

## 1

# Structure of Atom

## —Classical Mechanics

## CHAPTER

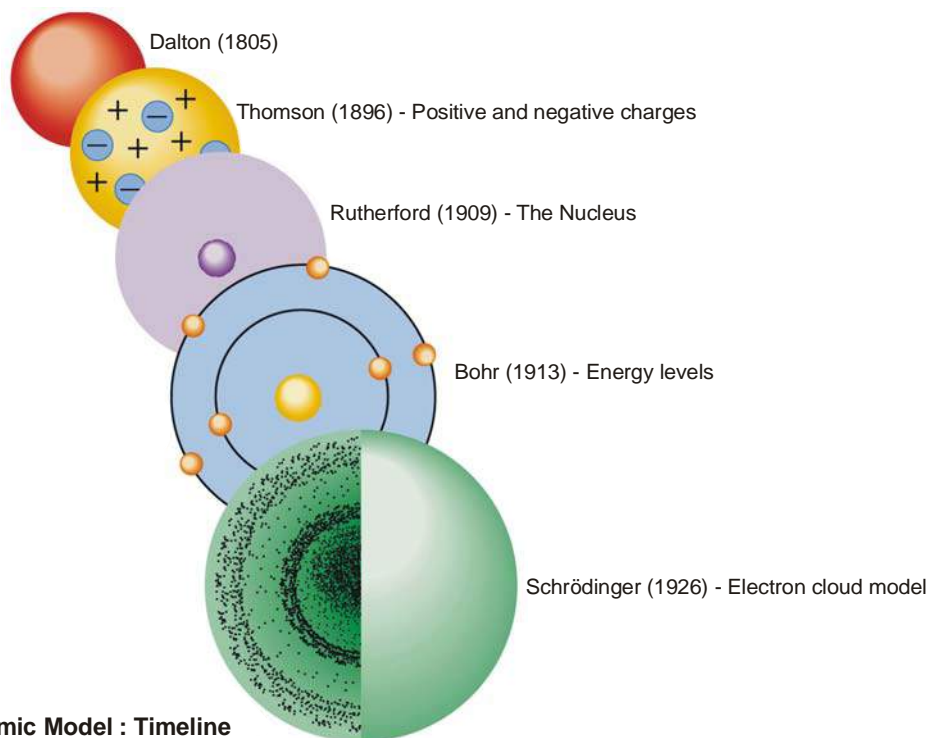
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**J**ohn Dalton (1805) considered that **all matter was composed of small particles called atoms**. He visualised the atom as a hard solid individual particle incapable of subdivision. At the end of the nineteenth century there accumulated enough experimental evidence to show that the atom is made of still smaller particles. These subatomic particles are called the **fundamental particles**. The number of subatomic particles now known is very large. For us, the three most important are the **proton, neutron and electron**. How these fundamental particles go to make the internal structure of the atom, is a fascinating story. The main landmarks in the evolution of atomic structure are :

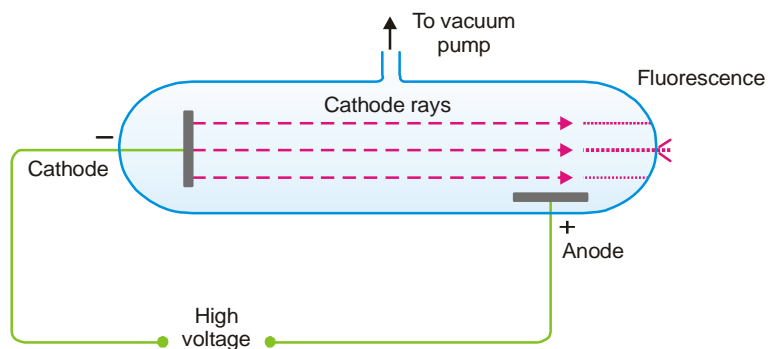
1896	J.J. Thomson's discovery of the electron and the proton
1909	Rutherford's Nuclear Atom
1913	Mosley's determination of Atomic Number
1913	Bohr Atom
1921	Bohr-Bury Scheme of Electronic Arrangement
1932	Chadwick's discovery of the neutron.



#### ■ Atomic Model : Timeline

### CATHODE RAYS – THE DISCOVERY OF ELECTRON

The knowledge about the electron was derived as a result of the study of the electric discharge in the **discharge tube** (J.J. Thomson, 1896). The discharge tube consists of a glass tube with metal electrodes fused in the walls (Fig. 1.1). Through a glass side-arm air can be drawn with a pump. The electrodes are connected to a source of high voltage (10,000 Volts) and the air partially evacuated. The electric discharge passes between the electrodes and the residual gas in the tube begins to glow. If virtually all the gas is evacuated from within the tube, the glow is replaced by faintly luminous 'rays' which produce fluorescence on the glass at the end far from the cathode. **The rays which proceed from the cathode and move away from it at right angles in straight lines are called Cathode Rays.**



■ **Figure 1.1**  
Production of cathode rays.

**PROPERTIES OF CATHODE RAYS**

1. They travel in straight lines away from the cathode and cast shadows of metallic objects placed in their path.
2. Cathode rays cause mechanical motion of a small pin-wheel placed in their path. Thus they possess kinetic energy and must be material particles.
3. They produce fluorescence (a glow) when they strike the glass wall of the discharge tube.
4. They heat up a metal foil to incandescence which they impinge upon.
5. Cathode rays produce X-rays when they strike a metallic target.
6. Cathode rays are deflected by the electric as well as the magnetic field in a way indicating that they are streams of minute particles carrying negative charge.

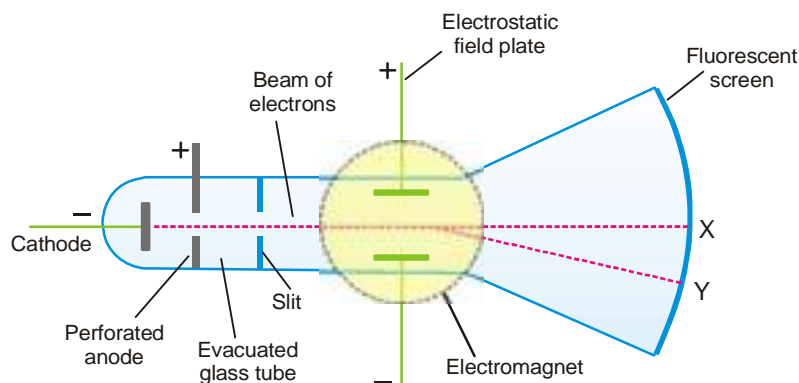
By counterbalancing the effect of magnetic and electric field on cathode rays, Thomson was able to work out the ratio of the charge and mass ( $e/m$ ) of the cathode particle. In SI units the value of  $e/m$  of cathode particles is  $-1.76 \times 10^{18}$  coulombs per gram. As a result of several experiments, Thomson showed that the value of  $e/m$  of the cathode particle was the same regardless of both the gas and the metal of which the cathode was made. This proved that the particles making up the cathode rays were all identical and were constituent parts of the various atoms. Dutch Physicist H.A. Lorentz named them **Electrons**.

Electrons are also obtained by the action of X-rays or ultraviolet light on metals and from heated filaments. These are also emitted as  $\beta$ -particles by radioactive substances. Thus it is concluded that **electrons are a universal constituent of all atoms**.

**MEASUREMENT OF  $e/m$  FOR ELECTRONS**

The ratio of charge to mass ( $e/m$ ) for an electron was measured by J.J. Thomson (1897) using the apparatus shown in Fig. 1.2.

Electrons produce a bright luminous spot at X on the fluorescent screen. Magnetic field is applied first and causes the electrons to be deflected in a circular path while the spot is shifted to Y. The radius of the circular path can be obtained from the dimensions of the apparatus, the current and number of turns in the coil of the electromagnet and the angle of deflection of the spot. An electrostatic field of known strength is then applied so as to bring back the spot to its original position. Then from the strength of the electrostatic field and magnetic field, it is possible to calculate the velocity of the electrons.



■ **Figure 1.2**  
**Measurement of  $e/m$  for electrons.**

Equating magnetic force on the electron beam to centrifugal force.

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

where  $B$  = magnetic field strength

$v$  = velocity of electrons

$e$  = charge on the electron

$m$  = mass of the electron

$r$  = radius of the circular path of the electron in the magnetic field.

This means

$$\frac{e}{m} = \frac{v}{Br} \quad \dots(1)$$

The value of  $r$  is obtained from the dimensions of the tube and the displacement of the electron spot on the fluorescent screen.

When the electrostatic field strength and magnetic field strength are counterbalanced,

$$Bev = Ee$$

where  $E$  is the strength of the electrostatic field.

$$\text{Thus} \quad v = \frac{E}{B} \quad \dots(2)$$

If  $E$  and  $B$  are known,  $v$  can be calculated and on substitution in equation (1), we get the value of  $e/m$ .

$$\frac{e}{m} = \frac{E}{B^2 r}$$

All the quantities on the right side of the equation can be determined experimentally. Using this procedure, the ratio  $e/m$  works out to be  $-1.76 \times 10^8$  per gram.

or  $e/m$  for the electron =  $-1.76 \times 10^8$  coulomb/g

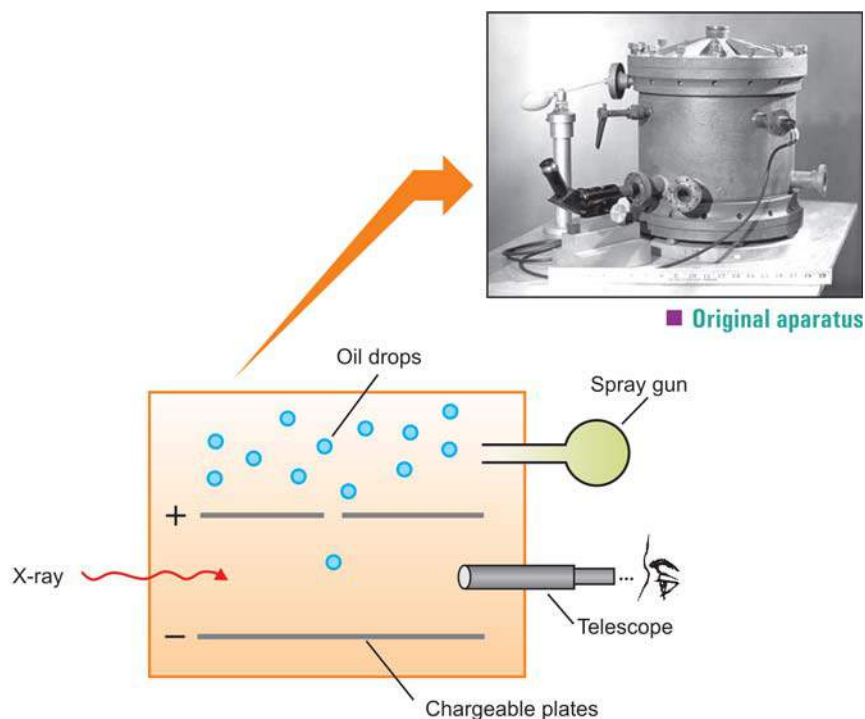
### DETERMINATION OF THE CHARGE ON AN ELECTRON

The absolute value of the charge on an electron was measured by R.A. Milikan (1908) by what is known as the **Milikan's Oil-drop Experiment**. The apparatus used by him is shown in Fig. 1.3. He sprayed oil droplets from an *atomizer* into the apparatus. An oil droplet falls through a hole in the upper plate. The air between the plates is then exposed to X-rays which eject electrons from air molecules. Some of these electrons are captured by the oil droplet and it acquires a negative charge. When the plates are earthed, the droplet falls under the influence of gravity.

He adjusted the strength of the electric field between the two charged plates so that a particular oil drop remained suspended, neither rising nor falling. At this point, the upward force due to the negative charge on the drop, just equalled the weight of the drop. As the X-rays struck the air molecules, electrons are produced. The drop captures one or more electrons and gets a negative charge,  $Q$ . Thus,

$$Q = ne$$

where  $n$  = number of electrons and  $e$  = charge of the electron. From measurement with different drops, Milikan established that electron has the charge  $-1.60 \times 10^{-19}$  coulombs.



■ **Figure 1.3**  
Milikan's apparatus for the Oil-drop experiment.

### Mass of Electron

By using the Thomson's value of  $e/m$  and the Milikan's value of  $e$ , the absolute mass of an electron can be found.

$$e/m = -1.76 \times 10^8 \text{ coulomb/g (Thomson)}$$

$$e = -1.60 \times 10^{-19} \text{ coulomb (Milikan)}$$

$$\therefore \frac{e}{e/m} = \frac{1.60 \times 10^{-19}}{1.76 \times 10^8}$$

$$\text{hence } m = 9.1 \times 10^{-28} \text{ g or } 9.1 \times 10^{-31} \text{ kg}$$

### Mass of an Electron relative to H

Avogadro number, the number of atoms in one gram atom of any element is  $6.023 \times 10^{23}$ . From this we can find the absolute mass of hydrogen atom.

$$\text{Mass of } 6.023 \times 10^{23} \text{ atoms of hydrogen} = 1.008 \text{ g}$$

$$\therefore \text{Mass of a hydrogen atom} = \frac{1.008}{6.023 \times 10^{23}} \text{ g}$$

$$= 1.67 \times 10^{-24} \text{ g}$$

$$\text{But mass of electron} = 9.1 \times 10^{-28} \text{ g}$$

$$\therefore \frac{\text{mass of H atom}}{\text{mass of electron}} = \frac{1.67 \times 10^{-24}}{9.1 \times 10^{-28}}$$

$$= 1.835 \times 10^3 = 1835$$

Thus an atom of hydrogen is 1835 times as heavy as an electron.

In other words, **the mass of an electron is  $\frac{1}{1835}$ th of the mass of hydrogen atom.**

### DEFINITION OF AN ELECTRON

Having known the charge and mass of an electron, it can be defined as :

**An electron is a subatomic particle which bears charge  $-1.60 \times 10^{-19}$  coulomb and has mass  $9.1 \times 10^{-28}$  g.**

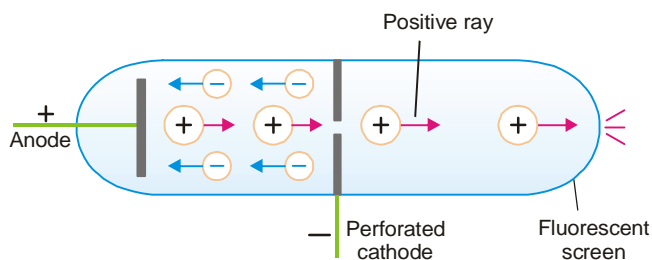
Alternatively, an electron may be defined as :

**A particle which bears one unit negative charge and mass 1/1835th of a hydrogen atom.**

Since an electron has the smallest charge known, it was designated as unit charge by Thomson.

### POSITIVE RAYS

In 1886 Eugen Goldstein used a discharge tube with a hole in the cathode (Fig. 1.4). He observed that while cathode rays were streaming away from the cathode, there were coloured rays produced simultaneously which passed through the perforated cathode and caused a glow on the wall opposite to the anode. Thomson studied these rays and showed that they consisted of particles carrying a positive charge. He called them **Positive rays**.



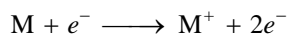
■ **Figure 1.4**  
**Production of Positive rays.**

### PROPERTIES OF POSITIVE RAYS

- (1) They travel in a straight line in a direction opposite to the cathode.
- (2) They are deflected by electric as well as magnetic field in a way indicating that they are positively charged.
- (3) The charge-to-mass ratio ( $e/m$ ) of positive particles varies with the nature of the gas placed in the discharge tube.
- (4) They possess mass many times the mass of an electron.
- (5) They cause fluorescence in zinc sulphide.

### How are Positive rays produced ?

When high-speed electrons (cathode rays) strike molecule of a gas placed in the discharge tube, they knock out one or more electrons from it. Thus a positive ion results



These positive ions pass through the perforated cathode and appear as positive rays. When electric discharge is passed through the gas under high electric pressure, its molecules are dissociated into atoms and the positive atoms (ions) constitute the positive rays.

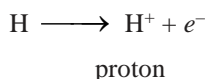
### Conclusions from the study of Positive rays

From a study of the properties of positive rays, Thomson and Aston (1913) concluded that atom consists of at least two parts :

- (a) the electrons ; and  
 (b) a positive residue with which the mass of the atom is associated.

## PROTONS

E. Goldstein (1886) discovered protons in the discharge tube containing hydrogen.



It was J.J. Thomson who studied their nature. He showed that :

- (1) The actual mass of proton is  $1.672 \times 10^{-24}$  gram. **On the relative scale, proton has mass 1 atomic mass unit (amu).**
- (2) **The electrical charge of proton is equal in magnitude but opposite to that of the electron.**  
 Thus proton carries a charge  $+1.60 \times 10^{-19}$  coulombs or + 1 elementary charge unit.

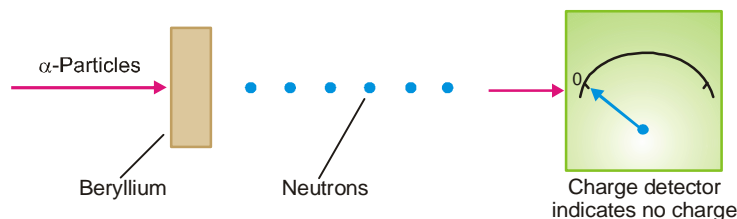
Since proton was the lightest positive particle found in atomic beams in the discharge tube, it was thought to be a unit present in all other atoms. Protons were also obtained in a variety of nuclear reactions indicating further that **all atoms contain protons.**

**Thus a proton is defined as a subatomic particle which has a mass of 1 amu and charge + 1 elementary charge unit.**

**A proton is a subatomic particle which has one unit mass and one unit positive charge.**

## NEUTRONS

In 1932 Sir James Chadwick discovered the third subatomic particle. He directed a stream of alpha particles ( ${}^4_2\text{He}$ ) at a beryllium target. He found that a new particle was ejected. It has almost the same mass ( $1.674 \times 10^{-24}$  g) as that of a proton and has no charge.

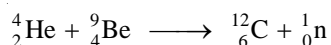


■ **Figure 1.5**  
**α-Particles directed at beryllium sheet eject neutrons**  
**whereby the electric charge detector remains unaffected.**

He named it *neutron*. The assigned relative mass of a neutron is approximately one atomic mass unit (amu). Thus :

**A neutron is a subatomic particle which has a mass almost equal to that of a proton and has no charge.**

The reaction which occurred in Chadwick's experiment is an example of artificial transmutation where an atom of beryllium is converted to a carbon atom through the nuclear reaction.



## SUBATOMIC PARTICLES

We have hitherto studied the properties of the three principal fundamental particles of the atom, namely the *electron*, *proton*, and *neutron*. These are summarised in Table 1.1.

TABLE 1.1. CHARGE AND MASS OF ELECTRON, PROTON AND NEUTRON

Particle	Symbol	Mass		Charge	
		amu	grams	Units	Coloumbs
Electron	$e^-$	$\frac{1}{1835}$	$9.1 \times 10^{-28}$	- 1	$- 1.60 \times 10^{-19}$
Proton	$p^+$	1	$1.672 \times 10^{-24}$	+ 1	$+ 1.60 \times 10^{-19}$
Neutron	$n$ or $n^0$	1	$1.674 \times 10^{-24}$	0	0

Nearly all of the ordinary chemical properties of matter can be examined in terms of atoms consisting of electrons, protons and neutrons. Therefore for our discussion we will assume that atom contains only these three principal subatomic particles.

### Other Subatomic Particles

Besides electrons, protons and neutrons, many other subatomic particles such as *mesons*, *positrons*, *neutrinos* and *antiprotons* have been discovered. A great deal of recent research is producing a long list of still other subatomic particles with names *quarks*, *pions* and *gluons*. With each discovery, the picture of atomic structure becomes increasingly complex. Fortunately, the three-particle (electron, proton, neutron) picture of the atom still meets the needs of the chemists.

### ALPHA PARTICLES

Alpha particles are shot out from radioactive elements with very high speed. For example, they come from radium atoms at a speed of  $1.5 \times 10^7$  m/sec. Rutherford identified them to be **di-positive helium ions**,  $\text{He}^{2+}$  or  ${}^4_2\text{He}$ . Thus an alpha particle has 2+ charge and 4 amu mass.

$\alpha$ -Particles are also formed in the discharge tube that contains helium,



**It has twice the charge of a proton and about 4 times its mass.**

### Conclusion

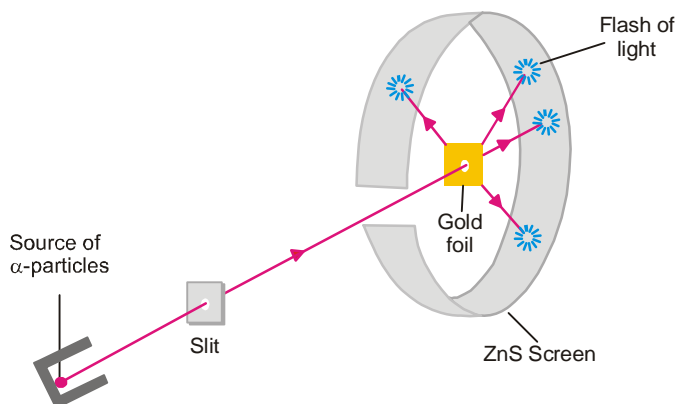
Though  $\alpha$ -particle is not a fundamental particle of the atom (or subatomic particle) but because of its high energy  $\left(\frac{1}{2}mv^2\right)$ , Rutherford thought of firing them like bullets at atoms and thus obtain information about the structure of the atom.

- (1) **He bombarded nitrogen and other light elements by  $\alpha$ -particles when  $\text{H}^+$  ions or protons were produced. This showed the presence of protons in atoms other than hydrogen atom.**
- (2) **He got a clue to the presence of a positive nucleus in the atom as a result of the bombardment of thin foils of metals.**

### RUTHERFORD'S ATOMIC MODEL – THE NUCLEAR ATOM

Having known that atom contains electrons and a positive ion, Rutherford proceeded to perform experiments to know as to how and where these were located in the atom. In 1909 Rutherford and Marsden performed their historic **Alpha Particle-Scattering Experiment**, using the apparatus illustrated in Fig. 1.6. They directed a stream of very highly energetic  $\alpha$ -particles from a radioactive source against a thin *gold foil* provided with a circular fluorescent zinc sulphide screen around it. Whenever an  $\alpha$ -particle struck the screen, a tiny flash of light was produced at that point.

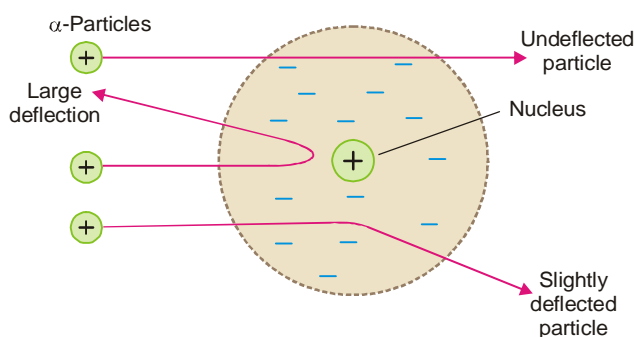




■ **Figure 1.6**

**Rutherford and Marsden's  $\alpha$ -particle scattering experiment.**

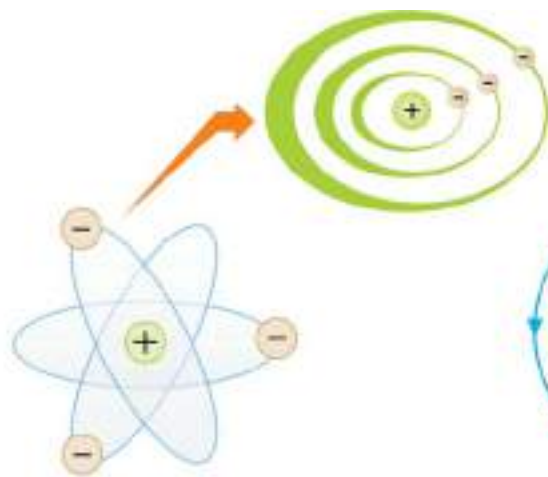
Rutherford and Marsden noticed that most of the  $\alpha$ -particles passed straight through the gold foil and thus produced a flash on the screen behind it. This indicated that gold atoms had a structure with plenty of empty space. To their great astonishment, tiny flashes were also seen on other portions of the screen, some time in front of the gold foil. This showed that gold atoms deflected or 'scattered'  $\alpha$ -particles through large angles so much so that some of these bounced back to the source. Based on these observations, Rutherford proposed a model of the atom which is named after him. This is also called the **Nuclear Atom**. According to it :



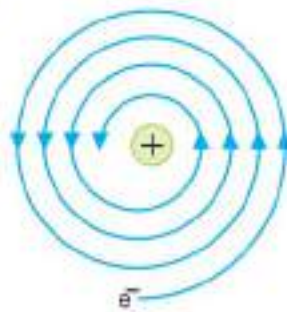
■ **Figure 1.7**

**How nuclear atom causes scattering of  $\alpha$ -particles.**

- (1) **Atom has a tiny dense central core or the nucleus which contains practically the entire mass of the atom, leaving the rest of the atom almost empty.** The diameter of the nucleus is about  $10^{-13}$  cm as compared to that of the atom  $10^{-8}$  cm. If the nucleus were the size of a football, the entire atom would have a diameter of about 5 miles. It was this empty space around the nucleus which allowed the  $\alpha$ -particles to pass through undeflected.
- (2) **The entire positive charge of the atom is located on the nucleus, while electrons were distributed in vacant space around it.** It was due to the presence of the positive charge on the nucleus that  $\alpha$ -particle ( $\text{He}^{2+}$ ) were repelled by it and scattered in all directions.
- (3) **The electrons were moving in orbits or closed circular paths around the nucleus like planets around the sun.**



■ **Figure 1.8**  
Rutherford's model of atom ; electrons  
orbiting around nucleus.



■ **Figure 1.9**  
Orbiting electron would radiate energy  
and spiral into the nucleus.

#### Weakness of Rutherford Atomic Model

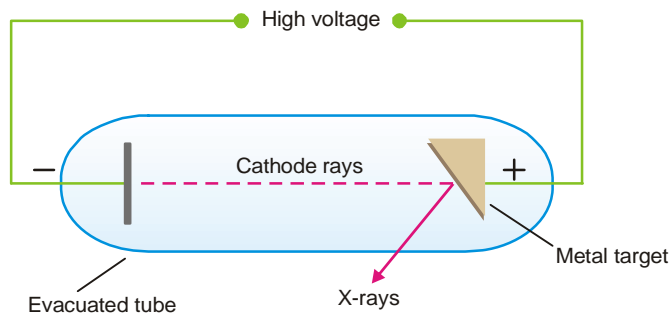
The assumption that electrons were orbiting around the nucleus was unfortunate. According to the classical electromagnetic theory if a charged particle accelerates around an oppositely charged particle, the former will radiate energy. If an electron radiates energy, its speed will decrease and it will go into spiral motion, finally falling into the nucleus. This does not happen actually as then the atom would be unstable which it is not. This was the chief weakness of Rutherford's Atomic Model.

#### MOSLEY'S DETERMINATION OF ATOMIC NUMBER

The discovery that atom has a nucleus that carries a positive charge raised the question : What is the magnitude of the positive charge? This question was answered by Henry Mosley in 1913.

Hitherto atomic number was designated as the 'position number' of a particular element in the Periodic Table. Mosley found that when cathode rays struck different elements used as anode targets in the discharge tube, characteristic X-rays were emitted. The wavelength of these X-rays decreases in a regular manner in passing from one element to the next one in order in the Periodic Table.

Mosley plotted the atomic number against the square root of the frequency of the X-rays emitted and obtained a straight line which indicated that atomic number was not a mere 'position number' but a fundamental property of the atom. He further made a remarkable suggestion that the wavelength (or frequency) of the emitted X-rays was related to the number of positive charges or protons in the nucleus. The wavelength changed regularly as the element that came next in the Periodic Table had one proton (one unit atomic mass) more than the previous one. Mosley calculated the number of units of positive charge on the nuclei of several atoms and established that :

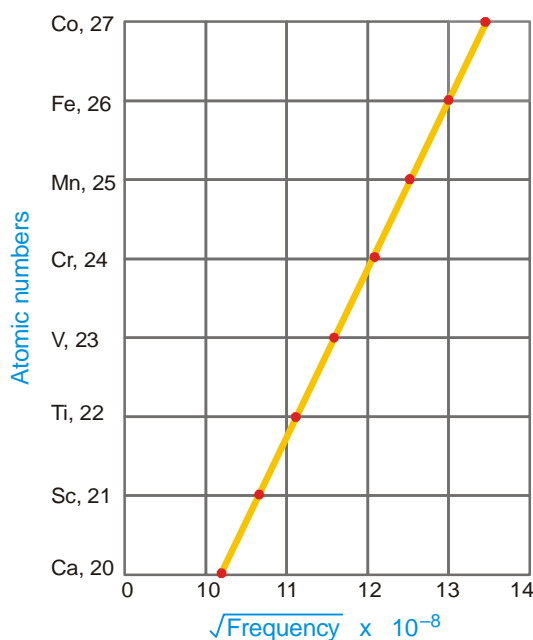


■ **Figure 1.10**  
Production of X-rays.

**Atomic Number of an element is equal to the number of protons in the nucleus of the atom of that element.**

Since the atom as a whole is electrically neutral, the atomic number ( $Z$ ) is also equal to the number of extranuclear electrons. Thus hydrogen (H) which occupies first position in the Periodic Table has atomic number 1. This implies that it has a nucleus containing one proton (+ 1) and one extranuclear electron (– 1).

Now the term Atomic Number is often referred to as the **Proton Number**.



■ **Figure 1.11**

**Mosley's plot of the square root of X-ray frequencies against atomic number for the elements calcium through cobalt.**

### WHAT IS MASS NUMBER ?

The total number of protons and neutrons in the nucleus of an atom is called the Mass Number,  $A$ , of the atom.

In situations where it is unnecessary to differentiate between protons and neutrons, these elementary particles are collectively referred to as **nucleons**. **Thus mass number of an atom is equal to the total number of nucleons in the nucleus of an atom.**

Obviously, the mass number of an atom is a whole number. Since electrons have practically no mass, the entire atomic mass is due to protons and neutrons, each of which has a mass almost exactly one unit. Therefore, **the mass number of an atom can be obtained by rounding off the experimental value of atomic mass (or atomic weight) to the nearest whole number.** For example, the atomic mass of sodium and fluorine obtained by experiment is 22.9898 and 26.9815 amu respectively. Thus their mass numbers are 23 for sodium and 27 for fluorine.

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

### COMPOSITION OF THE NUCLEUS

Knowing the atomic number ( $Z$ ) and mass number ( $A$ ) of an atom, we can tell the number of protons and neutrons contained in the nucleus. By definition :

Atomic Number,  $Z$  = Number of protons

Mass Number,  $A$  = Number of protons + Number of neutrons

$\therefore$  The number of neutrons is given by the expression :

$$N = A - Z$$

**SOLVED PROBLEM.** Uranium has atomic number 92 and atomic weight 238.029. Give the number of electrons, protons and neutrons in its atom.

#### SOLUTION

Atomic Number of uranium = 92

$\therefore$  Number of electrons = 92

and Number of protons = 92

Number of neutrons ( $N$ ) is given by the expression

$$N = A - Z$$

Mass Number ( $A$ ) is obtained by rounding off the atomic weight

$$= 238.029 = 238$$

$\therefore$   $N = 238 - 92 = 146$

**Thus uranium atom has 92 electrons, 92 protons and 146 neutrons.**

The composition of nuclei of some atoms is given in Table 1.2.

**TABLE 1.2. COMPOSITION OF THE NUCLEUS OF SOME ATOMS**

Atom	Mass Number (A)	Atomic Number (Z)	COMPOSITION	
			Protons = Z	Neutrons = A - Z
Be	9	4	4	5
F	19	9	9	10
Na	23	11	11	12
Al	27	13	13	14
P	31	15	15	16
Sc	45	21	21	24
Au	197	79	79	118

## QUANTUM THEORY AND BOHR ATOM

Rutherford model laid the foundation of the model picture of the atom. However it did not tell anything as to the position of the electrons and how they were arranged around the nucleus.

Rutherford recognised that electrons were orbiting around the nucleus. But according to the classical laws of Physics an electron moving in a field of force like that of nucleus, would give off radiations and gradually collapse into the nucleus. Thus Rutherford model failed to explain why electrons did not do so.

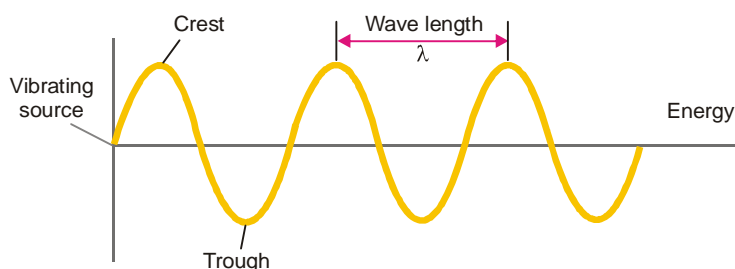
Neils Bohr, a brilliant Danish Physicist, pointed out that the old laws of physics just did not work in the submicroscopic world of the atom. He closely studied the behaviour of electrons, radiations and atomic spectra. In 1913 Bohr proposed a new model of the atom based on the modern Quantum theory of energy. With his theoretical model he was able to explain as to why an orbiting electron did not collapse into the nucleus and how the atomic spectra were caused by the radiations emitted when electrons moved from one orbit to the other. Therefore to understand the Bohr theory of the atomic

structure, it is first necessary to acquaint ourselves with the nature of electromagnetic radiations and the atomic spectra as also the Quantum theory of energy.

### Electromagnetic Radiations

Energy can be transmitted through space by electromagnetic radiations. Some forms of *radiant energy* are radio waves, visible light, infrared light, ultraviolet light, X-rays and  $\gamma$ -radiations.

Electromagnetic radiations are so named because they consist of waves which have electrical and magnetic properties. An object sends out energy waves when its particles move up and down or *vibrate* continuously. Such a vibrating particle causes an intermittent disturbance which constitutes a wave. A wave conveys energy from the vibrating object to a distant place. The wave travels at right angle to the vibratory motion of the object.



■ **Figure 1.12**  
Illustration of wave motion caused by a vibrating source.

Waves similar to electromagnetic waves are caused when a stone is thrown in a pond of water. The stone makes the water molecules vibrate up and down and transmit its energy as waves on water surface. These waves are seen travelling to the bank of the pond.

A wave may be produced by the actual displacement of particles of the medium as in case of water or sound waves. However, electromagnetic waves are produced by a periodic motion of charged particles. Thus vibratory motion of electrons would cause a wave train of oscillating electric field and another of oscillating magnetic field. These electromagnetic waves travel through empty space with the speed or velocity of light.

### Characteristics of Waves

A series of waves produced by a vibrating object can be represented by a wavy curve of the type shown in Fig. 1.12. The tops of the curve are called *crests* and the bottoms *troughs*. Waves are characterised by the following properties :

#### Wavelength

**The wavelength is defined as the distance between two successive crests or troughs of a wave.**

Wavelength is denoted by the Greek letter  $\lambda$  (lambda). It is expressed in centimetres or metres or in *angstrom* units. One angstrom,  $\text{\AA}$ , is equal to  $10^{-8}$  cm. It is also expressed in nanometers ( $1\text{ nm} = 10^{-9}$  m). That is,

$$\begin{aligned} 1 \text{ \AA} &= 10^{-8} \text{ cm} = 10^{-10} \text{ m} & \text{or} & & 1 \text{ cm} &= 10^8 \text{ \AA} & \text{and} & & 1 \text{ m} &= 10^{10} \text{ \AA} \\ 1 \text{ nm} &= 10^{-9} \text{ m} \end{aligned}$$

#### Frequency

**The frequency is the number of waves which pass a given point in one second.**

Frequency is denoted by the letter  $\nu$  (nu) and is expressed in *hertz* (hz).

It is noteworthy that a **wave of high frequency (*b*) has a shorter wavelength, while a wave of low frequency (*a*) has a longer wavelength.**

### Speed

The speed (or velocity) of a wave is the distance through which a particular wave travels in one second.

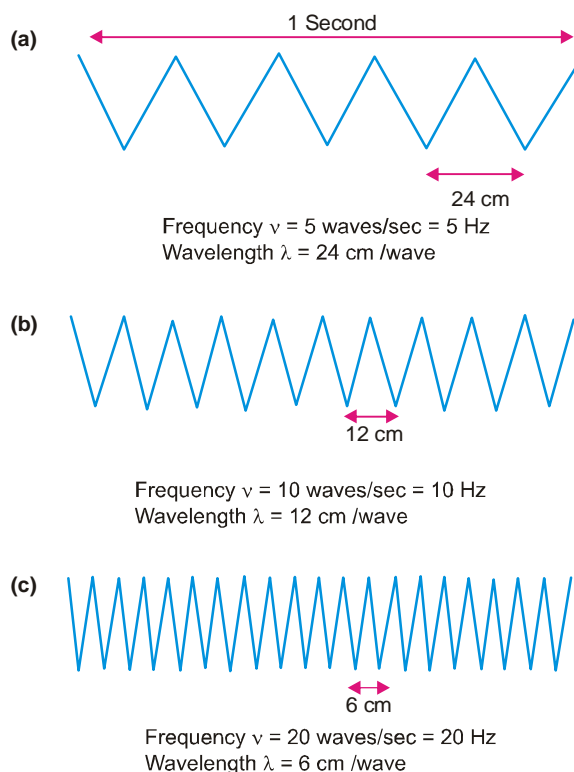
Speed is denoted by  $c$  and it is expressed in cm per second. If the speed of a wave is  $c$  cm/sec, it means that the distance travelled by the wave in one second is  $c$  cm. Speed is related to frequency and wavelength by the expression

$$c = \nu\lambda$$

or

$$\text{Speed} = \text{Frequency} \times \text{Wavelength}$$

The various types of electromagnetic radiations have different wavelengths and frequencies. As evident from Fig. 1.13, all types of radiations travel with the same speed or velocity. This velocity has been determined experimentally and it comes out to be  $3 \times 10^{10}$  cm/sec = 186,000 miles per second which is, in fact, the velocity of light.



■ **Figure 1.13**  
**Waves of different wavelengths and frequencies.**  
In all three cases; velocity =  $\lambda \times \nu = 120$  cm/sec.

### Wave Number

Another quantity used to characterise radiation is the *wave number*. This is reciprocal of the wavelength and is given the symbol  $\bar{\nu}$  (nu bar). That is,

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

The wave number is the number of wavelengths per unit of length covered. Its units are  $\text{cm}^{-1}$  or  $\text{m}^{-1}$ .

**SOLVED PROBLEM.** The wavelength of a violet light is 400 nm. Calculate its frequency and wave number.

**SOLUTION.** We know that

$$\text{frequency, } \nu = \frac{c}{\lambda}$$

$$\text{Here } c = 3.0 \times 10^8 \text{ m sec}^{-1}; \lambda = 400 \text{ nm} = 400 \times 10^{-9} \text{ m}$$

$$\begin{aligned} \nu &= \frac{c}{\lambda} = \frac{3.0 \times 10^8 \text{ m sec}^{-1}}{400 \times 10^{-9} \text{ m}} \\ &= \frac{3}{400} \times 10^{17} \text{ sec}^{-1} \\ &= \frac{3000}{400} \times 10^{14} \text{ sec}^{-1} \\ &= 7.5 \times 10^{14} \text{ sec}^{-1} \end{aligned}$$

Also, wave number

$$\begin{aligned} \bar{\nu} &= \frac{1}{\lambda} \\ \bar{\nu} &= \frac{1}{400 \times 10^{-9} \text{ m}} \\ &= 25 \times 10^5 \text{ m}^{-1} \end{aligned}$$

**SOLVED PROBLEM.** The frequency of strong yellow line in the spectrum of sodium is  $5.09 \times 10^{14} \text{ sec}^{-1}$ . Calculate the wavelength of the light in nanometers.

**SOLUTION.** We know that wavelength,  $\lambda = \frac{c}{\nu}$

Here

$$c = 3.0 \times 10^8 \text{ m sec}^{-1}$$

$$\nu = 5.09 \times 10^{14} \text{ sec}^{-1} \text{ (given)}$$

Wavelength

$$\begin{aligned} \lambda &= \frac{3.0 \times 10^8 \text{ m sec}^{-1}}{5.09 \times 10^{14} \text{ sec}^{-1}} \\ &= \frac{3000}{5.09} \times 10^{-9} \text{ m} \\ &= 589 \times 10^{-9} \text{ m} \\ &= 589 \text{ nm} \end{aligned}$$

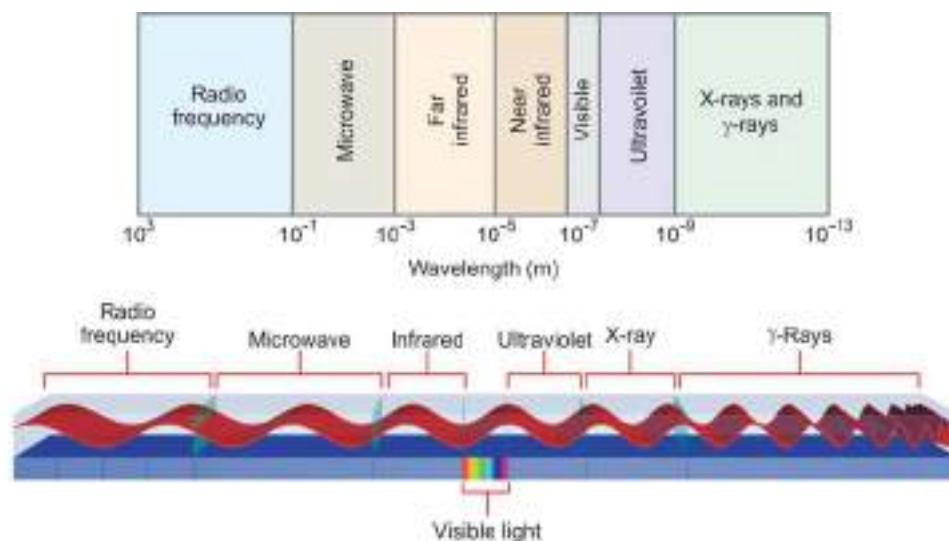
$$[\because 1 \text{ nm} = 10^{-9} \text{ m}]$$

## SPECTRA

A spectrum is an array of waves or particles spread out according to the increasing or decreasing of some property. An increase in frequency or a decrease in wavelength represent an increase in energy.

### THE ELECTROMAGNETIC SPECTRUM

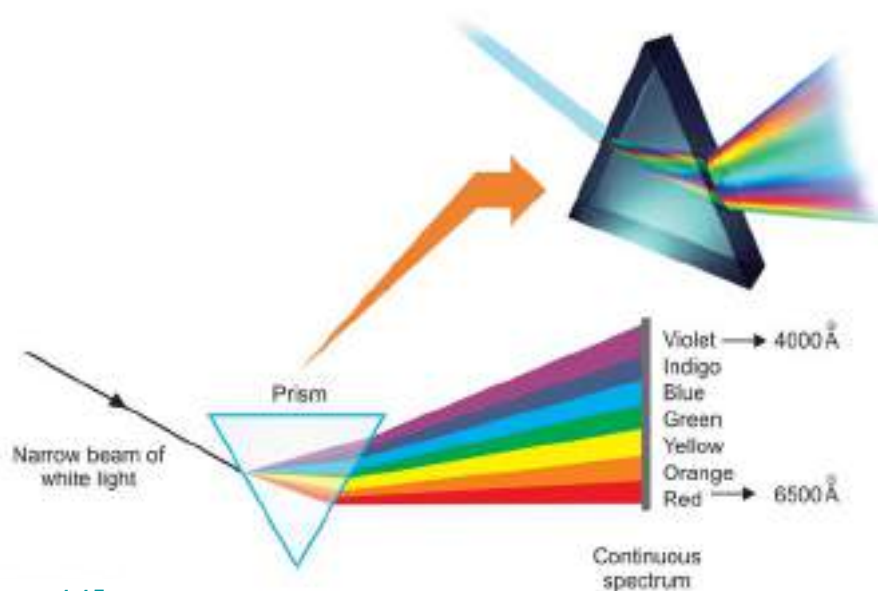
Electromagnetic radiations include a range of wavelengths and this array of wavelengths is referred to as the *Electromagnetic radiation spectrum* or simply *Electromagnetic spectrum*. The electromagnetic spectrum with marked wavelengths is shown in Fig. 1.14.



■ **Figure 1.14**  
Electromagnetic spectrum. Wavelength boundaries of each region are approximate.

### CONTINUOUS SPECTRUM

White light is radiant energy coming from the sun or from incandescent lamps. It is composed of light waves in the range  $4000\text{--}8000\text{ \AA}$ . Each wave has a characteristic colour. When a beam of white light is passed through a prism, different wavelengths are refracted (or bent) through different angles. When received on a screen, these form a continuous series of colour bands : violet, indigo, blue, green, yellow, orange and red (VIBGYOR). **This series of bands that form a continuous rainbow of colours, is called a Continuous Spectrum.**



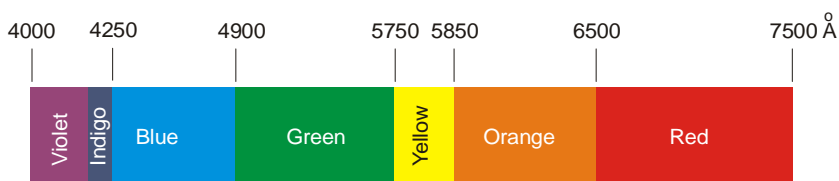
■ **Figure 1.15**  
The continuous spectrum of white light.



The violet component of the spectrum has shorter wavelengths (4000 – 4250 Å) and higher frequencies. The red component has longer wavelengths (6500 – 7500 Å) and lower frequencies. The invisible region beyond the violet is called **ultraviolet region** and the one below the red is called **infrared region**.

### ATOMIC SPECTRA

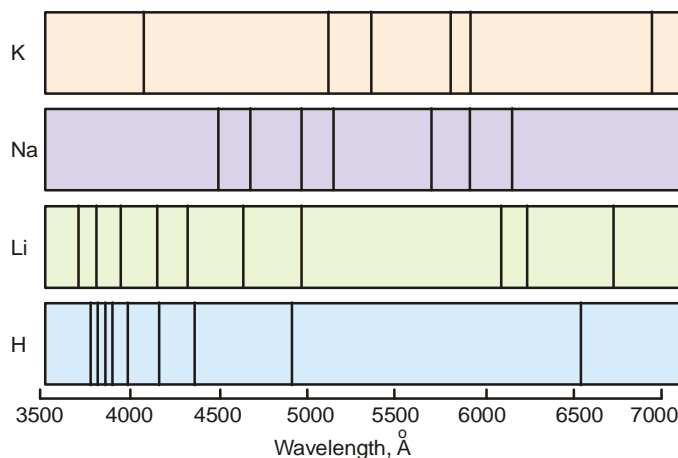
When an element in the vapour or the gaseous state is heated in a flame or a discharge tube, the atoms are excited (energised) and emit light radiations of a characteristic colour. The colour of light produced indicates the wavelength of the radiation emitted.



■ **Figure 1.16**

Wavelength range of colour bands in Å of continuous spectrum.

For example, a Bunsen burner flame is coloured yellow by sodium salts, red by strontium and violet by potassium. In a discharge tube, neon glows orange-red, helium-pink, and so on. If we examine the emitted light with a **Spectroscope** (a device in which a beam of light is passed through a prism and received on a photograph), the spectrum obtained on the photographic plate is found to consist of bright lines (Fig. 1.18). Such a spectrum in which each line represents a specific wavelength of radiation emitted by the atoms is referred to as the **Line spectrum** or **Atomic Emission spectrum** of the element. The emission spectra of some elements are shown in Fig. 1.17. An individual line of these spectra is called a **Spectral line**.



■ **Figure 1.17**

Emission spectra of K, Na, Li and H.

When white light composed of all visible wavelengths, is passed through the cool vapour of an element, certain wavelengths may be absorbed. These absorbed wavelengths are thus found missing in the transmitted light. The spectrum obtained in this way consists of a series of dark lines which is referred to as the **Atomic Absorption spectrum** or simply **Absorption spectrum**. The wavelengths of the dark lines are exactly the same as those of bright lines in the emission spectrum. The absorption spectrum of an element is the reverse of emission spectrum of the element.

Atomic spectral lines are emitted or absorbed not only in the visible region of the electromagnetic spectrum but also in the infrared region (**IR spectra**) or in the ultraviolet region (**UV spectra**).

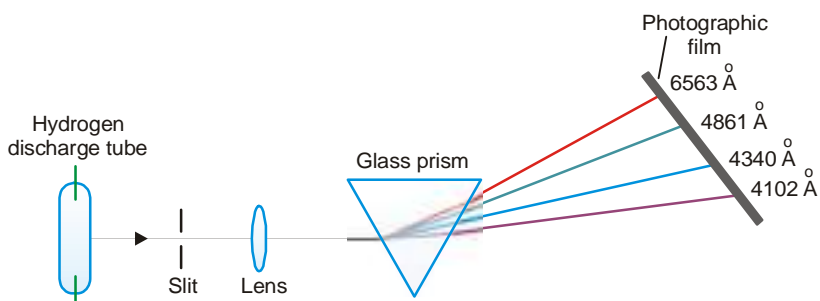
Since the atomic spectra are produced by emission or absorption of energy depending on the internal structure of the atom, each element has its own characteristic spectrum. Today spectral analysis has become a powerful method for the detection of elements even though present in extremely small amounts. The most important consequence of the discovery of spectral lines of hydrogen and other elements was that it led to our present knowledge of atomic structure.

### ATOMIC SPECTRUM OF HYDROGEN

The emission line spectrum of hydrogen can be obtained by passing electric discharge through the gas contained in a discharge tube at low pressure. The light radiation emitted is then examined with the help of a **spectroscope**. The bright lines recorded on the photographic plate constitute the atomic spectrum of hydrogen (Fig. 1.18).

In 1884 J.J. Balmer observed that there were four prominent coloured lines in the visible hydrogen spectrum :

- (1) a *red line* with a wavelength of 6563 Å.
- (2) a *blue-green line* with a wavelength 4861 Å.
- (3) a *blue line* with a wavelength 4340 Å.
- (4) a *violet line* with a wavelength 4102 Å.



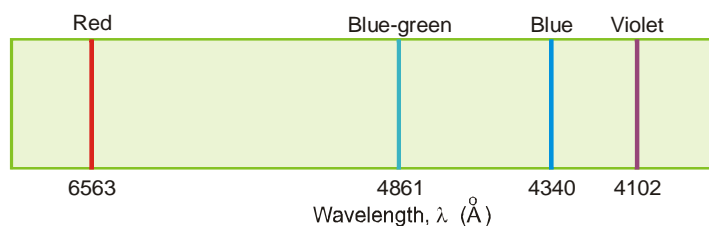
■ **Figure 1.18**

**The examination of the atomic spectrum of hydrogen with a spectroscope.**

The above series of four lines in the visible spectrum of hydrogen was named as the **Balmer Series**. By carefully studying the wavelengths of the observed lines, Balmer was able empirically to give an equation which related the wavelengths ( $\lambda$ ) of the observed lines. The **Balmer Equation** is

$$\frac{1}{\lambda} = R \left( \frac{1}{2^2} - \frac{1}{n^2} \right)$$

where  $R$  is a constant called the **Rydberg Constant** which has the value  $109,677 \text{ cm}^{-1}$  and  $n = 3, 4, 5, 6$  etc. That is, if we substitute the values of 3, 4, 5 and 6 for  $n$ , we get, respectively, the wavelength of the four lines of the hydrogen spectrum.



■ **Figure 1.19**

**Balmer series in the Hydrogen spectrum.**

In addition to Balmer Series, four other spectral series were discovered in the infrared and ultraviolet regions of the hydrogen spectrum. These bear the names of the discoverers. Thus in all we have **Five Spectral Series** in the atomic spectrum of hydrogen :

Name	Region where located
(1) Lyman Series	Ultraviolet
(2) Balmer Series	Visible
(3) Paschen Series	Infrared
(4) Brackett Series	Infrared
(5) Pfund Series	Infrared

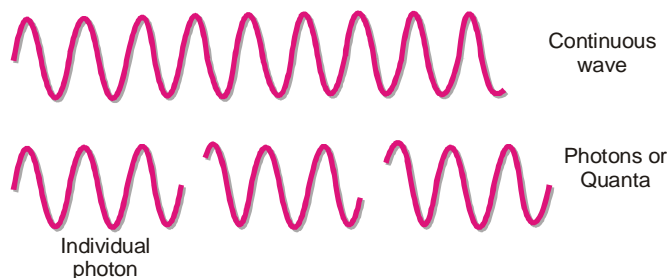
Balmer equation had no theoretical basis at all. Nobody had any idea how it worked so accurately in finding the wavelengths of the spectral lines of hydrogen atom. However, in 1913 Bohr put forward his theory which immediately explained the observed hydrogen atom spectrum. Before we can understand Bohr theory of the atomic structure, it is necessary to acquaint ourselves with the quantum theory of energy.

### QUANTUM THEORY OF RADIATION

The wave theory of transmission of radiant energy appeared to imply that energy was emitted (or absorbed) in continuous waves. In 1900 Max Planck studied the spectral lines obtained from hot-body radiations at different temperatures. According to him, light radiation was produced discontinuously by the molecules of the hot body, each of which was vibrating with a specific frequency which increased with temperature. Thus Planck proposed a new theory that a hot body radiates energy not in continuous waves but in small units of waves. The ‘unit wave’ or ‘pulse of energy’ is called **Quantum** (plural, *quanta*). In 1905 Albert Einstein showed that light radiations emitted by ‘excited’ atoms or molecules were also transmitted as particles or quanta of energy. These light quanta are called **photons**.

The general **Quantum Theory of Electromagnetic Radiation** in its present form may be stated as :

- (1) **When atoms or molecules absorb or emit radiant energy, they do so in separate ‘units of waves’ called quanta or photons.** Thus light radiations obtained from energised or ‘excited atoms’ consist of a stream of photons and not continuous waves.



■ **Figure 1.20**

**A continuous wave and photons.**

- (2) **The energy,  $E$ , of a quantum or photon is given by the relation**

$$E = h\nu \quad \dots(1)$$

where  $\nu$  is the frequency of the emitted radiation, and  $h$  the **Planck's Constant**. The value of  $h = 6.62 \times 10^{-27}$  erg sec. or  $6.62 \times 10^{-34}$  J sec.

We know that  $c$ , the velocity of radiation, is given by the equation

$$c = \lambda\nu \quad \dots(2)$$

Substituting the value of  $\nu$  from (2) in (1), we can write

$$E = \frac{hc}{\lambda}$$

Thus the magnitude of a quantum or photon of energy is directly proportional to the frequency of the radiant energy, or is inversely proportional to its wavelength,  $\lambda$ .

- (3) An atom or molecule can emit (or absorb) either one quantum of energy ( $h\nu$ ) or any whole number multiple of this unit.

Thus radiant energy can be emitted as  $h\nu$ ,  $2h\nu$ ,  $3h\nu$ , and so on, but never as  $1.5 h\nu$ ,  $3.27 h\nu$ ,  $5.9 h\nu$ , or any other fractional value of  $h\nu$  i.e.  $nh\nu$

Quantum theory provided admirably a basis for explaining the photoelectric effect, atomic spectra and also helped in understanding the modern concepts of atomic and molecular structure.

**SOLVED PROBLEM.** Calculate the magnitude of the energy of the photon (or quantum) associated with light of wavelength  $6057.8 \text{ \AA}$ . ( $\text{\AA} = 10^{-8} \text{ cm}$ )

### SOLUTION

- (a) Calculation of Frequency :

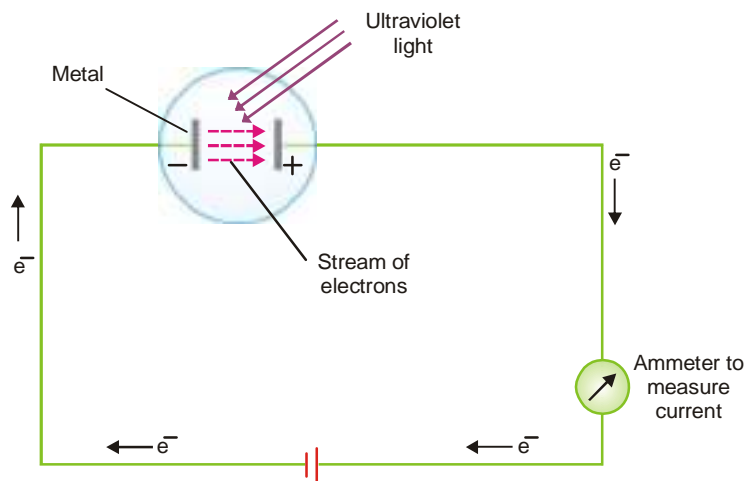
$$\begin{aligned} \nu &= \frac{c}{\lambda} = \frac{3.0 \times 10^{10} \text{ cm sec}^{-1}}{6057.8 \times 10^{-8} \text{ cm}} \\ &= 4.952 \times 10^{14} \text{ sec}^{-1} \end{aligned}$$

- (b) Calculation of Energy :

$$\begin{aligned} E &= h\nu = (6.625 \times 10^{-27} \text{ erg sec}) (4.952 \times 10^{14} \text{ sec}^{-1}) \\ &= 3.281 \times 10^{-12} \text{ erg} \end{aligned}$$

### PHOTOELECTRIC EFFECT

When a beam of light of sufficiently high frequency is allowed to strike a metal surface in vacuum, electrons are ejected from the metal surface. This phenomenon is known as **Photoelectric effect** and the ejected electrons **Photoelectrons**. For example, when ultraviolet light shines on Cs (or Li, Na, K, Rb) as in the apparatus shown in Fig 1.21, the photoelectric effect occurs.



■ **Figure 1.21**

Apparatus for measuring the photoelectric effect. When ultraviolet light shines on the metal, the emitted electrons flow to the anode and the circuit is completed. This current can be measured with the help of an ammeter.

With the help of this photoelectric apparatus the following observations can be made :

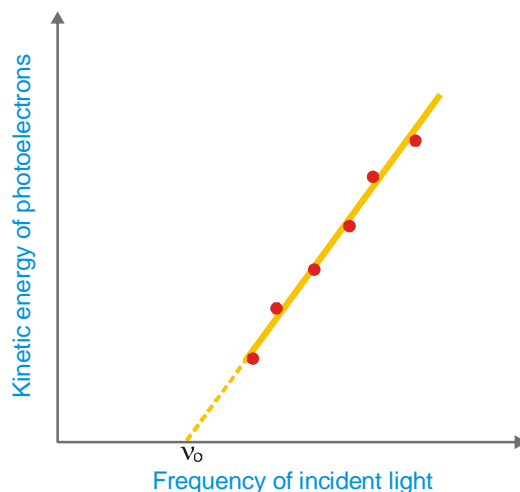
- (1) **An increase in the intensity of incident light does not increase the energy of the photoelectrons.** It merely increases their rate of emission.
- (2) **The kinetic energy of the photoelectrons increases linearly with the frequency of the incident light (Fig. 1.22).** If the frequency is decreased below a certain critical value (**Threshold frequency,  $\nu_0$** ), no electrons are ejected at all.

The Classical Physics predicts that the kinetic energy of the photoelectrons should depend on the intensity of light and not on the frequency. Thus it fails to explain the above observations.

### EINSTEIN'S EXPLANATION OF PHOTOELECTRIC EFFECT

In 1905 Albert Einstein, who was awarded Nobel Prize for his work on photons, interpreted the Photoelectric effect by application of the Quantum theory of light.

- (1) A photon of incident light transmits its energy ( $h\nu$ ) to an electron in the metal surface which escapes with kinetic energy  $\frac{1}{2}mv^2$ . **The greater intensity of incident light merely implies greater number of photons each of which releases one electron.** This increases the rate of emission of electrons, while the kinetic energy of individual photons remains unaffected.

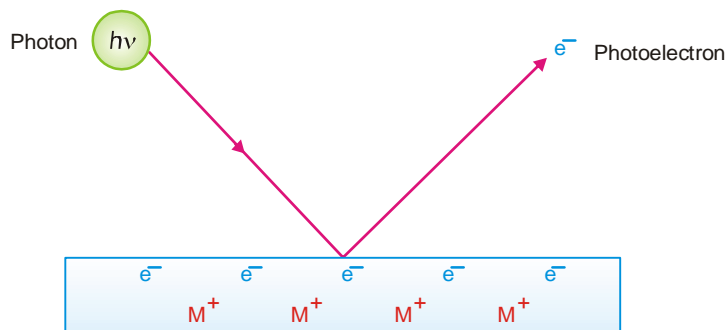


■ **Figure 1.22**  
Kinetic energy of photoelectrons plotted against frequency of incident light.

- (2) **In order to release an electron from the metal surface, the incident photon has first to overcome the attractive force exerted by the positive ion of the metal.** The energy of a photon ( $h\nu$ ) is proportional to the frequency of incident light. The frequency which provides enough energy just to release the electron from the metal surface, will be the *threshold frequency,  $\nu_0$* . For frequency less than  $\nu_0$ , no electrons will be emitted.

For higher frequencies  $\nu > \nu_0$ , a part of the energy goes to loosen the electron and remaining for imparting kinetic energy to the photoelectron. Thus,

$$h\nu = h\nu_0 + \frac{1}{2}mv^2 \quad \dots(1)$$



■ **Figure 1.23**

**It needs a photon( $h\nu$ ) to eject an electron with energy  $\frac{1}{2}mv^2$ .**

Where  $h\nu$  is the energy of the incoming photon,  $h\nu_0$  is the minimum energy for an electron to escape from the metal, and  $\frac{1}{2}mv^2$  is the kinetic energy of the photoelectron.  $h\nu_0$  is constant for a particular solid and is designated as  $W$ , the **work function**. Rearranging equation (1)

$$\frac{1}{2}mv^2 = h\nu - W \quad \dots(2)$$

This is the equation for a straight line that was experimentally obtained in Fig. 1.22. Its slope is equal to  $h$ , the Planck's constant. The value of  $h$  thus found came out to be the same as was given by Planck himself.

**SOLVED PROBLEM.** What is the minimum energy that photons must possess in order to produce photoelectric effect with platinum metal? The threshold frequency for platinum is  $1.3 \times 10^{15} \text{ sec}^{-1}$ .

**SOLUTION**

The threshold frequency ( $\nu_0$ ) is the lowest frequency that photons may possess to produce the photoelectric effect. The energy corresponding to this frequency is the minimum energy ( $E$ ).

$$\begin{aligned} E &= h\nu_0 \\ &= (6.625 \times 10^{-27} \text{ erg sec}) (1.3 \times 10^{15} \text{ sec}^{-1}) \\ &= \mathbf{8.6 \times 10^{-12} \text{ erg}} \end{aligned}$$

**SOLVED PROBLEM.** Calculate the kinetic energy of an electron emitted from a surface of potassium metal (work function =  $3.62 \times 10^{-12} \text{ erg}$ ) by light of wavelength  $5.5 \times 10^{-8} \text{ cm}$ .

**SOLUTION**

$$\begin{aligned} \nu &= \frac{c}{\lambda} \text{ where } c = \text{velocity of light } (3.0 \times 10^{10} \text{ cm sec}^{-1}) \\ \text{For } \lambda &= 5.5 \times 10^{-8} \text{ cm} \\ \nu &= \frac{c}{\lambda} = \frac{3.0 \times 10^{10} \text{ cm sec}^{-1}}{5.5 \times 10^{-8} \text{ cm}} = 5.5 \times 10^{17} \text{ sec}^{-1} \end{aligned}$$

$$\begin{aligned} \frac{1}{2}mv^2 &= h\nu - W \\ &= (6.6 \times 10^{-27} \text{ erg sec}) (5.5 \times 10^{17} \text{ sec}^{-1}) - 3.62 \times 10^{-12} \text{ erg} \\ &= 3.63 \times 10^{-9} \text{ erg} - 3.62 \times 10^{-12} \text{ erg} \\ &= \mathbf{3.63 \times 10^{-9} \text{ erg}} \end{aligned}$$

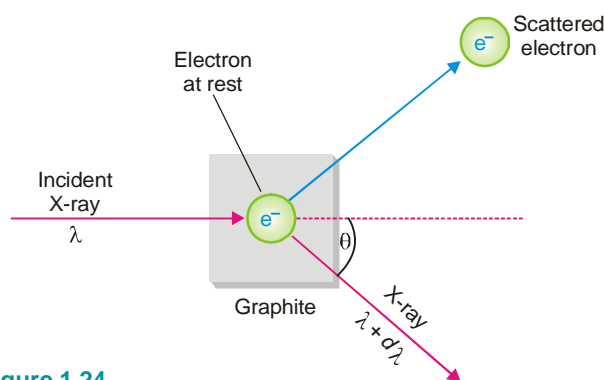
Thus the electron will be emitted with kinetic energy of  $3.63 \times 10^{-9} \text{ erg}$ .

## COMPTON EFFECT

In 1923 A.H. Compton provided one more proof to the quantum theory or the photon theory. He was awarded Nobel Prize in 1927 for his discovery of what is now called the **Compton Effect**. He demonstrated that : **When X-rays of wavelength  $\lambda'$  struck a sample of graphite, an electron was ejected and the X-rays scattered at an angle  $\theta$  had longer wavelength  $\lambda$ .**

### Explanation of Compton Effect

Compton said that it was like a ball hitting a stationary ball which is pushed away while the energy of the striking ball decreases. Thus he argued that light radiation (X-rays) consisted of particles (photons), as a continuous wave could not have knocked out the electron. **He visualised that a photon of incident light struck a stationary electron in graphite and hence lost some energy which resulted in the increase of wavelength.** This process could not have occurred unless light radiation consisted of particles or photons.



■ **Figure 1.24**  
**Compton scattering of X-rays.**

By assuming photon-electron collisions to be perfectly elastic, Compton found that the shift in wavelength,  $d\lambda$  was given by the expression

$$d\lambda = \frac{2h}{mc} \sin^2 \theta/2.$$

where  $h$  is Planck's constant,  $m$  the mass of an electron,  $c$  the velocity of light and  $\theta$  the angle of scattering. The expression shows that  $d\lambda$  is independent of the nature of the substance and wavelength of the incident radiation. Given the wavelength of a photon, one can calculate the momentum of the electron ejected.

## BOHR MODEL OF THE ATOM

Rutherford's nuclear model simply stated that atom had a nucleus and the negative electrons were present outside the nucleus. It did not say anything as to how and where those electrons were arranged. It also could not explain why electrons did not fall into the nucleus due to electrostatic attraction. In 1913 Niels Bohr proposed a new model of atom which explained some of these things and also the emission spectrum of hydrogen. Bohr's theory was based on Planck's quantum theory and was built on the following postulates.

### Postulates of Bohr's Theory

(1) **Electrons travel around the nucleus in specific permitted circular orbits and in no others.**

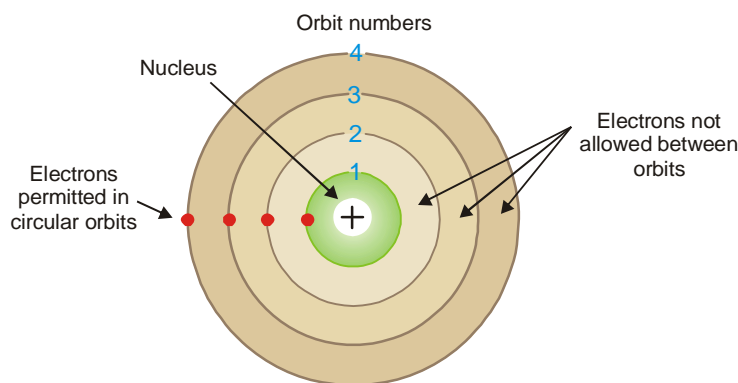
Electrons in each orbit have a definite energy and are at a fixed distance from the nucleus. The orbits are given the letter designation  $n$  and each is numbered 1, 2, 3, etc. (or K, L, M, etc.) as the distance from the nucleus increases.

(2) **While in these specific orbits, an electron does not radiate (or lose) energy.**

Therefore in each of these orbits the energy of an electron remains the same *i.e.* it neither loses nor gains energy. Hence the specific orbits available to the electron in an atom are referred to as **stationary energy levels** or simply **energy levels**.

(3) **An electron can move from one energy level to another by quantum or photon jumps only.**

When an electron resides in the orbit which is lowest in energy (which is also closest to the nucleus), the electron is said to be in the **ground state**. When an electron is supplied energy, it absorbs one quantum or photon of energy and jumps to a higher energy level. The electron then has potential energy and is said to be in an **excited state**.



■ **Figure 1.25**  
**Circular electron orbits or stationary energy levels in an atom.**

The quantum or photon of energy absorbed or emitted is the difference between the lower and higher energy levels of the atom

$$\Delta E = E_{\text{high}} - E_{\text{low}} = h\nu \quad \dots(1)$$

where  $h$  is Planck's constant and  $\nu$  the frequency of a photon emitted or absorbed energy.

(4) **The angular momentum ( $mvr$ ) of an electron orbiting around the nucleus is an integral multiple of Planck's constant divided by  $2\pi$ .**

$$\text{Angular momentum} = mvr = n \frac{h}{2\pi} \quad \dots(2)$$

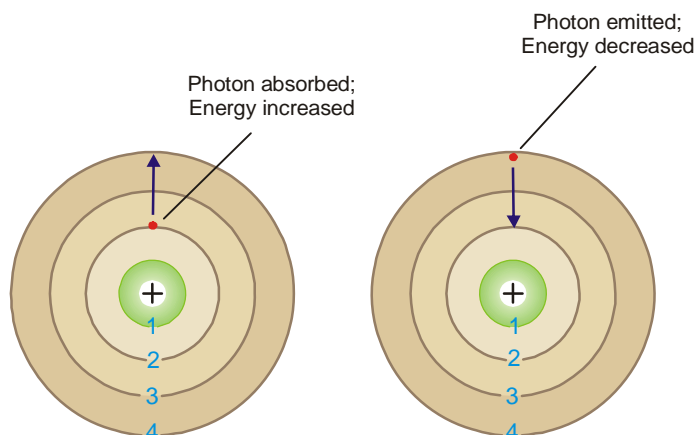
where  $m$  = mass of electron,  $v$  = velocity of the electron,  $r$  = radius of the orbit ;  $n = 1, 2, 3$ , etc., and  $h$  = Planck's constant.

By putting the values 1, 2, 3, etc., for  $n$ , we can have respectively the angular momentum

$$\frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi}, \text{ etc.}$$

There can be no fractional value of  $h/2\pi$ . Thus *the angular momentum is said to be quantized*. The integer  $n$  in equation (2) can be used to designate an orbit and a corresponding energy level  $n$  is called the atom's **Principal quantum number**.





■ **Figure 1.26**

**An electron absorbs a photon of light while it jumps from a lower to a higher energy orbit and a photon is emitted while it returns to the original lower energy level.**

Using the above postulates and some classical laws of Physics, Bohr was able to calculate the radius of each orbit of the hydrogen atom, the energy associated with each orbit and the wavelength of the radiation emitted in transitions between orbits. The wavelengths calculated by this method were found to be in excellent agreement with those in the actual spectrum of hydrogen, which was a big success for the Bohr model.

#### Calculation of radius of orbits

Consider an electron of charge  $e$  revolving around a nucleus of charge  $Ze$ , where  $Z$  is the atomic number and  $e$  the charge on a proton. Let  $m$  be the mass of the electron,  $r$  the radius of the orbit and  $v$  the tangential velocity of the revolving electron.

The electrostatic force of attraction between the nucleus and the electron (Coulomb's law),

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

The centrifugal force acting on the electron

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

Bohr assumed that these two opposing forces must be balancing each other exactly to keep the electron in orbit. Thus,

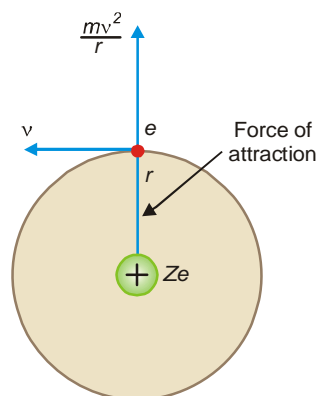
$$\frac{Ze^2}{r^2} = \frac{mv^2}{r}$$

For hydrogen  $Z = 1$ , therefore,

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

Multiplying both sides by  $r$

$$\frac{e^2}{r} = mv^2 \quad \dots(2)$$



■ **Figure 1.27**

**Forces keeping electron in orbit.**

According to one of the postulates of Bohr's theory, angular momentum of the revolving electron is given by the expression

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

or 
$$v = \frac{nh}{2\pi mr} \quad \dots(3)$$

Substituting the value of  $v$  in equation (2),

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

Solving for  $r$ ,

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

Since the value of  $h$ ,  $m$  and  $e$  had been determined experimentally, substituting these values in (4), we have

$$r = n^2 \times 0.529 \times 10^{-8} \text{ cm} \quad \dots(5)$$

where  $n$  is the principal quantum number and hence the number of the orbit.

When  $n = 1$ , the equation (5) becomes

$$r = 0.529 \times 10^{-8} \text{ cm} = \alpha_0 \quad \dots(6)$$

This last quantity,  $\alpha_0$  called the first **Bohr radius** was taken by Bohr to be the radius of the hydrogen atom in the ground state. This value is reasonably consistent with other information on the size of atoms. When  $n = 2, 3, 4$  etc., the value of the second and third orbits of hydrogen comprising the electron in the excited state can be calculated.

**SOLVED PROBLEM.** Calculate the first five Bohr radii.

#### SOLUTION

The equation (5) may be written as

$$\begin{aligned} r &= n^2 \times 0.529 \times 10^{-8} \text{ cm} \\ n = 1 ; r &= 1^2 \times 0.529 \times 10^{-8} = 0.529 \times 10^{-8} \text{ cm} \\ n = 2 ; r &= 2^2 \times 0.529 \times 10^{-8} = 2.12 \times 10^{-8} \text{ cm} \\ n = 3 ; r &= 3^2 \times 0.529 \times 10^{-8} = 4.76 \times 10^{-8} \text{ cm} \\ n = 4 ; r &= 4^2 \times 0.529 \times 10^{-8} = 8.46 \times 10^{-8} \text{ cm} \\ n = 5 ; r &= 5^2 \times 0.529 \times 10^{-8} = 13.2 \times 10^{-8} \text{ cm} \end{aligned}$$

#### Energy of electron in each orbit

For hydrogen atom, the energy of the revolving electron,  $E$  is the sum of its kinetic energy

$$\left( \frac{1}{2} mv^2 \right) \text{ and potential energy } \left( -\frac{e^2}{r} \right).$$

$$E = \frac{1}{2} mv^2 - \frac{e^2}{r} \quad \dots(7)$$

From equation (1)

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

Substituting the value of  $mv^2$  in (7)

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

or 
$$E = -\frac{e^2}{2r} \quad \dots(8)$$

Substituting the value of  $r$  from equation (4) in (8)

$$\begin{aligned} E &= -\frac{e^2}{2} \times \frac{4\pi^2 m e^2}{n^2 h^2} \\ &= -\frac{2\pi^2 m e^4}{n^2 h^2} \quad \dots(9) \end{aligned}$$

Substituting the values of  $m$ ,  $e$ , and  $h$  in (9),

$$E = \frac{-2.179 \times 10^{-11}}{n^2} \text{ erg/atom} \quad \dots(10)$$

or 
$$E = \frac{-2.179 \times 10^{-18}}{n^2} \text{ J per atom}$$

or 
$$E = \frac{-2.17 \times 10^{18} \times 6.02 \times 10^{23}}{n^2} \text{ J per mole}$$

or 
$$E = \frac{-1311.8}{n^2} \text{ kJ per mole}$$

or 
$$E = \frac{-313.3}{n^2} \text{ kcal per mole}$$

By using proper integer for  $n$  (quantum or orbit number), we can get the energy for each orbit.

**SOLVED PROBLEM.** Calculate the five lowest energy levels of the hydrogen atom.

### SOLUTION

From equation (10)

$$E = \frac{-2.179 \times 10^{-11} \text{ erg/atom}}{n^2}$$

Therefore the energy associated with the first five energy levels (or orbits) is :

$$n = 1 ; \quad E_1 = \frac{-2.179 \times 10^{-11}}{1^2} = -2.179 \times 10^{-11} \text{ erg/atom or } -1311.8 \text{ kJ mol}^{-1}$$

$$n = 2 ; \quad E_2 = \frac{-2.179 \times 10^{-11}}{2^2} = -0.5448 \times 10^{-11} \text{ erg/atom or } -327.9 \text{ kJ mol}^{-1}$$

$$n = 3 ; \quad E_3 = \frac{-2.179 \times 10^{-11}}{3^2} = -0.2421 \times 10^{-11} \text{ erg/atom or } -147.5 \text{ kJ mol}^{-1}$$

$$n = 4 ; \quad E_4 = \frac{-2.179 \times 10^{-11}}{4^2} = -0.1362 \times 10^{-11} \text{ erg/atom or } -82.0 \text{ kJ mol}^{-1}$$

$$n = 5 ; \quad E_5 = \frac{-2.179 \times 10^{-11}}{5^2} = -0.08716 \times 10^{-11} \text{ erg/atom or } -52.44 \text{ kJ mol}^{-1}$$

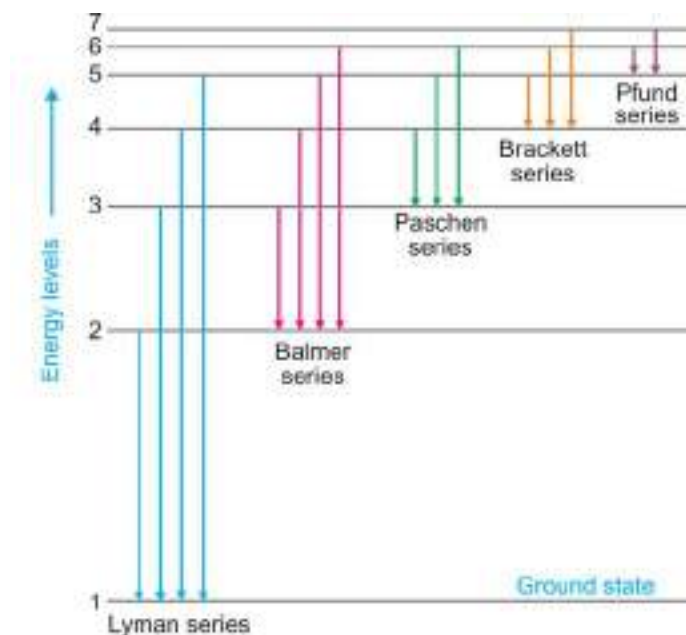
### Significance of Negative Value of Energy

The energy of an electron at infinity is arbitrarily assumed to be zero. This state is called *zero-energy* state. When an electron moves and comes under the influence of nucleus, it does some work and spends its energy in this process. Thus the energy of the electron decreases and it becomes less than zero *i.e.* it acquires a negative value.

### Bohr's Explanation of Hydrogen Spectrum

The solitary electron in hydrogen atom at ordinary temperature resides in the first orbit ( $n = 1$ ) and is in the lowest energy state (ground state). When energy is supplied to hydrogen gas in the *discharge tube*, the electron moves to higher energy levels *viz.*, 2, 3, 4, 5, 6, 7, etc., depending on the quantity of energy absorbed. From these high energy levels, the electron returns by jumps to one or other lower energy level. In doing so the electron emits the excess energy as a photon. This gives an excellent explanation of the various spectral series of hydrogen.

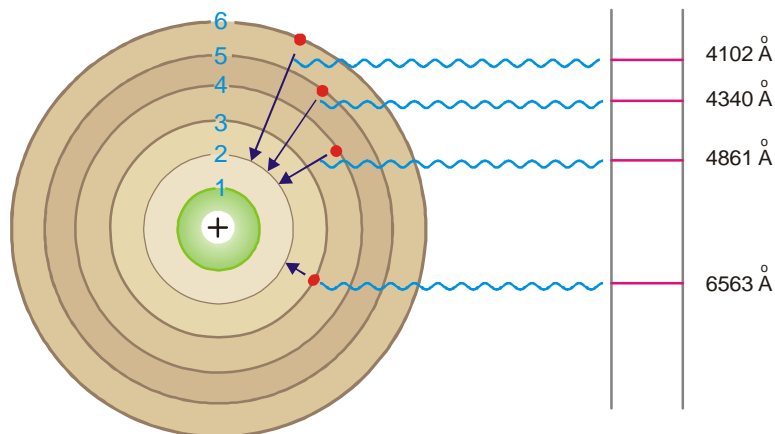
Lyman series is obtained when the electron returns to the ground state *i.e.*,  $n = 1$  from higher energy levels ( $n_2 = 2, 3, 4, 5$ , etc.). Similarly, Balmer, Paschen, Brackett and Pfund series are produced when the electron returns to the second, third, fourth and fifth energy levels respectively as shown in Fig. 1.28.



■ **Figure 1.28**  
Hydrogen spectral series on a Bohr atom energy diagram.

**TABLE 1.3. SPECTRAL SERIES OF HYDROGEN**

Series	$n_1$	$n_2$	Region	Wavelength $\lambda$ (Å)
Lyman	1	2, 3, 4, 5, etc.	ultraviolet	920-1200
Balmer	2	3, 4, 5, 6, etc.	visible	4000-6500
Paschen	3	4, 5, 6, 7, etc.	infrared	9500-18750
Brackett	4	5, 6, 7	infrared	19450-40500
Pfund	5	6, 7	infrared	37800-75000



■ **Figure 1.29**

**Explanation of spectral lines of hydrogen in visible region.**

**Value of Rydberg's constant is the same as in the original empirical Balmer's equation**

According to equation (1), the energy of the electron in orbit  $n_1$  (lower) and  $n_2$  (higher) is

$$E_{n_1} = -\frac{2\pi^2 me^4}{n_1^2 h^2}$$

$$E_{n_2} = -\frac{2\pi^2 me^4}{n_2^2 h^2}$$

The difference of energy between the levels  $n_1$  and  $n_2$  is :

$$\Delta E = E_{n_2} - E_{n_1} = \frac{2\pi^2 me^4}{h^2} \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad \dots(1)$$

According to Planck's equation

$$\Delta E = h\nu = \frac{hc}{\lambda} \quad \dots(2)$$

where  $\lambda$  is wavelength of photon and  $c$  is velocity of light. From equation (1) and (2), we can write

$$\frac{hc}{\lambda} = \frac{2\pi^2 e^4 m}{h^2} \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

or

$$\begin{aligned} \frac{1}{\lambda} &= \frac{2\pi^2 e^4 m}{h^3 c} \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \\ &= R \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad \dots(3) \end{aligned}$$

where  $R$  is **Rydberg constant**. The value of  $R$  can be calculated as the value of  $e$ ,  $m$ ,  $h$  and  $c$  are known. It comes out to be  $109,679 \text{ cm}^{-1}$  and agrees closely with the value of Rydberg constant in the original empirical Balmer's equation ( $109,677 \text{ cm}^{-1}$ ).

**Calculation of wavelengths of the spectral lines of Hydrogen in the visible region**

These lines constitute the Balmer series when  $n_1 = 2$ . Now the equation (3) above can be written as

$$\frac{1}{\lambda} = 109679 \left[ \frac{1}{2^2} - \frac{1}{n_2^2} \right]$$

Thus the wavelengths of the photons emitted as the electron returns from energy levels 6, 5, 4 and 3 were calculated by Bohr. The calculated values corresponded exactly to the values of wavelengths of the spectral lines already known. This was, in fact, a great success of the Bohr atom.

**SOLVED PROBLEM.** Find the wavelength in Å of the line in Balmer series that is associated with drop of the electron from the fourth orbit. The value of Rydberg constant is  $109,676 \text{ cm}^{-1}$ .

**SOLUTION**

The wavelengths of lines in Balmer series are given by

$$\frac{1}{\lambda} = R \left( \frac{1}{2^2} - \frac{1}{n^2} \right)$$

where  $\lambda$  = wavelength,  $R$  (Rydberg constant) =  $109,676 \text{ cm}^{-1}$ ;  $n = 4$ .

$$\begin{aligned} \therefore \frac{1}{\lambda} &= 109676 \left( \frac{1}{2^2} - \frac{1}{3^2} \right) = 109676 \left( \frac{9-4}{36} \right) \\ &= 109676 \times \frac{5}{36} \end{aligned}$$

$$\lambda = \frac{36}{109676 \times 5} = 6.561 \times 10^{-5} \text{ cm}$$

$$\lambda \text{ in } \text{\AA} = 6.561 \times 10^{-5} \times 10^8 = 6561 \text{ \AA}$$

$\therefore$  Wavelength of the spectral line is **6561 Å**

**SHORTCOMINGS OF THE BOHR ATOM**

- (1) The great success of the Bohr theory was in its ability to predict lines in the hydrogen atom spectrum. But **it was spectacularly unsuccessful for every other atom containing more than one electron.**
- (2) **We no longer believe in well-defined electron orbits as was assumed by Bohr.** In fact, in view of modern advances, like dual nature of matter, uncertainty principle, any mechanical model of the atom stands rejected.
- (3) **Bohr's model of electronic structure could not account for the ability of atoms to form molecules through chemical bonds.** Today we only accept Bohr's views regarding quantization as nobody has explained atomic spectra without numerical quantization and no longer attempted description of atoms on classical mechanics.
- (4) Bohr's theory could not explain the effect of magnetic field (Zeeman effect) and electric field (Stark effect) on the spectra of atoms.

**SOMMERFELD'S MODIFICATION OF BOHR ATOM**

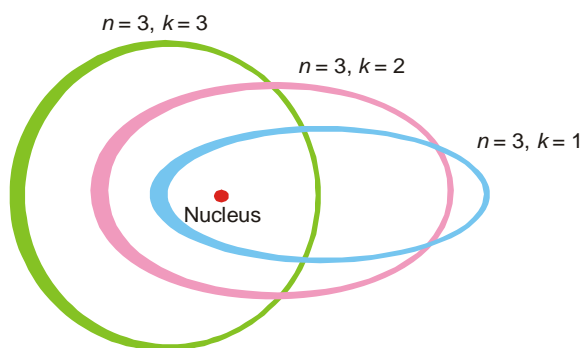
When spectra were examined with spectrometers, each line was found to consist of several closely packed lines. The existence of these multiple spectral lines could not be explained on the basis of Bohr's theory. Sommerfeld modified Bohr's theory as follows. **Bohr considered electron**

**orbits as circular but Sommerfeld postulated the presence of elliptic orbits also.** An ellipse has a major and minor axis. A circle is a special case of an ellipse with equal major and minor axis. The angular momentum of an electron moving in an elliptic orbit is also supposed to be quantized. Thus only a definite set of values is permissible. It is further assumed that the angular momentum can be an integral part of  $h/2\pi$  units, where  $h$  is Planck's constant. Or that,

$$\text{angular momentum} = \frac{kh}{2\pi}$$

where  $k$  is called the **azimuthal quantum number**, whereas the quantum number used in Bohr's theory is called the **principal quantum number**. The two quantum numbers  $n$  and  $k$  are related by the expression :

$$\frac{n}{k} = \frac{\text{length of major axis}}{\text{length of minor axis}}$$



■ **Figure 1.30**  
**Sommerfeld orbits in hydrogen atom.**

The values of  $k$  for a given value of  $n$  are  $k = n - 1, n - 2, n - 3$  and so on. A series of elliptic orbits with different eccentricities result for the different values of  $k$ . When  $n = k$ , the orbit will be circular. In other words  $k$  will have  $n$  possible values ( $n$  to 1) for a given value of  $n$ . However, calculations based on wave mechanics have shown that this is incorrect and the Sommerfeld's modification of Bohr atom fell through.

### ELECTRON ARRANGEMENT IN ORBITS

Having known that planetary electrons numerically equal to the atomic number are revolving about the atomic nucleus in closed orbits, the question arises as to how they are arranged in these orbits.

#### Langmuir Scheme

We are indebted to Langmuir for putting forward the first elaborate scheme of the arrangement of extranuclear electrons in 1919. His fundamental conception is that **the inert gases possess the most stable electron configuration and, therefore, contain complete electron orbits.** Since *helium* has two planetary electrons, the first orbit is considered fully saturated with 2 electrons. In the next inert gas *neon*, we have 10 planetary electrons and since 2 electrons would fully saturate the first orbit the remaining 8 will form the next stable orbit. Argon with atomic number 18 will similarly

**ELECTRONIC CONFIGURATION OF ELEMENTS**  
(ATOMIC NUMBERS ARE GIVEN AFTER THE SYMBOLS OF THE ELEMENTS)

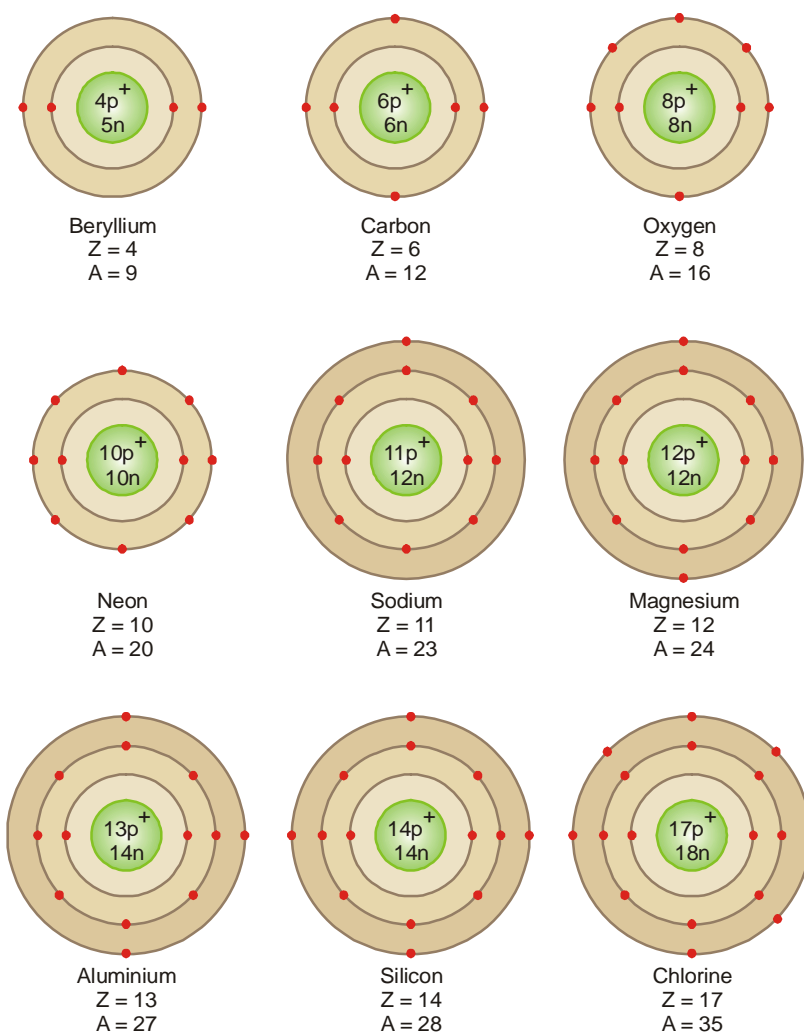
Group 0	Group 1		Group 2		Group 3		Group 4		Group 5		Group 6		Group 7		Group 8	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
	<b>H</b> 1												<b>H</b> 1			
	1												1			
<b>He</b> 2	<b>Li</b> 3		<b>Be</b> 4		<b>B</b> 5		<b>C</b> 6		<b>N</b> 7		<b>O</b> 8		<b>F</b> 9			
2	2, 1		2, 2		2, 3		2, 4		2, 5		2, 6		2, 7			
<b>Ne</b> 10	<b>Na</b> 11		<b>Mg</b> 12		<b>Al</b> 13		<b>Si</b> 14		<b>P</b> 15		<b>S</b> 16		<b>Cl</b> 17			
2, 8	2, 8, 1		2, 8, 2		2, 8, 3		2, 8, 4		2, 8, 5		2, 8, 6		2, 8, 7			
<b>Ar</b> 18	<b>K</b> 19		<b>Ca</b> 20		<b>Sc</b> 21		<b>Ti</b> 22		<b>V</b> 23		<b>Cr</b> 24		<b>Mn</b> 25		<b>Fe</b> 26	<b>Ni</b> 28
2, 8, 8	2, 8, 8, 1		2, 8, 8, 2		2, 8, 9, 2		2, 8, 10, 2		2, 8, 11, 2		2, 8, 12, 2		2, 8, 13, 2		2, 8, 14, 2	2, 8, 15, 2 2, 8, 16, 2
	<b>Cu</b> 29		<b>Zn</b> 30		<b>Ga</b> 31		<b>Ge</b> 32		<b>As</b> 33		<b>Se</b> 34		<b>Br</b> 35			
	2, 8, 17, 2		2, 8, 18, 2		2, 8, 18, 3		2, 8, 18, 4		2, 8, 18, 5		2, 8, 18, 6		2, 8, 18, 7			
<b>Kr</b> 36	<b>Rb</b> 37		<b>Sr</b> 38		<b>Y</b> 39		<b>Zr</b> 40		<b>Nb</b> 41		<b>Mo</b> 42		<b>Tc</b> 43		<b>Ru</b> 44	<b>Rh</b> 45 <b>Pd</b> 46
2, 8, 18, 8	2, 8, 18, 8, 1		2, 8, 18, 8, 2		2, 8, 18, 9, 2		2, 8, 18, 10, 2		2, 8, 18, 11, 2		2, 8, 18, 12, 2		2, 8, 18, 13, 2		2, 8, 18	2, 8, 18
	<b>Ag</b> 47		<b>Cd</b> 48		<b>In</b> 49		<b>Sn</b> 50		<b>Sb</b> 51		<b>Te</b> 52		<b>I</b> 53		14, 2	15, 2 16, 2
	2, 8, 18, 17, 2		2, 8, 18, 18, 2		2, 8, 18, 18, 3		2, 8, 18, 18, 4		2, 8, 18, 18, 5		2, 8, 18, 18, 6		2, 8, 18, 18, 7			
<b>Xe</b> 54	<b>Cs</b> 55		<b>Ba</b> 56		<b>La and Rare Earths (57-71)</b>		<b>Hf</b> 72		<b>Ta</b> 73		<b>W</b> 74		<b>Re</b> 75		<b>Os</b> 76	<b>Ir</b> 77 <b>Pt</b> 78
2, 8, 18, 18, 8	2, 8, 18, 18, 8, 1		2, 8, 18, 18, 8, 2		2, 8, 18, 18, 9, 2 to 2, 8, 18, 32, 9, 2		2, 8, 18, 32, 10, 2		2, 8, 18, 32, 11, 2		2, 8, 18, 32, 12, 2		2, 8, 18, 32, 13, 2		2, 8, 18, 32, 14, 2	2, 8, 18, 32, 15, 2 32, 16, 2
	<b>Au</b> 79		<b>Hg</b> 80		<b>Tl</b> 81		<b>Pb</b> 82		<b>Bi</b> 83		<b>Po</b> 84		<b>At</b> 85			
	2, 8, 18, 32, 17, 2		2, 8, 18, 32, 18, 2		2, 8, 18, 32, 18, 3		2, 8, 18, 32, 18, 4		2, 8, 18, 32, 18, 5		2, 8, 18, 32, 18, 6		2, 8, 18, 32, 18, 7			
<b>Rn</b> 86	<b>Fr</b> 87		<b>Ra</b> 88		<b>Ac</b> 89		<b>Th</b> 90		<b>Pa</b> 91		<b>U</b> 92					
2, 8, 18, 32, 18, 8	2, 8, 18, 32, 18, 8, 1		2, 8, 18, 32, 18, 8, 2		2, 8, 18, 32, 18, 9, 2		2, 8, 18, 32, 19, 9, 2		2, 8, 18, 32, 20, 9, 2		2, 8, 18, 32, 21, 9, 2					



have the similar arrangement 2, 8, 8. Proceeding in this manner the successive orbits would contain 2, 8, 8, 18, 32 electrons. Langmuir's scheme although quite correct for the first few elements, failed to explain the behaviour of higher elements.

### Bohr-Bury Scheme

In 1921, Bury put forward a modification of Langmuir scheme which is in better agreement with the physical and chemical properties of certain elements. At about the same time as Bury developed his scheme on chemical grounds, Bohr (1921) published independently an almost identical scheme of the arrangement of extra-nuclear electrons. He based his conclusions on a study of the emission spectra of the elements. Bohr-Bury scheme as it may be called, can be summarised as follows :



■ **Figure 1.31**

**Representation of some atomic models and their electron configuration elucidating Bohr-Bury theory.**

**Rule 1.** The maximum number of electrons which each orbit can contain is  $2 \times n^2$ , where  $n$  is the number of orbit.

The first orbit can contain  $2 \times 1^2 = 2$  ; second  $2 \times 2^2 = 8$  ; third  $2 \times 3^2 = 18$  ; fourth  $2 \times 4^2 = 32$ , and so on.

**Rule 2.** The maximum number of electrons in the outermost orbit is 8 and in the next-to-the outermost 18.

**Rule 3.** It is not necessary for an orbit to be completed before another commences to be formed. In fact, a new orbit begins when the outermost orbit attains 8 electrons.

**Rule 4.** The outermost orbit cannot have more than 2 electrons and next-to-outermost cannot have more than eight so long as the next inner orbit, in each case, has not received the maximum electrons as required by rule (1).

According to Bohr-Bury scheme the configuration of the inert gases is given in the table below :

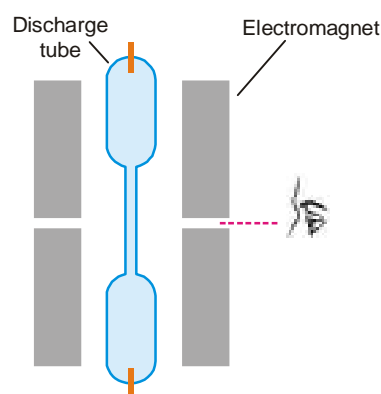
TABLE 1.4. ELECTRON CONFIGURATION OF INERT GASES							
Inert Gas	Atomic Number	Electron Orbits					
		1st (K)	2nd (L)	3rd (M)	4th (N)	5th (O)	6th (P)
Helium (He)	2	2	—	—	—	—	—
Neon (Ne)	10	2	8	—	—	—	—
Argon (Ar)	18	2	8	8	—	—	—
Krypton (Kr)	36	2	8	18	8	—	—
Xenon (Xe)	54	2	8	18	18	8	—
Radon (Rn)	86	2	8	18	32	18	8

A complete statement of the electron configuration of elements elucidating the various postulates of Bohr-Bury scheme is given in the table on page 31 for ready reference.

### ZEEMAN EFFECT

In 1896 Zeeman discovered that **spectral lines are split up into components when the source emitting lines is placed in a strong magnetic field**. It is called the Zeeman effect after the name of the discoverer. The apparatus used to observe Zeeman effect is shown in the Fig. 1.32.

It consists of electromagnets capable of producing strong magnetic field with pole pieces through which holes have been made lengthwise. Let a discharge tube or sodium vapour lamp emitting radiations be placed between the pole pieces. When the spectral lines are viewed axially through the hole in the pole pieces *i.e.*, parallel to the magnetic field, the line is found to split up into two components, one having shorter wavelength (higher frequency) and the other having higher wavelength (shorter frequency) than that of the original spectral line, which is no longer observable. The two



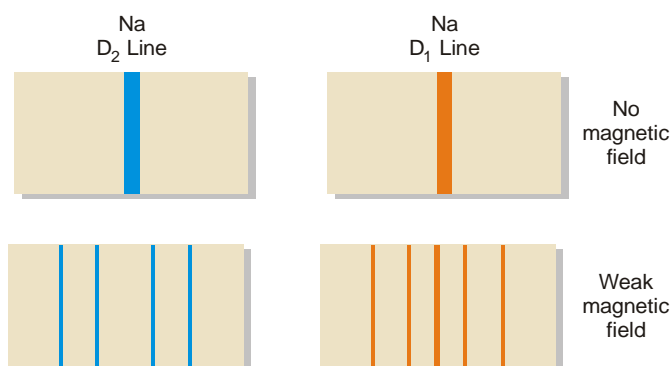
■ **Figure 1.32**  
Zeeman effect.

lines are symmetrically situated around the position of the original line and the change in wavelength is termed the Zeeman shift (denoted as  $d\lambda$ ). When viewed in a direction perpendicular to the applied field the lines split up into three, the central one having the same wavelength and frequency as that of the original line and the other two occupying the same position as observed earlier.

In order to explain Zeeman effect, let us consider motion of an electron in a particular orbit corresponding to its permitted angular momentum. The motion of the electron in an orbit is equivalent to a current in a loop of wire. If a current carrying loop of wire be placed in a magnetic field, it experiences a torque, and energy of the system depends upon the orientation of the loop with respect to magnetic field. The correct values of the energies are obtained if the components of the angular momentum of the electron along the direction of the magnetic field are restricted to the value

$$= m \times \frac{h}{2\pi}$$

where  $m = 0, \pm 1, \pm 2, \dots$  and so on. Corresponding to these values of  $m$ , a given line splits into as many lines. Hence for each frequency of a radiation emitted by the atom in the absence of magnetic field, there are several possible frequencies in the presence of it. This is, in fact, the cause of Zeeman Effect.



■ **Figure 1.33**  
Splitting of the  $D_2$  and  $D_1$  lines in the sodium spectrum by a weak magnetic field (Illustration of Zeeman effect).

The shift in the frequency  $d\lambda$  for each of the component lines is given by Lorentz's theoretically derived equation as

$$\text{Zeeman shift } d\lambda = \pm \frac{He\lambda^2}{4\pi mc}$$

where  $H$  is the strength of magnetic field,  $e$  the electronic charge,  $m$  the mass of electron,  $c$  the velocity of light and  $\lambda$  the wavelength of the original line in the absence of magnetic field. The equation can also be written as

$$\frac{e}{m} = \pm \frac{4\pi cd\lambda}{H\lambda^2}$$

The validity of the above equation can be tested experimentally by observing the Zeeman shift  $d\lambda$  for a given light source of known  $\lambda$  (say D-line of sodium) for a magnetic field of known strength  $H$  and calculating the value of  $e/m$  for the above equation. Lorentz found that the  $e/m$  of the electrons found by this method comes out to be the same as by any other method.

## EXAMINATION QUESTIONS

- Define or explain the following terms :
  - Neutrons
  - Nucleons
  - Atomic number
  - Mass Number
  - Photoelectric effect
  - Threshold energy
- Give an account of the experiment which led Rutherford to conclude that every atom has a positively charged nucleus which occupies a very small volume. What were the drawbacks of Rutherford's nuclear model of the atom? How did Bohr rectify the drawbacks of Rutherford model?
- State the postulates of Bohr's theory of the hydrogen atom. Derive an expression for the  $n$ th orbit of a hydrogen atom. Derive an expression for the radius of any orbit in the atom.
  - Calculate the energy of transition involving  $n_1 = 6$  to  $n_2 = 3$  in a hydrogen atom, given that Rydberg constant  $R = 109737.32 \text{ cm}^{-1}$  and  $h = 6.63 \times 10^{-34} \text{ J sec}$ .  
**Answer.** (b)  $1.818 \times 10^{-19} \text{ J}$
- Discuss Bohr's model of an atom. Show how it successfully explains the spectra of hydrogen atom.
  - Calculate the velocity of the electron in the first Bohr's orbit. ( $h = 6.625 \times 10^{-27} \text{ erg sec}$ ;  $r = 0.529 \text{ \AA}$ ;  $m = 9.109 \times 10^{-28} \text{ g}$ )  
**Answer.** (b)  $2.189 \times 10^8 \text{ cm sec}^{-1}$
- Explain Mosley's contribution towards the structure of the atom.
  - Give the defects of Rutherford's model of atom. What suggestions were given by Bohr to remove these defects?
- Calculate the radius of the third orbit of hydrogen atom. ( $h = 6.625 \times 10^{-27} \text{ erg sec}$ ;  $r = 0.529 \text{ \AA}$ ;  $m = 9.109 \times 10^{-28} \text{ g}$ ;  $e = 4.8 \times 10^{-10} \text{ esu}$ )  
**Answer.** (b)  $4.763 \times 10^{-8}$
- Calculate the wavelength of the first line in Balmer series of hydrogen spectrum. ( $R = 109677 \text{ cm}^{-1}$ )  
**Answer.** 1215 Å
- How does Bohr's theory explain the spectrum of hydrogen atom?
  - Calculate the wavelength associated with an electron moving with a velocity of  $1 \times 10^8 \text{ cm sec}^{-1}$ . Mass of an electron =  $9.1 \times 10^{-28} \text{ g}$   
**Answer.** (b)  $7.28 \times 10^{-8} \text{ cm}$
- A line at 434 nm in Balmer series of spectrum corresponds to a transition of an electron from the  $n$ th to 2nd Bohr orbit. What is the value of  $n$ ?  
**Answer.**  $n = 5$
- Explain Rutherford's atomic model. What are its limitations?
  - State and explain Ritz combination principle.
  - Calculate the radius of third orbit of hydrogen atom. ( $h = 6.625 \times 10^{-27} \text{ erg sec}$ ;  $m = 9.1091 \times 10^{-28} \text{ g}$ ;  $e = 4.8 \times 10^{-10} \text{ esu}$ )
  - Calculate the wavelength of first line in Balmer series of hydrogen spectrum. ( $R = \text{Rydberg's constant} = 109677 \text{ cm}^{-1}$ )  
**Answer.** (c)  $4.763 \times 10^{-8} \text{ cm}$  (d) 1215 Å
- Describe various series in hydrogen spectrum and calculate energy levels of hydrogen atom.
- Write Rutherford's experiment of scattering of  $\alpha$ -particles and give the drawbacks of atomic model.
- Write notes on :
  - Merits and demerits of Bohr's theory
  - Assumptions of Bohr's atomic model
- Based on Bohr's calculations, establish the energy expression of the rotating electron in hydrogen like atomic species.

15. Give an account of Bohr's theory of atomic structure and show how it explains the occurrence of spectral lines in the atomic spectra of hydrogen.
16. The electron energy in hydrogen atom is given by  $E = -21.7 \times 10^{-12}/n^2$  ergs. Calculate the energy required to remove an electron completely from the  $n = 2$  orbit. What is the longest wavelength (in cm) of light that can be used to cause this transition?  
**Answer.**  $-5.42 \times 10^{-12}$  erg;  $3.67 \times 10^{-5}$  cm
17. In a hydrogen atom, an electron jumps from 3rd orbit to first orbit. Find out the frequency and wavelength of the spectral line.  
**Answer.** 1025.6 Å (Agra BSc, 2000)
18. The energy of the electron in the second and third orbits of the hydrogen atom is  $-5.42 \times 10^{-12}$  erg and  $-2.41 \times 10^{-12}$  erg respectively. Calculate the wavelength of the emitted radiation when the electron drops from third to second orbit.  
**Answer.** 6600 Å (Kolkata BSc, 2000)
19. Calculate the wavelength in Å of the photon that is emitted when an electron in Bohr orbit  $n = 2$  returns to the orbit  $n = 1$  in the hydrogen atom. The ionisation potential in the ground state of hydrogen atom is  $2.17 \times 10^{-11}$  erg per atom.  
**Answer.** 1220 Å (Osmania BSc, 2000)
20. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition  $n = 4$  to  $n = 2$  of  $\text{He}^+$  transition?  
**Answer.**  $n = 2$  to  $n = 1$  (Baroda BSc, 2001)
21. (a) State postulates of Bohr's theory of an atom and derive an expression for radius of Bohr orbit of hydrogen atom.  
(b) Give any four limitations of Bohr's theory of an atom. (Nagpur BSc, 2002)
22. Describe Rutherford's model of the atom. How was it improved by Bohr? (Arunachal BSc, 2002)
23. Atomic hydrogen is excited to the 4th energy level from the ground state. Determine  
(a) the number of lines emitted and  
(b) the shortest wavelength present in the emission spectrum. ( $R_H = 109677 \text{ cm}^{-1}$ )  
**Answer.** (a) 3; (b) 972.55 Å (Vidyasagar BSc, 2002)
24. Radius of the first Bohr orbit of H-atom is 0.529 Å. Find the radii of the first and second Bohr orbit of  $\text{Li}^{2+}$  ion.  
**Answer.** (a) 0.1763 Å; (b) 0.7053 Å (Vidyasagar BSc, 2002)
25. If the energy difference between the ground state of an atom and its excited state is  $4.4 \times 10^{-19}$  J, what is the wavelength of the photon required to produce this transition?  
**Answer.**  $4.517 \times 10^{-7}$  m (Madras BSc, 2003)
26. Calculate the wavelength and energy of radiations emitted for the electronic transition from infinity ( $\infty$ ) to stationary state of the hydrogen atom. ( $R = 1.09678 \times 10^7 \text{ m}^{-1}$ ;  $h = 6.625 \times 10^{-34}$  Joule sec and  $c = 2.9979 \times 10^8 \text{ m sec}^{-1}$ )  
**Answer.**  $9.11 \times 10^{-6}$  m;  $217.9 \times 10^{-23}$  kJ (Gulbarga BSc, 2003)
27. The energy transition in hydrogen atom occurs from  $n = 3$  to  $n = 2$  energy level. ( $R = 1.097 \times 10^7 \text{ m}^{-1}$ ).  
(a) Calculate the wavelength of the emitted electron.  
(b) Will this electron be visible?  
(c) Which spectrum series does this photon belong to? (Jadavpur BSc, 2003)
28. Calculate the energy emitted when electrons of 1.0 g of hydrogen undergo transition giving the spectral line of lowest energy in the visible region of its atomic spectrum ( $R = 1.1 \times 10^7 \text{ m}^{-1}$ ;  $c = 3 \times 10^8 \text{ m sec}^{-1}$ ;  $h = 6.62 \times 10^{-34} \text{ J sec}$ )  
**Answer.** 182.5 kJ (Panjab BSc, 2004)

29. In hydrogen atom the energy of the electron in first Bohr's orbit is  $-1312 \times 10^5 \text{ J mol}^{-1}$ . What is the energy required for the excitation of second Bohr's orbit ? (Burdwan BSc, 2005)  
**Answer.**  $9.84 \times 10^5 \text{ J mol}^{-1}$
30. Calculate the wavelength in Å of the photon that is emitted when an electron in Bohr orbit  $n = 2$  returns to the orbit  $n = 1$  in the hydrogen atom. The ionisation potential in the ground state of hydrogen atom is  $2.17 \times 10^{-11}$  erg per atom. (Kalayani BSc, 2005)  
**Answer.** 1220 Å
31. A line at 434 nm in Balmer series of spectrum corresponds to a transition of an electron from the  $n$ th to 2nd Bohr orbit. What is the value of  $n$  ? (Gulbarga BSc, 2006)  
**Answer.**  $n = 5$
32. The energy transition in hydrogen atom occurs from  $n = 3$  to  $n = 2$  energy level. ( $R = 1.097 \times 10^7 \text{ m}^{-1}$ ).  
 (i) Calculate the wavelength of the emitted electron (ii) Will this electron be visible ? (iii) Which spectrum series does this photon belong to ? (Vikram BSc, 2006)  
**Answer.** 6564 Å ; Yes ; Balmer series
33. The energy of the electron in the second and third Bohr orbits of the hydrogen atom is  $-5.42 \times 10^{-12}$  erg and  $-2.41 \times 10^{-12}$  erg respectively. Calculate the wavelength of the emitted radiation when the electron drops from third to second orbit. (Calicut BSc, 2006)  
**Answer.** 6600 Å

### MULTIPLE CHOICE QUESTIONS

- Cathode rays are deflected by  
 (a) electric field only (b) magnetic field only  
 (c) electric and magnetic field (d) none of these  
**Answer.** (c)
- The  $e/m$  value for the particles constituting cathode rays is the same regardless of  
 (a) the gas present in cathode rays tube (b) the metal of which cathode was made  
 (c) both of these (d) none of these  
**Answer.** (c)
- The charge to mass ratio ( $e/m$ ) of positive particles  
 (a) varies with the nature of gas in discharge tube  
 (b) is independent of the gas in discharge tube  
 (c) is constant  
 (d) none of the above  
**Answer.** (a)
- A sub atomic particle which has one unit mass and one unit positive charge is known as  
 (a) hydrogen atom (b) neutron  
 (c) electron (d) proton  
**Answer.** (d)
- Atomic number of an element is equal to the number of \_\_\_\_\_ in the nucleus of the atom.  
 (a) neutrons (b) protons  
 (c) both the neutrons and protons (d) electrons  
**Answer.** (b)
- The mass number of an atom is equal to the number of \_\_\_\_\_ in the nucleus of an atom  
 (a) protons (b) neutrons

(c) electrons

(d) nucleons

**Answer.** (d)

7. If  $Z$  is the number of proton and  $A$  the number of nucleons, then the number of neutrons in an atom is given by

(a)  $A + Z$

(b)  $A - Z$

(c)  $Z - A$

(d) none of these

**Answer.** (b)

8. The mass number and atomic number of Phosphorus atom are 31 and 15 respectively. The number of neutrons in the nucleus is

(a) 15

(b) 16

(c) 31

(d) 46

**Answer.** (b)

9. In a sodium atom (atomic number = 11 and mass number = 23), the number of neutrons is

(a) equal to the number of protons

(b) less than the number of protons

(c) greater than the number of protons

(d) none of these

**Answer.** (c)

10. Which of the following is not correct for electromagnetic waves?

(a) the wavelength is the distance between two successive crests

(b) the frequency is the number of waves which pass a given point in one second

(c) the velocity of a wave is the distance covered by the particular wave in one second

(d) all electromagnetic waves have equal wavelengths

**Answer.** (d)

11. Which of the following relations is not correct?

(a)  $c = \lambda \times \nu$

(b)  $\bar{\nu} = \frac{1}{\lambda}$

(c)  $\bar{\nu} = \frac{1}{\lambda}$

(d)  $\lambda = c \div \nu$

**Answer.** (b)

12. The unit in which wave number is measured

(a) hertz

(b)  $\text{sec}^{-1}$

(c) nanometer

(d)  $\text{cm}^{-1}$

**Answer.** (d)

13. In the spectrum of hydrogen atom, the series which falls in ultraviolet region is

(a) Lyman series

(b) Balmer series

(c) Paschen series

(d) Brackett series

**Answer.** (a)

14. The Balmer series in the spectrum of hydrogen atom falls in

(a) ultraviolet region

(b) visible region

(c) infrared region

(d) none of these

**Answer.** (b)

15. The energy of a photon is given by the relation

(a)  $E = \frac{h \nu}{\lambda}$

(b)  $E = \frac{h c}{\lambda}$

(c)  $E = \frac{h \times c}{\nu}$

(d)  $E = \frac{\lambda \times c}{h}$

**Answer.** (b)

16. When a beam of light of sufficiently high frequency is allowed to strike a metal surface in vacuum, electrons are ejected from the metal surface. This phenomenon is called

(a) Black body radiation

(b) Photoelectric effect

(c) Zeeman effect

(d) Stark effect

**Answer.** (b)

17. In photoelectric effect, the kinetic energy of the photoelectrons increases linearly with the  
 (a) wavelength of the incident light (b) frequency of the incident light  
 (c) velocity of the incident light (d) none of these  
**Answer.** (b)
18. The kinetic energy of the photoelectrons emitted from the metal surface is given by the relation ( $\nu_0$  is the threshold frequency and  $\nu$  is the frequency of incident light)  
 (a)  $\frac{1}{2} m v^2 = h\nu - h\nu_0$  (b)  $\frac{1}{2} m v^2 = h\nu + h\nu_0$   
 (c)  $\frac{1}{2} m v^2 = h\nu$  (d)  $\frac{1}{2} m v^2 = h\nu_0$   
**Answer.** (a)
19. In Bohr's model of atom, the angular momentum of an electron orbiting around the nucleus is given by the relation  
 (a)  $m v r = \frac{h}{2\pi}$  (b)  $m v r = \frac{n h}{2\pi}$   
 (c)  $m v r = \frac{n^2 h^2}{4\pi}$  (d)  $m v r = \frac{n h}{4\pi}$   
**Answer.** (b)
20. The radius of first orbit in hydrogen atom according to Bohr's Model is given by the relation  
 (a)  $r = \frac{h^2}{4\pi^2 m e^2}$  (b)  $r = \frac{h}{4\pi^2 m e^2}$   
 (c)  $r = \frac{h^2}{4\pi m e^2}$  (d)  $r = \frac{h^2}{4\pi m e^4}$   
**Answer.** (a)
21. The radius of first orbit in hydrogen atom is  $0.529 \text{ \AA}$ . The radius of second orbit is given by  
 (a)  $\frac{1}{2} \times 0.529 \text{ \AA}$  (b)  $2 \times 0.529 \text{ \AA}$   
 (c)  $4 \times 0.529 \text{ \AA}$  (d)  $8 \times 0.529 \text{ \AA}$   
**Answer.** (c)
22. The energy of an electron in the first orbit in hydrogen atom is  $-313.6/n^2 \text{ kcal mol}^{-1}$ . The energy of the electron in 3rd orbit is given by the relation  
 (a)  $E_3 = \frac{-313.6}{3} \text{ kcal mol}^{-1}$  (b)  $E_3 = \frac{-313.6}{2} \text{ kcal mol}^{-1}$   
 (c)  $E_3 = \frac{-313.6}{9} \text{ kcal mol}^{-1}$  (d)  $E_3 = -313.6 \times 3 \text{ kcal mol}^{-1}$   
**Answer.** (c)
23. Lyman series is obtained when the electrons from higher energy levels return to  
 (a) 1st orbit (b) 2nd orbit  
 (c) 3rd orbit (d) 4th orbit  
**Answer.** (a)
24. A line in Pfund series is obtained when an electron from higher energy levels returns to  
 (a) 1st orbit (b) 3rd orbit  
 (c) 5th orbit (d) 6th orbit  
**Answer.** (c)
25. The energy of an electron in Bohr's atom \_\_\_\_\_ as we move away from the nucleus  
 (a) remains the same (b) decreases  
 (c) increases (d) sometimes increases, sometimes decreases  
**Answer.** (c)
26. When an electron drops from a higher energy level to a lower energy level, then  
 (a) the energy is absorbed (b) the energy is released  
 (c) the nuclear charge increases (d) the nuclear charge decreases  
**Answer.** (b)



27. The spectrum of hydrogen atom is similar to that of  
(a)  $H^+$  ion (b)  $He^+$  ion  
(c)  $Li^+$  ion (d)  $Na^+$  ion  
**Answer.** (b)
28. If  $r$  is the radius of first orbit, the radius of  $n$ th orbit of hydrogen atom will be  
(a)  $n^2 r$  (b)  $n r$   
(c)  $n/r$  (d)  $r/n$   
**Answer.** (a)
29. The ratio of radii of second and first orbit of hydrogen atom according to Bohr's model is  
(a) 2:1 (b) 1:2  
(c) 4:1 (d) 1:4  
**Answer.** (c)
30. The spectrum of helium is expected to be similar to that of  
(a) H-atom (b) Li atom  
(c)  $Li^+$  ion (d)  $Na^+$  ion  
**Answer.** (c)
31. Electromagnetic radiations with minimum wavelength is  
(a) ultraviolet (b) X-rays  
(c) infrared (d) radiowaves  
**Answer.** (b)
32. Which of the following statements is false?  
(a) electrons travel around the nucleus in specific permitted circular orbits  
(b) an electron does not lose energy as long as it moves in its specified orbits  
(c) an electron can jump from one energy level to another by absorbing or losing energy  
(d) the angular momentum of an electron is not quantised  
**Answer.** (d)
33. The idea of stationary orbits was first given by  
(a) Rutherford (b) JJ Thomson  
(c) Niels Bohr (d) Max Planck  
**Answer.** (c)
34. The maximum number of electrons that can be accommodated in an orbit is  
(a)  $2n$  (b)  $n^2$   
(c)  $2n^2$  (d)  $2n + 1$   
**Answer.** (c)
35. The maximum number of electrons in the outermost orbit is  
(a) 2 (b) 8  
(c) 18 (d) 32  
**Answer.** (b)
36. When the source emitting lines is placed in a strong magnetic field the spectral lines are split into its components. This effect is called  
(a) Compton effect (b) Zeeman effect  
(c) Rydberg effect (d) Photoelectric effect  
**Answer.** (b)
37. The number of electrons in the outermost shell of Potassium (at. no. 19) is  
(a) 1 (b) 2  
(c) 8 (d) 9  
**Answer.** (a)
38. An atom of silicon with atomic number 14 has the following number of electrons in the outermost shell  
(a) 1 (b) 2  
(c) 4 (d) 8  
**Answer.** (c)

39. Inert gases possess the most stable electronic configuration as they contain  
(a) fully filled outermost shell (b) half filled outermost shell  
(c) two electrons in the outermost shell (d) eight electrons in the outermost shell  
**Answer.** (d)
40. The effect of electric field on the spectra of atoms is called  
(a) Compton effect (b) Photoelectric effect  
(c) Stark effect (d) Zeeman effect  
**Answer.** (c)
41. Which one of the following species has the same number of electrons as an atom of Neon?  
(a)  $O^{2-}$  (b) Na  
(c) Mg (d)  $K^+$   
**Answer.** (a)
42. The energy of an electron in the first Bohr orbit for hydrogen is  
(a) 13.6 eV (b) -13.6 eV  
(c) 1.36 eV (d) -1.36 eV  
**Answer.** (b)
43. The energy of hydrogen atom in its ground state is -13.6 eV. The energy of the level corresponding to  $n = 3$  is  
(a) -4.53 eV (b) -2.265 eV  
(c) -1.51 eV (d) none of these  
**Answer.** (c)
44.  $E_n = -1311.8 \text{ kJ mol}^{-1}$ . If the value of  $E$  is  $-52.44 \text{ kJ mol}^{-1}$ , to which value ' $n$ ' corresponds?  
(a) 2 (b) 3  
(c) 4 (d) 5  
**Answer.** (d)
45. The spectral line lies in the Lyman series. It corresponds to the radiation emitted by an electron jumping from higher energy states to  
(a) first energy state (b) second energy state  
(c) third energy state (d) fifth energy state  
**Answer.** (a)
46. The ground state of an atom corresponds to a state of  
(a) maximum energy (b) minimum energy  
(c) zero energy (d) negative energy  
**Answer.** (b)
47. Balmer series in the spectrum of hydrogen atom lies in  
(a) ultraviolet region (b) visible region  
(c) infrared region (d) none of these  
**Answer.** (b)
48. The spectrum of H-atom is expected to be similar to that of  
(a)  $Li^+$  (b)  $Na^+$   
(c)  $He^+$  (d)  $K^+$   
**Answer.** (c)
49. An atom of Calcium (at. no. 20) contains \_\_\_\_\_ electrons in the third energy level.  
(a) 2 (b) 8  
(c) 10 (d) 18  
**Answer.** (b)
50. Out of the following pairs of elements which has the same number of electrons in the outer most energy level?  
(a) helium and lithium (b) boron and carbon  
(c) carbon and nitrogen (d) lithium and hydrogen  
**Answer.** (d)

## 2

# Structure of Atom —Wave Mechanical Approach

## CHAPTER

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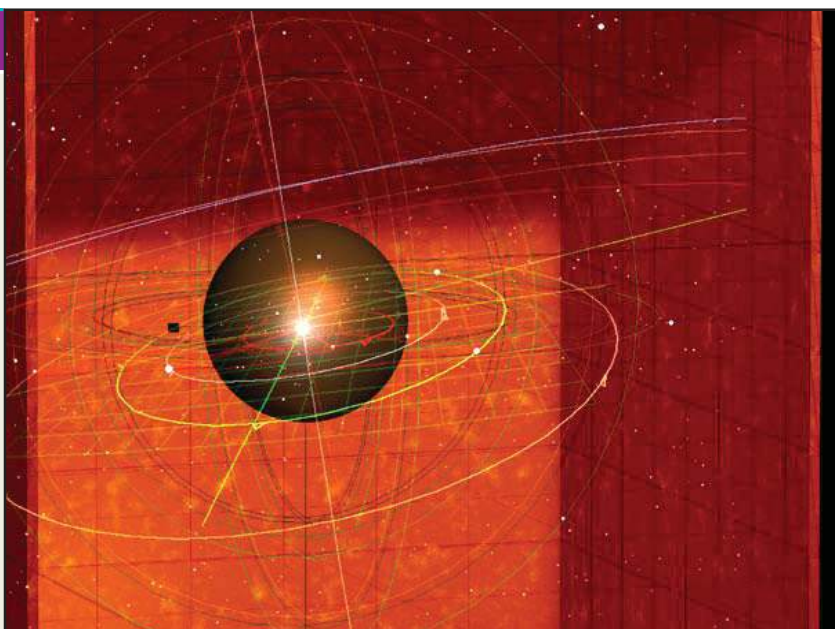
ENERGY DISTRIBUTION AND  
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## WAVE MECHANICAL CONCEPT OF ATOM

Bohr, undoubtedly, gave the first quantitative successful model of the atom. But now it has been superseded completely by the modern *Wave Mechanical Theory*. The new theory rejects the view that electrons move in closed orbits, as was visualised by Bohr. The Wave mechanical theory gave a major breakthrough by suggesting that the electron motion is of a complex nature best described by its wave properties and probabilities.

While the classical 'mechanical theory' of matter considered matter to be made of discrete particles (atoms, electrons, protons etc.), another theory called the 'Wave theory' was necessary to interpret the nature of radiations like X-rays and light. According to the wave theory, radiations as X-rays and light, consisted of continuous collection of waves travelling in space.

The wave nature of light, however, failed completely to explain the photoelectric effect *i.e.* the emission of electron from metal surfaces by the action of light. In their attempt to find a plausible explanation of radiations from heated bodies as also the photoelectric effect, Planck and Einstein (1905) proposed that energy radiations, including those of heat and light, are emitted

discontinuously as little ‘bursts’, quanta, or photons. This view is directly opposed to the wave theory of light and it gives particle-like properties to waves. **According to it, light exhibits both a wave and a particle nature, under suitable conditions.** This theory which applies to all radiations, is often referred to as the ‘**Wave Mechanical Theory**’.

With Planck’s contention of light having wave and particle nature, the distinction between particles and waves became very hazy. In 1924 Louis de Broglie advanced a complimentary hypothesis for material particles. According to it, the dual character—the wave and particle—may not be confined to radiations alone but should be extended to matter as well. In other words, matter also possessed particle as well as wave character. This gave birth to the ‘**Wave mechanical theory of matter**’. This theory postulates that electrons, protons and even atoms, when in motion, possessed wave properties and could also be associated with other characteristics of waves such as wavelength, wave-amplitude and frequency. **The new quantum mechanics, which takes into account the particulate and wave nature of matter, is termed the Wave mechanics.**

### de BROGLIE’S EQUATION

de Broglie had arrived at his hypothesis with the help of Planck’s Quantum Theory and Einstein’s Theory of Relativity. He derived a relationship between the magnitude of the wavelength associated with the mass ‘ $m$ ’ of a moving body and its velocity. According to Planck, the photon energy ‘ $E$ ’ is given by the equation

$$E = h\nu \quad \dots(i)$$

where  $h$  is Planck’s constant and  $\nu$  the frequency of radiation. By applying Einstein’s mass-energy relationship, the energy associated with photon of mass ‘ $m$ ’ is given as

$$E = mc^2 \quad \dots(ii)$$

where  $c$  is the velocity of radiation

Comparing equations (i) and (ii)

$$mc^2 = h\nu = h \frac{c}{\lambda} \quad \left( \because \nu = \frac{c}{\lambda} \right)$$

$$\text{or} \quad mc = \frac{h}{\lambda} \quad \dots(iii)$$

$$\text{or} \quad \text{mass} \times \text{velocity} = \frac{h}{\text{wavelength}}$$

$$\text{or} \quad \text{momentum } (p) = \frac{h}{\text{wavelength}}$$

$$\text{or} \quad \text{momentum} \propto \frac{1}{\text{wavelength}}$$

The equation (iii) is called **de Broglie’s equation** and may be put in words as : **The momentum of a particle in motion is inversely proportional to wavelength, Planck’s constant ‘ $h$ ’ being the constant of proportionality.**

The wavelength of waves associated with a moving material particle (matter waves) is called **de Broglie’s wavelength**. The de Broglie’s equation is true for all particles, but it is only with very small particles, such as electrons, that the wave-like aspect is of any significance. Large particles in motion though possess wavelength, but it is not measurable or observable. Let us, for instance consider de Broglie’s wavelengths associated with two bodies and compare their values.

#### (a) For a large mass

Let us consider a stone of mass 100 g moving with a velocity of 1000 cm/sec. The de Broglie’s wavelength  $\lambda$  will be given as follows :

$$\lambda = \frac{6.6256 \times 10^{-27}}{100 \times 1000} \quad \left( \lambda = \frac{h}{\text{momentum}} \right)$$

$$= 6.6256 \times 10^{-32} \text{ cm}$$

This is too small to be measurable by any instrument and hence no significance.

**(b) For a small mass**

Let us now consider an electron in a hydrogen atom. It has a mass =  $9.1091 \times 10^{-28}$  g and moves with a velocity  $2.188 \times 10^{-8}$  cm/sec. The de Broglie's wavelength  $\lambda$  is given as

$$\lambda = \frac{6.6256 \times 10^{-27}}{9.1091 \times 10^{-28} \times 2.188 \times 10^{-8}}$$

$$= 3.32 \times 10^{-8} \text{ cm}$$

This value is quite comparable to the wavelength of X-rays and hence detectable.

It is, therefore, reasonable to expect from the above discussion that **everything in nature possesses both the properties of particles (or discrete units) and also the properties of waves (or continuity)**. The properties of large objects are best described by considering the particulate aspect while properties of waves are utilized in describing the essential characteristics of extremely small objects beyond the realm of our perception, such as electrons.

### THE WAVE NATURE OF ELECTRON

de Broglie's revolutionary suggestion that moving electrons had waves of definite wavelength associated with them, was put to the acid test by Davison and Germer (1927). They demonstrated the physical reality of the wave nature of electrons by showing that a beam of electrons could also be *diffracted* by crystals just like light or X-rays. They observed that the diffraction patterns thus obtained were just similar to those in case of X-rays. It was possible that electrons by their passage through crystals may produce secondary X-rays, which would show diffraction effects on the screen. Thomson ruled out this possibility, showing that the electron beam as it emerged from the crystals, underwent deflection in the electric field towards the positively charged plate.

#### Davison and Germers Experiment

In their actual experiment, Davison and Germer studied the scattering of slow moving electrons by reflection from the surface of nickel crystal. They obtained electrons from a heated filament and passed the stream of electrons through charged plates kept at a potential difference of  $V$  *esu*. Due to the electric field of strength  $V \times e$  acting on the electron of charge  $e$ , the electrons emerge out with a uniform velocity  $v$  units. The kinetic energy  $\frac{1}{2}mv^2$  acquired by an electron due to the electric field shall be equal to the electrical force. Thus,

$$\frac{1}{2}mv^2 = Ve$$

or 
$$v = \sqrt{\frac{2Ve}{m}}$$

Multiplying by  $m$  on both sides,

$$mv = m \sqrt{\frac{2Ve}{m}} = \sqrt{2mVe} \quad \dots(i)$$

But according to de Broglie's relationship

$$mv = \frac{h}{\lambda} \quad \dots(ii)$$

Comparing (i) and (ii)

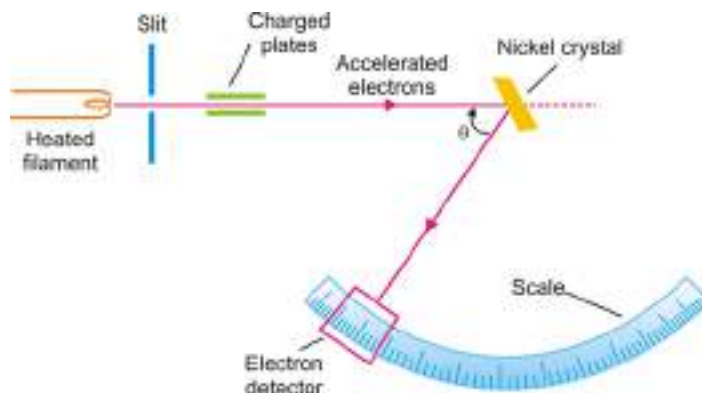
$$\frac{h}{\lambda} = \sqrt{2mVe}$$

$$\therefore \lambda = \frac{h}{\sqrt{2mVe}} = \sqrt{\frac{h^2}{2mVe}}$$

Substituting for  $h = 6.6256 \times 10^{-27}$  erg-sec,  $m = 9.1091 \times 10^{-28}$  g,  $e = 4.803 \times 10^{-10}$  esu, and changing  $V$  esu to  $V$  volts by using the conversion factor  $\frac{1}{3} \times 10^{-2}$ , we have

$$\begin{aligned} \lambda &= \sqrt{\frac{(6.6256 \times 10^{-27})^2 \times 0.33 \times 10^{-2}}{2 \times 9.1091 \times 10^{-28} \times 4.803 \times 10^{-10} V \text{ volts}}} \\ &= \sqrt{\frac{150}{V \text{ volts}}} \times 10^{-8} \text{ cm} = \sqrt{\frac{150}{V \text{ volts}}} \text{ \AA} \quad \dots(iii) \end{aligned}$$

If a potential difference of 150 volts be applied, the wavelength of electrons emerging out is  $\lambda = 1 \text{ \AA}$ . Similarly if a potential difference of 1500 volts be created, the electrons coming out shall have a wavelength  $0.1 \text{ \AA}$ . It is clear, therefore, that electrons of different wavelengths can be obtained by changing the potential drop. These wavelengths are comparable with those of X-rays and can undergo diffraction.



■ **Figure 2.1**  
**Schematic representation of the apparatus**  
**used by Davison and Germer.**

The electrons when they fall upon the nickel crystal, get diffracted. Electrons of a definite wavelength get diffracted along definite directions. The electron detector measures the angle of diffraction (say  $\theta$ ) on the graduated circular scale. According to Bragg's diffraction equation, the wavelength  $\lambda$  of the diffracted radiation is given by  $\lambda = d \sin \theta$ , where  $d$  is a constant ( $= 2.15$  for Ni crystal) and  $\theta$  the angle of diffraction. By substituting the experimental value of  $\theta$  in Bragg's equation ( $\lambda = d \sin \theta$ ), the wavelength of electrons may be determined. This wavelength would be found to agree with the value of  $\lambda$ , as obtained from equation (iii).

Since diffraction is a property exclusively of wave motion, Davison and Germer's 'electron diffraction' experiment established beyond doubt the wave nature of electrons. We have described earlier in this chapter that electrons behave like particles and cause mechanical motion in a paddle

wheel placed in their path in the discharge tube. This proves, therefore, that electrons not only behave like ‘particles’ in motion but also have ‘wave properties’ associated with them. It is not easy at this stage to obtain a pictorial idea of this new conception of the motion of an electron. But the application of de Broglie’s equation to Bohr’s theory produces an important result. The quantum restriction of Bohr’s theory for an electron in motion in the circular orbit is that the angular momentum ( $mvr$ ) is an integral multiple ( $n$ ) of  $h/2\pi$ . That is,

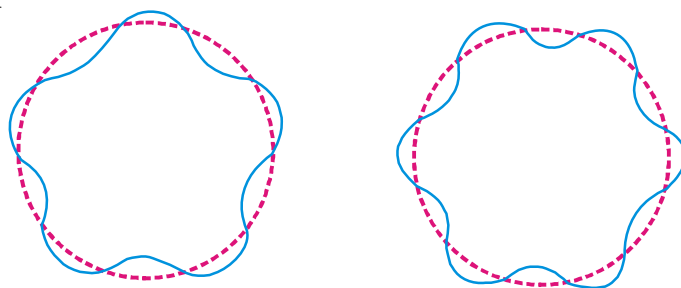
$$mvr = n \frac{h}{2\pi} \quad \dots \text{Bohr Theory}$$

On rearranging, we get

$$2\pi r = n \frac{h}{mv}$$

Putting the value of  $\frac{h}{mv}$  from equation (i), we have

$$2\pi r = n\lambda \quad \left( \because \lambda = \frac{h}{mv} \right)$$



■ **Figure 2.2**

**de Broglie's wave accommodated in Bohr's orbits.  
For these two wave trains the value of  $n$  is different.**

Now the electron wave of wavelength  $\lambda$  can be accommodated in Bohr's orbit only if the circumference of the orbit,  $2\pi r$ , is an integral multiple of its wavelength. Thus de Broglie's idea of standing electron waves stands vindicated. However, if the circumference is bigger, or smaller than  $n\lambda$ , the wave train will go out of phase and the destructive interference of waves causes radiation of energy.

**SOLVED PROBLEM.** Calculate the wavelength of an electron having kinetic energy equal to  $4.55 \times 10^{-25}$  J. ( $h = 6.6 \times 10^{-34}$  kg m<sup>2</sup> sec<sup>-1</sup> and mass of electron =  $9.1 \times 10^{-31}$  kg).

**SOLUTION**

$$\begin{aligned} \text{Kinetic energy of an electron} &= \frac{1}{2} mv^2 \\ &= 4.55 \times 10^{-25} \text{ J (given)} \\ &= 4.55 \times 10^{-25} \text{ kg m}^2 \text{ sec}^{-2} \end{aligned}$$

$$\begin{aligned} \text{or} \quad v^2 &= \frac{2 \times 4.55 \times 10^{-25}}{m} \\ &= \frac{2 \times 4.55 \times 10^{-25} \text{ kg m}^2 \text{ sec}^{-2}}{9.1 \times 10^{-31} \text{ kg}} \end{aligned}$$

$$\text{or} \quad v^2 = 1 \times 10^6 \text{ m}^2 \text{ sec}^{-2}$$

or

$$v = 1 \times 10^3 \text{ m sec}^{-1}$$

We know

$$\begin{aligned}\lambda &= \frac{h}{m \times v} \text{ (de Broglie equation)} \\ &= \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}}{(9.1 \times 10^{-31} \text{ kg}) \times (1 \times 10^3 \text{ m sec}^{-1})} \\ &= 7.25 \times 10^{-7} \text{ m} \\ &= 7.25 \times 10^{-7} \times 10^9 \text{ nm} \\ &= \mathbf{725 \text{ nm}}\end{aligned}$$

**SOLVED PROBLEM.** Calculate the wavelength of an  $\alpha$  particle having mass  $6.6 \times 10^{-27} \text{ kg}$  moving with a speed of  $10^5 \text{ cm sec}^{-1}$  ( $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$ )

**SOLUTION.** We know

$$\lambda = \frac{h}{mv} \text{ (de Broglie equation)}$$

Given

$$\begin{aligned}h &= 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1} \\ m &= 6.6 \times 10^{-27} \text{ kg} \\ v &= 1 \times 10^5 \text{ cm sec}^{-1} \\ &= 1 \times 10^3 \text{ m sec}^{-1}\end{aligned}$$

On substitution, we get

$$\begin{aligned}\lambda &= \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}}{6.6 \times 10^{-27} \text{ kg} \times 10^3 \text{ m sec}^{-1}} \\ &= \mathbf{1 \times 10^{-10} \text{ m}}\end{aligned}$$

### HEISENBERG'S UNCERTAINTY PRINCIPLE

One of the most important consequences of the dual nature of matter is the uncertainty principle developed by Werner Heisenberg in 1927. This principle is an important feature of wave mechanics and discusses the relationship between a pair of *conjugate properties* (those properties that are independent) of a substance. According to the uncertainty principle, it is impossible to know simultaneously both the conjugate properties accurately. For example, the position and momentum of a moving particle are interdependent and thus conjugate properties also. Both the position and the momentum of the particle at any instant cannot be determined with absolute exactness or certainty. If the momentum (or velocity) be measured very accurately, a measurement of the position of the particle correspondingly becomes less precise. On the other hand if position is determined with accuracy or precision, the momentum becomes less accurately known or uncertain. **Thus certainty of determination of one property introduces uncertainty of determination of the other.** The uncertainty in measurement of position,  $\Delta x$ , and the uncertainty of determination of momentum,  $\Delta p$  (or  $\Delta mv$ ), are related by Heisenberg's relationship as

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

or

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

where  $h$  is Planck's constant.

It may be pointed out here that there exists a clear difference between the behaviour of large objects like a stone and small particles such as electrons. **The uncertainty product is negligible in case of large objects.**



For a moving ball of iron weighing 500 g, the uncertainty expression assumes the form

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

$$\begin{aligned} \text{or} \quad \Delta x \times \Delta v &\geq \frac{h}{2\pi m} \\ &\geq \frac{6.625 \times 10^{-27}}{2 \times 3.14 \times 500} \approx 5 \times 10^{-31} \text{ erg sec g}^{-1} \end{aligned}$$

which is very small and thus negligible. Therefore for large objects, the uncertainty of measurements is practically nil.

But for an electron of mass  $m = 9.109 \times 10^{-28}$  g, the product of the uncertainty of measurements is quite large as

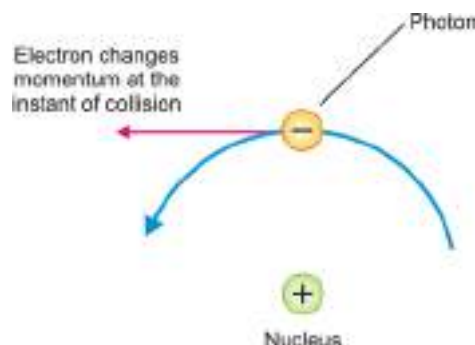
$$\begin{aligned} \Delta x \times \Delta v &\geq \frac{h}{2\pi m} \\ &\geq \frac{6.625 \times 10^{-27}}{2 \times 3.14 \times 9.109 \times 10^{-28}} \approx 0.3 \text{ erg sec g}^{-1} \end{aligned}$$

This value is large enough in comparison with the size of the electron and is thus in no way negligible. If position is known quite accurately *i.e.*,  $\Delta x$  is very small, the uncertainty regarding velocity  $\Delta v$  becomes immensely large and *vice versa*. It is therefore very clear that **the uncertainty principle is only important in considering measurements of small particles comprising an atomic system.**

#### Physical Concept of Uncertainty Principle

The physical concept of uncertainty principle becomes illustrated by considering an attempt to measure the position and momentum of an electron moving in Bohr's orbit. To locate the position of the electron, we should devise an instrument 'supermicroscope' to see the electron. A substance is said to be seen only if it could reflect light or any other radiation from its surface. Because the size of the electron is too small, its position at any instant may be determined by a supermicroscope employing light of very small wavelength (such as X-rays or  $\gamma$ -rays). A photon of such a radiation of small  $\lambda$ , has a great energy and therefore has quite large momentum. As one such photon strikes the electron and is reflected, it instantly changes the momentum of electron. Now the momentum gets changed and becomes more uncertain as the position of the electron is being determined (Fig. 2.3). Thus it is impossible to determine the exact position of an electron moving with a definite velocity (or possessing definite energy). It appears clear that the Bohr's picture of an electron as moving in an orbit with fixed velocity (or energy) is completely untenable.

As it is impossible to know the position and the velocity of any one electron on account of its small size, the best we can do is to speak of the probability or *relative chance* of finding an electron with a probable velocity. **The old classical concept of Bohr has now been discarded in favour of the probability approach.**



■ **Figure 2.3**

**The momentum of the electron changes when a photon of light strikes it, so does its position.**

**SOLVED PROBLEM.** Calculate the uncertainty in position of an electron if the uncertainty in velocity is  $5.7 \times 10^5 \text{ m sec}^{-1}$ .

**SOLUTION.** According to Heisenberg's uncertainty principle

$$\Delta x \times \Delta p = \frac{h}{4\pi}$$

or 
$$\Delta x \times m \Delta v = \frac{h}{4\pi}$$

or 
$$\Delta x = \frac{h}{4\pi m \times \Delta v}$$

Here 
$$\Delta v = 5.7 \times 10^5 \text{ m sec}^{-1}$$

$$h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$$

$$m = 9.1 \times 10^{-31} \text{ kg}$$

On substitution we get

$$\begin{aligned} \Delta x &= \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}}{4 \times 3.14 \times (9.1 \times 10^{-31} \text{ kg}) (5.7 \times 10^5 \text{ m sec}^{-1})} \\ &= \frac{6.6 \times 10^{-8}}{4 \times 3.14 \times 9.1 \times 5.7} \text{ m} \\ &= 1 \times 10^{-10} \text{ m} \end{aligned}$$

**SOLVED PROBLEM.** The uncertainty in the position and velocity of a particle are  $10^{-10} \text{ m}$  and  $5.27 \times 10^{-24} \text{ m sec}^{-1}$  respectively. Calculate the mass of the particle.

**SOLUTION.** We know 
$$\Delta x \times \Delta p = \frac{h}{4\pi}$$

or 
$$\Delta x \times m \Delta v = \frac{h}{4\pi}$$

or 
$$m = \frac{h}{4\pi \times \Delta x \times \Delta v}$$

Here 
$$h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$$

$$\Delta x = 1 \times 10^{-10} \text{ m}$$

$$\Delta v = 5.27 \times 10^{-24} \text{ m sec}^{-1}$$

Substituting the values, we get

$$\begin{aligned} m &= \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}}{4 \times 3.14 \times (1 \times 10^{-10} \text{ m}) (5.27 \times 10^{-24} \text{ m sec}^{-1})} \\ &= 0.10 \text{ kg} \\ &= 100 \text{ g} \end{aligned}$$

## SCHRÖDINGER'S WAVE EQUATION

In order to provide sense and meaning to the probability approach, Schrödinger derived an equation known after his name as **Schrödinger's Wave Equation**. Calculation of the probability of finding the electron at various points in an atom was the main problem before Schrödinger. **His equation is the keynote of wave mechanics and is based upon the idea of the electron as 'standing wave' around the nucleus.** The equation for the standing wave\*, comparable with that of a stretched string is

\* For the derivation of equation for a 'standing wave' in a stretched string, the reader may refer to a book on Physics (Sound).

$$\psi = A \sin 2\pi \frac{x}{\lambda} \quad \dots(a)$$

where  $\psi$  (pronounced as *sigh*) is a mathematical function representing the amplitude of wave (called *wave function*)  $x$ , the displacement in a given direction, and  $\lambda$ , the wavelength and  $A$  is a constant.

By differentiating equation (a) twice with respect to  $x$ , we get

$$\frac{d\psi}{dx} = A \frac{2\pi}{\lambda} \cos 2\pi \frac{x}{\lambda} \quad \dots(1)$$

$$\text{and} \quad \frac{d^2\psi}{dx^2} = -A \frac{4\pi^2}{\lambda^2} \sin 2\pi \frac{x}{\lambda} \quad \dots(2)$$

$$\text{But} \quad A \sin 2\pi \frac{x}{\lambda} = \psi$$

$$\therefore \quad \frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} \psi \quad \dots(3)$$

The K.E. of the particle of mass  $m$  and velocity  $v$  is given by the relation

$$\text{K.E.} = \frac{1}{2}mv^2 = \frac{1}{2} \frac{m^2v^2}{m} \quad \dots(4)$$

According to Broglie's equation

$$\lambda = \frac{h}{mv}$$

$$\text{or} \quad \lambda^2 = \frac{h^2}{m^2v^2}$$

$$\text{or} \quad m^2v^2 = \frac{h^2}{\lambda^2}$$

Substituting the value of  $m^2v^2$ , we have

$$\text{K.E.} = \frac{1}{2} \times \frac{h^2}{m\lambda^2} \quad \dots(5)$$

From equation (3), we have

$$\lambda^2 = -\frac{4\pi^2\psi}{\frac{d^2\psi}{dx^2}} \quad \dots(6)$$

Substituting the value of  $\lambda^2$  in equation (5)

$$\begin{aligned} \text{K.E.} &= -\frac{1}{2m} \cdot \frac{h^2}{4\pi^2\psi} \cdot \frac{d^2\psi}{dx^2} \\ &= -\frac{h^2}{8\pi^2m\psi} \cdot \frac{d^2\psi}{dx^2} \end{aligned}$$

The total energy  $E$  of a particle is the sum of kinetic energy and the potential energy

*i.e.*,

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

or

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

$$= -\frac{h^2}{8\pi^2m\psi} \cdot \frac{d^2\psi}{dx^2}$$

or

$$\frac{d^2\psi}{dx^2} = -\frac{8\pi^2m}{h^2} (E - \text{P.E.}) \psi$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} (E - \text{P.E.}) \psi = 0$$

This is Schrödinger's equation in one dimension. It need be generalised for a particle whose motion is described by three space coordinates  $x$ ,  $y$  and  $z$ . Thus,

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2m}{h^2} (E - \text{P.E.}) \psi = 0$$

This equation is called the **Schrödinger's Wave Equation**. The first three terms on the left-hand side are represented by  $\Delta^2\psi$  (pronounced as del-square sigh).

$$\Delta^2 \psi + \frac{8\pi^2m}{h^2} (E - \text{P.E.}) \psi = 0$$

$\Delta^2$  is known as **Laplacian Operator**.

The Schrödinger's wave equation is a second degree differential equation. It has several solutions. Some of these are imaginary and are not valid. If the potential energy term is known, the total energy  $E$  and the corresponding wave function  $\psi$  can be evaluated.

The wave function is always finite, single valued and continuous. It is zero at infinite distance. Solutions that meet these requirements are only possible if  $E$  is given certain characteristic values called **Eigen-values**. Corresponding to these values of  $E$ , we have several characteristic values of wavefunction  $\psi$  and are called **Eigen-functions**. As the eigen-values correspond very nearly to the energy values associated with different Bohr-orbits, the Bohr's model may be considered as a direct consequence of wave mechanical approach.

### Significance of $\psi$ and $\psi^2$

In Schrödinger's wave equation  $\psi$  represents the amplitude of the spherical wave. According to the theory of propagation of light and sound waves, the square of the amplitude of the wave is proportional to the intensity of the sound or light. A similar concept, modified to meet the requirement of uncertainty principle, has been developed for the physical interpretation of wave function  $\psi$ . This may be stated as the probability of finding an electron in an extremely small volume around a point. It is proportional to the square of the function  $\psi^2$  at that point. If wave function  $\psi$  is imaginary,  $\psi\psi^*$  becomes a real quantity where  $\psi^*$  is a complex conjugate of  $\psi$ . This quantity represents the probability  $\psi^2$  as a function of  $x$ ,  $y$  and  $z$  coordinates of the system, and it varies from one space region to another. Thus the probability of finding the electron in different regions is different. This is in agreement with the uncertainty principle and gave a death blow to Bohr's concept.

In Schrödinger's Wave Equation, **the symbol  $\psi$  represents the amplitude of the spherical wave**. For hydrogen atom, Schrödinger's Wave Equation gives the wave function of the electron (with energy =  $-2.18 \times 10^{-11}$  ergs) situated at a distance ' $r$ ',

$$\psi = C_1 e - C_2 r$$

where  $C_1$  and  $C_2$  are constants. The square of the amplitude  $\psi^2$  is proportional to the density of the wave. **The wave of energy or the cloud of negative charge is denser in some parts than in others.** Max Born interpreted the wave equations on the basis of probabilities. Even if an electron be considered as a particle in motion around the nucleus, the wave equation may be interpreted in terms of probability or relative chance of finding the electron at any given distance from the nucleus. The space characteristic of an electron is best described in terms of distribution function given by

$$D = 4\pi r^2 \psi^2$$

The numerical value of ' $D$ ' denotes the probability or chance of finding the electron in a shell of radius  $r$  and thickness  $dr$ , or of volume  $4\pi r^2 dr$ . Substituting for  $\psi$  we have,

$$D = 4\pi r^2 (C_1 e - C_2 r)^2$$

The probability of finding the electron is clearly a function of ' $r$ '. When  $r = 0$  or  $\infty$ , the probability function  $D$  becomes equal to zero. In other words, there is no probability of finding the electron at the nucleus or at infinity. However, it is possible to choose a value of  $r$  such that there is 90-95 percent chance of finding the electron at this distance. For the hydrogen atom, this distance is equal to  $0.53 \times 10^{-8}$  cm or  $0.53 \text{ \AA}$ . If the probability distribution be plotted against the distance  $r$  from the nucleus, the curve obtained is shown in Fig. 2.4. The probability distribution is maximum at the distance  $0.53 \text{ \AA}$  and spherically symmetrical. This distance corresponds to Bohr's first radius  $a_0$ . The graph can be interpreted as representing a contour that encloses a high-percentage of charge.

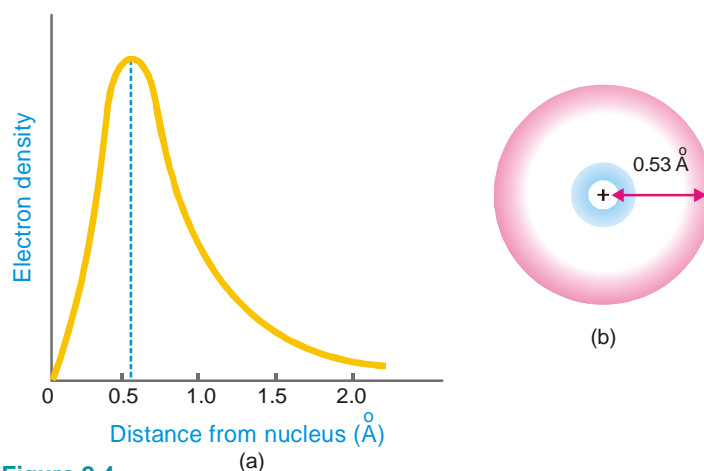
When the electron gets excited and it is raised from  $n$  to higher energy levels (say  $n = 2$  or  $n = 3$ ), the solution of wave equation gives sets of value of  $\psi^2$  which give different shapes to the space distribution of the electron.

### CHARGE CLOUD CONCEPT AND ORBITALS

The Charge Cloud Concept finds its birth from wave mechanical theory of the atom. The wave equation for a given electron, on solving gives a three-dimensional arrangement of points where it can possibly lie. There are regions where the chances of finding the electron are relatively greater. Such regions are expressed in terms of '**cloud of negative charge**'. We need not know the specific location of the electrons in space but are concerned with the negative charge density regions. Electrons in atoms are assumed to be vibrating in space, moving haphazardly but at the same time are constrained to lie in regions of highest probability for most of the time. **The charge cloud concept simply describes the high probability region.**

**The three-dimensional region within which there is higher probability that an electron having a certain energy will be found, is called an orbital.**

An orbital is the most probable space in which the electron spends most of its time while in constant motion. In other words, it is the spatial description of the motion of an electron corresponding to a particular energy level. **The energy of electron in an atomic orbital is always the same.**



■ **Figure 2.4**

**Shows the probability distribution of electron cloud :**

**(a) gives the graphical representation while**

**(b) depicts cross-section of the cloud.**

Each energy level corresponds to a three-dimensional electron wave which envelopes the nucleus. This wave possesses a definite 'size', 'shape' and 'orientation' and thus can be represented pictorially.

### QUANTUM NUMBERS

Bohr's electronic energy shells or levels, designated as Principal Quantum Numbers ' $n$ ', could

hardly explain the hydrogen spectrum adequately. Spectra of other elements that are quite complex, also remained unexplained by this concept. Many single lines of the spectra are found to consist of a number of closely related lines when studied with the help of sophisticated instruments of high resolving power. Also the spectral lines split up when the source of radiation is placed in a magnetic field (**Zeeman Effect**) or in an electrical field (**Stark Effect**).

To explain these facts, it is necessary to increase the number of ‘possible orbits’ where an electron can be said to exist within an atom. In other words, it is necessary to allow more possible energy changes within an atom (or a larger number of energy states) to account for the existence of a larger number of such observed spectral lines. Wave mechanics makes a provision for three more states of an electron in addition to the one proposed by Bohr. Like the energy states of Bohr, designated by  $n = 1, 2, 3, \dots$ , these states are also identified by numbers and specify the position and energy of the electron. Thus there are in all four such identification numbers called **quantum numbers** which fully describe an electron in an atom. Each one of these refers to a particular character.

### Principal Quantum Number ‘ $n$ ’

**This quantum number denotes the principal shell to which the electron belongs.** This is also referred to as **major energy level**. It represents the average size of the electron cloud *i.e.*, the average distance of the electron from the nucleus. This is, therefore, the main factor that determines the values of nucleus-electron attraction, or the energy of the electron. In our earlier discussion, we have found that the energy of the electron and its distance from the nucleus for hydrogen atom are given by

$$E_n = -\frac{313.3}{n^2} \text{ kcal}$$

$$\text{and} \quad r_n = 0.529 n^2 \text{ \AA}$$

where  $n$  is the principal quantum number of the shell.

The principal quantum number ‘ $n$ ’ can have non-zero, positive, integral values  $n = 1, 2, 3, \dots$  increasing by integral numbers to infinity. Although the quantum number ‘ $n$ ’ may theoretically assume any integral value from 1 to  $\infty$ , only values from 1 to 7 have so far been established for the atoms of the known elements in their ground states. In a polyelectron atom or ion, the electron that has a higher principal quantum number is at a higher energy level. An electron with  $n = 1$  has the lowest energy and is bound most firmly to the nucleus.

The letters K, L, M, N, O, P and Q are also used to designate the energy levels or shells of electrons with a  $n$  value of 1, 2, 3, 4, 5, 6, 7 respectively. There is a limited number of electrons in an atom which can have the same principal quantum number and is given by  $2n^2$ , where  $n$  is the principal quantum number concerned. Thus,

Principal quantum number ( $n =$ )	1	2	3	4
Letter designation	K	L	M	N
Maximum number of electrons ( $2n^2 =$ )	2	8	18	32

### Azimuthal Quantum number ‘ $l$ ’

This is also called secondary or subsidiary quantum number. It defines the spatial distribution of the electron cloud about the nucleus and describes the angular momentum of the electron. In other words, **the quantum number  $l$  defines the shape of the orbital occupied by the electron and the angular momentum of the electron.** It is for this reason that ‘ $l$ ’ is sometimes referred to as *orbital* or *angular quantum number*. For any given value of the principal quantum number  $n$ , the azimuthal quantum number  $l$  may have all integral values from 0 to  $n - 1$ , each of which refers to an *Energy sublevel* or *Sub-shell*. **The total number of such possible sublevels in each principal level is numerically equal to the principal quantum number of the level under consideration.** These sublevels

are also symbolised by letters  $s, p, d, f$  etc. For example, for principal quantum number  $n = 1$ , the only possible value for  $l$  is 0 *i.e.*, there is only one possible subshell *i.e.*  $s$ -subshell ( $n = 1, l = 0$ ). For  $n = 2$ , there are two possible values of  $l, l = 0$  and  $l = 2 - 1 = 1$ .

This means that there are two subshells in the second energy shell with  $n = 2$ . These subshells are designated as  $2s$  and  $2p$ . Similarly, when  $n = 3$ ,  $l$  can have three values *i.e.* 0, 1 and 2. Thus there are three subshells in third energy shell with designations  $3s, 3p$  and  $3d$  respectively. For  $n = 4$ , there are four possible values of azimuthal quantum number  $l$  ( $= 0, 1, 2$ , and  $3$ ) each representing a different sublevel. In other words, the fourth energy level consists of four subshells which are designated as  $4s, 4p, 4d$  and  $4f$ . Thus for different values of principal quantum numbers we have

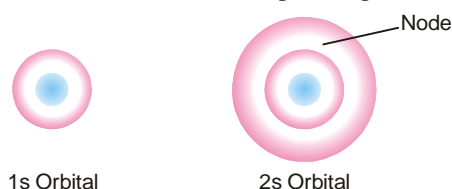
$n = 1$ $l = 0$ ( $1s$ )	$n = 2$ $l = 0$ ( $2s$ ) $l = 1$ ( $2p$ )	$n = 3$ $l = 0$ ( $3s$ ) $l = 1$ ( $3p$ ) $l = 2$ ( $3d$ )	$n = 4$ $l = 0$ ( $4s$ ) $l = 1$ ( $4p$ ) $l = 2$ ( $4d$ ) $l = 3$ ( $4f$ )	$n = 5$ $l = 0$ ( $5s$ ) $l = 1$ ( $5p$ ) $l = 2$ ( $5d$ ) $l = 3$ ( $5f$ ) $l = 4$ ( $5g$ )
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For a given value of principal quantum number the order of increasing energy for different subshells is

$$s < p < d < f \quad (\text{except for H atom})$$

### Magnetic Quantum Number ' $m$ '

**This quantum number has been proposed to account for the splitting up of spectral lines (Zeeman Effect).** An application of a strong magnetic field to an atom reveals that electrons with the same values of principal quantum number ' $n$ ' and of azimuthal quantum number ' $l$ ', may still differ in their behaviour. They must, therefore, be differentiated by introducing a new quantum number, the magnetic quantum number  $m$ . This is also called **Orientation Quantum Number** because it gives the orientation or distribution of the electron cloud. For each value of the azimuthal quantum number ' $l$ ', the magnetic quantum number  $m$ , may assume all the integral values between  $+l$  to  $-l$  through zero *i.e.*,  $+l, (+l-1), \dots, 0, \dots, (-l+1), -l$ . Therefore for each value of  $l$  there will be  $(2l+1)$  values of  $m_l$ . Thus when  $l=0, m=0$  and no other value. This means that **for each value of principal quantum number ' $n$ ', there is only one orientation for  $l=0$  ( $s$  orbital) or there is only one  $s$  orbital.** For  $s$  orbital, there being only one orientation, it must be spherically symmetrical about the nucleus. There is only one spherically symmetrical orbital for each value of  $n$  whose radius depends upon the value of  $n$ .

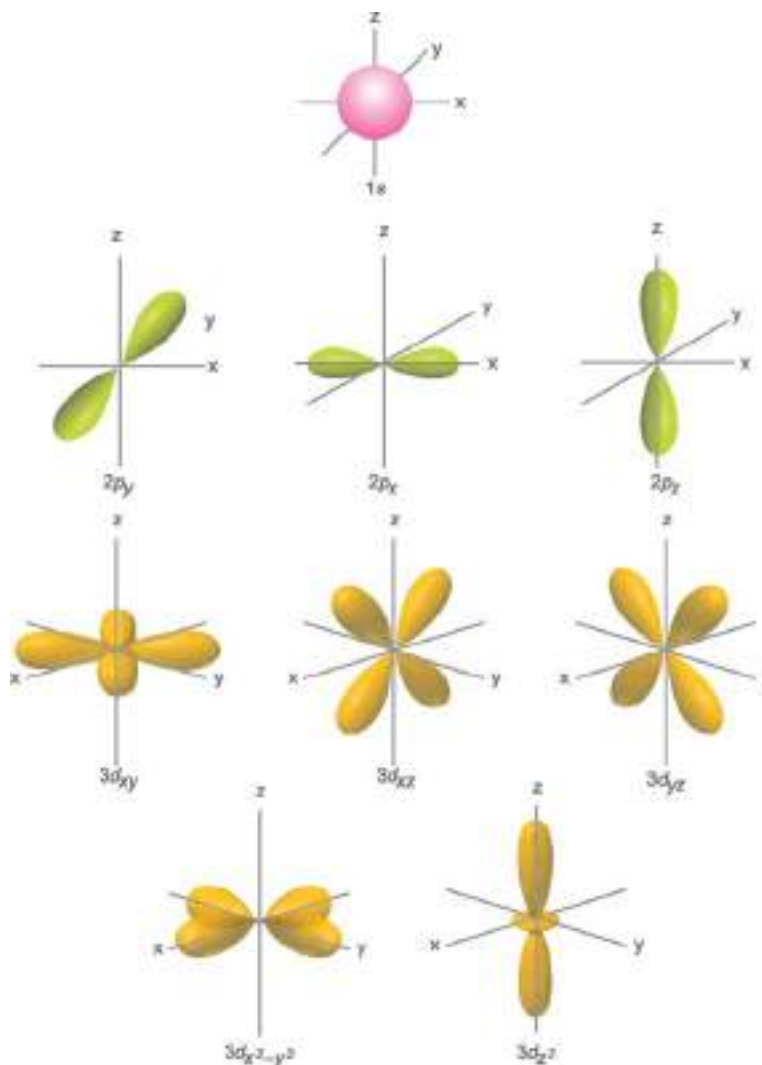


■ **Figure 2.5**  
**Spherical  $s$  orbitals, symmetrically disposed about the nucleus.**

For  $l = 1$  ( $p$  orbital), the magnetic quantum number  $m$  will have *three* values :  $+1, 0$  and  $-1$ ; so there are *three* orientations for  $p$  orbitals. These *three* types of  $p$  orbitals differ only in the value of magnetic quantum number and are designated as  $p_x, p_y, p_z$  depending upon the axis of orientation. The subscripts  $x, y$  and  $z$  refer to the coordinate axes. In the absence of a magnetic field, these three  $p$  orbitals are equivalent in energy and are said to be **three-fold degenerate** or **triply degenerate\***. In

\*Different orbitals of equivalent energy are called degenerate orbitals and are grouped together.

presence of an external magnetic field the relative energies of the three  $p$  orbitals vary depending upon their orientation or magnetic quantum number. This probably accounts for the existence of more spectral lines under the influence of an external magnetic field. The  $p$  orbitals are of dumb-bell shape consisting of two lobes. The two lobes of a  $p$  orbital extend outwards and away from the nucleus along the axial line. Thus the two lobes of a  $p$  orbital may be separated by a plane that contains the nucleus and is perpendicular to the corresponding axis. Such plane is called a **nodal plane**. **There is no likelihood of finding the electron on this plane.** For a  $p_x$  orbital, the  $yz$  plane is the nodal plane. The shapes and orientations of the  $p$  orbitals are given in Fig. 2.6.



■ **Figure 2.6**  
Shapes and orientation of  $s$ ,  $p$  and  $d$  orbitals.

For  $l = 2$  ( $d$  orbital), the magnetic quantum number are *five* ( $2 \times 2 + 1$ );  $+2, +1, 0, -1, -2$ . Thus there are five possible orientations for  $d$  orbitals which are equivalent in energy so long as the atom is not under the influence of a magnetic field and are said to be **five-fold degenerate** (Different orbitals of equivalent energy are called degenerate orbitals and are grouped together). The *five*  $d$  orbitals are

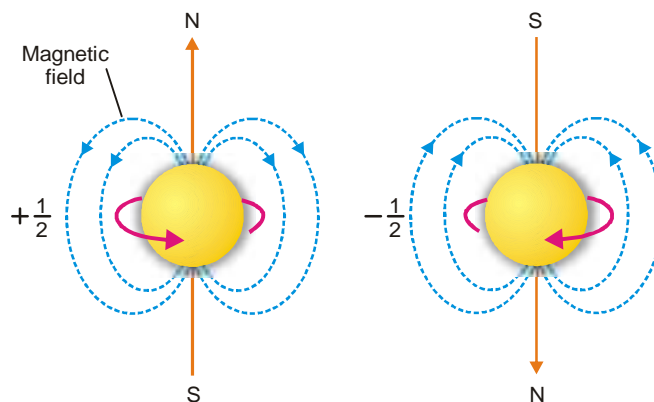


designated as  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ,  $d_{x^2-y^2}$ ,  $d_{z^2}$ . These orbitals have complex geometrical shapes as compared to  $p$  orbitals. The conventional boundary surfaces or shapes of five  $d_{z^2}$  orbitals are shown in Fig. 2.6. The shape of the  $d_{z^2}$  orbitals is different from others.

When  $l = 3$  ( $f$  orbital) the magnetic quantum number  $m$  can have *seven* ( $2 \times 3 + 1$ ) values as  $+3$ ,  $+2$ ,  $+1$ ,  $0$ ,  $-1$ ,  $-2$  and  $-3$ . These *seven* orientations give rise to a set of **seven-fold degenerate orbitals**. These seven orbitals possess very complicated shapes and orientation in space. The shapes of  $s$ ,  $p$  and  $d$  orbitals only are of interest to chemists.

### Spin Quantum Number ' $s$ '

**This quantum number has been introduced to account for the spin of electrons about their own axis.** Since an electron can spin clockwise or anticlockwise (in two opposite directions), there are two possible values of  $s$  that are equal and opposite. As quantum numbers can differ only by unity from each other, there are two values given to  $s$ ;  $+\frac{1}{2}$  and  $-\frac{1}{2}$  depending upon whether the electron spins in one direction or the other. These spins are also designated by arrows pointing upwards and downward as  $\uparrow$  and  $\downarrow$ . **Two electrons with the same sign of the spin quantum numbers are said to have parallel spins** while those having opposite signs of the spin quantum numbers are said to have **opposite spin** or **antiparallel spin** or **paired-up spin**.



■ **Figure 2.7**  
Clockwise and anticlockwise spins of electrons about their own axis produce opposite magnetic fields.

Since a spinning charge is associated with a magnetic field, an electron must have a magnetic moment associated with it.

The permitted values for each of these quantum numbers are given in the Table 2.1.

**SOLVED PROBLEM.** List all possible values of  $l$  and  $m$  for  $n = 2$ .

**SOLUTION.** Here, the principal quantum number  $n = 2$ . The azimuthal quantum number can have only two values. These are 0 and 1

When	$l = 0$	$m = 0$
and	$l = 1$	$m = +1, 0, -1$

**SOLVED PROBLEM.** Which of the following sets of quantum numbers are not allowable and why?

- |     |         |         |         |                    |
|-----|---------|---------|---------|--------------------|
| (a) | $n = 2$ | $l = 2$ | $m = 0$ | $s = +\frac{1}{2}$ |
| (b) | $n = 3$ | $l = 1$ | $m = 0$ | $s = -\frac{1}{2}$ |

(c)	$n = 1$	$l = 1$	$m = +1$	$s = +\frac{1}{2}$
(d)	$n = 2$	$l = 0$	$m = -1$	$s = 0$
(e)	$n = 3$	$l = 2$	$m = 2$	$s = -\frac{1}{2}$

**SOLUTION**

- (a) Not allowable as  $l$  cannot have value equal to 2 when  $n = 2$ .  
 (b) Allowable  
 (c) Not allowable as  $l$  cannot have value equal to 1 when  $n = 1$   
 (d) Not allowable as  $s$  cannot have value equal to 0.  
 (e) Allowable

**SOLVED PROBLEM.** What designation are given to the orbitals having

(a)	$n = 2$	$l = 1$
(b)	$n = 1$	$l = 0$
(c)	$n = 3$	$l = 2$
(d)	$n = 4$	$l = 3$

**SOLUTION**

(a)	when $n = 2$	and $l = 1$	the orbital is $2p$
(b)	when $n = 1$	and $l = 0$	the orbital is $1s$
(c)	when $n = 3$	and $l = 2$	the orbital is $3d$
(d)	when $n = 4$	and $l = 3$	the orbital is $4f$

**PAULI'S EXCLUSION PRINCIPLE**

The nature of an electron, its position and energy, is fully implied only by mentioning the values of four quantum numbers ascribed to it. Each electron is, therefore, fully characterised by a set of four quantum numbers ' $n$ ' – giving the size of electron orbital,  $l$  – its shape, and  $m$  – the orientation or disposition of the orbital and  $s$  the spin of the electron. Electrons having the same value of  $n$ , the principal quantum number, are said to belong to the same major energy level. However, the energies possessed by these electrons may yet be different owing to the different values of other quantum numbers assigned to them. In fact, the major energy levels are made of sublevels, given by the value of azimuthal quantum number ' $l$ '. A particular energy sublevel may be designated by  $s$ ,  $p$ ,  $d$  and  $f$ . Within each energy level, the various sublevels have slightly different energies which increase in the same order as the value of the azimuthal quantum number  $l$ . Therefore, for the major energy level  $n = 4$ , which has an  $s$  orbital ( $l = 0$ ),  $p$  orbitals ( $l = 1$ ),  $d$  orbitals ( $l = 2$ ) and  $f$  orbitals ( $l = 3$ ), the energy increases in the order  $s < p < d < f$ . An electron with the principal quantum number  $n$  and azimuthal quantum number  $l$  has always lesser energy than that of an electron with principal quantum number  $(n + 1)$  and the same azimuthal quantum number  $l$  i.e., the energy of a  $3s$  orbital is less than that of  $4s$  orbital and energy of  $4p$  orbitals is always more than the energy of  $3p$  orbitals, and so on. The other two quantum numbers namely magnetic and spin quantum numbers determine the maximum number of electrons that can be accommodated in orbitals of a sublevel. It is, therefore, the assignment of the four quantum numbers to the electrons which ultimately count to determine its energy and location in space within an atom.

TABLE 2.1. QUANTUM NUMBERS AND ELECTRON ACCOMMODATION

TABLE 2.1. QUANTUM NUMBERS AND ELECTRON ACCOMMODATION						
Principal Q-number $n$		Azimuthal Q-number $l$		Magnetic Quantum Number $m$	Spin Quantum Number $s$	Number of Electrons accommodated
1	K	0	$s$	0	$+\frac{1}{2}, -\frac{1}{2}$	2
2	L	0	$s$	0	$+\frac{1}{2}, -\frac{1}{2}$	2
		1	$p$	$+1, 0, -1$	$+\frac{1}{2}, -\frac{1}{2}$	6
3	M	0	$s$	0	$+\frac{1}{2}, -\frac{1}{2}$	2
		1	$p$	$+1, 0, -1$	$+\frac{1}{2}, -\frac{1}{2}$	6
		2	$d$	$+2, +1, 0, -1, -2,$	$+\frac{1}{2}, -\frac{1}{2}$	10
4	N	0	$s$	0	$+\frac{1}{2}, -\frac{1}{2}$	2
		1	$p$	$+1, 0, -1$	$+\frac{1}{2}, -\frac{1}{2}$	6
		2	$d$	$+2, +1, 0, -1 -2$	$+\frac{1}{2}, -\frac{1}{2}$	10
		3	$f$	$+3, +2, +1, 0, -1, -2, -3$	$+\frac{1}{2}, -\frac{1}{2}$	14

Wolfgang Pauli put forward an ingenious principle which controls the assignment of values of four quantum numbers of an electron. It applies certain restrictions on the values of electrons in an atom and hence the name ‘**exclusion principle**’. It is stated as : **No two electrons in an atom can have the same set of four identical quantum numbers.**

Even if two electrons have the same values for  $n$ ,  $l$  and  $m$ , they must have different values of  $s$ . Thus every electron in an atom differs from every other electron in total energy and, therefore, there can be as many electrons in a shell as there are possible arrangements of different quantum numbers. The arrangements of electrons using permitted quantum numbers  $n$ ,  $l$ ,  $m$  and  $s$  are given in the Table 2.1. Let us find out the maximum number of electrons that can be accommodated in an orbital. We have seen that the first shell ( $n = 1$ ) has only one orbital *i.e.*,  $1s$ . The possible arrangements for the quantum numbers are only two in accordance with Pauli’s exclusion principle.

$n$	$l$	$m$	$s$
1	0	0	$+\frac{1}{2}$ (1st electron)
1	0	0	$-\frac{1}{2}$ (2nd electron)

It follows, therefore, that a maximum of two electrons can be accommodated in an orbital and they must possess opposite spins.

Consider the second shell ( $n = 2$ ), there being four orbitals, one  $s$  orbital ( $l = 0$ ) and three  $p$  orbitals ( $l = 1$ ), the possible number of electrons having different set of quantum numbers can be as follows :

$n$	$l$	$m$	$s$	
2	0	0	$+\frac{1}{2}$	Two electrons accommodated in $2s$ orbital ( $l = 0$ )
2	0	0	$-\frac{1}{2}$	

2	1	+1	$+\frac{1}{2}$	} Six electrons in all the three $2p$ orbitals ( $l = 1$ ), two electrons each in $2p_x$ ( $m = +1$ ), $2p_y$ ( $m = -1$ ) and $2p_z$ ( $m = 0$ ) orbitals.
2	1	+1	$-\frac{1}{2}$	
2	1	-1	$+\frac{1}{2}$	}
2	1	-1	$-\frac{1}{2}$	
2	1	0	$+\frac{1}{2}$	}
2	1	0	$-\frac{1}{2}$	

The total number of electrons that can be accommodated in second shell is equal to  $2 + 6 = 8$ . Similarly it can be shown that the maximum number of electrons in the third and fourth shells is equal to 18 and 32 respectively. On the basis of the above direction and the Table 2.1 it follows that  $s$  sublevel may contain upto *two* electrons,  $p$  sublevel upto *six*,  $d$  sublevel upto *ten* and  $f$  sublevel may have upto *fourteen* electrons. Each sublevel can accommodate at the most twice the number of available orbitals at that sublevel.

**Pauli's exclusion principle is of immense value in telling the maximum number of electrons accommodated in any shell.**

### ENERGY DISTRIBUTION AND ORBITALS

In our earlier discussion we have seen that the energy of an electron is determined by the first two quantum numbers  $n$  and  $l$ , while the other two specify the orientation of the electron orbital in space and the spin. As we discuss the distribution of energy of the orbitals, the following two cases may arise :

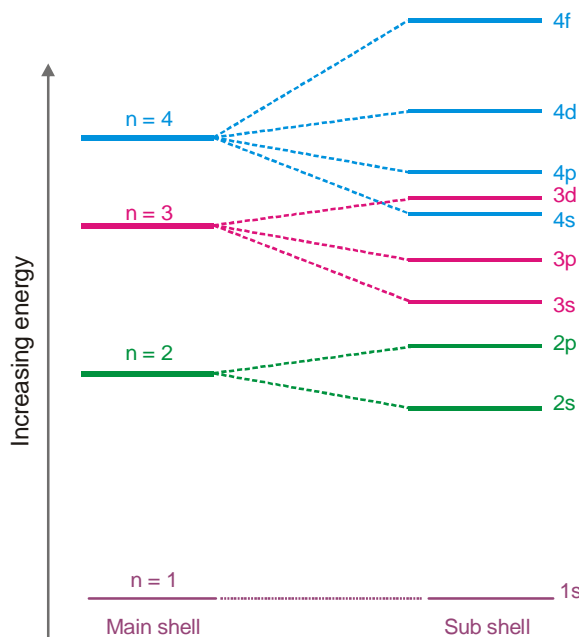
#### (a) Hydrogen and Hydrogen-like atoms

Hydrogen is the simplest of all atoms since there is only one electron in it. This single electron is expected normally to be present in the lowest energy state  $n = 1$ . The values of  $l$  and  $m$  are both zero and spin quantum numbers can be either  $+\frac{1}{2}$  or  $-\frac{1}{2}$ . When it absorbs energy, it may jump to higher energy levels given by  $n$  or a subshell thereon (represented by  $l$  values). The spectral study of hydrogen has revealed that its spectral lines correspond to the major energy levels only. Thus the energy value of an electron having a particular quantum is fixed, irrespective of the orbital to which it may belong. In other words, the energy associated with electrons in  $s$ ,  $p$ ,  $d$  and  $f$  orbitals of a particular principal quantum number is the same. For example, the energy level of  $3s$ ,  $3p$  and  $3d$  orbitals is equal (Fig. 2.8).

#### (b) Polyelectron atoms

Let us first consider a two electron atom. The second electron which may differ from the first electron in spin only, is also accommodated in the  $1s$  orbital, thereby completing the K shell. Unlike hydrogen, where there is no such completed shell, the energies of the subsequent electrons coming in various levels and sublevels will be affected. Thus it is this completed K shell that affects the energy of the electrons occupying subsequent energy levels. For atoms having more than two electrons, the nuclear charge is shielded from the outer electrons by the two K shell electrons. The effect of the completed K shell of electrons is to make the energy level of any orbital in a principal level  $n$  dependent upon the value of orbital quantum number  $l$ . The dependence of energy of orbitals of a shell on  $l$  ( $l = 0$  or  $s$ ,  $l = 1$  or  $p$  etc.) is because of the fact that  $s$  orbital electrons ( $l = 0$ ), for example, penetrate near the nucleus and are, therefore, less effectively shielded from the nuclear charge. The  $s$  electrons ( $l = 0$ ) being less shielded are drawn inwards and possess lesser energy than  $p$  orbital ( $l = 1$ ) electrons. The same argument can be extended for other values of  $l$ . Thus within each energy

level ' $n$ ', the various sublevels (different  $l$  values orbitals) exhibit slightly different energies. The orbitals at a principal level  $n$  get split up and come to possess different energies, which increase in the same order as the various values of  $l$ . Thus for a particular principal level, the energy of the sublevels is in the order  $s < p < d < f$ .



■ **Figure 2.8**  
Energy level schemes of Hydrogen atom.

The energy levels of 3s, 3p and 3d orbitals are different even though they belong to the same shell  $n = 3$ . However, **it may be noted that the energy of electrons in the same orbital is the same.** Thus all 3d orbitals ( $3d_{xy}$ ,  $3d_{yz}$ ,  $3d_{zx}$ ,  $3d_{z^2}$ ,  $3d_{x^2-y^2}$ ) or 4p orbitals ( $4p_x$ ,  $4p_y$ ,  $4p_z$ ) are at the same level of energy, irrespective of their orientation. It is also noteworthy from the above diagram that the order of increase of energy values of various orbitals approximately follows the sequence given below :

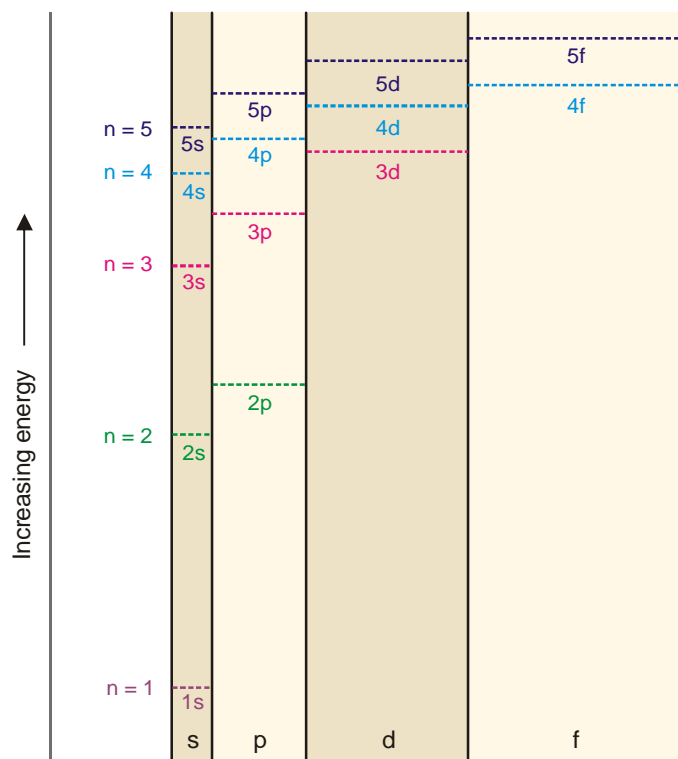
$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d$$

It is, therefore, clear that the 3d orbital electrons belonging to a lower shell ( $n = 3$ ) possess more energy than 4s orbital electrons which belong to higher shell ( $n = 4$ ). The 3d orbitals lie at a higher energy level than 4s orbital.

### DISTRIBUTION OF ELECTRONS IN ORBITALS

In passing along the periodic table of the elements from one element to the other, we find that one electron is added every time to the next atom. Where should the incoming electron go? The answer is provided by the possible values of the quantum numbers that can be assigned to the electron in accordance with Pauli's exclusion principle—prohibiting an orbital to accommodate two electrons with the same set of quantum numbers.

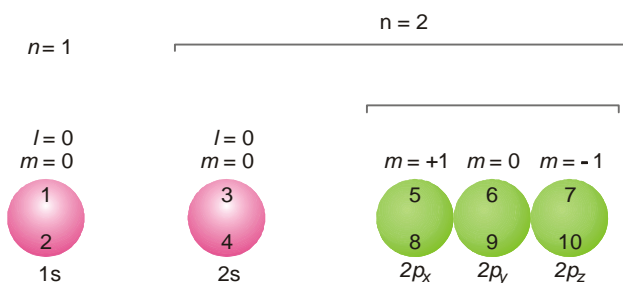
On the basis of magnetic measurements, which also help to determine the electronic configuration of elements, Hund put forward another empirical rule, popularly known after his name as **Hund's Rule of Maximum Multiplicity**. It states that : **Electrons are distributed among the orbitals of a subshell in such a way as to give the maximum number of unpaired electrons and have the same direction of spin.**



■ **Figure 2.9**

**Energy level scheme of polyelectron atoms.**

Thus the orbitals available at a subshell are first filled singly before they begin to pair. The following illustration shows the order of filling of electrons in the orbitals of  $n = 1$  and  $n = 2$  shells. The orbitals are shown by circles and the order of filling for the first ten electrons is indicated by the numbers entered in them.



■ **Figure 2.10**

**Order of filling of electrons in orbitals of  $n = 1$  and  $n = 2$  shells.**

It is also clear from the illustration that no two electrons in an orbital have the same values of all four quantum numbers. In fact, three are identical while the fourth quantum number *i.e.*, the spin quantum number is invariably different. The electrons in the  $p$  orbitals are arranged and accommodated such that they have all obtained one electron first (5th in  $2p_x$ , 6th in  $2p_y$ , 7th in  $2p_z$ ) and now they begin to pair up getting the 8th, 9th and 10th electrons respectively.

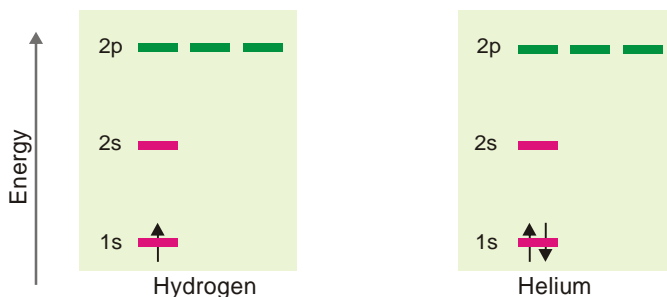
### SCHEMATIC REPRESENTATION OF ELECTRON CONFIGURATION

We have seen above that to define completely the state of an atom it is obligatory to refer to all the four quantum numbers ( $n$ ,  $l$ ,  $m$  and  $s$ ) of every electron in it. Since a simultaneous representation of all quantum numbers of each electron in a single symbolic notation seems quite difficult, it is customary to take into account the first two quantum numbers only while the other two can be inferred indirectly. The general symbolic notation employed for the purpose is  $nl^a$  where the numerical value of  $n = 1, 2, 3$  etc., represents the principal quantum number, the letter designate of  $l$  ( $s$  for  $l = 0$ ,  $p$  for  $l = 1$  and so on) stands for the orbital and the superscript  $a$  gives the number of electrons in the orbital. Thus  $3s^2$  indicates that two electrons are present in the first subshell ( $l = 0$ ) of the third shell ( $n = 3$ ). For instance, the distribution of seven electrons (of  $N$  atom) may be schematically represented as  $1s^2; 2s^2, 2p^3$  or more elaborately as  $1s^2; 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$ . By using the various designates of orbitals at a sublevel such as  $2p_x, 2p_y$  etc., the third quantum number  $m$  is also indicated (e.g.,  $2p_x$ , for  $m = +1$ ,  $2p_y$  for  $m = 0$  and  $2p_z$  for  $m = -1$ ). Spin quantum numbers are indirectly inferred. Whenever there are two electrons in an orbital, one of these has  $+\frac{1}{2}$  and the other  $-\frac{1}{2}$  as their spin quantum number.

It is a common practice to denote an orbital by a horizontal line or a circle or square and an electron by an arrow over it. The direction of the arrow indicates the spin, an upward arrow representing a clockwise spin while the downward arrow stands for the anticlockwise direction of spin. When there are more than one orbitals in a subshell (**degenerate orbitals**), they are shown by an equivalent number of horizontal lines at the same energy level. Let us now describe the electron configuration of first ten elements.

#### (a) Hydrogen and Helium

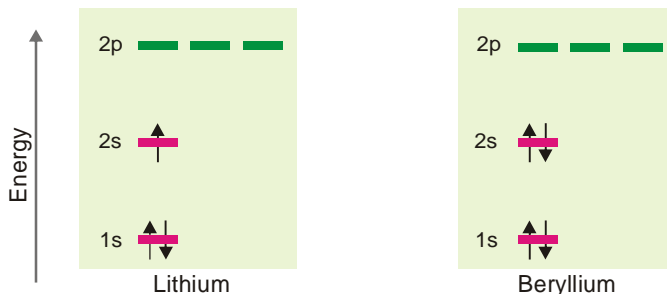
These have one and two electrons respectively which are accommodated in  $1s$  orbital while others remain vacant. The lone electron of hydrogen is filled in  $1s$  orbital and for helium the second electron would also go in  $1s$  orbital, since it could accommodate another electron with opposite spin.



■ **Figure 2.11**  
Electron configuration of Hydrogen and Helium.

#### (b) Lithium and Beryllium

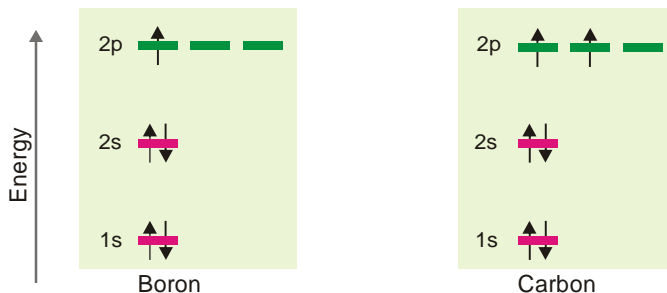
These have three and four electrons respectively. The third electron of Li enters in the  $2s$  orbital and the fourth electron of Be also enters in the same orbital, but has an opposite direction of spin.



■ **Figure 2.12**  
Electron configuration of Lithium and Beryllium.

**(c) Boron and Carbon**

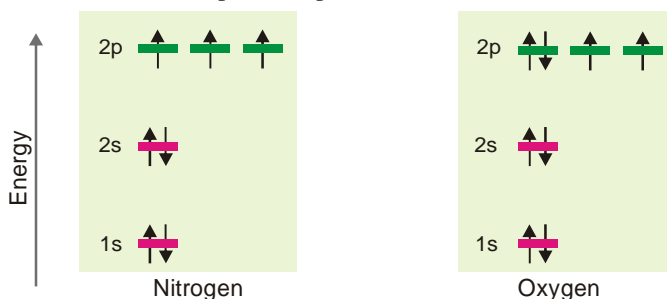
These atoms have five and six electrons respectively.  $1s$  and  $2s$  orbitals being completely filled with four electrons, the fifth electron of boron would go in one of the  $2p$  orbitals say  $2p_x$ . The sixth electron in carbon would prefer to be accommodated in another vacant  $2p$  orbital say ( $2p_y$ ) rather than going to  $2p_z$  orbital (Hund's rule). The two unpaired electrons shall have similar spins as indicated.

■ **Figure 2.13**

**Electron configuration of Boron and Carbon.**

**(d) Nitrogen and Oxygen**

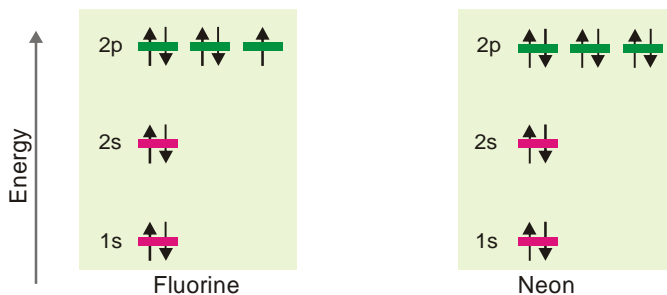
These atoms have seven and eight electrons respectively. After six electrons have been accommodated as above, there is a vacant  $2p_z$  orbital which will be the seat of the seventh electron possessing the same direction of spin. The eighth electron of the next element oxygen will go to pair up with the  $2p_x$  electron and has an antiparallel spin as shown below.

■ **Figure 2.14**

**Electron configuration of Nitrogen and Oxygen.**

**(e) Fluorine and Neon**

These atoms possess nine and ten electrons respectively which go to complete the other  $2p$  orbitals as shown in Fig. 2.15.

■ **Figure 2.15**

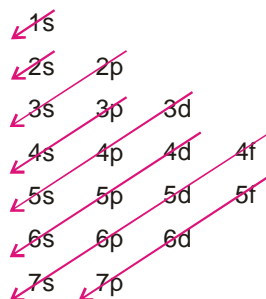
**Electron configuration of Fluorine and Neon.**



## GROUND-STATE ELECTRON CONFIGURATION OF ELEMENTS

So far we have considered the electron configuration of simple atoms. For complicated atoms which may contain many electrons and have many energy levels or orbitals, the ‘building up’ process for the electrons is governed by the following rules :

- Rule 1.** Each electron shell can hold a maximum of  $2n^2$  electrons where  $n$  is the shell number.
- Rule 2.** These electrons are accommodated in  $s$ ,  $p$ ,  $d$  and  $f$  orbitals, the maximum number of electrons in each type of orbitals being determined by its electron-holding capacity (for  $s = 2$ ,  $p = 6$ ,  $d = 10$  and  $f = 14$ ).
- Rule 3.** In the ground state of an atom, the electrons tend to occupy the available orbitals in the increasing order of energies, the orbitals of lower energy being filled first. This is called ‘building up principle’ or **Aufbau Principle** (*Aufbau* is a German expression meaning *building up or construction*). Lower energy orbitals are, therefore, better seats for electrons and better seats are occupied first. Fig 2.9 shows the energy level scheme of orbitals and this order can conveniently be remembered by the simple device given below.



■ **Figure 2.16**  
Aufbau order of orbitals for feeding in electrons.

The increasing order of energy of various orbitals is as follows :

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s \dots\dots$$

The energy of an orbital is determined by the sum of principal quantum number ( $n$ ) and the azimuthal quantum number ( $l$ ). This rule is called **( $n + l$ ) rule**. There are two parts of this rule :

- The orbitals with the lower value of  $(n + l)$  has lower energy than the orbitals of higher  $(n + l)$  value.
- When two orbitals have same  $(n + l)$  value, the orbital with lower value of  $n$  has lower energy. For example, let us compare the  $(n + l)$  value for  $3d$  and  $4s$  orbitals.

For  $3d$  orbital  $n = 3$ ,  $l = 2$  and  $n + l = 5$  and for  $4s$  orbital  $n = 4$ ,  $l = 0$  and  $n + l = 4$ .

Therefore,  $4s$  orbital is filled before  $3d$  orbital. Similarly, for  $4p$  and  $5s$  orbitals, the  $(n + l)$  values are  $(4 + 1)$  and  $(5 + 0)$  respectively. In this case  $4p$  orbital has lesser value of  $n$  and hence it has lower energy than  $5d$  orbital and is filled first.

It is, therefore, clear from above that  $4s$  orbital would be filled before  $3d$  orbitals (belonging to a lower shell *i.e.*, third) are filled because the latter have higher energy than the former.

- Rule 4.** Any orbital may have one or two electrons at the most. Two electrons can occupy the same orbital only if they have opposite spins (Pauli's exclusion principle).
- Rule 5.** 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 same spins (Hund's rule).

Actual electron configuration of atoms of all elements of the periodic table is given in Table 2.3. We find that these configurations are by and large the same as predicted by the Aufbau procedure. However, there are quite a few elements which exhibit slight variations from the standard pattern. Some anomalies are tabled below showing only the concerned orbitals.

**TABLE 2.2. ANOMALOUS ELECTRON CONFIGURATION OF SOME ELEMENTS**

Element	At. No.	Expected Configuration	Actual Configuration
Cr	24	$4d^4 4s^2$	$3d^5 4s^1$
Cu	29	$3d^9 4s^2$	$3d^{10} 4s^1$
Mo	42	$4d^4 5s^2$	$4d^5 5s^1$
Pd	46	$4d^8 5s^2$	$4d^{10} 5s^0$
Ag	47	$4d^9 5s^2$	$4d^{10} 5s^1$
Pt	78	$5d^8 6s^2$	$5d^9 6s^1$
Au	79	$5d^9 6s^2$	$5d^{10} 6s^1$

**TABLE 2.3. GROUND STATE ELECTRON CONFIGURATION OF ELEMENTS**

Z	Element	Electron configuration	Z	Element	Electron configuration
1	H	$1s^1$	21	Sc	$[\text{Ar}]3d^1 4s^2$
2	He	$1s^2$	22	Ti	$[\text{Ar}]3d^2 4s^2$
3	Li	$[\text{He}]2s^1$	23	V	$[\text{Ar}]3d^3 4s^2$
4	Be	$[\text{He}]2s^2$	24	Cr	$[\text{Ar}]3d^5 4s^1$
5	B	$[\text{He}]2s^2 2p^1$	25	Mn	$[\text{Ar}]3d^5 4s^2$
6	C	$[\text{He}]2s^2 2p^2$	26	Fe	$[\text{Ar}]3d^6 4s^2$
7	N	$[\text{He}]2s^2 2p^3$	27	Co	$[\text{Ar}]3d^7 4s^2$
8	O	$[\text{He}]2s^2 2p^4$	28	Ni	$[\text{Ar}]3d^8 4s^2$
9	F	$[\text{He}]2s^2 2p^5$	29	Cu	$[\text{Ar}]3d^{10} 4s^1$
10	Ne	$[\text{He}]2s^2 2p^6$	30	Zn	$[\text{Ar}]3d^{10} 4s^2$
11	Na	$[\text{Ne}]3s^1$	31	Ga	$[\text{Ar}]3d^{10} 4s^2 4p^1$
12	Mg	$[\text{Ne}]3s^2$	32	Ge	$[\text{Ar}]3d^{10} 4s^2 4p^2$
13	Al	$[\text{Ne}]3s^2 3p^1$	33	As	$[\text{Ar}]3d^{10} 4s^2 4p^3$
14	Si	$[\text{Ne}]3s^2 3p^2$	34	Se	$[\text{Ar}]3d^{10} 4s^2 4p^4$
15	P	$[\text{Ne}]3s^2 3p^3$	35	Br	$[\text{Ar}]3d^{10} 4s^2 4p^5$
16	S	$[\text{Ne}]3s^2 3p^4$	36	Kr	$[\text{Ar}]3d^{10} 4s^2 4p^6$
17	Cl	$[\text{Ne}]3s^2 3p^5$	37	Rb	$[\text{Kr}]5s^1$
18	Ar	$[\text{Ne}]3s^2 3p^6$	38	Sr	$[\text{Kr}]5s^2$
19	K	$[\text{Ar}]4s^1$	39	Y	$[\text{Kr}]4d^1 5s^2$
20	Ca	$[\text{Ar}]4s^2$	40	Zr	$[\text{Kr}]4d^2 5s^2$

Z	Element	Electron configuration	Z	Element	Electron configuration
41	Nb	[Kr]4d <sup>4</sup> 5s <sup>1</sup>	73	Ta	[Xe]4f <sup>14</sup> 5d <sup>3</sup> 6s <sup>2</sup>
42	Mo	[Kr]4d <sup>5</sup> 5s <sup>1</sup>	74	W	[Xe]4f <sup>14</sup> 5d <sup>4</sup> 6s <sup>2</sup>
43	Tc	[Kr]4d <sup>5</sup> 5s <sup>2</sup>	75	Re	[Xe]4f <sup>14</sup> 5d <sup>5</sup> 6s <sup>2</sup>
44	Ru	[Kr]4d <sup>7</sup> 5s <sup>1</sup>	76	Os	[Xe]4f <sup>14</sup> 5d <sup>6</sup> 6s <sup>2</sup>
45	Rh	[Kr]4d <sup>8</sup> 5s <sup>1</sup>	77	Ir	[Xe]4f <sup>14</sup> 5d <sup>7</sup> 6s <sup>2</sup>
46	Pd	[Kr]4d <sup>10</sup>	78	Pt	[Xe]4f <sup>14</sup> 5d <sup>9</sup> 6s <sup>1</sup>
47	Ag	[Kr]4d <sup>10</sup> 5s <sup>1</sup>	79	Au	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>1</sup>
48	Cd	[Kr]4d <sup>10</sup> 5s <sup>2</sup>	80	Hg	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup>
49	In	[Kr]4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>1</sup>	81	Tl	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>1</sup>
50	Sn	[Kr]4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>2</sup>	82	Pb	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>2</sup>
51	Sb	[Kr]4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>3</sup>	83	Bi	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>3</sup>
52	Te	[Kr]4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>4</sup>	84	Po	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>4</sup>
53	I	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>5</sup>	85	At	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>5</sup>
54	Xe	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>6</sup>	86	Rn	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>6</sup>
55	Cs	[Xe]6s <sup>1</sup>	87	Fr	[Rn]7s <sup>1</sup>
56	Ba	[Xe]6s <sup>2</sup>	88	Ra	[Rn]7s <sup>2</sup>
57	La	[Xe]5d <sup>1</sup> 6s <sup>2</sup>	89	Ac	[Rn]6d <sup>1</sup> 7s <sup>2</sup>
58	Ce	[Xe]4f <sup>1</sup> 5d <sup>1</sup> 6s <sup>2</sup>	90	Th	[Rn]6d <sup>2</sup> 7s <sup>2</sup>
59	Pr	[Xe]4f <sup>3</sup> 6s <sup>2</sup>	91	Pa	[Rn]5f <sup>2</sup> 6d <sup>1</sup> 7s <sup>2</sup>
60	Nd	[Xe]4f <sup>4</sup> 6s <sup>2</sup>	92	U	[Rn]5f <sup>3</sup> 6d <sup>1</sup> 7s <sup>2</sup>
61	Pm	[Xe]4f <sup>5</sup> 6s <sup>2</sup>	93	Np	[Rn]5f <sup>4</sup> 6d <sup>1</sup> 7s <sup>2</sup>
62	Sm	[Xe]4f <sup>6</sup> 6s <sup>2</sup>	94	Pu	[Rn]5f <sup>6</sup> 7s <sup>2</sup>
63	Eu	[Xe]4f <sup>7</sup> 6s <sup>2</sup>	95	Am	[Rn]5f <sup>7</sup> 7s <sup>2</sup>
64	Gd	[Xe]4f <sup>7</sup> 5d <sup>1</sup> 6s <sup>2</sup>	96	Cm	[Rn]5f <sup>7</sup> 6d <sup>1</sup> 7s <sup>2</sup>
65	Tb	[Xe]4f <sup>9</sup> 6s <sup>2</sup>	97	Bk	[Rn]5f <sup>9</sup> 7s <sup>2</sup>
66	Dy	[Xe]4f <sup>10</sup> 6s <sup>2</sup>	98	Cf	[Rn]5f <sup>10</sup> 7s <sup>2</sup>
67	Ho	[Xe]4f <sup>11</sup> 6s <sup>2</sup>	99	Es	[Rn]5f <sup>11</sup> 7s <sup>2</sup>
68	Er	[Xe]4f <sup>12</sup> 6s <sup>2</sup>	100	Fm	[Rn]5f <sup>12</sup> 7s <sup>2</sup>
69	Tm	[Xe]4f <sup>13</sup> 6s <sup>2</sup>	101	Md	[Rn]5f <sup>13</sup> 7s <sup>2</sup>
70	Yb	[Xe]4f <sup>14</sup> 6s <sup>2</sup>	102	No	[Rn]5f <sup>14</sup> 7s <sup>2</sup>
71	Lu	[Xe]4f <sup>14</sup> 5d <sup>1</sup> 6s <sup>2</sup>	103	Lr	[Rn]5f <sup>14</sup> 6d <sup>1</sup> 7s <sup>2</sup>
72	Hf	[Xe]4f <sup>14</sup> 5d <sup>2</sup> 6s <sup>2</sup>	104	Rf	[Rn]5f <sup>14</sup> 6d <sup>2</sup> 7s <sup>2</sup>

**Note :** The symbol in brackets indicates the electron core of the Noble gas.

**PERIODIC TABLE OF ELEMENTS  
(ELECTRON CONFIGURATIONS)**

Group number																				
		1	2											13	14	15	16	17	18	
		1A	2A											3A	4A	5A	6A	7A	8A	
Periods	1	1 H 1s <sup>1</sup>	2 He 1s <sup>2</sup>											5 B 2s <sup>2</sup> 2p <sup>1</sup>	6 C 2s <sup>2</sup> 2p <sup>2</sup>	7 N 2s <sup>2</sup> 2p <sup>3</sup>	8 O 2s <sup>2</sup> 2p <sup>4</sup>	9 F 2s <sup>2</sup> 2p <sup>5</sup>	10 Ne 2s <sup>2</sup> 2p <sup>6</sup>	
	2	3 Li 2s <sup>1</sup>	4 Be 2s <sup>2</sup>											13 Al 3s <sup>2</sup> 3p <sup>1</sup>	14 Si 3s <sup>2</sup> 3p <sup>2</sup>	15 P 3s <sup>2</sup> 3p <sup>3</sup>	16 S 3s <sup>2</sup> 3p <sup>4</sup>	17 Cl 3s <sup>2</sup> 3p <sup>5</sup>	18 Ar 3s <sup>2</sup> 3p <sup>6</sup>	
3	3B	21 Sc 3d <sup>1</sup> 4s <sup>2</sup>	22 Ti 3d <sup>2</sup> 4s <sup>2</sup>	23 V 3d <sup>3</sup> 4s <sup>2</sup>	24 Cr 3d <sup>5</sup> 4s <sup>1</sup>	25 Mn 3d <sup>5</sup> 4s <sup>2</sup>	26 Fe 3d <sup>6</sup> 4s <sup>2</sup>	27 Co 3d <sup>7</sup> 4s <sup>2</sup>	28 Ni 3d <sup>8</sup> 4s <sup>2</sup>	29 Cu 3d <sup>10</sup> 4s <sup>1</sup>	30 Zn 3d <sup>10</sup> 4s <sup>2</sup>			31 Ga 4s <sup>2</sup> 4p <sup>1</sup>	32 Ge 4s <sup>2</sup> 4p <sup>2</sup>	33 As 4s <sup>2</sup> 4p <sup>3</sup>	34 Se 4s <sup>2</sup> 4p <sup>4</sup>	35 Br 4s <sup>2</sup> 4p <sup>5</sup>	36 Kr 4s <sup>2</sup> 4p <sup>6</sup>	
	4	39 Y 4d <sup>1</sup> 5s <sup>2</sup>	40 Zr 4d <sup>2</sup> 5s <sup>2</sup>	41 Nb 4d <sup>4</sup> 5s <sup>1</sup>	42 Mo 4d <sup>5</sup> 5s <sup>1</sup>	43 Tc 4d <sup>5</sup> 5s <sup>2</sup>	44 Ru 4d <sup>7</sup> 5s <sup>1</sup>	45 Rh 4d <sup>8</sup> 5s <sup>1</sup>	46 Pd 4d <sup>10</sup>	47 Ag 4d <sup>10</sup> 5s <sup>1</sup>	48 Cd 4d <sup>10</sup> 5s <sup>2</sup>			49 In 5s <sup>2</sup> 5p <sup>1</sup>	50 Sn 5s <sup>2</sup> 5p <sup>2</sup>	51 Sb 5s <sup>2</sup> 5p <sup>3</sup>	52 Te 5s <sup>2</sup> 5p <sup>4</sup>	53 I 5s <sup>2</sup> 5p <sup>5</sup>	54 Xe 5s <sup>2</sup> 5p <sup>6</sup>	
5	5B	57 *La 5d <sup>1</sup> 6s <sup>2</sup>	72 Hf 5d <sup>2</sup> 6s <sup>2</sup>	73 Ta 5d <sup>3</sup> 6s <sup>2</sup>	74 W 5d <sup>4</sup> 6s <sup>2</sup>	75 Re 5d <sup>5</sup> 6s <sup>2</sup>	76 Os 5d <sup>6</sup> 6s <sup>2</sup>	77 Ir 5d <sup>7</sup> 6s <sup>2</sup>	78 Pt 5d <sup>9</sup> 6s <sup>1</sup>	79 Au 5d <sup>10</sup> 6s <sup>1</sup>	80 Hg 5d <sup>10</sup> 6s <sup>2</sup>			81 Tl 6s <sup>2</sup> 6p <sup>1</sup>	82 Pb 6s <sup>2</sup> 6p <sup>2</sup>	83 Bi 6s <sup>2</sup> 6p <sup>3</sup>	84 Po 6s <sup>2</sup> 6p <sup>4</sup>	85 At 6s <sup>2</sup> 6p <sup>5</sup>	86 Rn 6s <sup>2</sup> 6p <sup>6</sup>	
	6	89 †Ac 6d <sup>1</sup> 7s <sup>2</sup>	104 Rf 6d <sup>2</sup> 7s <sup>2</sup>	105 Db 6d <sup>3</sup> 7s <sup>2</sup>	106 Sg 6d <sup>4</sup> 7s <sup>2</sup>	107 Bh 6d <sup>5</sup> 7s <sup>2</sup>	108 Hs 6d <sup>6</sup> 7s <sup>2</sup>	109 Mt 6d <sup>7</sup> 7s <sup>2</sup>	110 (271.15)	111 (272.15)	112 (277)			113 (285)	114 (285)	115 (285)	116 (289)			
7	7	87 Fr 7s <sup>1</sup>	88 Ra 7s <sup>2</sup>																	

Lanthanides

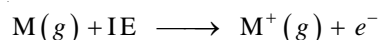
Actinides

We find from the table that irregularities involve the placing of one or two electrons from  $ns$  orbital in  $(n-1)d$  orbitals. There is very little energy difference between such  $s$  and  $d$  orbitals so that there is very little to choose from energy point of view. The deviations occur when  $d$  level orbitals are either almost full (e.g., Cu, Pd, Ag, Pt and Au) or half-full (Cr and Mo). The explanation for this deviation lies in the superior stability of completely filled or all half-filled orbitals than nearly filled or nearly half-filled orbitals. Thus  $d^5$  and  $d^{10}$  configurations are much more stable than  $d^4$  or  $d^8$  or  $d^9$ . Spectroscopic data and magnetic properties of elements justify the statement that **half-filled and completely filled subshells contribute to the stability.**

### IONISATION ENERGY

The process of removing an electron from an isolated atom to form a positive ion is called ionisation. Energy will be required to remove an electron from the atom against the force of attraction of the nucleus.

**The ionisation energy (IE) of an element is defined as the energy needed to remove a single electron from an atom of the element in the gaseous state.** That is,

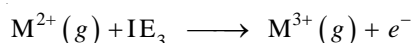
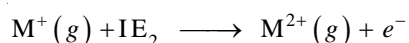
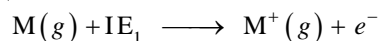


Since one, two or more electrons may be removed from the same atom, one after the other, we have as many ionisation energies of the element.

The **First ionisation energy ( $IE_1$ )**, is the energy needed to remove the first electron from the gaseous atom  $M$  to form  $M^+$  ion.

The **Second ionisation energy ( $IE_2$ )**, is the energy needed to remove a second electron, from the gaseous  $M^+$  ion to form  $M^{2+}$  ion.

Higher ionisation energies can be defined in the same way. We can depict the first, second and third ionisation energies in the form of equations as :



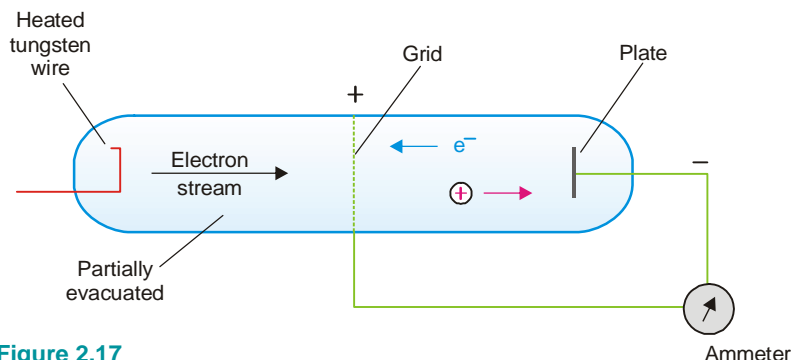
Ionisation energies are sometimes called **Ionisation potentials**. Ionisation energies are usually expressed in electron volts (eV) per atom, or in kilojoules per mole of atoms ( $\text{kJ mol}^{-1}$ ). For conversion,  $1\text{eV atom}^{-1} = 96.48\text{ kJ mol}^{-1}$ .

### MEASUREMENT OF IONISATION ENERGIES

The amount of energy required to detach an electron from an atom can be measured by supplying the required energy as thermal energy, electrical energy, or radiant energy. Thus ionisation energies can be determined from the spectrum of the element or by any of the two methods detailed below.

#### (1) The Electrical method

The apparatus used is shown in Fig. 2.17. The electrically heated tungsten wire emits electrons. The grid can be charged positively to different voltages which we read with a voltmeter. The plate opposite the grid has a small negative charge. When the potential to the grid is zero, no current flows between the grid and the plate. However if we give sufficient potential to the grid, the electrons emitted by the tungsten wire are accelerated towards the grid, pass through it and ionise the atoms between grid and plate. The electron ejected by each atom is attracted to grid and positive ion is attracted to plate. A current thus passes between grid and plate which is shown up by an ammeter. **The minimum grid voltage that just produces a current is called ionization potential.**



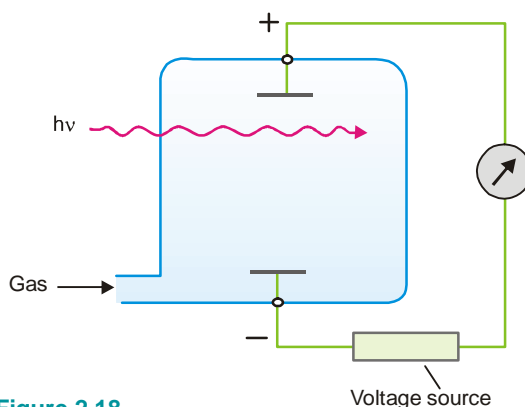
■ **Figure 2.17**  
Measurement of Ionisation energy.

If  $V$  be the ionization potential, the ionization energy (IE) is calculated as :

$$\begin{aligned} \text{IE} &= V \times \text{charge of electron} \times \text{Avogadro No} \\ &= V \times 1.60 \times 10^{-19} \times 6.02 \times 10^{23} \\ &= V \times 96.3 \text{ kJ mol}^{-1} \end{aligned}$$

## (2) Photo-ionisation Method

The gaseous atoms are introduced into a chamber containing two electrically charged plates (Fig. 2.18). As neutral atoms, they do not conduct electricity and no current flows between the plates. When radiant energy ( $h\nu$ ) is supplied to the gaseous atoms, ionisation will occur and electric current will flow. The frequency of the radiation used is gradually increased. The minimum frequency necessary to cause ionisation of the gaseous atoms, as shown by the flow of an electric current is noted. From this frequency the ionisation energy is calculated.



■ **Figure 2.18**  
Measurement of ionisation energy  
by photo-ionisation method.

## Order of Successive Ionisation Energies

The second ionisation energy ( $IE_2$ ) is larger than the first ionisation energy ( $IE_1$ ) because it is more difficult to detach an electron from a +ve ion than a neutral atom. The third ionisation energy ( $IE_3$ ) is still larger as the third electron has to be detached from a 2+ ion. Thus in general successive ionisation energies increase in magnitude. That is,

$$IE_1 < IE_2 < IE_3 < IE_4, \text{ and so on.}$$

For illustration, the first four ionisation energies for sodium and magnesium are listed below:



TABLE 2.4. IONISATION ENERGIES IN KILO JOULE PER MOLE ( $\text{KJ mol}^{-1}$ )

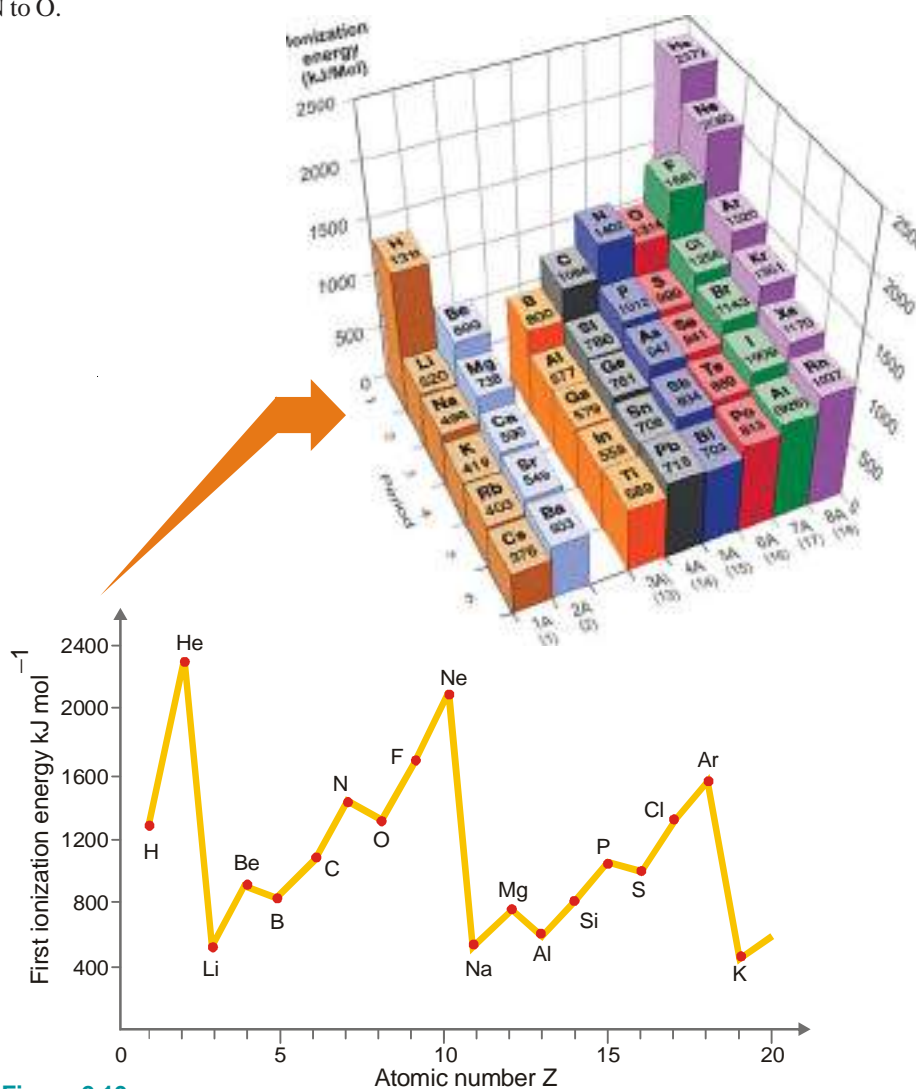
	$\text{IE}_1$	$\text{IE}_2$	$\text{IE}_3$	$\text{IE}_4$
Sodium	500	4600	6900	9500
Magnesium	740	1500	7700	10500

**Principal Trends in Ionisation Energies**

A graph of the first ionisation energies against atomic number ( $Z$ ) for the first 18 elements of the Periodic Table is shown in Fig. 2.19.

The important trends as illustrated by the graph are:

- (1) **Ionisation energies increase across a period.** *e.g.*, Li to Ne.
- (2) **Ionisation energies decrease down a group** *e.g.*, Li, Na, K.
- (3) **There are regular discontinuities in the increase trend across a period** *e.g.*, Be to B, and N to O.

■ **Figure 2.19**

Graph showing the variation of first ionisation energies with increase of atomic number.

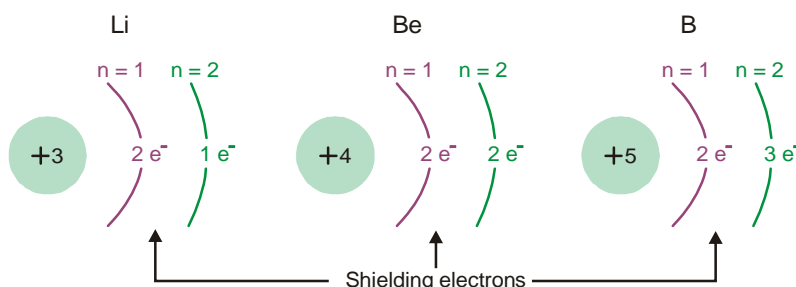
### Increase across a Period

As we pass from left to right in a period, the first ionisation energy shows a steady increase. Thus in Period 2 from Li to N, we have

	Li	Be	B	C	N
$IE_1$ (kJ mol <sup>-1</sup> )	525	906	805	1090	1400

#### Explanation

The outer-shell electrons in the elements of the same period are arranged in the same shell. For example, the build up of electrons in Period 2 from Li to B is shown in Fig. 2.20.



■ **Figure 2.20**  
Build up of atoms of elements for Li, Be, B.

Moving from Li to B, the positive charge on the nucleus increases whereas the distance between the nucleus and valence electrons decreases. Therefore more energy is required to remove an electron as we go from left to right in the Period. Since the number of screening electrons remains the same, they do not upset the increase trend.

### Decrease down a Group

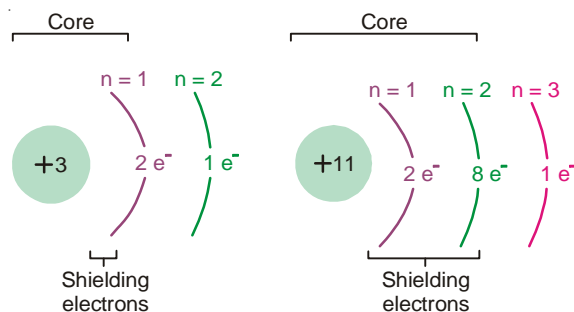
In the elements of a vertical Group of the Periodic table, the number of outer shell electrons is the same. But the following changes are noted from top to bottom.

- (1) **The principal quantum number  $n$  containing the valence electrons increases.**
- (2) **The nuclear charge (At. No.) increases.**
- (3) **The number of electrons in the inner shells (shielding electrons) increases.**

The net result of these changes is that the first ionisation energies down a group record a progressive decrease. Thus for Group IA we have

	Li	Na	K	Rb	Cs
$IE_1$ (kJ mol <sup>-1</sup> )	525	500	424	408	382

Let us explain the above decrease trend by taking example of lithium and sodium. They have the atomic structures.





Lithium and sodium both have one outer-shell electron. The number of shielding electrons in sodium is 10 while in lithium it is 2. If we assume that the inner shell electrons provide hundred percent screening, the core charge attracting the outer-shell electron would be :

	Nuclear charge	Shielding electrons	Core charge attracting outer-shell electron
Li	3	2	$3 - 2 = +1$
Na	11	2, 8	$11 - 10 = +1$

Thus the same net charge (+ 1) attracts the outer-shell electrons to the core. But the distance of the outer electron from the nucleus is greater in Na ( $n = 3$ ) than in Li ( $n = 1$ ). Therefore the force of attraction between the outer electron and the core will be less in Na than in Li. That explains the lower I E of Na compared to Li. By the same line of argument, the decrease trend in I E from element to element while going down a Group can be justified.

### Regular Discontinuities

As already discussed, the first ionisation energies increase across a period. But this increase trend is upset at the third and sixth element in a period. As clear from graph in Fig. 2.19, there are breaks at B and O which occupy the third and fifth positions respectively in the 2nd period. The I E<sub>1</sub> of B is less than that of Be and the I E<sub>1</sub> of O is less than that of N.

#### Explanation

(a) The electronic configuration of Be and B are :



The 2p orbital electron of B is already higher in energy than the 2s orbital electron. Therefore the removal of electron from B requires less energy and its I E<sub>1</sub> is lower.

(b) The electronic configuration of N and O is :



The 2p orbitals may be represented as

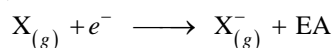


Whenever two electrons occupy a particular orbital, they repel each other. As a result it is easier to remove one of the paired 2p electrons from O than it is to remove an unpaired electron from N atom. Thus I E<sub>1</sub> of O is lower than that of N.

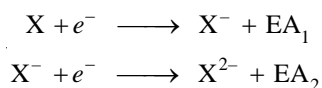
### ELECTRON AFFINITY

A neutral atom can accept an electron to form negative ion. In this process, in general, energy is released.

**Electron affinity (EA) of an element is the amount of energy released when an electron is added to a gaseous atom to form an anion.**



The energy involved in the addition of the first electron is called **first-electron affinity**; the energy involved in the addition of a second electron is called **second-electron affinity**; and so on. Thus,

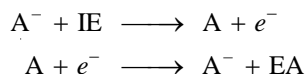


The electron affinity of an element measures the ease with which it forms an anion in the gas phase.

Electron affinities are difficult to measure and accurate values are not known for all elements. They are expressed in  $\text{kJ mol}^{-1}$ .

### Trends in Electron Affinities

The factors that determine the magnitude and sign of electron affinities are similar to those used to explain ionisation energies of elements. In fact, the electron affinity of a neutral atom may be thought of simply as equivalent to the ionisation energy of the singly charged negative ion of the atom.



The first-electron affinities of elements in the Periodic table are expected to show trends analogous to those of ionisation energies.

#### (a) Increase across a Period

The values of electron affinities for Period 2 are listed below.

Be	B	C	N	O	F	Ne
-240	23	123	0.00	142	323	-29 kJ mol <sup>-1</sup>

As we proceed from left to right, the general trend is the increase of electron affinities. Be, N and Ne are exceptions.

#### Explanation

Elements having relatively stable electronic configurations find it difficult to accept an electron readily. The atom of Be has the configuration  $1s^2 2s^2$ . The  $1s$  subshell is completely filled and, therefore, the electron being added must go to a subshell of considerably higher energy. This gives rise to negative electron affinity for Be.

The atom of N ( $1s^2 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$ ) has half-filled  $2p$  subshells, a condition of extra stability. Therefore the electron affinity of N would be less than expected.

The electron affinity of Neon is low because it has a stable outer-shell octet. Its atom shows little tendency to start a new shell.

#### (b) Decrease down a Group

The values of electron affinities for halogens (Group VII) are given below.

F	Cl	Br	I
332.6	349	324.7	296

The electron affinities show a general decrease from top to bottom. This is so because the valence shell is progressively farther from the nucleus. The value for fluorine, however, is out of line as it has a smaller atomic size than that of chlorine.

#### (c) Second electron affinity negative

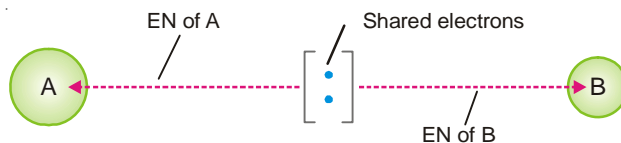
The second electron affinity of an element is always negative. This is on account of repulsion between the electron being added and the already negatively charged atom. For example,



### ELECTRONEGATIVITY

In a molecule A–B the electrons forming the covalent bond are attracted by atom A as well as by B. This attraction is measured in terms of what we call **electronegativity, EN**. It may be defined as :

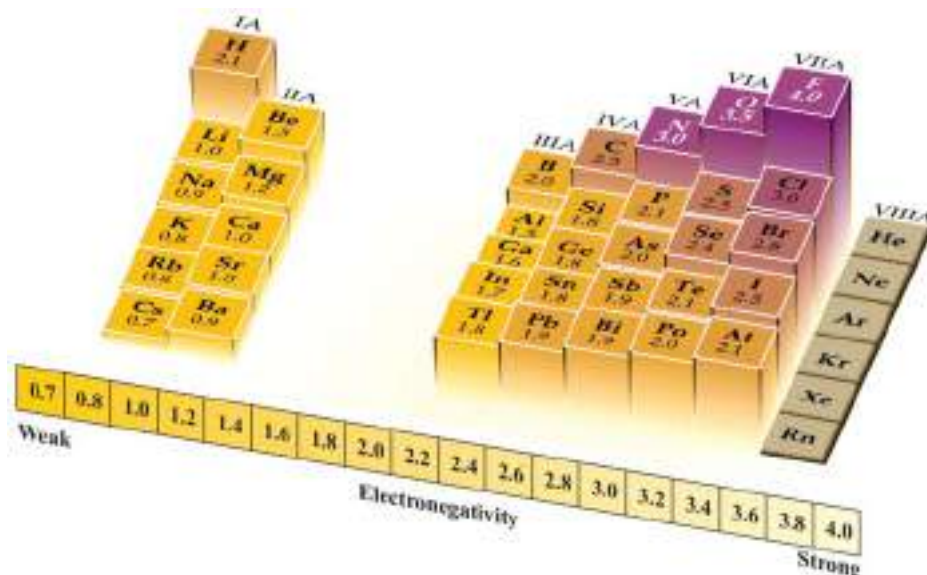
**The attraction exerted by an atom on the electron pair bonding it to another atom by a covalent bond.**



It is evident that an atom of high electronegativity will attract the shared electron pair away from one of lower electronegativity. Thus the former atom will acquire a partial negative charge while the other atom will get a partial positive charge.

### Electronegativity Values

Using measured values of bond energies, Pauling devised a set of electronegativity values. He allotted a value of 4 to the most electronegative atom, namely fluorine, and assigned values to the atoms of other elements.



### Trend in Electronegativities

The variations in electronegativities of elements in the Periodic table are similar to those of ionisation energies and electron affinities.

#### (1) Increase across a Period

The values of electronegativities increase as we pass from left to right in a Period. Thus for Period 2 we have

Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0

This is so because the attraction of bonding electrons by an atom increases with increase of nuclear charge (At. No.) and decrease of atomic radius. Both these factors operate as we move to the right in a Period.

#### (2) Decrease down a Group

The electronegativities of elements decrease from top to bottom in a Group. Thus for Group VII

we have

F	Cl	Br	I
4.0	3.0	2.8	2.5

The decrease trend is explained by more shielding electrons and larger atomic radius as we travel down a Group.

### Importance of Electronegativity

The electronegativities of elements are widely used throughout the study of Chemistry. Their usefulness will be discussed at appropriate places. The important applications of electronegativities are listed below.

- (1) **In predicting the polarity of a particular bond.** The polarity of a bond, in turn, shows the way how the bond would break when attacked by an organic reagent.
- (2) **In predicting the degree of ionic character of a covalent bond.**
- (3) **In predicting of inductive effects in organic chemistry.**
- (4) **In understanding the shapes of molecules.**

### EXAMINATION QUESTIONS

1. Define or explain the following terms :
 

(a) Planck's constant	(b) de Broglie equation
(c) Heisenberg's uncertainty principle	(d) Schrödinger's wave equation
(e) Principal quantum number	(f) Azimuthal quantum number
(g) Magnetic quantum number	(h) Zeeman effect
(i) Spin quantum number	(j) Pauli's exclusion principle
(k) Aufbau principle	(l) Hund's rule
2. What do you mean by the 'ionization potential' of an element? Why the first ionization potential of an element is less than the second ionization potential? How does the ionization potential of an element vary with atomic volume?
3. (a) What do you understand by the dual character of matter? Derive de Broglie's equation. How was it verified?  
 (b) A particle having a wavelength  $6.6 \times 10^{-4}$  cm is moving with a velocity of  $10^6$  cm sec<sup>-1</sup>. Find the mass of the particle. Planck's constant =  $6.62 \times 10^{-27}$  erg sec.  
**Answer.** (b)  $1.003 \times 10^{-29}$  g
4. (a) State and discuss Heisenberg's uncertainty principle.  
 (b) Draw energy level diagram valid for hydrogen and multi-electron atoms.  
 (c) Write Schrödinger wave equation.
5. Discuss the following :
  - (a) Hund's Rule of Maximum multiplicity.
  - (b) Pauli's Exclusion Principle.
6. What is the wavelength associated with a particle of mass 0.1 g moving with a speed of  $1 \times 10^5$  cm sec<sup>-1</sup> ( $h = 6.6 \times 10^{-27}$  erg sec)  
**Answer.**  $6.6 \times 10^{-31}$  cm
7. State Pauli's exclusion principle. Based on this principle show that the maximum number of electrons that can be accommodated in an orbit is 8 when  $n = 20$ .
8. The velocity of a ball being bowled by Kapil Dev is 25 m sec<sup>-1</sup>. Calculate the wavelength of the matter-

wave associated with the ball. Derive the equation you used. Weight of cricket ball = 158.5 g and  $h = 6.625 \times 10^{-27}$  erg sec.

**Answer.**  $1.67 \times 10^{-32}$  cm

9. Calculate the de Broglie wavelength for a ball of 200 g mass moving with a velocity  $3 \times 10^{10}$  cm sec<sup>-1</sup> and an electron moving with the same velocity. What do these values indicate?

**Answer.**  $1.04 \times 10^{-39}$  cm;  $2.4239 \times 10^{-10}$  cm

10. (a) Describe the Davison and Germer experiment for the verification of wave nature of electrons.  
(b) If an electron is accelerated by 100 volts, calculate the de Broglie wavelength associated with it. Also calculate the velocity acquired by the electron (Mass of electron =  $9.1 \times 10^{-28}$  g;  $h = 6.62 \times 10^{-27}$  erg sec).

**Answer.** (b)  $1.2247 \text{ \AA}$ ;  $5.940 \times 10^8$  cm sec<sup>-1</sup>

11. State Pauli's exclusion principle and show that the maximum number of electrons in a given shell is  $2n^2$  where  $n$  is the principal quantum number of the shell.

12. Derive Schrödinger wave equation for the wave mechanical model of an atom and discuss its application to hydrogen atom. What is the significance of  $\psi$  and  $\psi^2$  in it?

13. What are three quantum numbers used to describe an orbital? What property of an orbital is described by each quantum number? Specify the rule that governs the values of each quantum number.

14. What are quantum numbers? Mention all values of different quantum numbers when  $n = 2$ .

15. (a) Which other particles besides electron show particle-wave duality? Give two examples.

(b) Calculate the wavelength of a particle of mass 1.5 g moving with a velocity of 250 m sec<sup>-1</sup>.

**Answer.** (b)  $1.766 \times 10^{-31}$  cm

16. (a) Write a note on Heisenberg's uncertainty principle. How this principle goes against Bohr's theory?

(b) What is ionisation energy? What are the factors which affect the ionisation energy of an element? How ionisation energy changes among the elements in a group and in a period?

17. Write short notes on :

(a) Pauli's exclusion principle (b) Uncertainty principle

(c) Photoelectric effect (d) Aufbau principle

18. Calculate the momentum of a particle which has a de Broglie's wavelength of 0.1 nm.

**Answer.**  $6.6 \times 10^{-24}$  kg m<sup>2</sup> sec<sup>-1</sup>

19. The kinetic energy of an electron is  $4.55 \times 10^{-25}$  J. Calculate its wavelength ( $h = 6.6 \times 10^{-34}$  kg m<sup>2</sup> sec<sup>-1</sup>; mass of electron =  $9.1 \times 10^{-31}$  kg).

**Answer.**  $7.25 \times 10^{-1}$  m

20. The kinetic energy of a subatomic particle is  $5.60 \times 10^{-25}$  J. Calculate the frequency of the particle wave (Planck's Constant  $h = 6.6 \times 10^{-34}$  kg m<sup>2</sup> sec<sup>-1</sup>)

**Answer.**  $1.696 \times 10^9$  sec<sup>-1</sup>

21. Calculate the wavelength associated with an electron moving with a velocity of  $1 \times 10^8$  cm sec<sup>-1</sup>. (mass of the electron =  $9.1 \times 10^{-28}$  g).

**Answer.**  $7.28 \times 10^{-8}$  cm

22. Calculate the uncertainty in the velocity of a bullet of mass 10 g whose position at time  $t$  is known with uncertainty equal to  $1.0 \times 10^{-5}$  m.

**Answer.**  $5.628 \times 10^{-28}$  m sec<sup>-1</sup>

(Panjab BSc, 2000)

23. Calculate the uncertainty in the velocity of an electron if the uncertainty in position is  $1 \times 10^{-10}$  m.

**Answer.**  $5.76 \times 10^5$  m sec<sup>-1</sup>

(Madras BSc, 2000)

24. Calculate the uncertainty in the position of a particle when the uncertainty in the momentum is

(a)  $1 \times 10^{-7}$  kg m sec<sup>-1</sup> and

(b) zero

**Answer.** (a)  $5.72 \times 10^{-28}$  m;

(b)  $\infty$

(Delhi BSc, 2001)

25. Explain Heisenberg's uncertainty principle. How does it influence the concept of the electron ?

(Lucknow BSc, 2001)

26. What are postulates of Quantum Mechanics? (MD Rohtak BSc, 2002)
27. Write Schrödinger's wave equation for a single electron atom. (Nagpur BSc, 2002)
28. (a) Deduce de Broglie's relation for a matter wave and explain the terms involved in it.  
(b) Draw and explain the angular probability distribution curve for 1s electron. (Mizoram BSc, 2002)
29. (a) What is the significance of the wave function, ' $\psi$ '?  
(b) State and explain Heisenberg's uncertainty principle. (Mizoram BSc, 2002)
30. Give wave mechanical interpretation of an atomic orbital. Discuss qualitatively the probability distribution curves of s, p and d orbitals and hence draw the contour diagrams of all the 2p, 3p and 3d orbitals on x, y and z axis, showing the sign of wave functions. (Guru Nanak Dev BSc, 2002)
31. Describe the shapes of s and p orbitals on the basis of quantum mechanical concept. (Mizoram BSc, 2002)
32. A moving ball weighing 200 g is to be located within 0.2 Å. What is the uncertainty in the velocity? Comment on your result. (Given  $h = 6.626 \times 10^{-34}$  Joule sec)  
**Answer.**  $165.5 \times 10^{-24}$  m sec<sup>-1</sup> (Lucknow BSc, 2002)
33. Calculate de Broglie's wavelength of a xenon atom moving with a velocity of  $2.4 \times 10^2$  m sec<sup>-1</sup>. (Atomic weight of xenon is  $2.2 \times 10^{-25}$  kg)  
**Answer.** 30 Å (Arunachal BSc, 2002)
34. (a) Give de Broglie's relation for a particle of mass, m, moving with a velocity, v.  
(b) Calculate the uncertainty in velocity of a cricket ball of mass 150 g if the uncertainty in position is 1 Å. ( $h = 6.63 \times 10^{-34}$  J sec)  
**Answer.** (b)  $3.516 \times 10^{-24}$  m sec<sup>-1</sup> (Arunachal BSc, 2002)
35. An electron has a speed of  $3.0 \times 10^4$  cm sec<sup>-1</sup> accurate to 0.01%. Find out the uncertainty in the position of the electron. ( $h = 6.625 \times 10^{-27}$  erg sec,  $m = 9.11 \times 10^{-28}$  g)  
**Answer.**  $17.582 \times 10^{-22}$  Å (Vidyasagar BSc, 2002)
36. (a) Discuss probability distribution curves for s and p orbitals.  
(b) Discuss the following :  
(i) Wave nature of an electron  
(ii) Significance of wave function (Jammu BSc, 2002)
37. (a) Write the electronic configuration of the elements with atomic numbers : 10, 20, 29, 49 and 63  
(b) Write Hund's rule of maximum multiplicity.  
(c) What do you understand by wave function? (Jammu BSc, 2002)
38. (a) Give radial probability distribution curves for 2p and 3p orbitals and give their characteristics.  
(b) Draw energy level diagram for a multi-electron atom.  
(c) Write the ground state electronic configuration for Ce (Z = 58) and Sn (Z = 50). (Punjabi BSc, 2002)
39. State Schrödinger's wave equation. How this equation led to quantisation of energy? (Nagpur BSc, 2003)
40. Calculate uncertainty in momentum of electron, if uncertainty in position is  $10^{-8}$  m ( $h = 6.624 \times 10^{-34}$  J sec)  
**Answer.**  $5.27 \times 10^{-27}$  (Nagpur BSc, 2003)
41. (a) What is 'Effective Nuclear Charge'? What relation does it have with 'shielding' phenomenon?  
(b) Given that the first I.E. of Al is less than that of Mg. What about the second I.E. of Al compared to that of Mg? Why? (Delhi BSc, 2003)
42. Calculate the energy of a photon of wavelength 400 nm. ( $h = 6.62 \times 10^{-34}$  J sec.)  
**Answer.**  $0.04967 \times 10^{-17}$  Joule (Sambalpur BSc, 2003)
43. The wavelength of blue light is 480 nm. Calculate the frequency and wavelength of the light. ( $c = 3 \times 10^8$  m sec<sup>-1</sup>)  
**Answer.**  $6.25 \times 10^{14}$  sec<sup>-1</sup> and  $1.6 \times 10^{-15}$  m<sup>-1</sup> (Sambalpur BSc, 2003)
44. The uncertainty in the momentum of a particle is found to be  $2.5 \times 10^{-16}$  g cm<sup>-1</sup>. What is the uncertainty in its position? ( $h = 6.626 \times 10^{-27}$  erg sec)  
**Answer.**  $2110 \times 10^{-7}$  Å (Sambalpur BSc, 2003)

45. Determine the wavelength of a cricket ball having a mass  $4.0 \times 10^{-2}$  kg and velocity  $30 \text{ m sec}^{-1}$ . ( $h = 6.624 \times 10^{-34} \text{ J sec}$ )  
**Answer.**  $5.52 \times 10^{-24} \text{ \AA}$  (Nagpur BSc, 2003)
46. Calculate uncertainty in momentum of electron, if uncertainty in position is  $10^{-6} \text{ m}$ . ( $h = 6.624 \times 10^{-34} \text{ J sec}$ )  
**Answer.**  $0.527 \times 10^{-28} \text{ Ns}$  (Nagpur BSc, 2003)
47. Calculate de Broglie wavelength associated with a ball weighing 150 g thrown with a velocity of  $3 \times 10^3 \text{ cm sec}^{-1}$ . ( $h = 6.625 \times 10^{-27} \text{ erg sec}$ )  
**Answer.**  $0.0147 \times 10^{-30} \text{ cm}$  (Sambalpur BSc, 2004)
48. Calculate the de Broglie wavelength of an electron moving with a velocity of  $6 \times 10^5 \text{ m sec}^{-1}$ .  
**Answer.**  $1.456 \times 10^{-8} \text{ m}$  (Punjabi BSc, 2004)
49. Calculate the uncertainty in position of an electron if uncertainty in velocity is  $5.7 \times 10^5 \text{ m sec}^{-1}$ . ( $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$ ; mass of electron =  $9 \times 10^{-31} \text{ kg}$ )  
**Answer.**  $10^{-10} \text{ m}$  (Agra BSc, 2004)
50. A body moving with a speed of  $100 \text{ m sec}^{-1}$  has a wavelength of  $5 \times 10^{-36} \text{ m}$ . Calculate the mass of the body. ( $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$ )  
**Answer.**  $1.32 \text{ kg}$  (Panjab BSc, 2004)
51. Calculate the uncertainty in momentum of an electron if uncertainty in its position is approximately 100 pm. ( $5.0 \times 10^{-12} \text{ m}$ ).  
**Answer.**  $5.27 \times 10^{-25} \text{ kg m sec}^{-1}$  (Delhi BSc, 2004)
52. Calculate the wavelength associated with an electron moving with a velocity of  $1 \times 10^8 \text{ cm sec}^{-1}$ . (mass of the electron =  $9.1 \times 10^{-28} \text{ g}$ ).  
**Answer.**  $7.28 \times 10^{-8} \text{ cm}$  (Delhi BSc, 2005)
53. Calculate the de Broglie wavelength of an electron moving with a velocity of  $6 \times 10^5 \text{ m sec}^{-1}$ .  
**Answer.**  $1.456 \times 10^{-8} \text{ m}$  (Tripura BSc, 2005)
54. A body moving with a speed of  $100 \text{ m sec}^{-1}$  has a wavelength of  $5 \times 10^{-36} \text{ m}$ . Calculate the mass of the body. ( $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$ ).  
**Answer.**  $1.32 \text{ kg}$  (Banaras BSc, 2006)
55. Calculate the uncertainty in momentum of an electron if uncertainty in its position is approximately 100 pm. ( $5.0 \times 10^{-12} \text{ m}$ ).  
**Answer.**  $5.27 \times 10^{-25} \text{ kg m sec}^{-1}$  (Sambalpur BSc, 2006)
56. Calculate the uncertainty in the velocity of a bullet weighing 10 g whose position is known with an accuracy of  $\pm 0.1 \text{ nm}$ .  
**Answer.**  $0.527 \times 10^{-27} \text{ m sec}^{-1}$  (Panjab BSc, 2006)

### MULTIPLE CHOICE QUESTIONS

1. According to de Broglie's equation, the momentum of a particle in motion is \_\_\_\_\_ proportional to wavelength.  
 (a) inversely (b) directly  
 (c) is not (d) none of these  
**Answer.** (a)
2. The wavelength of large objects is of no significance as it is too \_\_\_\_\_ to be measurable.  
 (a) small (b) large  
 (c) heavy (d) none of these  
**Answer.** (a)

3. de Broglie equation is

(a)  $\lambda = h/m v$

(b)  $\lambda = m v/h$

(c)  $\lambda = h m v$

(d)  $\lambda = \frac{h v}{m}$

**Answer.** (a)

4. "It is impossible to determine simultaneously the position and velocity with accuracy of a small particle like electron". This statement is

(a) Heisenberg's uncertainty principle

(b) de Broglie principle

(c) Planck's law

(d) Aufbau's principle

**Answer.** (a)

5. The relation  $\Delta x \times \Delta p = \frac{h}{4\pi}$  represents

(a) de Broglie equation

(b) Heisenberg's uncertainty principle

(c) Schrödinger's wave equation

(d) Pauli's exclusion principle

**Answer.** (b)

6. In Schrödinger's wave equation, the symbol  $\psi$  represents the

(a) wavelength of the spherical wave

(b) amplitude of the spherical wave

(c) frequency of the spherical wave

(d) none of these

**Answer.** (b)

7. The energy of electron in an atomic orbital is always \_\_\_\_\_.

(a) different

(b) zero

(c) infinite

(d) same

**Answer.** (d)

8. An orbital is the space around the nucleus where the probability of finding electron is

(a) always zero

(b) maximum

(c) minimum

(d) always infinite

**Answer.** (b)

9. The Principal quantum number ' $n$ ' represents

(a) average size of the electron cloud

(b) average energy of the electron

(c) average distance of the electron from the nucleus

(d) all of the above

**Answer.** (d)

10. The Principal quantum number is related to the

(a) orbital angular momentum

(b) size and shape of the orbital

(c) orientation of the orbital

(d) average size of the orbital

**Answer.** (d)

11. The quantum number that defines the shape of the orbital occupied by the electron is

(a) principal quantum number

(b) azimuthal quantum number

(c) magnetic quantum number

(d) spin quantum number

**Answer.** (b)

12. The angular momentum of the electron is defined by the quantum number that is denoted as

(a)  $n$

(b)  $\ell$

(c)  $m$

(d)  $s$

**Answer.** (b)

13. The total number of sublevels in each principal level is equal to

(a) spin quantum number

(b) magnetic quantum number

(c) azimuthal quantum number

(d) principal quantum number

**Answer.** (d)

14. The quantum number which accounts for the splitting up of spectral lines (Zeeman effect) is

(a) principal quantum number

(b) azimuthal quantum number

(c) magnetic quantum number

(d) spin quantum number

**Answer.** (c)



15. For a given value of principal quantum number the order of increasing energy for different subshells is  
 (a)  $s < p < d < f$  (b)  $p < d < f < s$   
 (c)  $d < f < p < s$  (d)  $f < d < p < s$   
**Answer.** (a)
16. The  $p_x$ ,  $p_y$  and  $p_z$  orbitals are called degenerate orbitals as they have  
 (a) equal energy (b) same orientation in space  
 (c) same size (d) none of these  
**Answer.** (a)
17. A nodal plane separates the two lobes of a  $p$ -orbital. There is \_\_\_\_\_ likelihood of finding the electron on this plane.  
 (a) no (b) every  
 (c) either of these (d) none of these  
**Answer.** (a)
18. The total values of magnetic quantum number for a given value of azimuthal quantum number is  
 (a)  $2\ell$  (b)  $2\ell + 1$   
 (c)  $2\ell - 1$  (d)  $2\ell - 2$   
**Answer.** (b)
19. "No two electrons in an atom can have same set of four identical quantum numbers". It is the statement of  
 (a) Aufbau principle (b) Hund's rule  
 (c) Pauli's exclusion principle (d) none of these  
**Answer.** (c)
20. The orbital with  $n = 3$  and  $\ell = 2$  is  
 (a)  $3s$  (b)  $3p$   
 (c)  $3d$  (d)  $3f$   
**Answer.** (c)
21.  $4s$  orbital has lesser energy than  $3d$  orbital because it has  
 (a) greater value of  $n$  (b) lesser value of  $\ell$   
 (c) lesser value of  $n + \ell$  (d)  $\ell = 0$   
**Answer.** (c)
22. The maximum number of electrons that can be accommodated in  $f$ -subshell is  
 (a) 5 (b) 7  
 (c) 10 (d) 14  
**Answer.** (d)
23. The energy associated with electrons in  $s$ ,  $p$ ,  $d$  and  $f$  orbitals of a particular principal quantum number in hydrogen atom is in the order  
 (a)  $s = p = d = f$  (b)  $s < p < d < f$   
 (c)  $p < d < f < s$  (d)  $f < d < p < s$   
**Answer.** (a)
24. For a multi-electron atom, the energy associated with electrons in  $s$ ,  $p$ ,  $d$  and  $f$  orbitals of a particular quantum number is in the order  
 (a)  $s = p = d = f$  (b)  $s < p < d < f$   
 (c)  $p < d < f < s$  (d)  $d < f < s < p$   
**Answer.** (b)
25. The two electrons in the first shell will differ in the values for  
 (a)  $n$  (b)  $\ell$   
 (c)  $m$  (d)  $s$   
**Answer.** (d)
26. Which one of the following sets of quantum numbers is not allowed?
- |     | $n$ | $\ell$ | $m$ | $s$            |
|-----|-----|--------|-----|----------------|
| (a) | 1   | 0      | 1   | $-\frac{1}{2}$ |
| (b) | 2   | 1      | 0   | $+\frac{1}{2}$ |

- (c) 2 1 -2  $+\frac{1}{2}$   
 (d) 2 1 +2 0

**Answer.** (d)

27. Which of the following is incorrect for 3d orbital?

- |     | $n$ | $\ell$ | $m$ | $s$            |
|-----|-----|--------|-----|----------------|
| (a) | 3   | 0      | 0   | $+\frac{1}{2}$ |
| (b) | 3   | 1      | 0   | $+\frac{1}{2}$ |
| (c) | 3   | 2      | 0   | $+\frac{1}{2}$ |
| (d) | 3   | 1      | 2   | $+\frac{1}{2}$ |

**Answer.** (d)

28. The value of azimuthal quantum number for last electron of N-atom is

- (a) 0 (b) 1  
 (c) 2 (d) 3

**Answer.** (b)

29. The maximum number of electrons in a subshell is given by the equation

- (a)  $n^2$  (b)  $2n^2$   
 (c)  $2\ell - 1$  (d)  $2\ell + 1$

**Answer.** (d)

30. Out of the following, which is the correct set of quantum numbers for the outermost electron of potassium atom ( $Z = 19$ )?

- |     | $n$ | $\ell$ | $m$ | $s$            |
|-----|-----|--------|-----|----------------|
| (a) | 4   | 3      | 2   | $-\frac{1}{2}$ |
| (b) | 4   | 2      | 0   | $-\frac{1}{2}$ |
| (c) | 4   | 1      | 0   | $+\frac{1}{2}$ |
| (d) | 4   | 0      | 0   | $-\frac{1}{2}$ |

**Answer.** (d)

31. The number of unpaired electrons in oxygen atom is

- (a) 1 (b) 2  
 (c) 3 (d) 4

**Answer.** (b)

32. The number of unpaired electrons in chromium atom ( $Z = 24$ ) is

- (a) 1 (b) 2  
 (c) 3 (d) 6

**Answer.** (d)

33. In nitrogen atom there are three unpaired electrons. These are having \_\_\_\_\_ direction of spin.

- (a) same (b) different  
 (c) similar (d) none of these

**Answer.** (a)

34. The maximum number of electrons that can be accommodated in  $s$ ,  $p$ ,  $d$  and  $f$  orbitals is

- (a) 1, 2, 3 and 4 respectively (b) 1, 2, 4 and 8 respectively  
 (c) 2, 4, 6 and 8 respectively (d) 2, 6, 10 and 14 respectively

**Answer.** (d)

35. The sum of all quantum numbers of the electron of hydrogen atom is

- (a)  $-1/2$  (b) 1  
 (c)  $3/2$  (d)  $+1/2$

**Answer.** (c)

36. The sum of all quantum numbers of the last electron in lithium atom is

- (a)  $3/2$  (b) 2  
 (c)  $5/2$  (d) 3

**Answer.** (c)

37. The value of azimuthal quantum number for the electrons present in 5s-orbital is

- (a) 0 (b) 1  
 (c) 2 (d) 5

**Answer.** (a)

38. According to Pauli's exclusion principle two electrons can occupy the same orbital only if they have \_\_\_\_\_ direction of spin.  
(a) different (b) same  
(c) similar (d) none of these  
**Answer.** (a)
39. In the ground state of an atom, the electrons tend to occupy the available orbitals in the \_\_\_\_\_ order of energies.  
(a) increasing (b) decreasing  
(c) any (d) none of these  
**Answer.** (a)
40. Amongst  $3d$ ,  $4s$  and  $4p$  orbitals, the order of increasing energies is  
(a)  $3d < 4p < 4s$  (b)  $4s < 4p < 3d$   
(c)  $4p < 4s < 3d$  (d)  $3d < 4s < 4p$   
**Answer.** (d)
41. While comparing the energies of two orbitals we compare their  $(n + \ell)$  values the orbital with \_\_\_\_\_  $(n + \ell)$  value will have \_\_\_\_\_ energy.  
(a) lower, lower (b) higher, lower  
(c) lower, higher (d) none of these  
**Answer.** (a)
42. When two orbitals have the same  $(n + \ell)$  value, the orbital with lower value of \_\_\_\_\_ has lower energy.  
(a) principal quantum number (b) azimuthal quantum number  
(c) magnetic quantum number (d) spin quantum number  
**Answer.** (a)
43. After filling the  $4p$ -orbitals, an electron will enter in  
(a)  $4d$  (b)  $4f$   
(c)  $5s$  (d)  $3d$   
**Answer.** (c)
44. If the electronic configuration of nitrogen (at no = 7) is written as  $1s^2 2s^2 2p_x^2 2p_y^1$ , it would violate  
(a) Aufbau principle (b) Pauli's exclusion principle  
(c) Hund's rule of maximum multiplicity (d) none of these  
**Answer.** (c)
45. The outermost electronic configuration of manganese (at. no. = 25) is  
(a)  $3d^5 4s^2$  (b)  $3d^6 4s^1$   
(c)  $3d^7 4s^0$  (d)  $3d^6 4s^2$   
**Answer.** (a)
46. The subshell, which does not exist, has the quantum numbers  
(a)  $n = 2$   $\ell = 0$  (b)  $n = 2$   $\ell = 1$   
(c)  $n = 2$   $\ell = 2$  (d)  $n = 3$   $\ell = 0$   
**Answer.** (c)
47. The ground state electronic configuration of carbon atom has \_\_\_\_\_ pairs and \_\_\_\_\_ unpaired electrons  
(a) 2, 2 (b) 1, 2  
(c) 2, 1 (d) 2, 3  
**Answer.** (a)
48. Two electrons occupying the same orbital have different \_\_\_\_\_.  
(a) principal quantum number (b) azimuthal quantum number  
(c) magnetic quantum number (d) spin quantum number  
**Answer.** (d)
49. If the value of azimuthal quantum number is 2, there will be \_\_\_\_\_ values for magnetic quantum number.  
(a) 2 (b) 3  
(c) 4 (d) 5  
**Answer.** (d)

50. The energy needed to remove a single electron (most loosely bound) from an isolated gaseous atom is called  
(a) ionisation energy (b) electron affinity  
(c) kinetic energy (d) electronegativity  
**Answer.** (a)
51. Generally speaking, the ionisation energies increase when we move  
(a) from left to right in the periodic table (b) from top to bottom in a group  
(c) from right to left in the periodic table (d) none of these  
**Answer.** (a)
52. The ionisation energy of Boron ( $Z = 5$ ) is lesser than that of Beryllium ( $Z = 4$ ). It is because  
(a) Be has an incomplete  $2s$  orbital  
(b) Be has two pairs of electrons  
(c)  $2p$  orbital is already higher in energy than  $2s$  orbital  
(d) none of the above  
**Answer.** (c)
53. A neutral atom can accept an electron to form an anion. This process involves  
(a) loss of energy (b) gain of energy  
(c) no change in energy (d) none of these  
**Answer.** (a)
54. Electron affinity is expressed in  
(a)  $\text{g mol}^{-1}$  (b)  $\text{kJ mol}^{-1}$   
(c)  $\text{cal g}^{-1}$  (d)  $\text{kJ g}^{-1}$   
**Answer.** (b)
55. When we move from left to right across a period, the electron affinity in general  
(a) remains the same (b) decreases  
(c) increases (d) becomes zero  
**Answer.** (c)
56. The attraction exerted by an atom on the electron pair bonding it to another atom by covalent bond is called  
(a) ionisation energy (b) electron affinity  
(c) electronegativity (d) none of these  
**Answer.** (c)
57. The most electronegative element in the periodic table is  
(a) caesium (b) chlorine  
(c) fluorine (d) barium  
**Answer.** (c)
58. The values of electronegativities \_\_\_\_\_ as we move from left to right in a period.  
(a) increase (b) decrease  
(c) remain the same (d) none of these  
**Answer.** (a)
59. The electron affinities \_\_\_\_\_ from top to bottom in a group  
(a) increase (b) decrease  
(c) remain the same (d) none of these  
**Answer.** (b)
60. The second electron affinity of an element is always  
(a) zero (b) positive  
(c) negative (d) infinity  
**Answer.** (c)

## 3

Isotopes, Isobars  
and Isotones

## CHAPTER

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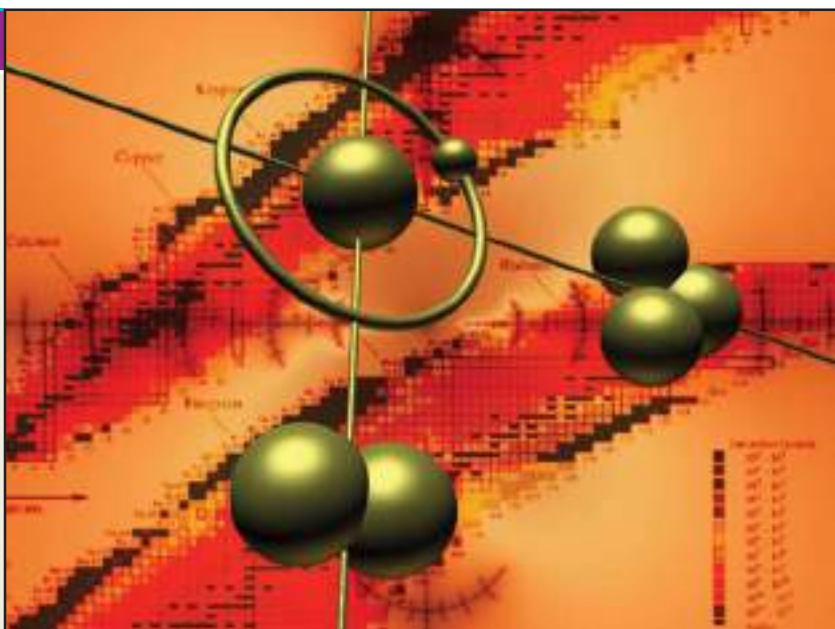
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## WHAT ARE ISOTOPES?

Contrary to Dalton's Atomic theory, all atoms of a given element are not necessarily identical. In fact, most elements have been shown to be composed of two or more types of atoms mixed in a fixed proportion.

- (1) The different atoms of such an element contain equal number of protons and, therefore, have the same atomic number.
- (2) The atoms which vary from one another have different number of neutrons in the nucleus. Thus they have different atomic masses.

**The atoms of an element which have the same number of protons and different number of neutrons are called Isotopes.**

Alternatively, isotopes may be defined as :

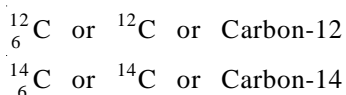
**The atoms of an element which have the same atomic number but different atomic masses or mass numbers.**

The name 'isotope' was assigned to them by Soddy because they have the same atomic number and hence occupied the same place in the periodic table (Greek, *isos* = same; *topos* = place). Isotopes have similar chemical properties as they have the same

electronic configuration. However, they differ in respect of physical properties which depend on atomic mass.

### SYMBOLIC REPRESENTATION OF ISOTOPES

In denoting particular isotopes of an element, the following notation has been internationally adopted. **The symbol of the element is written with atomic mass at the head and atomic number at the bottom.** Alternatively, the name of the element is followed by the atomic mass with a hyphen (-) in between. Thus the isotopes of carbon (atomic number 6) having atomic masses 12 and 14 may be written as



${}^{12}\text{C}$  or Carbon-12 reads 'carbon twelve', meaning isotope of carbon with a mass of approximately 12 amu.

### IDENTIFICATION OF ISOTOPES

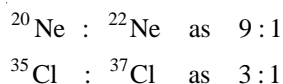
The positive rays produced in a discharge tube consist of nuclei of atoms. The deflection of positive rays in an electric and magnetic field is proportional to  $e/m$ , the charge on the particle divided by its mass. The nuclei obtained from an element consisting of a mixture of isotopes will have the same positive charge and, therefore, **their deflection will be inversely proportional to their masses.** Thus with a suitable application of electric and magnetic field, we can identify the isotopes present in a given element.

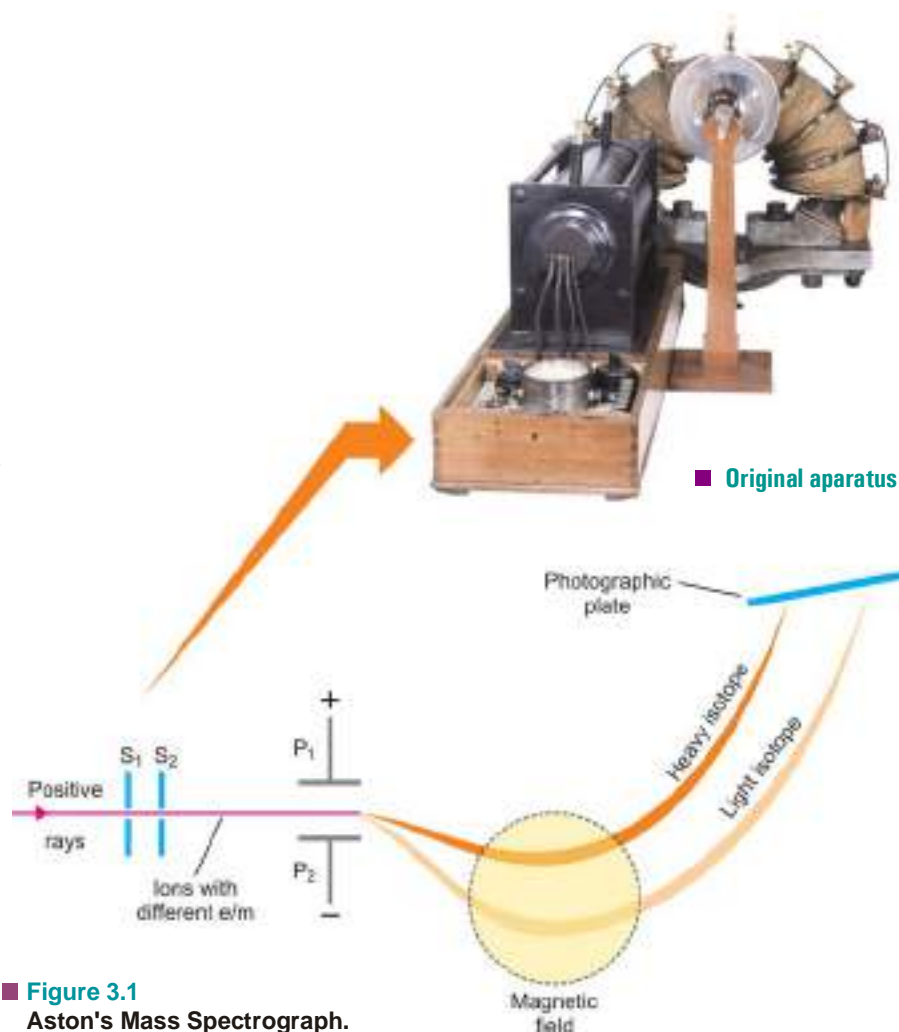
#### (1) Aston's Mass Spectrograph

In 1919 F.W. Aston developed an instrument known as the *Mass Spectrograph* which can accurately sort out the positive ions of different isotopes of an element and determine their masses (Fig. 3.1).

In this apparatus a beam of positive rays obtained from a gaseous element in the discharge tube, is rendered into a fine ribbon by passing through slits  $S_1$  and  $S_2$ . The fine beam consisting of positive ions of the various isotopes of the element is then sent between the electrostatically charged plates  $P_1$  and  $P_2$ . Here the beam of positive ions is deflected down toward the negative plate. The slow moving ions of the same isotope are deflected more than the faster ones which causes a broadening of the beam. Also, the heavier particles are deflected more (being slower) than the lighter ones and this brings about a separation of the various isotopes. The broadened beam of ions is then subjected to a magnetic field (shown by dashed circle) at right angles to the plane of the charged plates and is thus sent in a direction opposite to that caused by the electrostatic field, slower particles again being deflected most. By adjustment of the two fields all ions of the same mass come to focus on the same point on the photographic plate where a sharp line is obtained. Thus each line recorded on the photographic plate shows the existence of separate isotope. Further, the intensity of the line in comparison with the lines of other isotopes, gives the relative abundance of this particular isotope.

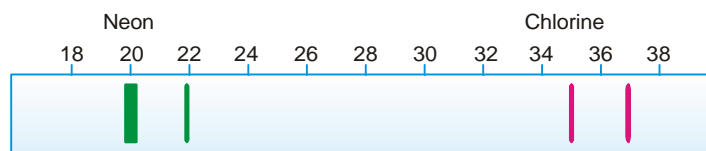
The mass of a particle corresponding to a line produced on the photographic plate is determined by comparing with a standard line produced by a particle of known mass (say,  $\text{O}^+ = 16$ ). For example, the examination of a sample of neon and chlorine by Aston's Mass Spectrograph showed that they were made of Ne-20, Ne-22 and Cl-35, Cl-37 respectively. The intensities of their lines showed that the relative abundance was





■ **Figure 3.1**  
Aston's Mass Spectrograph.

Thus Aston's Mass spectrograph not only helped in identifying the isotopes present in an element but also helped in determining the average atomic mass of a given element.



■ **Figure 3.2**  
Mass spectrographs of Neon and Chlorine.

**SOLVED PROBLEM.** A Sample of neon is found to consist of  $^{20}\text{Ne}$ ,  $^{21}\text{Ne}$  and  $^{22}\text{Ne}$  in the following percentages :

$^{20}\text{Ne}$	90.92
$^{21}\text{Ne}$	0.26
$^{22}\text{Ne}$	8.82

Calculate the atomic mass of neon.

**SOLUTION**

The atomic mass of an ordinary isotopic mixture is the average of the determined atomic masses of individual isotopes. Thus :

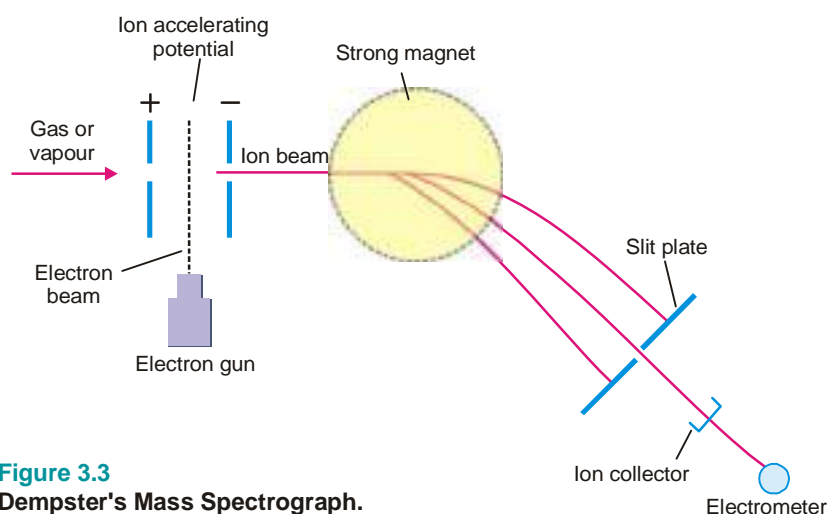
$$20 \times 0.9092 = 18.18$$

$$21 \times 0.0026 = 0.055$$

$$22 \times 0.0882 = 1.94$$

$$20.18$$

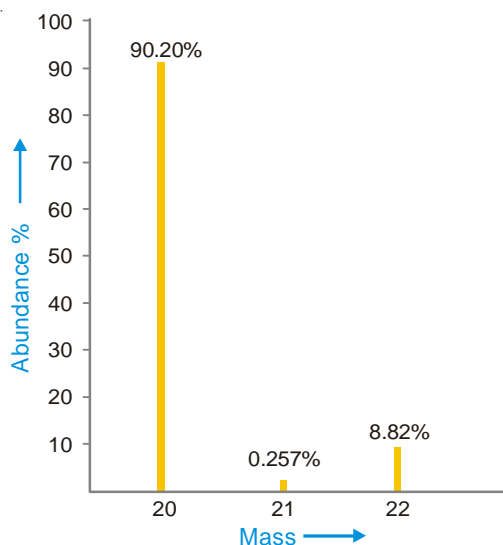
The atomic mass of neon is **20.18**.

**(2) Dempster's Mass Spectrograph**

**Figure 3.3**  
**Dempster's Mass Spectrograph.**

In this apparatus (Fig. 3.3) a slow stream of gas or vapour of the sample under examination is passed in between two perforated plates. Here it is bombarded by high-energy electrons shot out from an *electron gun*. The gas atoms are thus stripped of an electron and are converted to mono-positive ions (atom  $- e = \text{ion}^{1+}$ ). When a potential of 500 to 2000 volts is applied between the perforated accelerating plates, the positive ions are strongly attracted to the negative plate. The beam of positive ions moving with accelerated speed then enters the magnetic field at right angles to its path and is thus made to move in a circular path.

If  $V$  is the potential applied across the accelerating plates and  $e$  the charge on each positive particle, the electrical energy is  $Ve$ . This is imparted to the particles as kinetic energy,  $\frac{1}{2}mv^2$ . Thus,



**Figure 3.4**  
**A computer-plotted graph showing relative abundances of the three isotopes of neon against mass number.**



$$Ve = \frac{1}{2}mv^2 \quad \dots(1)$$

In the magnetic field of strength  $H$ , the magnetic force on the particle  $Hev$ , exactly balances the centrifugal force,  $mv^2/r$ ,  $r$  being the radius of the circular path. Thus,

$$\frac{mv^2}{r} = Hev \quad \dots(2)$$

Eliminating  $v$  between (1) and (2), we have

$$r = \sqrt{\frac{2Vm}{H^2e}}$$

or

$$\frac{m}{e} = \frac{H^2r^2}{2V} \quad \dots(3)$$

$e$ , being the unit electrical charge, and  $r$  (depending on particular apparatus) are constant. If during an experiment magnetic field  $H$  is kept the same, from (3) it follows that

$$m \propto \frac{1}{V}$$

Thus by adjusting the accelerating potential ( $V$ ), particles of mass  $m$  can be made to fall on the collector plate. Each ion sets up a minute electric current which passes to the electrometer. **The strength of the current thus measured, gives the relative abundance of the particles of mass  $m$ .** Similarly, the particles of the other isotopes having different masses are made to fall on the collector and current strength measured. The current strength in each case gives the relative abundance of the individual isotopes. By comparing the current strengths with an experiment performed with C-12 ion, the mass numbers of the various isotopes can be determined.

In the modern mass spectrographs, each ion strikes a detector, the ion current is amplified and fed to a recorder. The recorder makes a graph showing relative abundance plotted against mass number. A computer-plotted graph of neon isotopes is shown in Fig. 3.4.

### SEPARATION OF ISOTOPES

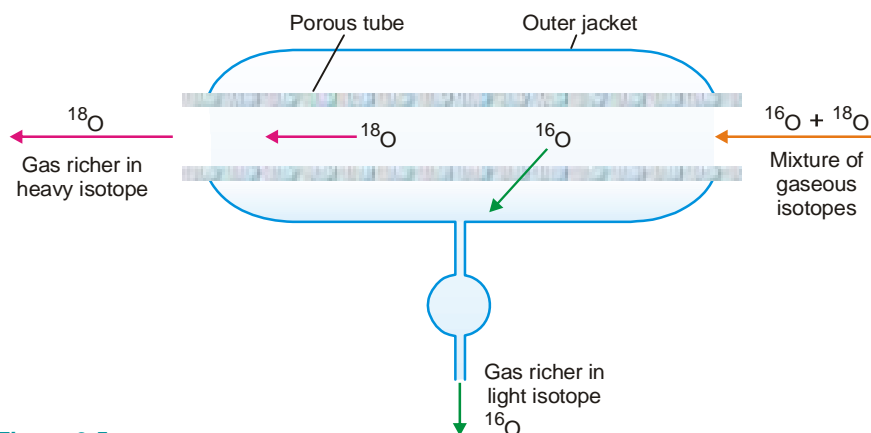
Since isotopes have exactly similar chemical properties, their separation by chemical means is out of question. **Their difference in those physical properties which depend on the mass of the atom has been utilised to effect their separation.** The methods commonly employed for the purpose are:

#### (1) Gaseous Diffusion

The rate of diffusion of a gas is inversely proportional to the square root of the molecular weight (*Graham's Law of Diffusion*).

$$\text{Rate of Diffusion} \propto \sqrt{\frac{1}{\text{Molecular weight}}}$$

Thus when a mixture of two gaseous isotopes is allowed to diffuse through a porous partition, **the lighter isotope passes through more rapidly than the heavier one.** The isotopes of neon ( $^{20}\text{Ne}$ ,  $^{22}\text{Ne}$ ) and oxygen ( $^{16}\text{O}$ ,  $^{18}\text{O}$ ) were separated by this method. The mixture of gaseous isotopes is passed through a porous tube sealed in an outer jacket (see Fig. 3.5). The lighter isotopes pass into the jacket, while the residual gas becomes richer in the heavier isotope. In actual practice a cascade of many 'Diffusion units' is used to achieve an appreciable separation. This process has been recently used for the separation of the gaseous fluorides  $^{235}\text{UF}_6$  and  $^{238}\text{UF}_6$ . It provides a procedure for effective separation of the isotopes of uranium, namely, U-238 and U-235 (needed for atomic energy).



■ **Figure 3.5**  
A unit of the 'diffusion cascade' for the separation of gaseous isotopes ( $^{16}\text{O}$ ,  $^{18}\text{O}$ ).

### (2) Thermal Diffusion

A long vertical tube with an electrical heated wire running down its axis is used. When a mixture of gaseous isotopes is introduced into the tube, **the lighter particles diffuse more rapidly to the central hot region**. Here they are carried upwards by convection currents. The heavier particles, on the other hand, travel to the cooler inner surface of the tube and sink to the bottom. Thus the lighter isotope collects at the top and the heavier one at the bottom. The isotopes of chlorine  $\text{Cl-35}$  and  $\text{Cl-37}$ , have been separated by this process. The fluorides of uranium have also been separated by thermal diffusion.

### (3) Distillation

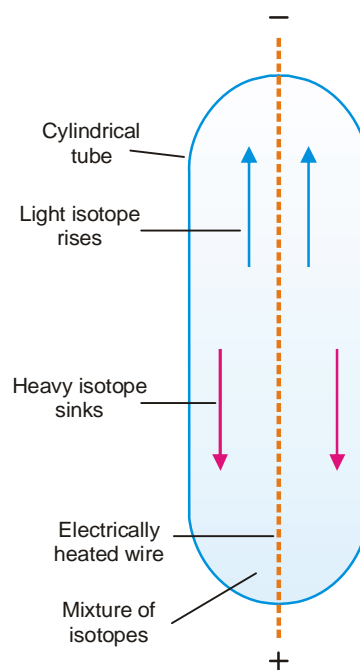
The lighter isotope will be distilled over first, leaving the heavier one behind. The isotopes of mercury were separated by this method. The frozen mercury from the cooled surface is removed, melted and evaporated under vacuum again. The whole process is repeated several times to separate the isotopes of mercury.

### (4) Ultracentrifuge

The mixture of isotopes is rotated in a high speed centrifuge. The heavier isotope is concentrated at the periphery. The separation depends essentially on the molecular mass and not its square root, causing better separation. The gaseous fluorides of  $\text{U-235}$  and  $\text{U-238}$  have been separated by this method.

### (5) Electromagnetic Separation

This method uses the principle of the Mass Spectrograph (Dempster). For example, the beam of ions of the isotopes of neon ( $\text{Ne-20}$ ,  $\text{Ne-21}$ ,  $\text{Ne-22}$ ) as obtained in the mass spectrograph, is then passed between the poles of a magnet. **The different isotopes are deflected to different extents and are collected in cooled chambers placed in appropriate positions.** Although the quantities obtained by this method are very small indeed, the separation is complete.



■ **Figure 3.6**  
Separation of isotopes by thermal diffusion.

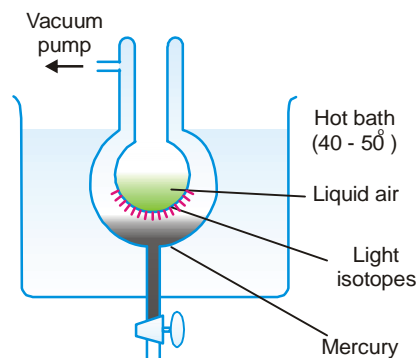
### (6) Fractional Electrolysis

Here the principle is that the rates of liberation of the isotopes of an element at an electrode during electrolysis are different. This is so because **the ions of the heavier isotope move slower, while those of the lighter isotope move faster to the opposite electrode.**

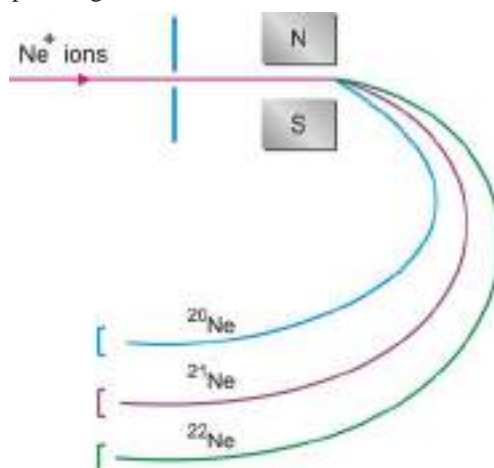
Urey (1931) separated the two isotopes of hydrogen, H-1 and H-2, by the electrolysis of acidified water. H-1 (protium) is liberated five times as rapidly as H-2 (deuterium) at the cathode. The residual water becomes richer in heavy water or deuterium oxide  $^2\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  which upon further electrolysis yields gas richer in deuterium.

### (7) Laser Separation

A laser is a very fine beam of electromagnetic radiation which consists of photons corresponding to a single wavelength, frequency or energy. All the waves in the beam are in phase with all troughs and peaks moving through space together.



■ **Figure 3.7**  
The separation of the isotopes of mercury by vacuum distillation.



■ **Figure 3.8**  
Separation of isotopes of Neon by using the principle of the Dempster's Mass Spectrograph.

In recent years, the development of lasers has been used for the separation of isotopes. If the laser light is of the appropriate wavelength, one isotope will absorb the energy, while another isotope will not. **The slight difference in absorption spectra of the two isotopes thus produced has been used to separate the more energetic isotope from the other.**

The laser method has been used successfully for the separation of isotopes of chlorine and sulphur. Potentially, laser isotope separation of uranium is 1000 times more efficient than gaseous diffusion separation.

### EXAMPLES OF ISOTOPES

Since isotopes of an element have the same atomic number, each of these contains equal number of protons. They have different atomic masses which is accounted for by the different number of neutrons present in the nucleus. Thus **the isotopes of an element are characterised by different number of neutrons in the nucleus.**

The atomic structure of an isotope with atomic number  $Z$  and mass number  $A$  (atomic mass in amu) can be given as follows :

- (1) The number of extranuclear electrons =  $Z$
- (2) The number of protons in the nucleus =  $Z$
- (3) The mass number  $A$  is equal to the total number of protons ( $Z$ ) and neutrons ( $N$ ) in the nucleus. That is,

$$A = Z + N$$

$$N = A - Z$$

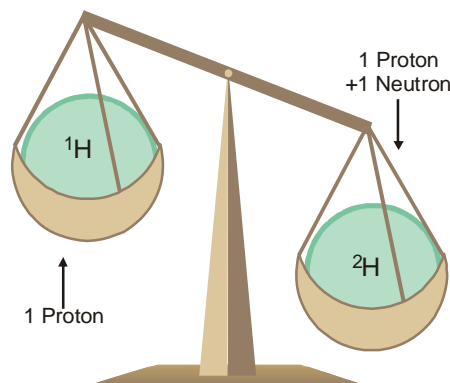
$\therefore$

### Isotopes of Hydrogen

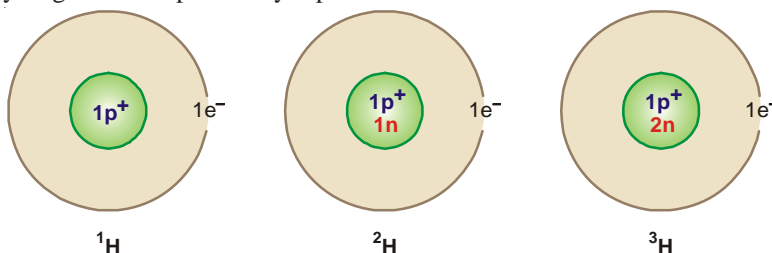
There are three isotopes of hydrogen : *protium* ( ${}^1_1\text{H}$ ), *deuterium* ( ${}^2_1\text{H}$  or  $\text{D}$ ), and *tritium* ( ${}^3_1\text{H}$  or  $\text{T}$ ). Protium is by far the most abundant in natural hydrogen, deuterium about 0.015% and tritium only one out of 10,000,000 hydrogen atoms.

#### Structure

The atomic number of the three isotopes of hydrogen is 1, while their mass numbers are : protium 1, deuterium 2, and tritium 3. Therefore each of the three isotopes has one extranuclear electron and one proton in the nucleus. The nucleus of protium is made of one proton only, while the number of neutrons ( $A - Z$ ) present in deuterium is  $2 - 1 = 1$ , and in tritium  $3 - 1 = 2$ . The structure of the three isotopes of hydrogen can be pictorially represented as :



■ Two isotopes of hydrogen



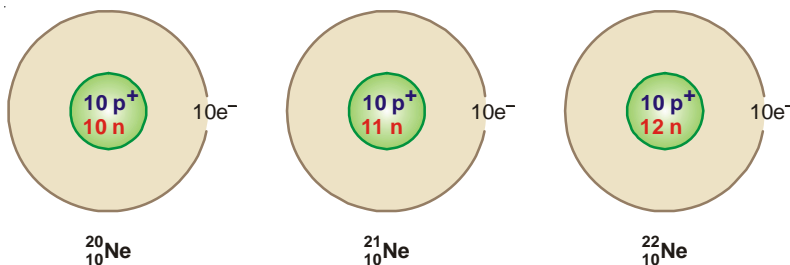
### Isotopes of Neon

Neon has been found to consist of three isotopes :  ${}^{20}_{10}\text{Ne}$ ,  ${}^{21}_{10}\text{Ne}$  and  ${}^{22}_{10}\text{Ne}$ . Their percentage abundance is

${}^{20}\text{Ne}$	${}^{21}\text{Ne}$	${}^{22}\text{Ne}$
90.92%	0.257%	8.82%

#### Structure

The atomic number of the three isotopes of neon is 10, while their mass numbers are 20, 21 and 22 respectively. Therefore each of these isotopes has ten extranuclear electrons and ten protons in the nucleus. The number of neutrons ( $A - Z$ ) are :  ${}^{20}\text{Ne}$ ,  $20 - 10 = 10$  ;  ${}^{21}\text{Ne}$ ,  $21 - 10 = 11$  ;  ${}^{22}\text{Ne}$ ,  $22 - 10 = 12$ . The atomic structure of the isotopes of neon can, therefore, be represented pictorially as:



### Isotopes of Oxygen

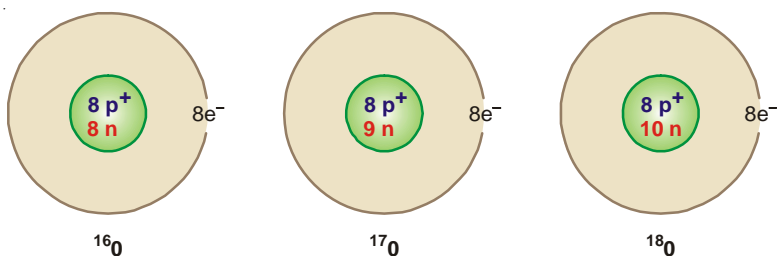
Oxygen has three isotopes :  ${}^{16}_8\text{O}$ ,  ${}^{17}_8\text{O}$  and  ${}^{18}_8\text{O}$ . These are found with the relative abundances of 99.759, 0.037 and 0.204 respectively.

#### Structure

The atomic number of the above three isotopes of oxygen is 8 while their mass numbers are 16, 17 and 18. Therefore each isotope has 8 extranuclear electrons and 8 protons in the nucleus. The number of neutrons ( $A - Z$ ) in the three isotopes is :

$$\begin{array}{ll} {}^{16}\text{O} & 16 - 8 = 8 \text{ neutrons} \\ {}^{17}\text{O} & 17 - 8 = 9 \text{ neutrons} \\ {}^{18}\text{O} & 18 - 8 = 10 \text{ neutrons} \end{array}$$

The complete atomic structure of the isotopes of oxygen can be pictorially represented as :



### Isotopes of Chlorine

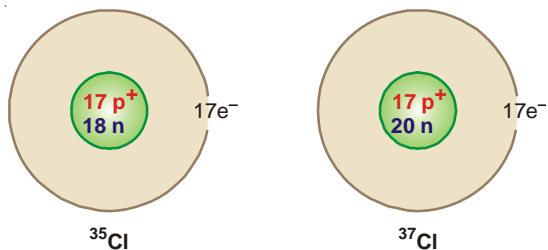
Chlorine is a mixture of two isotopes :  ${}^{35}_{17}\text{Cl}$  and  ${}^{37}_{17}\text{Cl}$ . Their percentage abundance is 75.53 and 24.47 respectively.

#### Structure

The atomic number of the two isotopes of chlorine is 17 while their mass numbers are 35 and 37. Therefore each isotope has 17 extranuclear electrons and 17 protons in the nucleus. The number of neutrons ( $A - Z$ ) in these isotopes is :

$$\begin{array}{ll} {}^{35}\text{Cl} & 35 - 17 = 18 \text{ neutrons} \\ {}^{37}\text{Cl} & 37 - 17 = 20 \text{ neutrons} \end{array}$$

The atomic structure of the isotopes of chlorine can be pictorially represented as :



### Isotopes of Uranium

There are three isotopes of uranium :



Natural uranium consists almost entirely of  $^{238}\text{U}$ , with about 0.72% of  $^{235}\text{U}$  and 0.006% of  $^{234}\text{U}$ . These isotopes are particularly important in atomic energy.

### Structure

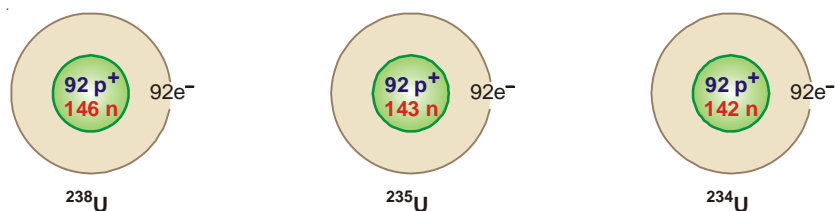
The atomic number of the three isotopes of uranium is 92 and their mass numbers are 238, 235 and 234. Thus each isotope has 92 extranuclear electrons and 92 protons. The number of neutrons ( $A - Z$ ) in these isotopes is :

$$^{238}\text{U} \quad 238 - 92 = 146 \text{ neutrons}$$

$$^{235}\text{U} \quad 235 - 92 = 143 \text{ neutrons}$$

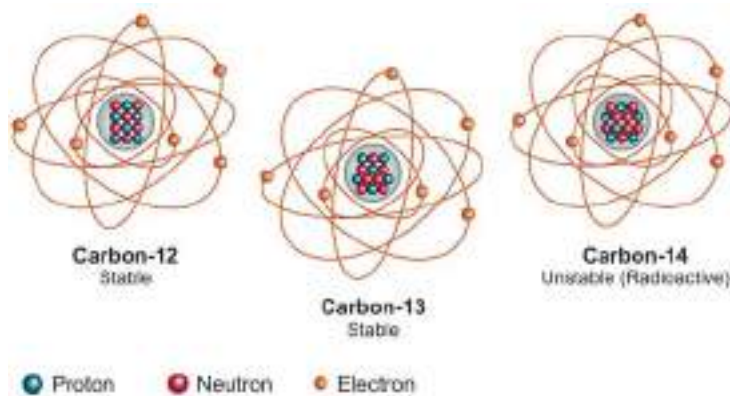
$$^{234}\text{U} \quad 234 - 92 = 142 \text{ neutrons}$$

The atomic structure of the three isotopes of uranium may be represented as :



Almost every element in nature exists as a mixture of isotopes. The isotopes of the elements with atomic numbers 1 to 10, and their structure is listed in Table 3.1. It may be noted that some elements *e.g.*, fluorine, are **monoisotopic**. These are found in nature only as a single isotope. About 20 elements are monoisotopic.

### ISOTOPES OF CARBON



Isotopes of an element are atoms of the element that have different numbers of neutrons in their nuclei. Carbon has three naturally occurring isotopes. The isotopes of carbon are carbon-12, which constitutes 98.89 of all carbon atoms and serves as the standard for the atomic mass scale; carbon-13, which is the only magnetic isotope, making it very important for structural studies of compounds containing carbon; and carbon-14, which is produced by cosmic rays bombarding the atmosphere. Carbon-14 is radioactive, with a half-life of 5760 years. The amount of carbon-14 remaining in historical artifacts can be used to estimate their age.

### ISOTOPIC EFFECTS

Although in many respects the chemistry of the isotopes of an element is the same, there are significant differences between them due to difference in masses. Thus the physical properties of the compounds of each isotope of an element are distinctly different from those of others. Similarly, reaction rates of the individual isotopes are also different.

**TABLE 3.1. THE NATURALLY OCCURRING ISOTOPES OF ELEMENTS WITH ATOMIC NUMBERS 1 TO 10**

Isotope	Atomic No. (Z)	Mass No. (A)	Protons (= Z)	Neutrons (= A – Z)	Electronic configuration		
Hydrogen-1	1	1	1	0	1	1s <sup>1</sup>	
Hydrogen-2	1	2	1	1	1	1s <sup>1</sup>	
Hydrogen-3	1	3	1	2	1	1s <sup>1</sup>	
Helium-3	2	3	2	1	2	1s <sup>2</sup>	
Helium-4	2	4	2	2	2	1s <sup>2</sup>	
Lithium-6	3	6	3	3	2, 1	1s <sup>2</sup>	2s <sup>1</sup>
Lithium-7	3	7	3	4	2, 1	1s <sup>2</sup>	2s <sup>1</sup>
Beryllium-9	4	9	4	5	2, 2	1s <sup>2</sup>	2s <sup>2</sup>
Boron-10	5	10	5	5	2, 3	1s <sup>2</sup>	2s <sup>2</sup> 2p <sup>1</sup>
Boron-11	5	11	5	6	2, 3	1s <sup>2</sup>	2s <sup>2</sup> 2p <sup>1</sup>
Carbon-12	6	12	6	6	2, 4	1s <sup>2</sup>	2s <sup>2</sup> 2p <sup>2</sup>
Carbon-13	6	13	6	7	2, 4	1s <sup>2</sup>	2s <sup>2</sup> 2p <sup>2</sup>
Carbon-14	6	14	6	8	2, 4	1s <sup>2</sup>	2s <sup>2</sup> 2p <sup>2</sup>
Nitrogen-13	7	13	7	6	2, 5	1s <sup>2</sup>	2s <sup>2</sup> 2p <sup>3</sup>
Nitrogen-14	7	14	7	7	2, 5	1s <sup>2</sup>	2s <sup>2</sup> 2p <sup>3</sup>
Nitrogen-16	7	16	7	9	2, 5	1s <sup>2</sup>	2s <sup>2</sup> 2p <sup>3</sup>
Oxygen-16	8	16	8	8	2, 6	1s <sup>2</sup>	2s <sup>2</sup> 2p <sup>4</sup>
Oxygen-17	8	17	8	9	2, 6	1s <sup>2</sup>	2s <sup>2</sup> 2p <sup>4</sup>
Oxygen-18	8	18	8	10	2, 6	1s <sup>2</sup>	2s <sup>2</sup> 2p <sup>4</sup>
Fluorine-19	9	19	9	10	2, 7	1s <sup>2</sup>	2s <sup>2</sup> 2p <sup>5</sup>
Neon-20	10	20	10	10	2, 8	1s <sup>2</sup>	2s <sup>2</sup> 2p <sup>6</sup>
Neon-21	10	21	10	11	2, 8	1s <sup>2</sup>	2s <sup>2</sup> 2p <sup>6</sup>
Neon-22	10	22	10	12	2, 8	1s <sup>2</sup>	2s <sup>2</sup> 2p <sup>6</sup>

**The differences in isotopes due to mass differences are termed Isotopic Effects.**

The isotopic effects show up clearly in the isotopes of hydrogen  ${}^1_1\text{H}$  and  ${}^2_1\text{H}$  (D). The differences in the physical properties of water from ordinary hydrogen  ${}^1_1\text{H}$  and heavy hydrogen D are listed in Table 3.2.

**TABLE 3.2. PHYSICAL PROPERTIES OF H<sub>2</sub>O AND D<sub>2</sub>O**

	H <sub>2</sub> O	D <sub>2</sub> O
Molecular weight	18.02	20.03
Density at 0°C, g cm <sup>-3</sup>	1.000	1.105
Melting point, 0°C	0.00	3.82
Boiling point, 0°C	100.00	101.42

The isotopic effects are also exhibited by the difference in the reaction rates of the two isotopes of hydrogen. Under similar conditions, the reaction of the heavy isotopes with chlorine is about six times slower than that of light isotope.



This difference in reaction rates is explained by the fact that the covalent bond formed by deuterium is slightly stronger than the corresponding bond with ordinary hydrogen. Hence a reaction that breaks a deuterium covalent bond is slower than the same reaction involving bond to light hydrogen.

There are several useful applications of isotopic effects. One method of separation of isotopes of hydrogen depends on the fact that the electrolysis of heavy water ( $\text{D}_2\text{O}$ ) is slower than the electrolysis of normal water. Pure heavy water is a valuable by-product of the electrolysis of water, since large quantities are required in nuclear reactors to moderate the rate of the uranium fission reaction.

### WHAT ARE ISOBARS?

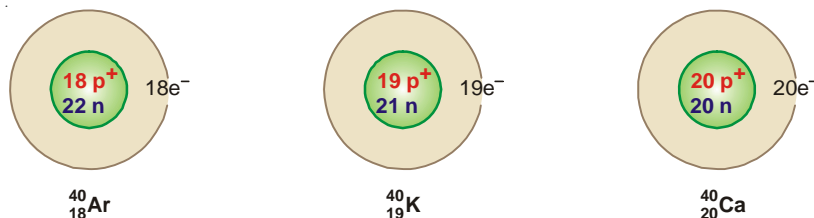
The atoms which have the same mass number but different atomic numbers are called isobars.

#### Isobars

The word isobar meaning 'equally heavy' is taken from the Greek *isos* = equal, and *barys* = heavy. For example,  $^{40}_{18}\text{Ar}$ ,  $^{40}_{19}\text{K}$ , and  $^{40}_{20}\text{Ca}$  are isobaric atoms. Similarly,  $^{235}_{92}\text{U}$ ,  $^{235}_{93}\text{Np}$ , and  $^{235}_{94}\text{Pu}$  are isobars.

#### Structure

Since isobars have the same mass number, the number of protons plus neutrons in the nucleus in each of these is equal. The number of protons being given by atomic number ( $Z$ ), the number of neutrons is, therefore, ( $A - Z$ ) where  $A$  is the mass number. The number of extranuclear electrons is equal to ( $Z$ ). Thus the atomic structure of the isobars  $^{40}_{18}\text{Ar}$ ,  $^{40}_{19}\text{K}$  and  $^{40}_{20}\text{Ca}$  is shown below :

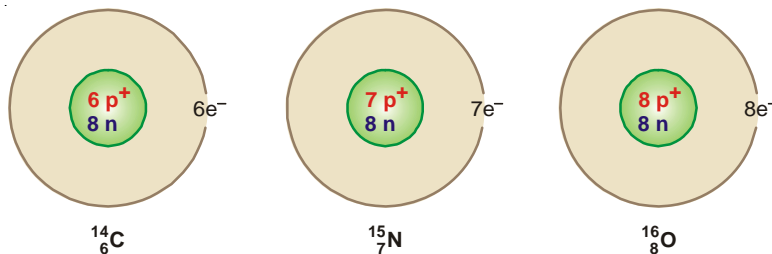


### WHAT ARE ISOTONES?

Atoms which have different atomic number and different atomic masses but the same number of neutrons are called Isotones.

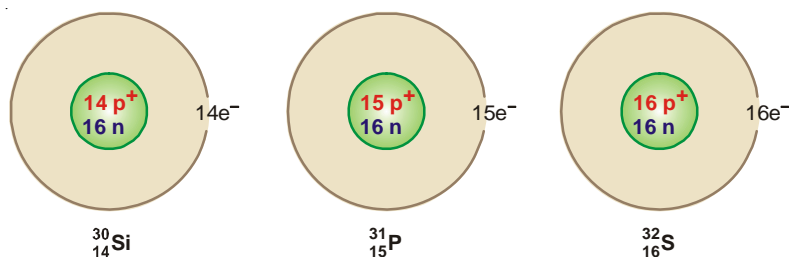
#### Examples of isotones

- (1)  $^{14}_6\text{C}$ ,  $^{15}_7\text{N}$  and  $^{16}_8\text{O}$  are isotones since each contains eight neutrons.



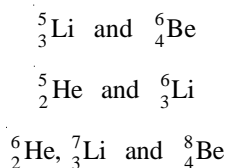


- (2)  $^{30}_{14}\text{Si}$ ,  $^{31}_{15}\text{P}$  and  $^{32}_{16}\text{S}$  are isotones. Each contains sixteen neutrons.



**Isotones are different elements having entirely different atomic structure.** They have different physical and chemical properties.

Some other examples of isotones are :



### EXAMINATION QUESTIONS

- Define or explain the following terms :
  - Isotopes
  - Rate of diffusion
  - Isobars
  - Isotones
- What are isotopes and isobars? Illustrate your answer with suitable examples.
  - Discuss the construction and working of Dempster's mass spectrograph.
- How is Aston's mass spectrograph used to detect the presence of an isotope? Describe briefly two methods of separation of isotopes.
- What are Isotopes and Isobars? Discuss the method by which isotopes can be separated from one another.
- What do you understand by isotopes and isobars?
  - Describe the working of Dempster's Mass Spectrograph.
- Write three isotopes of hydrogen and draw their structure.
- Discuss the construction, working and advantages of Aston's Mass Spectrograph.
- Describe the construction, working and the use of Dempster's Mass Spectrograph.
- Give the principle of the diffusion method for the separation of isotopes.
- Magnesium has naturally occurring isotopes with the following masses and abundances.

Isotope	Atomic mass (amu)	Fractional abundance
$^{24}_{12}\text{Mg}$	23.985	0.7870
$^{25}_{12}\text{Mg}$	24.986	0.1013
$^{26}_{12}\text{Mg}$	25.983	0.1117

Calculate the atomic mass of magnesium.

**Answer.** 24.31 amu

11. Calculate the fractional abundances for the two naturally occurring isotopes of copper. The masses of isotopes are 62.9298 and 64.9278 amu. The atomic mass of copper is 63.546 amu.

**Answer.** 0.692; 0.308

(Delhi BSc, 2000)

12. Calculate the atomic mass of boron, B, from the following data :

Isotope	Atomic mass (amu)	Fractional abundance
${}_5\text{B}^{10}$	10.013	0.1978
${}_5\text{B}^{11}$	11.009	0.8022

**Answer.** 10.8119 amu

(Bundelkhand BSc, 2001)

13. Naturally occurring boron consists of two isotopes whose atomic masses are 10.01 and 11.01. The atomic mass of naturally occurring boron is 10.81. Calculate the percentage of each isotope in natural boron.

**Answer.** Percentage of isotope with atomic mass 10.01 = 20

(Dibrugarh BSc, 2002)

Percentage of isotope with atomic mass 11.01 = 80

14. Describe in brief any two methods of separation of isotopes.

(Arunachal BSc, 2003)

15. Discuss the detection and separation of isotopes.

(Madras BSc, 2003)

16. What are isotones and nuclear isomerism? Give examples.

(Kerala BSc, 2003)

17. Define the terms : Isotope and Isobar. Give one example of each.

(Kerala BSc, 2004)

18. (a) How are nuclear masses determined with a mass spectrometer? Explain.

(b) Calculate the relative atomic mass of an element which consists of the following isotopes with the indicated relative abundance.

Isotope	Isotopic mass	Natural abundance
1	28.0	92.0
2	29.0	5.0
3	30.0	3.0

(Baroda BSc, 2005)

**Answer.** (b) 28.11

19. Silver has two naturally occurring isotopes with atomic masses 106.91 and 108.90 amu. The atomic mass of silver is 107.87 amu. Calculate the fractional abundances for these two isotopes.

**Answer.** 0.518; 0.482

(North Eastern Hill BSc, 2006)

### MULTIPLE CHOICE QUESTIONS

1. The atoms of an element which have the same number of protons and different number of neutrons are called

(a) isotopes  
(c) isotones

(b) isobars  
(d) isomers

**Answer.** (a)

2. Isotopes of an element have \_\_\_\_\_ atomic number but \_\_\_\_\_ mass numbers.

(a) same, same  
(c) same, different

(b) different, same  
(d) different, different

**Answer.** (c)

3. \_\_\_\_\_ occupy the same place in the periodic table.

(a) isobars  
(c) isotones

(b) isotopes  
(d) none of these

**Answer.** (b)

4. Isotopes have \_\_\_\_\_ chemical properties.

(a) same

(b) similar

- (c) different (d) none of these

**Answer.** (b)

5. The electronic configuration of isotopes of an element is \_\_\_\_\_.

- (a) same (b) similar  
(c) different (d) none of these

**Answer.** (a)

6. The physical properties of the isotopes which depend on the \_\_\_\_\_ of the atoms are used to separate them.

- (a) electronic configuration (b) mass  
(c) velocity (d) valence electrons

**Answer.** (b)

7. The mass number  $A$  is given by ( $Z$  is atomic number and  $N$  is number of neutrons)

- (a)  $A = Z - N$  (b)  $A = Z + N$   
(c)  $A = N - Z$  (d)  $A = 2(Z + N)$

**Answer.** (b)

8. An atom of \_\_\_\_\_ contains no neutrons.

- (a) hydrogen (b) deuterium  
(c) tritium (d) none of these

**Answer.** (a)

9. The difference between the number of neutrons and the protons is positive for

- (a) hydrogen atom (b) deuterium atom  
(c) tritium atom (d) none of these

**Answer.** (c)

10. An element with atomic number equal to one, exists in three isotopes namely  ${}_1\text{H}^1$ ,  ${}_1\text{H}^2$  and  ${}_1\text{H}^3$ . Which out of these has only one electron in its outermost shell.

- (a)  ${}_1\text{H}^1$  (b)  ${}_1\text{H}^2$   
(c)  ${}_1\text{H}^3$  (d) all the three

**Answer.** (d)

11. In which isotope of oxygen out of  $\text{O}^{16}$ ,  $\text{O}^{17}$  and  $\text{O}^{18}$  there are equal number of protons, electrons and neutrons.

- (a)  $\text{O}^{16}$  (b)  $\text{O}^{17}$   
(c)  $\text{O}^{18}$  (d) none of these

**Answer.** (a)

12. Which isotope of chlorine out of  ${}_{17}\text{Cl}^{35}$  and  ${}_{17}\text{Cl}^{37}$  has greater number of neutrons than the protons?

- (a)  ${}_{17}\text{Cl}^{35}$  (b)  ${}_{17}\text{Cl}^{37}$   
(c) neither of the two (d) both

**Answer.** (d)

13. The reaction rates of the individual isotopes are

- (a) the same (b) different  
(c) sometimes the same, sometimes different (d) none of these

**Answer.** (b)

14. The atoms which have the same mass number but different atomic numbers are called

- (a) isobars (b) isotopes  
(c) isotones (d) isomers

**Answer.** (a)

15. Which is true about the isobars?

- (a) they have same mass number and same atomic number  
(b) they have same mass number and different atomic number  
(c) they have different mass number and same atomic number  
(d) they have different mass number and different atomic number

**Answer.** (b)

16. Which of the following statements holds good for  ${}_{18}^{40}\text{Ar}$ ,  ${}_{19}^{40}\text{K}$  and  ${}_{20}^{40}\text{Ca}$

- (a) they have equal number of protons and electrons  
(b) they have equal number of protons and neutrons taken together

- (c) they have equal number of neutrons in their respective nuclei  
 (d) none of the above

**Answer.** (b)

17. Atoms which have different atomic numbers, different mass numbers but the same number of neutrons are called  
 (a) isotopes (b) isobars  
 (c) isotones (d) isomers

**Answer.** (c)

18. Which of the following statement is true for  $^{14}_6\text{C}$ ,  $^{15}_7\text{N}$  and  $^{16}_8\text{O}$ .  
 (a) they have equal number of protons (b) they have equal number of electrons  
 (c) they have equal number of neutrons (d) they have equal mass number

**Answer.** (c)

19. Which of the following pairs represents isotones?  
 (a)  $^1_1\text{H}^1$  and  $^1_1\text{H}^2$  (b)  $^{40}_{18}\text{Ar}$  and  $^{40}_{19}\text{K}$   
 (c)  $^{14}_6\text{C}$  and  $^{16}_8\text{O}$  (d)  $^{22}_{10}\text{Ne}$  and  $^{23}_{11}\text{Na}$

**Answer.** (c)

20. Which of the following pairs represents isobars?  
 (a)  $^{17}_8\text{O}$  and  $^{18}_8\text{O}$  (b)  $^{40}_{19}\text{K}$  and  $^{40}_{20}\text{Ca}$   
 (c)  $^{15}_7\text{N}$  and  $^{16}_8\text{O}$  (d)  $^{235}_{92}\text{U}$  and  $^{238}_{92}\text{U}$

**Answer.** (b)

21. An isotone of  $^{14}_6\text{C}$  is  
 (a)  $^{16}_8\text{O}$  (b)  $^{13}_6\text{C}$   
 (c)  $^{17}_8\text{O}$  (d)  $^{16}_7\text{N}$

**Answer.** (a)

22. Which of the following is isoelectronic with  $\text{Cl}^{-1}$ ?  
 (a)  $\text{S}^{2-}$  (b)  $\text{P}^{3-}$   
 (c)  $\text{K}^+$  (d) All

**Answer.** (d)

23. Two nuclei A and B are isotonic with mass numbers 15 and 16 respectively. If A contains 7 protons, then the number of protons in B would be  
 (a) 7 (b) 8  
 (c) 9 (d) 10

**Answer.** (b)

24.  $^{76}_{32}\text{Ge}$  is isotonic with  
 (a)  $^{77}_{32}\text{Ge}$  (b)  $^{78}_{33}\text{As}$   
 (c)  $^{78}_{32}\text{Ge}$  (d)  $^{77}_{33}\text{As}$

**Answer.** (d)

25. Which of the following atoms contains the largest number of neutrons?  
 (a)  $^{210}_{83}\text{Bi}$  (b)  $^{208}_{83}\text{Bi}$   
 (c)  $^{209}_{84}\text{Pb}$  (d)  $^{208}_{84}\text{Pb}$

**Answer.** (a)

26. The number of neutrons present in  $^{239}_{93}\text{Np}$  is  
 (a) 93 (b) 146  
 (c) 239 (d) 332

**Answer.** (b)

27. Which of the following properties of the element is a whole number?  
 (a) atomic mass (b) atomic volume  
 (c) atomic radius (d) atomic number

**Answer.** (d)

28. Which of the following is false about  $^{16}_8\text{O}$  and  $^{17}_8\text{O}$  ?  
 (a) both have eight protons (b) both have eight electrons  
 (c) both have eight neutrons (d) they have different rates of diffusion  
**Answer.** (c)
29. What is the relationship between  $^{27}_{13}\text{Al}^{3+}$  and  $^{23}_{11}\text{Na}^+$  ?  
 (a) they are isotopes (b) they are isobars  
 (c) they are isotones (d) they are isoelectronic  
**Answer.** (d)
30.  $^{24}_{11}\text{Na}$  and  $^{24}_{12}\text{Mg}$  are related to each other as  
 (a) isotopes (b) isobars  
 (c) isotones (d) isoelectronic  
**Answer.** (b)
31. The  $n/p$  ratio for  $^{16}_8\text{O}$  is the same as for  
 (a)  $^{12}_6\text{C}$  (b)  $^{14}_7\text{N}$   
 (c) both (d) none of these  
**Answer.** (c)
32. In the nucleus of  $^{40}_{18}\text{Ar}$ , the difference between the number of neutrons and protons is  
 (a) 4 (b) 18  
 (c) 22 (d) 40  
**Answer.** (a)
33. Amongst the three isotopes of Neon -  $^{20}_{10}\text{Ne}$ ,  $^{21}_{10}\text{Ne}$  and  $^{22}_{10}\text{Ne}$  the nucleus with lowest  $n/p$  ratio is  
 (a)  $^{22}_{10}\text{Ne}$  (b)  $^{21}_{10}\text{Ne}$   
 (c)  $^{20}_{10}\text{Ne}$  (d) all of these  
**Answer.** (c)
34. The number of neutrons is greatest in  
 (a)  $^{235}_{92}\text{U}$  (b)  $^{236}_{92}\text{U}$   
 (c)  $^{237}_{92}\text{U}$  (d)  $^{238}_{92}\text{U}$   
**Answer.** (d)
35. Calcium atom and  $\text{Ca}^{2+}$  ions have  
 (a) the same number of electrons (b) the same number of neutrons  
 (c) different number of protons (d) different number of neutrons  
**Answer.** (b)
36. The set of isoelectronic species is  
 (a)  $\text{Na}^+$   $\text{Ne}$   $\text{Mg}^{2+}$  (b)  $\text{Na}^+$   $\text{Mg}^{2+}$   $\text{Al}^{3+}$   
 (c)  $\text{Na}^+$   $\text{K}^+$   $\text{Ne}$  (d)  $\text{Ne}$   $\text{Cl}^-$   $\text{Na}$   
**Answer.** (b)
37. An atom of  $^{94}_{36}\text{Kr}$  contains  
 (a) 36 protons, 36 electrons and 36 neutrons (b) 94 protons, 94 electrons and 94 neutrons  
 (c) 36 protons, 58 electrons and 36 neutrons (d) 36 protons, 36 electrons and 58 neutrons  
**Answer.** (d)
38. In  $^{10}_5\text{B}$ , the  $n/p$  ratio is  
 (a) 1.0 (b) 1.25  
 (c) 1.50 (d) 2.0  
**Answer.** (a)
39. The nuclei  $^{130}_{52}\text{Te}$ ,  $^{130}_{54}\text{Xe}$  and  $^{130}_{56}\text{Ba}$  are isobars as they have  
 (a) different number of protons (b) different number of neutrons  
 (c) same mass number (d) different mass number  
**Answer.** (c)

40. Isotones have different physical and chemical properties as they have  
 (a) same number of neutrons (b) different number of protons (or electrons)  
 (c) same mass numbers (d) different mass numbers  
**Answer.** (b)
41. An element M has an atomic mass 19 and atomic number 9, its ion is represented by  
 (a)  $M^+$  (b)  $M^{2+}$   
 (c)  $M^-$  (d)  $M^{2-}$   
**Answer.** (c)
42. The nuclei, which are not identical but have the same number of nucleons, are called  
 (a) isotopes (b) isobars  
 (c) isotones (d) isoelectronic  
**Answer.** (b)
43. Which of the following are isotopes?  
 (a)  $17p + 18n$  and  $17p + 20n$  (b)  $19p + 20n$  and  $20p + 21n$   
 (c)  $18p + 20n$  and  $19p + 21n$  (d)  $20p + 20n$  and  $19p + 22n$   
**Answer.** (a)
44. In which of the species the number of neutrons is equal to the number of electrons?  
 (a)  ${}_6C^{12}$  (b)  ${}_7N^{15}$   
 (c)  ${}_8O^{17}$  (d)  ${}_9F^{19}$   
**Answer.** (a)
45. The triad of nuclei that is isotonic is  
 (a)  ${}_1H^1$  and  ${}_1H^2$  and  ${}_1H^3$  (b)  ${}_{92}^{235}U$ ,  ${}_{92}^{237}U$  and  ${}_{92}^{238}U$   
 (c)  ${}_{18}^{40}Ar$ ,  ${}_{19}^{40}K$  and  ${}_{20}^{40}Ca$  (d)  ${}_6^{14}C$ ,  ${}_7^{15}N$  and  ${}_8^{16}O$   
**Answer.** (d)
46.  ${}_{12}^{24}Mg^{2+}$  is isoelectronic with  
 (a)  ${}_{11}^{23}Na$  (b)  ${}_{13}^{27}Al$   
 (c)  ${}_{11}^{23}Na^+$  (d)  ${}_{12}^{24}Mg$   
**Answer.** (c)
47. In the nucleus of  ${}_{42}Mo^{96}$  the number of nucleons is  
 (a) 42 (b) 54  
 (c) 96 (d) 138  
**Answer.** (c)
48. The atomic mass of an element is not a whole number because  
 (a) nucleons are present in the nucleus  
 (b) the number of protons is different from the neutrons  
 (c) of the presence of isobars  
 (d) of the presence of isotopes  
**Answer.** (d)
49.  ${}_{88}Ra^{236}$  contains \_\_\_\_\_ neutrons in its nucleus.  
 (a) 88 (b) 236  
 (c) 148 (d) 324  
**Answer.** (c)
50. An element has atomic number 20. Its cation has 2 units positive charge. The number of electrons and protons in its cation are  
 (a) 18 e and 20 p (b) 20 e and 18 p  
 (c) 20 e and 20 p (d) 18 e and 18 p  
**Answer.** (a)

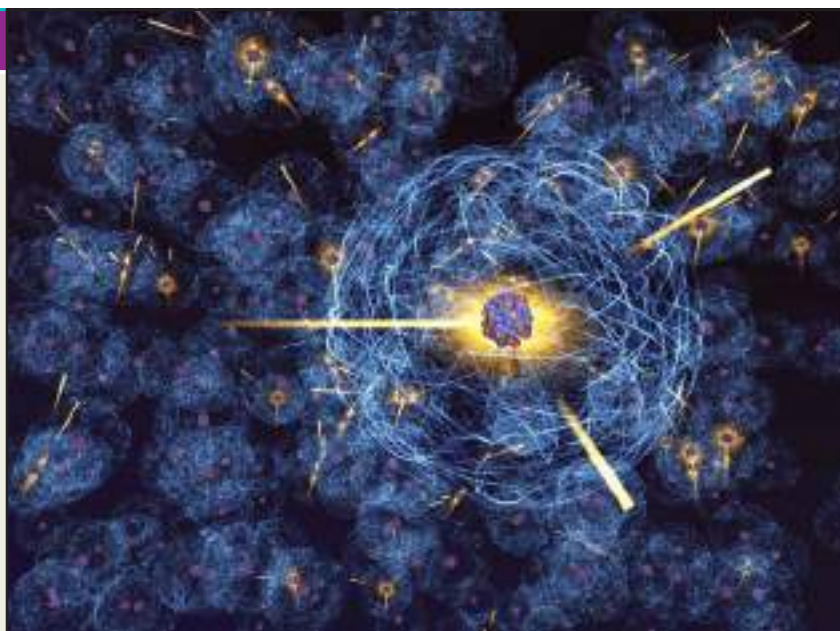
## 4

## Nuclear Chemistry

## CHAPTER

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A nuclear reaction is different from a chemical reaction. In a chemical reaction, atoms of the reactants combine by a rearrangement of extranuclear electrons but the nuclei of the atoms remain unchanged. In a nuclear reaction, on the other hand, it is the nucleus of the atom which is involved. The number of protons or neutrons in the nucleus changes to form a new element. **A study of the nuclear changes in atoms is termed Nuclear Chemistry.**

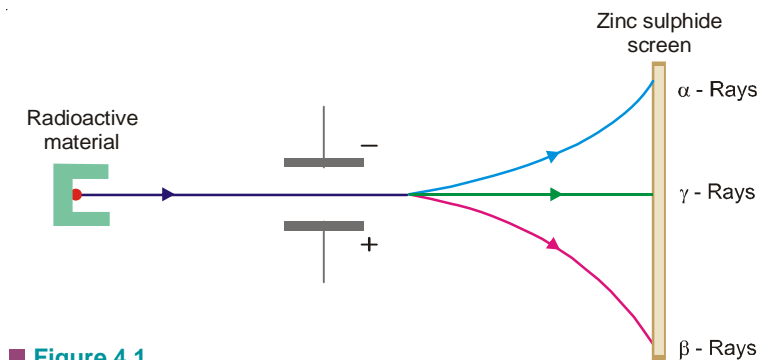
### RADIOACTIVITY

A number of elements such as uranium and radium are unstable. Their atomic nucleus breaks of its own accord to form a smaller atomic nucleus of another element. The protons and neutrons in the unstable nucleus regroup to give the new nucleus. This causes the release of excess particles and energy from the original nucleus, which we call **radiation**. The elements whose atomic nucleus emits radiation are said to be **radioactive**. The spontaneous breaking down of the unstable atoms is termed **radioactive disintegration or radioactive decay**.

**The disintegration or decay of unstable atoms accompanied by emission of radiation is called Radioactivity.**

### TYPES OF RADIATIONS

The radioactive radiations are of three types. These were sorted out by Rutherford (1902) by passing them between two oppositely charged plates (Fig. 4.1). The one bending towards the negative plate carried positive charge and were named  $\alpha$  (**alpha**) rays. Those bending towards the positive plate and carrying negative charge were called  $\beta$  (**beta**) rays. The third type of radiation, being uncharged, passed straight through the electric field and were named  $\gamma$  (**gamma**) rays.  $\alpha$ ,  $\beta$  and  $\gamma$  rays could be easily detected as they cause luminescence on the zinc sulphide screen placed in their path.



■ **Figure 4.1**  
Detection of  $\alpha$ ,  $\beta$  and  $\gamma$ -Rays.

### PROPERTIES OF RADIATIONS

Alpha ( $\alpha$ ), beta ( $\beta$ ) and gamma ( $\gamma$ ) rays differ from each other in nature and properties. Their chief properties are : (a) Velocity; (b) Penetrating power; (c) Ionisation.

#### ALPHA RAYS

(1) **Nature.** They consist of streams of  $\alpha$ -particles. **By measurement of their  $e/m$ , Rutherford showed that they have a mass of 4 amu and charge of +2.** They are **helium nuclei** and may be represented as  ${}^4_2\alpha$  or  ${}^4_2\text{He}$ .

(2) **Velocity.**  $\alpha$ -particles are ejected from radioactive nuclei with very high velocity, about one-tenth that of light.

(3) **Penetrating power.** Because of their charge and relatively large size,  $\alpha$ -particles have **very little power of penetration** through matter. They are stopped by a sheet of paper, 0.01 mm thick aluminium foil or a few centimetres of air.

(4) **Ionisation.** They cause **intense ionisation** of a gas through which they pass. On account of their high velocity and attraction for electrons,  $\alpha$ -particles break away electrons from gas molecules and convert them to positive ions.

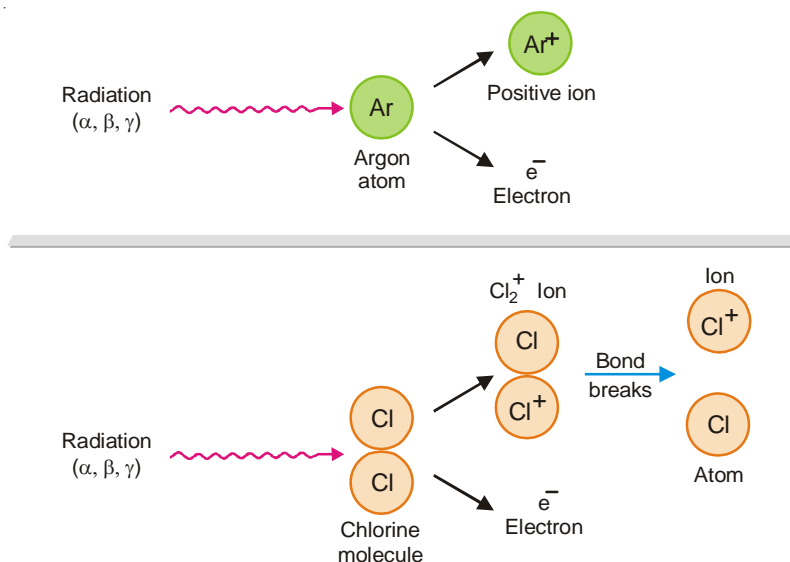
#### BETA RAYS

(1) **Nature.** They are streams of  $\beta$ -particles emitted by the nucleus. From their deflection electric and magnetic fields, Becquerel showed that  **$\beta$ -particles are identical with electrons.** They have very small mass (1/1827 amu) and charge of  $-1$ . A  $\beta$ -particle is symbolized as  ${}^0_{-1}\beta$  or  ${}^0_{-1}e$ .

(2) **Velocity.** They travel about **10 times faster than  $\alpha$ -particles.** Their velocity is about the same as of light.

(3) **Penetrating power.**  **$\beta$ -Particles are 100 times more penetrating in comparison to  $\alpha$ -particles.** This is so because they have higher velocity and negligible mass.  $\beta$ -particles can be stopped by about 1 cm thick sheet of aluminium or 1 m of air.





■ **Figure 4.2**

**Radiation energy knocks electrons out of atoms or molecules. This produces positive ions. Bond breaking often occurs in unstable molecular ions.**

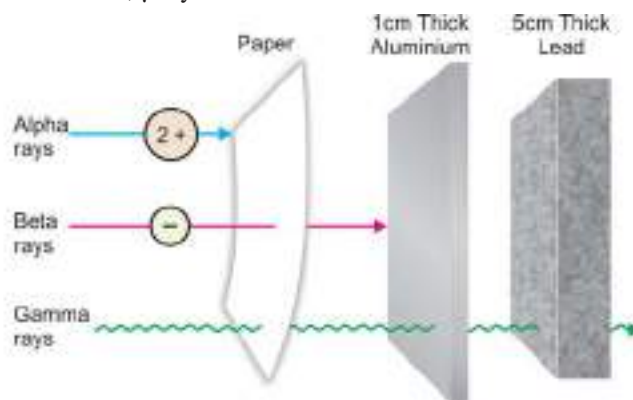
(4) **Ionisation.** The ionisation produced by  $\beta$ -particles in a gas is about **one-hundredth of that of  $\alpha$ -particles**. Though the velocity of  $\beta$ -particles is higher but the mass being smaller, their kinetic energy is much less than  $\alpha$ -particles. Hence they are poor ionisers.

### GAMMA RAYS

(1) **Nature.** Unlike  $\alpha$  and  $\beta$ -rays, they do not consist of particles of matter.  **$\gamma$ -Rays are a form of electromagnetic radiation** of shorter wavelength than X-rays. They could be thought of as high-energy photons released by the nucleus during  $\alpha$ - or  $\beta$ -emissions. They have no mass or charge and may be symbolized as  ${}^0_0\gamma$ .

(2) **Velocity.** Like all forms of electromagnetic radiation,  **$\gamma$ -rays travel with the velocity of light.**

(3) **Ionising power.** Their ionising power is very weak in comparison to  $\alpha$ - and  $\beta$ -particles. A  $\gamma$ -photon displaces an electron of the gas molecule to yield a positive ion. Since the chances of photon-electron collisions are small,  $\gamma$ -rays are weak ionisers.



■ **Figure 4.3**

**Penetrating powers of alpha, beta and gamma rays.**

(4) **Penetrating power.** Because of their high velocity and non-material nature,  $\gamma$ -rays are **most penetrating**. They cannot be stopped even by a 5 cm thick sheet of lead or several metres thick layer of concrete.

TABLE 4.1. COMPARISON OF PROPERTIES OF  $\alpha$ ,  $\beta$  AND  $\gamma$ -RAYS

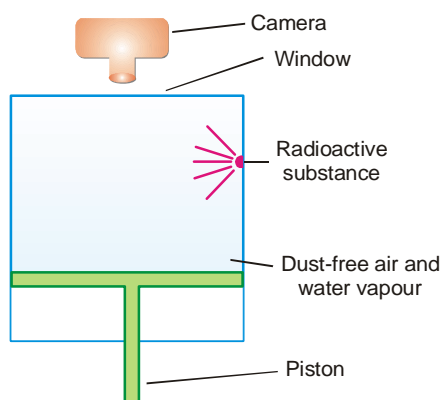
Property	$\alpha$ -rays	$\beta$ -rays	$\gamma$ -rays
Nature	helium nuclei ${}^4_2\text{He}$	fast electrons ${}^0_{-1}\text{e}$	electromagnetic radiation
Velocity	one-tenth of velocity of light	velocity of light	velocity of light
Penetrating Power	low	moderate	high
Stopped by	paper or 0.01 mm thick aluminium sheet	1 cm of aluminium	several cm thick lead/ concrete layer

### DETECTION AND MEASUREMENT OF RADIOACTIVITY

The radioactive radiation can be detected and measured by a number of methods. The important ones used in modern practice are listed below.

#### (1) Cloud Chamber

This technique (Fig. 4.4) is used for detecting radioactivity. The chamber contains air saturated with water vapour. When the piston is lowered suddenly, the gas expands and is supercooled. As an  $\alpha$ - or  $\beta$ -particle passes through the gas, ions are created along its path. These ions provide nuclei upon which droplets of water condense. The trail or cloud thus produced marks the track of the particle. The track can be seen through the window above and immediately photographed. Similarly,  $\alpha$ - or  $\beta$ -particles form a trail of bubbles as they pass through liquid hydrogen. The **bubble chamber method** gives better photographs of the particle tracks.



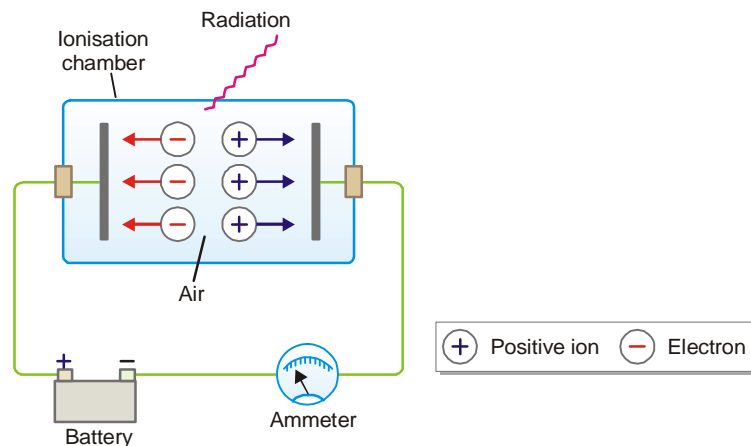
■ **Figure 4.4**  
Principle of Cloud Chamber.

#### (2) Ionisation Chamber

This is the simplest device used to measure the strength of radiation. An ionisation chamber is fitted with two metal plates separated by air. When radiation passes through this chamber, it knocks electrons from gas molecules and positive ions are formed. The electrons migrate to the anode and positive ions to the cathode.

Thus a small current passes between the plates. This current can be measured with an ammeter, and gives the strength of radiation that passes through the ionisation chamber. In an ionisation

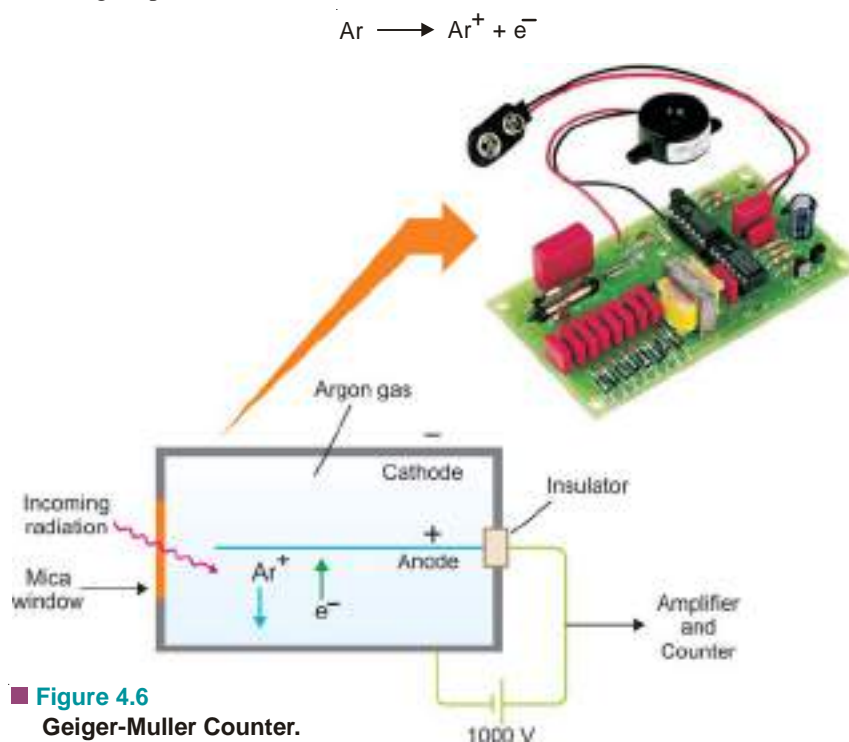
chamber called **Dosimeter**, the total amount of electric charge passing between the plates in a given time is measured. This is proportional to the total amount of radiation that has gone through the chamber.



■ **Figure 4.5**  
An Ionisation chamber used to measure the strength of radiation.

### (3) Geiger-Muller Counter

This device (Fig. 4.6) is used for detecting and measuring the rate of emission of  $\alpha$ - or  $\beta$ -particles. It consists of a cylindrical metal tube (cathode) and a central wire (anode). The tube is filled with argon gas at reduced pressure (0.1 atm). A potential difference of about 1000 volts is applied across the electrodes. When an  $\alpha$ - or  $\beta$ -particle enters the tube through the mica window, it ionises the argon atoms along its path.

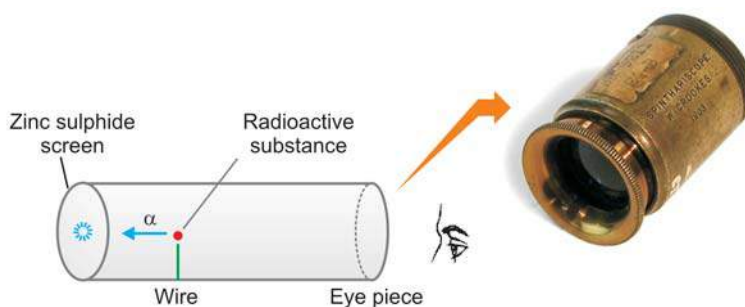


■ **Figure 4.6**  
Geiger-Muller Counter.

The argon ions ( $\text{Ar}^+$ ) are drawn to the cathode and electrons to anode. Thus for a fraction of a second, a pulse of electrical current flows between the electrodes and completes the circuit around. **Each electrical pulse marks the entry of one  $\alpha$ - or  $\beta$ -particle into the tube and is recorded in an automatic counter.** The number of such pulses registered by a radioactive material per minute, gives the intensity of its radioactivity.

#### (4) Scintillation Counter

Rutherford used a spinthariscopes (Fig. 4.7) for the detection and counting of  $\alpha$ -particles. The radioactive substance mounted on the tip of the wire emitted  $\alpha$ -particles. Each particle on striking the zinc sulphide screen produced a flash of light. These flashes of light (scintillations) could be seen through the eye-piece. With this device it was possible to count  $\alpha$ -particles from 50 to 200 per second.



■ **Figure 4.7**  
Spinthariscopes.

A **modern scintillation counter** also works on the above principle and is widely used for the measurement of  $\alpha$ - or  $\beta$ -particles. Instead of the zinc sulphide screen, a crystal of sodium iodide with a little thallium iodide is employed. The sample of the radioactive substance contained in a small vial, is placed in a 'well' cut into the crystal. The radiation from the sample hit the crystal wall and produce scintillations. **These fall on a photoelectric cell which produces a pulse of electric current for each flash of light.** This is recorded in a mechanical counter. Such a scintillation counter can measure radiation upto a million per second.

#### (5) Film Badges

A film badge consists of a photographic film encased in a plastic holder. When exposed to radiation, they darken the grains of silver in photographic film. The film is developed and viewed under a powerful microscope.

As  $\alpha$ - or  $\beta$ -particles pass through the film, they leave a track of black particles. These particles can be counted. In this way the type of radiation and its intensity can be known. However,  $\gamma$ -radiation darken the photographic film uniformly. The amount of darkening tells the quantity of radiation.

**A film badge is an important device to monitor the extent of exposure of persons working in the vicinity of radiation.** The badge-film is developed periodically to see if any significant dose of radiation has been absorbed by the wearer.

### TYPES OF RADIOACTIVE DECAY

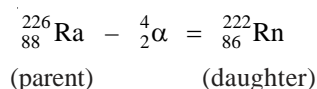
According to the theory put forward by Rutherford and Soddy (1903), radioactivity is a nuclear property. The nucleus of a radioactive atom is unstable. It undergoes decay or disintegration by spontaneous emission of an  $\alpha$ - or  $\beta$ -particle. This results in the change of proton-neutron composition of the nucleus to form a more stable nucleus. **The original nucleus is called the parent nucleus and the product is called the daughter nucleus.**

(1)  $\alpha$ -decay                      (2)  $\beta$ -decay

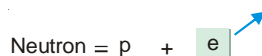
When a radioactive nucleus decays by the emission of an  $\alpha$ -particle ( $\alpha$ -**emission**) from the nucleus, the process is termed  $\alpha$ -decay. An alpha particle has four units of atomic mass and two units of positive charge. If  $Z$  be the atomic number and  $M$  the atomic mass of the parent nucleus, the daughter nucleus will have

atomic number =  $Z - 2$

For example, Radium decays by  $\alpha$ -emission to form a new element Radon.

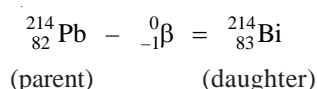


When a radioactive nucleus decays by  $\beta$ -particle emission ( **$\beta$ -emission**), it is called  $\beta$ -decay. A free  $\beta$ -particle or electron does not exist as such in the nucleus. It is produced by the conversion of a neutron to a proton at the moment of emission.

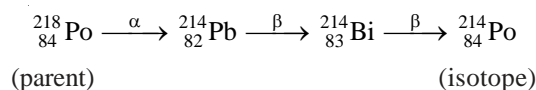


atomic number =  $Z + 1$

An example of  $\beta$ -decay is the conversion of lead-214 to bismuth-214,



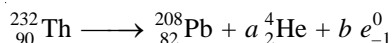
**One  $\alpha$ -emission and two  $\beta$ -emissions yield an isotope.** Let us consider the following series of changes.



The parent element  $^{218}_{84}\text{Po}$  emits an  $\alpha$ -particle and subsequently two  $\beta$ -particles, resulting in the formation of  $^{214}_{84}\text{Po}$  which is an isotope of the parent. Both the parent and the end-product have the same atomic number 84 but different mass numbers (218 and 214).

**SOLVED PROBLEM 1.** How many  $\alpha$  and  $\beta$  particles are emitted in passing down from  ${}^{232}_{90}\text{Th}$  to  ${}^{208}_{82}\text{Pb}$ .

**SOLUTION.** Let  $a$  be the number of  $\alpha$  particles and  $b$  be the number of  $\beta$  particles emitted during the radioactive transformation. It can be represented as



Comparing the mass numbers, we get

$$232 = 208 + 4 \times a + b \times 0$$

or

$$4a = 232 - 208 = 24$$

or

$$a = 6$$

Comparing the atomic numbers, we get

$$90 = 82 + 2 \times a + b(-1)$$

Substituting the value of  $a$ , we get

$$90 = 82 + 2 \times 6 - b$$

or

$$b = 94 - 90$$

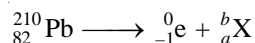
or

$$b = 4$$

Thus the number of  $\alpha$  particles emitted = 6 and the number of  $\beta$  particles emitted = 4

**SOLVED PROBLEM 2.**  ${}^{210}_{82}\text{Pb}$  is a  $\beta$ -emitter and  ${}^{226}_{88}\text{Ra}$  is an  $\alpha$ -emitter. What will be the atomic masses and atomic numbers of daughter elements of these radioactive elements? Predict the position of daughter elements in the periodic table.

**SOLUTION.** (a)  ${}^{210}_{82}\text{Pb}$  undergoes  $\beta$ -decay *i.e.*



Comparing the atomic masses, we have

$$210 = 0 + b$$

or

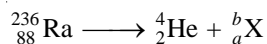
$$b = 210$$

and comparing the atomic numbers, we get

$$82 = -1 + a \text{ or } a = 83$$

Thus the daughter element will have the same atomic mass **210** and its atomic number will be **83**. It will occupy **one position right** to the parent element.

(b)  ${}^{236}_{88}\text{Ra}$  undergoes  $\alpha$  decay *i.e.*



Comparing the atomic masses, we get

$$236 = 4 + b \text{ or } b = 232$$

and comparing the atomic number, we get

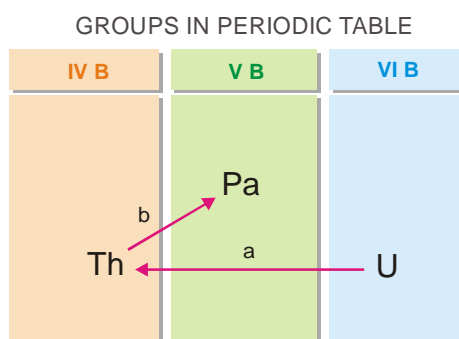
$$88 = 2 + a \text{ or } a = 86$$

Thus the daughter element will have atomic mass **232** and its atomic number will be **86**. It will occupy **two positions to the left** of the parent element.

### THE GROUP DISPLACEMENT LAW

The position number of an element in a Group of the Periodic Table corresponds to its atomic number. If the atomic number of a given element is changed, its Group also changes accordingly. We know that an  $\alpha$ -emission decreases the atomic number of the parent element by 2 and a  $\beta$ -emission increases the atomic number by 1. Thus : **in an  $\alpha$ -emission, the parent element will be displaced to a Group two places to the left and in a  $\beta$ -emission, it will be displaced to a Group one place to the right.**

This is called the **Group Displacement Law**. It was first stated by Fajans and Soddy (1913) and is often named after them as '*Fajans-Soddy Group Displacement Law*'.



■ **Figure 4.8**  
Illustration of Group Displacement Law.

### RADIOACTIVE DISINTEGRATION SERIES

A radioactive element disintegrates by the emission of an  $\alpha$ - or  $\beta$ - particle from the nucleus to form a new '*daughter element*'. This again disintegrates to give another '*daughter element*'. The process of disintegration and formation of a new element continues till a non-radioactive stable element is the product.

**The whole series of elements starting with the parent radioactive element to the stable end-product is called a Radioactive Disintegration Series.**

Sometime, it is referred to as a **Radioactive Decay Series** or simply **Radioactive Series**. All the natural radioactive elements belong to one of the three series :

- (1) The Uranium Series
- (2) The Thorium Series
- (3) The Actinium Series

#### The Uranium Series

It commences with the parent element uranium-238 and terminates with the stable element lead-206. It derives its name from uranium-238 which is the prominent member of the series and has the longest half-life. The Uranium series is illustrated in Fig. 4.9.

#### The Thorium Series

It begins with the parent element thorium-232 and ends with lead-208 which is stable. This series gets its name from the prominent member thorium-232.

#### The Actinium Series

It starts with the radioactive element uranium-235. The end-product is the stable element lead-207. This series derives its name from the prominent member actinium-227.

## THE URANIUM DISINTEGRATION SERIES

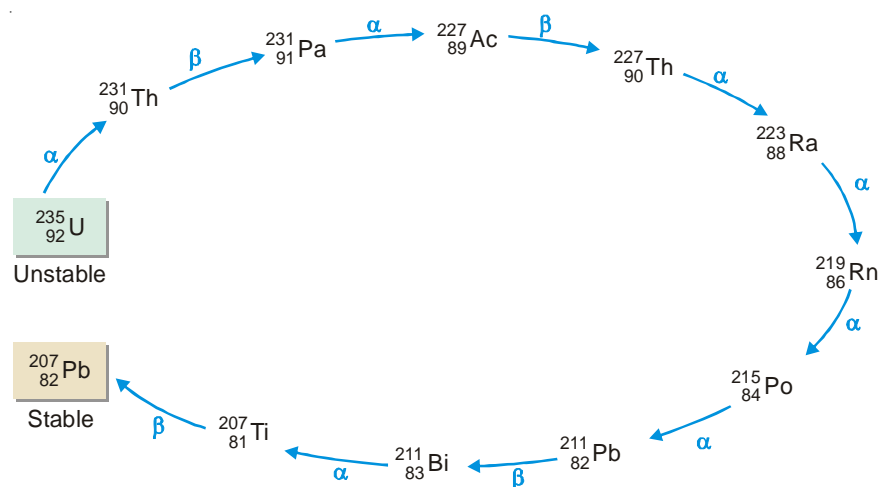
NUCLIDE	PARTICLE PRODUCED	HALF-LIFE
Uranium-238 ( $^{238}_{92}\text{U}$ )	$\alpha$	$4.51 \times 10^9$ years
↓		
Thorium - 234 ( $^{234}_{90}\text{Th}$ )	$\beta$	24.1 days
↓		
Protactinium-234 ( $^{234}_{91}\text{Pa}$ )	$\beta$	6.75 hours
↓		
Uranium-234 ( $^{234}_{92}\text{U}$ )	$\alpha$	$2.48 \times 10^5$ years
↓		
Thorium-230 ( $^{230}_{90}\text{Th}$ )	$\alpha$	$8.0 \times 10^4$ years
↓		
Radium-226 ( $^{226}_{88}\text{Ra}$ )	$\alpha$	$1.62 \times 10^3$ years
↓		
Radon-222 ( $^{222}_{86}\text{Rn}$ )	$\alpha$	3.82 days
↓		
Polonium-218 ( $^{218}_{84}\text{Po}$ )	$\alpha$	3.1 minutes
↓		
Lead-214 ( $^{214}_{82}\text{Pb}$ )	$\beta$	26.8 minutes
↓		
Bismuth-214 ( $^{214}_{83}\text{Bi}$ )	$\beta$	19.7 minutes
↓		
Polonium-214 ( $^{214}_{84}\text{Po}$ )	$\alpha$	$1.6 \times 10^{-4}$ second
↓		
Lead-210 ( $^{210}_{82}\text{Pb}$ )	$\beta$	20.4 years
↓		
Bismuth-210 ( $^{210}_{83}\text{Bi}$ )	$\beta$	5.0 days
↓		
Polonium-210 ( $^{210}_{84}\text{Po}$ )	$\alpha$	138.4 days
↓		
Lead-206 ( $^{206}_{82}\text{Pb}$ )	—	Stable

■ **Figure 4.9.**  
The Uranium Series.

#### The Neptunium Series

This series consists of elements which do not occur naturally. It commences with neptunium-237 and terminates at bismuth-200. It derives its name from the prominent member neptunium-237.





THE ACTINIUM SERIES

### RATE OF RADIOACTIVE DECAY

The decay of a radioactive isotope takes place by disintegration of the atomic nucleus. It is not influenced by any external conditions. Therefore the rate of decay is characteristic of an isotope and depends only on the number of atoms present. If  $N$  be the number of undecayed atoms of an isotope present in a sample of the isotope, at time  $t$ ,

$$-\frac{dN}{dt} \propto N$$

$$\text{or} \quad -\frac{dN}{dt} = \lambda N \quad \dots (1)$$

where  $-\frac{dN}{dt}$  means the rate of decrease in the number of radioactive atoms in the sample; and  $\lambda$  is the proportionality factor. This is known as the **decay constant** or **disintegration constant**. Putting  $dt = 1$  in equation (1) we have

$$-\frac{dN}{N} = \lambda \quad \dots (2)$$

Thus decay constant may be defined as the proportion of atoms of an isotope decaying per second.

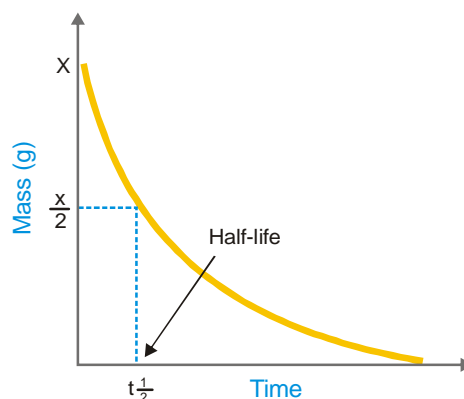
### UNITS OF RADIOACTIVITY

The standard unit of radioactivity (*i.e.* rate of disintegration) is *Curie* (c). A curie is a quantity of radioactive material decaying at the same rate as 1 g of Radium ( $3.7 \times 10^{10}$  dps). Rutherford is a more recent unit.

$$1 \text{ Rutherford} = 10^6 \text{ dps}$$

The S.I. unit is Becquerel

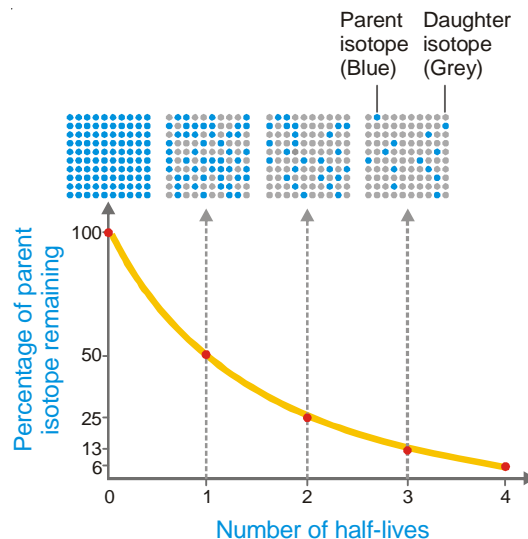
$$1 \text{ Bq} = 1 \text{ dps}$$



■ **Figure 4.10**  
Decay curve of a radioactive isotope of mass  $x$ .

### HALF-LIFE

The half-life or half-life period of a radioactive isotope is the time required for one-half of the isotope to decay. Or, it may be defined as the time for the radioactivity of an isotope to be reduced to half of its original value. Half-life period is characteristic of a radioactive element. For example, the half-life of radium is 1620 years. This means that 1 g of radium will be reduced to 0.5 g in 1620 years and to 0.25 g in further 1620 years; and so on. Some other radioactive elements may have half-life of a fraction of a second and for others it may be millions of years. The unit of half-life period is  $\text{time}^{-1}$ .



### THE ACTIVITY OF A RADIOACTIVE SUBSTANCE

It is defined as the **rate of decay or the number of disintegrations per unit time**. The activity of a sample is denoted by  $A$ . It is given by the expression :

$$A = \frac{dN}{dt} = \lambda N$$

The unit of activity is the **curie (Ci)** which is the rate of decay of  $3.7 \times 10^{10}$  disintegrations per second. The SI unit of activity is **becquerel (Bq)** which is defined as one disintegration per second.

The activity of a radioactive sample is usually determined experimentally with the help of a Geiger-Muller counter.

### CALCULATION OF HALF-LIFE

From equation (1) we can write

$$-\frac{dN}{N} = \lambda dt$$

On integration,

$$-\int \frac{dN}{N} = \lambda \int dt$$

$$\text{or} \quad -\ln N = \lambda t + X \text{ (constant)} \quad \dots(3)$$

If  $N_0$  is the number of atoms at time  $t = 0$ ,  $X = -\ln N_0$

Substituting the value of  $X$  in (3)

$$-\ln N = \lambda t - \ln N_0$$

$$\text{or} \quad \ln \left( \frac{N_0}{N} \right) = \lambda t$$

Using ordinary logs,

$$2.303 \log \left( \frac{N_0}{N} \right) = \lambda t \quad \dots(4)$$

At half-life time ( $t_{1/2}$ ),  $N = 1/2 N_0$

$$\therefore 2.303 \log \left( \frac{N_0}{\frac{1}{2} N_0} \right) = 2.303 \log 2 = \lambda t_{1/2}$$

$$\text{or} \quad 0.693 = \lambda t_{1/2}$$

$$\text{or} \quad t_{1/2} = \frac{0.693}{\lambda} \quad \dots(5)$$

The value of  $\lambda$  can be found experimentally by finding the number of disintegrations per second with the help of a Geiger-Muller counter. Hence, half-life of the isotope concerned can be calculated by using the relation (5).

**SOLVED PROBLEM 1.** Calculate the half-life of radium-226 if 1 g of it emits  $3.7 \times 10^{10}$  alpha particles per second.

### SOLUTION

Rate of decay = Rate of emission of  $\alpha$ -particles

We know that

$$\frac{dN}{dt} = \lambda N = 3.7 \times 10^{10} \text{ per second} \quad \dots(1)$$

The number of atoms of radium present ( $N$ ) in 1 g of sample,  $= \frac{6.023 \times 10^{23}}{226}$

From equation (5) stated earlier  $\lambda = \frac{0.693}{t_{1/2}}$

Substituting the value of  $\lambda$  and  $N$  in equation (1) above

$$\frac{dN}{dt} = \frac{0.693}{t_{1/2}} \times \frac{6.023 \times 10^{23}}{226} = 3.7 \times 10^{10}$$

Hence

$$t_{1/2} = \frac{0.693 \times 6.023 \times 10^{23}}{3.7 \times 10^{10} \times 226 \times 60 \times 60 \times 24 \times 365} \\ = \mathbf{1583 \text{ years}}$$

**SOLVED PROBLEM 2.** Calculate the disintegration constant of cobalt 60 if its half-life to produce nickel-60 is 5.2 years.

**SOLUTION**

From equation (5) stated earlier  $t_{1/2} = \frac{0.693}{\lambda}$

or 
$$\lambda = \frac{0.693}{t_{1/2}}$$

Substituting the value of  $t_{1/2}$ , we have  $\lambda = \frac{0.693}{5.2 \text{ yr}} = 0.13 \text{ yr}^{-1}$

**SOLVED PROBLEM 3.** The half-life period of radon is 3.825 days. Calculate the activity of radon. (atomic weight of radon = 222)

**SOLUTION**

We know that

$$dN = \lambda N \quad \dots (2)$$

where  $dN$  is the number of atoms disintegrating per second,  $\lambda$  is the decay constant and  $N$  is the number of atoms in the sample of radon.

**Calculation of  $\lambda$ :**

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{3.825 \times 24 \times 60 \times 60} = 2.096 \times 10^{-6} \text{ sec}^{-1}$$

**Calculation of  $N$ :**

From expression (1) above

$$N = \frac{dN}{\lambda} = \frac{3.7 \times 10^{10}}{2.096 \times 10^{-6}} = 1.7653 \times 10^{16} \text{ atoms}$$

Mass of  $6.02 \times 10^{23}$  atoms of radon = 222 g

$$\text{Mass of } 1.7653 \times 10^{16} \text{ atoms of radon} = \frac{222}{6.02 \times 10^{23}} \times 1.7653 \times 10^{16} \\ = 6.51 \times 10^{-6} \text{ g}$$

By definition, the activity of radon is its mass in grams which gives  $3.7 \times 10^{10}$  disintegrations per second. Therefore **activity of radon =  $6.51 \times 10^{-6}$  g curie.**

**CALCULATION OF SAMPLE LEFT AFTER TIME  $t$**

It follows from equation (4) stated earlier that

$$\log \left( \frac{N_0}{N} \right) = \frac{\lambda t}{2.303}$$

Knowing the value of  $\lambda$ , the ratio of  $N_0/N$  can be calculated. If the amount of the sample present to start with is given, the amount left after lapse of time  $t$  can be calculated.

**SOLVED PROBLEM 1.** Cobalt-60 disintegrates to give nickel-60. Calculate the fraction and the percentage of the sample that remains after 15 years. The disintegration constant of cobalt-60 is  $0.13 \text{ yr}^{-1}$ .

**SOLUTION**

$$\log \frac{N_0}{N} = \frac{\lambda t}{2.303} = \frac{(0.13 \text{ yr}^{-1})(15 \text{ yr})}{2.303} = 0.847$$

$$\frac{N_0}{N} = \text{antilog } 0.847 = 7.031$$

The fraction remaining is the amount at time  $t$  divided by the initial amount.

$$\frac{N}{N_0} = \frac{1}{7.031} = \mathbf{0.14}$$

Hence the fraction remaining after 15 years is 0.14 or 14 per cent of that present originally.

**SOLVED PROBLEM 2.** How much time would it take for a sample of cobalt-60 to disintegrate to the extent that only 2.0 per cent remains? The disintegration constant  $\lambda$  is  $0.13 \text{ yr}^{-1}$ .

**SOLUTION**

$$\frac{N}{N_0} = \frac{2}{100} = 0.02$$

or 
$$\frac{N_0}{N} = \frac{1}{0.02} = 50$$

From equation (4) stated earlier

$$\log \left( \frac{N_0}{N} \right) = \frac{\lambda t}{2.303}$$

$$\log 50 = \frac{(0.13 \text{ yr}^{-1}) t}{2.303}$$

or 
$$t = \frac{2.303 \log 50}{0.13 \text{ yr}^{-1}} = \mathbf{30 \text{ years}}$$

**SOLVED PROBLEM 3.** A sample of radioactive  $^{133}\text{I}$  gave with a Geiger counter 3150 counts per minute at a certain time and 3055 counts per unit exactly after one hour later. Calculate the half life period of  $^{133}\text{I}$ .

**SOLUTION.** Here  $N_0 = 3150$ ;  $N = 3055$ ;  $\frac{t_1}{2} = 1 \text{ hour}$ .

We know 
$$\lambda = \frac{0.693}{\frac{t_1}{2}} \text{ and } \lambda = \frac{2.303}{t} \log \frac{N_0}{N}$$

or 
$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log \frac{N_0}{N} = \frac{2.303}{1} \log \frac{3150}{3055}$$

or 
$$t_{1/2} = \mathbf{22.63 \text{ years}}$$

### AVERAGE LIFE

In a radioactive substance, some atoms decay earlier and others survive longer. **The statistical average of the lives of all atoms present at any time is called the Average life.** It is denoted by the symbol  $\tau$  and has been shown to be reciprocal of decay constant,  $\lambda$ .

$$\tau = \frac{1}{\lambda}$$

The average life of a radioactive element is related to its half-life by the expression :

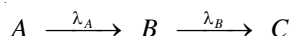
$$\text{Average life} = 1.44 \times \text{Half-life}$$

or 
$$\tau = 1.44 \times t_{1/2}$$

The average life is often used to express the rate of disintegration of a radioactive element. The average life of radium is 2400 years.

### RADIOACTIVE EQUILIBRIUM

Let a radioactive substance  $A$  decay to give another radioactive substance  $B$  which decays to form substance  $C$ . If  $\lambda_A$  and  $\lambda_B$  are the decay constants for the two changes, we can write



The rate of disintegration of  $A$  is also the rate of formation of  $B$ . When the rate of disintegration of  $A$  (or formation of  $B$ ) is equal to the rate of disintegration of  $B$ , the amount of  $B$  does not change with lapse of time. Then the radioactive equilibrium is said to be established between the substance  $A$  and the substance  $B$ . At this stage

$$\frac{dN_A}{dt} = \frac{dN_B}{dt}$$

where  $N_A$  and  $N_B$  are atoms of  $A$  and  $B$  present at the equilibrium.

Since 
$$\lambda_A N_A = \lambda_B N_B, \quad \frac{N_A}{N_B} = \frac{\lambda_B}{\lambda_A}$$

But 
$$\lambda \propto t_{1/2}$$

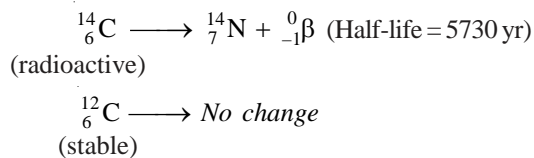
$$\therefore \frac{N_A}{N_B} = \frac{t_{1/2} \text{ of } B}{t_{1/2} \text{ of } A}$$

Thus the atoms of  $A$  and  $B$  are present in the ratio of their half-lives.

The radioactive equilibrium differs from a chemical equilibrium in that it is irreversible.

### RADIOACTIVE DATING

The age of an old piece of wood can be determined by radioactive dating technique. The atmosphere contains radioactive carbon dioxide,  $^{14}\text{CO}_2$ , and ordinary carbon dioxide,  $^{12}\text{CO}_2$ , in a fixed ratio. A plant while alive takes up both types of carbon dioxide and converts them to carbon-14 and carbon-12 photosynthesis. Thus a living plant contains radioactive carbon-14 and stable carbon-12 in a fixed ratio. When the plant dies, the uptake of carbon from the atmosphere stops. Now onward, carbon-12 remains unchanged but carbon-14 decays by beta-emission.



As a result,  $^{14}\text{C}/^{12}\text{C}$  decreases with lapse of time.

Therefore the concentration of carbon-14 declines with time. The concentration of carbon-14

can be measured by counting radioactivity. Knowing the concentration of carbon-14 in a given sample of old wood and that in a living plant, the age of the sample can be calculated.

**SOLVED PROBLEM.** The amount of carbon-14 in a piece of wood is found to be one-sixth of its amount in a fresh piece of wood. Calculate the age of old piece of wood.

### SOLUTION

Calculation of Decay constant :

The half-life of carbon-14 = 5730 years

$$\therefore \lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730 \text{ yr}}$$

Calculation of Age of Wood :

From expression (4) on page 89

$$t = \log \frac{{}^{14}\text{C}_0}{{}^{14}\text{C}_t} \times \frac{2.303}{\lambda}$$

or

$$\begin{aligned} t &= \log \frac{1}{1/6} \times \frac{2.303 \times 5730}{0.693} \\ &= \log 6 \times \frac{2.303 \times 5730}{0.693} \\ &= \frac{0.7782 \times 2.303 \times 5730}{0.693} \\ &= \mathbf{14818.5 \text{ years}} \end{aligned}$$

In a new method for determining the age of old wood (or fossil) the measurement of radioactivity is avoided. The ratio  ${}^{14}\text{C}/{}^{12}\text{C}$  is found with the help of a mass spectrometer in the old wood and fresh wood from a living plant. It is assumed that the ratio  ${}^{14}\text{C}/{}^{12}\text{C}$  in the fresh wood today is the same as it was at the time of death of the plant.

Let the ratio in the fresh plant at  $t = 0$  be

$$\frac{{}^{14}\text{C}_0}{{}^{12}\text{C}_0} = x \quad \dots(1)$$

Let the ratio in the old piece of wood at time  $t$  be

$$\frac{{}^{14}\text{C}_t}{{}^{12}\text{C}_t} = y \quad \dots(2)$$

Dividing (1) by (2)  $\frac{{}^{14}\text{C}_0}{{}^{12}\text{C}_0} \times \frac{{}^{12}\text{C}_t}{{}^{14}\text{C}_t} = \frac{x}{y}$

The concentration of carbon-12 does not change with time and  ${}^{12}\text{C}_0 = {}^{12}\text{C}_t$

Therefore  $\frac{{}^{14}\text{C}_0}{{}^{14}\text{C}_t} = \frac{x}{y} = \frac{1}{y/x}$

where the ratio in the old wood is  $y/x$  times the ratio in the living plant.

Knowing the value of  $y/x$ , the value of  $t$  can be found from the expression

$$t = \log \frac{{}^{14}\text{C}_0}{{}^{14}\text{C}_t} \times \frac{2.303}{\lambda}$$

**SOLVED PROBLEM.** A bone taken from a garbage pile buried under a hill-side had  $^{14}\text{C}/^{12}\text{C}$  ratio 0.477 times the ratio in a living plant or animal. What was the date when the animal was buried?

### SOLUTION

Half-life of carbon-14 is 5730 years

$$\therefore \lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730 \text{ yr}}$$

Substituting values in the expression

$$\begin{aligned} t &= \log \frac{{}^{14}\text{C}_0}{{}^{14}\text{C}_t} \times \frac{2.303}{\lambda} \\ &= \log \frac{1.0}{0.477} \times \frac{2.303 \times 5730}{0.693} = 6.1 \times 10^3 \\ &= \mathbf{6100 \text{ yr}} \end{aligned}$$

The animal was buried 6100 years ago.

## NUCLEAR REACTIONS

In a chemical reaction there is merely a rearrangement of extranuclear electrons. The atomic nucleus remains intact. A nuclear reaction involves a change in the composition of the nucleus. The number of protons and neutrons in the nucleus is altered. The product is a new nucleus of another atom with a different atomic number and/or mass number. Thus,

**A nuclear reaction is one which proceeds with a change in the composition of the nucleus so as to produce an atom of a new element.**

The conversion of one element to another by a nuclear change is called **transmutation**.

We have already considered the nuclear reactions of radioactive nuclei, producing new isotopes. Here we will consider such reactions caused by artificial means.

### DIFFERENCES BETWEEN NUCLEAR REACTIONS AND CHEMICAL REACTIONS

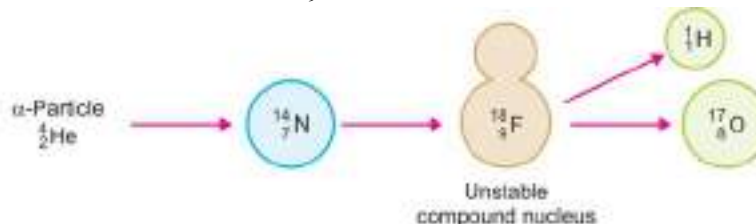
Nuclear Reactions	Chemical Reactions
1. Proceed by redistribution of nuclear particles.	1. Proceed by the rearrangement of extra-nuclear electrons.
2. One element may be converted into another.	2. No new element can be produced.
3. Often accompanied by release or absorption of enormous amount of energy.	3. Accompanied by release or absorption of relatively small amount of energy.
4. Rate of reaction is unaffected by external factors such as concentration, temperature, pressure and catalyst.	4. Rate of reaction is influenced by external factors.

## NUCLEAR FISSION REACTIONS

**In these reactions an atomic nucleus is broken or fissioned into two or more fragments.** This is accomplished by bombarding an atom by alpha particles ( ${}^4_2\text{He}$ ), neutrons ( ${}^1_0\text{n}$ ), protons ( ${}^1_1\text{H}$ ), deuterons ( ${}^2_1\text{H}$ ), etc. All the positively charged particles are accelerated to high kinetic energies by a device such as a *cyclotron*. This does not apply to neutrons which are electrically neutral. The projectile enters the nucleus and produces an unstable '**compound nucleus**'. It decomposes

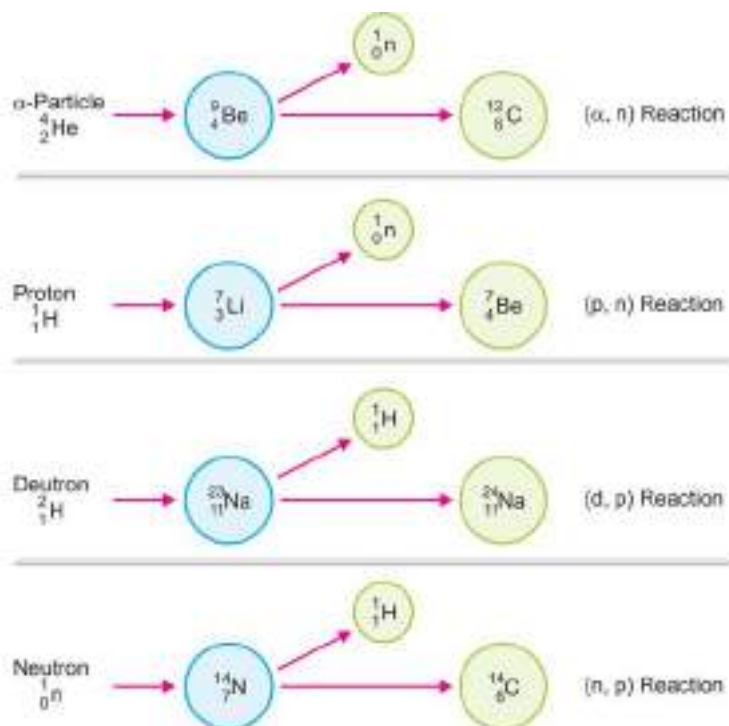


instantaneously to give the products. For example,  $^{14}_7\text{N}$  when struck by an  $\alpha$ -particle first forms an intermediate unstable compound nucleus,  $^{18}_9\text{F}$ , which at once cleaves to form stables  $^{17}_8\text{O}$ .



■ **Figure 4.11**  
Mechanism of a Nuclear fission reaction.

Other examples are,



■ **Figure 4.12**  
Representation of some Nuclear Fission reactions.  
Unstable compound nucleus is not shown.

Nuclear fission reactions are classified according to the projectile used and the particle that is emitted. In Fig. 4.12 the type of the reaction has been stated.

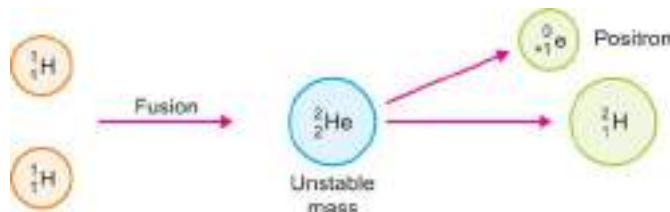
**It is noteworthy that neutrons are particularly useful as projectile.** Sir James Chadwick obtained these by bombarding beryllium-9 with  $\alpha$ -particles. Being electrically neutral, neutrons pierce the positive nucleus easily.

## NUCLEAR FUSION REACTIONS

**These reactions take place by combination or fusion of two small nuclei into a larger nucleus.** At extremely high temperatures the kinetic energy of these nuclei overweighs the electrical repulsions between them. Thus they coalesce to give an unstable mass which decomposes to give a stable large

nucleus and a small particle as proton, neutron, positron, etc. For example :

- (1) Two hydrogen nuclei,  ${}^1_1\text{H}$ , fuse to produce a deuterium nucleus,  ${}^2_1\text{H}$ .



- (2) Deuterium nucleus,  ${}^2_1\text{H}$ , and tritium nucleus,  ${}^3_1\text{H}$ , combine to give helium nucleus,  ${}^4_2\text{He}$  with the expulsion of a neutron.



#### DIFFERENCES BETWEEN NUCLEAR FISSION AND NUCLEAR FUSION

Nuclear Fission	Nuclear Fusion
1. A bigger (heavier nucleus splits into smaller (lighter) nuclei.	1. Lighter nuclei fuse together to form the heavier nucleus.
2. It does not require high temperature.	2. Extremely high temperature is required for fusion to take place.
3. A chain reaction sets in.	3. It is not a chain reaction.
4. It can be controlled and energy released can be used for peaceful purposes.	4. It cannot be controlled and energy released cannot be used properly.
5. The products of the reaction are radioactive in nature.	5. The products of a fusion reaction are non-radioactive in nature.
6. At the end of the reaction nuclear waste is left behind.	6. No nuclear waste is left at the end of fusion reaction.

#### NUCLEAR EQUATIONS

Similar to a chemical reaction, nuclear reactions can be represented by equations. **These equations involving the nuclei of the reactants and products are called nuclear equations.** The nuclear reactions occur by redistribution of protons and neutrons present in the reactants so as to form the products. Thus the total number of protons and neutrons in the reactants and products is the same. Obviously, **the sum of the mass numbers and atomic numbers on the two sides of the equation must be equal.**

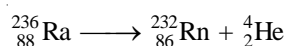
If the mass numbers and atomic numbers of all but one of the atoms or particles in a nuclear reaction are known, the unknown particle can be identified.

**How to write a Nuclear equation?**

- (1) Write the symbols of the nuclei and particles including the mass numbers (superscripts) and atomic numbers (subscripts) on the left (reactants) and right (products) of the arrow.
- (2) Balance the equation so that the sum of the mass numbers and atomic numbers of the particles (including the unknown) on the two sides of the equation are equal. Thus find the atomic number and mass number of the unknown atom, if any.
- (3) Then look at the periodic table and identify the unknown atom whose atomic number is disclosed by the balanced equation.

**Examples of Nuclear equations**

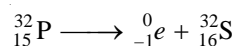
- (a) **Disintegration of radium-236** by emission of an alpha particle ( ${}^4_2\text{He}$ ),



<i>Mass Nos :</i>	Reactants = 236 ;	Products = 232 + 4 = 236
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<i>Atomic Nos :</i>	Reactants = 88 ;	Products = 86 + 2 = 88
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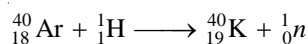
- (b) **Disintegration of phosphorus-32** by emission of a beta particle ( ${}^0_{-1}e$ ),



<i>Mass Nos :</i>	Reactants = 32 ;	Products : 0 + 32 = 32
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<i>Atomic Nos :</i>	Reactants = 15 ;	Products : 16 - 1 = 15
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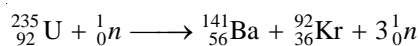
- (c) **Fission of argon-40** by bombardment with a proton  ${}^1_1\text{H}$ ,



<i>Mass Nos :</i>	Reactants = 40 + 1 = 41 ;	Products = 40 + 1 = 41
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<i>Atomic Nos :</i>	Reactants = 18 + 1 = 19 ;	Products = 19 + 0 = 19
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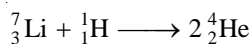
- (d) **Fission of uranium-235** by absorption of a neutron ( ${}^1_0n$ ),



<i>Mass No :</i>	Reactants = 235 + 1 = 236 ;	Products = 141 + 92 + 3 = 236
------------------	-----------------------------	-------------------------------

<i>Atomic Nos :</i>	Reactants = 92 + 0 = 92 ;	Products = 56 + 36 + 0 = 92
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- (e) **Fusion of lithium-7** and proton,  ${}^1_1\text{H}$ ,



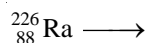
<i>Mass Nos :</i>	Reactants = 7 + 1 = 8 ;	Products = 2 × 4 = 8
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<i>Atomic Nos :</i>	Reactants = 3 + 1 = 4 ;	Products = 2 × 2 = 4
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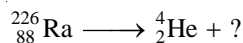
**SOLVED PROBLEM 1.** Write the nuclear equation for the change that occurs in radium-226 when it emits an alpha particle.

**SOLUTION**

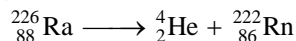
**Step 1** Write the symbol of the parent atom with its mass number and atomic number (from periodic table) on the left-hand side of the equation.



**Step 2** Write the symbol for the alpha particle on the right-hand side of the equation.



**Step 3** Complete the equation by writing the symbol of an isotope that has an atomic number  $88 - 2 = 86$  and mass number  $226 - 4 = 222$ . As shown by the periodic table, the isotope with atomic number 86 is radon, Rn. Thus,



**Step 4** Check that the mass numbers and atomic numbers on the two sides of the equation are balanced.

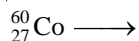
$$\text{Mass Nos :} \quad 226 = 4 + 222$$

$$\text{Atomic Nos :} \quad 88 = 2 + 86$$

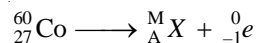
**SOLVED PROBLEM 2.** Cobalt-60 decays by emission of a beta particle. Predict the atomic number, mass number, and name of the isotope formed.

### SOLUTION

**Step 1** Write the symbol of the cobalt with mass number and atomic number (from the periodic table) on the left-hand side of the equation.



**Step 2** If the unknown product isotope is  $X$  with mass number  $M$  and atomic number  $A$ , the nuclear equation may be written as

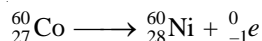


**Step 3** Since the sum of mass numbers and atomic numbers are equal on the two sides of the equation,

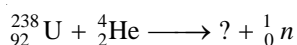
$$M = 60$$

$$A = 27 + 1 = 28$$

**Step 4** Consult the periodic table and find the element whose atomic number is 28. This is nickel, Ni. Therefore, the complete equation for the decay of cobalt-60 is



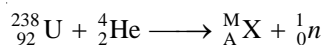
**SOLVED PROBLEM 3.** Complete the nuclear equation



### SOLUTION

Let the unknown atom be  $X$  with mass number  $M$  and atomic number  $A$ .

We can write the above nuclear equation as



But the sum of mass numbers on the two sides of the equation is equal. Thus,

$$238 + 4 = M + 1$$

or,

$$M = 242 - 1 = 241$$

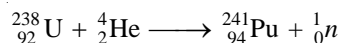
Also

$$92 + 2 = A + 0$$

or

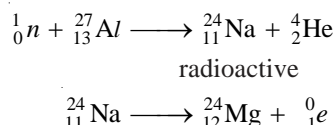
$$A = 94$$

Find the isotope of atomic number 94 from the periodic table. It is plutonium, Pu. Thus the completed nuclear equation is



### ARTIFICIAL RADIOACTIVITY

Many stable nuclei when bombarded with high speed particles produce unstable nuclei that are radioactive. The radioactivity produced in this manner by artificial means is known as **artificial radioactivity** or **induced radioactivity**. The artificial isotopes disintegrate in a definite fashion and have specific half-life. For example, aluminium-27 when bombarded with a neutron emits an alpha particle and forms sodium-24 which is radioactive. It disintegrates spontaneously by emission of a beta particle ( ${}_{-1}^0e$ ) and the product is magnesium-24. Sodium-24 has half-life of 24 hours.



### NUCLEAR ISOMERISM

Sometimes  $\alpha$  and  $\beta$ -decays may produce a pair of nuclei that have the same number of protons and neutrons but different radioactive properties.

**A pair of nuclei having same number of protons and neutrons but different half-lives are called nuclear isomers.** The phenomenon is called **nuclear isomerism**.

#### Example of Nuclear isomerism

Uranium-Z and Uranium-X<sub>2</sub> constitute a pair of nuclear isomers. Both nuclei contain 91 protons and 143 neutrons, and are isotopes. They exhibit  $\beta$ -ray activity with half-lives 6.7 hr and 1.14 min respectively.

#### Explanation

The  $\alpha$ - or  $\beta$ -decay of a radionuclide first leaves it in an excited state. This is then converted into the ground state nucleus. The excited and the ground state nuclei thus produced are called nuclear isomers. The nuclear isomers may be isotopic or isobaric.

### ENERGY RELEASED IN NUCLEAR REACTIONS

#### Einstein's Equation Relating Mass and Energy

According to Albert Einstein, mass can be converted into energy and *vice versa*. His famous equation relating mass and energy is

$$E = mc^2 \quad \dots(1)$$

where  $E$  = energy ;  $m$  = mass and  $c$  = velocity of light. In nuclear reactions, a change in mass,  $\Delta m$ , is accompanied by release of energy,  $\Delta E$ . Thus equation (1) may be written as

$$\Delta E = \Delta mc^2 \quad \dots(2)$$

If we substitute the value  $3.00 \times 10^{10}$  cm/sec for the velocity of light, the equation (2) directly gives the relation between the energy change in ergs and the mass change in grams.

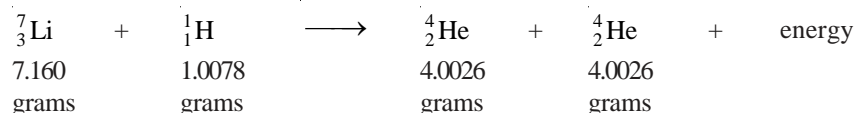
$$\Delta E \text{ (in ergs)} = 9.00 \times 10^{20} \times \Delta m \text{ (in grams)} \quad \dots(3)$$

Making use of the conversion factor  $1 \text{ erg} = 2.39 \times 10^{-11} \text{ kcal}$ , we can express the energy change in k cal.

$$\Delta E = 9.00 \times 10^{20} \text{ erg} \times \frac{2.39 \times 10^{-11}}{1 \text{ erg}} \times \Delta m$$

$$\text{or} \quad \Delta E \text{ (in kcal)} = 2.15 \times 10^{10} \times \Delta m \text{ (in grams)} \quad \dots(4)$$

Very often, in a nuclear reaction, the mass of the products is less than that of the reactants. The mass difference is converted into energy. Therefore by using equation (4), we can calculate the amount of energy released in a particular reaction. For example, in the equation



The atomic mass difference between the reactants and products is 0.0186 gram. Using equation (4)

$$\begin{aligned}
 \Delta E &= 2.15 \times 10^{10} \times \Delta m \\
 &= 2.15 \times 10^{10} \times 0.0186 \\
 &= 4.0 \times 10^8 \text{ k calories}
 \end{aligned}$$

### MASS DEFECT

We know that atomic nucleus consists of protons and neutrons; collectively known as nucleons. It is found that the measured mass of nucleus is always less than the sum of the masses of the individual protons and neutrons which make it up. Let us take the example of helium,  ${}^4_2\text{He}$ . It consists of two protons and two neutrons. Its mass may be calculated as :

$$\begin{aligned}
 \text{mass of the protons} &= 2 \times 1.00815 \\
 \text{mass of the neutrons} &= 2 \times 1.00899 \\
 &= 4.03428
 \end{aligned}$$

However, the experimental mass of the helium nucleus is only 4.00388. This is less by 0.03040 amu than that calculated above. This is called the mass defect of helium nucleus.

**The difference between the experimental and calculated masses of the nucleus is called the Mass defect or Mass deficit.**

$$(\text{experimental mass of nucleus}) - (\text{mass of protons} + \text{mass of neutrons}) = \text{mass defect}$$

### NUCLEAR BINDING ENERGY

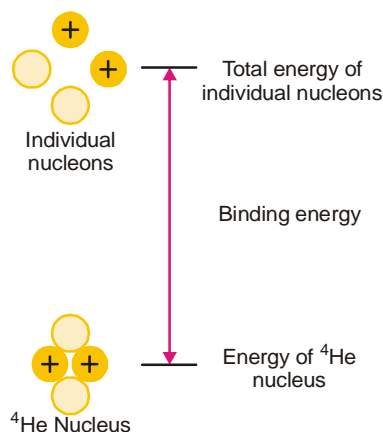
Atomic nucleus is made of protons and neutrons closely packed in a small volume. Although there exist intensive repulsive forces between the component protons, the nucleus is not split apart. This is so because the nucleons are bound to one another by very powerful forces. **The energy that binds the nucleons together in the nucleus is called the Nuclear binding energy.**

When a nucleus is formed from individual protons and neutrons, there occurs a loss of mass (mass defect). According to Einstein's theory, it is this mass defect which is converted into binding energy. **Hence binding energy is the energy equivalent of the mass defect.** The various nuclei have different binding energies.

Binding energy is a measure of the force that holds the nucleons together. Hence an energy equivalent to the binding energy is required to disrupt a nucleus into its constituent protons and neutrons. Since the nuclear energy is of an extremely high order, it is not easy to fission a nucleus.

### Calculation of Binding Energy

The binding energy of a nucleus can be calculated from its mass defect by using Einstein's equation,  $\Delta E = \Delta m \times c^2$ .



**Figure 4.13**  
A nucleus has a lower energy and a smaller mass than free nucleons.

**SOLVED PROBLEM.** What is the binding energy for  $^{11}_5\text{B}$  nucleus if its mass defect is 0.08181 amu ?

### SOLUTION

$$\Delta E = \Delta m \times c^2$$

....Einstein's equation

Here,

$$\Delta m = 0.08181 \text{ g/mole}$$

$$c = 3 \times 10^{10} \text{ cm/sec}$$

Substituting values in Einstein's equation,

$$\Delta E = (0.08181 \text{ g/mole}) (3 \times 10^{10} \text{ cm/sec})^2$$

$$= 7.4 \times 10^{19} \text{ ergs/mole}$$

No. of nuclei in one mole is  $6.02 \times 10^{23}$  (Avogadro's Law).

$\therefore$  Binding energy for  $^{11}_5\text{B}$  nucleus,  $\Delta E$ , may be expressed as

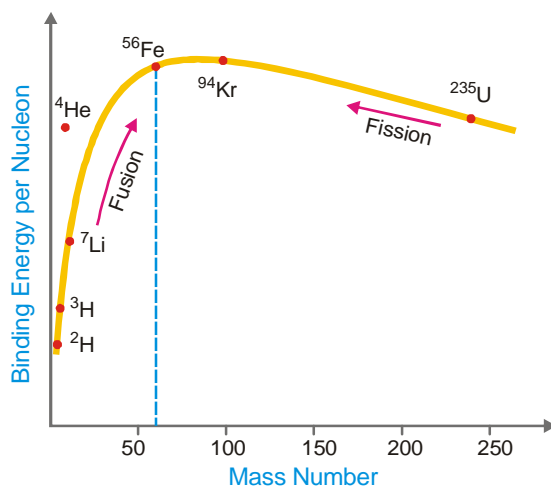
$$\Delta E = \frac{7.4 \times 10^{19}}{6.02 \times 10^{23}} = 1.2 \times 10^{-4} \text{ ergs/nucleus}$$

### Binding energy per nucleon

It can be calculated by dividing the total binding energy by the sum of the number of protons and neutrons present in the nucleus.

$$\text{Binding energy per nucleon} = \frac{\text{Binding energy of nucleus}}{\text{No. of protons} + \text{No. of neutrons}}$$

By plotting the binding energy per nucleon against the mass number, we get the graph shown in Fig. 4.14 This shows the relative stability of the various nuclei. **The greater the binding energy per nucleon the more stable is the nucleus.** Thus the nuclei of about 60 atomic mass having maximum energy per nucleon are most stable *e.g.*,  $^{56}\text{Fe}$ . The nuclei that are heavier or lighter than this have lower binding energies per nucleon and are less stable. Thus  $^{235}\text{U}$  undergoes fission into lighter and more stable isotopes as  $^{139}\text{Ba}$  and  $^{94}\text{Kr}$  with the release of energy. Similarly two or more lighter nuclei ( $^2\text{H}$ ,  $^3\text{H}$ ) with lower binding energy per nucleon combine or fuse together into a heavier and more stable nucleus. This is also accompanied by release of energy.



■ Figure 4.14

A curve of binding energy per nucleon versus mass number.

**Equivalence of amu and Energy**

Since 1 amu is exactly equal to  $\frac{1}{12}$  th of the mass of  $C^{12}$  atom, therefore

$$\begin{aligned} 1 \text{ amu} &= \frac{1}{12} \times \text{Mass of } C^{12} \text{ atom} \\ &= \frac{1}{12} \times \frac{\text{gram atomic mass of } C^{12}}{\text{Avagadro's Number}} \\ &= \frac{1}{12} \times \frac{12}{6.02 \times 10^{23}} \text{ g} \\ &= 1.66 \times 10^{-24} \text{ g} \end{aligned}$$

Also

$$E = mc^2$$

$\therefore$

$$\begin{aligned} E &= 1.66 \times 10^{-24} \text{ g} \times (3 \times 10^{10})^2 \\ &= 1.494 \times 10^{-3} \text{ erg} \\ &= \frac{1.494 \times 10^{-3}}{4.184 \times 10^7} \text{ cal} \quad [\because 1 \text{ cal} = 4.184 \times 10^7 \text{ erg}] \\ &= 0.356 \times 10^{-10} \text{ cal} \end{aligned}$$

or

$$\begin{aligned} E &= \frac{1.494 \times 10^{-3}}{10^7} \text{ joule} \quad [\because 1 \text{ joule} = 10^7 \text{ erg}] \\ &= 1.494 \times 10^{-10} \text{ J} \\ &= \frac{1.494 \times 10^{-10}}{1.602 \times 10^{-19}} \quad [\because 1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}] \\ &= 931.5 \times 10^6 \text{ eV} \\ &= 931.5 \text{ MeV} \end{aligned}$$

Thus

$$1 \text{ amu} = 931.5 \text{ MeV}$$

**SOLVED PROBLEM.** Calculate the binding energy per nucleon (in MeV) in He atom  ${}^4_2\text{He}$  which has a mass of 4.00260 amu. Mass of an electron = 1.008655 amu and mass of 1 hydrogen atom = 1.007825 mass.

**SOLUTION.** In Helium atom there are 2 electrons, 2 protons and 2 neutrons.

$$\begin{aligned} \therefore \quad \text{Mass of } 2p + 2e &= 2 \times \text{mass of 1 H atom} \\ &= 2 \times 1.007825 \text{ amu} \\ &= 2.01565 \text{ amu} \end{aligned}$$

$$\begin{aligned} \text{and} \quad \text{Mass of 2 neutrons} &= 2 \times 1.008665 \text{ amu} \\ \text{Mass of He atom} &= 2.01565 + 2.01733 \\ &= 4.03298 \text{ amu} \end{aligned}$$

$$\text{Actual mass of the atom} = 4.0026 \text{ amu (given)}$$

$$\begin{aligned} \therefore \quad \text{Mass defect} &= 4.0328 - 4.00260 \\ &= \mathbf{0.03038 \text{ amu}} \end{aligned}$$

$$\begin{aligned} \text{Binding Energy} &= 0.03038 \times 931.5 \text{ MeV} \\ &= 28.298 \text{ MeV} \quad [\because 1 \text{ amu} = 931.5 \text{ MeV}] \end{aligned}$$



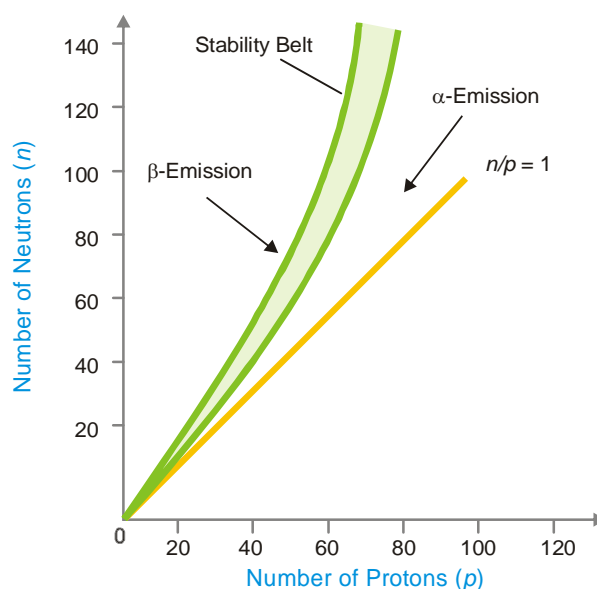
Binding energy per nucleon

$$\begin{aligned}
 &= \frac{\text{Binding Energy}}{\text{No. of Nucleons}} \\
 &= \frac{28.298}{4} = 7.0745 \text{ Mev}
 \end{aligned}$$

### NEUTRON-PROTON RATIO AND NUCLEAR STABILITY

Nuclei are composed of protons and neutrons. The protons would tend to fly apart due to repulsive forces between them. But the neutrons in some way hold the protons together within the nucleus. **The stability of a nucleus seems to depend on the neutron-to-proton ratio ( $n/p$ ) in the nucleus.** Fig. 4.15 shows the neutron-to-proton ratios for all known stable elements. Each point on the graph indicates the number of protons and neutrons in a particular stable nucleus. It is clear from the graph that :

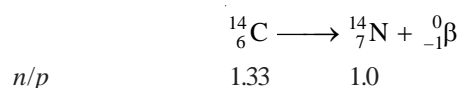
- (1) The lower elements (up to  $Z = 20$ ), the stable nuclei have about equal number of protons and neutrons i.e.,  $n/p = 1$ .
- (2) For higher elements to be stable, there must be more neutrons than protons i.e.,  $n/p > 1$ .
- (3) The shaded portion in Fig. 4.15 represents the region or belt of stability. The element whose  $n/p$  ratios lie inside the belt are stable.
- (4) A nucleus whose  $n/p$  lies above or below the stability belt is radioactive or unstable on account of unfavourable  $n/p$  ratio. It emits  $\alpha$ - or  $\beta$ - particles so as to move into the stability range.



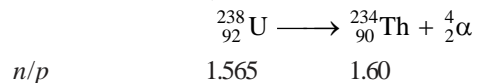
■ Figure 4.15

Neutron-proton ratios of stable nuclei.

(a) A nucleus that is above the stability belt emits a  $\beta$ -particle whereby a neutron is converted to proton. Thus  $n/p$  decreases and the nucleus becomes more stable or enters the stability belt. For example,



(b) A nucleus whose  $n/p$  lies below the stability belt emits an  $\alpha$ -particle and loses 2 protons and 2 neutrons. This results in a net increase of  $n/p$  and the new nucleus may enter the stability belt. For example,



The radioactive nuclei continue to emit  $\alpha$ - or  $\beta$ -particles, one after the other, till a stable nucleus is the end-product.

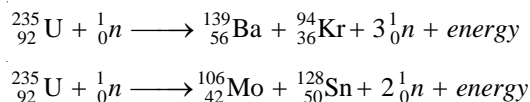
### NUCLEAR FISSION PROCESS

In 1939, Hahn and Stassmann discovered that a heavy atomic nucleus as of uranium-235 upon bombardment by a neutron splits apart into two or more nuclei. U-235 first absorbs a neutron to form an unstable 'compound nucleus'. The excited 'compound nucleus' then divides into two daughter nuclei with the release of neutrons and large amount of energy.

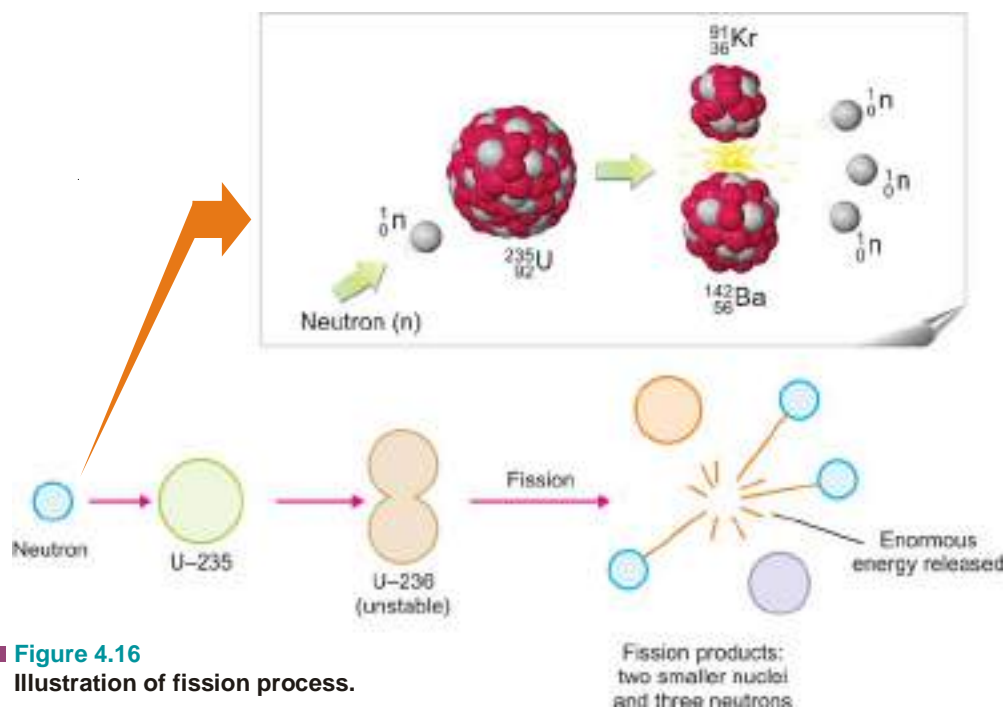
**The splitting of a heavy nucleus into two or more smaller nuclei is termed nuclear fission.**

The smaller nuclei formed as a result of fission are called **fission products**. The process of fission is always accompanied by the ejection of two or more neutrons and liberation of vast energy.

A given large nucleus can fission in many ways forming a variety of products. Thus the fission of U-235 occurs in about 35 ways. Two of these are given below in the form of equations.



In these fission reactions, the mass of the products is less than the mass of the reactant. A loss of mass of about 0.2 amu per uranium atom occurs. This mass is converted into a fantastic quantity of energy which is 2.5 million times of that produced by equivalent amount of coal.



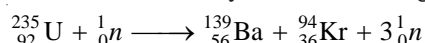
■ **Figure 4.16**  
Illustration of fission process.

### CHARACTERISTICS OF NUCLEAR FISSION

- (1) Upon capturing a neutron, a heavy nucleus cleaves into two or more nuclei.
- (2) Two or more neutrons are produced by fission of each nucleus.
- (3) Vast quantities of energy are produced as a result of conversion of small mass into energy.
- (4) All the fission products are radioactive, giving off beta and gamma radiations.

### NUCLEAR CHAIN REACTION

We know that U-235 nucleus when hit by a neutron undergoes the reaction,



Each of the three neutrons produced in the reaction strikes another U-235 nucleus, thus causing nine subsequent reactions. These nine reactions, in turn, further give rise to twenty seven reactions. This process of propagation of the reaction by multiplication in threes at each fission, is referred to as a **chain reaction**. Heavy unstable isotopes, in general, exhibit a chain reaction by release of two or three neutrons at each fission. It may be defined as :

**a fission reaction where the neutrons from a previous step continue to propagate and repeat the reaction.**

A chain reaction continues till most of the original nuclei in the given sample are fissioned. However, it may be noted that not all the neutrons released in the reaction are used up in propagating the chain reaction. Some of these are lost to the surroundings. Thus for a chain reaction to occur, the sample of the fissionable material should be large enough to capture the neutron internally. If the sample is too small, most neutrons will escape from its surface, thereby breaking the chain. **The minimum mass of fissionable material required to sustain a chain reaction is called critical mass.** The critical mass varies for each reaction. For U-235 fission reaction it is about 10 kg.

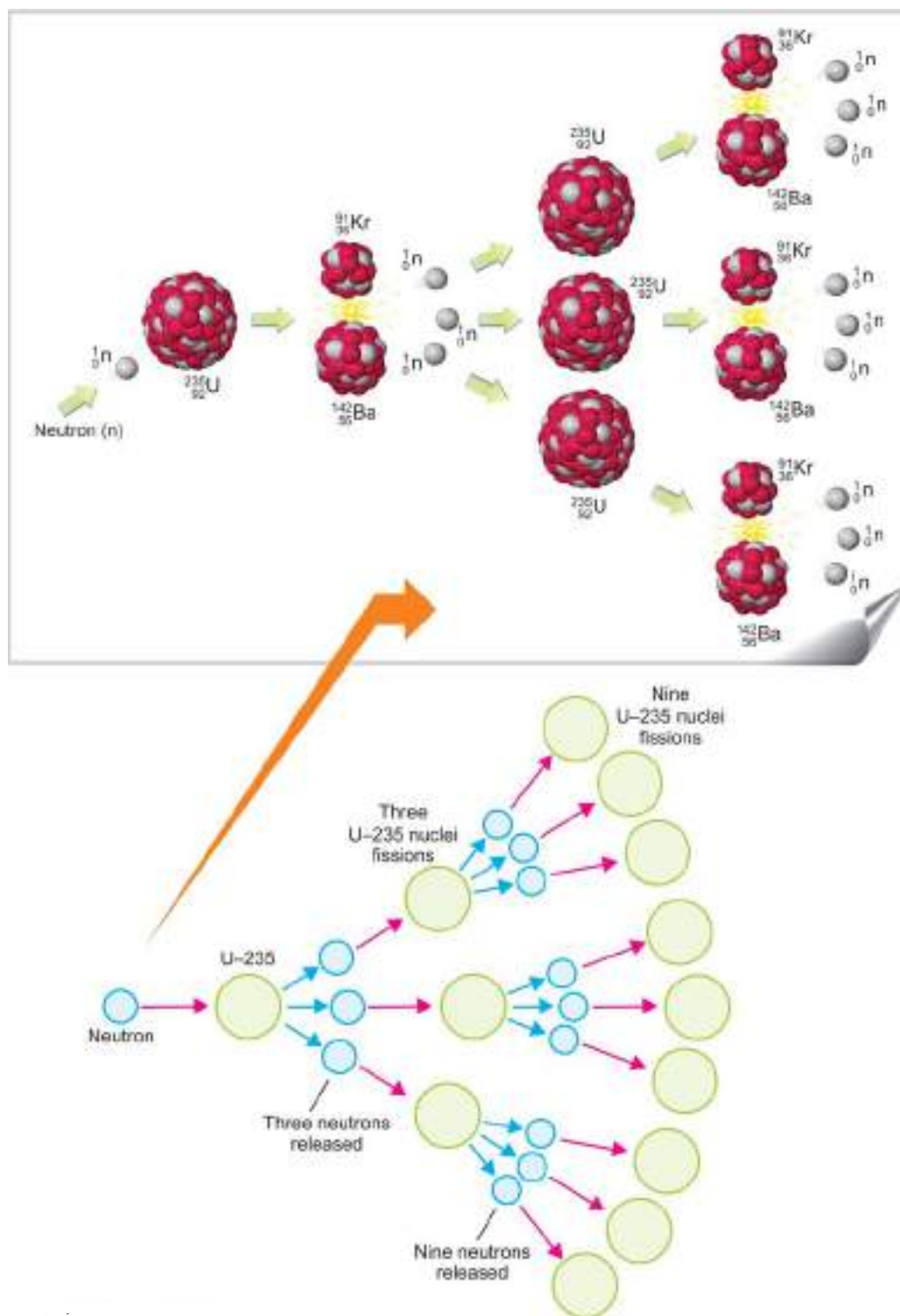
As already stated, even a single fission reaction produces a large amount of energy. A chain reaction that consists of innumerable fission reactions will, therefore, generate many times greater energy.

### NUCLEAR ENERGY

A heavy isotope as uranium-235 (or plutonium-239) can undergo nuclear chain reaction yielding vast amounts of energy. **The energy released by the fission of nuclei is called nuclear fission energy or nuclear energy.** Sometimes, it is incorrectly referred to as **atomic energy**.

The fission of U-235 or Pu-239 occurs instantaneously, producing incomprehensible quantities of energy in the form of heat and radiation. If the reaction is uncontrolled, it is accompanied by explosive violence and can be used in atomic bombs. However, when controlled in a reactor, the fission of U-235 is harnessed to produce electricity.





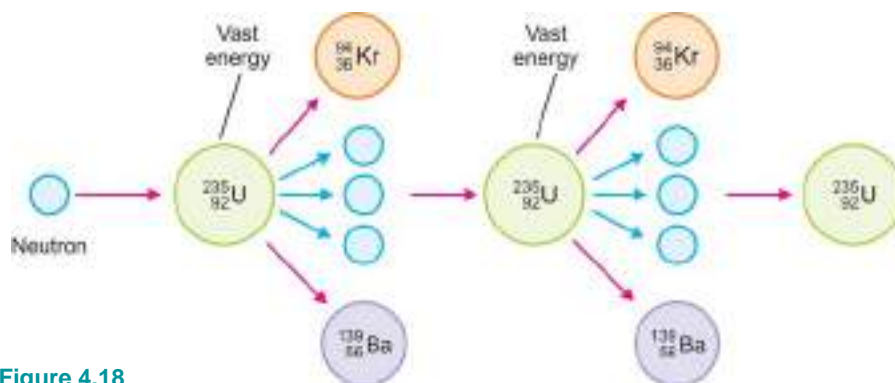
■ **Figure 4.17**

Illustration showing how U-235 fission chain reaction is propagated and multiplied. The products  $^{139}_{56}\text{Ba}$  and  $^{94}_{36}\text{Kr}$  are not shown.

## FIRST CHAIN REACTION



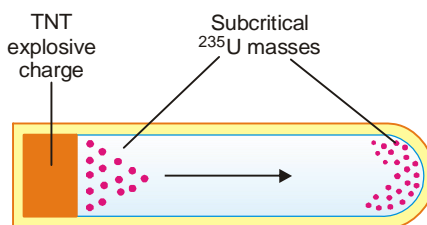
The first controlled nuclear fission chain reaction, directed by Italian-born American physicist Enrico Fermi, is captured here in a painting of the event, which took place under the sports stadium at the University of Chicago in December 1942. The event was the forerunner of all nuclear reactors.



■ **Figure 4.18**  
Chain reaction of Uranium-235 producing energy.

## THE ATOMIC BOMB

A bomb which works on the principle of a fast nuclear chain reaction is referred to as the **atomic bomb**. A design of such a bomb is shown in Fig. 4.19. It contains two subcritical masses of fissionable material,  $^{235}\text{U}$  or  $^{239}\text{Pu}$ . It has a mass of trinitrotoluene in a separate pocket. When TNT is detonated, it drives one mass of  $^{235}\text{U}$  into the other. A supercritical mass of the fissionable material is obtained. As a result of the instantaneous chain reaction, the bomb explodes with the release of tremendous heat energy. **Temperature developed in an atomic bomb is believed to be 10 million  $^{\circ}\text{C}$  (temperature of the sun).** Besides many radionuclei and heat, deadly gamma rays are released.



■ **Figure 4.19**  
A design used in atomic bombs to bring together two subcritical masses of  $^{235}\text{U}$ .

These play havoc with life and environment. If the bomb explodes near the ground, it raises tons of dust into the air. The radioactive material adhering to dust known as **fall out**. It spreads over wide areas and is a lingering source of radioactive hazard for long periods.

#### LITTLE BOY AND FAT MAN



#### ■ The First Atomic Bombs

*Little Boy* was the first nuclear weapon used in warfare. It exploded approximately 1,800 feet over Hiroshima, Japan, on the morning of August 6, 1945, with a force equal to 13,000 tons of TNT. Immediate deaths were between 70,000 to 130,000.

*Fat Man* was the second nuclear weapon used in warfare. Dropped on Nagasaki, Japan, on August 9, 1945, *Fat Man* devastated more than two square miles of the city and caused approximately 45,000 immediate deaths.

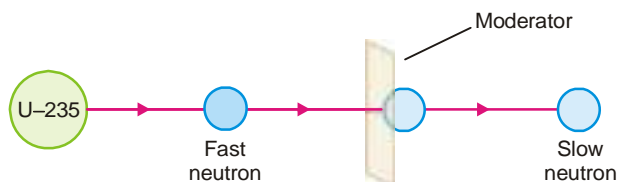
While *Little Boy* was a uranium gun-type device, *Fat Man* was a more complicated and powerful plutonium implosion weapon that exploded with a force equal to 20 kilotons of TNT.



## NUCLEAR REACTOR

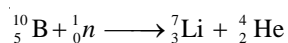
It has been possible to control fission of U-235 so that energy is released slowly at a usable rate. **Controlled fission is carried out in a specially designed plant called a nuclear power reactor or simply nuclear reactor.** The chief components of a nuclear reactor are :

- (1) **U-235 fuel rods** which constitute the 'fuel core'. The fission of U-235 produces heat energy and neutrons that start the chain reaction.
- (2) **Moderator** which slows down or moderates the neutrons. The most commonly used moderator is ordinary water. Graphite rods are sometimes used. Neutrons slow down by losing energy due to collisions with atoms/molecules of the moderator.



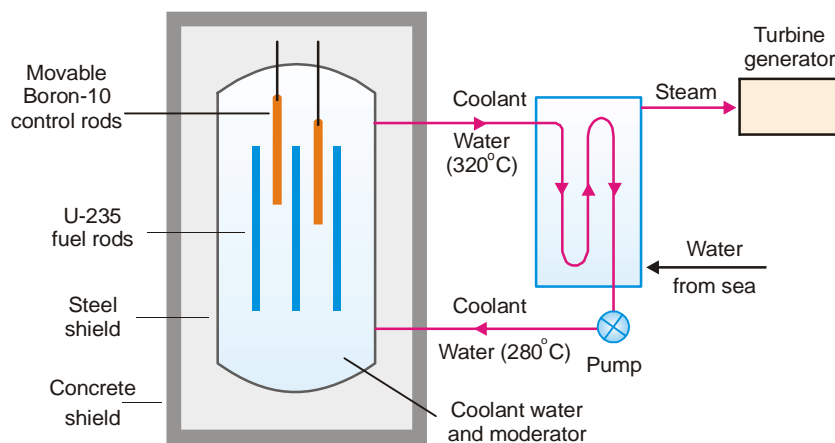
■ **Figure 4.20**  
Moderator slows down a fast neutron.

- (3) **Control rods** which control the rate of fission of U-235. These are made of boron-10 or cadmium, that absorbs some of the slowed neutrons.



Thus the chain reaction is prevented from going too fast.

- (4) **Coolant** which cools the fuel core by removing heat produced by fission. Water used in the reactor serves both as moderator and coolant. Heavy water ( $\text{D}_2\text{O}$ ) is even more efficient than light water.
- (5) **Concrete shield** which protects the operating personnel and environments from destruction in case of leakage of radiation.



■ **Figure 4.21**  
A light-water reactor producing electricity.

### Light-water Nuclear power plant

Most commercial power plants today are 'light-water reactors'. In this type of reactor, U-235 fuel rods are submerged in water. Here, water acts as coolant and moderator. The control rods of boron-10 are inserted or removed automatically from spaces in between the fuel rods.

The heat emitted by fission of U-235 in the fuel core is absorbed by the coolant. The heated coolant (water at 300°C) then goes to the *exchanger*. Here the coolant transfers heat to sea water which is converted into steam. The steam then turns the turbines, generating electricity. **A reactor once started can continue to function and supply power for generations.**

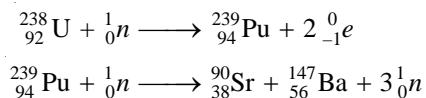
About 15 per cent of consumable electricity in U.S.A. today is provided by light water reactors. India's first nuclear plant went into operation in 1960 at Tarapur near Mumbai. Another plant has been set up at Narora in Uttar Pradesh. While such nuclear power plants will be a boon for our country, they could pose a serious danger to environments. In May 1986, the leakage of radioactive material from the Chernobyl nuclear plant in USSR played havoc with life and property around.

**Disposal of reactor waste poses another hazard.** The products of fission *e.g.*, Ba-139 and Kr-92, are themselves radioactive. They emit dangerous radiation for several hundred years. The waste is packed in concrete barrels which are buried deep in the earth or dumped in the sea. But the fear is that any leakage and corrosion of the storage vessels may eventually contaminate the water supplies.

#### Breeder Reactor

We have seen that uranium-235 is used as a reactor fuel for producing electricity. But our limited supplies of uranium-235 are predicted to last only for another fifty years. However, nonfissionable uranium-238 is about 100 times more plentiful in nature. This is used as a source of energy in the so-called breeder reactors which can supply energy to the world for 5,000 years or more.

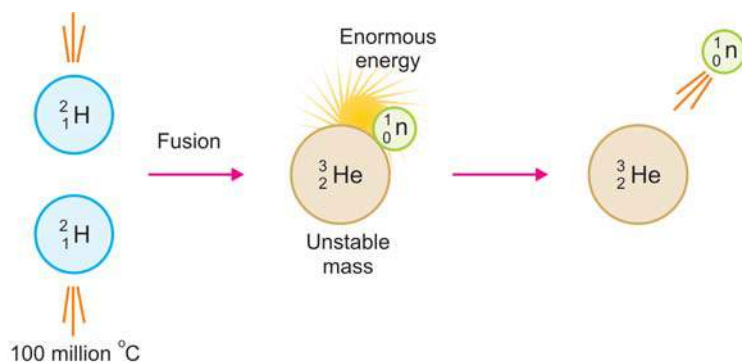
Here the uranium-235 core is covered with a layer or 'blanket' of uranium-238. The neutrons released by the core are absorbed by the blanket of uranium-238. This is then converted to fissionable plutonium-239. It undergoes a chain reaction, producing more neutrons and energy.



The above reaction sequence produces three neutrons and consumes only two. The excess neutron goes to convert more uranium to plutonium-239. **Thus the reactor produces or 'breeds' its own fuel and hence its name.** Several breeder reactors are now functioning in Europe. However, there is opposition to these reactors because the plutonium so obtained can be used in the dreaded H-bomb.

#### NUCLEAR FUSION PROCESS

This process is opposite of nuclear fission. Nuclear fusion may be defined as : **the process in which two light-weight nuclei combine or fuse to form a single heavier nucleus.**



■ **Figure 4.22**

**Illustration of fusion of two deuterium ( ${}^2_1\text{H}$ ) nuclei to form a single nucleus of helium ( ${}^3_2\text{He}$ ) with the release of a neutron and enormous energy.**

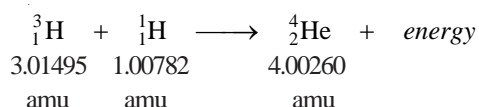


For example, two nuclei of deuterium ( ${}^2_1\text{H}$ ) undergo nuclear fusion to yield a heavier nucleus of helium-3. This fusion reaction takes place at a temperature of about 100 million  $^{\circ}\text{C}$ . The above fusion reaction may be stated in the form of an equation as :



Since fusion reactions occur at extremely high temperatures, these are also called **thermonuclear reactions**.

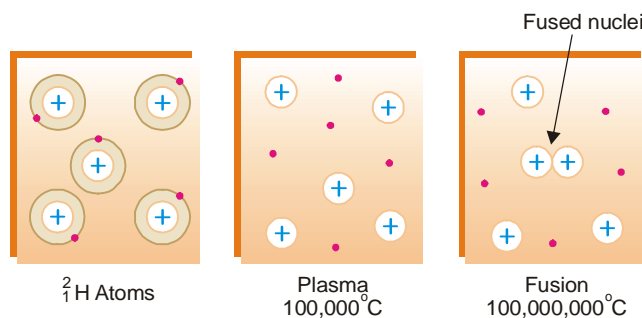
**In a fusion reaction, the mass of the reacting nuclei is greater than that of the nucleus formed.** The differential mass is manifested in the great amount of energy released in the reaction. For example,



The total mass of the reactants is 4.02277 amu which is 0.02017 amu greater than the mass of the product. The mass that is lost is converted into a lot of energy. A pair of reacting nuclei induces fusion of another pair of nuclei. In this way fantastic amounts of energy are generated. This is the basis of the H-bomb or **Hydrogen bomb**.

#### How Fusion occurs?

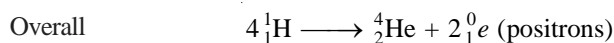
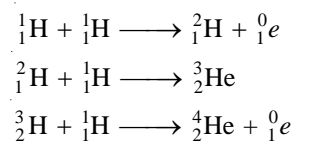
Let us explain the mechanism of fusion by taking the example of the fusion of deuterium ( ${}^2_1\text{H}$ ) cited above. At extremely high temperatures, 100 million  $^{\circ}\text{C}$  or more, atoms do not exist as such. At these temperatures, deuterium atoms are completely stripped of orbital electrons. Thus results a system containing positive nuclei and electrons, called **plasma**. In this state, the high kinetic energy of the nuclei can overcome electrostatic repulsions between them. The nuclei collide with such great force that they merge or fuse to form larger nuclei. (Fig. 4.23)



■ **Figure 4.23**  
Mechanism of fusion of  ${}^2_1\text{H}$ .

#### SOLAR ENERGY

The energy released by the sun results from a series of nuclear fusion reactions. The overall reaction consists of the fusion of four hydrogen nuclei (protons) to form helium nucleus. One mechanism suggested for the process is:

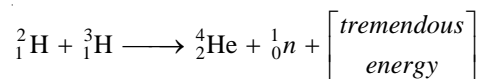


The fusion reactions in the sun take place at exceedingly high temperatures—greater than 40 million °C. Every second the sun loses  $4.3 \times 10^9$  kg (4, 20,000 tons) of mass by the fusion reactions. This mass is converted to energy. But the total mass of the sun is so great that its loss of mass is imperceptible. It is hoped that the sun will continue to pour energy on the earth for billions of years.



### HYDROGEN BOMB OR H-BOMB

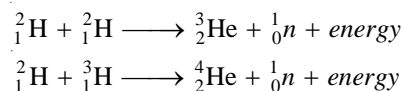
This deadly device makes use of the nuclear fusion of the isotopes of hydrogen. It consists of a small plutonium fission bomb with a container of isotopes of hydrogen. While the exact reaction used is a strictly guarded military secret, a fusion reaction between H-2 and H-3 may be the possible source of the tremendous energy released.



The 'fusion bomb' produces the high temperature required for nuclear fusion and triggers the H-bomb. The explosion of such a bomb is much more powerful than that of a fission bomb or atomic bomb. Fortunately, the H-bombs have been tested and not used in actual warfare. If they are ever used, it may mean the end of civilisation on earth.

### FUSION AS A SOURCE OF ENERGY IN 21st CENTURY

Almost likely that the world's energy source in the twenty-first century will be a fusion reactor. As indicated by the trends of research, it will be based on the reactions as:



A fusion reactor thus developed will be any time superior to a fission reactor for generating electricity.

1. The fusion fuel, deuterium ( ${}_1^2\text{H}$ ), can be obtained in abundance from heavy water present in sea water. The supplies of U-235 needed for a fission reactor are limited.
2. A fusion reaction produces considerably greater energy per gram of fuel than a fission reaction.
3. The products of fusion ( ${}_2^3\text{He}$ ,  ${}_2^4\text{He}$ ) are not radioactive. Thus, there will be no problem of waste disposal.

So far, it has not been possible to set up a fusion reactor. The chief difficulty is that the reactant nuclei must be heated to very high temperatures. A mixture of deuterium and tritium nuclei, for example, requires 30 million °C before they can fuse. So far no substance is known which can make a container that could withstand such high temperatures. However, scientists are making efforts to effect fusion at a lower temperature with the help of laser beams.

### EXAMINATION QUESTIONS

1. Define or explain the following terms :

- |                             |                            |
|-----------------------------|----------------------------|
| (a) Radioactivity           | (b) Radioactive substances |
| (c) Radioactive Decay       | (d) Half life period       |
| (e) Radioactive equilibrium | (f) Group displacement law |

- (g) Nuclear reactions (h) Nuclear fission reactions  
 (i) Nuclear fusion reactions (j) Mass defect  
 (k) Binding energy
2. (a) What is group displacement law of radioactivity? How does it throw light on the idea of radioactive isotopes?  
 (b) Radium has atomic number 226 and a half-life of 1600 years. Calculate the number of disintegrations produced per second from one gram of radium.  
**Answer.** (b)  $3.652 \times 10^{10}$  atoms
3. (a) Derive an expression for the decay constant for disintegration of a radioactive substance.  
 (b) The activity of a radioactive isotope reduces by 25% after 100 minutes. Calculate the decay constant and half-life period.  
**Answer.** (b)  $0.01386 \text{ min}^{-1}$ ; 50.007 min
4. Explain what you understand by the term Radioactive Dating. How the age of earth was determined?
5. How many  $\alpha$  and  $\beta$  particles will be emitted by an element  ${}^{218}_{84}\text{A}$  in changing to a stable isotope of  ${}^{206}_{82}\text{B}$ ?  
**Answer.** 3  $\alpha$ ; 4  $\beta$
6. (a) State and explain the group displacement law in radioactivity.  
 (b) Calculate the decay constant for  ${}^{108}\text{Ag}$ , if its half-life is 2.31 minutes.  
**Answer.** (b)  $0.3 \text{ minute}^{-1}$
7. (a) Write the significance of half-life period of a radioactive substance.  
 (b) The half-life of  ${}^{232}\text{Th}$  is  $1.4 \times 10^{10}$  years. Calculate its disintegration constant.  
**Answer.** (b)  $4.95 \times 10^{-11} \text{ year}^{-1}$
8. Complete the following nuclear reactions :  
 (i)  ${}^{15}_8\text{O} \rightarrow {}^0_{-1}\text{e} + ?$  (ii)  ${}^{238}_{92}\text{U} \rightarrow {}^{234}_{90}\text{Th} + ?$   
 (iii)  ${}^{236}_{92}\text{U} \rightarrow {}^{143}_{56}\text{Ba} + ? + {}^1_0\text{n}$  (iv)  ${}^{238}_{92}\text{U} + ? \rightarrow {}^{239}_{92}\text{U}$   
**Answer.** (i)  ${}^{15}_7\text{N}$ ; (ii)  ${}^4_2\text{He}$ ; (iii)  ${}^{92}_{36}\text{Kr}$ ; (iv)  ${}^1_0\text{n}$
9. (a) Define radioactivity. Discuss the liquid drop model for nuclear structure.  
 (b) Complete the following nuclear reactions :  
 (i)  ${}^{12}_6\text{C} + {}^2_1\text{M} \rightarrow ? + {}^4_2\text{He}$  (ii)  ${}^{27}_{13}\text{Al} + {}^1_0\text{n} \rightarrow {}^{24}_{11}\text{Na} + ?$   
 (iii)  ${}^{14}_7\text{N} + ? \rightarrow {}^{11}_6\text{C} + {}^4_2\text{He}$   
**Answer.** (b) (i)  ${}^{10}_5\text{B}$ ; (ii)  ${}^4_2\text{He}$ ; (iii)  ${}^1_1\text{H}$
10. (a) Explain what is meant by radioactive equilibrium. How does it differ from chemical equilibrium?  
 (b) A radioactive substance having half-life of 3.8 days, emitted initially  $7 \times 10^4$  alpha particles per second. In what time will its rate of emission reduces to  $2 \times 10^4$  alpha particles per second?  
**Answer.** (b) 6.870 days
11. Show how C-14 is used for radio-carbon dating. A freshly cut piece of plant gives 20.4 counts per minute per gram. A piece of wood antique gives 12.18 counts per minute per gram. What is the age in years of antique? It is assumed that the radioactivity is entirely due to C-14. The half life period of C-14 is 5760 years.  
**Answer.** 4287.43 years
12. Calculate the rate of disintegration of one gram of  ${}^{232}\text{Th}$  if its decay constant is  $1.58 \times 10^{-18} \text{ sec}^{-1}$ .  
**Answer.**  $4.0998 \times 10^3 \text{ dps}$
13. (a) Calculate the mass defect, binding energy and the binding energy per nucleon of  ${}^4_2\text{He}$  which has an isotopic mass of 4.0026 amu ( ${}^1_1\text{H} = 1.0081 \text{ amu}$ ;  ${}^1_0\text{H} = 1.0089 \text{ amu}$ )  
 (b) With the help of a diagram discuss the salient features of a nuclear power reactor.

(c) Explain the principle, construction and working of cyclotron.

**Answer.** (a) 0.0314 amu; 29.249 Mev; 7.312275 Mev

14. Write short notes on

(a) Radioactive series

(b) Nuclear Fission

(c) Tracer Technique

(d) Geiger-Muller counter

15. (a) What do you mean by Tracer Technique? Write different applications of Tracer-Techniques.

(b) The mass number and atomic number of a radioactive element Actinium are 227 and 89 respectively. Calculate the number of  $\alpha$  and  $\beta$  particles emitted, if the mass number and atomic number of the new element Lead are 207 and 82 respectively.

**Answer.** (b) 5  $\alpha$  and 3  $\beta$

16.  ${}_{84}\text{Po}^{210}$  decays with alpha to  ${}_{82}\text{Pb}^{206}$  with a half life of 138.4 days. If 1.0 g of  $\text{Po}^{210}$  is placed in a sealed tube, how much helium will accumulate in 69.2 days? Express the answer in  $\text{cm}^3$  at STP.

**Answer.** 31.248  $\text{cm}^3$

17. (a) What is group displacement law in radioactivity? What is binding energy and how it is related to Mass number of the nucleus?

(b) A radioactive isotope has half-life of 20 days. What is the amount of isotope left over after 40 days if the initial amount is 5 g?

**Answer.** (b) 1.25 g

18. (a) Define radioactive constant and derive the relation between decay constant and number of particles left at time  $t$ .

(b) Half-life period of thorium is 24.5 minutes. How much thorium would be left after 30 minutes if the initial amount of thorium is one gram?

**Answer.** (b) 0.429 g

19. Calculate the number of  $\lambda$  and  $\beta$  particles emitted in the conversion of Thorium,  ${}_{90}\text{Th}^{232}$ , to Lead,  ${}_{82}\text{Pb}^{206}$ .

**Answer.** 6  $\alpha$  and 4  $\beta$

(Delhi BSc, 2000)

20. A sample of  $\text{U}^{238}$  (half life =  $4.5 \times 10^9$  years) ore is found to contain 23.8 g of  $\text{U}^{238}$  and 20.6 g of  $\text{Pb}^{206}$ . Calculate the age of the ore.

**Answer.**  $4.50 \times 10^9$  years

(Bundelkhand BSc, 2000)

21. The half life of Cobalt-60 is 5.26 years. Calculate the percentage activity after eight years.

**Answer.** 34.87%

(Nagpur BSc, 2000)

22. Calculate the time required for a radioactive sample to lose one-third of the atoms of its parent Isotope. The half life is 33 min.

**Answer.** 19.31 min

(Bhopal BSc, 2000)

23. An old wooden article shows 2.0 counts per minute per gram. A fresh sample of wood shows 15.2 counts per minute per gram. Calculate the age of the wooden article. ( $t_{1/2}$  of  $\text{C}^{14}$  = 5760 years)

**Answer.** 1686.6 years

(Gulbarga BSc, 2000)

24. The mass number and atomic number of a radioactive element Actinium are 227 and 89 respectively. Calculate the number of  $\alpha$  and  $\beta$  particles emitted if the mass number and atomic number of the new element Lead are 207 and 82 respectively.

**Answer.** 5  $\alpha$  and 3  $\beta$

(Calicut BSc, 2000)

25. Calculate the age of the tooth in which  $\text{C}^{14}$  activity is 20% of the activity found at the present time ( $t_{1/2}$  for  $\text{C}^{14}$  = 5580 years)

**Answer.** 12961.4 years

(Delhi BSc, 2001)

26. A piece of wood recovered in excavation has 30% as much  ${}_{6}\text{C}^{14}$  as a fresh wood today. Calculate the age of excavated piece assuming half life period of  ${}_{6}\text{C}^{14}$  as 5700 years.

**Answer.** 9908 years

(Madurai BSc, 2001)

27. The activity of a radioactive sample falls to 85% of the initial value in four years. What is the half life of the sample? Calculate the time by which activity will fall by 85%.  
**Answer.** 17.05 years; 46.735 years (Mysore BSc, 2001)
28. Write short notes on  
(a) Carbon dating (b) Nuclear reaction (Lucknow BSc, 2001)
29. Derive an expression for the disintegration constant of a radioactive element and show that decay of the element is exponential. (Lucknow BSc, 2001)
30. (a) Write a note on Nuclear Fission and Nuclear Fusion.  
(b) What are nuclear reactions? How are they classified? Explain with examples.  
(HS Gaur BSc, 2002)
31. (a) What is Group displacement law? Explain with examples.  
(b) How does discovery of isotopes help in explaining fractional atomic weight of elements? Mention some applications of radioactivity. (Arunachal BSc, 2002)
32. Write notes on  
(a) Nuclear Fusion (b) Nuclear Binding Energy  
(c) Tracers and their applications (Mizoram BSc, 2002)
33. Define binding energy of a nucleus. Explain with the help of binding energy curve, the stability of the nuclei. (Nagpur BSc, 2002)
34. (a) Give the details of the application of  $C^{14}$  isotope in carbon dating. How the age of an old wooden sample is determined?  
(b) The rate of disintegration of an old wooden sample was found 25% as compared to a fresh identical sample. Find out the age of the old sample. (Half life of  $C^{14} = 5760$  years)  
**Answer.** (b) 11525 years (Bundelkhand BSc, 2002)
35. (a) How many  $\alpha$  and  $\beta$ -particles are emitted for the transformation  
$${}_{90}^{232}\text{Th} \rightarrow {}_{82}^{208}\text{Pb}$$
  
(b) What is a nuclide? Mention different kinds of nuclides with suitable examples.  
(c) What is a nuclear reactor? Describe its main parts briefly. (Sambalpur BSc, 2003)
36. (a) Calculate the (i) Mass Defect (ii) Binding energy per nucleon of  ${}_6C^{12}$ . (Given  $C^{12} = 12.0038$  amu;  $H^1 = 1.0081$  amu;  $n^1 = 1.0089$  amu)  
(b) What is artificial radioactivity? Give two examples. (Goa BSc, 2003)
37. (a) Discuss the stability of nucleus under the following heads:  
(i) binding energy per nucleon  
(ii) neutron-proton ratio and odd-even rule  
(b) What is the difference between Fission and Fusion reactions?  
(c) How do two isotopes of elements differ in the number of nucleons. (Aligarh BSc, 2003)
38. (a) What is group displacement law of radioactivity? How does it throw light on the idea of radioactive isotopes?  
(b) The half-life of radioactive isotope is 47.2 sec. Calculate  $N/N_0$  left after one hour.  
**Answer.** (b)  $1.12 \times 10^{-23}$  (Arunachal BSc, 2003)
39. Give the postulates of theory of radioactive emissions. (Arunachal BSc, 2003)
40. Write short notes on :  
(a) Mass defect (b) Packing fraction  
(c) Nuclear Fission (d) Half life period (Arunachal BSc, 2003)
41. (a) What is group displacement law of radioactivity? How does it throw light on the idea of radioactive isotopes?  
(b) Explain :  
(i) Radioactive dating (ii) Average life  
(iii) Radioactive equilibria (Arunachal BSc, 2003)

42. Explain :  
 (a) Why  ${}_{13}\text{Al}^{27}$  is stable while  ${}_{13}\text{Al}^{24}$  is radioactive in nature?  
 (b) The atomic weight of lithium is variable while in other members of group I it is fixed.  
*(Delhi BSc, 2003)*
43. Calculate the half life and average life period of a radioactive element if its decay constant is  $7.37 \times 10^{-3} \text{ hour}^{-1}$ .  
**Answer.** 0.0261 sec; 0.0376 sec *(Sambalpur BSc, 2003)*
44.  ${}_{92}\text{U}^{238}$  undergoes a series of changes emitting  $\alpha$  and  $\beta$  particles and finally  ${}_{82}\text{Pb}^{206}$  is formed. Calculate the number of  $\alpha$  and  $\beta$  particles which must have been ejected during the series.  
**Answer.** 8  $\alpha$  and 6  $\beta$  *(Panjab BSc, 2004)*
45. Radioisotope  ${}_{15}\text{P}^{32}$  has a half life of 15 days. Calculate the time in which the radioactivity of its 1 mg quantity will fall to 10% of the initial value.  
**Answer.** 49.84 days *(Osmania BSc, 2004)*
46. An old wooden article shows 2.0 counts per minute per gram. A fresh sample of wood shows 15.2 counts per minute per gram. Calculate the age of the wooden article ( $t_{1/2}$  of  $\text{C}^{14} = 5460$  years)  
**Answer.** 16861 years *(Banaras BSc, 2004)*
47. Explain the difference between Nuclear Fission and Nuclear Fusion. *(Agra BSc, 2005)*
48. (a) Write briefly on nuclear fission and nuclear fusion.  
 (b) A radioactive isotope has half-life period of 20 days. What is the amount of the isotope left over after 40 days if the initial concentration is 5 g?  
**Answer.** (b) 1.25 g *(Delhi BSc, 2005)*
49. (a) Discuss the stability of nucleus in terms of neutron-proton ratio and binding energy.  
 (b) 2 g of radioactive element degraded to 0.5 g in 60 hours. In what time will it be reduced to 10% of its original amount?  
**Answer.** (b) 4.56 hours *(Mysore BSc, 2006)*

### MULTIPLE CHOICE QUESTIONS

1. Which is the correct symbol for an alpha particle?  
 (a)  ${}^4_2\text{He}$  (b)  ${}^1_0\text{n}$   
 (c)  ${}^0_{-1}\text{e}$  (d)  ${}^1_1\text{p}$   
**Answer.** (a)
2. Of the following, which is the most damaging when ingested?  
 (a) beta emitters (b) alpha emitters  
 (c) gamma emitters (d) all of these  
**Answer.** (b)
3. An alpha particle is  
 (a) an electron (b) one neutron and one proton  
 (c) two protons and two neutrons (d) an X-ray emission  
**Answer.** (c)
4. By what type of decay process might  ${}^{214}\text{Pb}$  convert to  ${}^{214}\text{Bi}$ ?  
 (a) beta decay (b) alpha decay  
 (c) gamma decay (d) electron capture  
**Answer.** (a)

5. The curie is a measure of the
- (a) lethal threshold for radiation exposure
  - (b) number of alpha particles emitted by exactly 1 g of a radioactive substance
  - (c) number of disintegrations per second of a radioactive substance
  - (d) total energy absorbed by an object exposed to a radioactive source

**Answer.** (c)

6. Of the following processes, which one does not change the atomic number?
- (a) gamma emission
  - (b) alpha emission
  - (c) positron emission
  - (d) beta emission

**Answer.** (a)

7. Which of these nuclides is most likely to be radioactive?

- (a)  $^{39}_{19}\text{K}$
- (b)  $^{27}_{13}\text{Al}$
- (c)  $^{127}_{53}\text{I}$
- (d)  $^{243}_{95}\text{Am}$

**Answer.** (d)

8. The beta particle consists of

- (a) high-energy rays
- (b) 1 neutron
- (c) 2 neutrons and 2 protons
- (d) 1 electron

**Answer.** (d)

9. Lab coats and gloves provide shielding from

- (a) alpha radiation
- (b) alpha and beta radiation
- (c) alpha, beta, and gamma radiation
- (d) gamma radiation

**Answer.** (b)

10. When an alpha particle is released in nuclear decay, the mass number of the nucleus undergoing decay

- (a) stays the same
- (b) increases by 4
- (c) decreases by 4
- (d) decreases by 2

**Answer.** (c)

11. Which one of the following processes could not result in the conversion of strontium to rubidium?

- (a) gamma emission
- (b) proton emission
- (c) electron capture
- (d) positron emission

**Answer.** (a)

12. Alpha decay of  $^{226}\text{Ra}$  will yield which of the following nuclides?

- (a)  $^{222}\text{Rn}$
- (b)  $^{230}\text{Th}$
- (c)  $^{222}\text{Fr}$
- (d)  $^{222}\text{Th}$

**Answer.** (a)

13. In a Geiger-Müller counter, one “count” is directly due to

- (a) a secondary electron
- (b) a primary electron
- (c) many electrons and ions
- (d) a beta particle

**Answer.** (c)

14.  $^8_3\text{Li}$  decays to  $^8_4\text{Be}$ . What type of decay is this?

- (a) positron emission
- (b) beta
- (c)  $\gamma$ -ray
- (d) alpha

**Answer.** (b)

15. \_\_\_\_\_ rays consist of He nuclei, while \_\_\_\_\_ rays are electromagnetic radiation.

- (a) beta, alpha (b) alpha, beta  
(c) alpha, gamma (d) gamma, beta

**Answer.** (c)

16. Which type of radioactive decay results in an increase in atomic number?

- (a) positron emission (b) alpha emission  
(c) gamma emission (d) beta emission

**Answer.** (d)

17. When  $^{249}\text{Cf}$  is bombarded with  $^{10}\text{B}$ ,  $^{257}\text{Lr}$  is formed. What other particle(s) is/are produced?

- (a)  $^0_{-1}\text{e}$  (b)  $^1_0\text{n}$   
(c)  $^0_1\text{e}$  (d)  $^1_1\text{p}$

**Answer.** (b)

18. Which combination of the number of protons and the number of neutrons is most common among the naturally occurring non-radioactive nuclides?

- (a) even protons; even neutrons (b) odd protons; even neutrons  
(c) even protons; odd neutrons (d) odd protons; odd neutrons

**Answer.** (a)

19. Which form of radioactivity is most penetrating?

- (a) alpha particles (b) beta particles  
(c) neutrons (d) gamma rays

**Answer.** (d)

20. In electron capture,

- (a) gamma rays are emitted (b) a neutron is formed  
(c) a positron is formed (d) an alpha particle is emitted

**Answer.** (b)

21. The spontaneous transformation of one nuclide into others occurs only if

- (a) the process is endothermic  
(b) the process results in a neutron/proton ratio of 1:0 in the products  
(c) sufficient energy can be absorbed from the surroundings to drive the process  
(d) the combined mass of the products is less than the mass of the original nuclide

**Answer.** (d)

22. What particle is released when Ga-75 decays to Ge-75?

- (a) neutron (b) beta  
(c) gamma (d) alpha

**Answer.** (b)

23. What particle is missing in the following bombardment reaction?  $\text{Al}^{27} + ? = ^1_0\text{n} + \text{P}^{30}$

- (a) neutron (b) beta  
(c) proton (d) alpha

**Answer.** (d)

24. What would be the immediate product of neutron absorption by  $^{107}\text{Ag}$ ?

- (a)  $^{107}\text{Pd}$  (b)  $^{109}\text{In}$   
(c)  $^{108}\text{Cd}$  (d)  $^{108}\text{Ag}$

**Answer.** (d)

25. When a nuclide undergoes beta decay,

- (a) the atomic number remains unchanged and the mass number increases by one  
(b) the mass number remains unchanged and the atomic number decreases by one



- (c) the mass number remains unchanged and the atomic number increases by one  
(d) the atomic number remains unchanged and the mass number decreases by one

**Answer.** (c)

26. The half-life of  $^{32}\text{P}$ , which is used as a label on red blood cells to determine blood volume, is 14.3 days. How many days are required for the activity of a sample of  $^{32}\text{P}$  to drop to 5.00% of its initial level?
- (a) 26.8 days (b) 42.8 days  
(c) 61.8 days (d) 0.209 days

**Answer.** (c)

27. The half-life of Sulfur-35 is 88 days. If 8.0 g of Sulfur-35 exists on day one, what fraction will remain after 264 days?
- (a) 0.5 g (b) 4.0 g  
(c) 0 g (d) 1.0 g

**Answer.** (d)

28. When Xenon-123 emits a gamma ray, what is the product?

- (a)  $^{123}_{54}\text{Xe}$  (b)  $^{123}_{53}\text{I}$   
(c)  $^{119}_{52}\text{Te}$  (d)  $^{123}_{55}\text{Cs}$

**Answer.** (a)

29. The cloth shroud from around a mummy is found to have a  $^{14}\text{C}$  activity of 8.9 disintegrations per minute per gram of carbon as compared with living organisms that undergo 15.2 disintegrations per minute per gram of carbon. From the half-life for  $^{14}\text{C}$  decay,  $5.73 \times 10^3$  yr, calculate the age of the shroud.
- (a)  $9.3 \times 10^{-5}$  yr (b)  $4.4 \times 10^3$  yr  
(c)  $6.5 \times 10^{-5}$  yr (d)  $1.92 \times 10^3$  yr

**Answer.** (b)

30.  $^{198}\text{Au}$  has a half-life of 2.70 days. Assuming you start with a 10.0 mg sample of  $^{198}\text{Au}$ , how much will remain after 10.0 days?
- (a) 0.246 mg (b) 130 mg  
(c) 0.768 mg (d) 9.44 mg

**Answer.** (c)

31. The half-life for the beta decay of  $^{233}\text{Pa}$  is 27.4 days. How many days must pass to reduce a 5.00 g sample of  $^{233}\text{Pa}$  to 0.625 g?
- (a) 109.6 days (b) 54.8 days  
(c) 82.2 days (d) 27.4 days

**Answer.** (c)

32. The half-life of tritium (Hydrogen-3) is 12.3 yr. If 48.0 mg of tritium is released from a nuclear power plant during the course of an accident, what mass of this nuclide will remain after 49.2 yr?
- (a) 6.0 mg (b) 3.0 mg  
(c) 24.0 mg (d) 12.0 mg

**Answer.** (b)

33. How old is a fossil bone whose  $^{14}\text{C}$  content is 15.0 percent that of living bone?
- (a) 25400 yr (b) 15600 yr  
(c) 380 yr (d) 6810 yr

**Answer.** (b)

34. Iodine-131 has a half-life of 8 days. How many grams of I-131 in a 4.0 g sample remain after 24 days?
- (a) 2.0 g (b) 1.0 g

- (c) 0.50 g (d) 0.0 g

**Answer.** (c)

35. The half-life of  $^{45}\text{Ca}$  is 165 days. After 1.0 year, what percentage of the original sample of  $^{45}\text{Ca}$  remains?

- (a) 10.9 percent (b) 99.6 percent  
(c) 2.16 percent (d) 21.6 percent

**Answer.** (d)

36. What particle is produced when Phosphorus-29 decays to silicon-29?

- (a) positron (b) beta  
(c) gamma (d) alpha

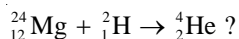
**Answer.** (a)

37. The bombardment of which isotope by a neutron produces  $^{198}\text{Au}$  and proton?

- (a)  $^{199}_{81}\text{Tl}$  (b)  $^{197}_{80}\text{Hg}$   
(c)  $^{198}_{80}\text{Hg}$  (d)  $^{197}_{78}\text{Pt}$

**Answer.** (c)

38. Complete and balance the following nuclear equation by selecting the missing particle.



- (a)  $^{22}_{13}\text{Al}$  (b)  $^{22}_{11}\text{Na}$   
(c)  $^{26}_{13}\text{Al}$  (d)  $^{20}_{10}\text{Ne}$

**Answer.** (b)

39. What is the product of beta decay of  $^{159}_{64}\text{Gd}$ ?

- (a)  $^{159}_{65}\text{Tb}$  (b)  $^{159}_{63}\text{Eu}$   
(c)  $^{159}_{64}\text{Gd}$  (d)  $^{155}_{62}\text{Sm}$

**Answer.** (a)

40. Which of the following is the nuclear equation for bismuth-214 undergoing beta decay?

- (a)  $^{214}_{83}\text{Bi} \rightarrow ^0_1\text{e} + ^{214}_{84}\text{Po}$  (b)  $^{214}_{83}\text{Bi} \rightarrow ^0_1\text{e} + ^{214}_{82}\text{Pb}$   
(c)  $^{214}_{83}\text{Bi} \rightarrow ^0_1\text{e} + ^{214}_{84}\text{Po}$  (d)  $^{214}_{83}\text{Bi} \rightarrow ^0_1\text{e} + ^{214}_{82}\text{Pb}$

**Answer.** (a)

41. When Zinc-73 decays by beta emission, the product of decay is

- (a)  $^{74}_{29}\text{Cu}$  (b)  $^{73}_{29}\text{Cu}$   
(c)  $^{73}_{31}\text{Ga}$  (d)  $^{72}_{30}\text{Zn}$

**Answer.** (c)

42. When  $^{27}_{13}\text{Al}$  is bombarded by an alpha particle, the products are a proton and another nuclide. What is the other nuclide?

- (a)  $^{31}_{16}\text{S}$  (b)  $^{27}_{12}\text{Mg}$   
(c)  $^{30}_{14}\text{Si}$  (d)  $^{31}_{13}\text{Al}$

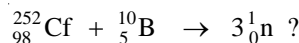
**Answer.** (c)

43. The nucleus of an atom of radioactive I-131 used in thyroid imaging contains  
(a) 53 protons and 75 neutrons (b) 53 protons and 78 neutrons  
(c) 53 electrons and 78 neutrons (d) 53 neutrons and 78 protons  
**Answer.** (b)
44. What is the product of the alpha decay of Rn-220?  
(a) Po-216 (b) Rn-220  
(c) Rn-216 (d) Ra-224  
**Answer.** (a)
45. A short-time exposure to a radiation dose of 100 to 200 rems will result in what health effect?  
(a) death of half the exposed population within 30 days after exposure  
(b) there are no detectable clinical effects  
(c) nausea and marked decrease in white blood cells  
(d) a slight temporary decrease in white blood cell counts  
**Answer.** (c)
46. When a nuclide undergoes electron capture,  
(a) the mass number remains unchanged and the atomic number decreases by one  
(b) the atomic number remains unchanged and the mass number increases by one  
(c) the mass number remains unchanged the atomic number increases by one  
(d) the atomic number remains unchanged and the mass number decreases by one  
**Answer.** (a)
47. What nuclide forms as a result of the positron emission of  $^{12}_{7}\text{N}$ ?  
(a)  $^{13}_{6}\text{C}$  (b)  $^{11}_{7}\text{N}$   
(c)  $^{12}_{6}\text{C}$  (d)  $^{12}_{8}\text{O}$   
**Answer.** (c)
48.  $^{232}_{90}\text{Th}$  undergoes a series of alpha and beta emissions resulting in the final stable product,  $^{208}_{82}\text{Pb}$ . How many alpha and beta emissions occur in this series?  
(a) 4 alpha, 6 beta (b) 8 alpha, 6 beta  
(c) 12 alpha, 4 beta (d) 6 alpha, 4 beta  
**Answer.** (d)
49. What is the product formed from  $^{207}\text{Po}$  by positron emission?  
(a)  $^{203}\text{Pb}$  (b)  $^{207}\text{Bi}$   
(c)  $^{208}\text{At}$  (d)  $^{206}\text{Bi}$   
**Answer.** (b)
50. Which of the following statements about the biological effects of radiation is false?  
(a) Radiation can cause leukemia  
(b) Ionizing radiation is more dangerous than non-ionising radiation  
(c) Radon is absorbed through the skin  
(d) Radon is harmful because it decays to polonium  
**Answer.** (c)
51. When a  $^{235}\text{U}$  nucleus is struck by a thermal neutron, fission occurs with the release of neutrons. If the fission fragments are  $^{90}\text{Sr}$  and  $^{144}\text{Xe}$ , how many neutrons are released?  
(a) 3 (b) 4  
(c) 1 (d) 2  
**Answer.** (d)
52. What other product occurs when Ac-222 releases an alpha particle?

- (a) Db-218 (b) Ra-218  
(c) Fr-218 (d) Ac-218

**Answer.** (c)

53. Complete and balance the following nuclear equation by selecting the missing particle:



- (a)  ${}_{103}^{261}\text{Lr}$  (b)  ${}_{103}^{259}\text{Lr}$   
(c)  ${}_{93}^{241}\text{Np}$  (d)  ${}_{93}^{239}\text{Np}$

**Answer.** (b)

54. The nuclide Iron-56 has a mass defect of 0.52840 amu. What is the binding energy per nucleon in Mev?

- (a) 8.81 Mev (b)  $9.79 \times 10^{-17}$  Mev  
(c)  $8.81 \times 10^3$  Mev (d) 494 Mev

**Answer.** (a)

55. The mass defect for  ${}^{12}\text{C}$  is 0.0990, meaning that six protons and six neutrons have a mass that is 0.0990 amu more than the mass of the  ${}^{12}\text{C}$  nucleus. What is the binding energy of the  ${}^{12}\text{C}$  nucleus per nucleon in kJ?

- (a)  $1.23 \times 10^{-15}$  kJ (b)  $1.23 \times 120^{-12}$  kJ  
(c)  $4.11 \times 10^{-24}$  kJ (d)  $1.48 \times 10^{-14}$  kJ

**Answer.** (a)

56. The combustion of one mol of graphite releases 393.5 kJ of energy. What is the mass change that accompanies the loss of this energy?

- (a)  $4.372 \times 10^{-12}$  kg (b)  $3.542 \times 10^{22}$  kg  
(c)  $1.312 \times 10^{-3}$  kg (d) none of these

**Answer.** (a)

57. Plutonium-239 is produced from  ${}^{238}\text{U}$  in breeder reactor. This might involve

- (a) neutron absorption followed by emission of two positrons  
(b) alpha particle absorption followed by emission of three protons  
(c) proton absorption followed by positron emission  
(d) neutron absorption followed by emission of two beta particles

**Answer.** (d)

58. What particle is produced when Plutonium-242 decays to Uranium-238?

- (a) gamma (b) alpha  
(c) positron (d) beta

**Answer.** (b)

59. In a living organism, the  ${}^{14}\text{C}$  concentration

- (a) remains approximately constant  
(b) continually increases  
(c) continually decreases  
(d) varies unpredictably during the lifetime of the organism

**Answer.** (a)

60. Which equation represents alpha emission from  ${}^{196}\text{Po}$ ?

- (a)  ${}_{84}^{196}\text{Po} \rightarrow {}_{82}^{192}\text{Pb} + {}_2^4\text{He}$  (b)  ${}_{84}^{196}\text{Po} + {}_2^4\text{He} \rightarrow {}_{82}^{192}\text{Pb}$   
(c)  ${}_{84}^{196}\text{Po} \rightarrow {}_{86}^{200}\text{Rn} + {}_2^4\text{He}$  (d)  ${}_{84}^{196}\text{Po} + {}_2^4\text{He} \rightarrow {}_{86}^{200}\text{Rn}$

**Answer.** (a)

61. Hydrogen burning  
(a) is the reaction sequence that is proposed to take place in normal stars  
(b) requires very large kinetic energy in the colliding nuclei in order to overcome huge activation energies associated with electrostatic repulsion  
(c) results in the conversion of hydrogen nuclei to helium nuclei  
(d) all of above  
**Answer.** (d)
62. The energy produced by the Sun involves which of the following nuclei?  
(a) Pu (b) Li  
(c) U (d) H  
**Answer.** (d)
63. From a kinetics standpoint, the radioactive decay of radium is a \_\_\_\_\_-order process, and the primary reactions in nuclear fusion in the sun are \_\_\_\_\_-order processes.  
(a) first, first (b) first, third  
(d) first, second (d) second, second  
**Answer.** (c)
64. Radiation is used in cancer treatment to  
(a) destroy cancer causing substances (b) relieve pain  
(c) obtain images of the diseased region (d) destroy cancer cells  
**Answer.** (d)
65. The amount of fissionable material large enough to maintain the chain reaction in nuclear fission is called the  
(a) moderator (b) critical mass  
(c) mass defect (d) nuclear binding energy  
**Answer.** (b)
66. Food irradiation is used to  
(a) precook food (b) kill insects  
(c) kill micro-organisms (d) increase nutrient value  
**Answer.** (c)
67. The radioisotopes used for diagnosis in nuclear medicine  
(a) have short half lives (b) travel rapidly through tissue  
(c) are usually gamma emitters (d) all of these  
**Answer.** (d)
68. The purpose of a moderator in a nuclear reactor is  
(a) to prevent corrosion of the core components  
(b) to slow the fission neutrons so that they can be captured to sustain the chain reaction  
(c) to cool the core to prevent melt down  
(d) to dissolve the fission products for disposal  
**Answer.** (b)
69. Fission reactions can be run continuously to generate electric power commercially because  
(a) the reactors generate more readily fissionable fuel than they consume  
(b) more neutrons are produced in the fission reactions than are consumed  
(c) supercritical neutrons split into protons and electrons  
(d) the different isotopes of uranium interconvert under reaction conditions to form the necessary Uranium-235  
**Answer.** (b)

70. A cyclotron is used to get

- (a) energetic ions
- (b) positrons
- (c) magnetic fields
- (d) neutrons

**Answer.** (a)

71. The reaction of  $\text{H}^3$  and  $\text{H}^2$  to form  $\text{He}^4$  and a neutron is an example of

- (a) a fission reaction
- (b) a fusion reaction
- (c) both fission and fusion reactions
- (d) neither a fission or fusion reaction

**Answer.** (b)

72. Nuclear fusion

- (a) takes place in the sun
- (b) uses large nuclides
- (c) is used in atomic bombs
- (d) takes place in a fusion reactor

**Answer.** (a)

73. Usually, the largest dose of radiation that a person gets is from

- (a) cigarettes
- (b) natural background radiation
- (c) medical X-rays
- (d) nuclear power plants

**Answer.** (b)

74. A moderator in a nuclear reactor serves to

- (a) accelerate neutrons
- (b) diminish the nuclear binding energy
- (c) provide fissionable isotopes
- (d) slow neutrons

**Answer.** (d)

## 5

Chemical Bonding  
– Lewis Theory

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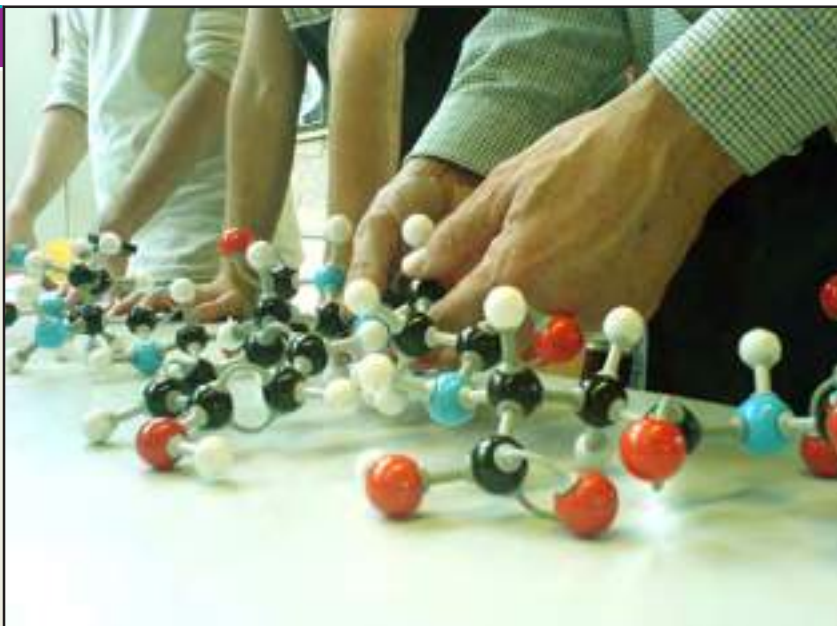
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## TERMS AND DEFINITIONS

## Chemical Bond

Molecules of chemical substances are made of two or more atoms joined together by some force, acting between them. This force which results from the interaction between the various atoms that go to form a stable molecule, is referred to as a *Chemical Bond*.

**A chemical bond is defined as a force that acts between two or more atoms to hold them together as a stable molecule.**

As we will study later, there are three different types of bonds recognised by chemists :

- (1) Ionic or Electrovalent bond
- (2) Covalent bond
- (3) Coordinate covalent bond

There is a fourth type of bond, namely, the metallic bond which we will consider later in this chapter.

## Definition of Valence

The term valence (or valency) is often used to state the potential or capacity of an element to combine with other elements.

At one time, it was useful to define valence of an element as : the number of hydrogen atoms or twice the number of oxygen atoms with which that element could combine in a binary compound (containing two different elements only).

In hydrogen chloride (HCl), one atom of chlorine is combined with one atom of hydrogen and the valence of chlorine is 1. In magnesium oxide (MgO), since one atom of magnesium holds one atom of oxygen, the valence of magnesium is 2.

By the above definition, we would assign a valence of 2 to sulphur in  $\text{H}_2\text{S}$ , but 4 to sulphur in  $\text{SO}_2$ . Some elements have fractional valence in certain compounds, while there are elements that have variable valencies. The concept of valence as a mere number could not explain these facts. This concept, in fact, was very confusing and has lost all value.

As already stated, there are three different type of bonds that are known to join atoms in molecules. Although no precise definition of valence is possible, we can say that : **Valence is the number of bonds formed by an atom in a molecule.**

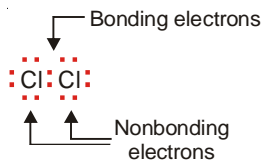
### Valence Electrons

The electrons in the outer energy level of an atom are the ones that can take part in chemical bonding. These electrons are, therefore, referred to as the valence electrons.

The electronic configuration of Na is 2, 8, 1 and that of Cl is 2, 8, 7. Thus sodium has one valence electron and chlorine 7. It is important to remember that **for an A group element of the periodic table (H, O, K, F, Al etc.) the group number is equal to the number of valence electrons.**

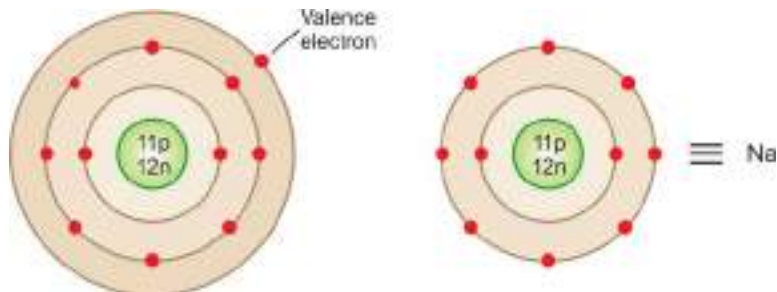
### Bonding and Non-bonding Electrons

**The valence electrons actually involved in bond formation are called bonding electrons.** The remaining valence electrons still available for bond formation are referred to as non-bonding electrons. Thus :



### Lewis Symbols of Elements

A Lewis symbol of an element consists of an element's symbol and surrounding dots to represent the number of valence electrons. In this notation, **the symbol of an element represents the nucleus plus the inner normally filled levels (or shells) of the atom.** For illustration, the symbol Na stands for the nucleus of sodium atom plus 2, 8 electrons in the inner two levels.



■ Figure 5.1

The Lewis symbol Na represents the nucleus and the electrons arranged in the inner two levels as 2, 8, minus the valence electrons.



To represent a Lewis symbol for an element, write down the symbol of the element and surround the symbol with a number of dots (or crosses) equal to the number of valence electrons. The position of dots around the symbol is not really of any significance. The bonding electrons are shown at appropriate positions, while the rest of the electrons are generally given in pairs. The Lewis symbols for hydrogen, chlorine, oxygen and sulphur may be written as :



The structural formulae of compounds built by union of Lewis symbols for the component atoms, are referred to as **Electron-dot formulas, or Electron-dot structures or Lewis structures**. For this purpose, the valence electrons actually involved in bond formation may be shown by crosses (x) or dots (•) for the sake of distinction.

Now we will proceed to discuss the common types of chemical bonds in the light of the electronic theory of valence.

### ELECTRONIC THEORY OF VALENCE

As Bohr put forward his model of the atom so electronic configuration of elements was known. G.N. Lewis and W. Kossel, working independently, used this knowledge to explain 'why atoms joined to form molecules'. They visualised that noble gas atoms had a stable electronic configuration, while atoms of all other elements has unstable or incomplete electronic configuration. In 1916, they gave the **electronic theory of valence**. It states that : **In chemical bond formation, atoms interact by losing, gaining, or sharing of electrons so as to acquire a stable noble gas configuration**. Each noble gas, except helium, has a valence shell of eight electrons (Table 5.1).

TABLE 5.1. ELECTRONIC CONFIGURATION OF NOBLE GASES

Noble gas	At. No.	Electrons in principal shells
He	2	2
Ne	10	2, 8
Ar	18	2, 8, 8
Kr	36	2, 8, 18, 8
Xe	54	2, 8, 18, 18, 8
Rn	86	2, 8, 18, 32, 18, 8

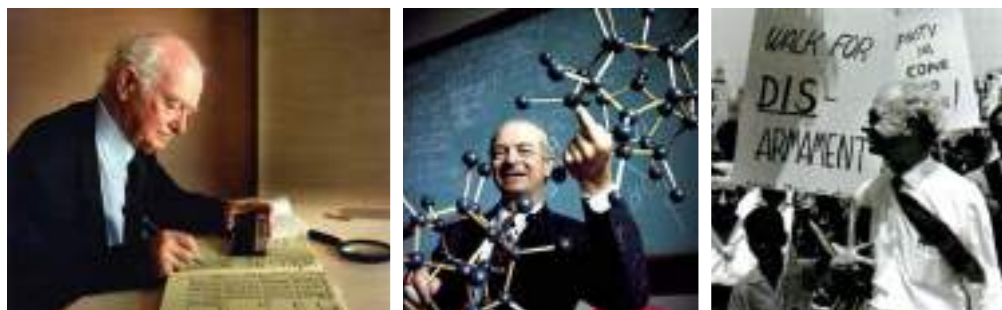
While atoms of noble gases possess a stable outer shell of eight electrons or **octet**, atoms of most other elements have incomplete octets. They may have less than 8 electrons or in excess. Thus, the electronic theory or valence could well be named as the **Octet theory of Valence**. It may be stated as : **Atoms interact by electron-transfer or electron-sharing, so as to achieve the stable outer shell of eight electrons**.

The tendency for atoms to have eight electrons in the outer shell is also known as the **Octet Rule** or the **Rule of Eight**. Since helium has two electrons in the outer shell, for hydrogen and lithium, having one and three (2, 1) electrons respectively, it is the **Rule of two** which will apply. We will see later in this chapter that there are quite a few exceptions to the rule of eight in covalent compounds.

### IONIC BOND

This type of bond is established by transfer of an electron from one atom to another. Let us consider a general case when an atom *A* has one electron in the valence shell and another atom *B* has seven electrons. *A* has one electron in excess and *B* has one electron short than the stable octet. Therefore, *A* transfers an electron to *B* and in this transaction both the atoms acquire a stable electron-octet. The resulting positive ion (cation) and negative ion (anion) are held together by electrostatic attraction.

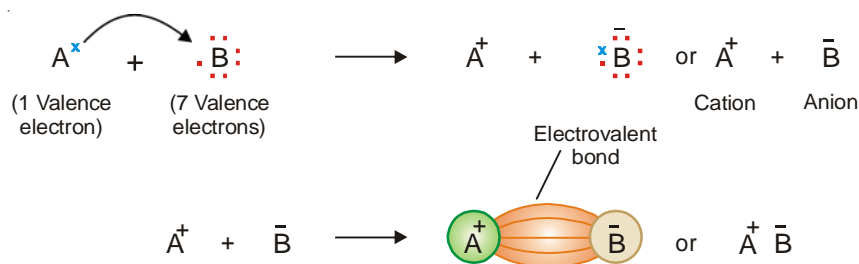
## LINUS CARL PAULING



Linus Pauling won the Nobel Prize in Chemistry in 1954 for his work on chemical bonding. He also received the Nobel Peace Prize in 1962 for his campaign against nuclear testing.

Linus Carl Pauling (February 28, 1901 – August 19, 1994) was an American quantum chemist and biochemist. Pauling is widely regarded as the premier chemist of the twentieth century. He pioneered the application of quantum mechanics to chemistry and in 1954 was awarded the Nobel Prize in chemistry for his work describing the nature of chemical bonds. He also made important contributions to crystal and protein structure determination, and was one of the founders of molecular biology. He came near to discovering the “double helix,” the ultrastructure of DNA, when Watson and Crick made the discovery in 1953.

Pauling received the Nobel Peace Prize in 1962 for his campaign against above-ground nuclear testing, and is the only person to win two unshared Nobel prizes. Later in life, he became an advocate for greatly increased consumption of vitamin C and other nutrients. He generalized his ideas to define orthomolecular medicine, which is still regarded as unorthodox by conventional medicine. He popularized his concepts, analyses, research and insights in several successful but controversial books centered around vitamin C and orthomolecular medicine.



**The electrostatic attraction between the cation (+) and anion (–) produced by electron-transfer constitutes an Ionic or Electrovalent bond.**

The compounds containing such a bond are referred to as **Ionic or Electrovalent Compounds**.

### CONDITIONS FOR FORMATION OF IONIC BOND

The conditions favourable for the formation of an ionic bond are :

#### (1) Number of valence electrons

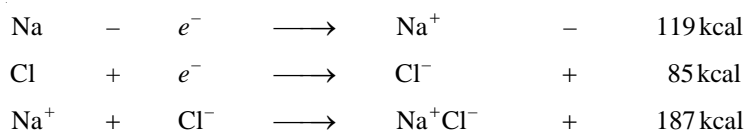
The atom A should possess 1, 2 or 3 valence electrons, while the atom B should have 5, 6 or 7 valence electrons. The elements of group IA, IIA and IIIA satisfy this condition for atom A and those of groups VA, VIA, and VIIA satisfy this condition for atom B.

**(2) Net lowering of Energy**

To form a stable ionic compound, there must be a net lowering of the energy. In other words energy must be released as a result of the electron transfer and formation of ionic compound by the following steps :

- The removal of electron from atom  $A$  ( $A - e^- \rightarrow A^+$ ) requires input of energy, which is the ionization energy (IE). It should be low.
- The addition of an electron to  $B$  ( $B + e^- \rightarrow B^-$ ) releases energy, which is the electron affinity of  $B$  (EA). It should be high.
- The electrostatic attraction between  $A^+$  and  $B^-$  in the solid compound releases energy, which is the electrical energy. It should also be high.

If the energy released in steps (b) and (c) is greater than the energy consumed in step (a), the overall process of electron transfer and formation of ionic compound results in a net release of energy. Therefore, ionisation of  $A$  will occur and the ionic bond will be formed. For example, in case of formation of sodium chloride (NaCl), we have



The net energy released is  $187 + 85 - 119 = 153$  kcal. Since the overall process results in a lowering of energy, the ionic bond between Na and Cl will be formed.

**(3) Electronegativity difference of A and B**

From the line of argument used in (2), we can say that atoms  $A$  and  $B$  if they have greatly different electronegativities, only then they will form an ionic bond. In fact, a difference of 2 or more is necessary for the formation of an ionic bond between atoms  $A$  and  $B$ . Thus Na has electronegativity 0.9, while Cl has 3.0. Since the difference is  $(3.0 - 0.9) = 2.1$ , Na and Cl will form an ionic bond.

**FACTORS GOVERNING THE FORMATION OF IONIC BOND****(1) Ionisation Energy**

The ionisation energy of the metal atom which loses electron(s) should be low so that the formation of +vely charged ion is easier. *Lower the ionisation energy greater will be the tendency of the metal atom of change into cation and hence greater will be the ease of formation of ionic bond.* That is why alkali metals and alkaline earth metals form ionic bonds easily. Out of these two, alkali metals form ionic bonds easily as compared to alkaline earth metals. *In a group the ionisation energy decreases as we move down the group and therefore, the tendency to form ionic bond increases in a group downward.* Due to this reason Cs is the most electropositive atom among the alkali metals.

**(2) Electron Affinity**

The atom which accepts the electron and changes into anion should have high electron affinity. *Higher the electron affinity more is the energy released and stable will be the anion formed.* The elements of group VI A and VII A have, in general, higher electron affinity and have high tendency to form ionic bonds. Out of these two, *the elements of group VII A (halogens) are more prone to the formation of ionic bond than the elements of group VI A.* In moving down a group the electron affinity decreases and, therefore, the tendency to form ionic bond also decreases.

**(3) Lattice Energy**

After the formation of cations and anions separately, they combine to form ionic compound.



In this process, energy is released. It is called Lattice Energy. It may be defined as “the amount of energy released when one mole of an ionic compound is formed from its cations and anions.”

Greater the lattice energy, greater the strength of ionic bond. The value of lattice energy depends upon the following two factors :

(a) **Size of the ions**

In order to have the greater force of attraction between the cations and anions their size should be small as the force of attraction is inversely proportional to the square of the distance between them.

(b) **Charge on Ions**

Greater the charge on ions greater will be the force of attraction between them and, therefore, greater will be the strength of the ionic bond.

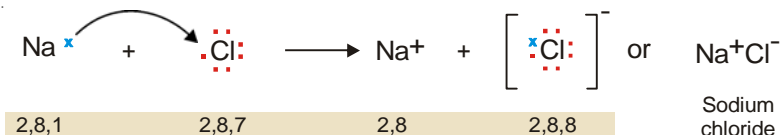
Necessary for the formation of an ionic bond between atoms A and B. Thus Na has electronegativity 0.9, while Cl has 3.0. Since the difference is  $(3.0 - 0.9) = 2.1$ , Na and Cl will form an ionic bond.

### SOME EXAMPLES OF IONIC COMPOUNDS

Here we will discuss the formation of **Lewis formula** or **Electron dot formula** of some binary ionic compounds, for illustration.

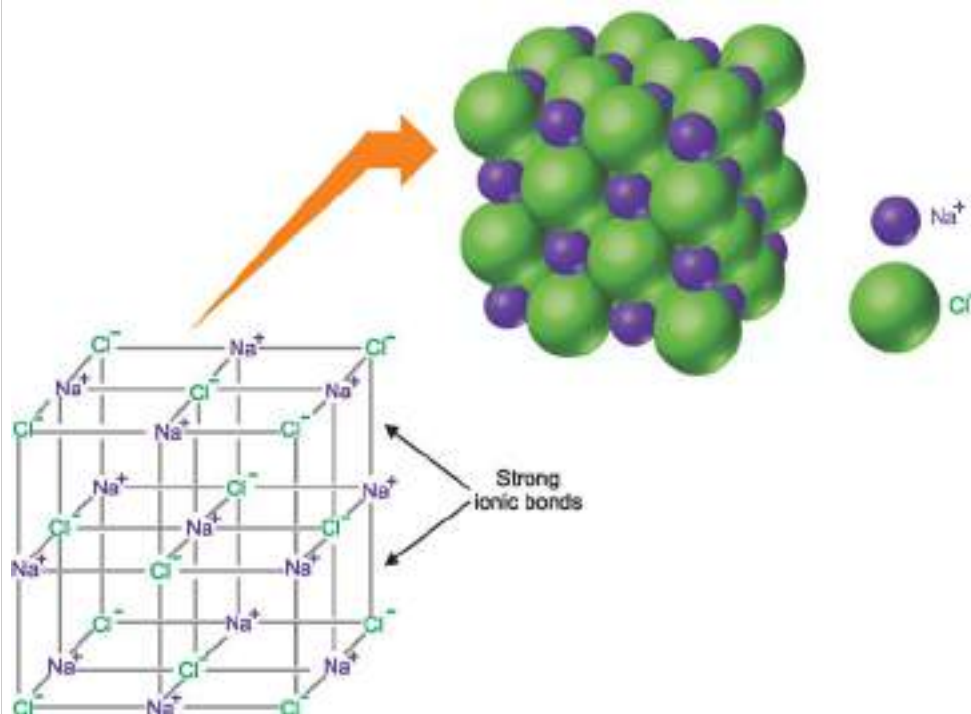
#### Sodium Chloride, NaCl

A simple sodium chloride molecule is formed from an atom of sodium (Na) and one atom of chlorine (Cl). Na (2, 8, 1) has one valence electron, while Cl (2, 8, 7) has seven. Na transfers its valence electron to Cl, and both achieve stable electron octet. Thus Na gives  $Na^+$  and Cl gives  $Cl^-$  ion, and the two are joined by an ionic bond.



**Ionic Compounds Exist as Crystals.** The (+) and (−) ions attract each other with electrostatic force that extends in all directions. This means that ions will be bonded to a number of oppositely charged ions around them. Therefore in solid state, single ionic molecules do not exist as such. Rather many (+) and (−) ions are arranged systematically in an alternating cation-anion pattern called the crystal lattice. The crystal lattice of NaCl is shown in Fig. 5.2. It will be noticed that here a large number of  $Na^+$  and  $Cl^-$  ions are arranged in an orderly fashion so as to form a cubic crystal. Each  $Na^+$  ion is surrounded by 6  $Cl^-$  ions and each  $Cl^-$  ion is surrounded by 6  $Na^+$  ions. This makes a network of  $Na^+$  and  $Cl^-$  ions which are tightly held together by electrostatic forces between them.

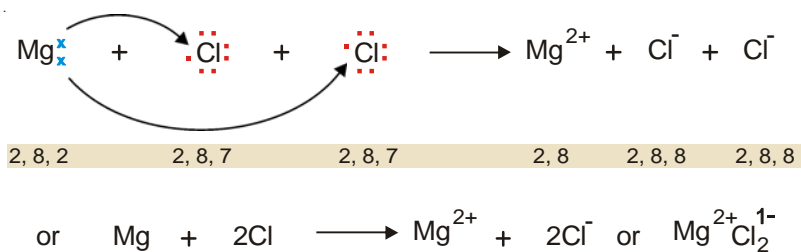
Although discrete molecules  $\text{Na}^+\text{Cl}^-$  do not exist in the solid form of ionic compounds, independent molecules do exist in the vapour form of such compounds.



**Figure 5.2**  
Ionic crystal of Sodium Chloride.

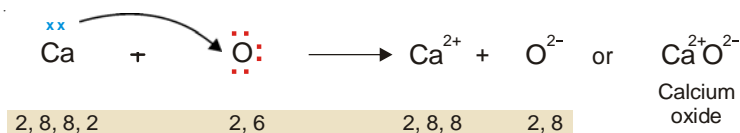
### Magnesium Chloride, $\text{Mg}^{2+}\text{Cl}_2^{1-}$ ( $\text{MgCl}_2$ )

Magnesium (Mg) has two valence electrons, while chlorine (Cl) has seven. The magnesium atom transfers its two electrons, one to each chlorine atom, and thus all the three atoms achieve the stable octet. In this way Mg atom gives  $\text{Mg}^{2+}$  ion and the two Cl atoms give  $2\text{Cl}^{1-}$ , forming  $\text{Mg}^{2+}\text{Cl}_2^{1-}$  (or  $\text{MgCl}_2$ ).



### Calcium Oxide, $\text{Ca}^{2+}\text{O}^{2-}$ ( $\text{CaO}$ )

Calcium (Ca) has two valence electrons, while oxygen (O) has six. Calcium atom transfers its two valence electrons to the same oxygen atom. Thus both Ca and O achieve the stable electron-octet, forming  $\text{Ca}^{2+}$  and  $\text{O}^{2-}$  ions. Thus is obtained the molecule of calcium oxide,  $\text{Ca}^{2+}\text{O}^{2-}$ .

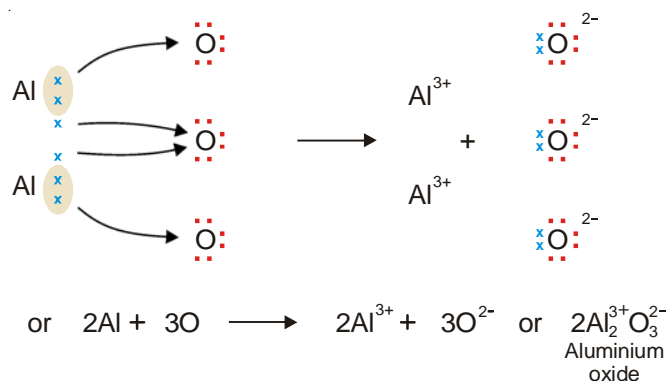


### Aluminium Oxide, $\text{Al}_2^{3+}\text{O}_3^{2-}$ ( $\text{Al}_2\text{O}_3$ )

Here the aluminium atom (Al) has three electrons in the valence shell (2, 8, 3), while oxygen has six (2, 6). Two atoms of aluminium transfer their six electrons to three oxygen atoms. Thus are the electron-octets of the two Al atoms and three O atoms achieved. The two Al atoms deprived of three electrons each, give  $2\text{Al}^{3+}$  ions, while the three O atoms having gained two electrons each give  $3\text{O}^{2-}$  ions. In this way, we get  $\text{Al}_2^{3+}\text{O}_3^{2-}$  or  $\text{Al}_2\text{O}_3$ .

### CHARACTERISTICS OF IONIC COMPOUNDS

The ionic compounds are made of (+) and (−) ions held by electrostatic forces in a crystal lattice. Each ion is surrounded by the opposite ions in alternate positions in a definite order in all directions. This explains the common properties of ionic compounds.



#### (1) Solids at Room Temperature

On account of strong electrostatic forces between the opposite ions, these ions are locked in their allotted positions in the crystal lattice. Since they lack the freedom of movement characteristic of the liquid state, they are solids at room temperature.

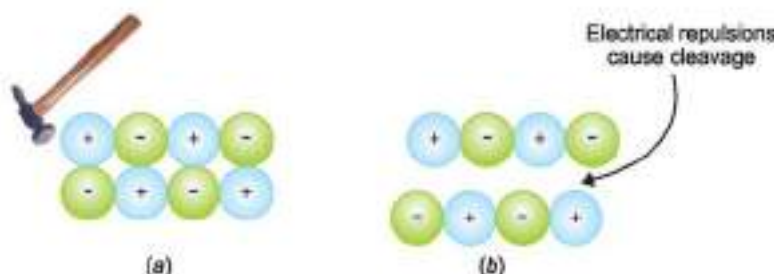
#### (2) High Melting Points

Ionic compounds have high melting points (or boiling points). Since the (+) and (−) ions are tightly held in their positions in the lattice, only at high temperature do the ions acquire sufficient kinetic energy to overcome their attractive forces and attain the freedom of movement as in a liquid. Thus ionic compounds need heating to high temperatures before melting.

#### (3) Hard and brittle

The crystals of ionic substances are hard and brittle. Their hardness is due to the strong electrostatic forces which hold each ion in its allotted position.

These crystals are made of layers of (+) and (−) ions in alternate positions so that the opposite ions in the various parallel layers lie over each other. When external force is applied to a layer of ions (Fig. 5.3), with respect to the next, even a slight shift brings the like ions in front of each other. The (+) and (−) ions in the two layers thus repel each other and fall apart. The crystal cleaves here.

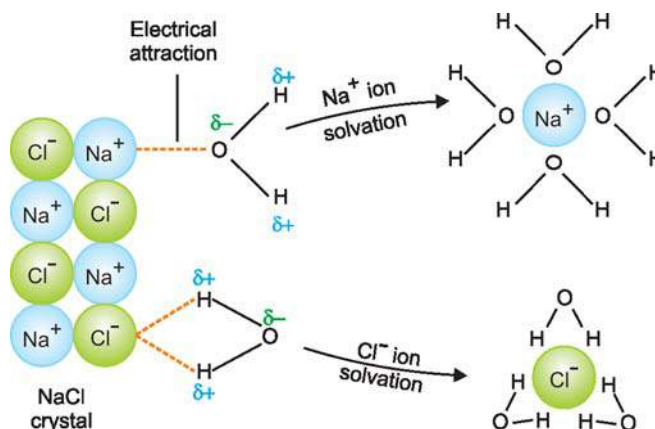


■ **Figure 5.3**

(a) Two layers of (+) and (–) ions in a crystal. (b) When force is applied to one layer it slips over the other so that similar ions come above one another and electrical repulsions between them cause cleavage of the crystal.

#### (4) Soluble in water

When a crystal of an ionic substance is placed in water, the polar water molecules detach the (+) and (–) ions from the crystal lattice by their electrostatic pull. These ions then get surrounded by water molecules and can lead an independent existence and are thus dissolved in water. By the same reason, non-polar solvents like benzene ( $C_6H_6$ ) and hexane ( $C_6H_{14}$ ) will not dissolve ionic compounds.



■ **Figure 5.4**

**Solvation of NaCl in water.**

#### (5) Conductors of electricity

Solid ionic compounds are poor conductors of electricity because the ions are fixed rigidly in their positions. In the molten state and in water solutions, ions are rendered free to move about. Thus molten ionic compounds or their aqueous solutions conduct a current when placed in an electrolytic cell.

#### (6) Do not exhibit isomerism

The ionic bond involving electrostatic lines of force between opposite ions, is non-rigid and non-directional. The ionic compounds, therefore, are incapable of exhibiting stereoisomerism.

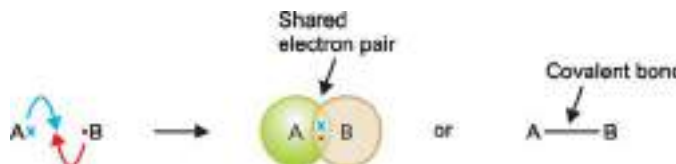
#### (7) Ionic reactions are fast

Ionic compounds give reactions between ions and these are very fast.



## COVALENT BOND

The electron transfer theory could not explain the bonding in molecules such as  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{Cl}_2$  etc., and in organic molecules, that had no ions. It was G.N. Lewis who suggested that two atoms could achieve stable 2 or 8 electrons in the outer shell by sharing electrons between them. Let us consider a general case where an atom  $A$  has one valence electron and another atom  $B$  has seven valence electrons. As they approach each other, each atom contributes one electron and the resulting electron pair fills the outer shell of both the atoms. Thus  $A$  acquires stable 2 electrons and  $B$ , 8 electrons in the outer shell.



The shared pair is indicated by a dash (—) between the two bonded atoms. A shared pair of electrons constitutes a **Covalent bond** or **Electron-pair bond**.

In fact, the positive nuclei of atoms  $A$  and  $B$  are pulled towards each other by the attraction of the shared electron pair. At the same time, the nuclei of two atoms also repel each other as do the two electrons. It is the net attractive force between the shared electrons and the nuclei that holds the atoms together. Thus an alternative definition of a covalent bond would be :

**The attractive force between atoms created by sharing of an electron-pair.**

The compounds containing a covalent bond are called **covalent compounds**.

## CONDITIONS FOR FORMATION OF COVALENT BOND

The conditions favourable for the formation of covalent bonds are :

### (1) Number of valence electrons

Each of the atoms  $A$  and  $B$  should have 5, 6 or 7 valence electrons so that both achieve the stable octet by sharing 3, 2 or 1 electron-pair.  $\text{H}$  has one electron in the valence shell and attains duplet. The non-metals of groups VA, VIA and VIIA respectively satisfy this condition.

### (2) Equal electronegativity

The atom  $A$  will not transfer electrons to  $B$  if both have equal electronegativity, and hence electron sharing will take place. This can be strictly possible only if both the atoms are of the same element.

### (3) Equal sharing of electrons

The atoms  $A$  and  $B$  should have equal (or nearly equal) electron affinity so that they attract the bonding electron pair equally. Thus equal sharing of electrons will form a nonpolar covalent bond. Of course, precisely equal sharing of electrons will not ordinarily occur except when atoms  $A$  and  $B$  are atoms of the same element, for no two elements have exactly the same electron affinity.

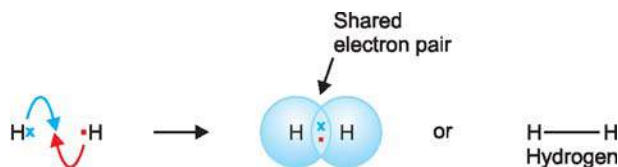
## SOME EXAMPLES OF COVALENT COMPOUNDS

The construction of Lewis structures of simple covalent compounds will be discussed.

### Hydrogen, $\text{H}_2$

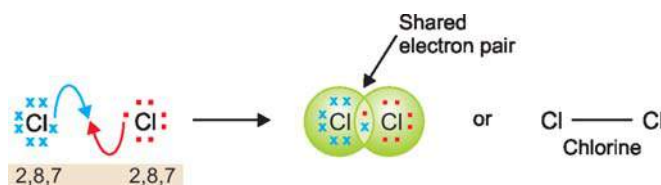
Hydrogen molecule is made of two  $\text{H}$  atoms, each having one valence electron. Each contributes an electron to the shared pair and both atoms acquire stable helium configuration. Thus stable  $\text{H}_2$  molecule results.





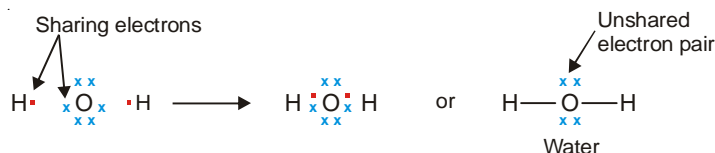
### Chlorine, $\text{Cl}_2$

Each Cl atom (2, 8, 7) has seven valence electrons. The two Cl atoms achieve a stable electron octet by sharing a pair of electrons.



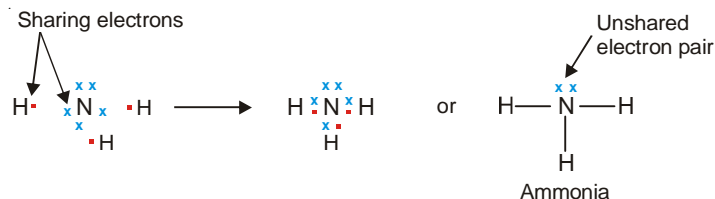
### Water, $\text{H}_2\text{O}$

Oxygen atom (2, 6) has six valence electrons and can achieve the stable octet by sharing two electrons, one with each H atom. Thus Lewis structure of water can be written as :



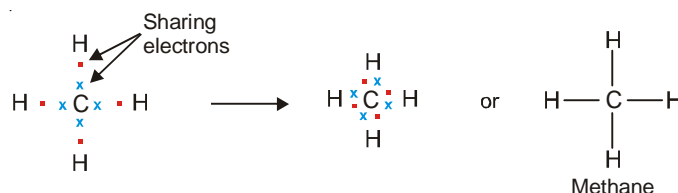
### Ammonia, $\text{NH}_3$

Nitrogen atom (2, 5) has five valence electrons and can achieve the octet by sharing three electrons, one each with three H atoms. This gives the following Lewis structure for ammonia :



### Methane, $\text{CH}_4$

Carbon atom (2, 4) has four electrons in the valence shell. It can achieve the stable octet by sharing these electrons with four H atoms, one with each H atom. Thus the Lewis structure of methane can be written as :

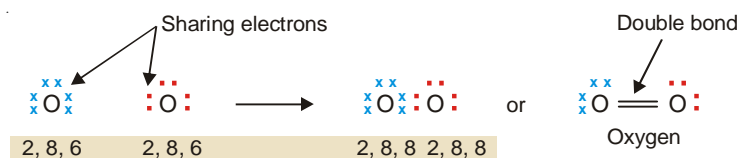


### EXAMPLES OF MULTIPLE COVALENT COMPOUNDS

In many molecules, we find that in order to satisfy the octet, it becomes necessary for two atoms to share two or three pairs of electrons between the same two atoms. The sharing of two pairs of electrons is known as a **Double bond** and the sharing of three pairs of electrons a **Triple bond**. Let us consider some examples of compounds containing these multiple covalent bonds in their molecules.

#### Oxygen, $O_2$

The conventional Lewis structure of oxygen is written by sharing of two pairs of electrons between two O atoms (2, 6). In this way both the O atoms achieve the octet.



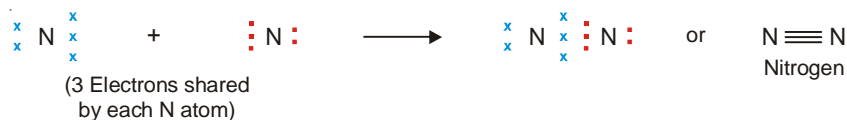
The above structure of oxygen implies that all the electrons in oxygen,  $O_2$ , are paired whereby the molecule should be diamagnetic. However, experiment shows that  $O_2$  is paramagnetic with two unpaired electrons. This could be explained by the structure.



Although writing Lewis structures work very well in explaining the bonding in most simple molecules, it should be kept in mind that it is simply the representation of a theory. In this case, the theory just doesn't work.

#### Nitrogen, $N_2$

The two atoms of nitrogen (2, 5), each having five electrons in the valence shell, achieve the octet by sharing three electron pairs between them.



#### Carbon Dioxide, $CO_2$

Carbon (2, 4) has four valence electrons. It shares two electrons with each O atom (having six valence electrons). Thus the C atom and both the O atoms achieve their octet.



### CHARACTERISTICS OF COVALENT COMPOUNDS

While the atoms in a covalent molecule are firmly held by the shared electron pair, the individual molecules are attracted to each other by weak van der Waals forces. Thus the molecules can be separated easily as not much energy is required to overcome the intermolecular attractions. This explains the general properties of covalent compounds.

#### (1) Gases, liquids or solids at room temperature

The covalent compounds are often gases, liquids or relatively soft solids under ordinary conditions. This is so because of the weak intermolecular forces between the molecules.

#### (2) Low melting points and boiling points

Covalent compounds have generally low melting points (or boiling points). The molecules are

held together in the solid crystal lattice by weak forces. On application of heat, the molecules are readily pulled out and these then acquire kinetic energy for free movement as in a liquid. For the same reason, the liquid molecules are easily obtained in the gaseous form which explains low boiling points of covalent liquids.

### (3) Neither hard nor brittle

While the ionic compounds are hard and brittle, covalent compounds are neither hard nor brittle. There are weak forces holding the molecules in the solid crystal lattice. A molecular layer in the crystal easily slips relative to other adjacent layers and there are no 'forces of repulsion' like those in ionic compounds. Thus the crystals are easily broken and there is no sharp cleavage between the layers on application of external force.

### (4) Soluble in organic solvents

In general, covalent compounds dissolve readily in nonpolar organic solvents (benzene, ether). The kinetic energy of the solvent molecules easily overcomes the weak intermolecular forces.

Covalent compounds are insoluble in water. Some of them (alcohols, amines) dissolve in water due to hydrogen-bonding.

### (5) Non-conductors of electricity

Since there are no (+) or (–) ions in covalent molecules, the covalent compounds in the molten or solution form are incapable of conducting electricity.

### (6) Exhibit Isomerism

Covalent bonds are rigid and directional, the atoms being held together by shared electron pair and not by electrical lines of force. This affords opportunity for various spatial arrangements and covalent compounds exhibit stereoisomerism.

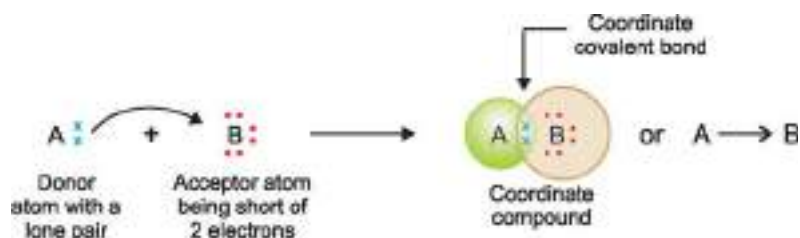
### (7) Molecular reactions

The covalent compounds give reactions where the molecule as a whole undergoes a change. Since there are no strong electrical forces to speed up the reaction between molecules, these reactions are slow.

## CO-ORDINATE COVALENT BOND

In a normal covalent bond, each of the two bonded atoms contributes one electron to make the shared pair. In some cases, a covalent bond is formed when both the electrons are supplied entirely by one atom. Such a bond is called **co-ordinate covalent** or **dative bond**. It may be defined as : **a covalent bond in which both electrons of the shared pair come from one of the two atoms (or ions)**. The compounds containing a coordinate bond are called **coordinate compounds**.

If an atom *A* has an unshared pair of electrons (**lone pair**) and another atom *B* is short of two electrons than the stable number, coordinate bond is formed. *A* donates the lone pair to *B* which accepts it. Thus both *A* and *B* achieve the stable 2 or 8 electrons, the lone pair being held in common.



The atom *A* which donates the lone pair is called the **donor**, while *B* which accepts it the **acceptor**. The bond thus established is indicated by an arrow pointing from *A* to *B*. Although the arrow head

indicates the origin of the electrons, once the coordinate bond is formed it is in no way different from an ordinary covalent bond.

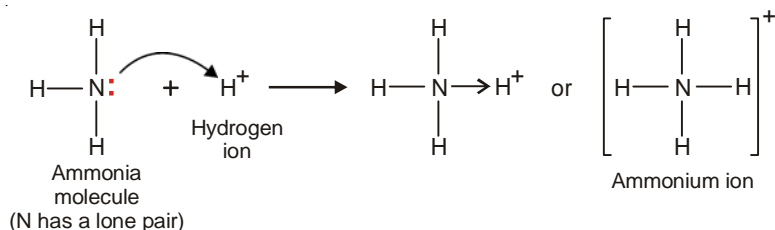
**The molecule or ion that contains the donor atom is called the ligand.**

### SOME EXAMPLES OF COORDINATE COMPOUNDS OR IONS

Lewis structures of some common molecules or ions containing a coordinate covalent bond are listed below.

#### Ammonium ion, $\text{NH}_4^+$

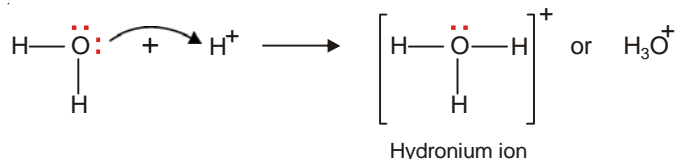
In ammonia molecule, the central N atom is linked to three H atoms and yet N has an unshared pair of electrons. The  $\text{H}^+$  ion furnished by an acid has no electron to contribute and can accept a pair of electrons loaned by N atom. Thus,  $\text{NH}_3$  donates its unshared electrons to  $\text{H}^+$  forming ammonium ion.



All the N–H bonds in  $\text{NH}_4^+$  are identical, once the coordinate bond  $\text{N} \rightarrow \text{H}^+$  is established.

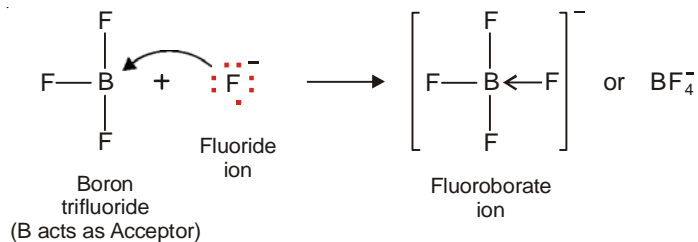
#### Hydronium ion, $\text{H}_3\text{O}^+$

The oxygen atom in water molecule is attached to two H atoms by two covalent bonds. There are still two unshared pairs of electrons with the O atom. The O atom donates one of these pairs of electrons to  $\text{H}^+$  ion and the hydronium ion is thus formed.



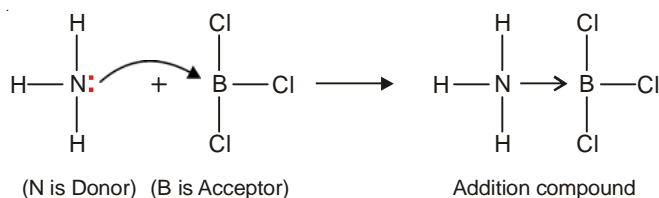
#### Fluoroborate ion, $\text{BF}_4^-$

It is formed when a boron trifluoride molecule ( $\text{BF}_3$ ) shares a pair of electrons supplied by fluoride ion ( $\text{F}^-$ ).



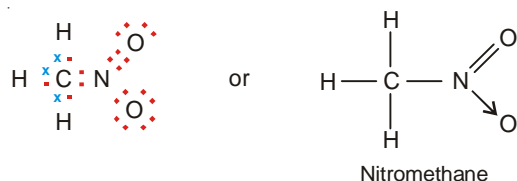
#### Addition compound of $\text{NH}_3$ with $\text{BCl}_3$

The N atom of ammonia molecule ( $\text{NH}_3$ ) has lone pair while B atom in boron trichloride ( $\text{BCl}_3$ ) is short of two electrons than stable octet. An addition compound is formed as the N atom donates its lone pair to B atom of  $\text{BCl}_3$ .



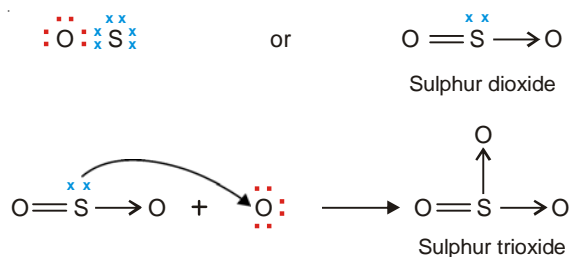
### Nitromethane, $\text{CH}_3\text{NO}_2$

The Lewis structure of nitromethane is shown below. Here the N atom has five valence electrons, three of which are used in forming a covalent bond with C atom and two covalent bonds with O atom. The N atom is still left with two unshared electrons which are donated to another O atom.



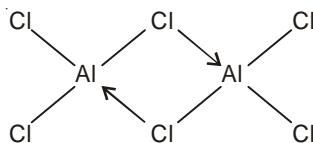
### Sulphur dioxide, $\text{SO}_2$ , and Sulphur trioxide, $\text{SO}_3$

Sulphur achieves its octet by forming two covalent bonds with one O atom, giving SO. The S atom in SO has two lone pairs, one of which is shared with a second O atom to form sulphur dioxide,  $\text{SO}_2$ . The S atom in  $\text{SO}_2$  still has one lone pair which it donates to a third O atom forming the sulphur trioxide ( $\text{SO}_3$ ) molecule.



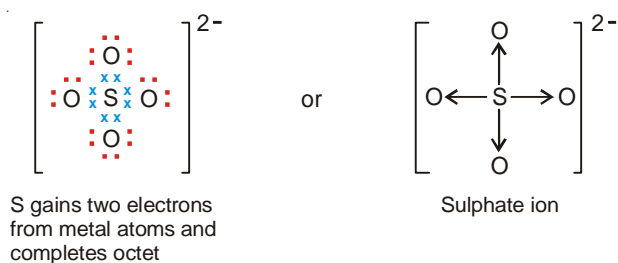
### Aluminium Chloride, $\text{Al}_2\text{Cl}_6$

Aluminium atom has three valence electrons which it shares with three Cl atoms, forming three covalent bonds. Thus the Al atom acquires six electrons in its outer shell. Now Cl atom has three lone pairs, one of which is donated to the Al atom of another molecule  $\text{AlCl}_3$ . Thus both Al atoms achieve octet and stable  $\text{Al}_2\text{Cl}_6$  results.



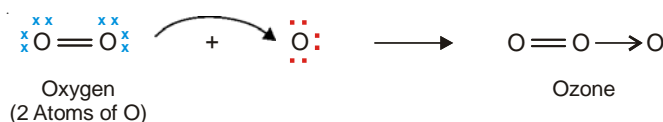
### Sulphate ion, $\text{SO}_4^{2-}$

Sulphur has six valence electrons (2, 8, 6) and achieves the octet by gaining two electrons from metal atoms (say two Na atoms). The four pairs of electrons around the S atom are then donated to four oxygen atoms each of which has six electrons. Thus the Lewis structure for  $\text{SO}_4^{2-}$  ion may be written as :



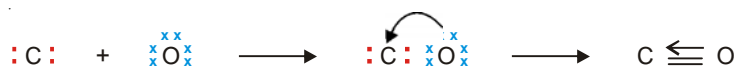
### Ozone, O<sub>3</sub>

Oxygen molecule is made of two oxygen atoms joined by two covalent bonds. Each O atom in O<sub>2</sub> has two unshared pairs of electrons. When one pair of these is donated to a third O atom which has only six electrons, a coordinate bond is formed. Thus the Lewis structure of ozone may be represented as :



### Carbon Monoxide, CO

Carbon atom has four valence electrons while oxygen atom has six. By forming two covalent bonds between them, O atom achieves octet but C atom has only six electrons. Therefore O donates an unshared pair of electron to C, and a coordinate covalent bond is established between the two atoms. Lewis structure of CO may be written as :

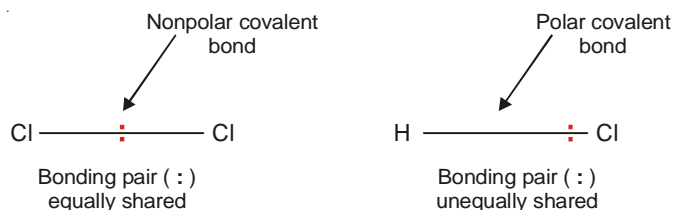


### COMPARISON OF IONIC AND COVALENT BONDS

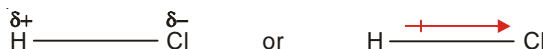
Ionic Bond	Covalent Bond
<ol style="list-style-type: none"> <li>1. Formed by transfer of electrons from a metal to a non-metal atom.</li> <li>2. Consists of electrostatic force between (+) and (-) ions.</li> <li>3. Non-rigid and non-directional; cannot cause isomerism.</li> </ol> <p><b>Properties of Compounds</b></p> <ol style="list-style-type: none"> <li>1. Solids at room temperature.</li> <li>2. High melting and boiling points.</li> <li>3. Hard and brittle.</li> <li>4. Soluble in water but insoluble in organic solvents.</li> <li>5. Conductors of electricity</li> <li>6. Undergo ionic reactions which are fast.</li> </ol>	<ol style="list-style-type: none"> <li>1. Formed by sharing of electrons between nonmetal atoms.</li> <li>2. Consists of a shared pair of electrons between atoms.</li> <li>3. Rigid and directional : causes stereoisomerism.</li> </ol> <p><b>Properties of Compounds</b></p> <ol style="list-style-type: none"> <li>1. Gases, liquids or soft solids.</li> <li>2. Low melting and boiling points.</li> <li>3. Soft, much readily broken</li> <li>4. Insoluble in water but soluble in organic solvents.</li> <li>5. Non-conductors of electricity.</li> <li>6. Undergo molecular reactions which are slow.</li> </ol>

### POLAR COVALENT BONDS

In the  $H_2$  or  $Cl_2$  molecule, the two electrons constituting the covalent bond are equally shared by the two identical nuclei. Due to even distribution of (+) and (−) charge, the two bonded atoms remain electrically neutral. Such a bond is called **nonpolar covalent bond**. However, when two different atoms are joined by a covalent bond as in  $HCl$ , the electron pair is not shared equally.



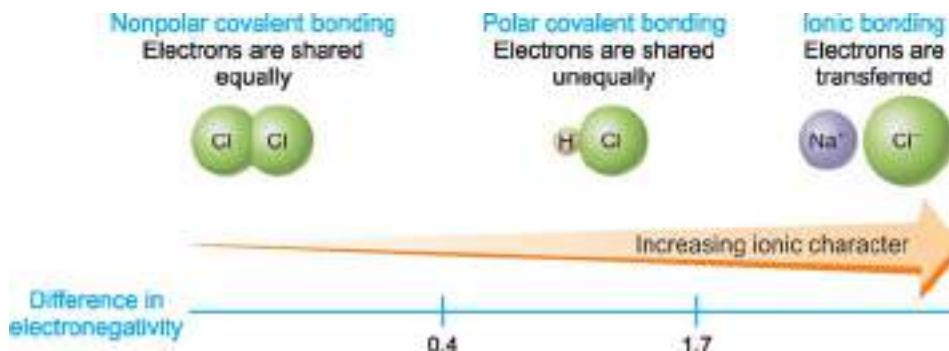
Due to a greater attraction of one nucleus ( $Cl$ ) for the electrons, the shared pair is displaced towards it. This makes one end of the bond partially positive ( $\delta_+$ ) and the other partially negative ( $\delta_-$ ).



**A covalent bond in which electrons are shared unequally and the bonded atoms acquire a partial positive and negative charge, is called a polar covalent bond.**

A molecule having partial positive and negative charge separated by a distance is commonly referred to as a **Dipole** (*two poles*). The dipole of a bond is indicated by an arrow from positive to negative end with a crossed tail as shown above in  $HCl$  molecule.

Since two atoms of different elements do not have exactly the same attraction for electrons in a bond, all bonds between unlike atoms are polar to some extent. The amount of polarity of a bond is determined by the difference of electronegativity (or tendency to attract electrons) of the two bonded atoms. **The greater the difference of electronegativity between two atoms, greater the polarity.** A graph showing the % age ionic character and difference in electronegativity between the two atoms is shown in Fig. 5.5.

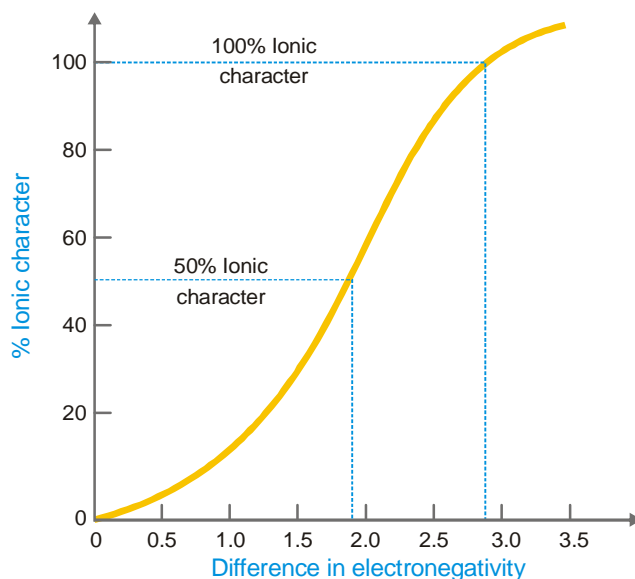


As a matter of fact, if this difference is around 1.9 and 2.9, the bond is generally ionic, meaning that one atom has gained complete control of the electron pair in the bond.

The percentage ionic character of a bond can be calculated by using the equation

$$\% \text{age ionic character} = 16 [X_A - X_B] + 3.5 [X_A - X_B]^2$$

This equation was given by Hannay and Smith.



■ **Figure 5.5**  
Graph between % ionic character and difference in electronegativity.

**SOLVED PROBLEM.** Calculate the percentage ionic character of C–Cl bond in  $\text{CCl}_4$  if the electronegativities of C and Cl are 3.5 and 3.0 respectively.

**SOLUTION**

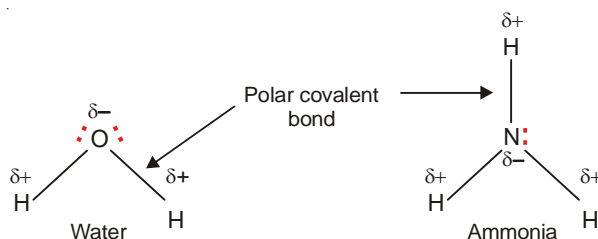
$$\% \text{age ionic character} = 16 [X_A - X_B] + 3.5 [X_A + X_B]^2$$

$$\text{Give } X_A = 3.5 \text{ and } X_B = 3.0$$

$$\begin{aligned} \therefore \% \text{age ionic character} &= 16 (3.5 - 3.0) + 3.5 (3.5 - 3.0)^2 \\ &= 8.0 + 0.875 \\ &= \mathbf{8.875\%} \end{aligned}$$

**Examples of Polar Covalent Bonds**

Water molecule ( $\text{H}_2\text{O}$ ) contains two O–H covalent bonds. The electronegativity of O is 3.5 and that of H is 2.1. Thus both the bonds are polar and water has a polar molecule.



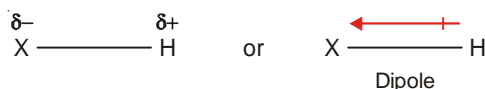
In ammonia molecule, there are three N–H bonds. The electronegativity of N is 3.0 and that of H is 2.1. Therefore all the N–H bonds are polar and ammonia has a polar molecule.

The electronegativity of fluorine (F) is 4.0 and that of H is 2.1. The difference of electronegativities being very great, the molecule H–F has a strong dipole.

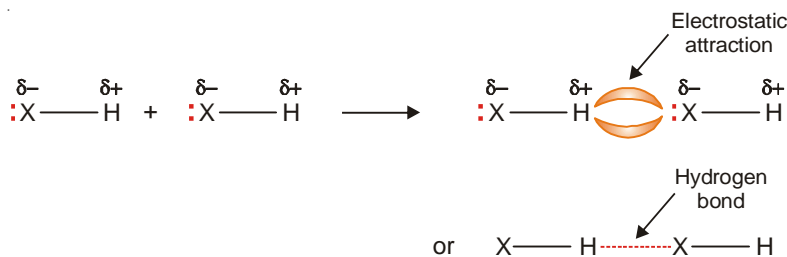


**HYDROGEN BONDING (H-Bonding)**

When hydrogen (H) is covalently bonded to a highly electronegative atom X (O, N, F), the shared electron pair is pulled so close to X that a strong dipole results.



Since the shared pair is removed farthest from H atom, its nucleus (the proton) is practically exposed. The H atom at the positive end of a polar bond nearly stripped of its surrounding electrons, exerts a strong electrostatic attraction on the lone pair of electrons around X in a nearby molecule. Thus :



The electrostatic attraction between an H atom covalently bonded to a highly electronegative atom X and a lone pair of electrons of X in another molecule, is called **Hydrogen Bonding**. Hydrogen bond is represented by a dashed or dotted line.

**POINTS TO REMEMBER**

- (1) Only O, N and F which have very high electronegativity and small atomic size, are capable of forming hydrogen bonds.
- (2) Hydrogen bond is longer and much weaker than a normal covalent bond. Hydrogen bond energy is less than 10 kcal/mole, while that of covalent bond is about 120 kcal/mole.
- (3) Hydrogen bonding results in long chains or clusters of a large number of 'associated' molecules like many tiny magnets.
- (4) Like a covalent bond, hydrogen bond has a preferred bonding direction. This is attributed to the fact that hydrogen bonding occurs through *p* orbitals which contain the lone pair of electrons on X atom. This implies that the atoms  $\text{X}-\text{H}\cdots\text{X}$  will be in a straight line.

**CONDITIONS FOR HYDROGEN BONDING**

The necessary conditions for the formation of hydrogen bonding are

**(1) High electronegativity of atom bonded to hydrogen**

The molecule must contain an atom of high electronegativity such as F, O or N bonded to hydrogen atom by a covalent bond. The examples are HF, H<sub>2</sub>O and NH<sub>3</sub>.

**(2) Small size of Electronegative atom**

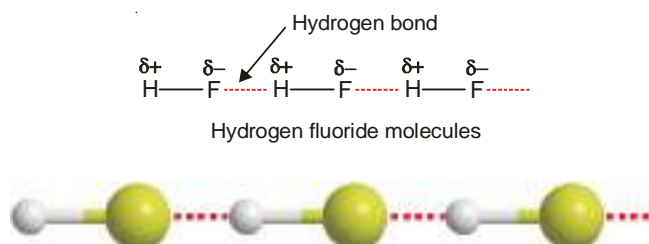
The electronegative atom attached to H-atom by a covalent bond should be quite small. Smaller the size of the atom, greater will be the attraction for the bonded electron pair. In other words, the polarity of the bond between H atom and electronegative atom should be high. This results in the formation of stronger hydrogen bonding. For example, N and Cl both have 3.0 electronegativity. But hydrogen bonding is effective in NH<sub>3</sub> in comparison to that in HCl. It is due to smaller size of N atom than Cl atom.

### EXAMPLES OF HYDROGEN-BONDED COMPOUNDS

When hydrogen bonding occurs between different molecules of the same compound as in HF,  $\text{H}_2\text{O}$  and  $\text{NH}_3$ , it is called **Intermolecular hydrogen bonding**. If the hydrogen bonding takes place within single molecule as in 2-nitrophenol, it is referred to as **Intramolecular hydrogen bonding**. We will consider examples of both types.

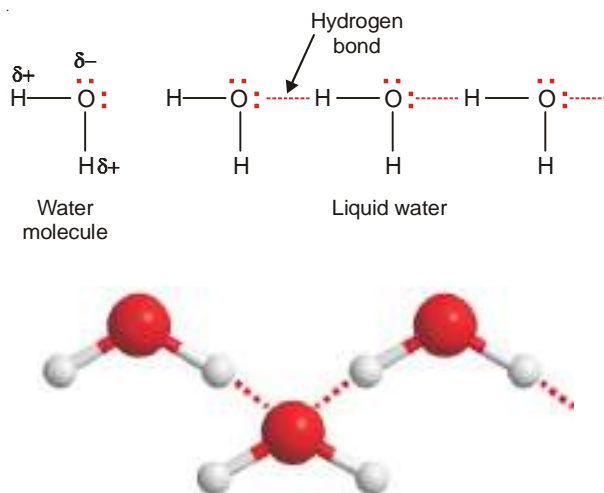
#### Hydrogen Fluoride, HF

The molecule of HF contains the strongest polar bond, the electronegativity of F being the highest of all elements. Therefore, hydrogen fluoride crystals contain infinitely long chains of H–F molecules in which H is covalently bonded to one F and hydrogen bonded to another F. The chains possess a zig-zag structure which occurs through  $p$  orbitals containing the lone electron pair on F atom.



#### Water, $\text{H}_2\text{O}$

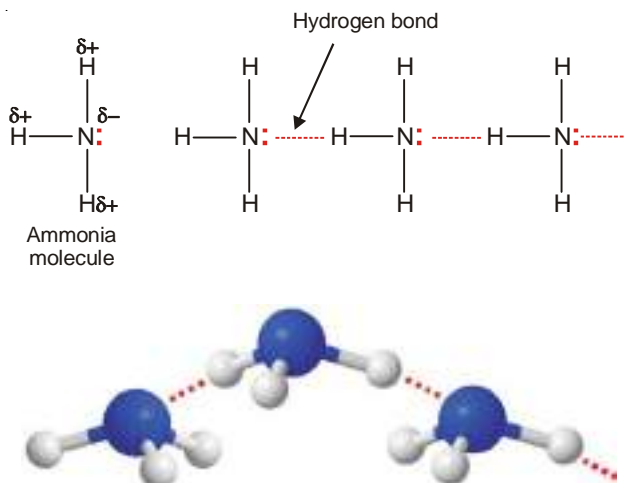
In  $\text{H}_2\text{O}$  molecule, two hydrogen atoms are covalently bonded to the highly electronegative O atom. Here each H atom can hydrogen bond to the O atom of another molecule, thus forming large chains or clusters of water molecules.



Each O atom still has an unshared electron pair which leads to hydrogen bonding with other water molecules. Thus liquid water, in fact, is made of clusters of a large number of molecules.

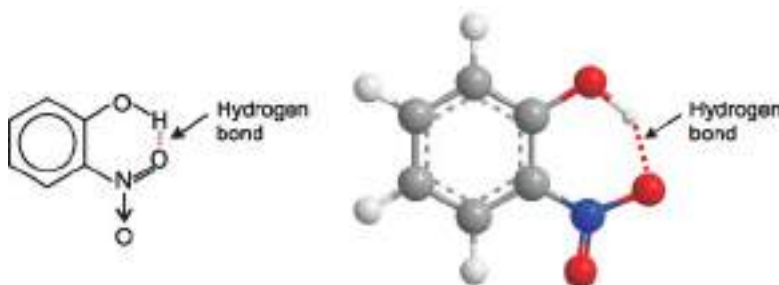
#### Ammonia, $\text{NH}_3$

In  $\text{NH}_3$  molecules, there are three H atoms covalently bonded to the highly electronegative N atom. Each H atom can hydrogen bond to N atom of other molecules.



## 2-Nitrophenol

Here hydrogen bonding takes place within the molecule itself as O–H and N–H bonds are a part of the same one molecule.

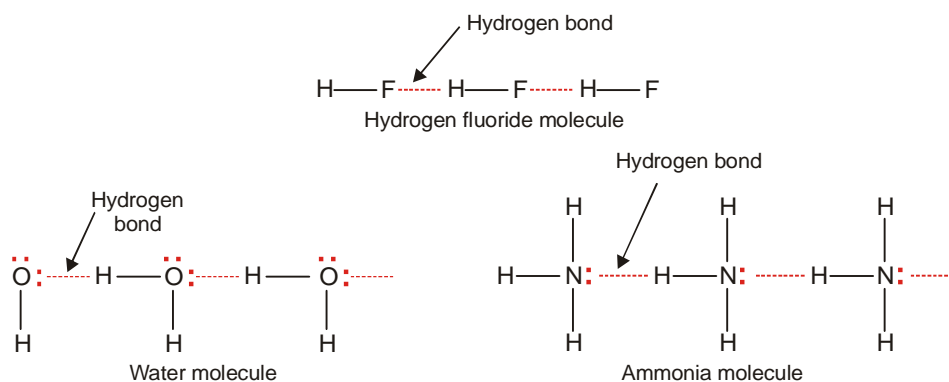


## TYPES OF HYDROGEN-BONDING

Hydrogen bonding is of two types :

### (1) Intermolecular Hydrogen bonding

This type of hydrogen bonding is formed between two different molecules of the same or different substances *e.g.* hydrogen bonding in HF, H<sub>2</sub>O, NH<sub>3</sub> etc. It is shown in the following diagram (Fig. 5.6).



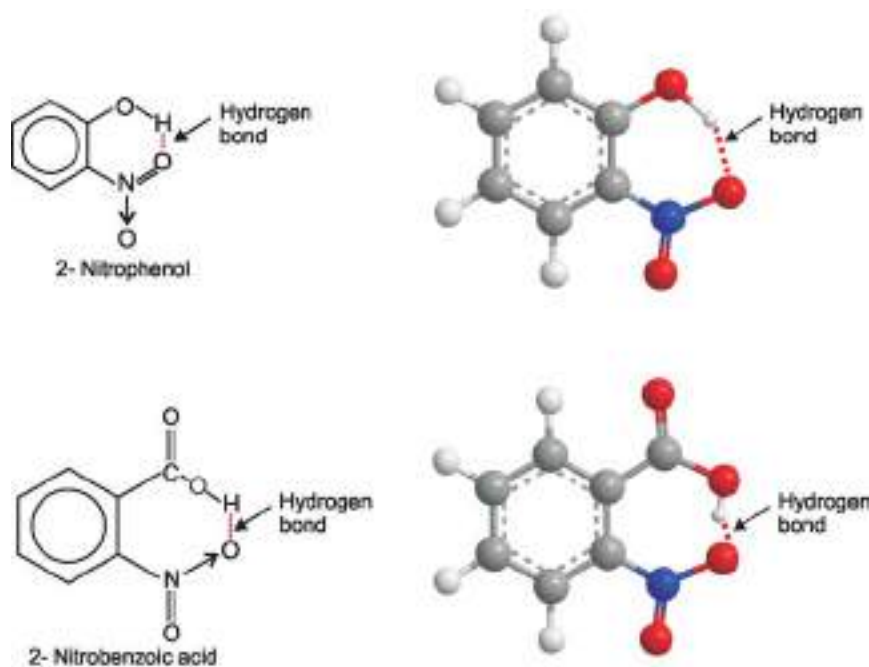
■ **Figure 5.6**

Intermolecular hydrogen bonding in HF, H<sub>2</sub>O and NH<sub>3</sub>.

This type of hydrogen bonding results in the formation of associated molecules. Generally speaking, the substances with intermolecular hydrogen bonding have high melting points, boiling points, viscosity, surface tension etc.

### (2) Intramolecular Hydrogen bonding

This type of hydrogen bonding is formed between the hydrogen atom and the electronegative atom present within the same molecule. It results in the cyclisation of the molecule. Molecules exist as discrete units and not in associated form. Hence intramolecular hydrogen bonding has no effect on physical properties like melting point, boiling point, viscosity, surface tension, solubility etc. For example intramolecular hydrogen bonding exists in *o*-nitrophenol, 2-nitrobenzoic acid etc. as shown below :



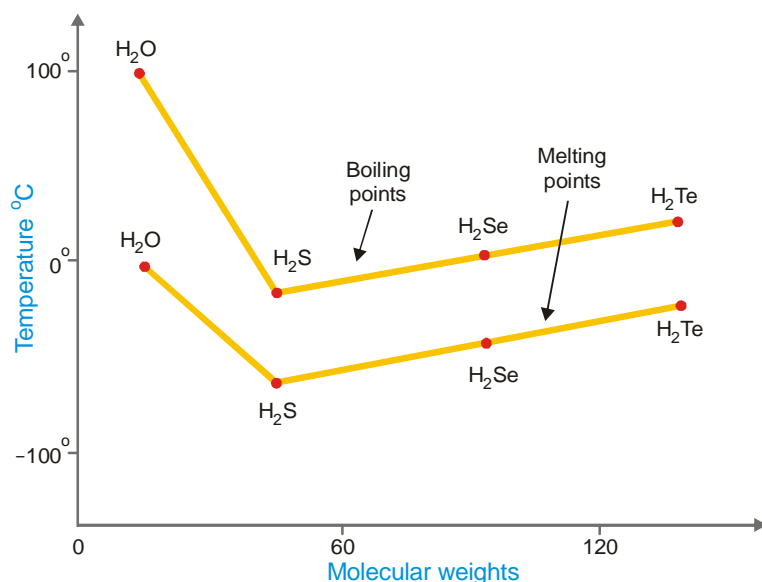
■ **Figure 5.7**  
Intramolecular hydrogen bonding.

## CHARACTERISTICS OF HYDROGEN-BONDED COMPOUNDS

### (1) Abnormally high boiling and melting points

The compounds in which molecules are joined to one another by hydrogen bonds, have unusually high boiling and melting points. This is because here relatively more energy is required to separate the molecules as they enter the gaseous state or the liquid state. Thus the hydrides of fluorine (HF), oxygen ( $\text{H}_2\text{O}$ ) and nitrogen ( $\text{NH}_3$ ) have abnormally high boiling and melting points compared to other hydrides of the same group which form no hydrogen bonds. In Fig. 5.8 are shown the boiling points and melting points of the hydrides of VIA group elements plotted against molecular weights.

It will be noticed that there is a trend of decrease of boiling and melting points with decrease of molecular weight from  $\text{H}_2\text{Te}$  to  $\text{H}_2\text{S}$ . But there is a sharp increase in case of water ( $\text{H}_2\text{O}$ ), although it has the smallest molecular weight. The reason is that the molecules of water are 'associated' by hydrogen bonds between them, while  $\text{H}_2\text{Te}$ ,  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{S}$  exist as single molecules since they are incapable of forming hydrogen bonds.

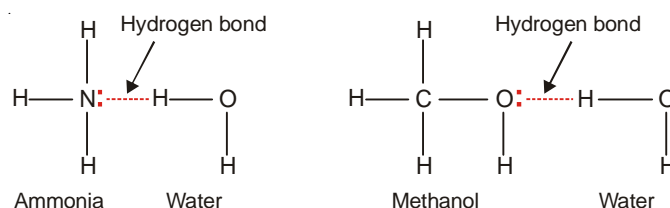


■ Figure 5.8

Boiling and melting point curves of the hydrides of VIA group showing abrupt increase for water (H<sub>2</sub>O) although it has the lowest molecular weight.

### (2) High solubilities of some covalent compounds

The unexpectedly high solubilities of some compounds containing O, N and F, such as NH<sub>3</sub> and CH<sub>3</sub>OH in certain hydrogen containing solvents are due to hydrogen bonding. For example, ammonia (NH<sub>3</sub>) and methanol (CH<sub>3</sub>OH) are highly soluble in water as they form hydrogen bonds.



### (3) Three dimensional crystal lattice

As already stated, **hydrogen bonds are directional and pretty strong to form three dimensional crystal lattice.** For example, in an ice crystal the water molecules (H<sub>2</sub>O) are held together in a tetrahedral network and have the same crystal lattice as of diamond. This is so because the O atom in water has two covalent bonds and can form two hydrogen bonds. These are distributed in space like the four covalent bonds of carbon. The tetrahedral structural units are linked to other units through hydrogen bonds as shown in Fig. 5.6.

Since there is enough empty space in its open lattice structure ice is lighter than water, while most other solids are heavier than the liquid form.

### Water as an Interesting Liquid

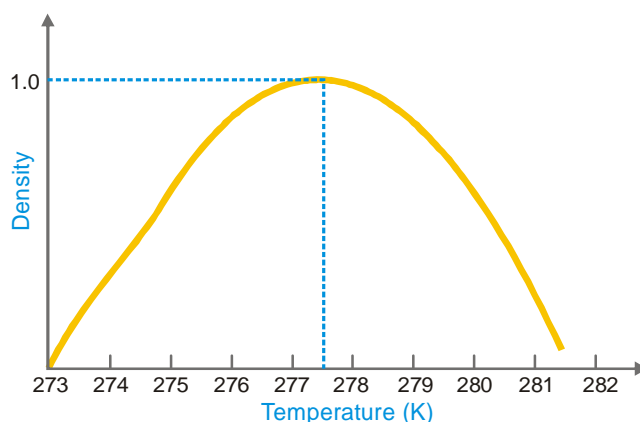
Water is very interesting solvent with unusual properties. It dissolves many ionic compounds and polar organic compounds. It has high heat of vaporisation, high heat of fusion, high specific heat with melting point 273 K and boiling point 373 K. Its structure as shown above is very interesting as it explains many properties :

**(1) Ice (solid) is lighter than water (Liquid)**

The structure of water is tetrahedral in nature. Each oxygen atom is linked to two H-atoms by covalent bonds and other two H-atoms by hydrogen bonding. In this solid state (Ice), this tetrahedral structure is packed resulting in open cage like structure with a number of vacant space. Hence in this structure the volume increases for a given mass of liquid water resulting in lesser density. Due to this reason ice floats on water.

**(2) Maximum density of water at 277 K (4°C)**

On melting ice, the hydrogen bonds break and water molecules occupy the vacant spaces. This results in decrease in volume and increase in density ( $d = m/v$ ). Hence density of water keeps on increasing when water is heated. This continues upto 277 K (4°C). Above this temperature water molecules start moving away from one another due to increase in kinetic energy. Due to this volume increases again and density starts decreasing. This behaviour of water is shown in the fig. 5.9.



■ **Figure 5.9**  
A plot of density versus temperature (water).

**EXCEPTIONS TO THE OCTET RULE**

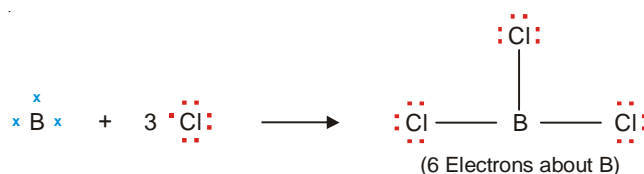
For a time it was believed that all compounds obeyed the Octet rule or the Rule of eight. However, it gradually became apparent that **quite a few molecules had non-octet structures**. Atoms in these molecules could have number of electrons in the valence shell short of the octet or in excess of the octet. Some important examples are :

**(1) Four or six electrons around the central atom**

A stable molecule as of beryllium chloride,  $\text{BeCl}_2$ , contains an atom with four electrons in its outer shell.



The compound boron trifluoride,  $\text{BF}_3$ , has the Lewis structure :

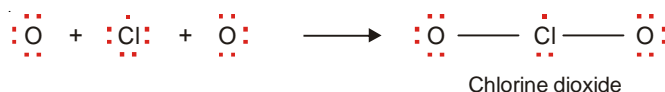


The boron atom has only six electrons in its outer shell.

Beryllium chloride and boron trifluoride are referred to as **electron-deficient compounds**.

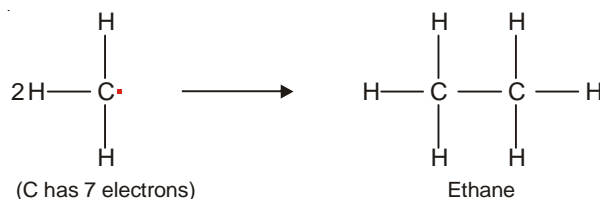
### (2) Seven electrons around the central atom

There are a number of relatively stable compounds in which the central atom has seven electrons in the valence shell. A simple example is chlorine dioxide,  $\text{ClO}_2$ .



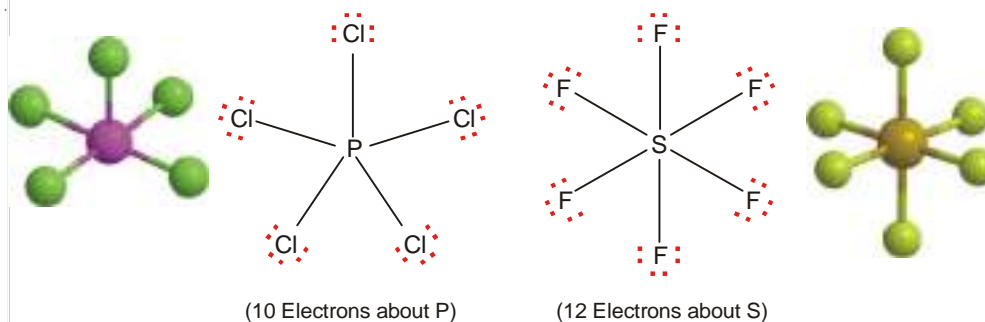
The chlorine atom in  $\text{ClO}_2$  has seven electrons in its outer shell.

Methyl radical ( $\text{CH}_3$ ) has an odd electron and is very short lived. When two methyl free radicals collide, they form an ethane molecule ( $\text{C}_2\text{H}_6$ ) to satisfy the octet of each carbon atom. **Any species with an unpaired electron is called a free radical.**



### (3) Ten or more electrons around the central atom

Non-metallic elements of the third and higher periods can react with electronegative elements to form structures in which the central atom has 10, 12 or even more electrons. The typical examples are  $\text{PCl}_5$  and  $\text{SF}_6$ .



The molecules with more than an octet of electrons are called **superoctet structures**.

In elements C, N, O and F the octet rule is strictly obeyed because only four orbitals are available (one  $2s$  and three  $2p$ ) for bonding. In the elements P and S, however,  $3s$ ,  $3p$ , and  $3d$  orbitals of their atoms may be involved in the covalent bonds they form. Whenever an atom in a molecule has more than eight electrons in its valence shell, it is said to have an **expanded octet**.

### VARIABLE VALENCE

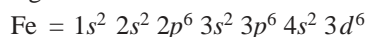
Some elements can display two or more valences in their compounds. The transition metals belong to this class of elements. The Electronic Structure of some of these metals is given below :

TABLE 5.2. ELECTRONIC STRUCTURE OF THE TWO OUTERMOST SHELLS OF SOME TRANSITION METALS

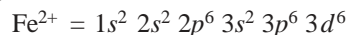
Sc	$3d^1 4s^2$	Ag	$4d^{10} 5s^1$
Cr	$3d^5 4s^1$	La	$5d^1 6s^2$
Mn	$3d^5 4s^2$	Os	$5d^6 6s^2$
Fe	$3d^6 4s^2$	Ir	$5d^7 6s^2$
Co	$3d^7 4s^2$	Pt	$5d^9 6s^2$
Cu	$3d^{10} 4s^1$	Au	$5d^{10} 6s^1$

Most of the transition metals have one or two outer-shell electrons and they form monovalent or bivalent positive ions. But because some of the  $d$  electrons are close in energy to the outermost electrons, these can also participate in chemical bond formation. Thus transition metals can form ions with variable valence. For example, copper can form  $\text{Cu}^{1+}$  and  $\text{Cu}^{2+}$  ions and iron can form  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions.

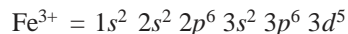
The complete electronic configuration of an iron atom is



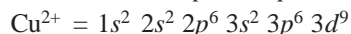
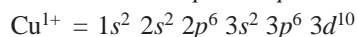
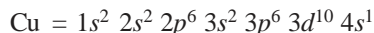
It can form  $\text{Fe}^{2+}$  by losing two  $4s$  electrons,



When iron loses two  $4s$  electrons and one of the three  $3d$  electrons, it forms  $\text{Fe}^{3+}$  ion



Copper forms  $\text{Cu}^{1+}$  and  $\text{Cu}^{2+}$  ions by losing one  $4s$  electron, and one  $4s$  and  $3d$  electron respectively



It may be noted that the structures of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{1+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$ , etc., are not isoelectronic with any of the noble gases, and hence the  $d$  electrons being unstable are available for bond formation. (The atoms and ions that have the same number of electrons are said to be **Isoelectronic**).

## METALLIC BONDING

The valence bonds that hold the atoms in a metal crystal together are not ionic, nor are they simply covalent in nature. Ionic bonding is obviously impossible here since all the atoms would tend to give electrons but none are willing to accept them. Ordinary covalent bonding is also ruled out as, for example, sodium atom with only one outer-shell electron could not be expected to form covalent bonds with 8 nearest neighbouring atoms in its crystal. **The peculiar type of bonding which holds the atoms together in metal crystal is called the Metallic Bonding.**

Many theories have been proposed to explain the metallic bonding. Here we will discuss the simplest of these : The Electron Sea Model.

## THE ELECTRON SEA MODEL

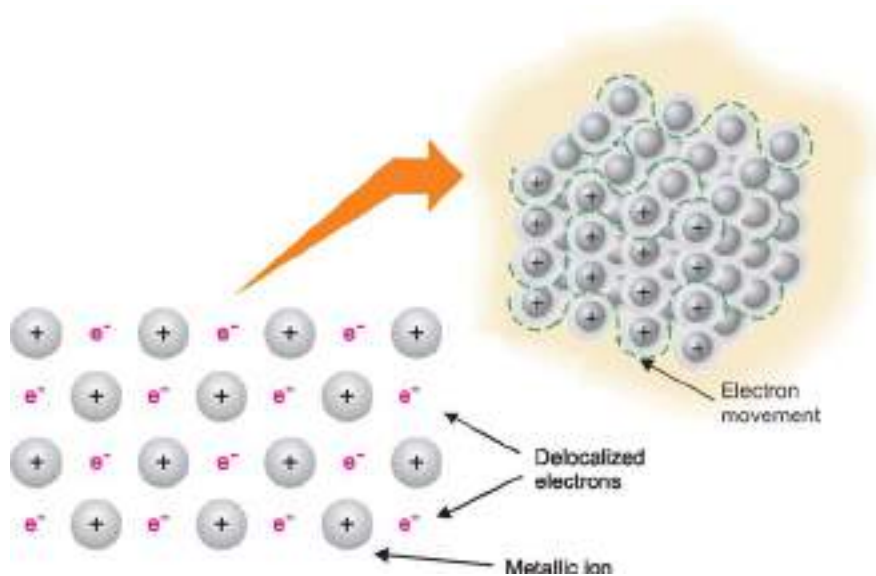
Metal atoms are characterised by :

- (1) **Low ionization energies** which imply that the valence electrons in metal atoms can easily be separated.
- (2) **A number of vacant electron orbitals in their outermost shell.** For example, the magnesium atom with the electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^0$  has three vacant  $3p$  orbitals in its outer electron shell.



There is considerable overlapping of vacant orbitals on one atom with similar orbitals of adjacent atoms, throughout the metal crystal. Thus it is possible for an electron to be delocalized and move freely in the vacant molecular orbital encompassing the entire metal crystal. The delocalized electrons no longer belong to individual metal atoms but rather to the crystal as a whole.

As a result of the delocalization of valence electrons, the positive metal ions that are produced, remain fixed in the crystal lattice while the delocalized electrons are free to move about in the vacant space in between. The metal is thus pictured as a network or lattice of positive ions of the metal immersed in a 'sea of electrons' or 'gas of electrons'. This relatively simple model of metallic bonding is referred to as the **Electron Sea model** or the **Electron Gas model** (Fig. 5.10.)



■ **Figure 5.10**

**The Electron Sea model of metallic bonding.**

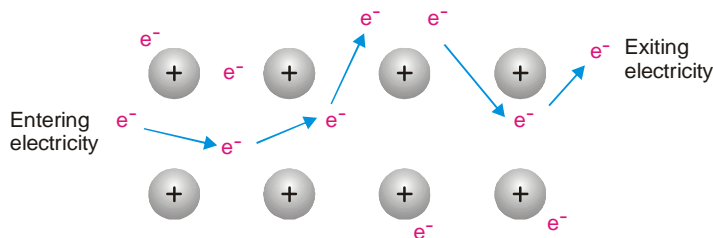
A metallic bond is the electrostatic force of attraction that the neighbour positive metallic ions have for the delocalized electrons.



**The electron sea model of metallic bonding explains fairly well the most characteristic physical properties of metals.**

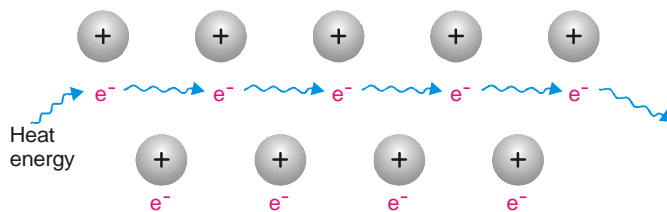
(1) **Luster or Reflectivity.** The delocalized mobile electrons of the 'electron sea' account for this property. Light energy is absorbed by these electrons which jump into higher energy levels and return immediately to the ground level. In doing so, the electrons emit electromagnetic radiation (light) of the same frequency. Since the radiated energy is of same frequency as the incident light, we see it as a reflection of the original light.

(2) **Electric Conductivity.** Another characteristic of metals is that they are good conductors of electricity. According to the electron sea model, the mobile electrons are free to move through the vacant space between metal ions. When electric voltage is applied at the two ends of a metal wire, it causes the electrons to be displaced in a given direction. The best conductors are the metals which attract their outer electrons the least (low ionization energy) and thus allow them the greatest freedom of movement.



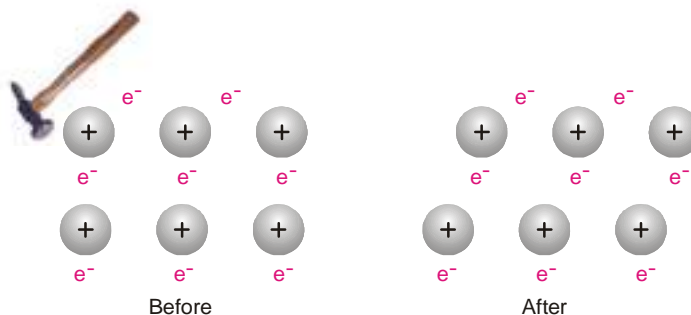
■ **Figure 5.11**  
Electrical conductivity by flow of electrons  
based on Electron Sea model.

(3) **Heat Conductivity.** If a metal is heated at one end, the heat is carried to the other end. The mobile electrons in the area of the ‘electron sea’ around one end of the metal easily absorb heat energy and increase their vibrational motion. They collide with adjacent electrons and transfer the added energy to them. Thus the mobility of the electrons allows heat transfer to the other end (Fig. 5.12).



■ **Figure 5.12**  
Heat conduction through a metal.

(4) **Ductility and Malleability.** The ductility and malleability of metals can also be explained by the electron sea model. In metals the positive ions are surrounded by the sea of electrons that ‘flows’ around them. If one layer of metal ions is forced across another, say by hammering, the internal structure remains essentially unchanged (Fig. 5.13). The sea of electrons adjusts positions rapidly and the crystal lattice is restored. This allows metals to be ductile and malleable. However, in ionic crystals of salts *e.g.*, sodium chloride, displacement of one layer of ions with respect to another brings like charged ions near to each other. The strong repulsive forces set up between them can cause the ionic crystals to cleave or shatter. **Thus ionic crystals are brittle.**



■ **Figure 5.13**  
When force is applied to the upper layer of cations it slips  
to the right without changing the environments.  
illustration of malleability and ductility.

(5) **Electron Emission.** When enough heat energy is applied to a metal to overcome the attraction between the positive metal ions and an outer electron, the electron is emitted from the metallic atom. When the frequency and, therefore, the energy of the light that strikes the metal is great enough to overcome the attractive forces, the electron escapes from the metal with a resultant decrease in the energy of the incident photon (**Photoelectric effect**).

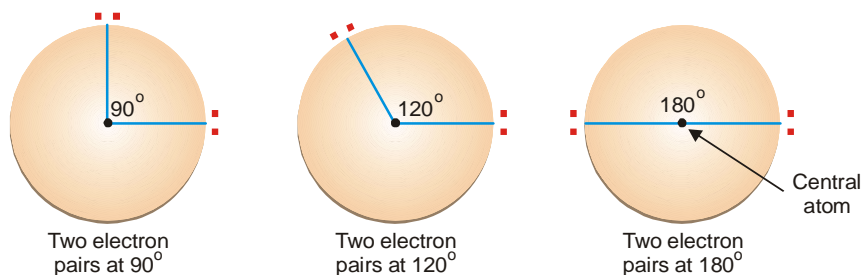
### GEOMETRIES OF MOLECULES

So far we have depicted molecules by Lewis structures in the flat plane of paper. But **all molecules containing three or more atoms are three-dimensional**. The shape of a particular molecule is determined by the specific arrangement of atoms in it and the bond angles. Molecular shapes may be linear, bent (or angular), trigonal planar, pyramidal or tetrahedral.

The shapes of molecules can be determined in the laboratory by modern methods such as X-ray and electron diffraction techniques. Molecular shapes are important because they are helpful in the investigation of molecular polarity, molecular symmetry or asymmetry. Physical and chemical properties of compounds depend on these factors. VSEPR theory throws light on the three dimensional shapes of molecules.

### VSEPR THEORY

The Lewis structure of a molecule tells us the number of pairs of electrons in the valence shell of the central atom. These electron pairs are subject to electrostatic attractions between them. On this basis, R.G.Gillespie (1970) proposed a theory called the **Valence-Shell Electron Pair Repulsion or VSEPR** (pronounced as ‘Vesper’) **theory**. It states that : **The electron pairs (both lone pairs and shared pairs, surrounding the central atom will be arranged in space as far apart as possible to minimise the electrostatic repulsion between them.**



■ **Figure 5.14**

**Arrangement of two electron pairs on circle at 90°, 120° and at 180°. Placement of electron pairs at 180° puts them the farthest apart, thereby minimising the electrostatic repulsion.**

Let us consider the simplest case of an atom with two electron pairs. We wish to place the electron pairs on the surface of a sphere such that they will be as far apart as possible so as to minimise repulsion between them. Fig. 5.14 illustrates it by showing some possible placements of the two electron pairs. The arrangement in which the electron pair-central atom-electron pair angles is 180°, makes the electron pairs farthest apart. **This arrangement is called linear because the electron pairs and the central atom are in a straight line.**

VSEPR theory is simple but remarkably powerful model for predicting molecular geometries and bond angles. While working out the shapes of molecules from this theory, it must be remembered :

(1) **Multiple bonds behave as a single electron-pair bond** for the purpose of VSEPR. They represent a single group of electrons.

(2) **Order of repulsions** between lone pair and lone pair ( $lp-lp$ ), lone pair and bonding pair ( $lp-bp$ ), and bonding pair and bonding pair ( $bp-bp$ ) is

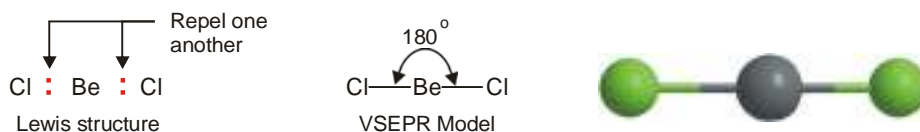
$$lp-lp \gg lp-bp > bp-bp$$

**When a molecule has lone pairs of electrons, the bonding electron pairs are pushed closer and thus the bond angle is decreased.**

Now we proceed to work out the shapes of some common molecules with the help of VSEPR theory.

### (1) Linear Molecules

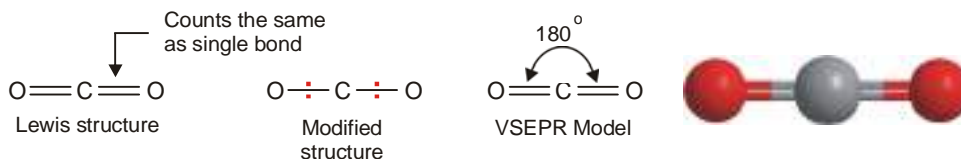
(a) **Beryllium chloride,  $\text{BeCl}_2$** . It has the Lewis structure



■ **Figure 5.15**  
Geometry of  $\text{BeCl}_2$  molecule.

The central atom Be has two bonding electron pairs and no unshared electron. According to VSEPR theory, the bonding pairs will occupy positions on opposite sides of Be forming an angle of  $180^\circ$ . An angle of  $180^\circ$  gives a straight line. Therefore,  $\text{BeCl}_2$  molecule is linear. In general, **all molecules as A–B–A which have only two bonds and no unshared electrons are linear.**

(b) **Carbon dioxide,  $\text{CO}_2$** . It has the structure



■ **Figure 5.16**  
Geometry of  $\text{CO}_2$  molecule.

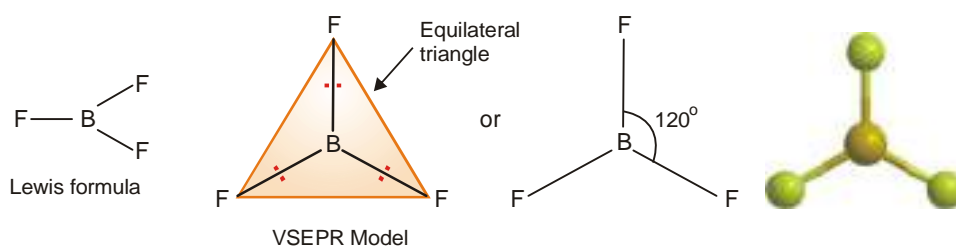
The central C atom has no unshared electron. We know that a double bond counts the same as a single bond in VSEPR model. Thus  $\text{CO}_2$  is a linear molecule.

Similarly, it can be shown that hydrogen cyanide ( $\text{H}-\text{C}\equiv\text{N}$ ) and acetylene ( $\text{H}-\text{C}\equiv\text{C}-\text{H}$ ) are linear molecules.



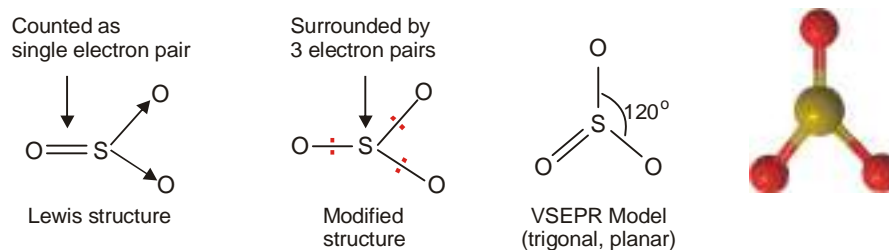
### (2) Trigonal Planar Molecules

(a) **Boron trifluoride,  $\text{BF}_3$** . Its Lewis structure shown that the central atom B has three bonding electron pairs and no unshared electrons. VSEPR theory says that the three bonding electron pairs will be as far apart as possible. This can be so if these electron pairs are directed to the corners of an equilateral triangle. Thus VSEPR model of  $\text{BF}_3$  molecule has three F atoms at the corners of the triangle with B atom at its centre. All the four atoms (three F and one B) lie in the same plane. Therefore, the shape of such a molecule is called **trigonal planar**. The bond angle is  $120^\circ$ .



■ **Figure 5.17**  
Geometry of  $\text{BF}_3$  molecule.

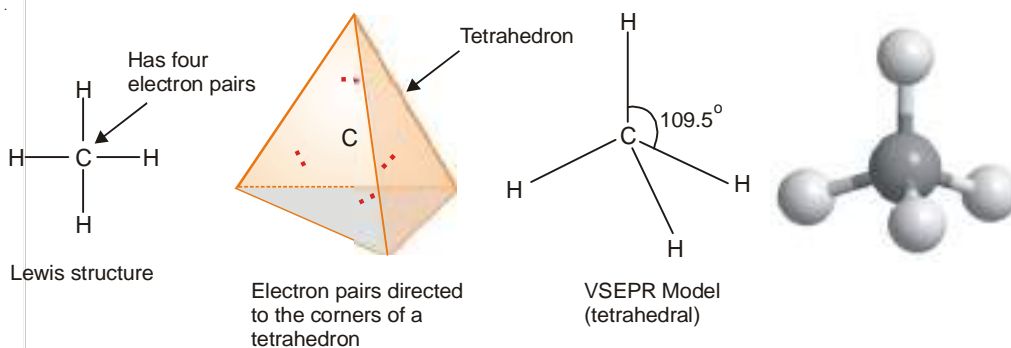
(b) **Sulphur trioxide,  $\text{SO}_3$ .** In the Lewis structure of  $\text{SO}_3$ , the central S atom is joined with two O atoms by covalent bonds. The third O atom is joined with S by a double bond. But a double bond is counted as a single electron pair for the purpose of VSEPR model. Therefore, in effect, S has three electron pairs around it. Thus like  $\text{BF}_3$ ,  $\text{SO}_3$  has trigonal planar geometry.



■ **Figure 5.18**  
Geometry of  $\text{SO}_3$  molecule.

### (3) Tetrahedral Molecules

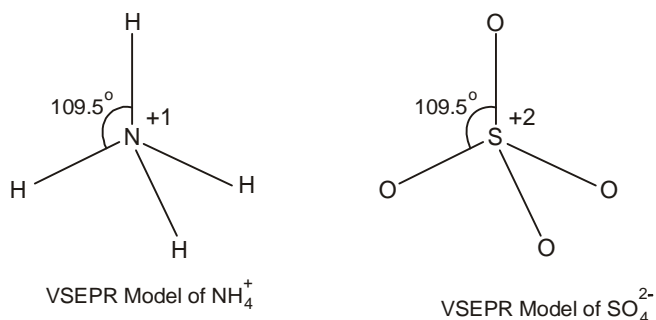
(a) **Methane,  $\text{CH}_4$ .** Lewis structure of methane shows that the central C atom has four bonding electron pairs. These electron pairs repel each other and are thus directed to the four corners of a regular tetrahedron. A regular tetrahedron is a solid figure with four faces which are equilateral triangles. All bond angles are  $109.5^\circ$ .



■ **Figure 5.19**  
Geometry of  $\text{CH}_4$  molecule.

Similarly,  $\text{CCl}_4$  in which the central C atom is bonded to four other atoms by covalent bonds has tetrahedral shape.

(b) **Ammonium ion,  $\text{NH}_4^+$ , and Sulphate ion,  $\text{SO}_4^{2-}$ .** The N atom in  $\text{NH}_4^+$  and S atom in  $\text{SO}_4^{2-}$  have four electron pairs in the valence shell. These are directed to the corners of a tetrahedron for maximum separation from each other. Thus both  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  have tetrahedral shape.

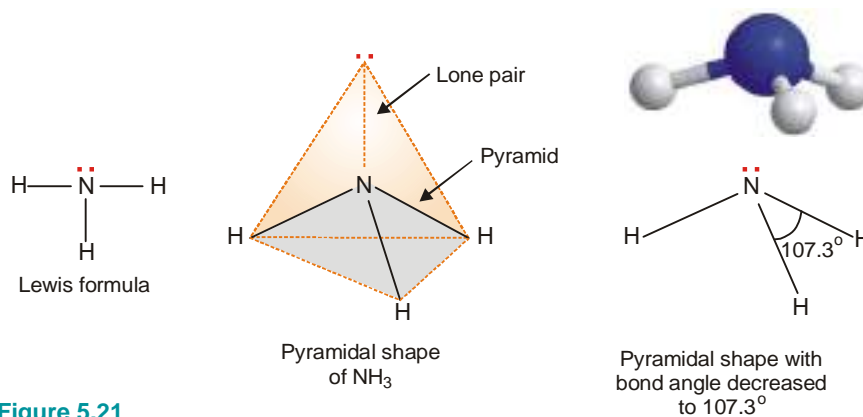


■ **Figure 5.20**  
Geometry of  $\text{NH}_4^+$  ion and  $\text{SO}_4^{2-}$  ion.

#### (4) Pyramidal Molecules

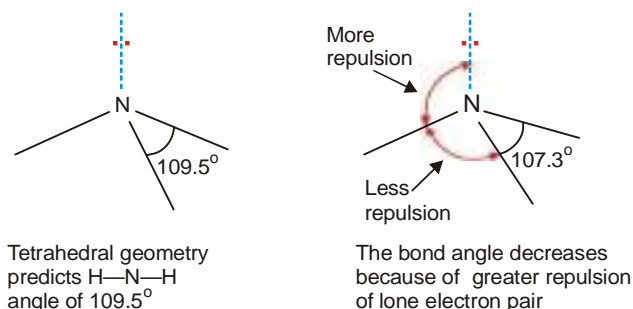
(a) **Ammonia molecule.** The Lewis structure of  $\text{NH}_3$  shows that the central N atom has three bonding electrons and one lone electron pair. The VSEPR theory says that these electron pairs are directed to the corners of a tetrahedron. Thus we predict that H–N–H bond angle should be  $109.5^\circ$ . But the shape of a molecule is determined by the arrangement of atoms and not the unshared electrons. Thus, if we see only at the atoms, we can visualise  $\text{NH}_3$  molecule as a pyramid with the N atom located at the apex and H atoms at the three corners of the triangular base.

According to VSEPR theory, **a lone pair exerts greater repulsion on the bonding electron pairs than the bonding pairs do on each other.** As a result, the bonds of  $\text{NH}_3$  molecule are pushed slightly closer. This explains why the observed bond angle H–N–H is found to be  $107.3^\circ$  instead of  $109.5^\circ$  predicted from tetrahedral geometry.



■ **Figure 5.21**  
Geometry of  $\text{NH}_3$  molecule.

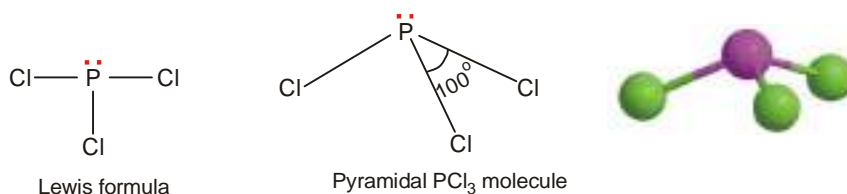
**All molecules in which the N atom is joined to three other atoms by covalent bonds, have pyramidal shape.** For example, amines  $\text{RNH}_2$ ,  $\text{R}_2\text{NH}$  and  $\text{R}_3\text{N}$  have pyramidal shape.



■ Figure 5.22

Why the angle H—N—H in  $\text{NH}_3$  molecule is  $107.3^\circ$  while the tetrahedral angle is  $109.5^\circ$ ?

(b) **Phosphorus trichloride,  $\text{PCl}_3$ .** The structural formula indicates that the central phosphorus atom has three bonding electron pairs and one lone electron pair. Thus, like  $\text{NH}_3$  it has pyramidal shape and the observed bond angle Cl—P—Cl is  $100^\circ$ .

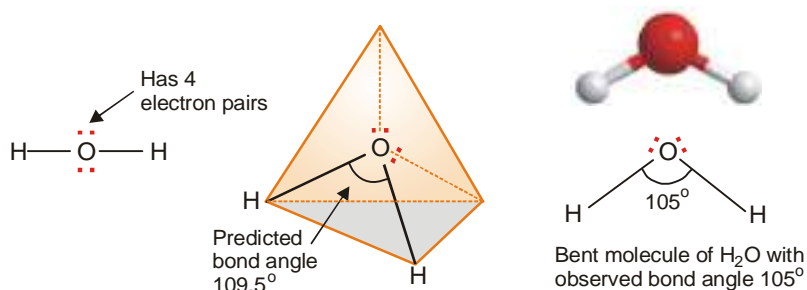


■ Figure 5.23

Geometry of  $\text{PCl}_3$  molecule.

### (5) Bent or Angular Molecules

(a) **Water,  $\text{H}_2\text{O}$ .** In the structural formula of  $\text{H}_2\text{O}$ , the O atom is bonded to two H atoms by covalent bonds and has two lone pairs. Thus O is surrounded by two bonding electron pairs and two



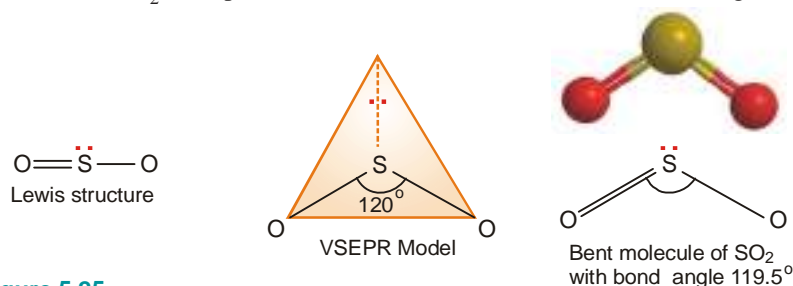
■ Figure 5.24

Geometry of  $\text{H}_2\text{O}$  molecule.

unshared electron pairs. VSEPR theory says that in order to secure maximum separation between them, the four electron pairs are directed to the corners of a tetrahedron. If we look at the three atoms (and ignore the unshared pairs), the atoms HOH lie in the same plane and the predicted bond angle is  $109.5^\circ$ . But with two unshared pairs repelling the bonding pairs, the bond angle is compressed to  $105^\circ$ , the experimental value. Thus the  $\text{H}_2\text{O}$  molecule is flat and bent at an angle at the O atom. Such a molecule is called a **bent molecule** or **angular molecule**.

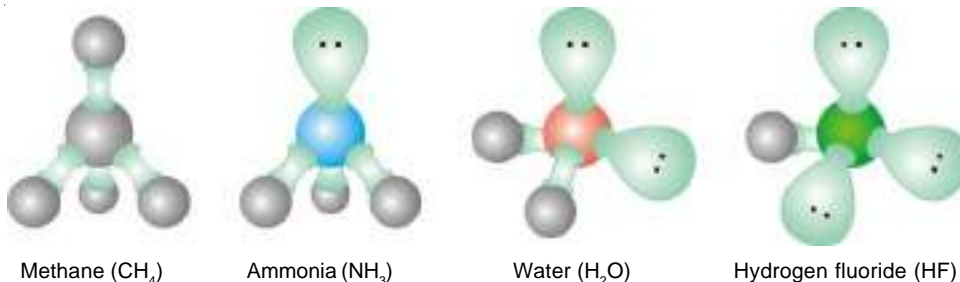


(b) **Sulphur dioxide,  $\text{SO}_2$ .** The Lewis structure of  $\text{SO}_2$  is given below. The S atom is bonded to one O by a double bond and to the other O by a single bond. It has an unshared electron pair. In VSEPR model a double bond is counted as a single electron pair. That way, the S atom is surrounded by three electron pairs, two bonding pairs and one unshared pair. For maximum separation the three electron pairs are directed to the corners of an equilateral triangle. The predicted bond angle is  $120^\circ$ . But with the unshared electron pair repelling the bonding electron pairs, the bond angle is actually reduced somewhat. Thus  $\text{SO}_2$  has a planar bent molecule with the observed bond angle  $119.5^\circ$ .



■ **Figure 5.25**  
Geometry of  $\text{SO}_2$  molecule.

### SUMMARY : SHAPES OF MOLECULES



The directional nature of covalent bonds is shown in the diagrams of molecules above. The shape of the methane molecule is tetrahedral because the four bonding pairs of electrons repel each other equally, and the equilibrium position of all four bonding electron pairs is tetrahedral.

### HOW TO WORK OUT THE SHAPE OF A MOLECULE

It is possible to work out the shape of a small molecule that has a formula  $\text{XY}_n$  by applying a few simple rules. We will use ammonia as an example to illustrate the idea.

- Rule 1** First find the number of bonding pairs of electrons in the molecule. The number of bonding pairs of electrons in the molecule  $\text{NH}_3$  can be seen in the formula. There must be three bonding pairs of electrons holding the three hydrogens onto the nitrogen.
- Rule 2** Find the number of valence electrons (electrons in the outer energy level) on an atom of the central atom (The one of which there is only one.) Nitrogen is in group V, so the nitrogen has five electrons in the outer energy level.
- Rule 3** Find the number of lone pairs on the central atom by subtracting the number of bonding pairs (3) from the valence electrons (5) to find the number of electrons (2) that will make up lone pairs of electrons. Divide this number by 2 to find the number of lone pairs,  $2/2 = 1$ .
- Rule 4** Distribute all the electron pairs around the central atom and learn the angles they will make from molecules with no lone pairs.
- Rule 5** Learn that the repulsion between lone pairs of electrons is greater than the repulsion between bonding pairs, and subtract  $2^\circ$  from the bond angles for every lone pair.
- Rule 6** Learn the names of the shapes. The shapes are named from the position of the atoms and not the position of the orbitals.

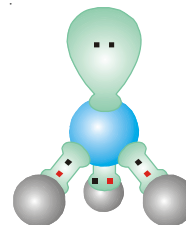

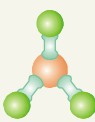
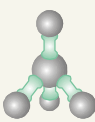

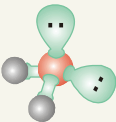




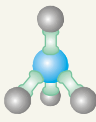

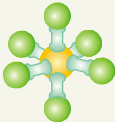
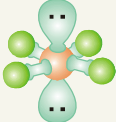

TABLE OF SHAPES

Formula	$\text{BeCl}_2$ Beryllium chloride	$\text{BCl}_3$ Boron trichloride	$\text{CH}_4$ Methane	$\text{NH}_3$ Ammonia	$\text{H}_2\text{O}$ Water
Bonding Pairs	2	3	4	3	2
Valence Electrons	2	3	4	5	6
Lone Pairs	0	0	0	1	2
Angles between bonding pairs	$180^\circ$	$120^\circ$	$109.5^\circ$	$107^\circ$	$105^\circ$
Name of shape	Linear	Trigonal Planar	Tetrahedral	Trigonal Pyramid	Bent
					

There is one more rule to learn, and it concerns the shape of polyatomic ions.

**Rule 2(a)** If the molecule is an ion, e.g. ammonium ( $\text{NH}_4^+$ ), subtract 1 from the number of valence electrons for every + charge on the ion and add 1 to the valence number for every - charge, then proceed as before.

### SOME MORE EXAMPLES

Formula	$\text{NH}_4^+$	$\text{PCl}_5$	$\text{SF}_6$	$\text{XeF}_4$	$\text{ICl}_3$
Bonding Pairs	4	5	6	4	3
Valence Electrons	5	5	6	8	7
Rule 2(a)	$5 - 1 = 4$				
Lone Pairs	0	0	0	2	2
Angles between bonding pairs	$109.5^\circ$	$90^\circ$ & $120^\circ$	$90^\circ$	$90^\circ$	$90^\circ$
Name of shape	Tetrahedral	Trigonal Bipyramid	Octahedron	Square	T shape
					

## EXAMINATION QUESTIONS

- Define or explain the following terms :
  - Octet rule
  - Covalent bond
  - Polar covalent bond
  - Intermolecular H-bonding
  - VSEPR theory
  - Ionic bond
  - Co-ordinate covalent bond
  - Hydrogen bonding
  - Intramolecular H-bonding
- Compare the properties of ionic and covalent compounds.
  - State whether the following compounds are ionic or covalent.
    - $\text{AlCl}_3$
    - $\text{HgF}_2$
- Draw the structure of NaCl crystal and give the co-ordination number of  $\text{Na}^+$ .
  - Which of the two is more covalent and why in the following pairs
    - AgCl and AgI
    - LiCl and KCl
- In methane, ammonia and water molecule the bond angle is decreasing. Explain giving reasons.
- Explain the formation of covalent bond between two atoms of chlorine in a chlorine molecule on the basis of octet rule.
  - Define (i) Ionic bond; (ii) Co-ordinate bond; and (iii) Metallic bond
- What do you understand by 'Stable configuration'? What are the ways by which an atom can attain stable configuration?
  - Write the electronic configuration of any two of the following compounds :
    - Phosphorus pentachloride
    - Sulphuric acid
    - Lithium fluoride
- What type of bonds do you expect in the following cases? Give reasons :
  - between a very small cation and a large anion.
  - between atoms having a very large difference in electronegativities,
  - between atoms of the same element.
- Explain qualitatively the valence bond theory with reference to Hydrogen molecule.
- Compare the properties of ionic and covalent compounds. Give two examples of each type of compounds.
- Indicate the type of bonding that exists in the following solids :
  - Ice
  - Naphthalene
  - Diamond
  - Potassium chloride
- Write Lewis dot formulae of : (a) HOCl (b)  $\text{BF}_3$  (c)  $\text{NH}_4^+$ .
- Show the formation of a co-ordinate bond in ozone molecule and discuss briefly the electron gas model of the metallic bond and how it explains the electrical conductivity of metals.
- What is electronegativity? How is the concept of electronegativity used to predict the bond types between hetero atoms?
- Account for the variation of bond angles between the pairs (i)  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$  ( $104.5^\circ$  and  $92^\circ$ ) and (ii)  $\text{H}_2\text{O}$  and  $\text{OF}_2$  ( $104.5^\circ$  and  $101.1^\circ$ ).
- Describe the structures of water, ammonia and methane molecules in terms of the electron pair repulsion theory. Explain why the bond angles are different in the three molecules.
- What is a co-ordinate covalent bond? How does it differ from a normal covalent bond?
- Discuss the shape of the following molecules on the basis of VSEPR theory :
$$\text{NH}_3, \text{CH}_4, \text{PCl}_3$$
- Explain the formation of  $\text{NH}_3$  molecule if no hybridization of  $s$  and  $p$ -orbitals of nitrogen is assumed.

Give diagrammatic representation also.

19. Explain :  
(a) The structure of  $H_2$  molecule according to V.B. theory.  
(b) Ionic bond and Metallic bond.
20. Two elements  $X$  and  $Y$  occur in the same period and their atoms have two and seven valence electrons respectively. Write down the electronic structure of the most probable compound between  $X$  and  $Y$ . Will the bond between  $X$  and  $Y$  be predominantly ionic or covalent?  
**Answer.**  $XY_2$ ; Ionic
21. Using VSEPR theory, identify the type of hybridisation and draw the structure of  $OF_2$ . What are the oxidation states of O and F?
22. Account for : The experimentally found N—F bond length in  $NF_3$  is greater than the sum of single covalent radii of N and F.
23. Which of the following compounds contain bonds that are predominantly ionic in character :  $MgO$ ,  $Ca_3P_2$ ,  $AlCl_3$ ,  $Mg_2Si$  and  $CsF$ .  
**Answer.**  $CsF$ ,  $Mg_2Si$  and  $MgO$
24. Classify the bonds in the following as ionic, polar covalent or covalent : (a)  $HCl$  (b)  $NaCl$  and (c)  $NCl_3$ .  
**Answer.**  $HCl$  - Polar covalent,  $NaCl$  - Ionic and  $NCl_3$  - Covalent
25. Predict the geometry of the following molecules using VSEPR theory.  
(a)  $CCl_4$  (b)  $AlCl_3$   
(c)  $H_2Se$   
**Answer.** (a) Tetrahedral (b) Trigonal planar (c) Bent
26. Predict the geometry of the following ions having VSEPR model.  
(a)  $H_3O^+$  (b)  $NO_2^-$   
(c)  $ClO_2^-$   
**Answer.** (a) Pyramidal (b) Bent (c) Bent
27. Calculate the percentage ionic character of C—Cl bond in  $CCl_4$ , if the electronegativities of C and Cl are 3.5 and 3.0 respectively.  
**Answer.** 8.875%
28. The experimentally determined dipole moment,  $m$ , of  $KF$  is  $2.87 \times 10^{-29}$  coulomb meter. The distance,  $d$ , separating the centers of charge in a  $KF$  dipole is  $2.66 \times 10^{-3}$  m. Calculate the percent ionic character of  $KF$ .  
**Answer.** 67.4%
29. The dipole moment of  $KCl$  is  $3.336 \times 10^{-29}$  coulomb meter which indicates that it is highly polar molecule. The interionic distance between  $K^+$  and  $Cl^-$  in this molecule is  $2.6 \times 10^{-10}$  m. Calculate the dipole moment of  $KCl$  molecule if there were opposite charges of one fundamental unit localised at each nucleus. Calculate the percentage ionic character of  $KCl$ .  
**Answer.** 80%
30. What is meant by an ionic bond? What are the conditions necessary for the formation of an ionic bond?  
(Agra BSc, 2000)
31. Describe the basic ideas of the VSEPR theory. Explain the application of the theory for predicting the shapes of the molecules,  $BCl_3$ ,  $NH_3$ ,  $H_2O$  and  $SF_6$ .  
(Delhi BSc, 2001)
32. (a) What are electrovalent compounds? Discuss various factors which affect the formation of these compounds.  
(b) What do you understand by hydrogen bonds? Classify them with examples. Explain why water has abnormally high boiling point.  
(Baroda BSc, 2002)
33. Why bond angles of  $H_2O$  and  $NH_3$  are  $104.5^\circ$  and  $107^\circ$  respectively although central atoms are  $sp^3$  hybridized.  
(Aligarh BSc, 2002)
34. Define Lattice energy. Discuss the factors on which it depends.

35. (a) Why melting and boiling points of ionic compounds are usually higher than covalent compounds?  
 (b) Discuss the geometry and shape of  $\text{PF}_5$  molecule.  
 (c) Write a short note on hydrogen bonding. (Arunachal BSc, 2003)
36. Each of the concepts of covalency and electrovalency relates to an idealised state of chemical bonding which often does not exist in real compounds. Discuss how far this statement is valid and give two examples with suitable explanation of cases where such non-ideality in fact arises. (Delhi BSc, 2003)
37. Strength of hydrogen bond in  $\text{H-F}$  is more than in  $\text{H}_2\text{O}$  but still  $\text{HF}$  is a gas and  $\text{H}_2\text{O}$  is a liquid at room temperature. Explain. (Delhi BSc, 2004)
38. (a) The bond angle  $\angle\text{H-N-H}$  in ammonia is  $107^\circ$  while bond angle  $\angle\text{H-O-H}$  in water is about  $104^\circ$ . Why?  
 (b) A covalent bond is stronger than a metallic bond. Why? (Sambalpur BSc, 2004)
39. Explain intermolecular and intramolecular hydrogen bonding with one example for each. (Agra BSc, 2005)
40. Based on metallic bond, explain why metals are :  
 (a) good conductors of electricity (b) malleable and ductile  
 (c) having characteristic lustre (Mysore BSc, 2006)

### MULTIPLE CHOICE QUESTIONS

1. The valency of an element is  
 (a) the combining capacity of one atom of it  
 (b) the number of bonds formed by its one atom  
 (c) the number of hydrogen atoms that combine with one atom of it  
 (d) all the above  
**Answer.** (d)
2. The octet rule is  
 (a) the tendency of atoms to have eight electrons in the outermost shell  
 (b) the tendency of atoms to have eight pairs of electrons in the valency shell  
 (c) the tendency of the molecule to have a total of eight electrons  
 (d) the tendency of atoms to have eight non-bonding electrons  
**Answer.** (a)
3. An ionic bond is formed between  
 (a) two metal atoms (b) two non-metal atoms  
 (c) one metal atom and one non-metal atom (d) one metal atom and one metalloid atom  
**Answer.** (c)
4. Factors governing the formation of an ionic bond are  
 (a) low ionisation energy of metal and high electron affinity of non-metal atom  
 (b) high ionisation energy of metal and high electron affinity of non-metal atom  
 (c) low ionisation energy of metal atom and low electron affinity of non-metal atom  
 (d) high ionisation energy of metal and low electron affinity of non-metal atom  
**Answer.** (a)
5. The lattice energy is the amount of energy that  
 (a) is released when one cation combines with one anion  
 (b) is released when one mole of cations combine with one mole of anions  
 (c) is released when one mole of an ionic compound is formed from its cations and anions

(d) is absorbed when one mole of an ionic compound is formed from its cation and anions

**Answer.** (c)

6. The most favourable conditions for the formation of an ionic compound is

- (a) low charge on ions, small cation and small anion
- (b) high charge on ions, large cation and large anion
- (c) high charge on ions, small cation and large anion
- (d) low charge on ions, large cation and small anion

**Answer.** (c)

7. Ionic compounds are generally

- (a) solids having large melting points and good conductors of electricity
- (b) gases having low melting points and poor conductors of electricity
- (c) solids having low melting points and good conductors of electricity
- (d) solids having high melting points and bad conductors of electricity

**Answer.** (a)

8. A covalent bond involves

- (a) sharing of electrons between a metal and a non-metal atom
- (b) sharing of electrons between two metal atoms
- (c) sharing of electrons between two atoms having similar electronegativity
- (d) sharing of electrons between two atoms having a large difference in electronegativity

**Answer.** (c)

9. The total number of electron pairs in a nitrogen molecule is

- (a) 2
- (b) 3
- (c) 5
- (d) 7

**Answer.** (d)

10. The covalent compounds are soluble in

- (a) all acids
- (b) all bases
- (c) all solvents
- (d) non-polar solvents

**Answer.** (d)

11. The compounds which contain both ionic and covalent bonds are

- (a)  $\text{CHCl}_3$  and  $\text{CCl}_4$
- (b)  $\text{KCl}$  and  $\text{AlCl}_3$
- (c)  $\text{KCN}$  and  $\text{NaOH}$
- (d)  $\text{H}_2$  and  $\text{CH}_4$

**Answer.** (c)

12. A co-ordinate bond is formed by

- (a) complete transfer of electrons
- (b) sharing of electrons contributed by both the atoms
- (c) sharing of electrons contributed by one atom only
- (d) none of these

**Answer.** (c)

13. The types of bonds present in sulphuric acid molecules are

- (a) only covalent
- (b) ionic and covalent
- (c) co-ordinate and covalent
- (d) co-ordinate, covalent and ionic

**Answer.** (d)

14. The common feature among the species  $\text{O}_3$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}_3\text{O}^+$  and  $\text{AlCl}_3$  is that

- (a) they contain only ionic bonds
- (b) they contain only covalent bonds
- (c) they contain co-ordinate bond
- (d) they contain covalent and ionic bonds

**Answer.** (c)

15. The species  $\text{CO}$ ,  $\text{CN}^-$  and  $\text{N}_2$  are

- (a) isoelectronic
- (b) having co-ordinate bond
- (c) having low bond energies
- (d) having polar bonds

**Answer.** (a)

16. The polarity of a covalent bond is due to  
(a) lesser electronegativity difference between two atoms  
(b) greater electronegativity difference between two atoms  
(c) lesser bond energy  
(d) greater bond energy  
**Answer.** (b)
17. A  $\text{CO}_2$  molecule contains two polar bonds but the net dipole moment is zero. It is because  
(a) the molecule has symmetrical linear geometry  
(b) the molecule is non-linear  
(c) the electronegativity difference between the two atoms is too large  
(d) the electronegativity difference between the two atoms is too small  
**Answer.** (a)
18. Among  $\text{BeF}_2$ ,  $\text{BF}_3$ ,  $\text{NH}_3$  and  $\text{CCl}_4$ , the molecule with net dipole moment is  
(a)  $\text{BeF}_2$  (b)  $\text{BF}_3$  (c)  $\text{NH}_3$  (d)  $\text{CCl}_4$   
**Answer.** (c)
19. The common feature among the molecules  $\text{HF}$ ,  $\text{H}_2\text{O}$ ,  $\text{HCl}$  and  $\text{NH}_3$  is  
(a) intramolecular H-bonding (b) intermolecular H-bonding  
(c) that they contain no polar bonds (d) that their dipole moment is zero  
**Answer.** (b)
20. Methanol is soluble in water due to  
(a) covalent bond nature (b) ionic bond nature  
(c) hydrogen bonding (d) its poisonous nature  
**Answer.** (c)
21. Among  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{Te}$ , the substance with highest boiling point is  
(a)  $\text{H}_2\text{O}$ ; due to hydrogen bonding  
(b)  $\text{H}_2\text{S}$ ; due to large size of S atom  
(c)  $\text{H}_2\text{Se}$ ; due to large electronegativity difference  
(d)  $\text{H}_2\text{Te}$ ; due to largest size of Te atom  
**Answer.** (a)
22. In ice crystal, the  $\text{H}_2\text{O}$  molecules are held together in a  
(a) planar structure (b) linear structure  
(c) tetrahedral three dimensional structure (d) none of these  
**Answer.** (c)
23. The density of ice (solid) is lesser than that of water (liquid) because it has  
(a) open cage like structure with no empty spaces  
(b) open cage like structure with large empty spaces  
(c) intermolecular H-bonding  
(d) intramolecular H-bonding  
**Answer.** (b)
24. The density of water is maximum at  
(a) 273 K (b) 277 K (c) 281 K (d) 285 K  
**Answer.** (b)
25. Among  $\text{BeCl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$  and  $\text{PCl}_5$ , the octet rule is not observed in  
(a)  $\text{BeCl}_2$  only (b)  $\text{PCl}_5$  only (c)  $\text{BeCl}_2$  and  $\text{PCl}_5$  (d)  $\text{CHCl}_3$  and  $\text{CCl}_4$   
**Answer.** (c)
26. An example of electron deficient compound among  $\text{BF}_3$ ,  $\text{CF}_4$ ,  $\text{PF}_5$  and  $\text{SF}_6$  is  
(a)  $\text{BF}_3$  (b)  $\text{CF}_4$  (c)  $\text{PF}_5$  (d)  $\text{SF}_6$   
**Answer.** (a)

27. The transition metals show variable valency because of  
(a) the availability of vacant  $d$ -orbitals (b) their tendency to form complex ions  
(c) their ability to form coloured ions (d) none of these  
**Answer.** (a)
28. The electrical conductivity of metals is due to  
(a) mobile protons in the nucleus (b) mobile nucleus in the nucleus  
(c) mobile electrons in outer vacant spaces (d) none of these  
**Answer.** (c)
29. According to VSEPR theory,  
(a) the lone pairs only decide the structure of the molecule  
(b) the bond pairs only decide the structure of the molecule  
(c) the lone pairs and bond pairs both decide the structure of the molecule  
(d) none of these  
**Answer.** (c)
30. In which of the following, the central atom is surrounded by four electron pairs  
(a)  $\text{H}_2\text{O}$  (b)  $\text{NH}_3$  (c)  $\text{CH}_4$  (d) All  
**Answer.** (d)
31. The molecule among  $\text{CCl}_4$ ,  $\text{PCl}_3$ ,  $\text{SF}_4$  and  $\text{NH}_3$  that does not contain lone pairs of electrons around the central atom is  
(a)  $\text{CCl}_4$  (b)  $\text{PCl}_3$  (c)  $\text{SF}_4$  (d)  $\text{NH}_3$   
**Answer.** (a)
32. Which of the following are isostructural  
(a)  $\text{SO}_2$  and  $\text{CO}_2$  (b)  $\text{SO}_2$  and  $\text{H}_2\text{O}$  (c)  $\text{BCl}_3$  and  $\text{CHCl}_3$  (d)  $\text{NH}_3$  and  $\text{CH}_4$   
**Answer.** (b)
33. The molecular shapes of  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{CH}_4$  are  
(a) similar with 2, 1 and 0 lone pairs of electrons respectively  
(b) similar with 0, 1 and 2 lone pairs of electrons respectively  
(c) different with 0, 1 and 2 lone pairs of electrons respectively  
(d) different with 2, 1 and 0 lone pairs of electrons respectively  
**Answer.** (d)
34. The molecule of  $\text{NH}_3$  is  
(a) tetrahedral with bond angle  $109^\circ 28'$  (b) pyramidal with bond angle  $107^\circ 20'$   
(c) trigonal with bond angle  $120^\circ$  (d) linear with bond angle  $180^\circ$   
**Answer.** (b)
35. The  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  ions have  
(a) tetrahedral geometry (b) triangular geometry  
(c) pyramidal geometry (d) square planar geometry  
**Answer.** (a)
36. Which is incorrect?  
(a) all molecules with polar bonds have dipole moment  
(b) all molecules with polar bonds may or may not have dipole moment  
(c) the greater the difference in electronegativity between two atoms, greater is the polarity  
(d) if the electronegativity difference between two atoms is greater than 1.7, the bond will be ionic  
**Answer.** (a)
37. The favourable conditions for the formation of H-bonding are  
(a) high electronegativity and small size of the atom bonded to H-atom  
(b) low electronegativity and large size of the atom bonded to H-atom  
(c) high electronegativity and large size of the atom bonded to H-atom

(d) low electronegativity and small size of the atom bonded to H-atom

**Answer.** (a)

38. The strength of hydrogen bonding lies in between

- (a) covalent and ionic bond (b) metallic and covalent bond  
(c) van der Waal's and covalent bond (d) metallic and ionic bond

**Answer.** (d)

39. The bond angles in a trigonal bipyramid molecules are

- (a)  $90^\circ$  (b)  $120^\circ$  (c)  $109.5^\circ$  (d)  $120^\circ, 90^\circ$

**Answer.** (d)

40.  $\text{CO}_2$  has zero dipole moment whereas  $\text{H}_2\text{O}$  has a dipole moment. It is because

- (a)  $\text{H}_2\text{O}$  is linear while  $\text{CO}_2$  is a bent molecule  
(b) of intermolecular H-bonding in  $\text{H}_2\text{O}$  molecules  
(c)  $\text{CO}_2$  is linear while  $\text{H}_2\text{O}$  is a bent molecule  
(d)  $\text{CO}_2$  is a gas while  $\text{H}_2\text{O}$  is a liquid at room temperature

**Answer.** (c)

41. Which of the following does not obey the octet rule?

- (a)  $\text{PCl}_5$  (b)  $\text{H}_2\text{O}$  (c)  $\text{NH}_3$  (d)  $\text{CCl}_4$

**Answer.** (a)

42. The total number of electrons that take part in forming bonds in  $\text{O}_2$  is

- (a) 2 (b) 4 (c) 6 (d) 8

**Answer.** (d)

43. CO is isoelectronic with

- (a)  $\text{C}_2\text{H}_2$  (b)  $\text{CN}^-$  (c)  $\text{O}_2^+$  (d)  $\text{O}_2^-$

**Answer.** (b)

44.  $\text{CO}_2$  is isostructural with

- (a)  $\text{H}_2\text{O}$  (b)  $\text{NO}_2$  (c)  $\text{H}_2\text{S}$  (d)  $\text{C}_2\text{H}_2$

**Answer.** (d)

45. In a bond between two atoms X and Y, the shared electron pair does not lie in the centre. The bond is

- (a) single bond (b) non-polar bond (c) polar bond (d) co-ordinate bond

**Answer.** (c)

46. The maximum number of Hydrogen bonds formed by a water molecule is

- (a) 1 (b) 2 (c) 3 (d) 4

**Answer.** (b)

47. Out of the following, intramolecular Hydrogen bonding exists in

- (a) water (b)  $\text{H}_2\text{S}$  (c) 2-nitrophenol (d) 4-nitrophenol

**Answer.** (c)

48. In a compound, hydrogen bonding exists but there is no effect on physical properties like m. pt., b. pt. etc. It shows the presence of

- (a) weak van der Waal's forces (b) intramolecular hydrogen bonding  
(c) intermolecular hydrogen bonding (d) resonance in the molecule

**Answer.** (b)

49. Which one of the following is the most polar

- (a)  $\text{H} - \text{F}$  (b)  $\text{H} - \text{Cl}$  (c)  $\text{H} - \text{Br}$  (d)  $\text{H} - \text{I}$

**Answer.** (a)



## 6

Chemical Bonding  
– Orbital Theory

## CHAPTER

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With a knowledge of the electronic structure of atoms and their orbitals as background, we now proceed to discuss the behaviour of atoms when their ‘atomic orbitals’ interact to form chemical bonds.

Free atoms have a random motion and possess energies. Farther the atoms are more will be the energy of the system, giving it lesser stability. Two or more atoms unite to form a molecule because in doing so the energy of the system is lowered and thus the ‘molecule’ becomes stable in comparison to separate atoms. **In other words, a stable chemical union or bond between two (or more) atoms comes into existence only if the energy is lowered when the atoms come in close proximity.**

By the term ‘energy’ here, we mean the sum of the kinetic and potential energies. The kinetic energy of atoms finds its origin in the unabated motion of the electrons. The potential energy of a system in which atoms A and B approach each other can be due to

- Electron-electron repulsions
- Nucleus-nucleus repulsions
- Nucleus-electron attractions.