1. The Electronic Structure of Atoms

1.1 Investigations into the structure of the Atom

Daltonâ€™s assumption that atoms were indivisible has been found to be incorrect. The observations disproving this assumption were first made in the Crookeâ€™s discharge tube experiments. Crooke noticed that a stream of rays was emitted from the cathode when electric current was passed through a tube containing gas at very low pressures. The rays travelled towards the anode. Figure 1.1 shows a Crookeâ€™s discharge tube. He called the rays cathode rays because they originated from the cathode.

Many scientists have performed experiments to determine the components and structure of the atom. Some of these experiments are discussed here.

Electrons
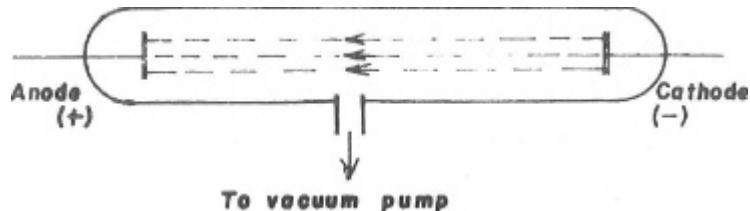
Figure 1.1: William Crookeâ€™s discharge tube

J. J. Thompson investigated the nature of these cathode rays using modified cathode ray tubes. Figure 1.2 represents Thompsonâ€™s cathode ray tube. Our present day television sets and fluorescent tubes are modifications of cathode ray tubes.
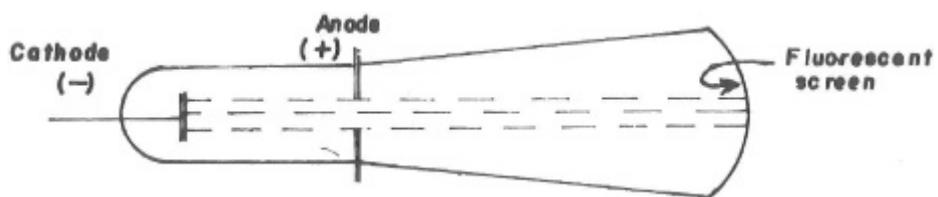

Figure 1.2: J.J. Thompsonâ€™s cathode ray tube.

Thompson's experiments demonstrated that:

(i) The cathode rays cause the fluorescent screen to glow with a green light when the rays fall on it.
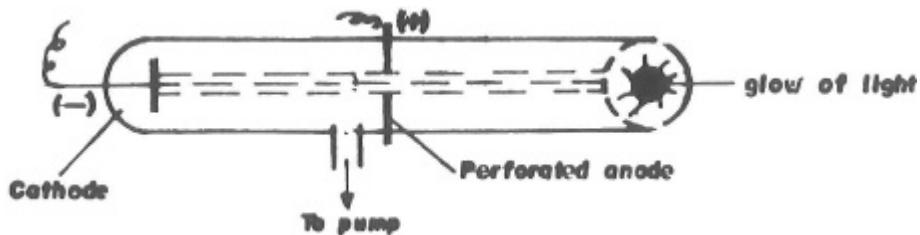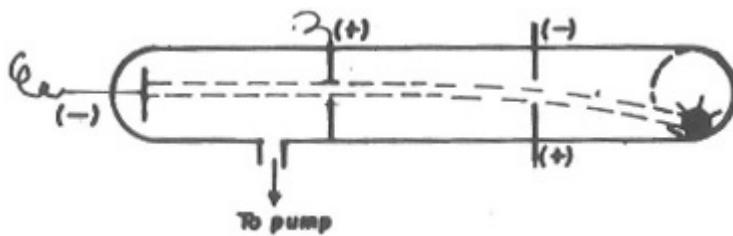
Figure 1.3: A glow on the fluorescent screen

(ii) The rays are bent towards me positive electrode (anode) when an electric field is placed on their path.
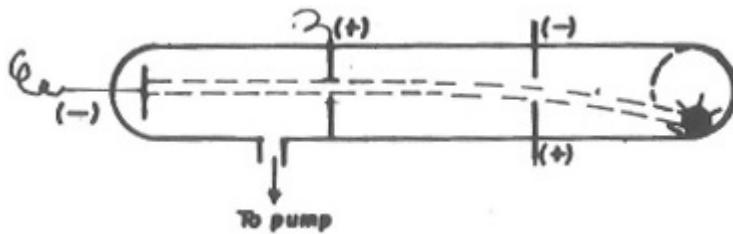

Figure 1.4: Deflection of cathode rays by an electric field.

(iii) A magnetic field has a similar effect on the rays as the electric field.
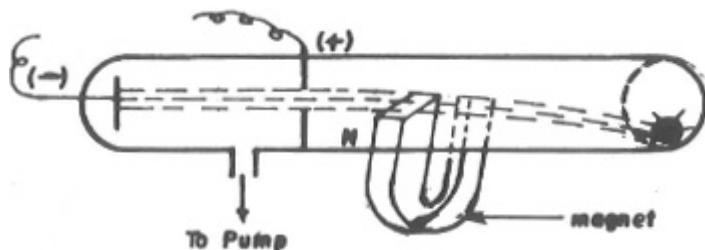
Figure 1.5: Deflection of cathode rays by a magnet.

(iv) An object placed behind the perforated anode casts a shadow on the screen.
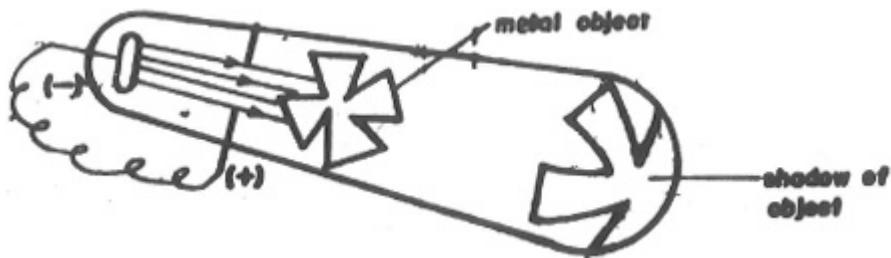
Figure 1.6: Cathode rays cast a shadow of objects in their path.

(v)   The rays penetrate sheets of metals such as 1 mm thick aluminium, without casting a shadow.

(iv)   The rays can impart mechanical motion on a tiny paddle wheel.
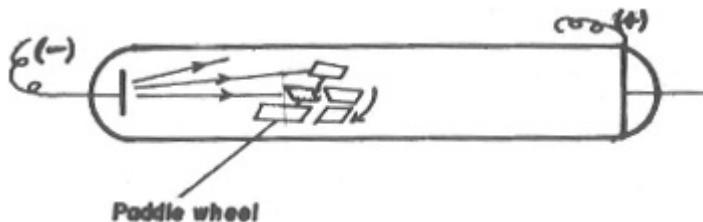
Figure 1.7: Cathode rays impart motion on a paddle wheel

(vii) No matter what metal was used as cathode and no matter what residual gas was in the tube, the mass and charge of the particles making up the rays remain constant.

Explanations:

(a)   The bending of the rays by both electric and magnetic fields suggests that cathode rays are negatively charged particles. They are bent towards the positive plate of an electric field, and towards the north pole of a magnet.

(b)   The casting of the shadow of an object in their path on the screen shows that the rays travel in straight lines.

(c)   Even the very small hydrogen atoms cannot pass through a metal. That the cathode rays can pass through aluminium foil indicates that they are smaller particles than atoms.

(d)   They are able to rotate a paddle wheel because they are particles which possess some (though neglible) mass.

(e)   The constant mass and charge of the particles irrespective of the nature of the cathode or the residual gas proves that they are basic constituents of matter. These particles are called electrons. Millikan subsequently determined the charge of an electron in his famous 'Oil drop' experiment.

SUMMARY OF THE OBSERVATION IN THE CATHODE RAY EXPERIMENT AND THE CORRESPONDING DEDUCTIONS

Observations	Deductions
(i) Rays are deflected towards the positive plate.	They are negatively charged
(ii) Rays pass through a thin sheet of aluminium foil.	They are smaller than atoms
(iii) Rays cause the wheels of a small paddle to rotate	They possess mechanical energy
(iv) The rays cast shadows of objects placed in their path.	They travel in straight lines
(v) The rays cause scintillation.	They can conduct electricity Protons

Protons

Further experiments involving the passage of electric current through discharge tubes containing gases at reduced pressures led to the discovery of protons by Goldstein. He found that if the cathode was perforated, charged particles travelled in the opposite direction to the cathode rays. These particles were bent towards the cathode of an electric field in their path, and towards the south pole of a magnet. Their masses and charges depended on the nature of the residual gas in the tube. The lightest particles were obtained when hydrogen was the residual gas. This was found to have the same mass as the hydrogen atom, and to have an equal but opposite charge as the cathode ray. This particle was shown to be hydrogen atom from which an electron has been struck off. It is known as a proton.
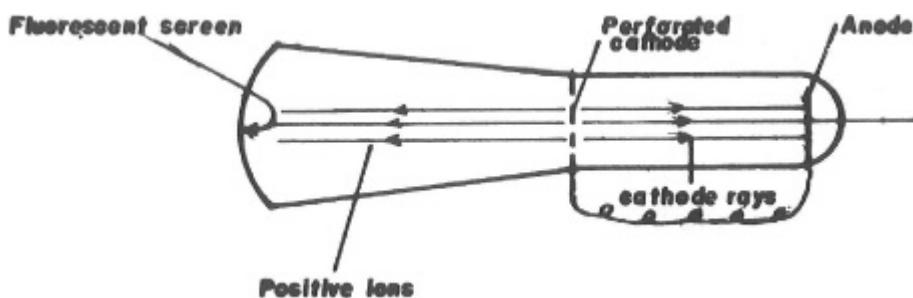
Figure 1.8: J.J. Thompson's apparatus for studying protons

Neutrons

Before 1932, chemists represented the atom in different ways because there was no agreement on how to account for the mass of each atom in relation to the number of protons in die atom. Rutherford then suggested that there could be another particle in the atom with the same mass as a proton but with no charge. He called it the neutron. The neutron was subsequently discovered in 1932 by Chadwick, a

former student of Sir Rutherford. The particle was found to be nearly as heavy as the proton. This confirmed Rutherford's prediction.

EXERCISE 1.1

1.   What experimental findings suggest that:
   (a)   electrons are fundamental constituents of matter?
   (b)   electrons are negatively charged?
   (c)   cathode rays are particles?
   (d)   protons are positively charged?

2.   What argument led Rutherford to the suggestion that there must be a neutral particle in the nucleus of an atom, of equal mass with the proton, long before its discovery?

Rutherford's Nuclear Atom

In 1909 H. Geiger, E' Masden and Rutherford devised an experiment which was a key step in the development of the modern atomic structure. They bombarded a thin gold foil with alpha particles and observed that most of the alpha particles passed through the foil in straight lines (undeflected). A small fraction was deflected to various degrees. A smaller fraction was turned back by almost 180°.

Figure 1.9 shows the arrangement of the apparatus, while Figure 1.10 shows the manner of deflection of the rays.
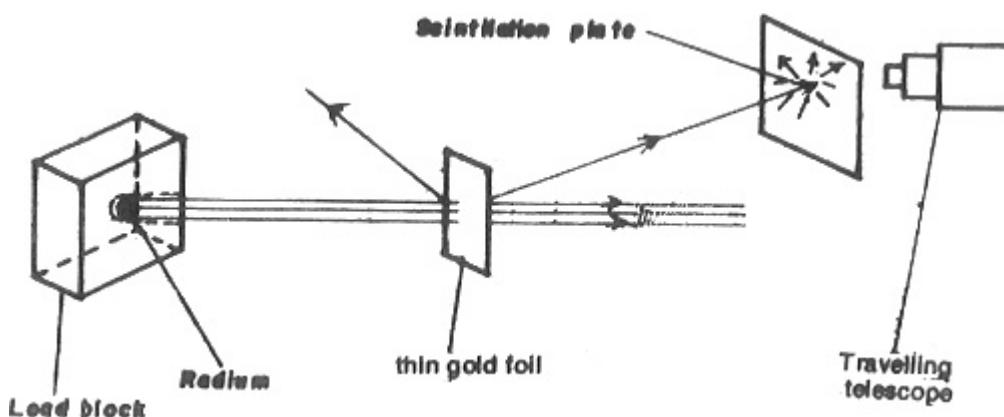

Figure 1.9: Rutherford's apparatus for the nuclear atom experiment

The telescope was used to locate the rays after passing through the foil. The rays appeared on the zinc sulphide screen as tiny flashes.
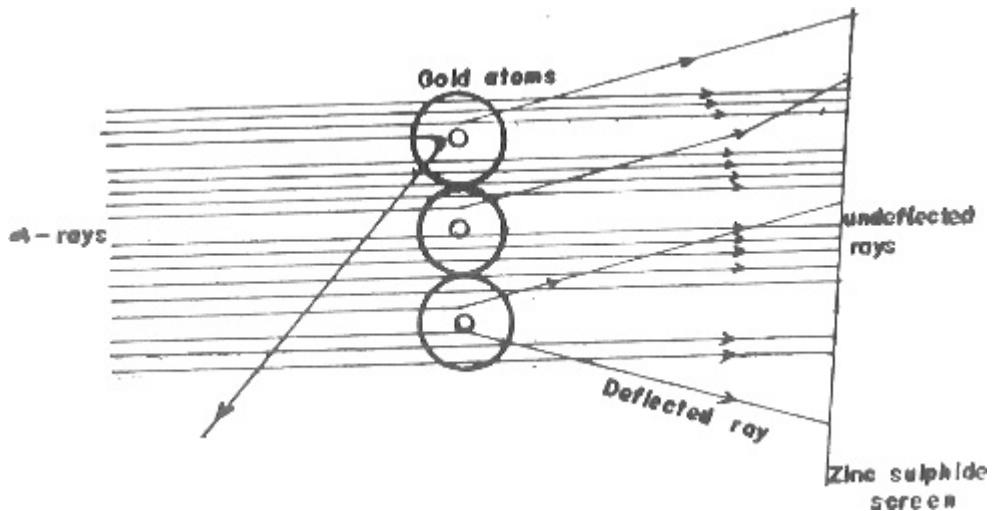
Figure 1.10: Interaction of α–rays with gold atoms

Rutherford regarded the thin foil as containing only a few layers of atoms. Most of the alpha-particles suffered no deflection because a greater part of the atom consists of empty space. This open space allowed the alpha particles to pass through undeflected. The few deflections that occured were due to some alpha particles which approached positively charged parts of the atom, i.e the nucleus. The deflections were few because the nucleus is very small, so that only few alpha particles got near it. The fewer particles that approached it directly were repelled. They suffered near complete reversal of their direction of motion.

Rutherford therefore proposed the model in Figure 1.11 as the structure of an atom.
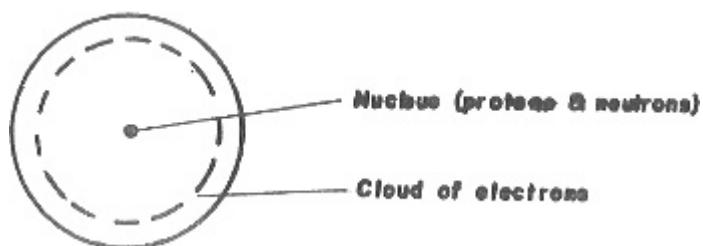
Figure 1.11: Rutherford's model of an atom.

Since like charges repel, chemists needed to explain why protons in the nuclei of atoms heavier than hydrogen are able to stay together. Every atom with two or more protons also has two or more neutrons. The heavy atoms have greater number of neutrons than protons. A possible explanation is that the neutrons serve to bind the protons together. For neutrality to be maintained, the number of protons in the nucleus of an atom is equal to the number of electrons around that neucleus.

EXERCISE 1.2

(i)   Platinum and gold have about the same density. If platinum foil were used in the alpha-particle scattering experiment, would the scattering pattern be different? Explain.

(ii)   The diameter of the hydrogen nucleus is about 10^{-12} nm. The diameter of the space enclosed by the rotating electron in a hydrogen atom is about 10^{-7} nm. What is the ratio of the diameter of the hydrogen atom to the hydrogen nucleus?
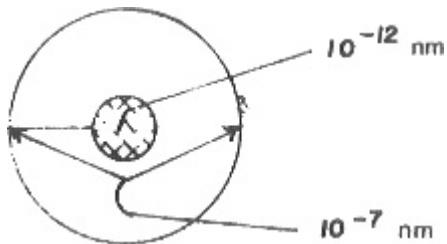
Figure 1.12: Dimensions of the hydrogen atom

Moseley's Experiment on Atomic Number

X-rays were discovered in 1895 by Rontgen. They are formed in a Crooke's tube when electrons strike a metal target. The x-rays come out through the walls of the glass tube, Figure 1.13.
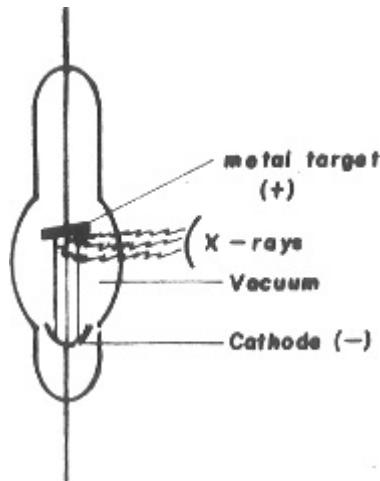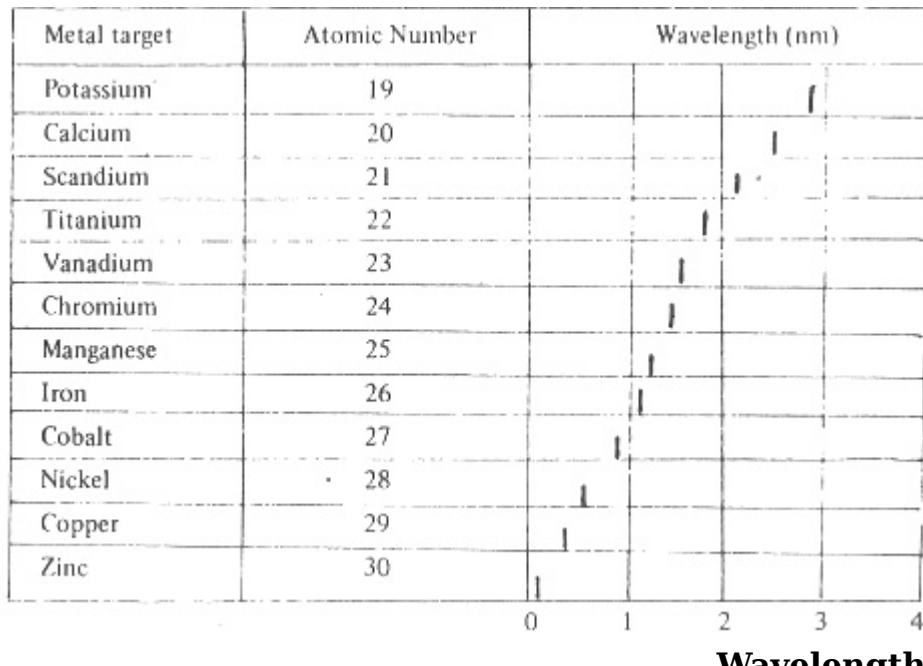
Figure 1.13: An X-ray tube

Working in Rutherford's laboratory, Moseley in 1913 found that x-ray spectra consisted of groups of lines. Each line represented a definite wavelength. They occured at regular intervals when elements with increasing atomic masses were used as targets. For example, with manganese as target, there was a line at a wavelength of 0.21 nm. There was another at 0.193 nm with iron as target, and 0.1*79* nm for cobalt as target. The wavelengths of x-rays from other metals are shown in Table 1.1.

TABLE 1.1:   Wavelengths of X-rays obtained with various metal targets

Metal target	Atomic Number	Wavelength (nm)
Potassium	19	
Calcium	20	
Scandium	21	
Titanium	22	
Vanadium	23	
Chromium	24	
Manganese	25	
Iron	26	
Cobalt	27	
Nickel	28	
Copper	29	
Zinc	30	

0   1   2   3   4

Wavelengths (nm)

The interpretation of these results was that there is a fundamental property of the atoms of the elements which increases regularly as the atomic number increases. Moseley thought this property was the number of protons in the nucleus of each atom. Thus, this experiment showed that the elements arose by a stepwise addition of one proton to the nucleus of a preceding one.

EXERCISE 1.3

Why did Moseley not attribute the fundamental property to the number of electrons in the atoms of the elements? What is the relationship between this number and the atomic number of an element?

The Mass Spectrometer

The mass spectrometer is a modern instrument used for measuring the relative masses of atoms of the elements and molecules of compounds. Information obtained from it has added to our knowledge of the structure of the nucleus of an atom.
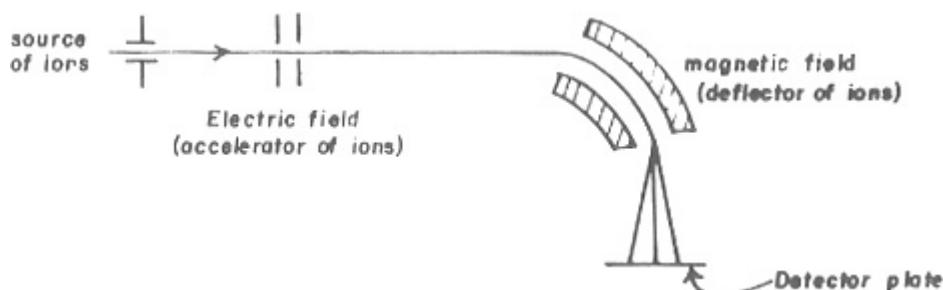

Figure 1. 14: Schematic diagram of a mass spectrometer

In a mass spectrometer, when a stream of electrons is passed at

high speed through the gaseous atoms of an element, electrons are struck off from the outer most shells of the atoms, producing positively charged ions. The ions so produced are then accelerated by an electric field in a discharge tube. On getting to a magnetic field further away from their source, the paths of the ions are bent. The extent to which each ion's path is bent depends solely on its mass, provided all die ions are travelling with the same speed, and carry equal charges. The lightest ions are bent to the greatest extent and the heaviest to the least extent. A line is inscribed on the detector plate where ions of the same mass strike it. The intensity of each line depicts the relative abundance of ions of that mass.

When a single element is injected into the mass spectrometer, several lines are often produced on the detector plate. Oxygen, for example, produces three lines corresponding to masses 16, 17 and 18. The line for mass 16 is the most intense. Those for masses 17 and 18 are less intense.

Figure 1.15: Lines on a detector plate when oxygen is used

The explanation for atoms of the same element falling at different points on the detector plate is that such atoms have different masses. Atoms of the same element which have different masses are called isotopes. Such atoms contain the same number of protons, but different number of neutrons in their nuclei. Oxygen has three isotopes: oxygen – 16 which has eight protons, eight neutons and a mass number of 16; oxygen – 17 which has eight protons, nine neutons and a mass number of 17; oxygen – 18 which has eight protons, ten neutrons and a mass number of 18.

We have discussed isotopy in Book 1 and listed a number of common elements with their isotopes.

EXERCISE 1.4

Chlorine occurs as two isotopes: Cl^{35} (75%), and Cl^{37} (25%). How many lines will appear on the detector plate if chlorine is injected into the mass spectrometer? Which isotope will give the more intense line?

TABLE 1.2: Summary of experimental evidence for atomic structure

Experiment	Evidence
1. Cathode ray experiments	Sub-atomic particles:– electrons, protons, neutrons.

2.	Natural radioactivity	α, β and γ radiation from atoms, further evidence for sub-atomic particles.
3.	Experiments of Rutherford and his aides.	Structure of atom:– a massive nucleus containing protons and neutrons, and electrons in the rest of the space.
4.	Moseley's experiment.	Atomic number:– stepwise addition of protons to the nucleus, producing new elements.
5.	Mass spectrometer	Isotopes:– atoms of the same element with different masses because they contain different numbers of neutrons in their nuclei.
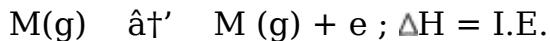
1.2   Arrangement of Electrons in Atoms

Niels Bohr proposed in 1913, that electrons move round the nuclei of atoms in orbits (or shells) to explain why electrons in an atom are not attracted to the positively charged nuclei. If a vehicle makes a sharp bend to the left, passengers in it experience a force tending to throw them outwards to the right. This is known as a centrifugal force. This force, acting on an electron as it moves round the nucleus in a shell, counterbalances the force of attraction which the positively charged nucleus has on the electron:

But how are the electrons arranged in a shell? What evidences do we have for any proposed order of arrangement?

Evidence from Ionization Energy

The energy required to remove the most loosely bound electron from a gascous atom is its first ionization energy, I.E.

$M(g) \rightarrow M^+(g) + e ; \triangle H = I.E.$

If one electron is removed, the remaining electrons become more strongly bound to the positively charged ion that results from the removal. Thus, more energy is required to remove a second electron. The second ionization energy is therefore usually higher than the first. Similarly, the third is higher than the second, and so on. The first, second and third ionization energies of the first twenty elements are given in Table 1.3.

TABLE 1.3: Ionization energies of the first twenty elements (kJ mol^{-1})

Element	Atomic Number (number of elecrons)	1st I.E.	2nd I.E.	3rd I.E.
Hydrogen	1	1310	–	–
Helium	2	2370	5250	–
Lithium	3	520	7300	11800
Beryllium	4	900	1760	14800
Boron	5	800	2420	3660
Carbon	6	1090	2350	4610
Nitrogen	7	1400	2860	4580
Oxygen	8	1310	3390	5300
Fluorine	9	1680	3380	6040
Neon	10	2080	3960	6150
Sodium	11	490	4560	6910
Magnesium	12	740	1450	7730
Aluminium	13	580	1820	2740
Silicon	14	790	1580	3230
Phosphorus	15	1060	1900	2910
Sulphur	16	1000	2260	3380
Chlorine.	17	1260	2300	3850
Argon	18	1520	2660	3950
Potassium	19	420	3070	4440
Calcium	20	590	1150	4940

EXERCISE 1.5:

Plot a graph of first ionization energy against number of electrons for the elements in Table 1.3. Join the adjacent points with straight lines. Observe the following features of the graph:

(a)   Elements with atomic numbers 2, 10 and 18 (i.e with 2, 10, 18 electrons) appear at the top of the graph. Why?

(b)   Elements with 3, 11 and 19 electrons appear at the bottom. Why?

(c)   The second ionization energies of the elements with 3, 11 and 19 electrons are much higher than those of their neighbouring elements. Why?

Explanations of the ionization energy figures: A close study of the ionization energies in Table 1.3 reveals the following facts:

(a)   Helium, neon and argon have very high first ionization energies because they have stable electronic arrangements from which it is difficult to remove an electron. The low reactivity of these elements supports this.

(b)   The first ionization energies of lithium, sodium and potassium are very low compared with the values for helium, neon and argon which preceded them. This is attributed to the fact that new shells begin with lithium, sodium and potassium. That is, the first shell takes a maximum of two electrons as in helium. The third electron

of lithium goes into the second shell which is further away from the nucleus. The second shell takes a maximum of eight electrons which it does in neon. An eleventh electron goes into the third shell from where it is easy to remove, because it is further away from the nucleus.

(c)   The second ionization energies of lithium, sodium and potassium are very high. This is attributed to the fact that the energies of the shells are widely different. In lithium, the second electron has to be lost from the first shell, the first having been lost from the second shell which contained only one electron. In sodium, the second electron has to be lost from the second shell, the first having been lost from the third shell which contained only one electron.

EXERCISE 1.6:

Explain the high difference in third ionization energies of magnesium (7740 kJ mol^{-1}), and aluminium, (2740 kJ mol^{-1}).

1.3   Atomic Spectra and Electronic Arrangements in Atoms

The Bohr theory of electrons revolving round the nuclei in orbits or shells was not able to explain all the characteristics of atoms. It did not, for example, explain the atomic spectra emitted when electric current was passed through gaseous elements at low pressures in discharge tubes. Before discussing atomic spectra, let us first consider the nature of electromagnetic radiations.

Wave Motion

Water waves are the most common forms of wave motion.
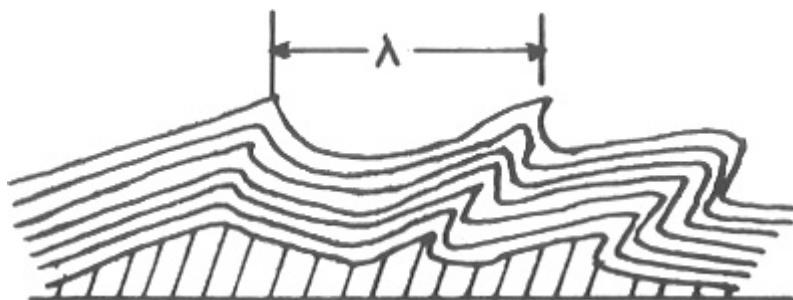

Figure 1.16: Waves in a body of water.
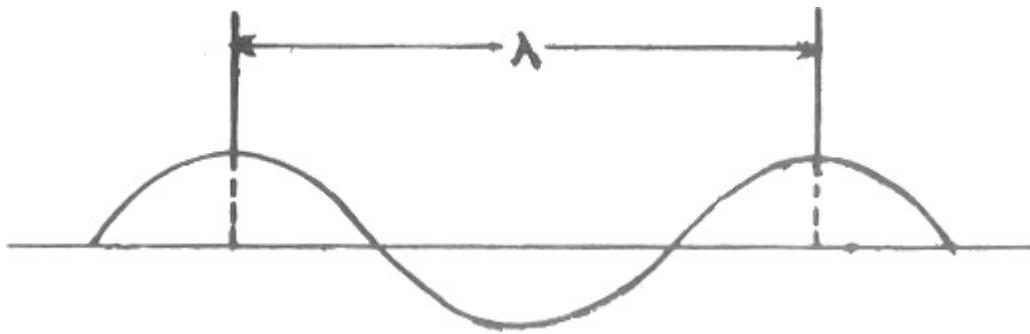
Figure 1.17: Wave motion.

The distance between the crests in two waves is known as the wavelength, λ. Another characteristic often measured in a wave motion is the number of waves passing a given point per unit time. This is known as the frequency' v, of the wave motion. The relationship between wavelength and frequency is given by the equation:

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

where c is the velocity of light (3 × 10^{10}cm sec^{-1}).

All forms of electromagnetic radiation, be they gamma rays, x-rays, visible light, ultraviolet rays, infrared rays, radio waves, or any other type, travel as waves. A device which can break up white light into its constituent wavelengths is illustrated in Figure 1.18.
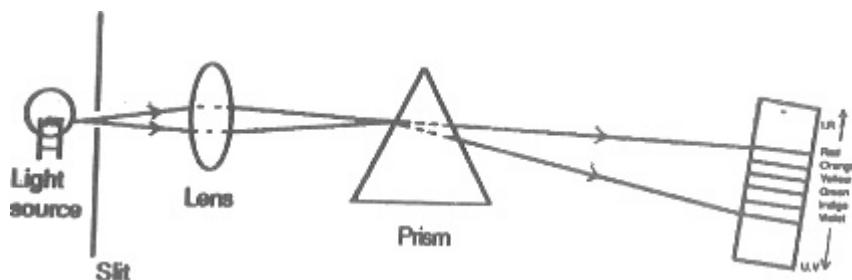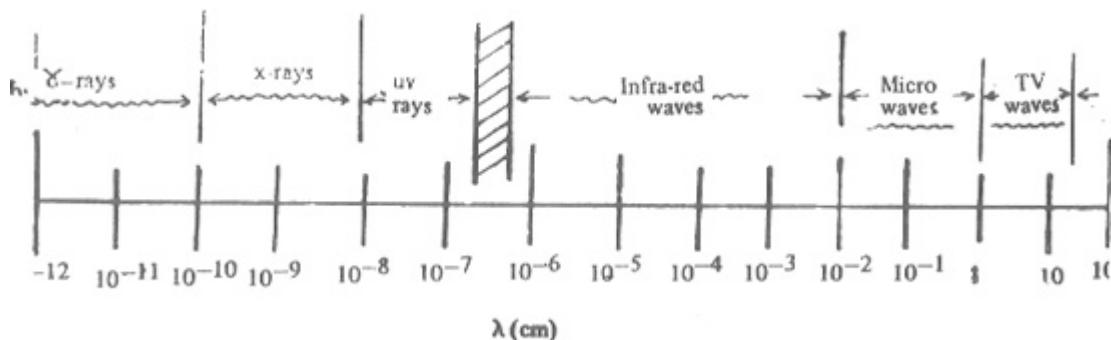
Figure 1.18: The continuous spectrum of white light.

The light source could be an electric bulb or the sunlight. It is passed through a narrow slit so that only a small beam is selected. A convex lens focuses the beam on a prism which breaks it up into its constituent wavelengths. Each wavelength in the visible region produces a particular colour. The colours gradually fade, one into another. If a photographic film is placed at the position of the screen and later developed, the film is seen to be darkened beyond where red and violet colours appear. This shows that there are frequencies in white light which are not detected by the human eye. The frequencies beyond the red are called infrared rays, those beyond the violet are the ultra violet rays.

TABLE 1.4: Wavelength ranges of electromagnetic radiation.

EXERCISE 1.7

Using the relationship,

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

where c $= 3 \times 10^{10}$ cm sec^{-1}, calculate the frequency range of the radio waves in cycles sec^{-1}. (Take wavelength range to be 10 – 10^4 cm.)

Answer: 3×10^9 - 3×10^6 cycles sec^{-1}

Light as a form of Energy

We feel the energy of the sun's rays. Plants convert this same energy to chemical energy by a process known as photosynthesis. These are evidences that light is a form of energy. An experimental proof is the ignition of a combustible material, such as kerosene, by focusing the sun's rays on it, using a lens, as shown in Figure 1.19.
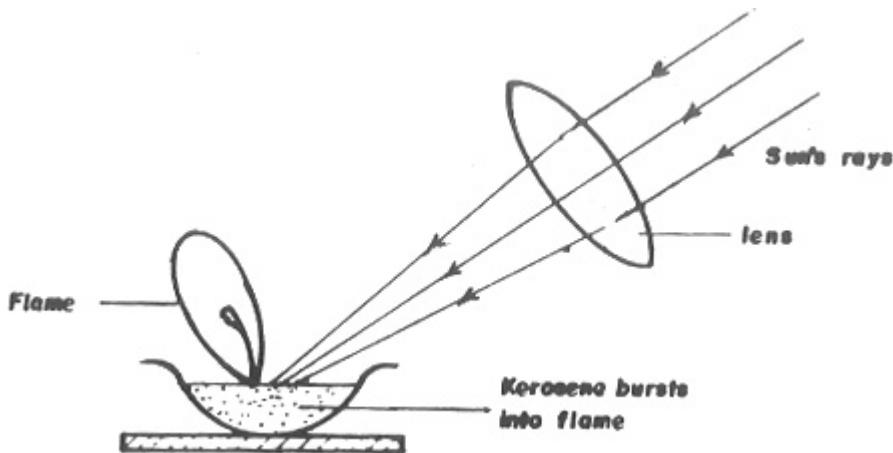

Figure 1.19: Using a lens to ingnite kerosene.

Light carries its energy in bundles. Each bundle, called a photon or a quantum, contains an amount of energy which depends on the frequency of the radiation. The relationship between the energy and frequency is given by :

$$E = h\upsilon$$

where h is a proportionality constant called Planck's constant.

Since $v = \dfrac{c}{\lambda}$

$\bar{E} = \dfrac{hc}{\lambda}$

So, the energy of a photon of light is proportional to the frequency but inversely proportional to the wavelength of radiation.

Atomic Spectra

(a)   **Absorption spectrum:** If hydrogen gas is put into a discharge tube at low pressure and electric current at high voltage is passed through the metal plates at opposite ends of the tube, a pale-blue coloured light is observed. If this light is passed through a prism arranged as shown in Figure 1.20, a line spectrum, made up of black lines on a white screen is obtained. This is an absorption spectrum of hydrogen. Figure 1.21 shows this absorption spectrum, indicating the missing wavelengths of white light which are responsible for the black lines.
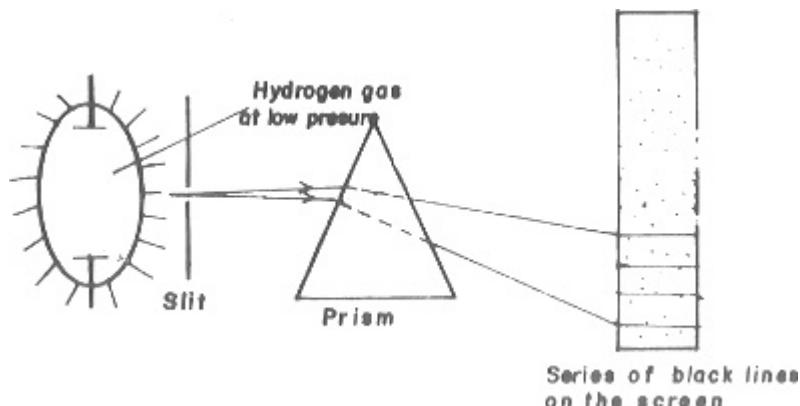
*Figure 1.20: Apparatus forgetting the hydrogen absorption spectrum*
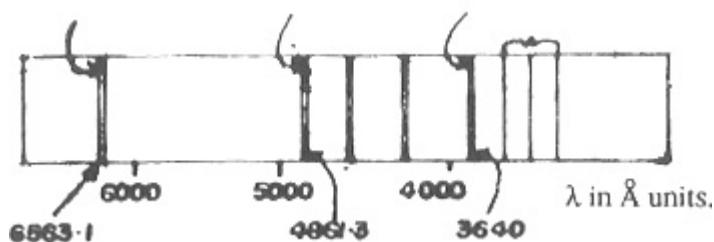
Figure 1.21: The hydrogen absorption spectrum

The explanation for the missing wavelengths is that electrons in hydrogen atoms absorb photons of energy from white light and jump to shells of higher energy level. The light reaching the screen has thus lost the absorbed wavelengths.

(b)   **Emission spectrum:** If the same discharge tube is used as a

source of light, the spectrum again consists of lines (Figure 1.22). These are bright lines on a dark background.
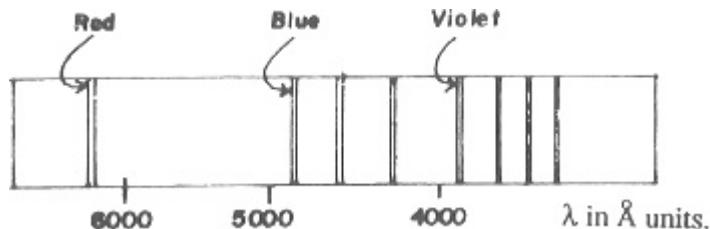
Figure 1.22: Hydrogen emission spectrum

This is an emission spectrum. The wavelengths that were missing from the absorption spectrum are the ones present in the emission spectrum. On return to their lower energy levels, the electrons that jumped to shells of higher energies now emit photons of light corresponding in energy to what they absorbed. The emission appears on the screen as bright colours. This is why wavelengths missing in the absorption spectrum are the ones appearing in the emission spectrum.

Emission
Spectrum

Absorption
Spectrum
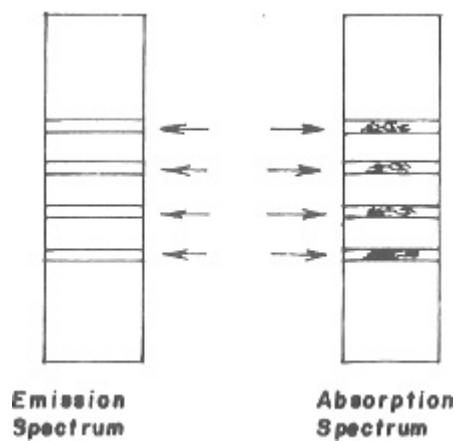
Figure 1.23: Missing wavelengths in an absorption spectrum appear in emission spectrum

When all electrons in an atom are in their lowest energy levels, the atom is said to be in the ground state. When some electrons absorb some photons of light and jump into shells of higher energy levels, the atom is said to be excited.

The Spectrum of the Hydrogen Atom

The hydrogen atom has a single electron in the K shell. If it absorbs a photon of light to move into a higher energy level, we should expect a single black line in its absorption spectrum. When this electron returns to the ground state it should give rise to a single colour or line in the emission spectrum, corresponding to the missing wavelength of the absorption spectrum. But in practice, a complex spectrum consisting of several lines is obtained (Figure 1.21 and 1.22).

The complex spectrum of hydrogen is explained thus: a sample of hydrogen vapour contains many molecules which are made up of two atoms each. The single electron of each atom is capable of absorbing and re-emitting different number of photons of energy. While some absorb enough energy to go into the L shell, other absorb enough to take them into the M, N, O, etc, shells. The appropriate wavelengths are found missing in the hydrogen absorption spectrum. Similarly, the wavelengths of the radiation they re-emit will correspond to the different energies absorbed. The energy difference between two levels is calculated from the equation: E = hv (h and v have already been defined).
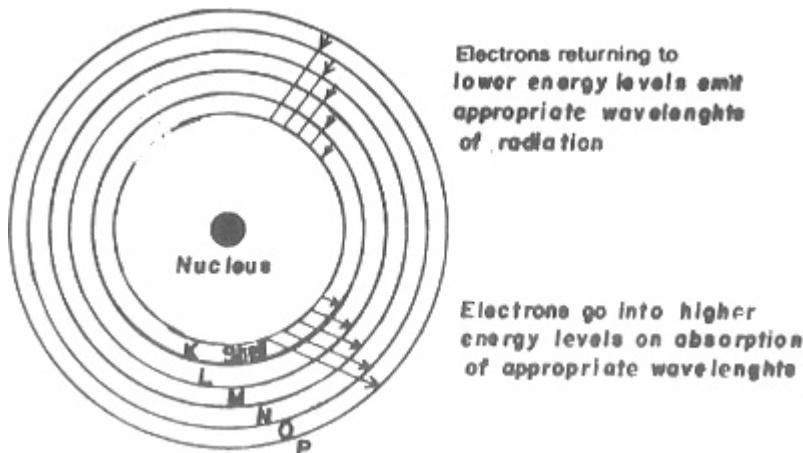
Figure 1.24: Energy levels of electrons and Bohr's explanation of the hydrogen spectrum

Worked Example

If the energy difference between two electronic energy levels is 6.63 kJ mol^{-1}, calculate the frequency of the electromagnetic radiation emitted when an electron drops from the higher to the lower energy level. (Planck's constant = 6.63 × 10^{-34}Js).

Solution:

$$E_1 - E_2 = hv$$

i.e $6.63 \times 10^3 = 6.63 \times 10^{-34} \ v$

$\therefore \quad v = \dfrac{6.63 \times 10^3}{6.63 \times 10^{-34}} \ s^{-1}$

$\quad = \dfrac{10^3}{10^{-34}} \ s^{-1}$

$\quad = 10^{37} \ s^{-1}$

1.4 Quantum Numbers

The spectra of atoms with many electrons are more complex than that of hydrogen. Each line is seen to be composed of several very closely

spaced lines. By solving a classical wave equation, Schrodinger was able to explain the fine structure. Each shell was considered to be composed of a number of sub-energy levels.

The different energy levels correspond to different numbers, called quantum numbers, which result from the solution of the wave equation. One such number is the principal quantum number, n. This has to do with the energy electrons possess due to their distance from the nucleus. The second, called azimuthal quantum number. It has to do with the energy electrons possess due to their angular momentum. The magnetic quantum number, m, corresponds to the energy derived from their orientation in space. The last in the series, the spin quantum number, s, corresponds to the energy electrons derive from their clockwise or anticlockwise spin.

* n may have integral values from 1 upwards, i.e. 1, 2, 3.....
* L may have intergral values from zero to (n - 1).
* m may have intergral values from +L to -L
* s may have two values only, $+\frac{1}{2}$ or $-\frac{1}{2}$ (clockwise or anticlockwise spin).

If n = 1, L can have only one value: zero and since m has values from +L to -L, then m is also zero; s can have its two values: $+\frac{1}{2}$ or $-\frac{1}{2}$. So there are only two sets of values for electrons having the principal quantum number n = 1. These are tabulated in Table 1.5.

TABLE 1.5: Sets of quantum number values for n = 1

n	L	m	s
1	0	0	$+\frac{1}{2}$
1	0	0	$-\frac{1}{2}$

For n = 2, L has two volues: 0 of 1. m may have values: + 1, 0, or -1. The following sets of quantum numbers result as shown in Table 1.6 for n = 2.

TABLE 1.6: Sets of quantum number values fer n = 2

n	l	m	s	
2	0	0	$+\frac{1}{2}$	
2	0	0	$-\frac{1}{2}$	
2	1	+1	$+\frac{1}{2}$	8 sets of values
2	1	+1	$-\frac{1}{2}$	
2	1	0	$+\frac{1}{2}$	
2	1	0	$-\frac{1}{2}$	
2	1	-1	$+\frac{1}{2}$	
2	1	-1	$-\frac{1}{2}$	

EXERCISE 1.8:

How many sets of values are there for electrons with principal quantum number 3? Tabulate them.

Answer: 18 sets of values.

Significance of Quantum Numbers

The quantum numbers have significance for the energy of the electrons and their arrangement in space.

The principal quantum number, n, represents the main energy level of the electron.

It has the same significance as the K, L, M. . . shells. But each energy level is no longer associated with a fixed radius. When n = 1, the electron is in its lowest energy level, called its ground state. Higher values of n correspond to higher energy levels.

The Azimuthal quantum number, L, determines the shape of the area in space where the electron is located.

This is also called the orbital of the electron. For l = 0, the orbital is a sphere around the nucleus. It is called an s–orbital.
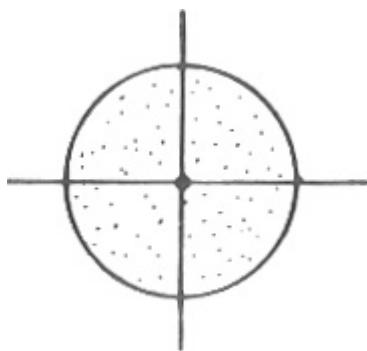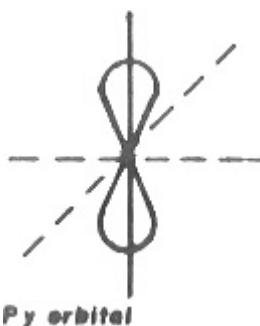
Figure 1.25: Shape of an s–orbital

No matter the value of n, the s–orbital has the same shape. For l= 1, the orbi-tals are dumb-bell shaped. They are called p–orbitals. There are three such dumb-bell shapes, depending on the values of m when l = 1. They stretch along the three cartesian co-ordinates, as illustrated in Figure 1.26.
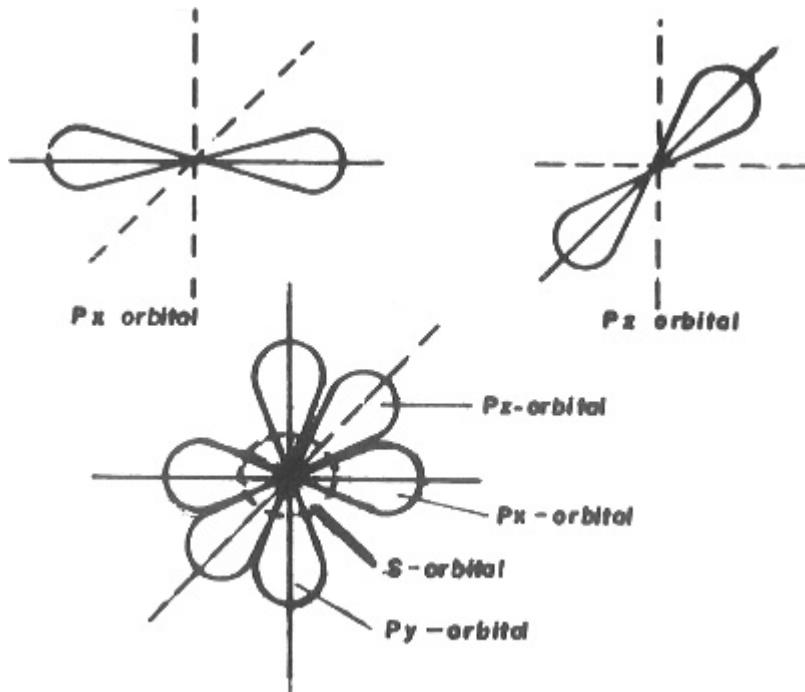
P y orbital

Figure 1.26: P–orbitals

For L = 2, there are five orbitals, called d–orbitals. Their shapes are more complex and need not concern us now. For L = 3, there are seven orbitals, called f–orbitals which have even more complex shapes.

Each orbital, whether s–, p–, d– or f–, takes a maximum of two electrons with opposite spins, (s = +½ or -½). Within a given principal quantum number, the s–orbital is of lowest energy, followed by the p–orbital, then the d– orbital. The f–orbital is of highest energy. The three p–orbitals have equal energies, so do the five d–orbitals and the seven f–orbitals.

Table 1.7 is a summary of the orbitals in the first four shells from the nucleus.

TABLE 1.7: Orbitale associated with quantum numbers of the first four shells

Shell	Values of n	Values of l	Values of m	Number and type of orbital		Total number of electrons
K	1	0	0	1	s	2
L	2	0	0	1	s	
		1	+1, 0, − 1	3	p	8
M	3	0	0	1	s	
		1	+1, 0.− 1	3	p	18
		2	+2, +1, 0, − 1, − 2	5	d	
N	4	0	0	1	s	
		1	+ 1, 0, − 1	3	p	32
		2	+ 2, +1, 0, − 1, −2	5	d	
		3	+3, +2, +1, 0, − 1, −2, −3	7		

We may regard elements following one another consecutively in the horizontal rows of the periodic table as resulting from a stepwise addition of one proton to the nucleus, and one electron to the orbitals. The last added electron goes into an available orbital with lowest energy level. This way, we can account for the position of each element in the periodic table.

This principle of stepwise addition of electrons is known as the "Aufbau" principle.

Hund's rule of maximum multiplicity is part of the principle.

Hund's rule states that if two or more orbitals of equal energies, such as the three p—orbitals, or the five d—orbitals. are available,electrons enter them singly first before pairing takes place.

Figure 1.27 is a schematic diagram of the relative energy levels of the orbitals.
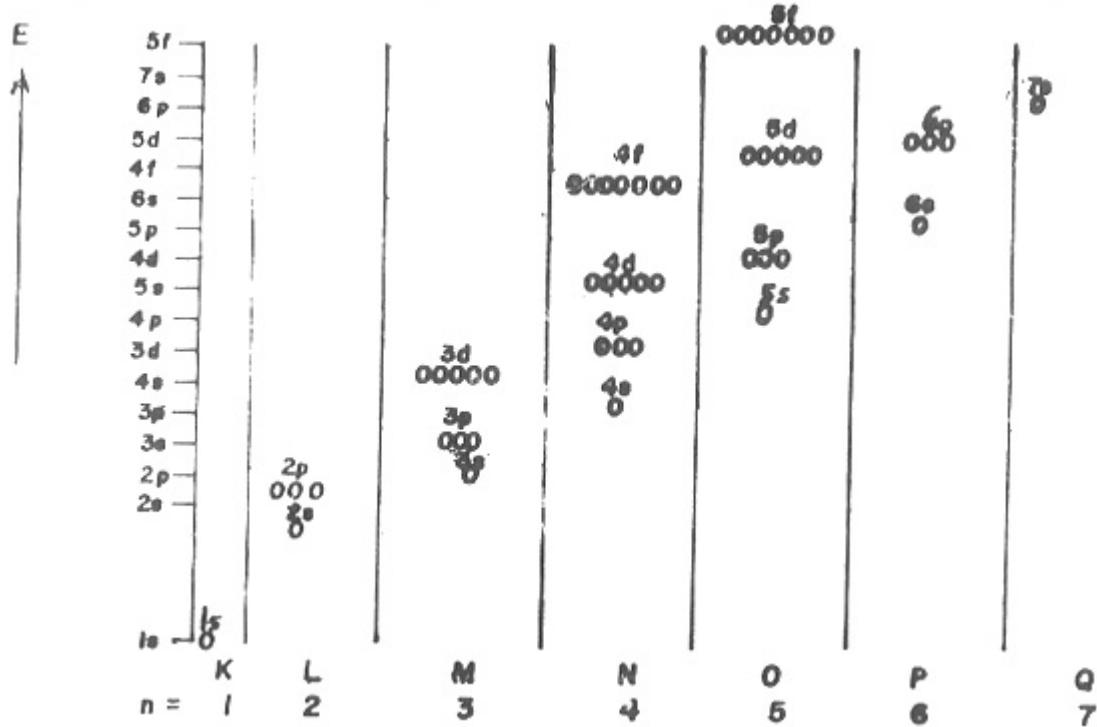
Figure 1.27: Energy level diagram of the orbitals.

A formula for remembering this increasing order of energies is given in Table 1.8.
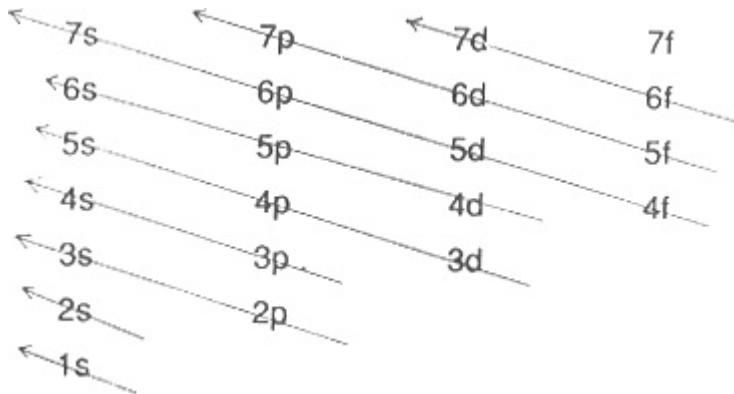
TABLE 1.8: The "Aufbau" Principle
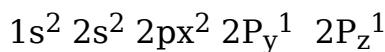
1.5 Electronic Configurations of the First 30 Elements

By representing an electron with an arrow, **(1)**, and a pair of electrons by **(⇅)**, the electronic configurations of the first ten elements can be written as in Table 1.9, following the "Aufbau" principle.

TABLE 1.9: **Electronic configurations of the first 20 elements**

Atomic Number	Symbol	Electronic configuration				
		1s	2s	2P$_X$	2P$_Y$	2P$_Z$
1	H	↑				
2	He	↑↓				
3	Li	↑↓	↑			
4	Be	↑↓	↑↓			
5	B	↑↓	↑↓	↑		
6	C	↑↓	↑↓	↑	↑	
7	N	↑↓	↑↓	↑	↑	↑
8.	O	↑↓	↑↓	↑↓	↑	↑
9	F	↑↓	↑↓	↑↓	↑↓	↑
10	Ne	↑↓	↑↓	↑↓	↑↓	↑↓

An alternative way of representing the electronic configurations of atoms is to write the number of electrons in each orbital as a superscript. By this notation, the electronic configuration for oxygen, atomic number 8, is:

$$1s^2\ 2s^2\ 2px^2\ 2P_y^1\ 2P_z^1$$

or $1s^2\ 2s^2\ 2p^4$, for short.

The electronic configurations of the third row elements, by this notation, are given in Table 1.10.

TABLE 1.10: Electronic configuration of the third row elements

Atomic Number	Symbol	Electronic configuration
11	Na	$1s^2\ 2s^2\ 2p^6\ 3s^1$
12	Mg	$1s^2\ 2s^2\ 2p^6\ 3s^2$
13	Al	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^1$
14	Si	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^1\ 3p_y^1$
15	P	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$
16	S	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^1\ 3p_z^1$
17	Cl	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1$
18	Ar	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^2$

EXERCISE 1.9:

Potassium, atomic number 19, begins a new shell (n = 4), after argon. Write down its electronic configuration, and that of calcium, atomic number 20.

The 3d-orbitals have higher energy levels than the 4s, but lower than the 4p. So the 3d-orbitals are filled after the 4s but before the

4p–orbitals. Ten electrons enter into the five 3d-orbitals, singly first, before pairing takes place. Their filling gives rise to the first series of ten transition elements, scandium to zinc. Table 1.11 gives the electronic configurations of the elements in the first transition cries.

TABLE 1.11: Electronic configurations of the first transition metal series

Element	Atomic Number	Electronic configuration
Sc	21	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^1$
Ti	22	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^2$
V	23	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^3$
Cr	24	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^1$ $3d^5$
Mn	25	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^5$
Fe	26	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^6$
Co	27	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^7$
Ni	28	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^8$
Cu	29	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^1$ $3d^{10}$
Zn	30	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^{10}$

By the arrow-notation, the electronic configuration of scandium is:

EXERCISE 1.10:

Using the arrow notation and recalling Hund's rule, write down the electronic configurations of manganese, iron and cobalt.

Eectron-dot symbol representation

It is convenient when discussing bonding, to express electrons in the last shells of an atom by dots around the symbol of the element. The dot symbol of hydrogen is H·, that of helium is He: The electron-dot symbols of the first twenty elements are shown in Table 1.12.

TABLE 1.12: Electron-dot symbols of the first twenty elements

ns^1	ns^2	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6
H.	He:						
Li.	Be:	B:	C:	:N:	:O:	:F:	:Ne:
Na.	Mg:	Al:	Si:	:P:	:S:	:Cl:	:Ar:
K˙	Ca:						

The electron-dot symbols reveal at a glance, the periodicity of electronic configurations of the elements, which gives rise to periodicity in properties.

1.6 Periodicity of properties

The periodicity of properties, especially reactions, of the elements was discussed in Book 2. Here, we are concerned with periodicity in the elementary properties on which those reactions depend.

Atomic Size

Atomic size is not easily defined because the exact position of the outermost electron, which should mark the size of an atom, is not fixed. However, atomic volume, which is atomic mass divided by density of the element could be used to represent atomic size for solid elements. The density of gases is temperature dependent. So, atomic volume for gaseous elements is meaningless.

EXERCISE 1.11:

Table 1.13 gives the atomic masses and densities of the alkali metals.

TABLE 1.13:

Element	Atomic Number	Atomic mass (g)	Density (g cm^{-3})	Atomic volume (cm^3)
Li	3	6.94	0.53	?
Na	11	22.99	0.97	?
K	19	39.1	0.86	?
Rb	37	85.47	1.53	?
Cs	55	132.91	1.90	?

Calculate the atomic volume of each alkali metal.
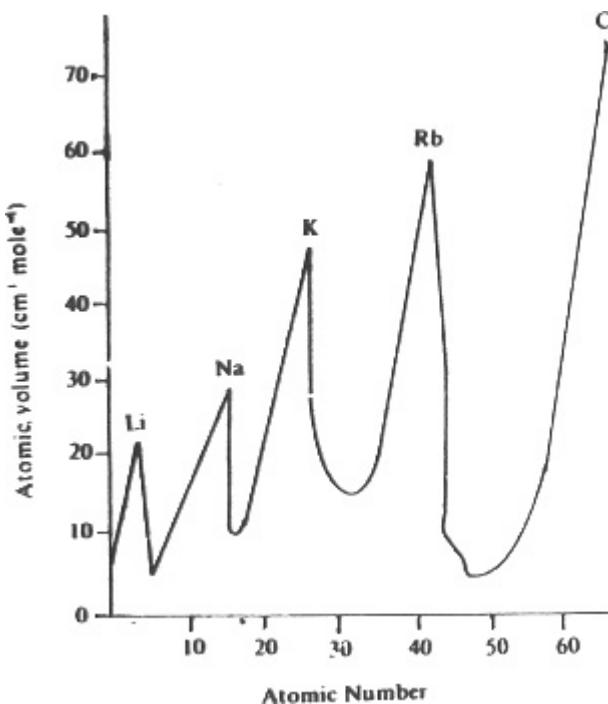
FIGURE 1.28: plot of atomic volume Versus atomic number

Figure 1.28 is a plot of atomic volume against atomic number of the elements. The periodicity of atomic volume is evident from this plot. Lithium, sodium, potassium, etc, are seen to have higher atomic volumes than other members of their periods. This is because these alkali metals start new shells. The contraction of atomic volume in going from left to right in a given period is due to the greater attraction the increased nuclear charge has for the outer electrons which are added to the same shell. The effective nuclear charge which attracts the outer electrons to the nucleus increases from left to right in a given period because of the increase in the number of protons in the same direction.

Atomic Radius

True relative sizes of the elements are not obtained from atomic volume because elements exist in many forms. Atomic radius is preferred, but its value depends on what neighbours the atom has. However, half the inter-nuclear distance between two atoms has been accepted as a measure of atomic radius in solids and gases. This distance is slightly less than the actual atomic radius in covalent compounds. It is called the covalent radius. However, the covalent radius is a good approximation for most purposes.
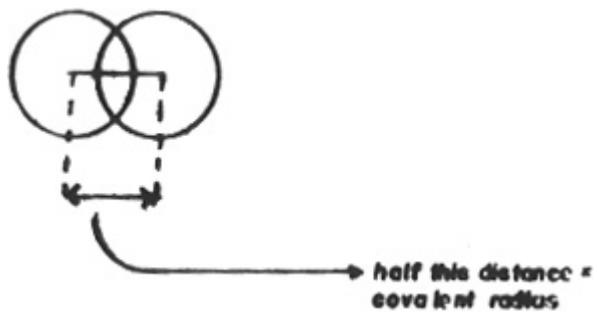
Figure 1.29: covolent radius

Three factors determine the radius of an atom (and hence size of the atom). They are:

(i)   the attractive force between the nucleus and the outermost electrons;

(ii) the shielding (screening) effect on the outermost electrons by inner electrons;

(iii) the number of shells occupied by electrons.

For elements in the same group, the first and second factors tend to cancel out. Hence the atomic radii for elements in the same group depend on the number of occupied shells. Since the atomic number and shell number increases down the group atomic radius also increases down the groups.

Taking the alkali metals for example, lithium ($1s^2\ 2s^1$) has electrons in the first two shells only. Sodium ($1s^2\ 2s^2\ 2p^6\ 3s^1$) has electrons in three shells, and potassium ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$) has electrons in four shells. This successive addition of new shells continues down the group and in other groups too, leading to increase in atomic radius down a given group.

For elements in a horizontal row (period), the number of occupied shells is the same. The addition of one proton and one electron in moving from one element to another, causes an increase in the electrostatic attraction between the nucleus and the last electron added because this last electron is added to the same shell as others before it. Therefore, atomic radius decreases from left to right across the periods.

A plot of atomic radius against atomic number therefore gives a series of curves, Figure 1.30, rising whenever a new shell is started, and falling gradually again.
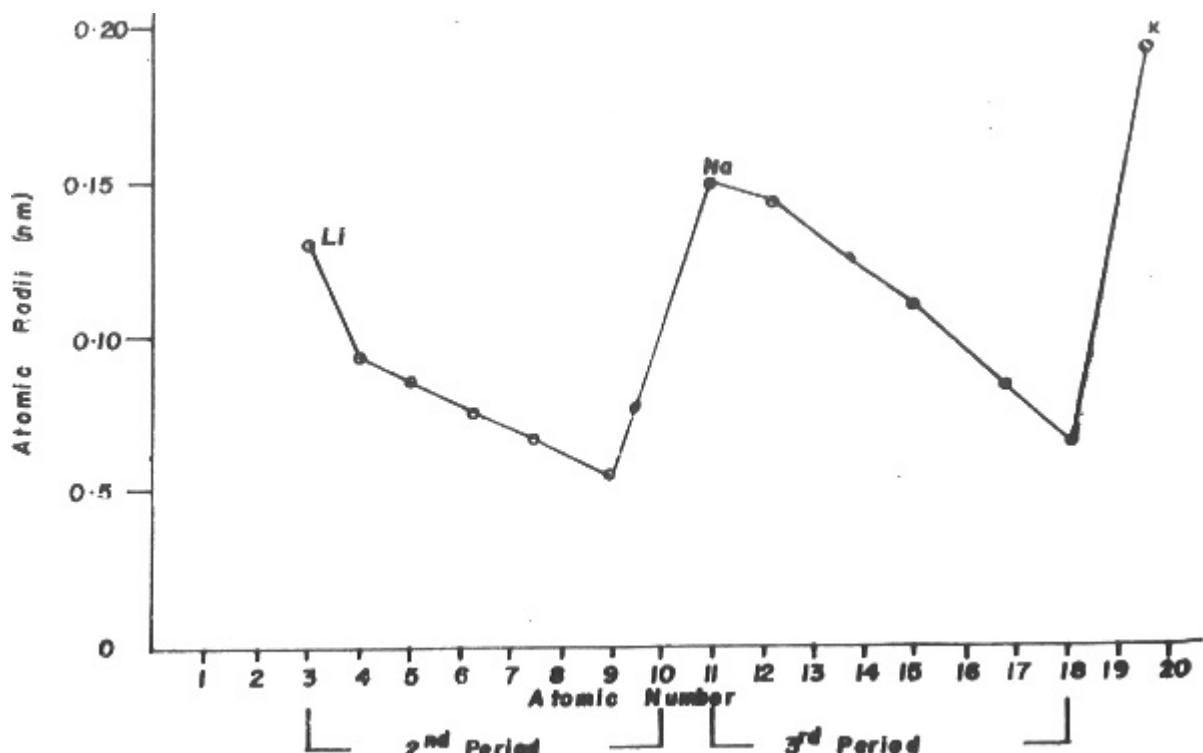
Figure 1. 30: A plot of atomic radius against atomic number

Ionic Radii

Metals form ions by the loss of valence electrons, which usually results in the shedding off of one shell. The radius of the ion formed is thus less than the radius of the atom from which it was formed. For ions in the same group, the number of shells left in the ions still increases as we go down the group. Thus ionic radii, increase down the group as is the case with atomic radii.

Within a period, the variation is not constant. For the metallic ions between lithium and carbon in period two, for example, there is an increase in the nuclear charge while the number of electrons left in the ions remains constant. Li^+, Be^{2+}, $-B^{3+}$, C^{4+} are species with the same number of electons and electronic configuration. They are said to be isoelectronic. The increase in nuclear charge from left to right, leads to decrease in ionic radii in that order.

The non-metals form ions by gain of electrons. Nitrogen gains three electrons to form the ion N^{3-}. Oxygen gains two electrons to form O^{2-}, while fluorine gains one electron to form $F^{â€''}$. Repulsion between the electrons leads to greater ionic radii than the atomic radii of the respective elements. The three additional electrons in N^{3-} repel more than the two in O^{2-}, etc. Thus, ionic radii decrease from N^{3-} towards $F^{â€''}$. This trend is shown in Figure 1.31.
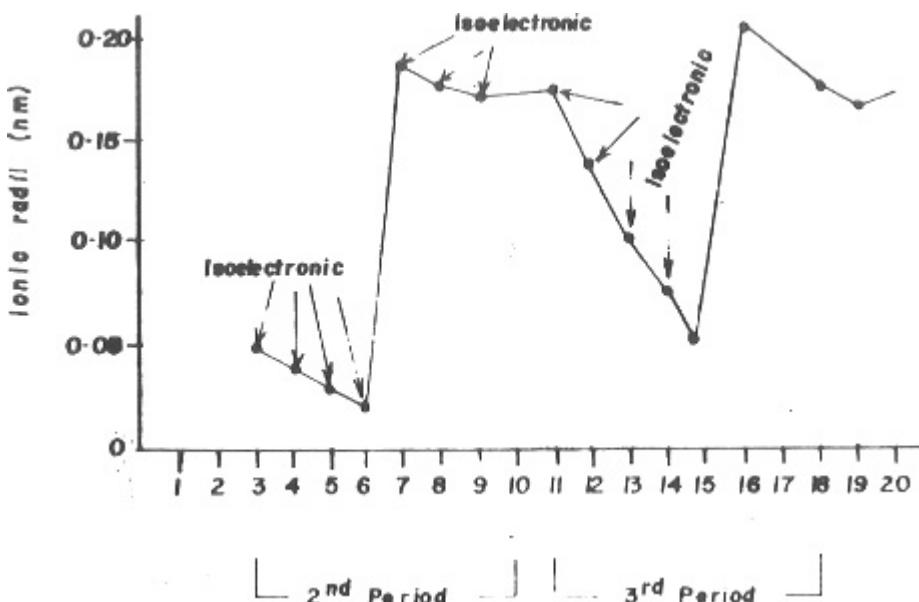
Figure 1.31: Plot of ionic radius vs. atomic number

Ionization Energy

Ionization energy has earlier been defined as the energy required for the process:

$$M(g) \rightarrow M^+(g) + e^-$$

Ionization energy is high if:

(i)   nuclear charge is high, or

(ii)   atomic radius is small.

For elements in the same group, the effect of increasing nuclear charge down the group is balanced by the shielding effect of the completely filled inner shells on the outer electrons. Thus, ionization energy depends mainly on the atomic radius and not on the nuclear charge for elements in the same group. As a result, ionization energy decreases down the group.
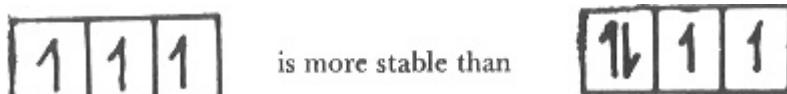
The phenomenon of shielding effect is observed among elements in the same group. Though atomic number increases from top to bottom for elements in the same group (implying that nuclear charge increases down the group, and resulting in outermost electrons being held by progressively stronger forces down the group) the outermost electrons are not held by progressively stronger forces. This is because electrons in the completely filled inner orbitals shield the outermost electrons from the influence of the nuclear charge.

In a given period, ionisation energy increases from left to right because:

(i)   atomic radii decrease in this order, which implies that the outermost electrons become more strongly bound to the nucleus;

(ii)   nuclear charges increase in this order, which also means that outermost electrons become more strongly bound to the nucleus.

This general trend is reversed between beryllium and boron. The electronic configurations of these elements are $1s^2\ 2s^2$ and $1s^2\ 2s^2\ 2p^1$ respectively. An electron is pulled out from a 2s—orbital in beryllium, but from a 2p—orbital in boron. Since the 2s—orbital is a bit nearer the nucleus than the 2p—orbital, more energy is required to pull out an electron from beryllium than from boron, hence the reverse. Similar reversals occur, for the same reason, between magnesium and aluminium in period 3, and between zinc and gallium in period 4.

Another reversal occurs between nitrogen and oxygen in period 2, and between elements in similar positions in periods 3 and 4. Here, the singly-filled p—orbitals are more stable than when pairing has started. That is:

Electron-electron repulsion in the paired p—orbital is responsible for the decreased stability and for the lower ionization energies of oxygen than nitrogen; sulphur than phosphorus; and selenium than arsenic.

A plot of ionization energy against atomic number shows a reverse of the curves in the plot of atomic radii against atomic number. The alkali metals which are top in the plot of atomic radii versus atomic number, are now at the bottom in the plot of ionization energy versus atomic number. Instead of a decrease, the curve rises from an alkali metal to a noble gas, then falls as another alkali metal starts a new shell.
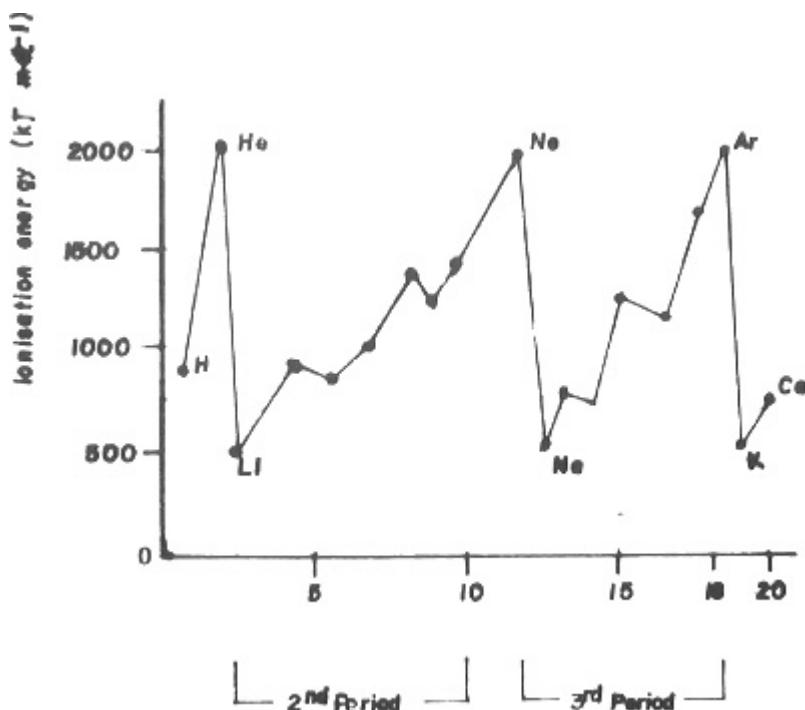
Figure 1.32: Plot of ionization energy against atomic number

Electron Affinity

Electron affinity is a measure of the ease of gain of electron. It is the energy released when a gaseous atom accepts an electron to form a gaseous negative ion.

Electron affinity is the energy involved in the process $E(g) + e^-$ $\rightarrow$ E^- (g).

Table 1.14 gives the electron affinities of some elements.

TABLE 1.14: Electron affinities of elements at OK (in kJ mol^{-1})

Group	I	II	III	IV	V	VI	VII	O
	H 72							He −54
	Li 57	Be −66	B 15	C 120	N −31	O 142	F 333	Ne −99
	Na 21	Mg −67	Al 26	Si 135	P 60	S 196	Cl 348	
							Br 342	
							I 297	

The general trend in electron affinity is a decrease down each group. Nitrogen, oxygen and fluorine have unexpectedly low values because the atoms are very small. This means that their electrons are spread

over a small area, resulting in high electron densities. The atoms therefore tend to repel any additional electrons. After these first elements of the groups, the general trend of decrease in electron affinity down the groups prevails. The reason for this order of change is because of the increase in atomic radius down the group.

The values of electron affinities of the elements depend on the electronic configurations of their atoms. The noble gases which have stable electronic configurations have no tendency to accept electrons. They have zero electron affinity. The halogens require only one electron each to attain stable electronic configurations. Their electron affinities are therefore very high. The group 6 elements require two electrons per atom to attain stable electronic configurations. After one electron has been added, it becomes more difficult to add another. Their electron affinities are therefore lower than those of the group 7 elements. Generally, electron affinity increases across the period from left to right, among the non-metals.

Electron affinity figures are known for only a few elements. Therefore, it i*s* not a very useful property of the elements.

Electronegativity

In covalent bond formation each atom donates as well as accepts an electron. We say that the two atoms share a pair of electrons contributed by them. Electronegativity is a measure of how readily the atoms do this. Electronegativity is defined as the relative ability of an atom in a molecule to attract electrons. Though, it is not measurable, it can be estimated. One way of estimating its value is to take the average value of ionization energy and electron affinity of the element. Table 1.15 lists the electronegativity values of the elements.

TABLE 1.15 : Electronegativity scale (Pauling)

Groups	I	II	III	IV	V	VI	VII	VIII
	H 2.1							He —
	Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne —
	Na 0.9	Mg 1.2	Al 1.5	Si 1.9	P 2.1	S 2.5	Cl 3.0	Ar —
	K 0.8	Ca 1.0	Ga 1.6	Ge 1.7	As 2.0	Se 2.0	Br 2.8	Kr —
	Rb 0.8	Sr 1.0					I 2.5	Xe —

Both ionization energy and electron affinity increase from left to

right across the periods, and decrease from top to bottom in the groups. Their average values, which is a measure of electronegativity, should therefore also increase from left to right in the periods and decrease from top to bottom in the groups. This is evident in Table 1.15.

EXERCISE 1.12:

1.   Where in the periodic table would you expect to find the most electronegative element, and why?

2.   Why are there no values of electronegativities for the noble gases?

CHAPTER SUMMARY

• The evidences available for the detailed structure of the atom are derived from many sources. Information about the nucleus of the atom is given by:

(i) natural radioactivity in which atoms disintegrate to atoms of lighter elements, emitting sub-atomic particles.

(ii) cathode ray tube experiments, in which J.J. Thompson and others studied the nature of electrons, protons and neutrons.

(iii) Rutherford's experiment in which the nucleus was found to be made up of a small hard core where the protons are concentrated, and a much larger space where electrons revolve round the nucleus.

(iv) Moseley's experiment which showed that the number of protons in a nucleus increases gradually from one element to another.

• Information about the arrangement of the electrons within the atom is provided by:

(i) ionization energies of atoms, which are energies required to remove successive outermost electrons from atoms.

(ii) atomic spectra (absorption or emission) which indicate energy level differences between different electrons in an atom.

(iii) the "Aufbau" principle – which is the principle of stepwise addition of electrons to atomic orbitals to form new elements.

(iv) Hund's rule of maximum multiplicity, which states that when two or more orbitals of equal energy (same energy level) are available, electrons enter them singly before pairing takes place.

• Quantum numbers:

(i) The principal quantum number, n, represents main energy

levels of electrons.

(ii) The azimuthal quantum number, L, represents the sub-energy levels (orbitals) into which the main energy levels (shells) are divided.

(iii) The magnetic quantum number, m, represents the energy which electrons have due to their orientation in space.

(iv) The spin quantum number, s, represents the energy which electrons have due to their clockwise or anti-clockwise spin.

ASSESSMENT

1. The first five ionization energies of carbon, in kJ mol^{-1}, are as follows:
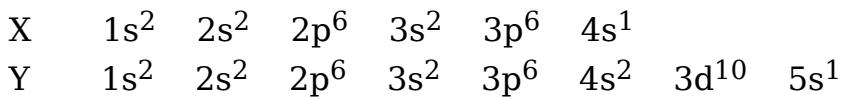
1st	2nd	3rd	4th	5th
1090	2350	4610	6220	3780

    Explain the magnitudes in terms of the electronic configuration of carbon. How many valence electrons has carbon? Explain your answer.

2. What contributions to the development of the atomic structure were made by the following: (i) Lord Rutherford, (ii) J. J. Thompson, (iii) J. Chadwick, and (iv) H.J.G. Moseley?

3.   If the diameter of the nucleus of a hydrogen atom is 10^{-12} cm and the diameter of the hydrogen atom 10^{-7} cm, calculate the ratio of atomic volume to nuclear volume in a hydrogen atom.

4. If the energy difference between two electronic energy levels in an atom is 3.0 kJ mol^{-1}, calculate the wavelength of electromagnetic radiation absorbed when an electron jumps from the lower into the higher energy level.

    Take Planck's constant as 6.63×10^{-34} Js.

5. Lise the conditions that cause two atoms to combine to form:
    (i)   an ionic bond,
    (ii) a covalent bond,
    (iii) a polar covalent bond.

6. What experimental evidence points to the quantization of electromagnetic radiation?

7. Explain the complexity of the hydrogen atomic spectrum.

8. What is the physical significance of each of the quantum numbers?

9. Draw an s – and the p– orbitals of a carbon atom. Explain the tetravalence of carbon.

10. Write down the electronic configuration of oxygen (atomic number 8), neon (atomic number 10), and sulphur (atomic number 15).

11.   Account for:
    (i)   the tetrahedral structure of methane,
    (ii)   the fact that the H-N-H angle in ammonia is 107Â°,
    (iii) the planar structure of BF_3 .

12.   Consider the two electronic configurations:
    X $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^1$
    Y $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^{10}$ $5s^1$

    Which of the following statements is false.
    A. Energy is required to change X to Y.
    B. X represents a potassium atom.
    C. Less energy is required to remove an electron from Y than from
        X.
    D. X and Y represent different elements.