Unit - 02

Atomic Structure

After studying this unit, the students will be able to:

- Summarize Bohr's atomic theory. (Applying)
- Use Bohr's model for calculating radii of orbits. (Understanding)
- Use Bohr's atomic model for calculating energy of electron in a given orbit of hydrogen atom.
- Relate energy equation (for electron) to frequency, wavelength and wave number of radiation emitted or absorbed by electron.
- Explain production, properties, types and uses of X – rays. (Understanding)
- Define photon as a unit of radiation energy. (Remembering)
- Describe the concept of orbitals. (Understanding)
- Explain the significance of quantized energies of electrons. (Applying)
- Distinguish among principal energy levels, energy sub levels and atomic orbitals. (Understanding)
- Describe the general shapes of s, p and d orbitals. (Understanding)
- Relate the discrete – line spectrum of hydrogen to energy levels of electrons in the hydrogen atom. (Applying)
- Describe the hydrogen atom using the Quantum Theory. (Understanding)
- Use the Aufbau principle, the Pauli Exclusion Principle and Hund's rule to write the electronic configuration of the elements. (Applying)
- Describe the orbitals of hydrogen atom in order of increasing energy. (Understanding)
- Explain the sequence of filling of electrons in many electron atoms. (Applying)
- Write electron configuration of atoms. (Applying)

Teaching	Assessment	Weightage %
10	01	08

Introduction

A Greek philosopher Democritus for the first time in the fifth century B.C, suggested that all kinds of matter is composed of small microscopic particles known as atoms that cannot be further divided. Later in 19th Century, after the development of John Dalton's atomic theory, several important discoveries were made that led to a new understanding of the atom. A number of experiments proved that the atom is divisible and consists of subatomic particles called electrons, neutrons and protons. Most of the mass of an atom is concentrated in a central unit called nucleus, which contains protons and neutrons. The nucleus is surrounded by orbits, which have the light particles electrons, which are responsible for most of the volume occupied by the atom. The electron was the first subatomic particle to be discovered, followed by discoveries of the proton and the neutron. These sub-atomic particles are of much significance for a chemist, since the arrangement of these particles within an atom determines its physical and chemical properties.

In the previous grades, you have learnt about the discoveries of the nucleus, Rutherford's atomic model, Bohr's atomic model and shell. In this unit, you will be able to calculate the atomic radii, energy, wavelength and frequency of radiations absorbed or emitted by electronic transitions. You will also learn about the production, properties and types of X – rays, hydrogen spectrum and quantum numbers which will improve your existing understanding of the atom.

> ***Tidbit***
>
> Word atom is derived from the Greek word 'atomos' meaning indivisible.

2.1 Discharge Tube Experiments (The Discovery of Electron)

The development of John Dalton's atomic theory led towards the invention of new instruments. For example, the Crookes tube or gas discharge tube, developed by Sir William Crookes, opened the door to discover the subatomic particles of an atom. The discovery of electron is attributed to the knowledge derived from discharge tube experiments.

A gas discharge tube consists of a glass tube. Two metallic electrodes, acting as cathode and anode are sealed in the walls of a glass tube. The tube is attached to a vacuum pump by means of a small tube, so that the conduction of electricity through a gas may be studied at any desired value of low pressure. A high voltage source is connected to the electrodes.

William Crookes conducted a series of experiments in the late 19th century using a gas discharge tube to study the passage of electric current through gases. His apparatus was consisted of a glass tube with meal electrodes, anode and cathode, on the two ends of the tube. The tube can be connected to a vacuum pump so that the electrical conduction through the gas may be studies at any desired value of low pressure. A high voltage sources is connected to the electrodes.

It was observed by Crookes, that the gas inside the tube, at ordinary pressure, did not conduct electricity, even when the electrodes were connected to a source of very high potential, of reduced by means of the vacuum pump and the electrodes were connected to a high voltage of 5000 – 10,000 volts, an electric discharge was observed through the gas, producing a uniform glow inside the tube. This happened at a pressure of about 0.1mm Hg. When the pressure inside the tube was further reduced to about 0.01mm Hg, the original uniform glow disappeared and the whole tube was filled up by dark space and no luminous discharge was observed. At this stage, the electrical resistance between the two electrodes became very high and it became difficult to maintain the discharge, unless the potential difference between the electrodes was very high (approximately 10,000 volts). Under this condition some rays (faint fluorescent light) was produced which created fluorescence on the glass wall opposite to the cathode. When different gases were used in the discharge tube, under similar conditions, with different metals used as electrodes, the same rays were produced. These rays were called cathode rays by Goldstein (1886), since these were originated from cathode.

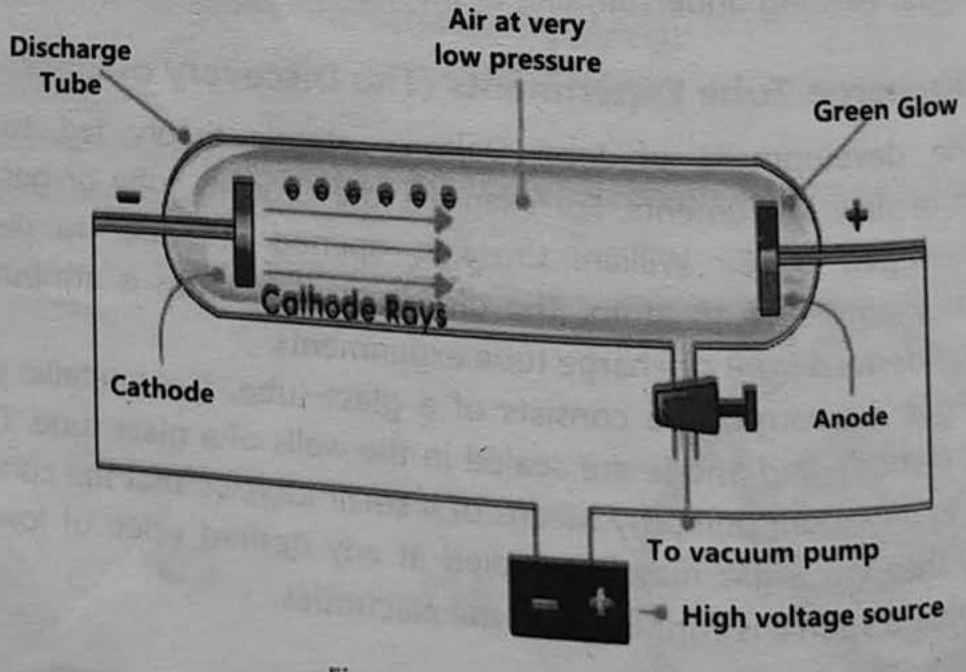


Figure 2.1 Cathode ray tube

Later J.J. Thomson and other scientists made further investigations on cathode rays and its properties which ultimately lead to the discovery of electron which were by then called cathode rays.

Note: Crookes used cold cathode at his time in this system. The gas particles inside the tube were ionized at anode and became positively charged particles which were attracted towards cathode due to its negative charge and collided with it with high speed which resulted in emission of electrons from cathode. These electrons then rushed towards anode. In modern cathode ray tube, hot cathode is used. Due to high temperature the electrons are energized and expelled from the cathode due to attraction of anode and move with high speed towards anode. However, in addition to thermionic effect, the phenomenon of ionization of gas (as in the case of cold cathode) cannot be ignored in this case.

2.1.1 Characteristics of Cathode Rays

Later on, a number of experiments, performed by various scientists, showed that the cathode rays have the following characteristics.

i. These rays travel in straight lines perpendicular to the cathode surface and away from the cathode.
ii. They produce a sharp shadow if an opaque object is placed in their path as shown in figure 2.2.
iii. These rays produce fluorescence (a glow) when they strike the wall of the discharge tube.
iv. These rays heat up the metal on which they fall.
v. These rays can move a small pin wheel placed in their path as shown in figure 2.3, as these rays are bunch of moving particles with definite mass and kinetic energy.
vi. These rays produce X-rays when they strike heavy metal anode.
vii. These rays can ionize the gases.
viii. These rays can cause a chemical change in a material on which they fall, as they have reducing effect.
ix. These rays can penetrate metallic sheets like Aluminum and Gold.
x. Cathode rays are negatively charged particles as when these rays are through an electric field, they are deflected towards positively charge plate/ electrode as shown in figure 2.4.
xi. These rays are also deflected by magnetic field as shown in figure 2.5.
xii. The charge to mass ratio (e/m) of cathode rays (electron) is 1.7588×10^{11} C/kg.
xiii. Charge (e) on cathode rays (electron) is 1.6022×10^{-19} C.

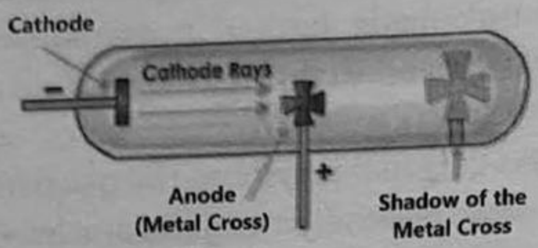


Fig 2.2 Cathode Rays Casting Shadows

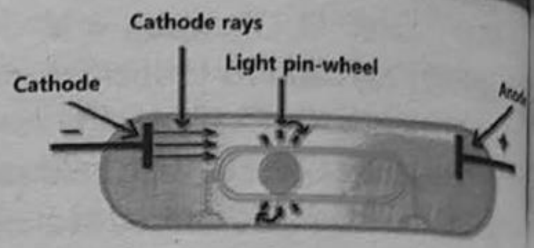


Fig 2.3 Cathode Rays, Rotating light Pin-Wheel

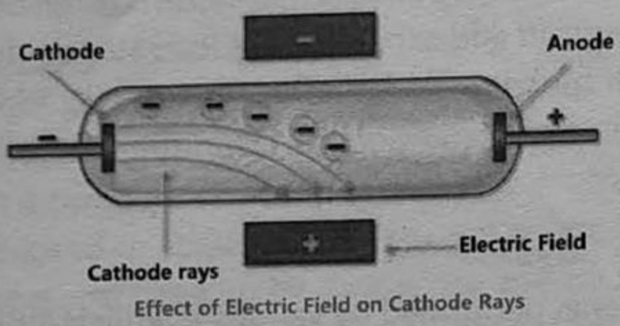


Figure 2.4 Cathode rays, deflecting in an electric field

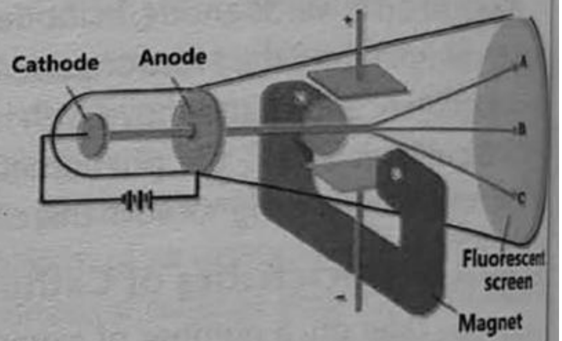


Figure 2.5 Cathode rays, deflecting magnetic field

On the basis of the above characteristics, it was concluded that the cathode rays were in fact negatively charged particles. G. J. Stoney gave these particles the name "electrons".

2.1.2 Mass of the Electron

The e/m ratio of electron is 1.7588×10^{11}C/kg and the charge is 1.6022×10^{-19}C. Making use of these two values the mass of electron "m" can be calculated as,

The charge to mass ratio, $\frac{e}{m} = 1.7588\times10^{11}\,\text{C/kg}$ (2.1)

The charge on an electron, $e = 1.6022\times10^{-19}\,\text{C}$

Putting the value of 'e', in equation (2.1), you get,

$$\frac{1.6022\times10^{-19}\,\text{C}}{m} = 1.7588\times10^{11}\,\text{C/kg}$$

By cross multiplication,

$$m \times 1.7588\times10^{11}\,\text{C/kg} = 1.6022\times\times10^{-19}\,\text{C}$$

$$m = \frac{1.6022\times10^{-19}\,\text{C}}{1.7588\times10^{11}\,\text{C.kg}^{-1}}$$

or $m = 9.1069\times10^{-31}\,\text{kg}$

or $m = 9.1069\times10^{-28}\,\text{g}$

Reading Check

What is a gas discharge tube? Write the conditions that are necessary for the production of cathode rays.

2.1.3 Canal Rays or Positive Rays – The Discovery of Proton

From a number of experiments, it was concluded that beside cathode rays (electrons) which carry negative charge, there are some positively charged particles present in an atom because atom as a whole is an electrically neutral particle.

In 1886, Eugen Goldstein used a discharge tube with holes (perforation) in the cathode. He observed that while cathode rays were moving away from the cathode, there were some other rays (streams of dim luminous glow), produced at the same time, moving towards cathode and passed through the perforated cathode and caused a glow on the wall opposite to the anode. These were called the canal rays because they were coming from perforations (canals). It was concluded that these rays must be positively charged and hence named positive rays.

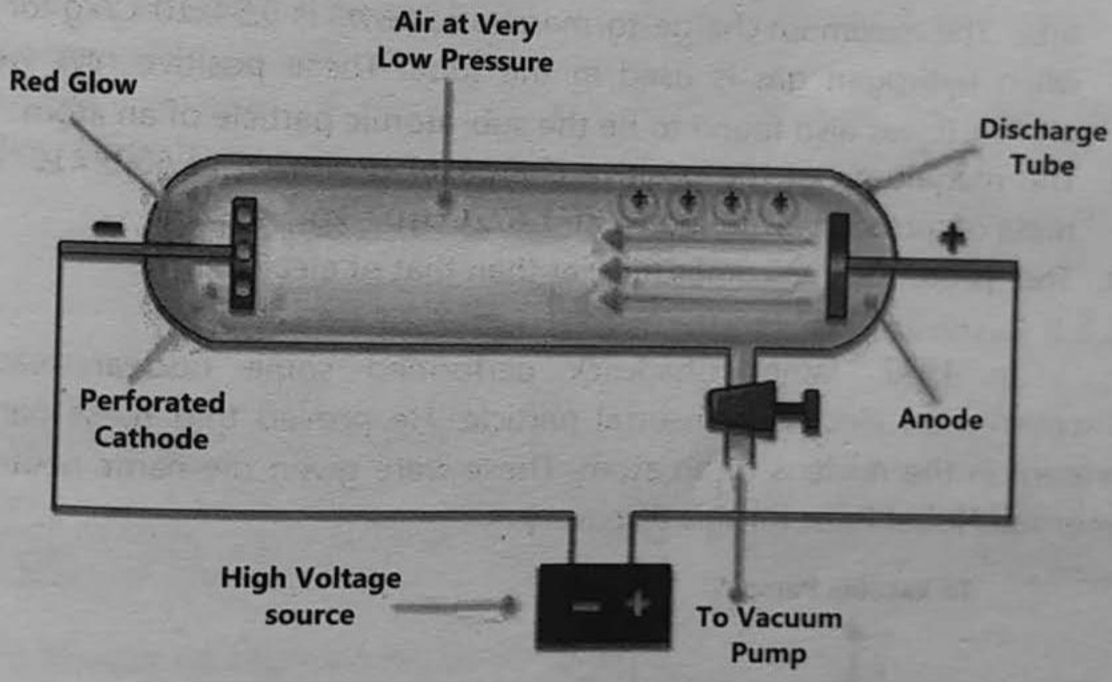


Figure 2.6 Canal ray tube

2.1.4 Positive Rays Production

When high-speed electrons (cathode rays) collide with the molecules of remaining gas in the discharge tube, they knock out one or more electrons from them. Thus, positive ions (cation) are produced.

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

These ions are positively charged and attracted by the cathode, some of which pass through the perforated cathode and strike at the walls of the tube.

2.1.5 Characteristic of Canal Rays or Positive Rays

Some of the characteristics of canal rays or positive rays are,

i. These rays travel in straight lines perpendicular to the anode surface.
ii. These rays have particle nature because these rays can move a small wheel placed in their path.
iii. These rays are deflected by electric and magnetic field in opposite directio electron.
iv. Their attraction towards cathode shows that they are positively char particles.
v. They produce fluorescence when strike with zinc sulphide (ZnS) layer.
vi. The charge-to-mass ratio (*e/m*) of positive rays is always less than cath rays.
vii. The e/m ratio changes with the nature of the gas placed in the disch tube. The maximum charge-to-mass ratio (*e/m*) is 9.54×10^{7}C/kg for these when hydrogen gas is used in the tube. These positive rays were na proton. It was also found to be the sub-atomic particle of an atom.
viii. The magnitude of the positive charge of proton is 1.6022×10^{-19}C and mass of proton was found to be 1.6726×10^{-27}kg.
ix. The proton is 1836 times heavier than that of electron.

2.1.6 Discovery of Neutron (Artificial Radioactivity)

In 1932, James Chadwick performed some nuclear reactions discovered an electrically neutral particle. He proved that these particles present in the nucleus of an atom. These were given the name neutron; he awarded Nobel Prize for this discovery.

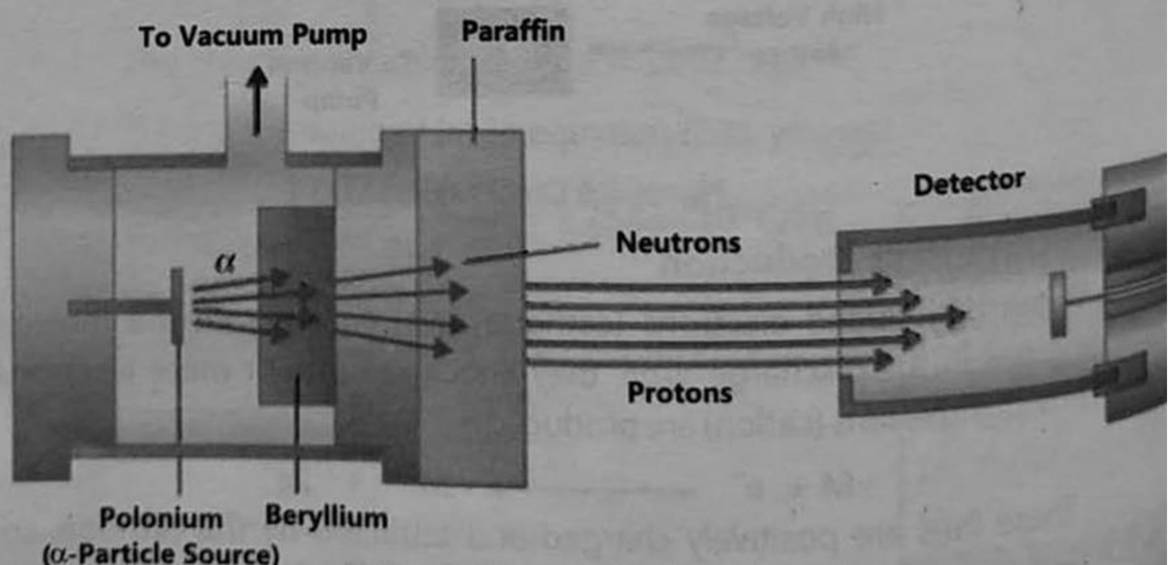


Figure 2.7 James Chadwick Experiment

He bombarded the nucleus of lighter atoms such as, Beryllium (Be) with α-particles produced from Polonium (Po). He observed that some highly penetrating radiations were produced. These radiations were neutral to the charge detector and were called neutrons. Examples of nuclear reactions (artificial Radioactivity) taking place are,

$$^{9}_{4}Be + ^{4}_{2}He\ (\alpha\text{- particle}) \longrightarrow ^{12}_{6}C + ^{1}_{0}n\ (\text{neutron})$$

$$^{27}_{13}Al + ^{4}_{2}He\ (\alpha\text{- particle}) \longrightarrow ^{30}_{15}P + ^{1}_{0}n\ (\text{neutron})$$

2.1.7 Characteristics of Neutron

Neutrons have the following characteristics.

i. Neutrons are highly penetrating particles.
ii. These particles carry no charge and are not deflected by electric or magnetic fields.
iii. These particles can knock out high-speed protons from substances like paraffin, water, cellulose etc.
iv. Neutron has mass 1.6749×10^{-27} kg and is 1842 times as heavy as electron.

Reading Check

Write an equation, which shows the production of neutron from the lighter atoms.

Table 2.1 Characteristics of the Three Fundamental Particles

Particles	Mass (kg)	Charge (C)	Unit Charge	Relative Atomic Mass (amu)
Electron	9.1069×10^{-31}	-1.6×10^{-19}	− 1	0.00055
Proton	1.6726×10^{-27}	$+1.6 \times 10^{-19}$	+ 1	1.0073
Neutron	1.6749×10^{-27}	0	0	1.0087

Bohr's Model of Hydrogen Atom

Rutherford atomic model set the foundation for the structure of an atom. According to the classical laws of Physics, an electron revolving around the nucleus, will lose energy continuously and will fall down into the nucleus. Thus, Rutherford model failed to explain why electrons did not do so.

In 1913, Neils Bohr proposed a new model of an atom based on the Quantum theory of energy and rectified the defects in Rutherford atomic model. With his model, he tried to explain why a revolving electron did not fall down into the nucleus.

The main postulates of the Bohr's model of an atom are,

1. Electrons are revolving around the nucleus in fixed circular paths called the orbits or shells. Each orbit is associated with a definite amount of energy. These orbits are also called energy levels.
2. The energy of the electron in an orbit is related to its distance from the nucleus. The farther the electron from the nucleus, the higher will be the energy.
3. As long as electrons are revolving around the nucleus in fixed circular orbit, they do not lose (radiate) or absorb energy.
4. When an electron jumps from a higher energy orbit to the lower energy orbit, it loses energy and when it jumps from lower energy orbit to higher energy orbit, it absorbs energy.

   The energy difference between two levels is given by,

   $\Delta E = E_2 - E_1 = h\nu$

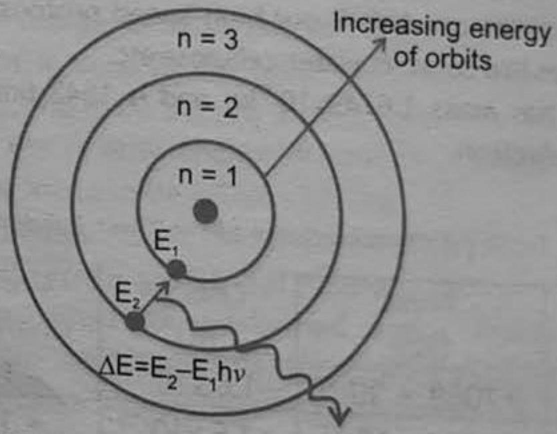


Figure 2.8 Energy Difference between Two Levels

Where, E_1 is the energy of lower orbit and E_2 is that of higher energy orbit. ΔE is the energy difference, h is the Planck's constant and ν is the frequency of radiation emitted or absorbed by the electron.

5. The angular momentum (mvr) of the electron in the hydrogen atom is quantized and can have values which are the whole number multiple of

$$mvr \propto \frac{h}{2\pi}$$

$$\text{that is; } mvr = \frac{nh}{2\pi}$$

Where, 'n' is the whole number say, 1, 2, 3, 4.... and represent the shell, 'm' is the mass of electron, 'v' is the velocity of electron, 'r' is the radius of the orbit in which electron are revolving and 'h' is the Planck's constant, its value is 6.6262×10^{-34} Js.

Based on these assumptions, Bohr presented a model for hydrogen atom that can best explain the spectrum of hydrogen atom.

2.2 Application of Bohr's Model

2.2.1 Derivation of Radius, Energy, Frequency, Wave Length and Wave Number

1. Derivation of Radius

Bohr had assumed that proton, being 1836 times heavier, remains stationary with respect to electron, which revolves around the nucleus in the hydrogen atom.

Consider an atom of hydrogen with atomic number 'Z'. It has 'Z' number of proton with nuclear charge 'Ze'. An electron of charge 'e' is revolving around the nucleus in circular path (orbit) of radius 'r', with velocity 'v'. According to Coulomb's law, the electrostatic force of attraction between the electron and the nucleus is given by,

$$F_{\text{Coulombic}} \propto \frac{q_1 q_2}{r^2}$$

$$F_{\text{Coulombic}} = k\frac{q_1 q_2}{r^2} \qquad (2.2)$$

As,

Charge on nucleus(proton), $q_1 = Ze$

Charge on electron, $q_2 = e$

$$F_{\text{Coulombic}} = k\frac{Ze.e}{r^2}$$

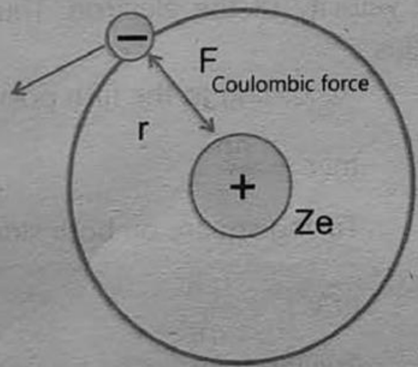


Figure 2.9: A hydrogen atom with atomic number 'Z'

Where the proportionality constant $k = \frac{1}{4\pi\varepsilon_o}$ and ε_o is the vacuum permittivity constant and is a measure of how easy it is for electrostatic force to pass through the vacuum (free space) and its value is $8.854 \times 10^{-12} C^2N^{-1}m^{-2}$. Putting the value of k in equation (2.2), you get

$$F_{\text{Coulombic}} = \frac{Ze^2}{4\pi\varepsilon_o r^2} \qquad (2.3)$$

This centripetal force, provided by the Columbic force of attraction is balanced by the centrifugal force, $\frac{mv^2}{r}$.

$$F_{Centrifugal} = \frac{mv^2}{r} \qquad (2.4)$$

As forces on both sides are equal, opposite and balance each other, so equating equation (2.3) and (2.4) you get,

For a stable orbit,

$$F_{Centrifugal} = F_{Coulombic}$$

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

Or $$mv^2 = \frac{Ze^2}{4\pi\varepsilon_o r} \qquad (2.5)$$

Rearranging $$r = \frac{Ze^2}{4\pi\varepsilon_o v^2 m} \qquad (2.6)$$

Equation (2.6) shows that radius is inversely proportional to the square of the velocity of the electron. Thus, electron moves faster in an orbit of smaller radius.

According to the fifth postulate of Bohr's atomic model, you have

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

Taking square on both sides, you have,

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

Solving for 'v^2'

$$v^2 = \frac{n^2h^2}{4\pi^2m^2r^2} \qquad (2.7)$$

Activity No. 1

Looking into the values of r_1, r_2, r_3 and r_4 and $r_2 - r_1$, $r_3 - r_2$ and $r_4 - r_3$, etc. What do you conclude about the spacing between the orbits?

Substituting the value of v^2 from equation (2.7) into equation (2.6) and solving for 'r', you get,

$$r = \frac{n^2h^2\varepsilon_o}{Ze^2\pi m} \qquad (2.8)$$

For hydrogen Z = 1, so the equation (2.8), for radius of hydrogen atom is,

$$r = n^2\left[\frac{\varepsilon_o h^2}{\pi e^2 m}\right] \qquad (2.9)$$

Where the terms in brackets are constant quantities, and are equal to,

$$\left[\frac{\varepsilon_o h^2}{\pi e^2 m}\right] = \alpha_o$$

$$\alpha_o = 0.529\,\mathring{A}$$

$$r = n^2 \times \alpha_o$$

$$r_n = n^2 \times 0.529\ \mathring{A} \qquad (2.10)$$

For hydrogen the radius of 1st and 2nd Bohr's orbits will be,

When, n = 1

$$r_1 = (1)^2 \times 0.529\,\mathring{A} = 1 \times 0.529\,\mathring{A} = 0.529\,\mathring{A}$$

When, n = 2

$$r_1 = (2)^2 \times 0.529\,\mathring{A} = 4 \times 0.529\,\mathring{A} = 2.116\,\mathring{A}$$

Example 2.1

Calculate the radius of 3rd and 4th orbits of hydrogen atoms.

Solution:

You have to calculate r_3 (for n=3) and r_4 (n=4), using equation (2.9),

n = 3

$$r_3 = n^2\,(0.529\,\mathring{A})$$

$$r_3 = (3)^2 \times 0.529\,\mathring{A} = 9 \times 0.529\,\mathring{A} = 4.761\,\mathring{A}$$

n = 4

$$r_4 = (4)^2 \times 0.529\,\mathring{A} = 16 \times 0.529\,\mathring{A} = 8.464\,\mathring{A}$$

Practice Problem 2.1

Calculate the radius of 5th and 6th orbits of hydrogen atom.

2. Derivation of Energy of the Electron in an Orbit

Electron in an atom possesses kinetic energy (K.E.) due to its motion and potential energy (P.E.) due to the attractive force between protons and electrons. The total energy of electron (E) in particular orbit is the sum of its K.E. and P.E.,

$$E = K.E. + P.E. \qquad (2.11)$$

Where $$K.E. = \frac{1}{2}mv^2 \qquad (a)$$

And P.E. is equal to the work done in bringing the electron from infinity (where there is no interaction with the nucleus) to a point at a distance 'r' from the nucleus (where interaction exists). In doing so work must be done, this is given by, Work done = P.E. = - force x distance (r)

Here the force of attraction between the electron and the nucleus is as given by equation (2.3), therefore,

$$P.E. = -\frac{Ze^2}{4\pi\varepsilon_0 r^2} \times r$$

$$P.E. = -\frac{Ze^2}{4\pi\varepsilon_0 r} \qquad (b)$$

Here the negative sign indicates that P.E. decreases when electron is brought from infinity to a point at a distance 'r' from the nucleus.

Putting values of K.E. and P.E. in equation (2.11), you get,

$$E = \frac{1}{2}mv^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} \qquad (2.12)$$

Now substituting the value of mv^2 from equation (2.5) into equation (2.12) you get,

$$E = \frac{1}{2}\left(\frac{Ze^2}{4\pi\varepsilon_0 r}\right) - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$E = -\frac{Ze^2}{8\pi\varepsilon_0 r} \qquad (2.13)$$

Now, putting the value of 'r' from equation (2.8), in equation (2.13) you get,

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

For n^{th} orbit, the energy of electron will be,

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

$$E_n = -\frac{e^4m}{8\varepsilon_o^2 h^2} \times \frac{Z^2}{n^2} \qquad (2.14)$$

For hydrogen atom, Z = 1, so,

$$E_n = -\frac{e^4m}{8\varepsilon_o^2 h^2}\left(\frac{1}{n^2}\right) \qquad (2.15)$$

By inserting the values for various parameters it comes out to be,

$$\frac{me^4}{8\varepsilon_o^2 h^2} = 2.18 \times 10^{-18} \text{J/atom}$$

Thus, equation 2.15 becomes as,

$$E_n = -2.18 \times 10^{-18}\left(\frac{1}{n^2}\right) \text{ J/atom}$$

Or

$$E_n = -2.18 \times 10^{-18}\left(\frac{1}{n^2}\right) \times \frac{6.022 \times 10^{23}}{1000} \text{kJ/mol}$$

$$E_n = -\frac{1312.36}{n^2} \text{ kJ/mol} \qquad (2.17)$$

Equations (2.16) and (2.17) show that energy of the electron in an atom depends on the value of 'n', it is, therefore, called the principal quantum number. Further, the energy state associated with, n = 1 is called the ground state energy and represents the lowest energy state. All energy states higher than n=1 are called excited state for hydrogen atom.

Activity No. 2

You may also try for $E_2 - E_1$, $E_3 - E_2$, $E_4 - E_3$ and $E_5 - E_4$ etc. to check what happens to the difference in energies between two successive energy levels (orbits) as you move away from the nucleus?

The energy associated with the electron in various orbits (different 'n' values), can be calculated using equation (2.17).

When n= 1, $E_1 = -1312.36$kJ/mol

n=2, $E_2 = -328.32$kJ/mol

n=3, $E_3 = -145.92$kJ/mol

It is evident from the above calculations that the energy of electron increases as the value of 'n' increases.

Practice Problem 2.2

Calculate the energy of 4th and 5th levels of the hydrogen atom.

3. Energy Difference between Two Orbits

You have the energy equation 2.14,

$$E = -\frac{e^4 m}{8\varepsilon_o^2 h^2} \times \frac{Z^2}{n^2}$$

Let E_1 be the energy of orbit n_1 and E_2 be the energy of the orbit n_2, then the above energy equation, for the two orbits

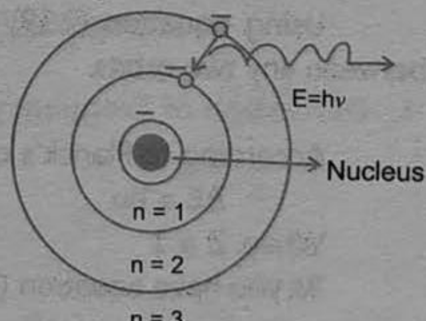


Fig 2.10 Energy Difference between Two Orbits

can be written as, $E_1 = -\frac{e^4m}{8\varepsilon_o^2h^2} \times \left(\frac{Z^2}{n_1^2}\right)$ for lower energy level,

and $E_2 = -\frac{e^4m}{8\varepsilon_o^2h^2} \times \left(\frac{Z^2}{n_2^2}\right)$ for higher energy level

Therefore, change in energy, $\Delta E = E_2 - E_1$

Then,

Putting the values in the above equation, you get,

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

For hydrogen atom, Z = 1, so,

$$\Delta E = \frac{e^4m}{8\varepsilon_o^2h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad (2.18)$$

As you have,

$$\frac{me^4}{8\varepsilon_o^2h^2} = 2.18 \times 10^{-18}\ \text{J/atom}$$

Thus, equation (2.18) becomes,

$$\Delta E = 2.18 \times 10^{-18}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\ \text{J/atom} \qquad (2.19)$$

Or

$$\Delta E = 1312.36\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\ \text{kJ/mol} \qquad (2.20)$$

Using equation (2.19) or (2.20), you can calculate the energy difference between any two orbits.

4. Derivation of Frequency, Wavelength and Wave Number

According to Planck's quantum theory,

$\Delta E = h\upsilon$

When, Z = 1

As you have equation (2.18)

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

Or

$$\Delta E = h\upsilon = \frac{e^4 m}{8\varepsilon_o^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad (2.21)$$

i. **Frequency**

For the calculation of frequency of radiation emitted or absorbed during electronic transitions between the orbits, the equation (2.21) becomes,

$$\upsilon = \frac{e^4 m}{8\varepsilon_o^2 h^2 \times h}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) Hz$$

$$\upsilon = \frac{e^4 m}{8\varepsilon_o^2 h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) Hz \quad (2.22)$$

ii. **Wave number**

The wave number of radiation can be calculated as,

The equation for velocity of radiation is,

$$c = \upsilon\lambda$$

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

As wave number $(\bar{\upsilon})$ is reciprocal of wavelength i.e.,

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

So, you can write,

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

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

or,

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

Putting the value of v from equation (2.22), you get,

$$\bar{\upsilon} = \frac{\upsilon}{c} = \frac{1}{\lambda} = \frac{e^4 m}{8\varepsilon_o^2 h^3 c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) m^{-1} \quad (2.23)$$

As you have,

$$\frac{me^4}{8\,\varepsilon_o^2 h^3 c} = R = 1.09678 \times 10^7 m^{-1}$$

Where R is called Rydberg's constant. Therefore, you can write the equation (2.23) as,

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

$$\bar{\upsilon} = 1.09678 \times 10^7 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) m^{-1} \quad ....(2.24)$$

Equation (2.23) and equation (2.24) give the value for the wave number of the photon emitted or absorbed, when electron jumps between any two orbits.

Reading Check

1. Write the equation used for the determination of radius of hydrogen atom.
2. Write the energy equation for the n^{th} orbit.

Practice Problem 2.3

In a hydrogen atom, an electron jumps from 3[rd] orbit to 1[st] orbit. Find out th frequency and wavelength of the spectral line.

2.2.2 Spectrum of Hydrogen Atom

Spectrum

A band or series of radiations in order of increasing or decreasing order o wavelengths or frequencies when light is resolved into it constituent radiations i called spectrum.

For example, spectrum of sunlight, hydrogen, electric bulb light. Th instrument used to study the spectra (plural of spectrum) is calle spectrophotometer. The spectrum from an ordinary light or sunlight consists of tw main parts, visible and invisible.

Spectrum is of two types.

a. Continuous spectrum
b. Line spectrum

a. Continuous Spectrum

The spectrum, which has no dark or bright spaces between lines, mean n clear boundary can be seen between the lines (colours) is called continuo spectrum.

Different colours diffuse into each other, so that the boundaries of differe colours cannot be marked, for example, rainbow, the spectrum of sunlight an ordinary tungsten filament lamp. When the sunlight or ordinary electric light i passed through a prism, it is dispersed into seven colours; these colours form th continuous spectrum as shown in the figure 2.11.

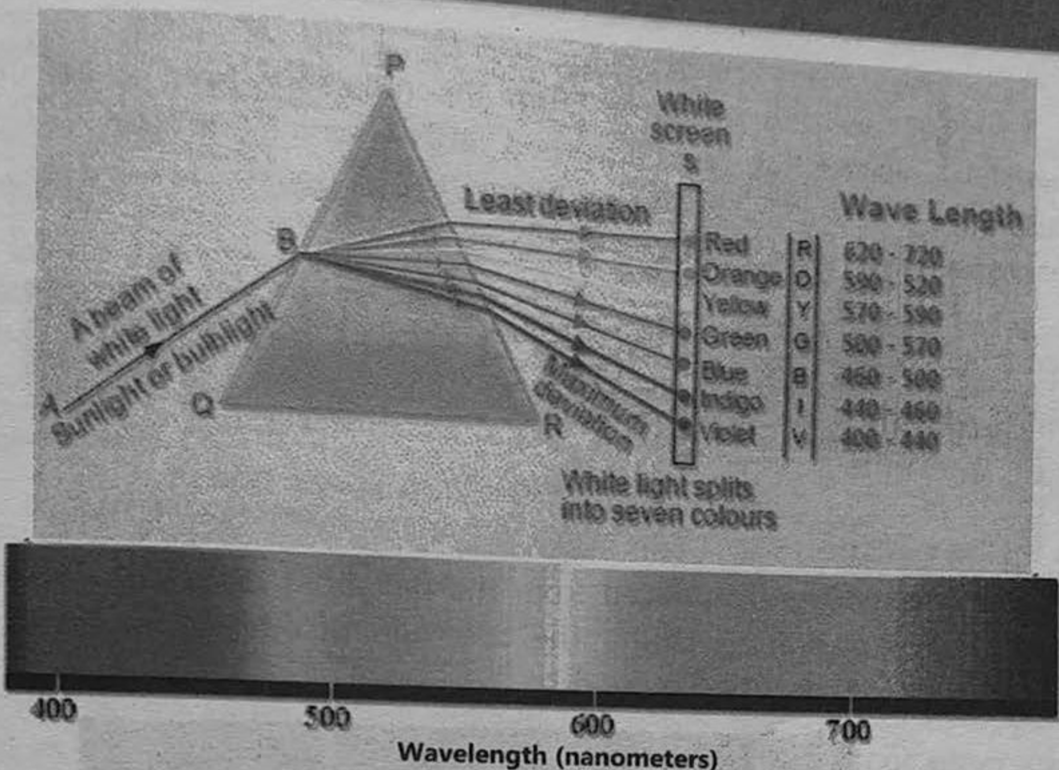


Figure 2.11 Continuous Spectrum of sun light

b. Line Spectrum

The spectrum, which consists of lines with dark or bright spaces between them, is called line spectrum. In this type of spectrum, there is a clear-cut boundary between the colour bands. Line spectrum is also called atomic spectrum. Each element emits light of definite wavelength. Therefore, various elements can be distinguished with the help of line spectrum as shown in the figure 2.12.


Sodium Spectrum


Helium Spectrum

Fig.2.12 Line Spectrum

The line spectrum may be,

i. Line absorption spectrum
ii. Line emission spectrum

Tidbit

Sodium (Na^+) ion impart yellow colour to the Bunsen flame, indicating that it absorbs (and then emits) radiation in this region, strontium (Sr^{+2}) ion gives red colour and potassium (K^+) ion gives violet colour to the Bunsen flame.

i. Line Absorption Spectrum

The spectrum produced from the radiations from which the rays of particular wavelength are absorbed after passing through the absorbing substance. The spectrum obtained consists of a series of dark lines in a bright background, is called atomic absorption spectrum.

Figure 2.13 Hydrogen Absorption Spectrum

ii. Line Emission Spectrum

The line spectrum produced from the radiations emitted by a substance is called the emission spectrum. The spectrum of emitted radiations produces bright lines with dark background.

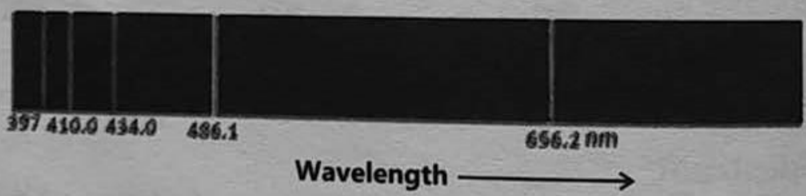


Figure 2.14 Hydrogen Line Emission Spectrum

Spectrum of Hydrogen Atom

Bohr proposed that the energy, which is emitted or absorbed by an atom, must have specific values. The change in energy when an electron moves to higher or lower energy levels is not continuous, rather, it is discrete (energy pulse).

When a hydrogen atom is excited and absorbs energy from surrounding, its electron is moved to higher energy level, a dark band is obtained but when an electron jumps from a higher energy orbit to the lower energy orbit, it radiates energy and bright band is formed in the line spectrum.

Experimentally the line emission spectrum of hydrogen can be obtained by passing electric discharge through the hydrogen gas contained in a discharge tube at low pressure. The light radiations emitted are then examined with the help of a **spectroscope.** The bright lines recorded on the photographic plate constitute the atomic spectrum of hydrogen as shown in figure 2.15.

In 1884, J. J. Balmer observed that there were four prominent coloured lines i.e. red, blue-green, blue-violet and violet in the visible hydrogen spectrum.

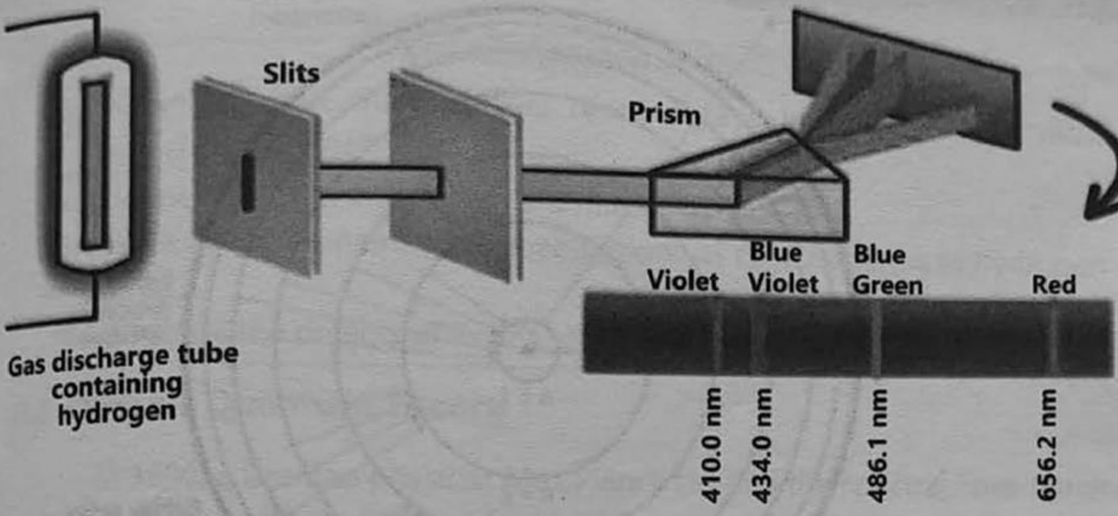


Figure 2.15 Atomic Spectrum of Hydrogen

The above series of four lines in the visible spectrum of hydrogen was named as the **Balmer Series.** In addition to Balmer Series, four other spectral series were discovered in the infrared and ultraviolet regions of the hydrogen spectrum. Thus, in all you have **Five Spectral Series** in the atomic spectrum of hydrogen and are named after the discoverer of these series. These are:

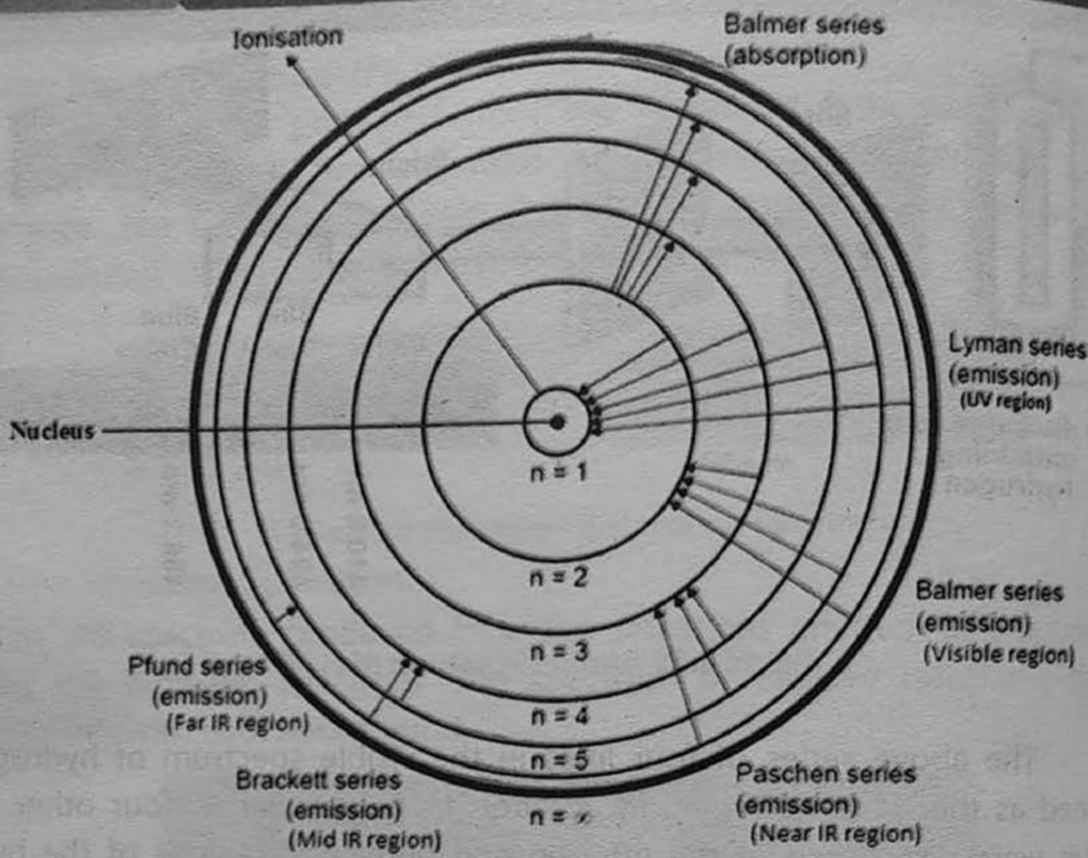
1. **Lyman Series** (Ultraviolet region), is obtained, when electron returns to its ground state, i.e. $n_1=1$ from higher energy levels, such as, $n_2= 2,3,4,5.$ etc.

2. **Balmer Series** (Visible region), is obtained, when electron returns to the 2nd energy level, i.e. $n_1 = 2$ from higher energy levels, $n_2 = 3,4,5,6$ etc.

3. **Paschen Series** (Near Infrared region), is obtained, when electron returns to the 3rd energy level, i.e. $n_1 = 3$ from higher energy levels, $n_2 = 4, 5, 6$ etc.

4. **Brackett Series** (Mid Infrared region), is obtained, when electron returns to the 4th energy level, i.e. $n_1 = 4$ from higher energy levels, $n_2 = 5, 6, 7$ etc.

5. **Pfund Series** (Far Infrared region), is obtained, when electron returns to the 5th energy level, i.e. $n_1 = 5$ from higher energy levels, $n_2 = 6, 7$ etc.



Spectral series	Emission	Absorption	Frequency
Lyman series	Down to n =1	Up from n =1	Ultraviolet
Balmer series	Down to n =2	Up from n =2	visible light
Paschen series	Down to n =3	Up from n =3	Near infrared
Brackett series	Down to n =4	Up from n =4	Mid infrared
Pfund series	Down to n =5	Up from n =5	Far infrared

Figure 2.16 Hydrogen Spectral Series in Various Regions

2.2.3 Defects of Bohr's Model

The great success of Bohr's model of atom lies in its ability to predict lines in the hydrogen spectrum. It also explains spectra of other hydrogen like simple ions like He^{+}, Li^{++}, Be^{+++} but fails to explain the following.

1. It is unsuccessful to explain the spectrum of more complicated atoms (multi electron system).
2. It cannot explain the multiplicity of the spectral lines (fine structure) observed under a high resolving power spectrometer.
3. It cannot explain the effect of magnetic field (Zeeman effect) and electric field (Stark effect) on the spectra of hydrogen atom.
4. Modern research no longer believe in well- defined electron orbits as assumed in Bohr's model.

Self-Assessment

1. Name any four characteristics of canal rays, including charge, mass and charge to mass ratio.
2. Define spectrum and name its different types.
3. Write down the names and their regions of spectral series of hydrogen atom.
4. What are the defects of Bohr's atomic model?

2.3 Planck's Quantum Theory

In 1900, a German physicist Max Planck studied the spectral lines obtained from hot black body at different temperatures. He observed that light radiation was produced discontinuously by the particles of the hot body, which were vibrating with a specific frequency. These vibrations increased with an increase in temperature. Thus, Planck proposed a new theory called Planck's quantum theory.

The main postulates of this Planck's quantum theory are,

1. Energy emitted or absorbed by a hot body is not in a continuous form but in small units of waves. These 'unit waves' or 'wave packets' or 'pulses of energy' are called quanta (singular Quantum). In case of light energy, the quantum of energy is often called photon.

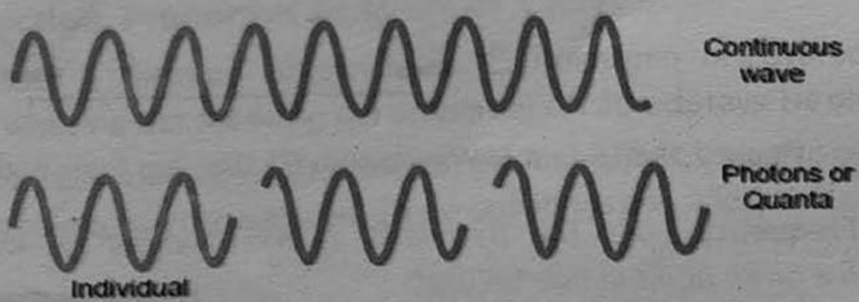


Figure 2.17 Continuous Wave and Photons or Quanta

2. The energy, E, associated with quantum or photon is directly proportional to frequency (υ) of the radiation.

$$E \propto \upsilon$$

Or $$E = h\upsilon \qquad (2.23)$$

This is called Planck's equation. Where 'υ' (nu) is the frequency of the emitted radiation and 'h' is the Planck's constant and its value is 6.6262×10^{-34} Js.

The frequency 'υ' is also related to wavelength and speed of radiation the equation,

$$c = \upsilon\lambda \qquad (2.24)$$

Where 'c' is the speed of light and 'λ' is the wavelength of any radiation.

3. A body can emit (or absorb) either one quantum ($h\upsilon$) or any whole number multiple of this unit.

   $E = nh\upsilon$

   Where n = 1, 2, 3... etc. It means energy is quantized.

2.3.1 Postulates with Derivation of $E = hc\bar{\upsilon}$

Wavelength (λ): *The wavelength is defined as the distance between adjacent crests or troughs of a wave.*

Wavelength is denoted by the Greek letter λ (lambda). It is expressed in centimeters or meters or in *angstrom* units. One angstrom, Å, is equal to 10^{-10} m. It is also expressed in nanometers (1nm = 10^{-9} m).

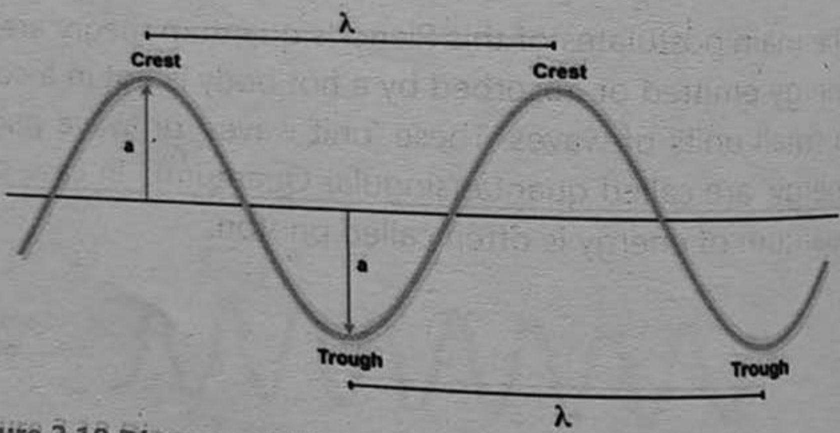


Figure 2.18 Diagram of Wavelength (λ) showing Crest and Trough

Frequency (υ): *The frequency is the number of waves, which pass through a given point in one second.*

Frequency is denoted by the letter υ (nu) and its unit is *hertz* (Hz)

Speed(c): *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 meter per second (ms^{-1}). The velocity of light is $3 \times 10^{8} ms^{-1}$ in vacuum.

Tidbit

υ = f, both are used as symbol of frequency. In chemistry, 'υ' is used as symbol of frequency and 'f' is used as symbol of frequency.

Wave number ($\bar{\upsilon}$): *It is the number of waves per unit length.* This is reciprocal of the wavelength and is given the symbol $\bar{\upsilon}$ (nu bar). That is,

$$\bar{\upsilon} = \frac{1}{\lambda} m^{-1} \text{ or } cm^{-1}$$

The frequency of a photon is inversely proportional to its wavelength,

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

We have also,

$c = \upsilon\lambda$ (where 'c' is the velocity of light)

$$\upsilon = \frac{c}{\lambda} \qquad (2.25)$$

As $E = h\upsilon$ (2.26)

Putting the value of υ in equation (2.26), you get,

$$E = \frac{hc}{\lambda} \qquad (2.27)$$

As you know $\bar{\upsilon} = \frac{1}{\lambda}$

Putting the value of $1/\lambda$ in equation (2.27), you get,

$$E = hc\bar{\upsilon} \qquad (2.28)$$

Thus, it can be concluded that the energy of photon is related to the frequency, wave length and wave number.

2.4 X – Rays

2.4.1 Production, Properties and Uses of X-Rays

In 1895, a German physicist, W. C. Roentgen discovered the X-rays accidentally while he was studying the properties of cathode rays. He observed that, *when high energy electrons (cathode rays) strike the heavy metal used as an anode, some sort of radiations are produced. These radiations are called X – rays.*

Production of X- Rays

X-Rays can be produced by a number of ways. The most important methods are

1. Roentgen method (Gas Tube)
2. Coolidge Method
3. By using betatron (an electron accelerating machine).

Roentgen Methods of X-Rays Production

It consists of special type of discharge tube as shown in the figure 2.19.

The pressure inside the tube is reduced to 0.001 mm of Hg. The voltage is kept 30,000 to 50,000 volts. The cathode is a heated filament and due to high potential difference between the cathode and anode, electrons are emitted from cathode and travel towards the anode where it strikes with high speed. Due to some electronic transition, high energy X-ray photons are emitted from the anode.

The cathode is concave shaped with its focus on the anode. The electrons emitted from cathode are focused on small portion of anode and X – rays are emitted from that small portion of anode.

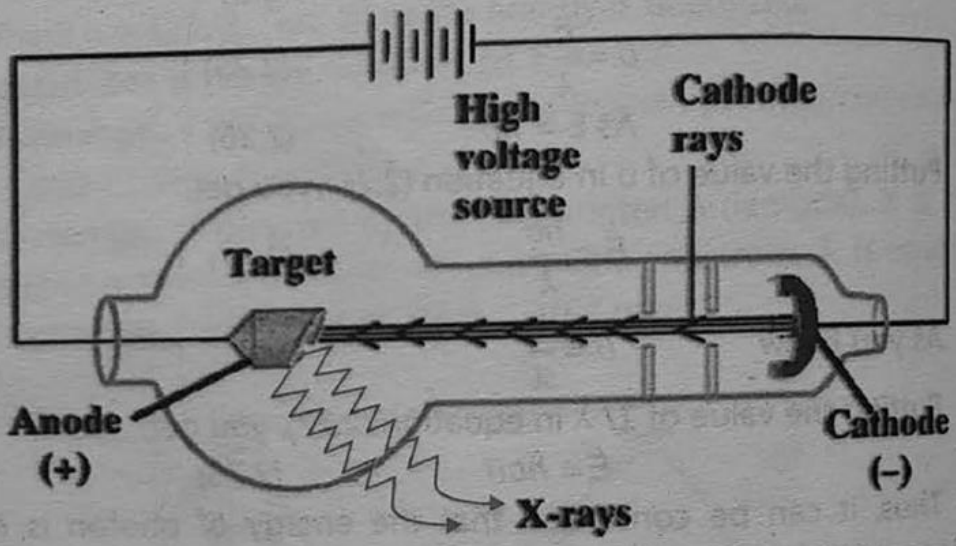


Figure 2.19 X – Rays Production by Roentgen Method

Properties of X-Rays

X–rays are electromagnetic radiations and have very high frequency (shorter wavelengths). The wavelength of the radiations constituting X-rays ranges from 10^{-2} Å to 10^{+2} Å (0.001 nm to 10nm). The following are the main properties of X –rays.

1. These rays travel in straight line.
2. These rays are not deflected by electric and magnetic field.
3. They are neutral in nature.
4. They have the ability to ionize the gases. The ionizing power depends on the intensity of the X – rays beam.
5. They can produce fluorescence in substances like NaCl, salts, glass etc.
6. These rays can be reflected and refracted.
7. These rays can be diffracted by crystalline substances.
8. These rays can penetrate through many substances. Their penetration

power is different in different substances.

9. These rays can blacken the photographic plate.

Uses of X-Rays

Following are the main uses of X-rays.

1. X-rays are used in the field of medicine due to different penetrating power through the flesh and bones of the body.
2. X-rays are used in the XRD analysis (X-rays diffraction analysis) for measuring space between the ionic layers of a crystalline substance.
3. X-rays are used for the ionization of gases.
4. X-rays were used by Watson and Crick to identify the double helix structure of DNA.

2.4.2 Types of X-Rays

There are two types of X-ray spectra

1. Continuous 2. Characteristic

1. Continuous X-rays

The continuous X-rays spectrum appears when an electron previously accelerated by a high potential difference is deflected by the nucleus of target atom of anode. This deflection results in loss of energy of the incoming electrons, which is released as X-ray photons. Thus, the maximum X-rays frequency possible emitted is equal to the maximum energy of the incoming electrons.

2. Characteristic X-rays

The second type of X-rays spectrum arises when an incoming electron has enough energy to remove an electron of target atom from its inner shell. The other electrons of atom will rearrange to fill the missing space and a set of X-rays lines will be emitted corresponding to these electron transitions from outer shells to inner shells.

This X-rays spectrum has definite series named as K-series, L-series etc. The production of these series is described as follow.

Supposes K–shell electron is knocked out from an atom creating a vacancy in the K–shell. Then electron from either, L, M, or N shell will quickly jump down in order to fill the vacancy in the K–shell, emitting the excess energy in the form of X-rays photon. An X-rays photon emitted due to transition of L–shell to the vacant space in the K-shell is called $K\alpha$ characteristics X-rays. The transition from M and N-shells to K-shell gives rise to $K\beta$ and $K\gamma$ characteristics X-rays, respectively. These X-rays are of high energy. Similarly L, M, and N series characteristics X-rays, relatively of low energy, are produced due to the ejection of electrons from L, M and N – shells, respectively, and produce Lα, Lβ, Mα, Mβ etc. characteristics X –rays.

Inside the same group of lines, α denotes a transition between two consecutive levels, β denotes a transition skipping one level, etc.

Every metal has its own characteristic X-rays line spectrum. This line spectrum is the characteristic of target material used. This characteristic X-rays spectrum has discrete spectral lines.

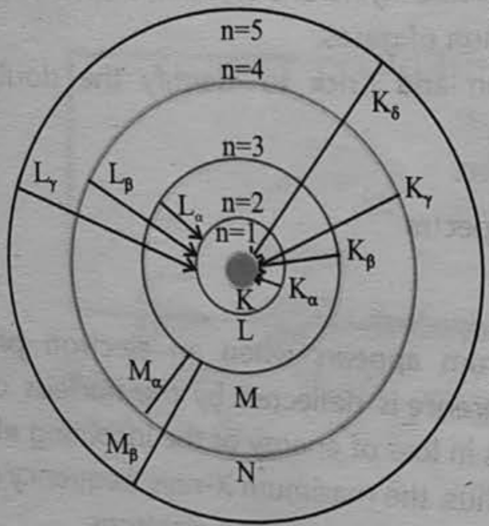


Figure 2.20 Inner - Shell transition

Tidbit

The spectral lines of x-rays could be classified into two different distinct groups, shorter wavelengths are identified by K- series and Longer wavelengths are identified by L-series and M-series etc.

2.4.3 X – Rays and Atomic Number (Z)

In 1913, Henry Moseley observed that the frequency of emitted X - rays depends upon on the material used as target element (anode). Greater the number of positive charge on the nuclei of the target element, greater will be the frequency of the emitted X - rays. Therefore, each element was assigned a characteristic number equal to the positive charges on the nucleus of the atom. The number of unit positive charges on the nucleus of an atom of an element is termed as atomic number; it is represented by 'Z'. Since the positive charge on the nucleus is due to the presence of protons inside the nucleus, the number of unit positive charge will directly indicate the number of protons. Thus, the atomic number of an element is the number of protons present in its nucleus.

Reading Check

- What are X- rays? Write its different types.
- Define Planck's quantum theory and prove that $E = hc\bar{\upsilon}$

2.4.4 Moseley's Experiment

Mosley used the discharge tube used by Roentgen for the discovery of X – rays. He performed a number of experiments and proved that positive charge on the nucleus was the fundamental property of the element. Moseley used different X-rays tubes with anodes of different materials and took spectrum of X – rays in each case, by allowing them to fall on a photographic plate. It was observed that the wavelength of X – rays depends on the element used as anode and excitation voltage.

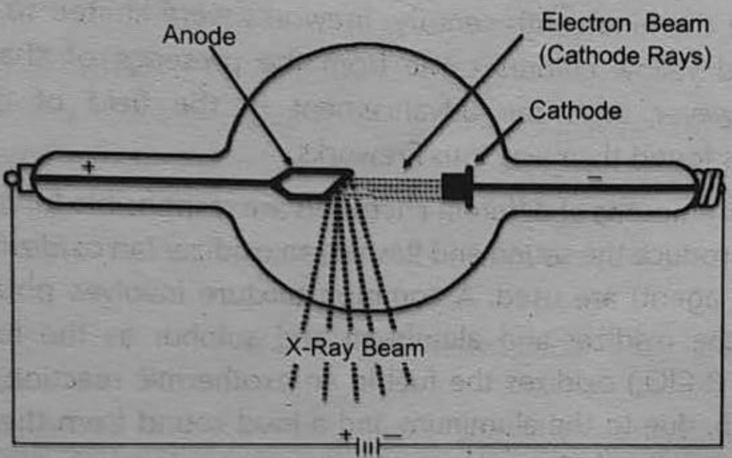


Figure 2.21 Moseley's Experiment (X- Rays tube)

2.4.5 Moseley's Law

Moseley showed that the square root of the frequency ($\sqrt{\upsilon}$) of a spectral line is directly related with the nuclear charge (Z), provided that the excitation potential is kept constant.

On the basis of results, he suggested that, "the square root of the frequency ($\sqrt{\upsilon}$) is directly proportional to the atomic number (Z) of an element."

Mathematically, it can be written as,

$$\sqrt{\upsilon} \propto Z$$

In order to get the accurate results, Mosley modified this relationship as,

> **Reading Check**
> Define Moseley's law.

$$\sqrt{\upsilon} \propto (Z-b)$$

Where 'b' is a constant and is known as screening constant. For spectral lines of K – series, b = 1. Thus,

$$\sqrt{\upsilon} = a\,(Z-b) \qquad (2.29)$$

Where "a" is the proportionality constant, equation (2.29) represents Moseley's law. It is used for the calculation of the atomic number Z, if the frequencies of the spectral lines are known.

STS Science, Technology and Society

Fireworks Display

The art of using mixtures of chemicals to produce fire is an ancient one. Before the nineteenth century, fireworks were limited to few chemicals. Orange and yellow colours came from the presence of charcoal and iron filings. However, with the advancement in the field of chemistry, new compounds found their way into fireworks.

Small amounts of different chemicals are responsible for most of the amazing effects. To produce the sound and flashes, an oxidizer (an oxidizing agent) and a fuel (a reducing agent) are used. A common mixture involves potassium perchlorate ($KClO_4$) as the oxidizer and aluminum and sulphur as the fuel. The potassium perchlorate ($KClO_4$) oxidizes the fuel in an exothermic reaction, which produces a brilliant flash, due to the aluminum and a loud sound from the rapidly expanding gases. For a colour effect, an element with a coloured emission spectrum is included. Recall that the electrons in atoms can be raised to higher-energy orbitals when the atoms absorb energy. The excited atoms then release this excess energy by emitting light of specific wavelengths, often in the visible region.

In fireworks, the energy to excite the electrons comes from the reaction between the oxidizer and fuel. Sodium imparts yellow colour in fireworks, red colour come from strontium salts. Barium salts give a green colour; copper salts give a blue colour in fireworks.

2.5 Quantum Numbers and Orbitals

Quantum numbers are certain numbers (which are a set of numerical values) that give information about the designation (energy, shape of orbital etc.) of an electron in an atom.

Quantum numbers are important because they can be used to determine the electronic configuration of an atom and the probable location of its electrons. There are four quantum numbers, three of which have been derived from the mathematical solution of the Schrödinger equation for the hydrogen atom. They are called the principle quantum number, the azimuthal quantum number and the magnetic quantum number. These quantum numbers will be used to describe atomic orbitals and to label electrons that reside in them. A fourth quantum number, called the spin quantum number was discovered independently and describes the behaviour of a specific electron and completes the description of electrons in atoms. These four quantum numbers are,

i. Principal quantum number (n)
ii. Azimuthal quantum number (l)
iii. Magnetic quantum number (m)
iv. Spin quantum number (s)

2.5.1 Principle Quantum Number (n)

This quantum number denotes the principal shell to which the electron belongs. This quantum number represents the main energy level or shell in which the electron is present. It represents the average distance of the electron from the nucleus. The principal quantum number 'n' can have non-zero, positive, integral values n = 1, 2, 3...

- An electron with $n = 1$, has the lowest energy and is bound most firmly to the nucleus.
- Higher the value of '*n*' means that the size of the energy level is larger, with a higher probability of finding an electron farther from the nucleus.
- Energy of the electron depends on the value of 'n', lower the value of 'n' lower will be the energy of the electron in that orbit and vice versa.

The letters K, L, M, N, O, P and Q are also used to designate the energy levels or shells of electrons with 'n' value of 1, 2, 3, 4, 5, 6, 7, respectively. The maximum number of electrons that is possible in any energy level of principal quantum number is calculated by the formula $2n^2$.

For example, if n = 1, maximum number of electrons possible = $2n^2 = 2\times(1)^2 = 2$ and so on.

2.5.2 Azimuthal Quantum Number (ℓ)

Chemists use a variety of names for the second quantum number. They are referred as angular momentum quantum number, the azimuthal quantum number, the secondary quantum number or the orbital-shape quantum number. Regardless of its name, the second quantum number refers to the energy sublevels within each principal energy level/shell.

Azimuthal Quantum Number defines the shape of the orbital occupied by the electron and the angular momentum of the electron. It also shows the number of sub-shell in a given shell. It also shows us the shape of orbital. This quantum number is represented by 'ℓ'.

For any given value of the principal quantum number, *n*, the azimuthal quantum number ℓ may have all whole number 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 energy level is numerically equal to the principal quantum number of the level under consideration.* These sublevels are also symbolized by letters s, p, d, f etc. The letters s, p, d and f have been taken from the old spectroscopic terms, *sharp, principal, diffused and fundamental* respectively. The values of 'ℓ' for different values of n are given in table 2.2.

Table2.2 Principle Quantum Number and values of Azimuthal Quantum Number

n value	ℓ value	Sub-shell	Should be written as	No. of sub-shell
1	0	s	1s	1
2	0,1	s, p	2s,2p	2
3	0,1,2	s, p, d	3s, 3p,3d	3
4	0,1,2,3	s, p, d, f	4s,4p,4d,4f	4

The value of 'ℓ' also determines the shape of the sub-shell. The shapes of sub-shell are due to revolution of electron around the nucleus, e.g. when ℓ=0 then it is s-orbital (sub-shell) and is spherical, when ℓ=1, the sub-shell is dumbbell shaped and is called p-sub-shell, when ℓ=2, the sub-shell is sausage shaped (double dumbbell) and is called the d sub-shell, and when ℓ=3, the sub-shell is even more complicated and is called the f sub-shell.

2.5.3 Magnetic Quantum Number (m)

This quantum number has been based upon the splitting up of spectral lines (Zeeman Effect). By applying a strong magnetic field to electrons with the same values of principal quantum number 'n' and of azimuthal quantum number 'ℓ', electrons may differ in their behaviour. Therefore, a new quantum number, called the magnetic quantum number, is introduced.

- This quantum number is also called *Orientation Quantum Number* because this quantum number indicates the orientation of the orbital in the space around the nucleus. This quantum number is represented by 'm' as it explains the magnetic properties of an electron.
- The number allowed to m, depends on the 'ℓ' values and ranges from –ℓ through 0 to + ℓ, making a total of (2ℓ + 1) values. i.e. when ℓ =0, m =0

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(sub-shell is 's'), when $\ell=1$, m= −1, 0, +1 (sub-shell is p, which is oriented in three directions x, y, z in space). That is to say, the sub-shell 'p' has three degenerate orbitals p_x, p_y and p_z, arranged in space along x, y and z axes.

When $\ell=2$, m = −2, −1, 0, +1, +2 (sub-shell is 'd', which implies that it has five space orientations due to five 'm' values and are designated as d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, d_{z^2}.

When $\ell=3$, m= −3, −2, −1, 0, +1, +2, +3 (sub-shell is 'f', having orientations in seven different directions in space.

The table 2.3 shows the possible magnetic quantum number values (m) for the corresponding azimuthal quantum number (ℓ).

Table 2.3 Relationships among Values of n, ℓ and m

n value	Possible values of ℓ	No of sub-shell	Sub-shell designation	Possible values of m	Number of orbitals in sub-shell	Total number of orbitals in shell
1	0	1=s	1s	0	1	1
2	0 1	2=s, p	2s 2p	0 1, 0, -1	1 3	4
3	0 1 2	3=s, p, d	3s 3p 3d	0 1, 0, -1 2,1,0,-1,-2	1 3 5	9
4	0 1 2 3	4=s, p, d, f	4s 4p 4d 4f	0 1, 0, -1 2,1,0,-1,-2 3,2,1,0,-1,-2,-3	1 3 5 7	16

2.5.4 Spin Quantum Number (m_s or s)

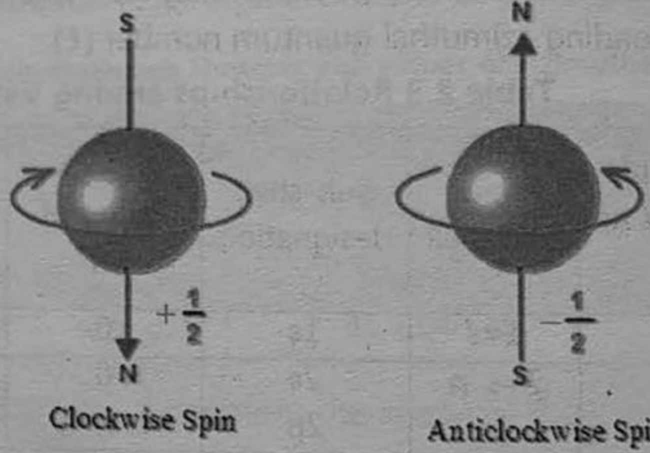
The spin quantum number describes the spin for a given electron on its axis. An electron can have one of two possible spin values, either clockwise or anti-clockwise direction. The direction of the spin can be found out by the application of an external magnetic field. Since an electron has equal probability to spin clockwise and anticlockwise direction on its own axis around the nucleus, so the value for s may be $-\frac{1}{2}$ or $+\frac{1}{2}$. The clockwise motion is assigned $+\frac{1}{2}$

'value and downward arrow (↓).The anticlockwise motion is assigned '$-\frac{1}{2}$ 'value and upward arrow (↑) i.e. s = $+\frac{1}{2}$ (↓) or s= $-\frac{1}{2}$ (↑) or

$$m_s = +\frac{1}{2} (\downarrow) \text{ or } -\frac{1}{2} (\uparrow) = \pm\frac{1}{2}$$

The probability of spin of electrons is supposed to be 50% clockwise and 50% anticlockwise.

A single orbital can hold a maximum of two electrons, with opposite spins



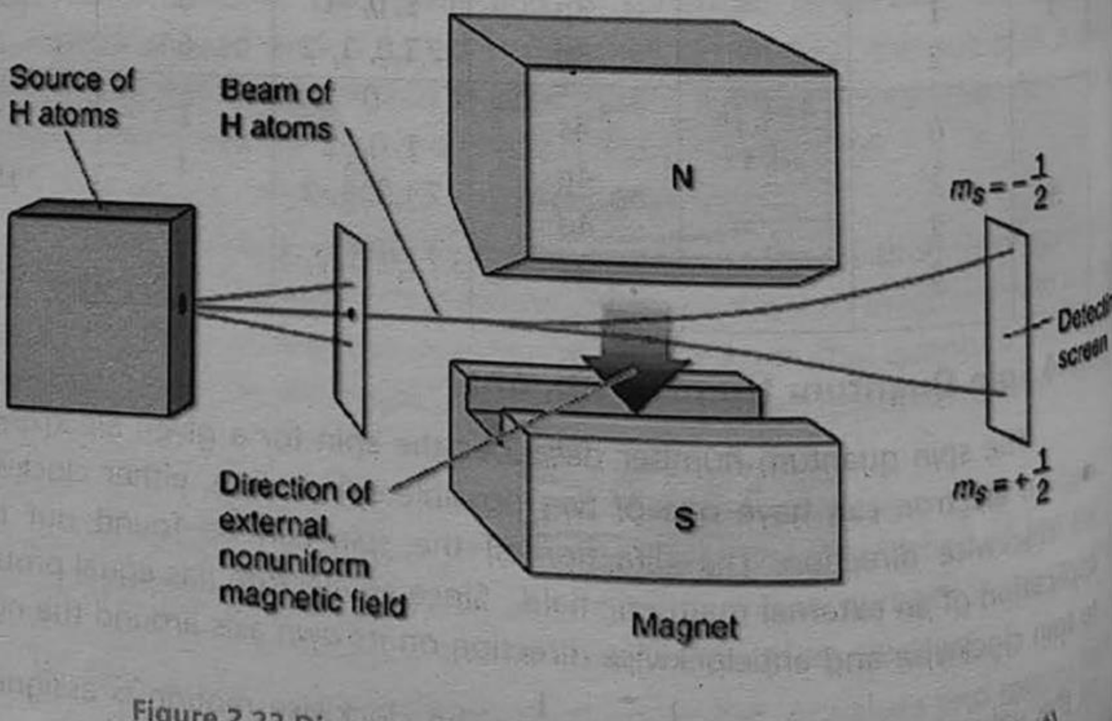


Figure 2.22 Discovery of Electron spins (Stern-Gerlach Experiment)

Two electrons, with the same spin, are said to have parallel spins and are represent by (↑↑) or (↓↓), while others are said to have anti-parallel or pair up spins and are represented by (↓↑) or (↑↓).

Reading Check

What are quantum numbers? Write the name of four quantum numbers.

2.5.5 Shapes of s, p and d Orbitals

Orbital have no physical existence. These are, in fact, regions of space around the nucleus; where there is maximum probability of finding an electron, with a definite amount of energy. These regions have no strict boundaries. An orbital is associated with a size, a three-dimensional shape and an orientation around the nucleus. Together, the size, shape and position of an orbital represent the probability of finding a specific electron around the nucleus of an atom. The overall shape of an atom is a combination of all its orbitals. Thus, the overall shape of an atom is spherical.

The type and shape of the orbital depend on the value of the azimuthal quantum number 'ℓ'.

i. **s- Orbital**

An electron for which $\ell = 0$ is located in an s orbital, regardless of the value of its principal quantum number n. This orbital is spherical in shape as shown in figure 2.23. It is found nearest to the nucleus. Its size increases with the increase in the value of 'n'. They are just like tennis ball.

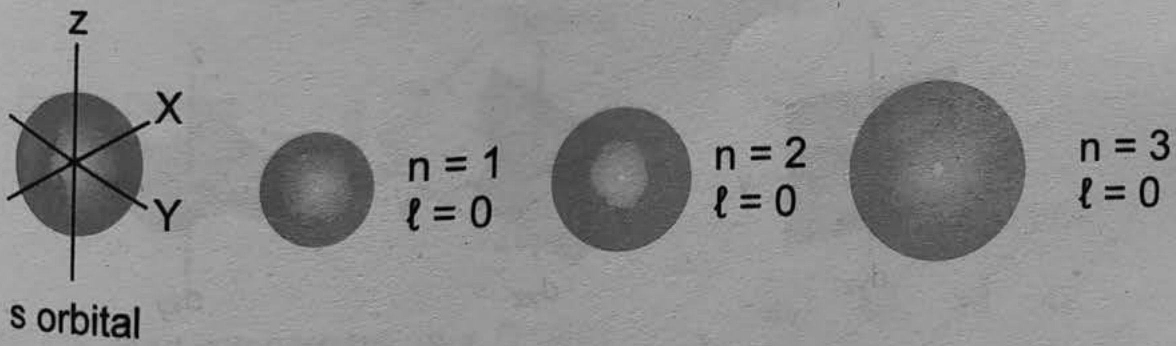


Figure 2.23 Shape of s orbital

ii. **p- Orbital**

Electrons for which $\ell = 1$, the value of 'm' include -1, 0, +1, which consist of three orbitals i.e. p-orbitals have three possible orientations. They are designated as p_x, p_y, p_z depending upon the axis of orientation. Each p-orbitals has two lobes one on each side of the nucleus. They are of dumbbell-shape, eac of which is perpendicular to the two others in three-dimensional space as show in figure 2.24.

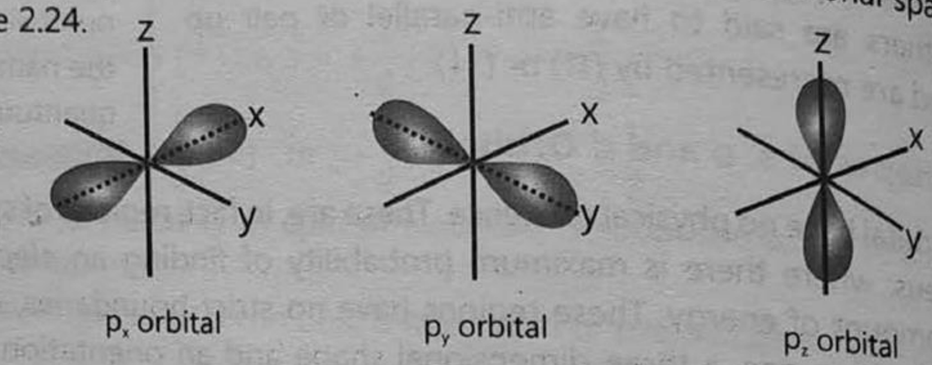


Figure 2.24 Shape and orientation of p orbitals

iii. d- Orbital

When $\ell = 2$, the values of 'm' include -2, -1, 0, +1, and +2, which consi of five d orbitals. The d-orbitals have five possible orientations. The five d-orbita are designated as d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, d_{z^2}. These orbitals have complex geometri shapes as compared to p-orbitals. The three d- orbitals d_{xy}, d_{yz}, d_{zx} have the lobes lying on the planes xy, yz, zx. The $d_{x^2-y^2}$ have somewhat similar structure d_{xy}. The shape of the d_{z^2} orbitals is different from others. The d_{z^2} resembles p orbital with an additional doughnut shaped space in the centre.

Even though the d_{z^2} appears to have a different shape than the others is still mathematically equivalent and exhibits the same properties (such as to energy) as the other d-orbitals as shown in figure 2.25.

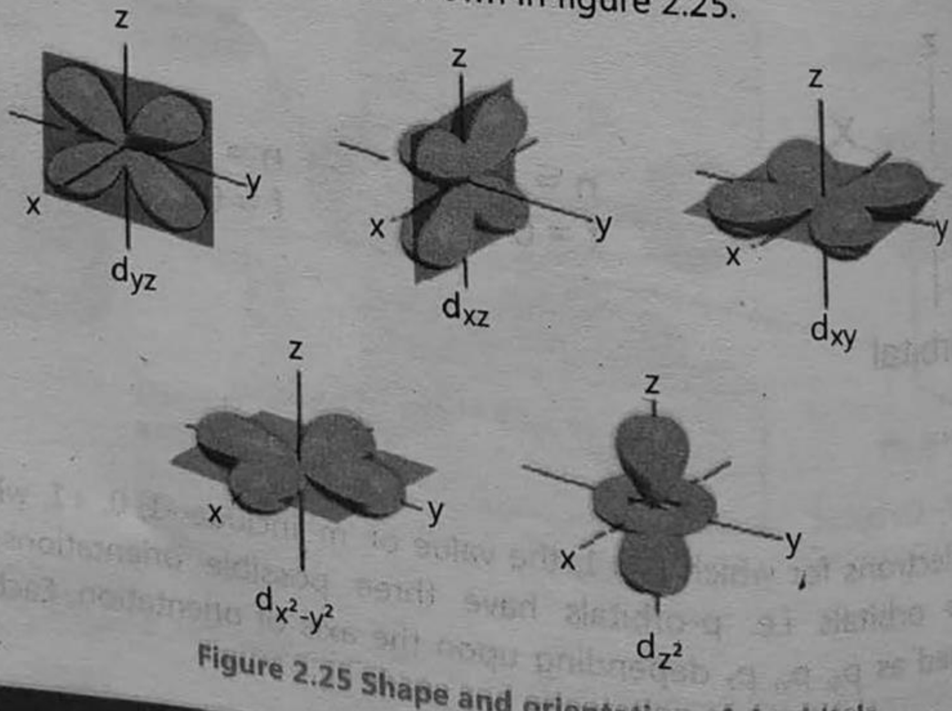


Figure 2.25 Shape and orientation of d orbitals

2.6 Electronic Configuration

The distribution or filling of electrons in the various sub – shells and orbitals of an atom is called electronic configuration.

There are three rules used for the distribution of electrons in the sub – shells and orbitals. These rules are,

2.6.1 Aufbau Principle (The building up Principle)

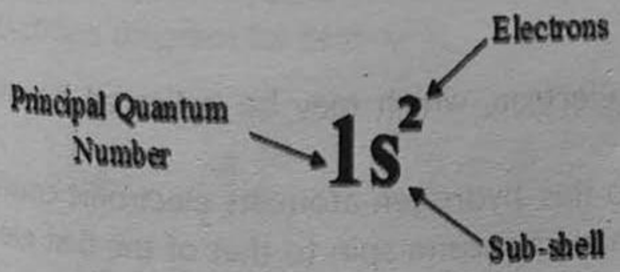
Aufbau is a German word meaning building up or construction. Aufbau principle states that electron fill orbitals that have the lowest-energy first. In other words, electrons are filled in different orbitals in the order of their increasing energies.

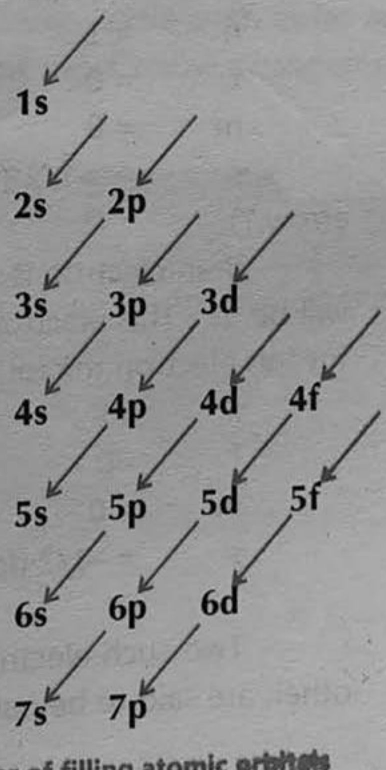
The energy of an orbital is determined by the sum of the principle quantum number (n) and the azimuthal quantum number (ℓ). This rule is also called $(n + \ell)$ rule. This rule consists of two parts.

i. The orbitals with the lower value $(n + \ell)$ have lower energy than the orbitals of higher $(n + \ell)$ value.

ii. When two orbitals have the same $(n + \ell)$ value, the orbitals with lower value of 'n' have lower energy and will be filled up first.

The notation for the electronic configuration includes the principal quantum number (n), the letter designation for azimuthal quantum number (s, p, d and f) and a superscript to indicate the number of electrons in the orbital or sub-shell e.g.





For example, let us compare the $(n + \ell)$ value of '3d' and '4s' orbitals,

For 3d orbitals $n = 3, \ell = 2$

$n + \ell = 3 + 2 = 5$

For 4s orbitals $n = 4, \quad \ell = 0$

$n + \ell = 4 + 0 = 4$

Figure 2.26 Order of filling atomic orbitals

Therefore, '4s' orbital is filled before '3d' orbital.

Similarly, for '4p' orbitals n =4, ℓ =1

$n + \ell = 4 + 1 = 5$

and '5s' orbitals, n = 5, ℓ = 0

$n + \ell = 5 + 0 = 5$

In this case, '4p' orbital has lesser value of 'n' and hence it has lower energy than '5s' orbital and is filled first. It is, therefore, clear 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.

Therefore, the order of filling various sub-shells(orbitals) according to 'n + ℓ' rule would be, $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6$, ... etc.

2.6.2 Pauli's Exclusion Principle

In 1925, Austrian physicist Wolfgang Pauli put forward a principle for the distribution of electrons in the orbitals. According to this principle, *In a given atom no two electrons can have the same set of four quantum numbers (n, ℓ, m and s).* An orbital can accommodate a maximum of two electrons and that these two electrons residing in the same orbital must have opposite spin.

For example, consider the hydrogen atom. Its electronic configuration is $1s^1$. Therefore, hydrogen atom has one electron. For this electron the four quantum numbers (n, ℓ, m and s) are,

n = 1

ℓ = 0

m = 0

s = +1/2 (for one electron, which may be indicated by an upward arrow,↑)

If an electron is added to this hydrogen atom, its electronic configuration will be $1s^2$. This electron must have opposite spin to that of the first electron, so for this electron the four quantum numbers (n, ℓ, m, and s) are,

n =1

ℓ =0

m = 0

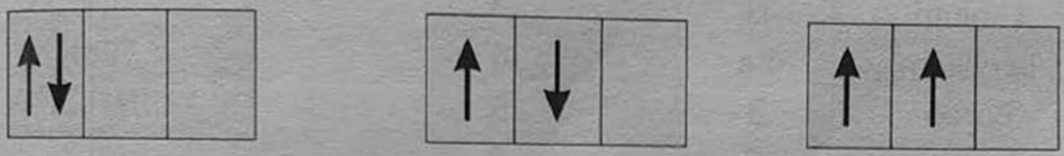
s = −1/2 (for other electron, which may be by a downward arrow, ↓)

Two such electrons, in the same orbital, with their spins opposite to each other, are said to be paired and are represented by (↓↑).

2.6.3 Hund's Rule

Hund's rule (named after the German physicist F. H. Hund), states that when a number of orbitals are available to the electrons and these orbitals have equal energies, the electrons will be arranged in these orbitals in such a way, so as to give maximum number of unpaired electrons and have the same direction of spin.

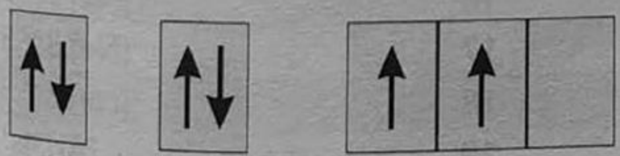
Carbon is an element, which has six electrons. The electron configuration of carbon (Z = 6) is $1s^2 2s^2 2p^2$. These three are the different ways of distributing two electrons among three *p* orbitals,



$2p_x 2p_y 2p_z$ (a) $2p_x 2p_y 2p_z$ (b) $2p_x 2p_y 2p_z$ (c)

All the above three arrangements are according to the Pauli Exclusion Principle. Therefore, you must find out which one will give the greatest stability. This answer is provided by *Hund's rule,* which states *that the most stable arrangement of electrons in sub-shells is the one with the greatest number of parallel spins.* The (c) arrangement satisfies this condition, while both in (a) and (b) the two electrons spins cancel each other. Thus, the most stable arrangement of electrons diagram for carbon is,

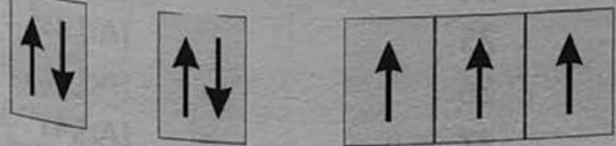
C



$1s^2$ $2s^2$ $2p^2$

The electronic configuration of nitrogen (Z = 7) is $1s^2 2s^2 2p^3$ and the electrons in orbitals are arranged as follow;

N



$1s^2$ $2s^2$ $2p^3$

Tidbit

Different orbitals belonging to the same sub-shell are degenerate (same energy) e.g., $2p_x$, $2p_y$ and $2p_z$ are degenerate orbitals.

The Hund's rule describes that all three 2*p* electrons have parallel spins to one another; the nitrogen atom contains three unpaired electrons.

2.6.4 Electronic Configurations

Based on the rules above, the electronic configurations of first forty elements in the periodic table are given in table 2.4.

Table 2.4 Electronic Configurations of First forty Elements

Element	Symbol	Atomic Number (Z)	Electronic configuration
Hydrogen	H	1	$1s^1$
Helium	He	2	$1s^2$
Lithium	Li	3	$[He],2s^1$
Beryllium	Be	4	$[He],2s^2$
Boron	B	5	$[He],2s^2,2p^1$
Carbon	C	6	$[He],2s^2,2p^2$
Nitrogen	N	7	$[He],2s^2,2p^3$
Oxygen	O	8	$[He],2s^2,2p^4$
Fluorine	F	9	$[He],2s^2,2p^5$
Neon	Ne	10	$[He],2s^2,2p^6$
Sodium	Na	11	$[Ne],3s^1$
Magnesium	Mg	12	$[Ne],3s^2$
Aluminum	Al	13	$[Ne],3s^2,3p^1$
Silicon	Si	14	$[Ne],3s^2,3p^2$
Phosphorous	P	15	$[Ne],3s^2,3p^3$
Sulphur	S	16	$[Ne],3s^2,3p^4$
Chlorine	Cl	17	$[Ne],3s^2,3p^5$
Argon	Ar	18	$[Ne],3s^2,3p^6$
Potassium	K	19	$[Ar],4s^1$
Calcium	Ca	20	$[Ar],4s^2$
Scandium	Sc	21	$[Ar],4s^2,3d^1$
Titanium	Ti	22	$[Ar],4s^2, 3d^2$
Vanadium	V	23	$[Ar],4s^2, 3d^3$
Chromium	Cr	24	$[Ar],4s^1, 3d^5$ (more stable)
Manganese	Mn	25	$[Ar],4s^2, 3d^5$
Iron	Fe	26	$[Ar],4s^2, 3d^6$
Cobalt	Co	27	$[Ar],4s^2, 3d^7$
Nickel	Ni	28	$[Ar],4s^2, 3d^8$

Copper	Cu	29	[Ar],$4s^1$, $3d^{10}$$_{(more\ stable)}$
Zinc	Zn	30	[Ar],$4s^2$, $3d^{10}$
Gallium	Ga	31	[Ar],$4s^2$, $3d^{10}$,$4p^1$
Germanium	Ge	32	[Ar],$4s^2$, $3d^{10}$,$4p^2$
Arsenic	As	33	[Ar,$4s^2$], $3d^{10}$,$4p^3$
Selenium	Se	34	[Ar],$4s^2$, $3d^{10}$,$4p^4$
Bromine	Br	35	[Ar],$4s^2$, $3d^{10}$,$4p^5$
Krypton	Kr	36	[Ar],$4s^2$, $3d^{10}$,$4p^6$
Rubidium	Rb	37	[Kr], $5s^1$
Strontium	Sr	38	[Kr], $5s^2$
Ytterbium	Y	39	[Kr],$5s^2$, $4d^1$
Zirconium	Zr	40	[Kr],$5s^2$, $4d^2$

Self-Assessment

1. Briefly write the Moseley experiment.
2. Explain the magnetic quantum number in detail.
3. What are the shapes of s, p and d orbitals?
4. Define Pauli's exclusion principle and Hund's rule.
5. What is mean by Aufbau principle?

KEY POINTS

- Electron, proton and neutron are the fundamental particles of all kinds matter.
- In discharge tube experiment, cathode rays are in fact electrons and the ca rays (when hydrogen gas is in the discharge tube) are protons.
- Electron is 1836 times lighter than proton.
- According to Planck's quantum theory, energy emitted or absorbed by a body does not propagate in continuous form but in form of sm units/packets of energy. The 'unit wave' or 'pulse of energy' is called quantu He proposed the equation $E = h\nu$, for the energy of quantum.
- Bohr rectified the Rutherford atomic model and developed an atomic mod for hydrogen on the basis of quantum theory in 1913.
- Bohr successfully gave equations for the calculation of radius and ener of orbits of electron and frequency, wavelength and wave number of radiatio released or absorbed during electronic transition between shells.
- Bohr explained the spectrum of hydrogen atom.
- X – rays are high frequency radiations, discovered by Roentgen. These ra are produced by hitting the metal surface by high-energy electron beam.
- According to Moseley, the number of positive charges in the nucleus is th fundamental property of an element.
- Moseley's law states that, the square root of the frequency ($\sqrt{\upsilon}$) of th emitted X – ray radiation is directly proportional to the atomic number (Z) o an element, $\sqrt{\upsilon} \propto Z$
- Quantum numbers are a set of numbers, which designate an electron in a atom. These are four in number i.e. principal quantum number (n), azimutha quantum number (ℓ), magnetic quantum number (m) and spin quantu number (m_s, or s)
- An orbital is a region of space around the nucleus where the probability finding electron is maximum.
- Aufbau principle, Pauli's exclusion principle, and Hund's rule are followed the distribution of electrons in different orbitals of multi electron atoms.

EXERCISE

Choose the Correct Option.

1. The e/m ratio of cathode rays is,
   a. 1.76×10^{23} C/kg
   b. 1.76×10^{11} C/kg
   c. 1.76×10^{-31} C/kg
   d. 1.76×10^{7} C/kg
2. The wave number ($\bar{\upsilon}$)of a radiation with $\lambda = 2 \times 10^{8}$nm will be,
   a. 0.5×10^{-8} nm^{-1}
   b. $10nm^{-1}$
   c. $5nm^{-1}$
   d. $100nm^{-1}$
3. For an electron in K-shell, the correct four quantum numbers are represented by,
   a. $n=1, \ell=0, m=0, s=+\frac{1}{2}$
   b. $n=2, \ell=0, m=0, s=+\frac{1}{2}$
   c. $n=1, \ell=1, m=0, s=-\frac{1}{2}$
   d. $n=2, \ell=2, m=+2, s=+\frac{1}{2}$
4. All are electromagnetic in nature except,
   a. IR rays
   b. X – Rays
   c. UV- rays
   d. cathode Rays
5. The energy associated with quantum of radiation is,
   a. $h\upsilon$
   b. $\frac{nh}{2\pi}$
   c. $2h\upsilon$
   d. $\frac{1}{2}h\upsilon$
6. Bohr's theory cannot be applied on,
   a. H
   b. H^{+}
   c. He^{+1}
   d. Li^{+2}
7. Which of the following sets of quantum numbers are not possible?
   a. $n = 3, \ell = 2, m = 0, s=-\frac{1}{2}$
   b. $n = 3, \ell = 3, m = -3, s=+\frac{1}{2}$
   c. $n = 4, \ell = 3, m = -3, s=+\frac{1}{2}$
   d. $n = 3, \ell = 1, m = 0, s=+\frac{1}{2}$

8. The frequency of a green light is $6x10^{14}$Hz, its wavelength is,
   a. 5nm b. 500nm c. 5000nm d. 100nm
9. Which of the following sub-shell do not exist?
   a. 1p b. 5d c. 6f d. 1s
10. All quantum numbers are obtained from solution of Schrödinger equat[illegible] except,
    a. Principal quantum number, n
    b. Magnetic quantum number, m
    c. Spin quantum number, s
    d. Azimuthal quantum number, ℓ
11. The maximum number of electrons in 3*s* orbital,
    a. 1 b. 2 c. 6 d. 10
12. The splitting of spectral lines in magnetic field is
    a. Stark effect
    b. Zeeman effect
    c. Aufbau principle
    d. Pauli exclusion principle
13. If the mass of electron is reduced to half, the Rydberg's constant,
    a. Becomes half
    b. Becomes double
    c. Remains unchanged
    d. Becomes one fourth
14. Which element has the electronic configuration of noble-gas notation [illegible] $5s^2$, $4d^2$
    a. Se b. Sr c. Zr d. Mo
15. The mathematical form of Moseley's law is
    a. $\sqrt{v} = b(z-a)$
    b. $\sqrt{v} = a(z-b)$
    c. $\sqrt{v} = \frac{a}{b}\sqrt{z}$
    d. $\sqrt{v} = \frac{b}{a}z$

Short Questions

1. Name any four properties of cathode rays.
2. How will you differentiate between a continuous and a line spectrum?
3. How did Moseley discover that the atomic number (Z) is the fundamental property of an element?
4. What are the shortcomings of Bohr's atomic model?
5. Can you give the reason that 4s orbital are written first than the 3d orbital.

Numerial Questions

1. Calculate the distance (Å) between the nucleus and an electron in the 5^{th} orbit of an excited hydrogen atom. Ans.: 13.225Å
2. What will be the wave number ($\bar{\upsilon}$) of the spectral line of an electron when it jumps from $n_2 = 4$ to $n_1 = 2$? Ans.: $20.58 \times 10^5 m^{-1}$
3. What is frequency of a radiation with wave number ($\bar{\upsilon}$) equal to $0.5 \times 10^8 m^{-1}$? Ans.: 1.5×10^{16}Hz
4. Calculate the wavelength of an electron when it moves with the velocity of light. Ans.: 2.424×10^{-12}m
5. What will be the energy (kJ/mol) of an electron residing in n=3 in hydrogen atom? Ans.: –145.817kJ/mol
6. How much energy is lost when an electron in hydrogen atom jumps from $n_2=3$ to $n_1=1$? Ans.: 1166.542kJ/mol

Descriptive Questions

1. (a) What is Planck's quantum theory? What are the postulates of this theory?
   (b) Prove that $E = hc\bar{\upsilon}$, where E = energy, h= Planck's constant, c = velocity of light, and $\bar{\upsilon}$ = wave number.
   (c) What will be energy of a radiation with $\lambda=2\times10^{-8}$m? Ans.: 9.939×10^{-18}J
2. (a) Write down the main postulates of Bohr's atomic model.
   (b) How can Bohr's model of atom be applied to hydrogen atom to calculate the radius of n^{th} shell? Ans: $\bar{\upsilon}=1.028\times10^7 m^{-1}$, $\lambda=9.72\times10^{-8}$m
3. (a) Derive expression using Bohr's model, for the energy difference (ΔE), frequency (ν) and wave number ($\bar{\upsilon}$) in hydrogen atom.
   (b) How does Bohr's model explain the hydrogen spectrum?
4. (a) What are X-rays? How are these rays produced?
   (b) Enlist some characteristics of X – rays.

5. (a) Define quantum numbers. What information is given by the sp quantum number? What are the possible values for this quantu number?
(b) What information is given by the magnetic quantum number?

6. (a) What is an orbital? How does it differ from an orbit?
(b) Discuss the shapes of s, p and d orbitals.
(c) Calculate the wave number and wavelength of a photon when the electron jumps from $n_2 = 4$ to $n_1 = 1$. Ans: $\bar{\upsilon} = 1.028 \times 10^{7} m^{-1}$, $\lambda = 9.72 \times 10$
(d) Identify the series of spectral lines to which this photon belongs?

Project:

- Take three different salts and identify unknown metal ion in them by using flame test.
- Construct a simple gas discharge tube from low cost substances, showing the electrodes, vacuum pump, power supply etc.