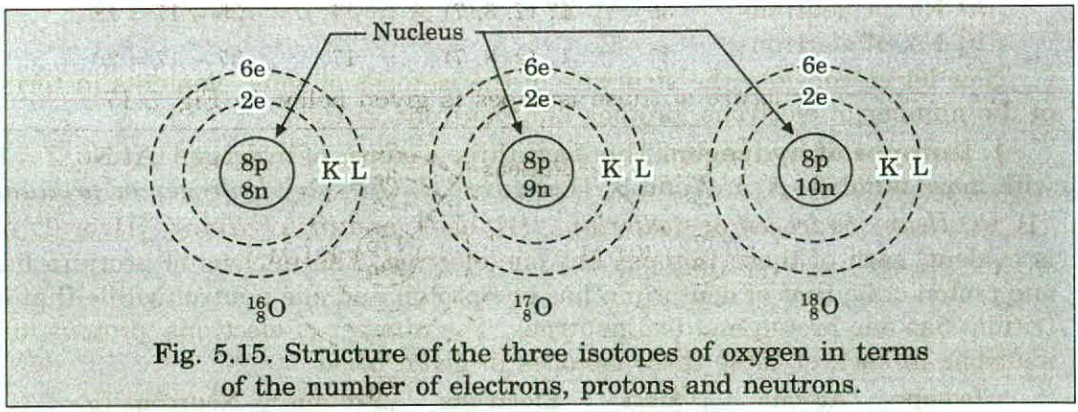


Fig. 5.15. Structure of the three isotopes of oxygen in terms of the number of electrons, protons and neutrons.

3. Isotopes of neon. Neon has three isotopes with atomic number, Z = 10, and mass number, A equal to 20, 21 and 22. These are thus represented as : $^{20}_{10}Ne$, $^{21}_{10}Ne$, $^{22}_{10}Ne$ respectively. The number of electrons, protons and neutrons in each of them is given below :

Isotope	Atomic number (Z)	Mass number (A)	Electrons (e) = Z	Protons (p) = Z	Neutrons (n) = (A–Z)
$^{20}_{10}Ne$	10	20	10 (2, 8)	10	20 – 10 = 10
$^{21}_{10}Ne$	10	21	10 (2, 8)	10	21 – 10 = 11
$^{22}_{10}Ne$	10	22	10 (2, 8)	10	22 – 10 = 12

The complete structure of these isotopes is shown below in Fig. 5.16.

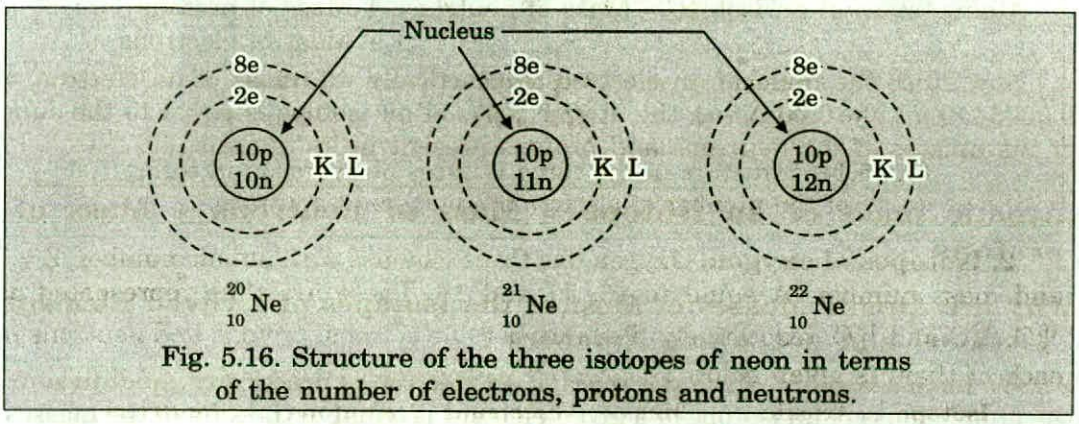


Fig. 5.16. Structure of the three isotopes of neon in terms of the number of electrons, protons and neutrons.

4. Isotopes of chlorine. Chlorine is a mixture of two isotopes with atomic number, Z = 17 and mass number, A equal to 35 and 37. Thus these are represented as $^{35}_{17}Cl$ and $^{37}_{17}Cl$ respectively. The number of electrons, protons and neutrons in each of these isotopes is as follows :

Isotope	Atomic number (Z)	Mass number (A)	Electrons (e) = Z	Protons (p) = Z	Neutrons (n) = (A–Z)
$^{35}_{17}Cl$	17	35	17 (2, 8, 7)	17	35 – 17 = 18
$^{37}_{17}Cl$	17	37	17 (2, 8, 7)	17	37 – 17 = 20

The complete structure of these isotopes is given below in Fig. 5.17 :

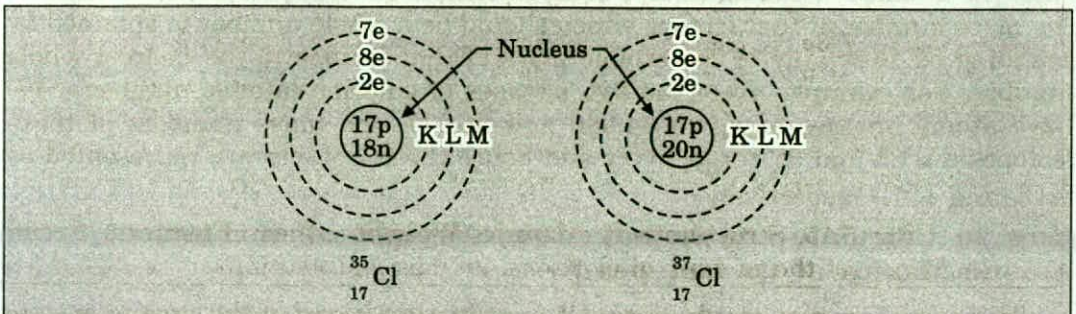


Fig. 5.17. Structure of the two isotopes of chlorine in terms of the number of electrons, protons and neutrons.

Almost all the elements are found in nature as a mixture of isotopes. The isotopes of some elements and their structure in terms of the number of electrons, protons and neutrons is given in Table 5.1.

It may be seen from the table that some elements like beryllium and fluorine are found in nature as a single isotope. Such elements are called **monoisotopic.** Only about 20 elements have been found to be monoisotopic.

What is Atomic Mass of an Isotope ?

We know that an atom is made up of neutrons, protons and electrons. The sum of the masses of these constituent particles in a given isotope of an element is known as its atomic mass. Thus :

Atomic mass of an isotope = Mass of neutrons + Mass of protons + Mass of electrons

Now since the mass of an electron in practically nil (mass of an electron = 0.0005449 *amu* ≈ 0.00 *amu*), the atomic mass of an isotope is equal to the sum of the masses of the neutrons and protons present in its nucleus, *i.e.*

Atomic mass of an isotope = Mass of neutrons + Mass of protons

Why are Atomic Masses of Most of the Isotopes of a Given Element Fractional and not Whole Numbers ?

We have seen that, since the mass of an electron is practically equal to zero, the atomic mass of an isotope of a given element is equal to the sum of the masses of neutrons and protons present in the nucleus of the isotope under consideration. Now since the mass of each of the protons and neutrons is not a whole number on the atomic weight scale (mass of a proton = 1.003757 *amu*, mass of a neutron = 1.00898 *amu*), the atomic mass of an isotope which is equal to the sum of the masses of the protons and neutrons is *not a whole number, i.e.* it is a fractional number. For example the atomic masses of the two isotopes of chlorine are 34.980 *amu* and 36.977 *amu* which are fractional numbers.

How to Calculate the Mass Number of an Isotope From its Atomic Masses ?

We have seen that mass number (A) of an isotope is a whole number. Now since the atomic mass of an isotope of an element is generally a fractional number, the mass number of that isotope which should be a whole number is obtained by rounding off the value of the atomic mass of that isotope to the nearest whole number. For example, since the two isotopes of chlorine (atomic number = 17) have atomic masses equal to 34.980 and 36.977, the mass numbers of these isotopes are 35 and 37 respectively and hence these isotopes are represented as $^{35}_{17}Cl$ and $^{37}_{17}Cl$ respectively.

How to Calculate the Actual Atomic Weight of an Element From Atomic Masses of its Isotopes ?

The atomic weight of an element is a statistical mean of the atomic masses of different isotopes of the elements. The value of atomic weight depends on the relative proportions of the various isotopes. For example :

(*i*) The actual atomic weight of neon which is found to consist of $^{20}_{10}Ne$, $^{21}_{10}Ne$ and $^{22}_{10}Ne$ isotopes in the percentage : ^{20}Ne = 90.92%, ^{21}Ne = 0.26% and ^{22}Ne = 8.82% is :

Table 5.1 Isotopes of some elements and their structure

Element and atomic number	Isotopes	Mass number (A)	Electrons, e = Z The distribution of electrons in K, L and M shells is given in bracket	Protons, p = Z	Neutrons, n = A–Z
Hydrogen (Z = 1)	$^{1}_{1}H$	1	1(1)	1	1–1 = 0
	$^{2}_{1}H$ or D	2	1(1)	1	2–1 = 1
	$^{3}_{1}H$ or T	3	1(1)	1	3–1 = 2
Helium (Z = 2)	$^{3}_{2}He$	3	2(2)	2	3–2 = 1
	$^{4}_{2}He$	4	2(2)	2	4–2 = 2
Lithium (Z = 3)	$^{6}_{3}Li$	6	3(2, 1)	3	6–3 = 3
	$^{7}_{3}Li$	7	3(2, 1)	3	7–3 = 4
Beryllium (Z = 4)	$^{9}_{4}Be$	9	4(2, 2)	4	9–4 = 5
Boron (Z = 5)	$^{10}_{6}B$	10	5(2, 3)	5	10–5 = 5
	$^{11}_{5}B$	11	5(2, 3)	5	11–5 = 6
Carbon (Z = 6)	$^{12}_{6}C$	12	6(2, 4)	6	12–6 = 6
	$^{13}_{6}C$	13	6(2, 4)	6	13–6 = 7
Nitrogen (Z = 7)	$^{14}_{7}N$	14	7(2, 5)	7	14–7 = 7
	$^{15}_{7}N$	15	7(2, 5)	7	15–7 = 8
Oxygen (Z = 8)	$^{16}_{8}O$	16	8(2, 6)	8	16–8 = 8
	$^{17}_{8}O$	17	8(2, 6)	8	17–8 = 9
	$^{18}_{8}O$	18	8(2, 6)	8	18–8 = 10
Fluorine (Z = 9)	$^{19}_{9}F$	19	9(2, 7)	9	19–9 = 10

Element and atomic number	Isotopes	Mass number (A)	Electrons, e = Z The distribution of electrons in K, L and M shells is given in bracket	Protons, p = Z	Neutrons, n = A–Z
Neon (Z = 10)	$^{20}_{10}Ne$	20	10(2, 8)	10	20–10 = 10
	$^{21}_{10}Ne$	21	10(2, 8)	10	21–10 = 11
	$^{22}_{10}Ne$	22	10(2, 8)	10	22–10 = 12
Chlorine (Z = 17)	$^{35}_{17}Cl$	35	17(2, 8, 7)	17	35–17 = 18
	$^{37}_{17}Cl$	37	17(2, 8, 7)	17	37–17 = 20
Argon (Z = 18)	$^{36}_{18}Ar$	36	18(2, 8, 8)	18	36–18 = 18
	$^{40}_{18}Ar$	40	18(2, 8, 8)	18	40–18 = 22

$$= \frac{90.92 \times 20 + 0.26 \times 21 + 8.82 \times 22}{(90.92 + 0.26 + 8.82)}$$

$$= \frac{1818.40 + 5.46 + 194.04}{100} = \frac{2017.90}{100}$$

$$= 20.1790 \approx 20.18$$

(*ii*) Ordinary chlorine consists of 75.4% of ^{35}Cl isotope and 24.6% of ^{37}Cl isotope. Hence its atomic weight as :

$$= \frac{75.4 \times 35 + 24.6 \times 37}{75.4 + 24.6} = 35.492$$

(*iii*) Two isotopes of ordinary hydrogen with mass numbers 1 and 2 have atomic masses equal to 1.007825 and 2.01473 and are in the ratio of 6400 : 1. Therefore, the atomic weight of hydrogen is :

$$= \frac{1.007825 \times 6400 + 2.01473 \times 1}{6400 + 1} = 1.0080$$

(*iv*) Two isotopes of Li have atomic masses equal to 6.017 *amu* and 7.018 *amu* and are present in the ratio 1 : 11.7. Thus the atomic weight of lithium is

$$= \frac{6.017 \times 1 + 7.018 \times 11.7}{1 + 11.7} = 6.93$$

List of Isotopes of Some Elements

The isotopes of some elements along with their atomic masses (in *amu*), mass numbers etc. are given in Table 5.2.

Table 5.2. Isotopes of some elements

Element	No. of Isotopes	Atomic Mass (amu)	Mass Number	Relative abundance of isotopes (%)	Actual atomic weight of the element
Boron (Z = 5)	2	10.016 11.012	10 11	18.5 81.5	10.811
Carbon (Z = 6)	2	12.003 13.007	12 13	98.8 1.2	12.0111
Nitrogen (Z = 7)	2	14.007 15.004	14 15	99.63 0.37	14.0067
Oxygen (Z = 8)	3	16.000 17.004 18.004	16 17 18	99.76 0.04 0.20	15.9994
Fluorine (Z = 9)	1	18.9984	19	100.00	18.9984
Neon (Z = 10)	3	19.993 21.000 21.998	20 21 22	90.92 0.26 8.82	20.183
Sodium (Z = 11)	1	22.9898	23	100.00	22.9898
Silicon (Z = 14)	3	27.985 28.985 29.983	28 29 30	92.3 4.6 3.1	28.086
Sulphur (Z = 16)	4	31.982 32.981 33.978 35.978	32 33 34 36	95.1 0.74 4.20 0.016	32.064
Chlorine (Z = 17)	2	34.980 36.977	35 37	75.4 24.6	35.453

Identification of Isotopes

Different isotopes of an element can be identified by any of the following mass spectrographs.

1. Aston's mass spectrograph. In 1919 Aston devised a mass spectrograph (Fig. 5.18) which can accurately sort out the positive ions of different isotopes of an element and determine their masses. In this spectrograph, a beam of positive rays obtained from a gaseous element in a discharge tube is passed through two slits S_1 and S_2 which are so arranged that only a thin ribbon of rays passes through an electric field. The thin rays consisting of positive ions of various isotopes of the element are sent between electrically charged plates P_1 and P_2. Here the beam of positive ions is deflected towards the negatively-charged plate, P_2.

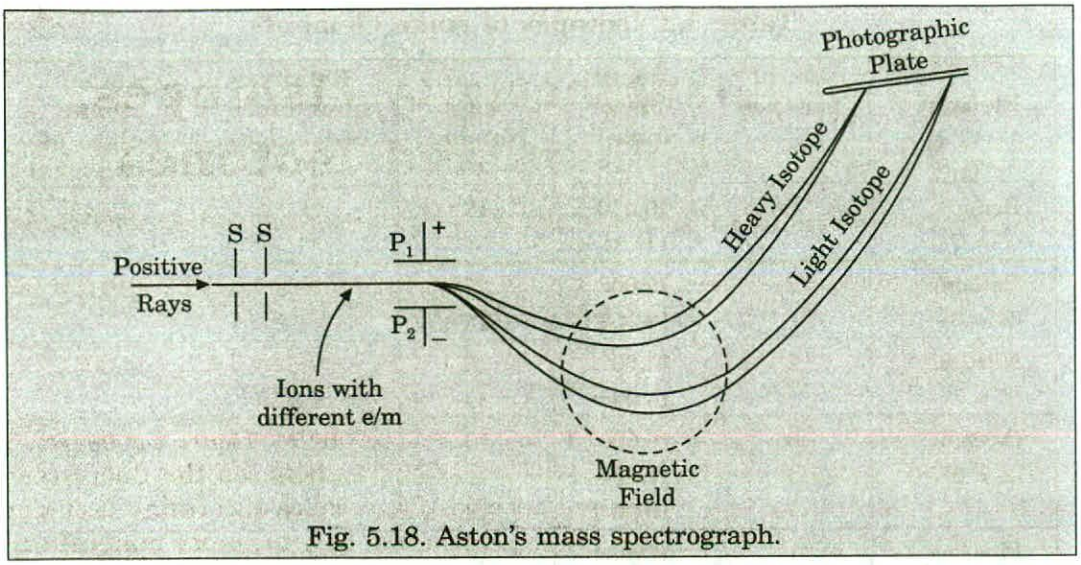


Fig. 5.18. Aston's mass spectrograph.

The angle of deflection depends on the mass, charge and velocity of particles constituting the positive rays. The slow moving ions of the same isotope are deflected more than the fast moving ions which cause a broadening of the beam. The broadened beam of ions is then allowed to pass through a magnetic field (shown by a dotted circle in the Figure) at right angles to the plane of the charged plates and is thus sent in a direction opposite to that caused by the electric field. Here also the slow moving particles (heavier particles) undergo maximum deflection. The strengths of electric and magnetic fields are so adjusted that all the ions of the same mass are focussed at the same point on the photographic plate where a sharp line or spot is obtained. The developed plate is known as **mass spectrogram.** Each line or spot seen on the photographic plate shows the existence of separate isotope. Further, the intensity of the line or spot in comparison with the lines of other isotopes gives the relative abundence of this particular isotope. This point is evident from the fact that an examination of the Aston's mass spectrogram of a sample of ordinary neon shows that the sample consists of two lines (see Fig. 5.19) which indicate that neon in a mixture of ^{20}Ne and ^{22}Ne isotopes. The relative intensities of these lines show that the relative abundance of these isotopes is as $^{20}Ne : {}^{22}Ne = 9 : 1$. Similarly the mass spectrogram of a sample of chlorine has two lines, indicating the presence of ^{35}Cl and ^{37}Cl isotopes (Fig. 5.19). The relative intensities of these lines show that the relative abundance of these isotopes is as : $^{35}Cl : {}^{37}Cl = 3 : 1$.

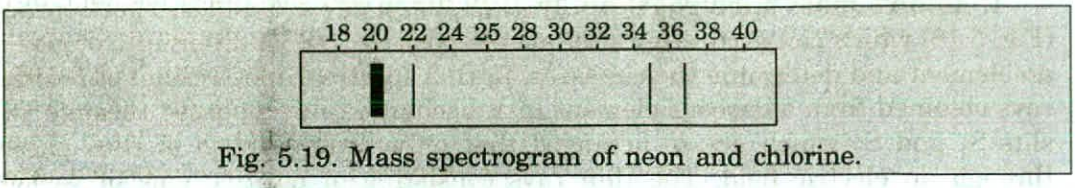


Fig. 5.19. Mass spectrogram of neon and chlorine.

Aston's mass spectrograph not only helps in identifying the isotopes present in an element but also helps in determining the actual atomic weight of a given element as is clear from the following example.

Example. *A sample of ordinary neon is found to consist of ^{20}Ne, ^{21}Ne and ^{22}Ne isotopes in the percentage ^{20}Ne = 90.92%, ^{21}Ne = 0.26% and ^{22}Ne = 8.82%. Calculate the actual atomic weight of neon.*

Solution. Actual atomic weight of neon

$$= \frac{90.92\times 20\times 0.26\times 21 + 8.82\times 22}{90.92 + 0.26 + 8.82}$$

$$= \frac{1818.40 + 5.46 + 194.04}{100} = \frac{2017.90}{100}$$

$$= 20.1790 \approx 20.18$$

2. Dempster's mass spectrograph. This spectrograph is shown in Fig. 5.20. In this apparatus a slow stream of gas or vapour of the sample is allowed to pass in between two perforated plates. Between these plates the stream is bombarded with the help of high-energy electrons which are produced by an electric gun. The gas atoms (A) are thus ionised and are converted into monopositive ions (A^+) ($A \xrightarrow{-e^-} A^+$). Now when a potential of 500 – 2000 volts is applied between the perforated accelerating plates, the positively-charged ions are strongly attracted towards the negatively charged plate. The positively-charged ions moving with accelerated speed then enter the magnetic field at right angles to their path and are thus made to move in a circular path.

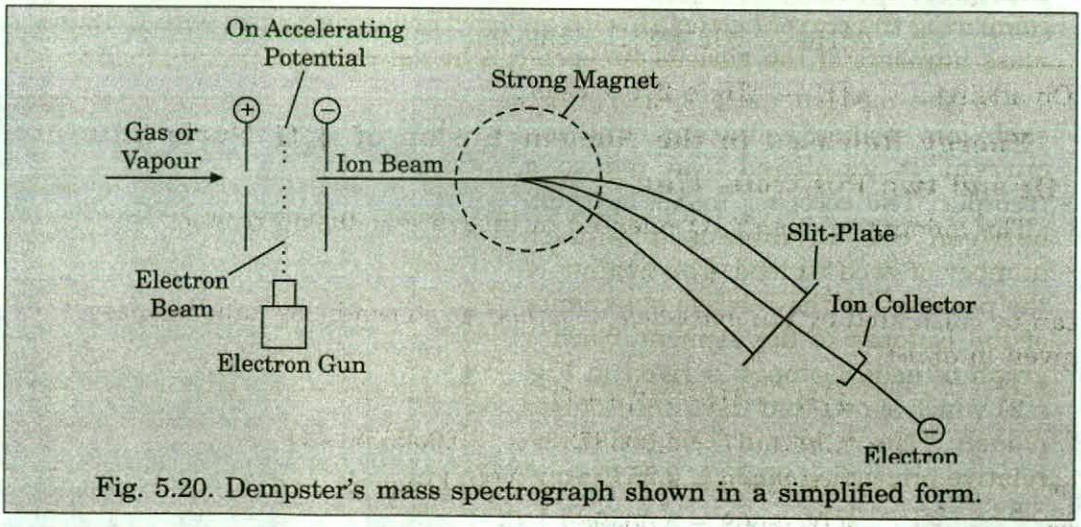


Fig. 5.20. Dempster's mass spectrograph shown in a simplified form.

Principle. If V is the potential applied between the accelerating plates and e is the charge on each positive particle, then the electrical energy is equal to Ve. This energy is imparted to the positive particles as kinetic energy, 1/2 mv^2, *i.e.*

$$Ve = \frac{1}{2}mv^2 \qquad ...(1)$$

Here m is the mass and v is the velocity of the particle.

If the strength of the magnetic field is H, then the magnetic force acting on the particle is equal to HeV which is again equal to centrifugal force, mv^2/r (r = radius of the circular path). Thus :

$$Hev = \frac{mv^2}{r} \qquad ...(2)$$

or $$H^2e^2 = \frac{m^2v^2}{r^2}$$

Since $$Ve = \tfrac{1}{2}mv^2 \qquad \text{[From eqn. (1)]}$$

$$\frac{H^2e^2}{Ve} = \frac{m^2v^2}{r^2} \times \frac{2}{mv^2} = \frac{2m}{r^2}$$

or $$e/m = \frac{2V}{H^2r^2} \qquad ...(3)$$

In the above equation [eqn. (3)], e, being the unit electrical charge, is constant. The radius (r) of the circular path is constant for a given spectrograph. Now if the strength of the magnetic field (H) is kept constant, than m is proportional to 1/V, *i.e.*

$$m \propto \frac{1}{V}$$

Thus by adjusting the accelerating potential (V), positively charged particles of mass m are made to fall on the collector plate. Each particle sets up a minute electric current which passes to the electrometer. The strength of the current thus gives the relative abundance of the individual particles (*i.e.* isotopes). By comparing the current strength with an experiment performed with C-12 ion, the mass numbers of the various isotopes can be determined.

In the modern mass spectrograph each ion strikes a detector, the ion current is amplified and fed to a recorder. The recorder makes a graph between the abundance and mass number of each isotope. The heights of the peaks gives the relative abundance of the isotopes of the element. Such a graph of neon isotopes is given in Fig. 5.21 which shows that the three isotopes namely ^{20}Ne, ^{21}Ne and ^{22}Ne are in the relative proportion 90.20%, 0.257%, and 8.82% respectively.

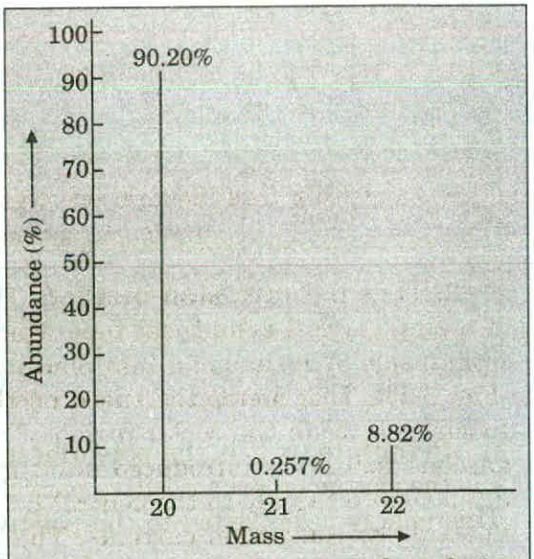


Fig. 5.21. Graph between the relative abundance (%) of the three isotopes of neon against their mass numbers.

Separation of Isotopes

Since all the isotopes of a given element have similar properties, it is almost impossible to separate them by chemical methods. However, some physical methods have been used for this purpose. In these methods the difference in physical properties of the isotopes

which depend on the mass of the atom has been utilised. Some of the physical methods are discussed below :

1. Gaseous diffusion method. According to Grahm's law of diffusion, the rate of diffusion (r) of a gas is inversely proportional to the square root of its molecular weight (M), *i.e.*

$$r \propto \sqrt{\frac{1}{M}}$$

Thus if a mixture consisting of two gaseous isotopes is allowed to diffuse through a porous partition, the lighter isotope passes through the porous partition more rapidly than the heavier one. Gaseous ^{20}Ne and ^{22}Ne isotopes of neon, and ^{16}O and ^{18}O isotopes of oxygen have been separated by this method. The separation of gases ^{16}O and ^{18}O isotopes has been shown in Fig. 5.22. The mixture of gaseous isotopes is passed through a porous tube sealed in an outer jacket. The lighter isotope (^{16}O isotope) passes into the jacket while the heavier isotope (^{18}O isotope) goes into the residual gas.

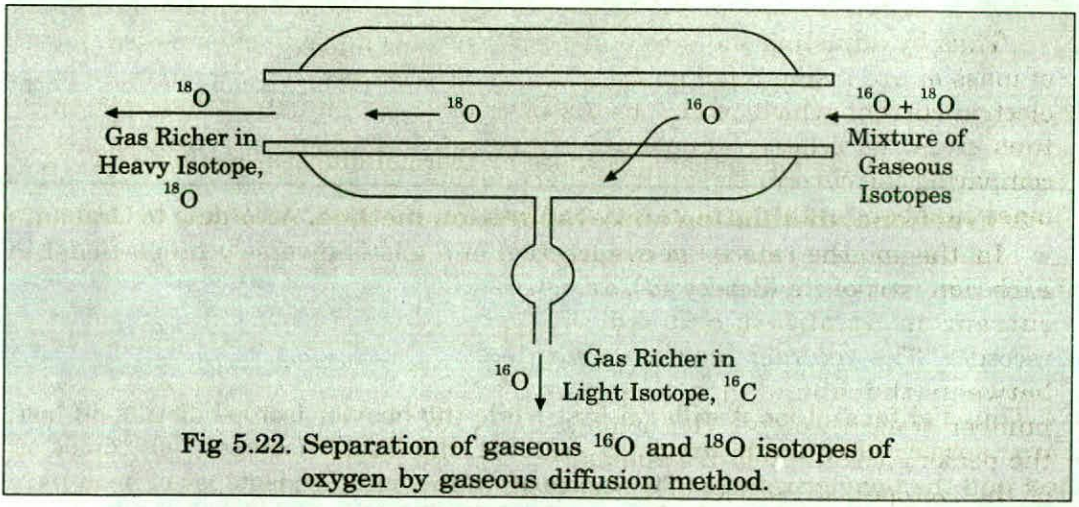


Fig 5.22. Separation of gaseous ^{16}O and ^{18}O isotopes of oxygen by gaseous diffusion method.

2. Thermal diffusion method. The apparatus used in this method consists of a long vertical cylindrical tube which is heated electrically to 600°C or above from inside by means of a thin platinum wire running down the axis of the tube (Fig. 5.23). This method is based on the tendency of heavier molecules of a gas to concentrate in the cooler region of the vertical tube. Thus when a mixture of gaseous isotopes is introduced into the tube, the molecules of the lighter isotope diffuse more rapidly to the central hot region of the tube. Here they are carried upwards by convection currents. The molecules of heavier isotope travel to the cooler inner surface of the tube and thus sink to the bottom. Thus lighter isotope collects at the top while the heavier isotope collects at the bottom. The process is repeated several times. This method has been used by Clausius for the separation of ^{35}Cl and ^{37}Cl isotopes of chlorine.

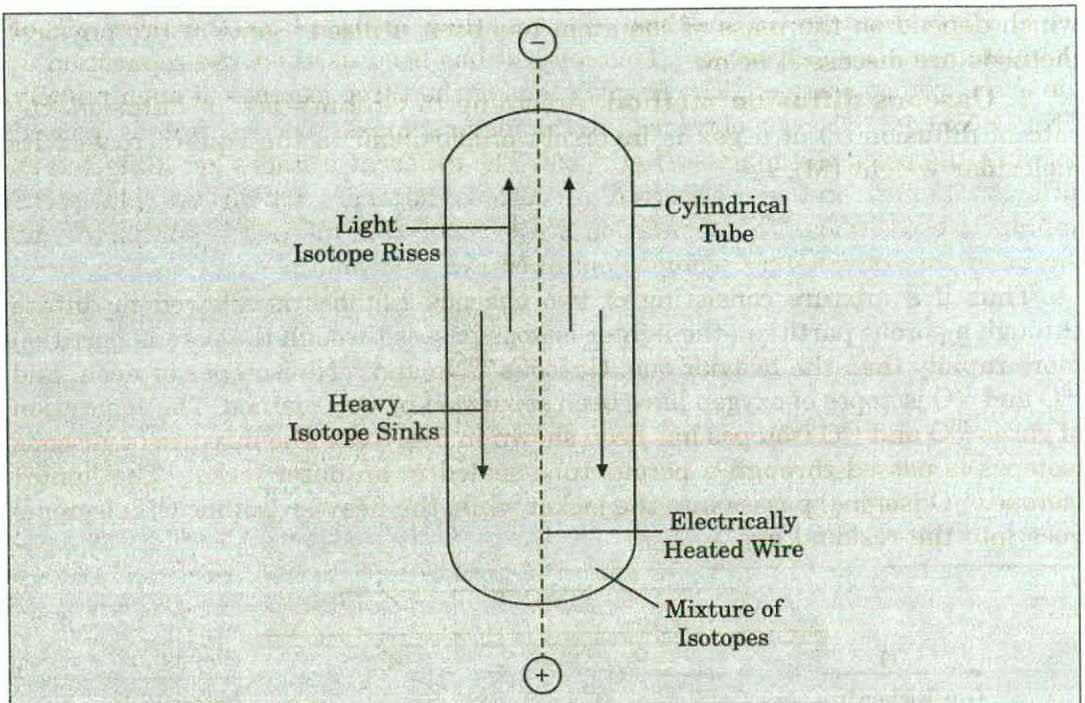


Fig. 5.23. Separation of isotopes by thermal diffusion method.

3. Fractional distillation and evaporation method. According to Graham's law of diffusion, the rate (r) of evaporation of a gas is inversely proportional to the square root of its density (d), *i.e.*

$$r \propto \sqrt{\frac{1}{d}}$$

Thus lighter isotope distills off first while the heavier isotope distills off last. For example, when liquid oxygen is distilled, the lighter isotope (^{16}O) comes off first and the heavier isotope (^{18}O) comes off in the end. The isotopes of neon have been separated by this method.

The separation of the two isotopes of Hg has been achieved by fractional evaporation at 40°C to 50°C in vacuum as shown in Fig. 5.24. The vapours of Hg are condensed on a surface cooled in liquid air which is placed a little above the evaporating Hg. After some time the liquid Hg left behind is found to consist of mostly heavier isotope which is taken out by opening stop-cock at the bottom. The frozen Hg collected at the cooler surface and consists of lighter isotope. It is removed, melted and evaporated under vacuum again. The whole process is repeated several times.

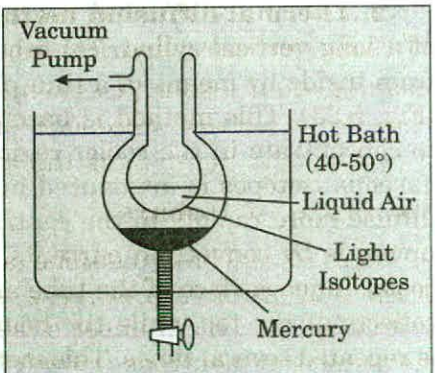


Fig. 5.24. Separation of the two isotopes of mercury by fractional evaporation

4. Electromagnetic method. This method is based on the principle of Dempster's mass spectrograph. This method has been used for the separation of the three isotopes of neon. The beam of ions of the three isotopes of neon namely ^{20}Ne, ^{21}Ne and ^{22}Ne as obtained in Dempster's mass spectrograph is passed between the poles of a magnet (Fig. 5.25). The different isotopes get difflected at different angles and are collected in cooled chambers which are placed in appropriate positions. The separation achieved by this method is complete, but the quantities of different isotopes obtained are very small.

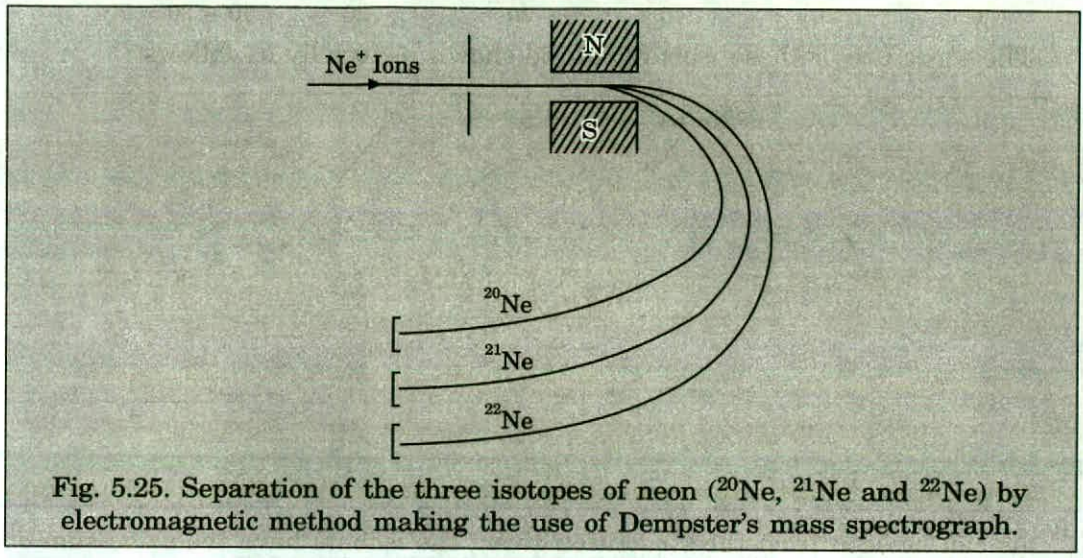


Fig. 5.25. Separation of the three isotopes of neon (^{20}Ne, ^{21}Ne and ^{22}Ne) by electromagnetic method making the use of Dempster's mass spectrograph.

Isobars

What are Isobars ?

The atoms of different elements which have the same mass number but different atomic number are called **isobars.** Since isobars have the same mass number, these can also be defined as atoms of different elements which have the same sum of protons and neutrons in the necleus of each of these atoms but different atomic number. The word *isobar* has been derived from the Greek word meaning *equally heavy* (*isos* = equal; *barys* = heavy). $^{40}_{18}Ar$, $^{40}_{19}K$ and $^{40}_{20}Ca$ are the examples of isobars, since each of them has the same mass number *i.e.* the sum of protons and neutrons is the same.

Structure of Isobars

Since isobars have the same mass number (A), the sum of protons and neutrons in the nucleus of each of these isobars is equal. Quite obviously the number of protons (p) and the number of electrons (e) is equal to atomic number (Z) while the number of neutrons (n) will be equal to (A–Z). Thus :

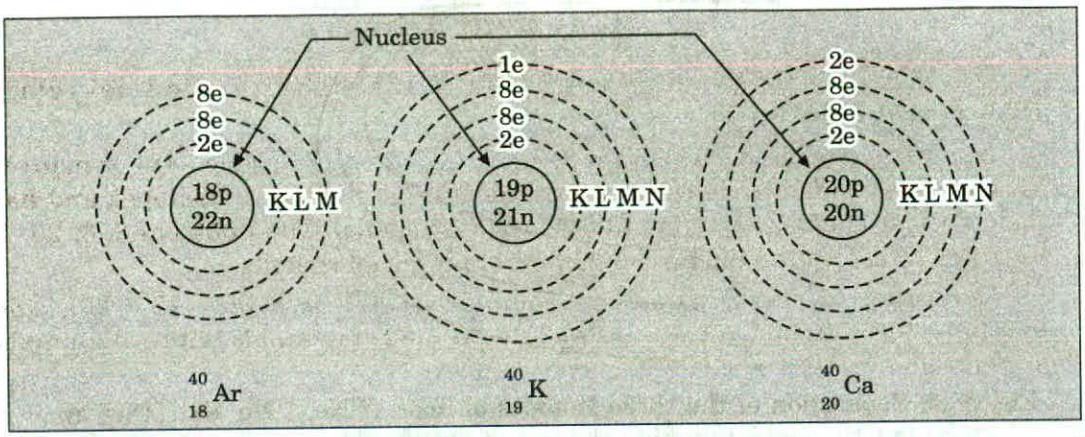
$$p = Z = e \qquad ...(i)$$

$$n = (A - Z) \qquad ...(ii)$$

On the basis of equations (*i*) and (*ii*), the number of electrons, protons and neutrons in each of the three isobars namely $^{40}_{18}Ar$, $^{40}_{19}K$ and $^{40}_{20}Ca$ is shown below :

Isobars	Atomic number (Z)	Mass number (A)	Electrons (e) = Z	Protons (p) = Z	Neutrons (n) = (A–Z)
$^{40}_{18}Ar$	18	40	18	18	40 – 18 = 22
$^{40}_{19}K$	19	40	19	19	40 – 19 = 21
$^{40}_{20}Ca$	20	40	20	20	40 – 20 = 20

The structure of these isobars can be shown pictorially as follows :



As can be seen from the structures given, the isobars have the same sum of protons and neutrons in the nucleus.

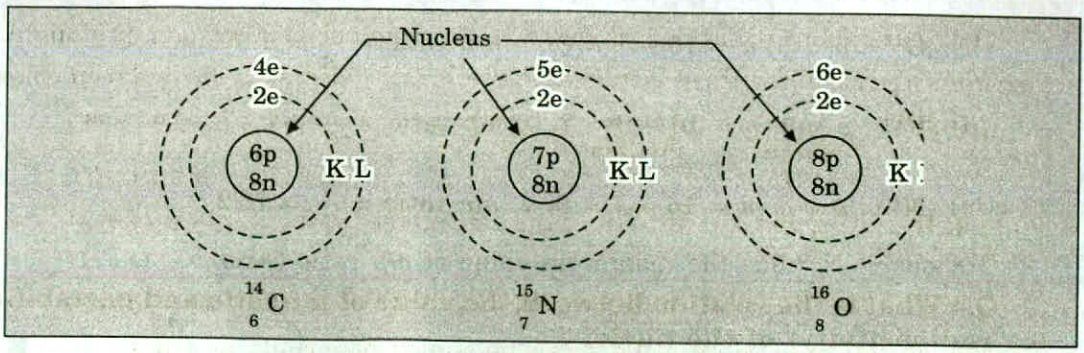
Isotones

What are Isotones ?

The atoms of different elements which have the same number of neutrons but different atomic number are called **isotones.** Since isotones have different atomic number, these can also be defined as the atoms of different elements which have the same number of neutrons but different number of protons and electrons. $^{14}_{6}C$, $^{15}_{7}N$ and $^{16}_{8}O$ are isotones, since each has the same number of neutrons as shown below :

Isotones	Atomic number (Z)	Mass number (A)	Electrons (e) = Z	Protons (p) = Z	Neutrons (n) = (A–Z)
$^{14}_{6}C$	6	14	6	6	14 – 6 = 8
$^{15}_{7}N$	7	15	7	7	15 – 7 = 8
$^{16}_{8}O$	8	16	8	8	16 – 8 = 8

The structure of these isotones can be shown pictorially as follows :



Questions with Answers

Q.1 What are magic numbers ? How is the stability of nuclei related with magic number ?

Ans : The nuclei which contain 2, 8, 20, 50, 82 or 126 protons (p) or neutrons (n) have been found to be extra stable, have large number of isotopes and have their nuclear shells completely-filled (*i.e* closed shells). The numbers 2, 8, 20, 50, 82 and 126 are called magic numbers for the nuclear shells.

Examples of stable nuclei (*i*) The nuclei $_{18}Ar^{38}$ (n = 38 – 18 = 20), $_{40}Zr^{90}$ (n = 90 – 40 = 50) and $_{56}Ba^{138}$ (n = 138 – 56 = 82) are stable, since the number of neutrons in these nuclei are magic numbers.

(*ii*) $_{2}He^{4}$ (p = 2, n = 4 – 2 = 2), $_{8}O^{16}$ (p = 8, n = 16 – 8 = 8), $_{20}Ca^{40}$ (p = 20, n = 40 – 20 = 20) and $_{82}Pb^{208}$ (p = 82, n = 208 – 82 = 126) nuclei are extra stable, since both the numbers of protons (p) and netrons (n) in these nuclei are magic numbers.

(*iii*) The end products in thorium ($4n$), uranium [$(4n + 2)$] and actinium [$(4n + 3)$] series are $_{82}Pb^{208}$, $_{82}Pb^{206}$ and $_{82}Pb^{207}$ respectively. All these isotopes are stable nuclei of $_{82}Pb$, since the number of protons (p = 82) in each isotope is a magic number.

Q.2 Which of the following nuclei would you expect to be radioactive and why ?

$$\mathbf{^{4}_{2}He,\ ^{39}_{20}Ca,\ ^{210}_{85}At.}$$

Ans : (*i*) $^{4}_{2}He$ has protons = 2, neutrons = 2, *i.e.*, both are magic numbers. Hence, it is expected to be *stable* (*non-radioactive*).

(*ii*) $^{39}_{20}Ca$ has protons = 20 (even number) and neutrons = 19 (odd number). 20 is one of the magic numbers. Nevertheless, n/p ratio is less than 1. Hence, it would lie below the stability belt. Hence, it is expected to be *radioactive*.

(*iii*) $^{210}_{85}At$ is *radioactive* as there is no stable nuclei with atomic number > 83.

Q.3 which of the following species has the maximum value of n/p ratio ? (*i*) Ne^{16} (*ii*) O^{16} (*iii*) F^{16} (*iv*) N^{16}

Ans : (*i*) $_{10}Ne^{16}$: p = 10, n = 16 – 10 = 6, $\therefore$ n/p ratio = $\dfrac{6}{10}$ = 0.60

(*ii*) $_8O^{16}$: $p = 8$, $n = 16 - 8 = 8$, $\therefore$ n/p ratio $= \frac{8}{8} = 1.00$

(*iii*) $_9F^{16}$: $p = 9$, $n = 16 - 9 = 7$, $\therefore$ n/p ratio $= \frac{7}{9} = 0.77$

(*iv*) $_7N^{16}$: $p = 7$, $n = 16 - 7 = 9$, $\therefore$ n/p ratio $= \frac{9}{7} = 1.22$

Obviously $_7N^{16}$ has the maximum value of n/p ratio (**Ans**).

Q.4 What is the relation between the value of n/p ratio and unstability (or radioactivity) of the nuclei ?

Ans : The nuclei having higher value of n/p ratio (or lower value of p/n ratio) are more unstable and hence are radioactive.

Q.5 In the emission of a $\bar{\beta}$-particle the atomic number of the daughter element increases by 1. Explain why ?

Ans : Let us consider the following nuclear reaction which involves $\bar{\beta}$-emmission.

$$_6C^{14} \longrightarrow {}_7N^{14} + {}_{-1}e^0 + {}_0\upsilon^0$$

$p = 6$	$p = 7$	$\bar{\beta}$-particle	Neutrino
$n = A - p$	$n = A - p$		
$= 14 - 6$	$= 14 - 7$		
$= 8$	$= 7$		

This reaction shows that the number of protons increases by 1 ($6 \rightarrow 7$) and that of neutrons decreases by 1 ($8 \rightarrow 7$). The increase in the number of protons is due to the fact thus one neutron is converted into proton.

$$_0n^1 \rightarrow {}_{+1}p^1 + {}_{-1}e^0$$

Due to the increase in the number of protons the atomic number of the daughter element increases by 1.

Q.6 Calculate the amount of a radioactive element ($t_{1/2}$ = 140 days) to which 1 g of the element will reduce in 560 days.

Ans : $N_0 = 1$ g, $t = 560$ days, $t_{1/2} = 140$ days.

$\therefore$ No. of half-lives in 560 days $(n) = \frac{t}{t_{1/2}}$

$$= \frac{560}{140} = 4$$

$\therefore$ Amount of the element left after 560 days or 4 half-periods

$$= \frac{N_0}{2^n} = \frac{1}{2^4}\,g = \frac{1}{16}\,\mathbf{g}\ \textbf{(Ans)}$$

Q.7 I^{131} has half-life period of 13.3 hours. After 79.8 hours, what fraction of I^{131} will remain ?

Ans : $t_{1/2}$ = 13.3 hours

$\therefore$ No. of half-lives in 79.8 hours = $\frac{79.8}{13.3}$ = 6 half-lives

Amount left after n half-lives (N) = $\frac{N_0}{2^n}$

or Fraction left $\left(\frac{N}{N_0}\right) = \frac{1}{2^n} = \frac{1}{2^6} = \frac{1}{64}$.

Q.8 $^{234}_{90}Th \rightarrow 7\alpha + 6\beta + {}^{A}_{Z}X$. **Identify** $^{A}_{Z}X$.

Ans : $^{234}_{90}Th \rightarrow 7\,^{4}_{2}\alpha + 6\,^{0}_{-1}\beta + {}^{A}_{Z}X$

Balancing the atomic number and mass number on both sides, we have

$$234 = 7 \times 4 + 6 \times 0 + A$$

or $$A = 234 - 28 = 206$$

$$90 = 7 \times 2 + 6\,(-1) + Z$$

or $$Z = 90 - 14 + 6 = 82$$

Hence, $^{A}_{Z}X$ is $^{206}_{82}Pb$.

Q.9 ^{227}Ac has a half-life of 22.0 years with respect to radioactive decay. The decay follows two parallel paths, one leading to ^{227}Th and the other to ^{223}Fr. The percentage yields of these two daughter nuclides are 2.0 and 98.0 respectively. What are the decay constants (λ) for each of the separate paths ?

Ans : The decay of ^{227}Ac into ^{227}Th and ^{223}Fr can be shows as :

$$^{227}Ac \xrightarrow{\lambda_1} {}^{227}Th\left(2\% = \frac{2}{100}\right)$$

$$^{227}Ac \xrightarrow{\lambda_2} {}^{223}Fr\left(98\% = \frac{98}{100}\right)$$

Here λ_1 and λ_2 are the disintegration constants for the two paths and over all disintegration constant is λ.

$$\lambda = \frac{0.693}{t_{1/2} \text{ of } {}^{227}Ac} = \lambda_1 + \lambda_2$$

or $$\frac{0.693}{22 \text{ yrs}} = \lambda_1 + \lambda_2$$

or $$\lambda_1 + \lambda_2 = 0.0315 \text{ yrs}^{-1}$$

Fractional yield of ^{227}Th $= \frac{2}{100} = \frac{\lambda_1}{\lambda_1 + \lambda_2}$

or $$\frac{2}{100} = \frac{\lambda_1}{0.0315}$$

This equatian gives λ_1 = **6.3×10^{-4} yrs^{-1} (Ans)**

Similarly,

Fractional yield of $^{223}Fr = \frac{98}{100} = \frac{\lambda_2}{\lambda_1 + \lambda_2}$

or $$\frac{98}{100} = \frac{\lambda_2}{0.0315}$$

This equantian gives λ_2 = **308.7×10^{-4} yrs^{-1} (Ans)**

Q.10 ^{64}Cu (half-life = 12.8 *h*) decays by β^- emission (38%), β^+ emission (19%) and electrons capture (43%). Write the decay products and calculate partial half-lives for each of the decay processes.

Ans.

$^{64}_{29}Cu$ $(t_{1/2} = 12.8\ h)$

(*i*) $-\beta^-(-_{-1}e^0)$, $K_1(t_1)$ → $^{64}_{30}Zn + {}_{-1}e^0$

(*ii*) $-\beta^+(-_{+1}e^0)$, $K_2(t_2)$ → $^{64}_{28}Ni + {}_{+1}e^0$

(*iii*) $+_{-1}e^0$, $K_3(t_3)$ → $^{64}_{28}Ni$

If t_1, t_2 and t_3 are the half-life for the partial processes (*i*), (*ii*) and (*iii*) respectively, then :

$$t_1 = \frac{0.693}{K_1} = \frac{0.693}{0.38\ K}$$

(Here K_1 is the disintegration constant for process (*i*) and K is the rate constant for the over all process)

$$= \frac{0.693}{0.38 \times 0.693 / t_{1/2} \text{ of Cu}}$$

$$= \frac{0.693 \times t_{1/2} \text{ of Cu}}{0.38 \times 0.693} = \frac{12.8}{0.38} = \textbf{33.68 hr (Ans.)}$$

Similarly :

$$t_2 = \frac{12.8}{0.19} = \textbf{67.37 hr (Ans.)}$$

and, $$t_3 = \frac{12.8}{0.43} = \textbf{29.77 hr (Ans.)}$$

University Questions

1. Describe the nature and properties of the rays emitted by radioactive materials. *(Meerut 1981)*
2. Describe the properties of α, β and γ-rays. *(North Bengal 81; Kerala 80; Saugar 82)*

3. Select any two members of the same radioactive series : $_{92}U^{238}$, $_{88}Ra^{224}$, $_{82}Pb^{206}$, $_{92}U^{235}$, $_{82}Pb^{208}$, $_{86}Rn^{22}$, $_{83}Bi^{214}$. *(Lucknow 85)*

4. Name the different radioactive series you know. How can you find that a particular isotope belongs to which radioactive series? To which radioactive series respectively $_{90}Th^{231}$, $_{82}Pb^{266}$ and $_{89}Ac^{228}$ belong? *(Kanpur 86)*

5. Calculate the value of disintegration constant for $_{86}Rn^{222}$, if its half-life period is 3.82 days. *(Kanpur 85)*

6. If the activity of a radioactive element drops to 1/6 of its initial value in one hour and twenty minutes, what are its disintegration constant and half-life period. *(Raj. 84)*

7. Explain the theory of radioactive disintegration. *(Meerut 1981)*

8. Write short note on "Isotopes". *(Calicut 80; Banaras 80; Saugar 82; Raj. 81, 84; MD Rohtak 84; Garhwal 88)*

9. Explain the principle of Aston's mess spectrograph. *(Raj. 82; Bundelkhand 80)*

10. Why can the isotopes of an element not be separated by chemical methods ? *(Himachal 82; Kashmir 83; GND 82)*

11. Discuss Dempster's mass spectrographic method for the identification of isotopes. *(GND 82)*

12. Write a note on "Separation of isotopes". *(Jiwaji 84)*

13. Write a note on "Isobars". *(Calicut 80; Banaras 80; Saugar 82; Raj. 81, 84; MD Rohtak 84; Garhwal 88; Madras 87; Andhra 87)*

14. What is the difference between isotope and isotone ? Explain with examples. *(Meerut M.Sc. 89)*

15. Discuss the applications of radioactive isotopes. *(Kanpur 99)*

16. Discuss the uses of isotopes as tracers. *(Gujrat 2003)*

17. Name the isotopes of hydrogen. *(Nagpur 2003)*

18. (*i*) What do you mean by half-hfe period of a radioactive element ? Deduce the formula for it.

(*ii*) 1 gram of $_{79}Au^{198}$ ($T_{1/2}$ = 65 hrs) emits a β-particle and gives a stable isotope of Hg. Calculate the amount of Hg after 260 hrs.

(*iii*) Write a note on "Disintegration Series" or "Radioactive Equilibrium".

(*iv*) Write the differences between nuclear changes and chemical changes.

(*iv*) Write a note on "Group Displacement Law". How many α and β particles should be emitted to change $_{90}Th^{232}$ to $_{82}Pb^{208}$ (stable). *(Meerut 2009)*