2 ATOMIC STRUCTURE

Student Learning Outcomes [C-11-A-01 to C-11-A-25]

After studying this chapter, students will be able to:

- Describe protons, neutrons, and electrons in terms of their relative charge and relative masses. **(Understanding)**
- Recognize that the terms atomic and proton number represent the same concept. **(Understanding)**
- Recognize that the terms mass and nucleon number represent the same concept. **(Understanding)**
- Explain the change in atomic and ionic radius across a period and down a group. **(Understanding)**
- Describe the behaviour of beams of protons, neutrons and electrons moving at the same velocity in an electric field. **(Understanding)**
- Determine the number of protons, neutrons, and electrons present in both atoms and ions given atomic or proton number, mass or nucleon number and charge. **(Knowledge)**
- Relate Quantum Numbers to electronic distribution of elements. **(Understanding)**
- Account for the variation in successive ionization energies of an element. **(Understanding)**
- Define terms related to electronic configuration (some examples include: shells, sub-shells, orbitals, principal quantum number (n), ground state). **(Knowledge)**
- Describe the order of increasing energy of the sub-shells (s. p, d, and f). **(Understanding)**
- Describe that, each atomic shell and sub-shell are further divided into degenerate orbitals having the same energy. **(Understanding)**
- Apply Aufbau principle, Pauli's exclusion principle and Hund's rule to write the electronic configuration of elements. **(Application)**
- Describe the number of orbitals making up s, p, d, and f sub-shells, and the number of electrons that can fill s, p, d, and f sub-shells. **(Understanding)**
- Describe the shapes of s, p, and d orbitals. **(Understanding)**
- Determine the electronic configuration of elements and their ions with proton numbers. (Some examples include: (a) simple configuration e.g., 2, 8. (b) Sub-shells e.g., $1s^2$, $2s^2$, $2p^6$, $3s^1$. (c) students should be able to determine both of these from periodic table and are not required to memorize these. (d) Students should understand that chemical properties of an atom are governed by valence electrons). **(Knowledge and Application).**
- Explain the electronic configurations to include the number of electrons in each shell, sub-

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shell and orbitals. **(Understanding)**

- Explain the electronic configurations in terms of energy of the electrons and inter-electron repulsion. **(Understanding)**
- Determine the electronic configuration of atoms and ions given the proton or electron number and charge. **(Understanding)**
- Describe free radical as a species with one or more unpaired electrons. **(Understanding)**
- Illustrate the importance of electronic configurations and development of new materials for electronic devices. (For example, semiconductors such as silicon has a specific electronic configuration that makes them ideal for their use in electronic devices) **(Understanding)**
- Deduce the electronic configurations of elements using successive ionization energy data. **(Application)**
- Deduce the position of an element in the periodic table using successive ionization energy data. **(Application)**
- Explain that ionization energies are due to the attraction between the nucleus and the outer electrons. **(Understanding)**
- Explain how ionization energy helps account for the trends across the period and down a group of the periodic table. **(Understanding)**
- Explain the factors influencing the ionization energies of elements in terms of nuclear charge, atomic/ionic radius, shielding by inner shells and sub-shells and spin pair repulsion. **(Understanding)**

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2.1 ATOMIC NUMBER, PROTON NUMBER AND NUCLEON NUMBER; IDENTITY OF AN ELEMENT

In 1913, **Moseley** observed that when different elements were bombarded with cathode rays, the X–rays of some characteristic frequencies were produced. It was found that the square root of frequency of the X–rays was directly proportional to the atomic number of an element Z.

$$\sqrt{\text{frequency}}\ (\nu)\ \alpha\ Z$$

He concluded that this number, i.e. the atomic number Z was a fundamental property of an element. It is also called **proton number**. The number of protons and neutrons in the nucleus of an atom is collectively called its nucleon number (A), also known as mass number.

Atomic number is related to the mass number by the following equation

$$A = Z + N$$

For example, an atom of an element X having atomic number Z and mass number A is described as ${}^{A}_{Z}X$, e.g. ${}^{27}_{13}Al$. Number of neutrons in an atom can be calculated as

$$N = A - Z$$

Let us consider $^{27}_{13}Al$,

Atomic number/ proton number (Z) = 13

Mass number/ nucleon number (A) = 27

$$N = 27 - 13 = 14$$

Similarly, the number of electrons, protons, and neutrons can be justified for an ion as in the following example:

$^{27}_{13}Al$ atom loses three electrons to form Al^{3+}, then;

No. of protons = 13

No. of neutrons =14

No of electrons = 13 – 3 = 10

Similarly, $^{35}_{17}Cl$ gains an electron to form Cl^{-} ion;

No. of protons = 17

No. of neutrons =18

No of electrons = 17+1 = 18

When gain of electrons happens by the neutral atoms, say $^{16}_{8}O$ to $_{8}O^{2-}$, $^{31}_{15}P$ to $_{15}P^{3-}$ and $^{32}_{16}S$ to $_{16}S^{2-}$, the number of neutrons, protons and electrons are as in **Table 2.1**.

Table 2.1 Number of protons, electrons and neutrons in different ions

Species	Neutrons	Protons	Electrons
O^{2-}	8	8	10
S^{2-}	16	16	18
P^{3-}	16	15	18

Thus the atomic number and proton number represent the same concept.

2.2 EFFECT OF ELECTRIC FIELD ON FUNDAMENTAL PARTICLES

The behaviour of particles in an electric field depends upon their masses and charges. If we allow the beams of electrons, protons and neutrons to pass one by one at the same speed through an electric field, they show their behaviours as follows:

1. Neutrons being neutral are not deflected but travel in a straight path perpendicular to the direction of electric field.
2. Protons being positively charged are deflected towards the negative plate.
3. Electrons being negatively charged are deflected towards the positive plate, to greater extent since they are $\frac{1}{1836}$ times lighter than protons.

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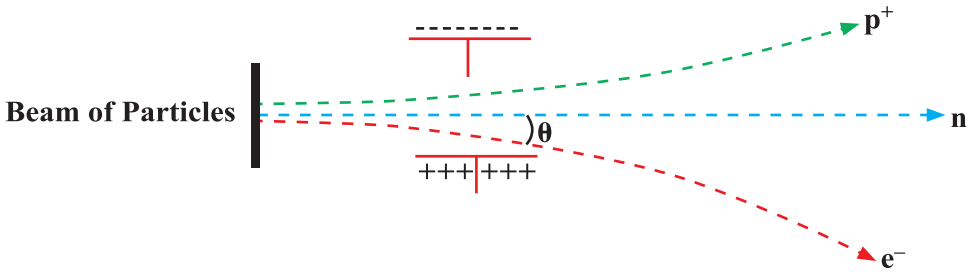

Figure 2.1 Behaviour of proton, electron and neutron in the electric field

The amount of deviation from its original direction of movement is measured in two ways.

(i) Angle of deflection $\propto \frac{\text{charge}}{\text{mass}}$ (ii) Radius of deflection $\propto \frac{\text{mass}}{\text{charge}}$

This is possible if we imagine that after deflection, the particle moves in a circular path. Hence, the factors affecting the radius of deflection are reciprocal to that for the angle of deflection.

2.2.1 Properties of Fundamental Particles

The **Table 2.2** shows the properties of three fundamental particles electron, proton and neutron present in an atom.

Table 2.2 Properties of three fundamental particles

Particle	Charge (coulomb)	Relative charge	Mass (kg)	Mass (amu)
Proton	$+1.6022 \times 10^{-19}$	+1	1.6726×10^{-27}	1.0073
Neutron	0	0	1.6750×10^{-27}	1.0087
Electron	-1.6022×10^{-19}	−1	9.1095×10^{-31}	5.4858×10^{-4}

Quick Check 2.1

a) Calculate the number of neutrons in the following elements.

(i) $^{39}_{19}K$ (ii) $^{35}_{17}Cl$ (iii) $^{40}_{18}Ar$

b) Which of electron, proton and neutron is deflected the most in the magnetic field?

2.3 EXPERIMENTAL EVIDENCES FOR THE ELECTRONIC CONFIGURATION

The modern theory of electronic structure originates from the Bohr model of atom. Evidence for this and later models of the atoms derives principally from two sources; atomic spectra and ionization energies.

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2.3.1 Atomic Spectra

When an element in its gaseous state is heated to high temperatures or subjected to electrical discharge, radiation of certain wavelengths is emitted. The spectrum of this radiation contains coloured lines and is called atomic emission spectrum. The atomic emission spectrum of hydrogen is shown in **Figure 2.2 (a).**

When a beam of white light is passed through a gaseous sample of an element in cold state, certain wavelengths are absorbed. The wavelengths of the white light that has been absorbed by the atoms show up as dark lines on the spectrum. The spectrum of this radiation is called an atomic absorption spectrum. The atomic absorption spectrum of hydrogen is shown in **Figure 2.2 (b)**. The wavelengths of the dark lines in the absorption spectrum are exactly the same as those of coloured lines in the emission spectrum.

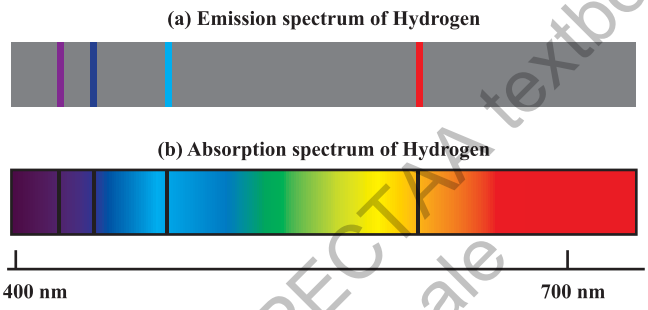

Figure 2.2 (a) Atomic emission spectrum of hydrogen **(b)** atomic absorption spectrum of hydrogen

Each element has a unique arrangement of electrons and thus a unique range of fixed energy levels. It follows that the wavelengths and frequencies of the radiation absorbed or emitted when electrons jump from one energy level to another must also be unique. This uniqueness convinces us to conclude that every element has its own characteristic spectrum. Therefore, every element is identified by its characteristic spectrum. Hence, we can say that atomic spectra are the finger prints of the elements. **Figure 2.3** shows the emission spectra of some elements.

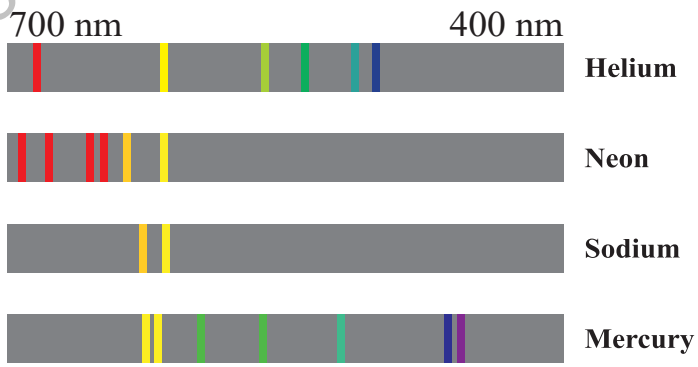

Figure 2.3 Spectral series of various elements as plotted by a spectrometer

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2.3.2 Ionization Energy and Energy Levels (Electronic Shells)

A major difference between electrons in different types of shells is their energy. We can investigate the electronic configuration of the atoms by measuring experimentally the energies of the electrons within them. This can be done by measuring ionization energies. Ionization energies are used to investigate the electronic configurations of elements in two ways.

i. Successive ionization energies of the same element

ii. First ionization energies for different element

i) Successive Ionization Energies of the Same Element

We can look at an atom of a particular element and measure the energy required to remove each of its electrons, one by one.

$$X \longrightarrow X^{+} + e^{-} \qquad \Delta Hi_1$$

$$X^{+} \longrightarrow X^{2+} + e^{-} \qquad \Delta Hi_2$$

$$X^{2+} \longrightarrow X^{3+} + e^{-} \qquad \Delta Hi_3$$

We can continue to remove electrons from an atom until only the nucleus is left. We call this sequence of ionization energies, successive ionization energies. The successive ionization energies show clearly the arrangement of electrons in shells around the nucleus.

If we take the magnesium atom as an example, and measure the energy required to remove successively the first electron, the second, the third, and so on. We obtain a graph when the ionization energies values are plotted against number of electrons as in **Figure 2.4**. This plot shows that successive ionization energies increase when we move from the valence shell to the inner shells. First two electrons are removed from the outermost shell and require lower energy for their removal. But, a large increase occurs when the third electron is removed. This is because when two electrons of the outer shell have been removed, the next has to be removed from the shell that is very much closer to the nucleus.

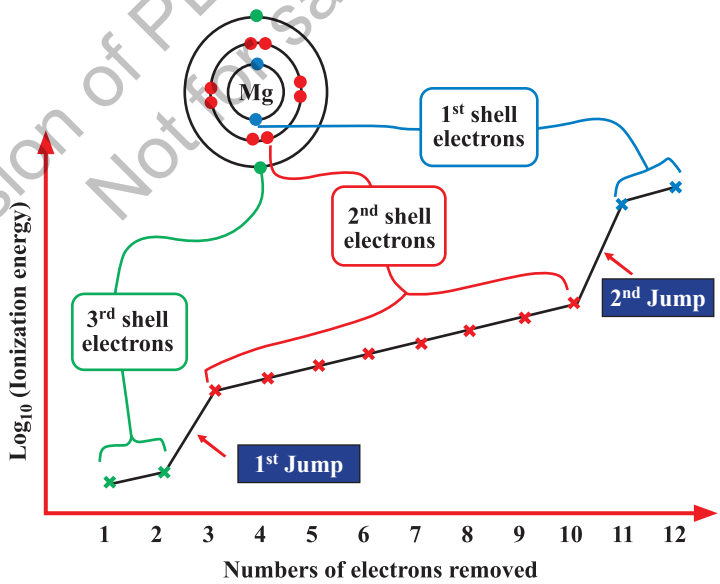

Figure 2.4 A plot of the successive ionization energies of Mg

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The next seven electrons are removed successively from the second shell and a gradual increase in ionization energy is observed. A similar but much more enormous jump occurs when the eleventh and twelfth electrons are removed. These electrons are removed from the first shell, right next to the nucleus. Hence, over all, we observe two large jumps in the successive ionization energies. These two large jumps in the series of successive ionization energies are very good evidence that the electron in the magnesium atoms exist in three different shells.

ii) First ionization energies of different elements

The second way in which ionization energies show us the details of electronic configuration is to look at how the first ionization energies of elements vary with atomic numbers. **Figure 2.5** shows a plot for the first 88 elements.

This graph tells us the following:

- All ionization energies are strongly endothermic; it takes energy to remove an electron from an atom.
- As we go down a particular group, for example, from helium to neon to argon, or from lithium to sodium to potassium, ionization energies decrease. The larger the atom, the easier is to separate an electron from it. Actually, down the group, number of shells increases, hold of nucleus on the valence electrons decreases, hence removal of electrons becomes easier.
- The ionization energies generally increase on going across a period. The group 1 elements, the alkali metals, have the lowest ionization energy within each period, and the noble gases have the highest. It is due to the reason that across the period shell number remains same. As the proton number increases, electrons are added in the same shell. Therefore, nucleus attracts the valence electrons more strongly. As a result, ionization energy increases across the period.

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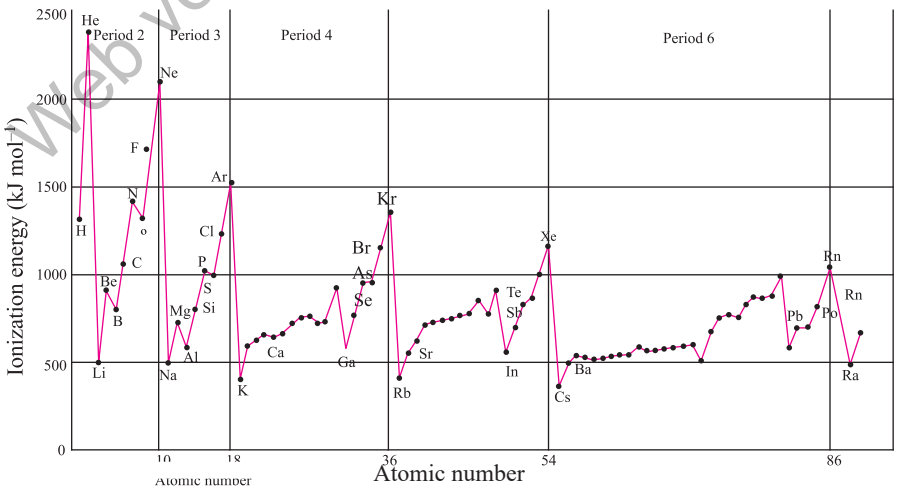

Figure 2.5 A plot of the ionization energies of elements against atomic number

Quick Check 2.2

a) Write equations that describe:
- i. 1st ionization energy of calcium
- ii. 3rd ionization energy of potassium
- iii. 2nd ionization energy of lithium
- iv. 5th ionization energy of sulfur

b) For the element aluminium (Z = 13), draw a sketch graph between the $\log_{10}$ of the successive ionization energies (y-axis) against the number of electrons removed (x-axis).

c) The first ΔH_{i1} and the second ΔH_{i2} ionization energies (kJ/mol) of a few elements are given in table.

Element	ΔH_{i1}	ΔH_{i2}
I	2372	5251
II	520	7300
III	900	1760
IV	1680	3380

Which of the above element is likely to be:
- i. a reactive metal
- ii. a reactive non-metal
- iii. a noble gas
- iv. a metal that forms a stable binary halide of the formula AX_2 (X = halogen)

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2.4 QUANTUM NUMBERS

The Bohr model was a one-dimensional model that used one quantum number to describe the distribution of electrons in the atom. The only important information was the size and energy of the orbit, which was described by the n-quantum number. Since Schrodinger's model allowed the electron to occupy three-dimensional space, therefore, it required three coordinates, or three quantum numbers, to describe the orbitals in which electrons can be found. The three quantum numbers that come from Schrödinger's wave equations are the principal (**n**), azimuthal (ℓ), and magnetic (**m**) quantum numbers. These quantum numbers describe the size, shape, and orientation in space of the orbitals in an atom.

2.4.1 Principal Quantum Number (n)

The principal quantum number, n, can have positive integral values 1,2,3,4… designated by K, L, M, N.... This quantum number, n, describes the size and energy of the orbital. The larger 'n' is, the greater the average distance of an electron in the shell or orbital from the nucleus. An increase in 'n' also means that the electron has a higher energy and is therefore less tightly bound to the nucleus.

The principal quantum number, n, can also be used to calculate the maximum number of electrons in a shell by the formula $2n^2$. Therefore shells K, L, M and N can accommodate maximum electrons. 2,8,18, 32 respectively.

2.4.2 Azimuthal Quantum Number (ℓ)

Azimuthal quantum number (ℓ) can have integral values 0 to (n–1) for each value of n. This quantum number describes the shape of the orbital. The values of 'ℓ' are integers that depend on the value of the principal quantum number. If n= 1, there is only one possible value of 'ℓ', i.e. ℓ =0 (n-1, where n = 1). If n=2, there are two values of 'ℓ ' , i.e. 0 and 1. If n=3 there are, three values of 'ℓ' , i.e. 0,1 and 2. Similarly, if n=4, there are four values of 'ℓ', i.e. 0, 1, 2 and 3. The values of 'ℓ ' are designated by the letters **s**, **p**, **d**, and **f**, with which stand for **sharp**, **principal**, **diffused** and **fundamental**, respectively, describing spectral lines. The number of electrons in a subshell can be calculated by the formula $2(2\ell+1)$ as given in the **Table 2.3**.

Table 2.3 Shapes of orbital

Value of ℓ	0	1	2	3
Orbital designation	s	p	d	f
shape of orbital	spherical	polar (dumb bell)	cloverleaf (double dumbbell)	complicated
No. of electrons in a subshell, $2(2\ell+1)$	2	6	10	14

The number of subshells in a shell is equal to its shell number. For example 1st, 2nd, 3rd, and 4th shells have one, two, three and four subshells respectively.

Table 2.4 Relationship between n, ℓ and subshells

Shell	Principal Quantum Number (n)	Azimuthal Quantum Number (ℓ)	Subshells	No. of Subshells
K	1	0	1s	1
L	2	0 , 1	2s, 2p	2
M	3	0, 1, 2	3s, 3p, 3d	3
N	4	0, 1, 2, 3	4s, 4p, 4d, 4f	4

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2.4.3 Magnetic Quantum Number (m)

The magnetic quantum number '**m**' describes the orientation of an orbital in space, within a subshell. The value of m depends on the value of ℓ. For a certain value of ℓ, there are (2ℓ + 1) integral values of m, i.e. $-\ell$……0……..$+\ell$. The values of m indicate the number of orbitals in a subshell. If ℓ = 0, (s-subshell) there is only one possible value of m, i.e. 0. It means s-subshell has only 1 orbital. If ℓ=1, (p-subshells) there are three values of m; -1,0 and +1. It means p-subshells has three orbitals.

If ℓ=2, (d-subshell), there are five values of m. It means d-subshells have 5 orbitals.

Did you Know?

Splitting of small fine lines in the presence of maginatic field and there three dimensional orientation in space indicate the presence of orbitals in subshells.

If ℓ =3, (f-subshell) there are seven values of m. It means f-subshells have 7 orbitals.

Orbitals of the same subshell have same energy and are called degenerate orbitals. These degenerate orbitals are differentiated from each other in the presences of magnetic field, hence the name of this quantum number, i.e. magnetic quantum number. The relationship between the azimuthal and magnetic quantum numbers is provided in **Table 2.5.**

Table 2.5 Relationship between ℓ and m

Subshell	Azimuthal Quantum Number (ℓ)	Magnetic Quantum Number (m) ($-\ell$----- 0---- ℓ+)	Number of Degenerate Orbitals (2ℓ+1)
s	0	0	One orbital
p	1	-1, 0 , +1	Three degenerate p-orbitals
d	2	+2, +1, 0, -1, -2	Five degenerate d-orbitals
f	3	+3, +2, +1, 0, -1, -2, -3	Seven degenerate f-orbitals

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Spin Quantum Number (s)

Electrons also have spin motion around their own axes. According to electromagnetic theory, a spinning charge generates a magnetic field. This motion causes an electron to behave like a magnet. **Figure 2.6** shows the two possible spinning motions of an electron. One is clockwise and the other is anticlockwise. The values of s are $+\frac{1}{2}$ and $-\frac{1}{2}$, as in **Figure 2.6.**

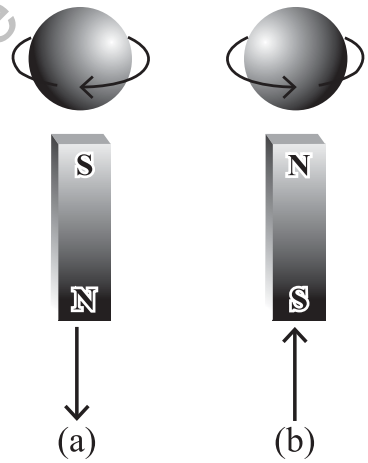


Figure 2.6 (a) clockwise **(b)** counterclockwise spins of an electron.

The clockwise spin is represented by an arrow (↓) pointing downwards, while the anticlockwise spin is represented by an arrow (↑) pointing upwards.

Thus it takes three quantum numbers to describe an orbital but forth quantum number to differentiate between the two electrons that can occupy an orbital.

Did you Know?

In the nth principal quantum number, there are n subshells consisting of n^2 orbitals with a maximum number of $2n^2$ electrons.

Quick Check 2.3

a) What information about an electron in an atom can be obtained from:
- i. Principal quantum number
- ii. Azimuthal quantum number
- iii. Magnetic quantum number
- iv. Spin quantum number

b) For an electron(s):
- i. If n=2 and $\ell = 1$, how many orientations in space are possible?
- ii. If n=3 and $\ell = 2$, which shell and subshell does the electron belong to?
- iii. If $\ell=2$, find all possible values of m and maximum number of electrons for m.

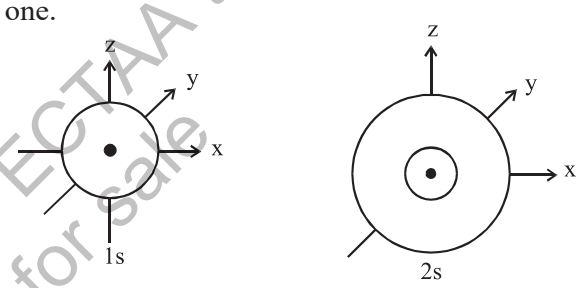
2.5 SHAPES OF ATOMIC ORBITALS

An atomic orbital is defined as the three dimensional region in space around the nucleus in which the probability of finding the electron is maximum.

Let us discuss the different orbitals one by one.

2.5.1 s-orbital

The shape of an 's' orbital is spherical. The electronic density around the nucleus in an s orbital is uniformly distributed in all directions. With the increase in the principal quantum number, the size of s orbital also becomes larger as in **Figure 2.7**.

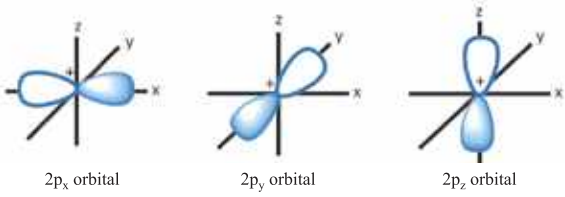


(a) n = 1, l = 0, m = 0 (b) n = 2, l = 0, m = 0

Figure 2.7 Boundary surface for (a) 1s (b) 2s.

2.5.2 p-orbitals

The distribution of electron density for a 2p orbital is shown in **Figure 2.8**. The electron density is not distributed in a spherically symmetric fashion as in an s orbital. Rather, a p orbital has two lobes on any of the axis. The p orbitals are named as p_x, p_y, and p_z accordingly to their axes.



ℓ = 1, m = +1 **ℓ = 1, m = –1** **ℓ = 1, m = 0**

Figure 2.8 Shapes of three 2p orbitals

2.5.3 d and f orbitals

In a given shell, 'd' orbitals have different shapes and orientations in space. The d_{xy}, d_{xz}, and d_{yz} lie in the xy, xz, and yz planes, respectively. The lobes of the $d_{x^2-y^2}$ lie along the x and y axes. The d_{z^2} orbital has two lobes along the z-axis and a "doughnut" in the xy plane.

The shapes for the five d orbitals (ℓ = 2,) are shown in **Figure 2.9.**

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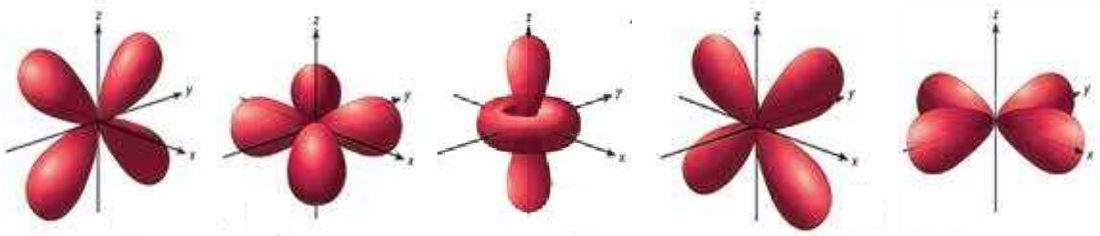

d_{yz} d_{xy} d_{z^2} d_{xz} $d_{x^2-y^2}$

Figure 2.9 Shapes of five d orbitals

An f subshell has seven orientations in space, i.e. there are seven f orbitals. However, the shapes of f orbitals are very complicated.

Quick Check 2.4

a) What does an orbital represent according to the wave mechanical model of atom?

b) There are three orientations of p-orbital due to three values of magnetic quantum number. Justify it.

2.6 ELECTRONIC CONFIGURATION

Electronic configuration is the distribution of electrons among available shells, subshells, or orbitals of an atom or ion. Each group of orbitals in a subshell is labeled by its subshell notation. An electron in an orbital is shown by an arrow. The arrow points upward, when s = +½ and downward when s = –½. The orbital diagram of boron ($^{11}_{5}B$) is as follows

$$^{11}_{5}B = \overset{\uparrow\downarrow}{1s}\ \overset{\uparrow\downarrow}{2s}\ \overset{\uparrow}{2p_x}\ \overset{0}{2p_y}\ \overset{0}{2p_z}$$

2.6.1 Distribution of Electrons in Shells

The electronic configuration of an atom describes the distribution of electrons in its atomic shells. The shells, denoted as K, L, M, N, and so on, correspond to the principal quantum number (n) of the orbitals.

Each shell has a specific capacity for electrons:

K shell (n=1): 2 electrons maximum

L shell (n=2): 8 electrons maximum

M shell (n=3): 18 electrons maximum

N shell (n=4): 32 electrons maximum

For example:

	K	L	M
$_{11}Na$:	2	8	1
$_{17}Cl$:	2	8	7

2.6.2 Distribution of Electrons in Subshells

In case of subshells, the electronic configuration is described by a notation that lists the subshell symbols, one after the other. Each symbol has a superscript on the right. This gives the number of electrons in the subshell. Following rules are applied to fill the orbitals of multi-electron atoms.

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Aufbau principle

Aufbau principle is also known as the **building up principle**. This principle says that the subshells in an atom are filled with electrons in an increasing order of their energy values.

Since, the energy of a subshell in the absence of any magnetic field, depends upon the principal quantum number (n) and the azimuthal quantum number (ℓ), hence the order of filling subshells with electrons may be obtained from the summation (n + ℓ). Following rules must be considered while applying (n + ℓ) rule:

a) The subshell having lower (n + ℓ) value has lower energy and is filled first. For example, 4s orbital has (n + ℓ) = 4 + 0 = 4 and 3d orbital has (n + ℓ) = 3+2 = 5. Since (n + ℓ) value of 4s orbital is lower than that of 3d, hence 4s subshell has lower energy than 3d and 4s will be filled first.

b) In case there are two subshells having equal (n + ℓ) values, then the subshell with lower 'n' value will be filled first. For example, both 4p and 3d subshells have n+ℓ value equal to 5 (4p=4+1=5) and (3d = 3+2=5); 3d subshell will be preferred to be filled because of its low n value.

According to this rule the energy wise arrangement of subshells should be.

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s

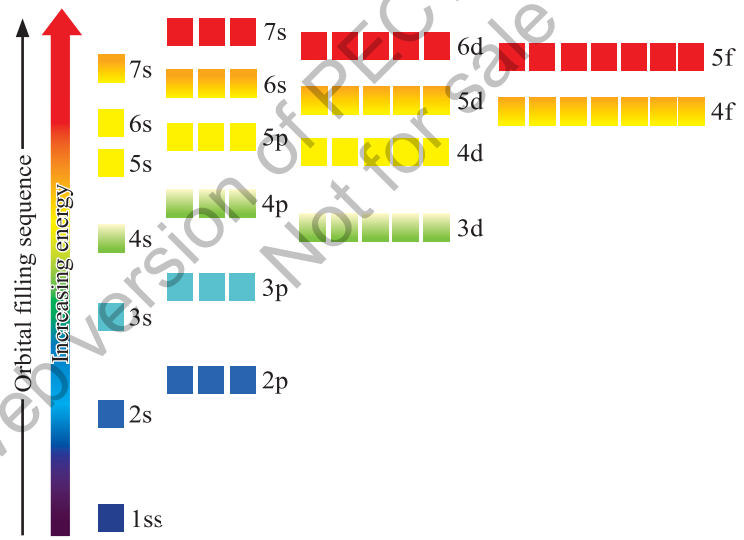

Figure 2.10 Arrangement of subshells in increasing energy order

So, the order of filling of various subshells with electrons obtained by this rule is given below **Figure 2.10**.

For example, the configuration of $^{9}_{4}Be$ atom with two electrons in the '1s' subshell and two electrons in the '2s' subshell is written $1s^2 2s^2$.

The electronic configuration of $_{11}Na$ in subshells is $1s^2 2s^2 2p^6 3s^1$. The subshell electronic configuration of different elements is provided in **Table 2.6**.

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Table 2.6 Electronic configuration of ground states of elements Z = 1 –36.

Z	Element	Configuration	Z	Element	Configuration
1.	H	$1s^1$	19.	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
2.	He	$1s^2$	20.	Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
3.	Li	$1s^2 2s^1$	21.	Sc	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$
4.	Be	$1s^2 2s^2$	22.	Ti	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
5.	B	$1s^2 2s^2 2p^1$	23.	V	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
6.	C	$1s^2 2s^2 2p^2$	24.	Cr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
7.	N	$1s^2 2s^2 2p^3$	25.	Mn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
8.	O	$1s^2 2s^2 2p^4$	26.	Fe	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
9.	F	$1s^2 2s^2 2p^5$	27.	Co	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
10.	Ne	$1s^2 2s^2 2p^6$	28.	Ni	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$
11.	Na	$1s^2 2s^2 2p^6 3s^1$	29.	Cu	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
12.	Mg	$1s^2 2s^2 2p^6 3s^2$	30.	Zn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$
13.	Al	$1s^2 2s^2 2p^6 3s^2 3p^1$	31.	Ga	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$
14.	Si	$1s^2 2s^2 2p^6 3s^2 3p^2$	32.	Ge	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$
15.	P	$1s^2 2s^2 2p^6 3s^2 3p^3$	33.	As	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$
16.	S	$1s^2 2s^2 2p^6 3s^2 3p^4$	34.	Se	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$

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2.6.3 Distribution of Electrons in Orbitals

The filling of electrons in orbitals is represented by box diagrams, where each box represents an orbital, as shown in **Figure 2.11**.

- Each box represents an atomic orbital.
- Each orbital can occupy maximum of two electrons.
- An electron is represented by an arrow.
- The boxes (orbitals) can be arranged in order of increasing energy from bottom to top.

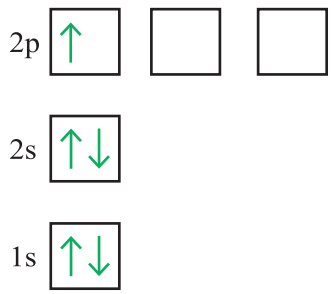

Figure 2.11 The electronic configuration of boron in terms of orbitals

The following rules are obeyed while filling orbitals with electrons.

i) Pauli's exclusion principle

According to this principle. No two electrons in an atom can have the same values for all the four quantum numbers or, "Two electrons in an orbital will always have opposite spins".

In the first shell of helium (**He**) atom, there are two electrons. They are present in 1s orbital. According to the concept of quantum numbers and Pauli's exclusion principal, the values of their **quantum numbers are:**

Table 2.7 values of quantum numbers of two electrons in the same orbital

Electron	n	l	m	s
Electron 1	1	0	0	$+\frac{1}{2}$ (anticlockwise)
Electron 2	1	0	0	$-\frac{1}{2}$ (clockwise)

The two electrons having the same values of **'n'**, ***'l'*** and **'m'** can have different values of **'s'**. It means that their spins are in the opposite directions.

ii) Hund's rule

This rule gives an idea for filling electrons into the orbitals having equal energies. For example, three p-orbtials, *i.e.,* p_x, p_y and p_z have equal energy. To understand it, let us take an example in which three electrons are to be filled into three p-orbitals. There are two different ways to do this as shown below:

Which of the two is correct? The answer is given by Hund's rule, which states that,

When degenerate orbitals are available and more than two electrons are to be placed in them, they should be placed in separate orbitals with the same spin rather than in the same orbital with opposite spins.

According to the Hund's rule, the correct way of filling three electrons in three p orbitals is that in which each orbital is singly occupied. Electronic configuration in terms of orbitals in carbon, nitrogen and oxygen is provided in **Figure 2.12**.

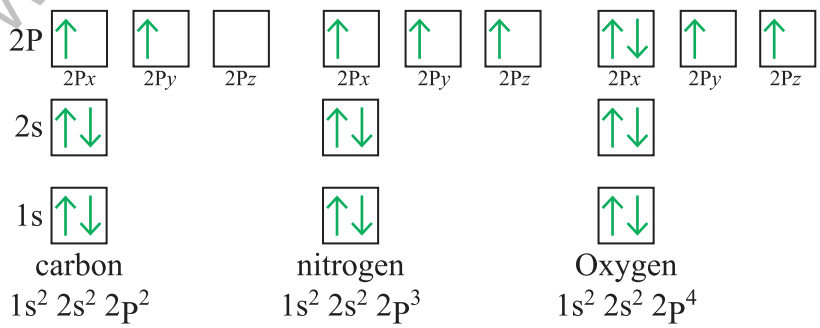

Figure 2.12 Electronic configuration in terms of orbitals in carbon, nitrogen and oxygen

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The electronic configurations of some elements of the periodic table in the light of the above-mentioned principles are given in **Table 2.6.**

2.7 ELECTRONIC CONFIGURATION AND THE PERIODIC TABLE

We have seen that the electronic configurations of elements are related to their position in the periodic table. The periodic table is structured so that elements with the same pattern of outer-shell (valence) electronic configuration are arranged in same groups.

You can easily write the electron configuration of an element based on its location in the periodic table. The pattern is summarized in **Table 2.8.** Notice that the elements can be grouped in terms of the type of orbital into which the electrons are placed.

On the left are two columns of elements. These elements, known as the alkali metals and alkaline earth metals (groups 1 and 2), are those in which the s orbitals are being filled. We see that the group 1 and 2 elements all have ns^1 and ns^2 outer configurations respectively. When we jump to group 13 elements, we find that they have ns^2np^1 configuration. On the right is a block of six columns. These are the elements in which the outermost 'p' orbitals are being filled. In the middle of the table is a block of ten columns that contain the transition metals. In these, the d orbitals are being filled. Below the main portion of the table are two rows that contain fourteen columns. These elements are often referred to as the f-block elements. These are the ones in which the 'f' orbitals are being filled. Recall that the numbers 2, 6, 10, and 14 are precisely the number of electrons that can fill the s, p, d, and f subshells, respectively.

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Quick Check 2.5

a) With the help of periodic table, write the electronic configurations for the following elements by giving the appropriate noble-gas inner core plus the electrons beyond it (i) $_{48}Cd$; (ii) $_{57}La$.

b) Write the complete electron configuration for antimony (Sb) with atomic number 51.

c) How many unpaired electrons are there in each atom of $_{51}Sb$?

d) Write down the electronic configuration of valence shell of the following in terms of orbitals:

i) $_{13}Al$ ii) $_{14}Si$ iii) $_{28}Ni$

2.7.1 Valence electrons

The electrons in an atom in the outermost shell are called **valence electrons**. These are such electrons that are primarily involved in chemical reactions. The similarities among the configurations of valence electrons account for similarities of the chemical properties among groups of elements.

Table 2.8 shows a periodic table which include the valence shell configurations. Note the similarity in electronic configuration within any group (column) of elements.

Table 2.8 The electronic distribution of elements of modern periodic table

1 H $1s^1$																	2 He $1s^2$
3 Li $2s^1$	4 Be $2s^2$											5 B $2s^2 2p^1$	6 C $2s^2 2p^2$	7 N $2s^2 2p^3$	8 O $2s^2 2p^4$	9 F $2s^2 2p^5$	10 Ne $2s^2 2p^6$
11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^2 3p^1$	14 Si $3s^2 3p^2$	15 P $3s^2 3p^3$	16 S $3s^2 3p^4$	17 Cl $3s^2 3p^5$	18 Ar $3s^2 3p^6$
19 K $4s^1$	20 Ca $4s^2$	21 Sc $4s^2 3d^1$	22 Ti $4s^2 3d^2$	23 V $4s^2 3d^3$	24 Cr $4s^1 3d^5$	25 Mn $4s^2 3d^5$	26 Fe $4s^2 3d^6$	27 Co $4s^2 3d^7$	28 Ni $4s^2 3d^8$	29 Cu $4s^1 3d^{10}$	30 Zn $4s^2 3d^{10}$	31 Ga $4s^2 3d^{10} 4p^1$	32 Ge $4s^2 3d^{10} 4p^2$	33 As $4s^2 3d^{10} 4p^3$	34 Se $4s^2 3d^{10} 4p^4$	35 Br $4s^2 3d^{10} 4p^5$	36 Kr $4s^2 3d^{10} 4p^6$
37 Rb $5s^1$	38 Sr $5s^2$	39 Y $5s^2 4d^1$	40 Zr $5s^2 4d^2$	41 Nb $5s^1 4d^4$	42 Mo $5s^1 4d^5$	43 Tc $5s^1 4d^6$	44 Ru $5s^1 4d^7$	45 Rh $5s^1 4d^8$	45 Pd $4d^{10}$	47 Ag $5s^1 4d^{10}$	48 Cd $5s^2 4d^{10}$	49 In $5s^2 4d^{10} 5p^1$	50 Sn $5s^2 4d^{10} 5p^2$	51 Sb $5s^2 4d^{10} 5p^3$	52 Te $5s^2 4d^{10} 5p^4$	53 I $5s^2 4d^{10} 5p^5$	54 Xe $5s^2 4d^{10} 5p^6$
55 Cs $6s^1$	56 Ba $6s^2$	57 La $6s^2 5d^1$	72 Hf $6s^2 4f^{14} 5d^2$	73 Ta $6s^2 4f^{14} 5d^3$	74 W $6s^2 4f^{14} 5d^4$	75 Re $6s^2 4f^{14} 5d^5$	76 Re $6s^2 4f^{14} 5d^6$	77 Ir $6s^2 4f^{14} 5d^7$	78 Pt $6s^2 4f^{14} 5d^9$	79 Au $6s^2 4f^{14} 5d^{10}$	80 Hg $6s^2 4f^{14} 5d^{10}$	81 Tl $6s^2 4f^{14} 5d^{10} 6p^1$	82 Pb $6s^2 4f^{14} 5d^{10} 6p^2$	83 Bi $6s^2 4f^{14} 5d^{10} 6p^3$	84 Po $6s^2 4f^{14} 5d^{10} 6p^4$	85 At $6s^2 4f^{14} 5d^{10} 6p^5$	86 Rn $6s^2 4f^{14} 5d^{10} 6p^6$
87 Fr $7s^1$	88 Ra $7s^2$	89 Ac $7s^2 6d^1$	104 Rf $7s^2 5f^{14} 6d^2$	105 Db $7s^2 5f^{14} 6d^3$	106 Sg $7s^2 5f^{14} 6d^4$	107 Bh $7s^2 5f^{14} 6d^5$	108 Hs $7s^2 5f^{14} 6d^6$	109 Mt $7s^2 5f^{14} 6d^7$	110 Ds $7s^2 5f^{14} 6d^8$	111 Rg $7s^2 5f^{14} 6d^9$	112 Cn $7s^2 5f^{14} 6d^{10}$	113 Nh $7s^2 5f^{14} 6d^{10} 7p^1$	114 Fl $7s^2 5f^{14} 6d^{10} 7p^2$	115 Mc $7s^2 5f^{14} 6d^{10} 7p^3$	116 Lv $7s^2 5f^{14} 6d^{10} 7p^4$	117 Ts $7s^2 5f^{14} 6d^{10} 7p^5$	118 Og $7s^2 5f^{14} 6d^{10} 7p^6$

58 Ce $6s^2 4f^1 5d^1$	59 Pr $6s^2 4f^3$	60 Nd $6s^2 4f^4$	61 Pm $6s^2 4f^5$	62 Sm $6s^2 4f^6$	63 Eu $6s^2 4f^7$	64 Gd $6s^2 4f^7 5d^1$	65 Tb $6s^2 4f^9$	66 Dy $6s^2 4f^{10}$	67 Ho $6s^2 4f^{11}$	68 Er $6s^2 4f^{12}$	69 Tm $6s^2 4f^{13}$	70 Yb $6s^2 4f^{14}$	71 Lu $6s^2 4f^{14} 5d^1$
90 Th $7s^2 6d^2$	91 Pa $7s^2 5f^2 6d^1$	92 U $7s^2 5f^3 6d^1$	93 Np $7s^2 5f^4 6d^1$	94 Pu $7s^2 5f^6$	95 Am $7s^2 5f^7$	96 Cm $7s^2 5f^7 6d^1$	97 Bk $7s^2 5f^9$	98 Cf $7s^2 5f^{10}$	99 Es $7s^2 5f^{11}$	100 Fm $7s^2 5f^{12}$	101 Md $7s^2 5f^{13}$	102 No $7s^2 5f^{14}$	103 Lr $7s^2 5f^{14} 6d^1$

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2.7.2 Classification of elements of periodic table

The main-group or representative elements all have valence-shell configurations $ns^a\ np^b$. They have some choice of 'a' and 'b'. In other words, the outer 's' or 'p' subshell is being filled. Similarly, in the d-block transition elements, a 'd' subshell is being filled. In the f-block transition elements or inner-transition elements, an 'f' subshell is being filled.

There is a definite pattern to the order of filling of the subshells as we go through the elements in the periodic table. From this we can write down the building-up order. The overall sketch of periodic table is given in **Table 2.9**. This shows the blocks of elements.

Table 2.9 Modern periodic table showing s, p, d and f-block elements.

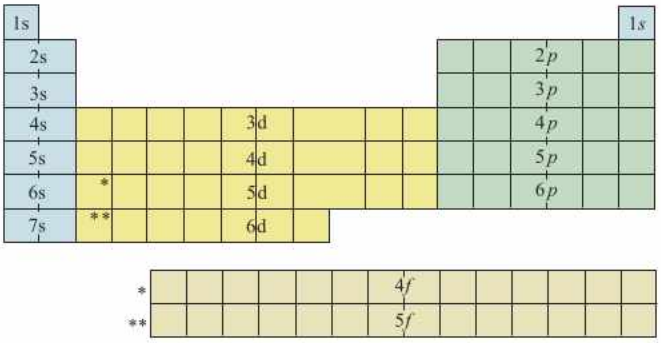

Table 2.9 shows a periodic table indicating this pattern. For example, in the blue colored area, an '*ns*' subshell is being filled. In the green colored area, an np subshell is being filled. In the yellow area, an (n – 1) *d* subshell is being filled. In the light golden area (n–2) *f* subshell is being filled.

We start building-up order by starting with the first period, in which the '1*s*' subshell is being filled. In the second period, we have '2*s*'; then staying in the same period but jumping across, we have '2*p*'. In the third period, we have '3*s*' and '3*p*'; in the fourth period, '4*s*', '3*d*' and then '4*p*'. This pattern should become clear enough to visualize with a periodic table.

The classification of elements of periodic table has been done into metals, non-metals, representative, transition elements, periods, groups and blocks (s, p, d, f). This division is done on the basis of electronic configuration and their valence electrons. The chemical properties of various categories of elements discussed above can be easily assessed.

Quick Check 2.6

a) An element has the electronic configuration

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^5.$$

i. Which block in the Periodic Table does this element belong to?
ii. Which group does it belong to?
iii. Which period does it belong to?
iv. Identify this element.

b) Which block, group and period in the periodic table does the element with the electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$ belong to? Name it.

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2.8 ELECTRONIC CONFIGURATION OF IONS AND FREE RADICALS

2.8.1 Ions

Positive ions are formed when electrons are removed from atoms. The sodium ion, Na^+ (proton number = 11), has 10 electrons. So, its electronic configuration is $1s^2\ 2s^2\ 2p^6$.

Note that this is the same as the electronic configuration of neon, the element with 10 electrons in each atom.

Negative ions are formed when atoms gain electrons. The sulfide ion, S^{2-} (proton number = 16), has 18 electrons. Its electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$, which is the same as argon, the element with 18 electrons in each atom.

Note that, in general, electrons in the outer subshell are removed when metal atoms form the positive ions. However, the d-block elements behave slightly differently. Reading across the Periodic Table from potassium to zinc, the 4s subshell fills before the 3d subshell. But when atoms of a d-block element lose electrons to form ions, the 4s electrons are lost first.

For example:

Ti atom: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$

Ti^{2+} ion: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2$

Cr atom: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

Cr^{3+} ion: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

2.8.2 Free radicals

"A free radical is a species that has one or more unpaired electrons".

An example of a simple free radical is free chlorine atom $:\ddot{\underset{..}{C}}\dot{\ell}:$. The electronic configuration of this radical is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$. In the 2p subshell, two orbitals have paired electrons whereas, the third one contains a single unpaired electron. The unpaired electron is shown by a single dot as in $Cl^{\bullet}$. Apart from single atoms, groups of atoms can also be free radicals. For example, $OH^{\bullet}$, $CH_3^{\bullet}$, etc.

Quick Check 2.7

Write electronic configurations for the following ions and free radicals:

i. $Al^{\bullet}$ ($Z = 13$) **ii.** O^{2-} ($Z = 8$) **iii.** Fe3+ ($Z = 26$) **iv.** Cu^{2+} ($Z = 29$) **v.** $Cu^{\bullet}$ ($Z = 29$)

2.9 ELECTRONIC CONFIGURATION AND THE FORMATION OF SEMICONDUCTORS

Semiconductors are materials that can conduct electricity under some conditions. They are used in many electronic devices, including smartphones, laptops, and cars.

Example of the elements that can act as semiconductors are silicon, germanium and arsenic etc. The formation of semiconductors is possible because of a unique electronic configuration of these elements. Let us consider the example of Si and explore how it can be converted into a P-type and N-type semiconductors. The electron configuration of $_{14}Si = 2, 8, 4$, meaning that it has 4 electrons in its valence shell. In the pure crystalline form, each Si atom is bonded to four other Si atoms. In this form, there is no possibility of electronic conduction through the Si crystal as in **Figure 2.13**.

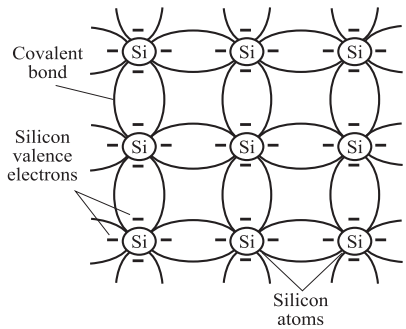

Figure 2.13 A crystal of pure silicon

2.9.1 P-type semiconductor formation

Impurity atoms with three valence electrons (like Al) are added to the pure semiconductor. Some of the trivalent atoms take place of the Si atoms in the crystals. The silicon atoms cannot make four bonds due to the lack of electrons. For this reason, there are created holes in the crystal lattice, which act as positive charge carriers as shown in **Figure 2.14 (a)**. This process creates a positive-type semiconductor or P-type semiconductor. Electrons from an external current source can move through the semiconductor and it can act as a conductor.

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2.9.2 N-type semiconductor formation

When impurity atoms with five valence electrons (like phosphorus) are added to the pure semiconductor, some of Si atoms are replaced with the pentavalent phosphorus atoms. The Si atoms in the vicinity of these atoms can make four bonds and the fifth electron is an extra electron. These impurity atoms contribute extra electrons to the crystal lattice, which become free to move and act as negative charge carriers as in **Figure 2.14 (b)**. The result is an N-type semiconductor that can conduct electricity when connected to an external source.

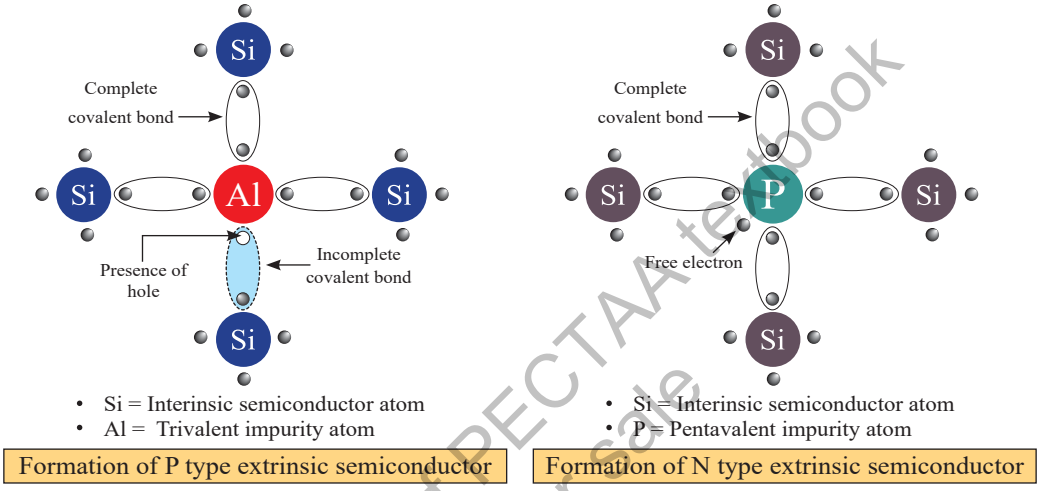

Figure 2.14 Doping and the formation of P-type and N-type semiconductor

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EXERCISE

MULTIPLE CHOICE QUESTIONS

Q.1 Four choices are given for each question. Select the correct choice.

I. The quantum number 'm' of a free gaseous atom is associated with:

a) the effective volume of the orbital

b) the shape of the orbital

c) the spatial orientation of the orbital

d) the energy of the orbital in the absence of a magnetic field

II. When 3d subshell is completely filled, the next entering electron goes into:

a) 4f b) 4s

c) 4p d) 4d

III. Quantum number values for 2p orbitals are:

a) n = 2, l = 1 b) n = 1, l = 2

c) n = 1, l = 0 d) n = 2, l = 0

IV. An electron having the set of values: n = 4, l = 0, m = 0 and s = +1/2 lies in:

a) 2s b) 3s

c) 4s d) 4p

V. The quantum number values (n, ℓ, m) for the fourth electron of $_4^9$Be atom are:

a) 1, 0, 0 b) 2, 0, 0

c) 2, 1, 0 d) 1, 1, 1

VI. The correct order of first ionization energies is:

a) F > He > Mg > N > O b) He > F > N > O > Mg

c) He > O > F > N > Mg d) N > F > He > O > Mg

VII. A p orbital has a characteristic shape with how many lobes?

a) 1 b) 2

c) 3 d) 4

VIII. The three p orbitals in a given energy level are oriented:

a) Along the same axis.

b) At 45° to each other.

c) Mutually perpendicular to each other along the x, y, and z axes.

d) In a complex tetrahedral arrangement.

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IX. How many d orbitals are there in a given energy level?

a) 1 b) 3

c) 5 d) 7

X. What information does the principal quantum number (n) gives us about orbitals:

a) Size b) Shape

c) Size and shape d) Spin

XI. How many unpaired electrons are present in an atom of cobalt?

a) Two b) Three

c) Four d) Five

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a) There are three orientations of p-orbital due to three values of magnetic quantum number. Justify it.

b) 'I_3' of Mg is much bigger than its 'I_2'. Justify.

c) Among the elements Li, K, Ca, S and Kr which one has the lowest first ionization energy? Which has the highest first ionization.

d) Consider the electronic configuration of the potassium atom (atomic number 19).

(i) Write the full electronic configuration of potassium using the s, p, d, f notation.

(ii) Explain why the 4s subshell is filled before the 3d subshell in potassium, even though the principal quantum number of the 3d subshell is lower.

e) i) An atom of element X has an atomic number of 17 and a mass number of 35. Determine the number of protons, neutrons, and electrons in this atom.

(ii) If this element forms an ion with a charge of -1, how many protons, neutrons, and electrons will be present in the ion?

f) In the ground state of mercury $_{80}Hg$:

i. How many electrons occupy atomic orbitals with n = 3?

ii. How many electrons occupy 4d atomic orbitals?

iii. How many electrons occupy $4p_z$ atomic orbital?

iv. How many electrons in the valence shell have spin "up" (s = -½)?

g) The successive ionization energies for an unknown element are

I_1 = 896 kJ/mol, I_2 = 1752 kJ/mol

I_3 = 14,807 kJ/mol I_4 = 17,948 kJ/mol

To which family in the periodic table, does the unknown element most likely belong?

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i) Consider the following ionization energies for aluminium:

$Al_{(g)} \longrightarrow Al^{+}_{(g)} + e^{-}$ I_1 = 580 kJ/mol

$Al^{+}_{(g)} \longrightarrow Al^{2+}_{(g)} + e^{-}$ I_2 = 1815 kJ/mol

$Al^{2+}_{(g)} \longrightarrow Al^{3+}_{(g)} + e^{-}$ I_3 = 2740 kJ/mol

$Al^{3+}_{(g)} \longrightarrow Al^{4+}_{(g)} + e^{-}$ I_4 = 11,600 kJ/mol

(i) Account for the trend in the values of the ionization energies.

(ii) Explain the large increase from I_3 to I_4.

(iii) List the four aluminium ions given in order of increasing size, and explain your ordering.

h) (i) State the general order of filling orbitals up to the 4p subshell.

(ii) Explain why the 4s subshell is filled before the 3d subshell, according to the Aufbau principle.

i) Draw the orbital box diagram for the valence electrons of a phosphorus atom (atomic number 15), ensuring that your diagram adheres to Hund's rule and the Pauli Exclusion Principle.

DESCRIPTIVE QUESTIONS

Q.3 What are quantum numbers? Describe briefly principal and spin quantum numbers.

Q4. Draw the shapes of s, p and d-orbitals. Justify these by keeping in view the azimuthal and magnetic quantum numbers.

Q.5 What do you mean by successive ionization energies? How the electronic shell structure of magnesium (Mg) is derived from the successive ionization energies?

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