CHAPTER 2

ATOMIC STRUCTURE

SLOs: After completing this lesson, the student will be able to:

1. Describe that, each atomic shell and sub-shell are further divided into degenerate orbitals having the same energy.
2. Describe protons, neutrons, and electrons in terms of their relative charge and relative masses.
3. Recognize that the terms atomic and proton number represent the same concept.
4. Describe the behaviour of beams of protons, neutrons and electrons moving at the same velocity in an electric field
5. 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.
6. Explain the change in atomic and ionic radius across a period and down a group.
7. 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).
8. Define terms related to electronic configuration (some examples include: shells, sub-shells, orbitals, principal quantum number (n), ground state).
9. Relate Quantum Numbers to electronic distribution of elements.

10. 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.
11. Apply Aufbau principle, Pauli's exclusion principle and Hund's rule to write the electronic configuration of elements.
12. Describe the order of increasing energy of the sub-shells (s, p, d, and f).
13. Explain the electronic configurations to include the number of electrons in each shell, sub-shell and orbitals.
14. Explain the electronic configurations in terms of energy of the electrons and inter-electron repulsion.
15. Determine the electronic configuration of atoms and ions given the proton or electron number and charge.
16. 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)
17. Describe the shapes of s, p, and d orbitals.
18. Describe free radical as a species with one or more unpaired electrons.
19. Explain that ionization energies are due to the attraction between the nucleus and the outer electrons.
20. Explain how ionization energy helps account for the trends across the period and down a group of the periodic table.
21. Account for the variation in successive ionization energies of an element.
22. 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.
23. Deduce the electronic configurations of elements using successive ionization energy data.
24. Deduce the position of an element in the periodic table using successive ionization energy data.
25. Explain how a mass spectrometer can be used to determine the relative atomic mass of an element from its isotopic composition.
26. Perform calculations involving non-integer relative atomic masses and abundance of isotopes from given data, including mass spectra.
27. Explain the concept of emission spectra. Use the concept of emission spectra to deduce the electronic configuration of elements.

2.1 BRIEF HISTORY OF ATOMIC MODELS

Based on discharge tube experiments a series of discoveries which started during the later part of 19th century modified Daltonian concept of atomic structure. Later on Neil Bohr's atomic model further clarified the picture of atom. His model was the first approach to the quantized energy levels or electronic shells with fixed energy. He was successful to calculate the radius of hydrogen atom and the energy of the electron in any shell of H atom. The emission spectrum of hydrogen was well explained by Bohr but when high resolution spectrophotometers were made, fine spectrum originated with splitted spectral lines, these lines were splitting in electric and magnetic field giving

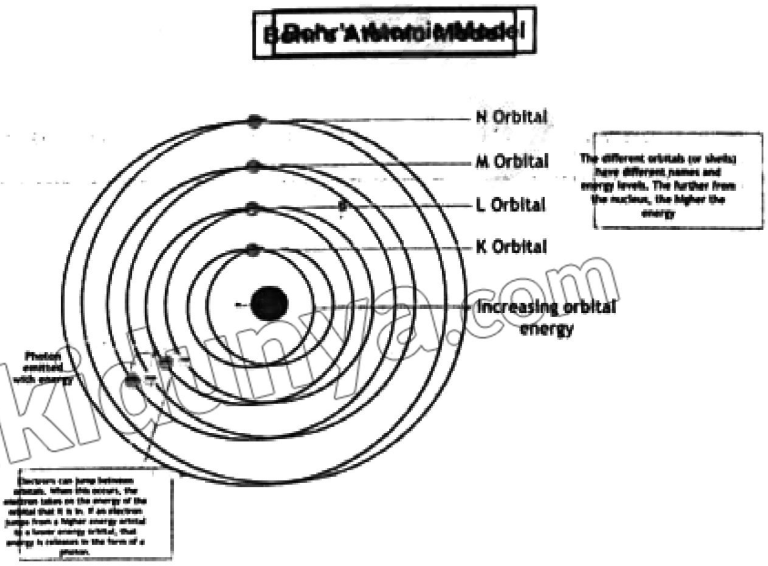


Figure 2.1: Bohr's Atomic Model

rise the stark effect and zeeman effect respectively, which were obviously not explained by Bohr. This new spectral advancement made the atomic structure more complicated.

These discoveries were followed by Heisenberg's uncertainty principle, which gave rise the concept of subshells and orbitals as the comprising parts of an electronic shell.

2.1.1 Sub-Atomic Particles

Electron:

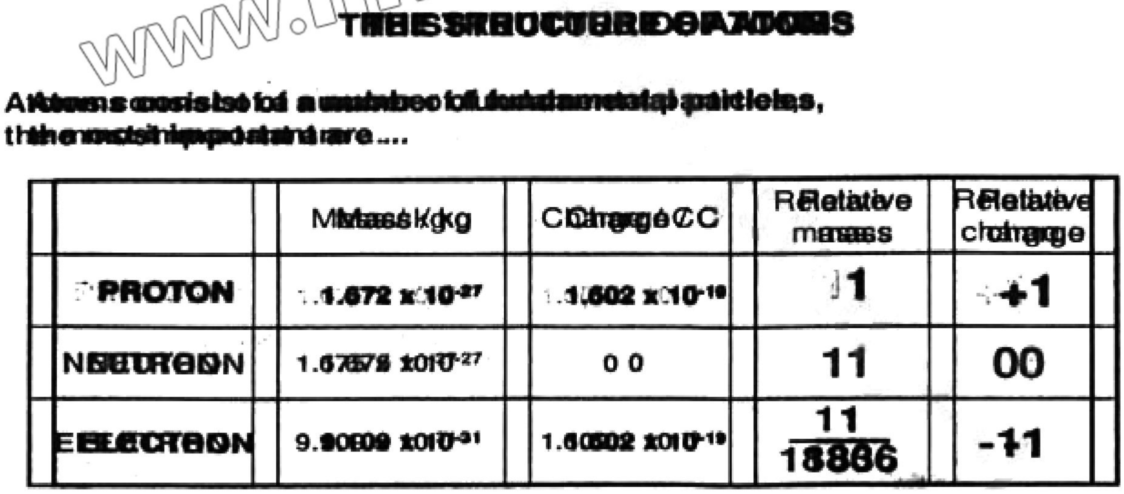
It is negatively charged subatomic particle with a charge 1.6022×10^{-19} C. Its relative charge is -1. Its mass is 9.1095×10^{-31}kg.It was discovered by J.J. Thomson. These particles are deflected towards positive pole of electric field.

Proton:

This is positively charged subatomic particle with a charge equal to that of electron, but it is 1836 times heavier than an electron as its mass is 1.6727×10^{-27} kg. It's relative charge is +1.It is deflected towards negative pole of electric field, thus electron and proton are electromagnetic in nature.

Neutron:

Neutron carries no charge as it passes by the electric and magnetic fields un-deflected. It is more massive than proton. Its mass is 1.6750×10^{-27}kg.



THE STRUCTURE OF ATOMS

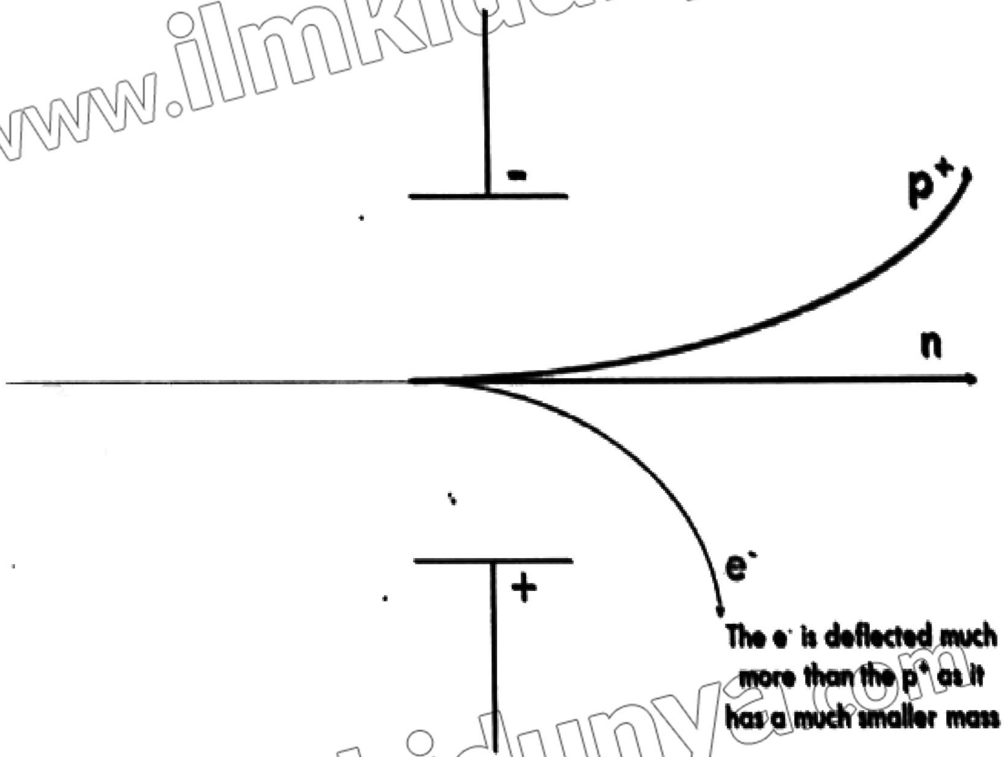
Atoms consist of a number of fundamental particles, the most important are ....

	Mass/kg	Charge/C	Relative mass	Relative charge
PROTON	1.672×10^{-27}	1.602×10^{-19}	1	+1
NEUTRON	1.675×10^{-27}	0	1	0
ELECTRON	9.109×10^{-31}	1.602×10^{-19}	$\frac{1}{1836}$	-1

2.1.2 Behaviour of electron, proton and neutron in electric field

In the presence of an electric field, electrons and protons undergo opposing forces due to their opposite charges. Electrons, being negatively charged, move against the electric field towards positive pole, while positively charged protons move in the direction of the electric field, towards negative pole. Neutrons, being electrically neutral, generally experience negligible forces and exhibit no deviation in an electric field.

When electrons, protons, and neutrons share the same velocity, their paths diverge *due to the* electric forces acting on electrons and protons. Electrons curve against the electric field, protons curve with it, and neutrons, having no net charge, continue along their path with minimal deflection, their turning curvature also depend on the trajectory force or velocity.



The e- is deflected much more than the p+ as it has a much smaller mass

Figure 2.2: Path of positively and negatively charged particles through the uniform electric field.

2.1.3 Atomic Number and Mass Number

Atomic number is the number of protons in the nucleus of an atom. Since atom is a neutral particle, it means that the number of electrons revolving around the nucleus are equal to the number of protons present in the nucleus. Atomic number is represented by Z.

Mass number or nucleon number represent the total number of protons and neutrons in the nucleus. It is represented by A. Mass number is approximately equal to the atomic mass of an atom.

Atomic number+ Number of neutrons= Mass number

(P+N=A)

Number of Protons=Number of electrons (in a neutral atom).

Number of electrons in a cation= Atomic number - magnitude of charge on cation

Number of electrons in an anion = Atomic number + magnitude of charge on anion.

Concept Assessment Exercise 2.1

1. How many electrons are present in the following species:

Mg^{+2}, Al^{+3}, S^{-2},

2.	Find out number of electrons protons and neutrons of the following species using the atomic number. (Use periodic table). Mg^{+2}, Cl^{-1}, Al^{+3}, S^{-2}

2.1.4 Atomic and Ionic Radius

The average distance of nucleus from the outermost electrons is called radius of an atom. It is the measure of size of an atom as the boundary of electronic cloud is not very well defined so the term average is used.

Periodic Trends

Across the period from left to right in main groups the atomic and Ionic radius decrease as the nuclear charge increases. From left to right the shielding effect remains constant. However, in transition metal series it increases as the electrons are configured in the inner shell d-orbitals.

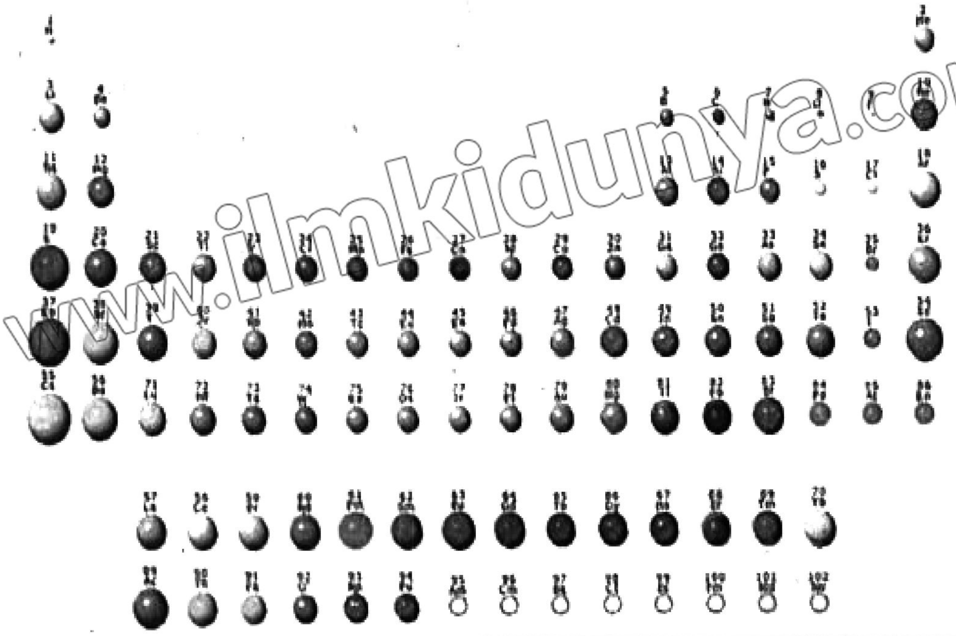
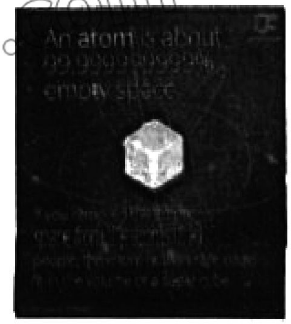


Figure 2.3: Atomic and ionic radii

In a group from top to bottom the atomic radius increases universally in the whole periodic table. This is due to increasing number of shells, one in each period and the shielding effect increases due to intervening electrons.

Ionic Radius

The cations are always smaller than their parent atoms due to increase in effective nuclear charge and decrease in the electron- electron repulsion in the valence shell due to removal of electrons.



Similarly, the anions are bigger than the parent atoms.

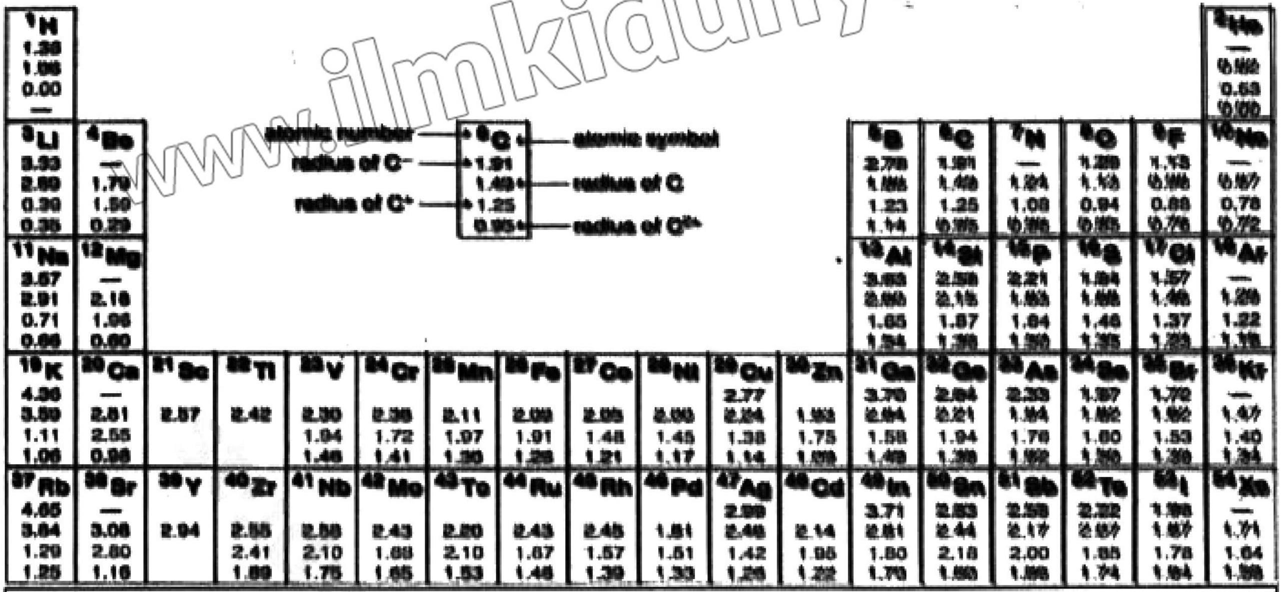


Figure 2.4: Periodic table of nonrelativistic classic turning radii

From top to bottom in a group the trend of Ionic radius is the same as that of atomic radius, it goes on increasing. This is due to the same charge on the ions throughout the group.

This is debateable in the period from left to right because in a period each element does not usually form Ion with the same charge. The charge on the ion depends upon the valence shell electronic configuration, which changes from left to right. If we consider the same charge on each ion in periodic table from left to right in a period the trend will be the same, that is, the decrease as that of the atomic radii.

It is important to understand that atomic and ionic radii and their trends because they affect a lot of other properties of the atom for example ionization energies, electronegativities, bond energies, bond lengths and oxidizing or reducing powers.

Concept Assessment Exercise 2.2

1. As you move from left to right across a period in the periodic table, the atomic radius generally ________.
2. Down a group in the periodic table, the atomic radius tends to ________.
3. When an atom loses electrons to become a cation, its ionic radius ________ compared to its atomic radius.
4. Among elements, as you move from top to bottom within a group, the ionic radius of cations tends to ________, while the ionic radius of anions tends to ________.
5. In general, nonmetals tend to form ________ ions with ________ ionic radii compared to their atomic radii.

2.2 QUANTUM NUMBERS

The approach of expressing the presence of electrons around the nucleus in digital/ mathematical way gave rise the concept of quantum numbers.

A set of four numerals, called quantum numbers are assigned to each electron present in an atom. No matter how bigger the electronic cloud in an atom is, the specific set of quantum numbers are enough to specify the exact location of an electron in an atom. The energies of electrons might be expected to depend upon the first two quantum numbers i.e principal quantum number and azimuthal quantum number.

1. Principal Quantum Number

This quantum number is the expression of Bohr's shell in quantum form. It is represented by n, which has possible values

$$n=1,2,3\ldots$$

The principal quantum number also depicts the period number in the periodic table, because each period starts with the new shell. This number represents the Bohr's shell.

If n is greater the energy of the shell is greater so is its size. Principal quantum Number arose from the emission spectrum of hydrogen which was first of all explained by Bohr and Max Planck. Each spectral line in the emission spectrum is explained by the possible jumps within shells of H atoms.

2. Azimuthal Quantum Number

The azimuthal quantum number which is denoted by l describes the shapes of orbitals of electronic shells. An orbital is a space around the nucleus where the probability of finding the electron is maximum. One shell may be comprising of more than one subshells or orbitals. Azimuthal quantum number determines the orbital's angular momentum of the electron and specifies the subshell within a given principal energy level (n). The values of l range from 0 to n - 1.

Possible values: $l=0,1,2,3\ldots$

The presence of subshells is related to the fine spectral lines in the spectrum. Number of subshells in a shell depends upon the shell number, bigger the shell, more are the number of subshells in it and more electrons can be accommodated in it. Azimuthal quantum number is also *related* with the position of element in the periodic table. s,p,d, and f orbitals represent the blocks in the periodic table.

Table showing possible quantum numbers

n	l	m_l	m_s	Number of orbitals	Orbital Name	Number of electrons	Total Electrons
1 (K shell)	0	0	½ - ½	1	1s	2	2
2 (L Shell)	0	0	½ - ½	1	2s	2	8
	1	-1, 0, +1	½ - ½	3	2p	6	
3 (M-shell)	0	0	½ - ½	1	3s	2	18
	1	-1, 0, +1	½ - ½	3	3p	6	
	2	-2, -1, 0, +1, +2	½ - ½	5	3d	10	
4 (L-shell)	0	0	½ - ½	1	4s	2	32
	1	-1, 0, +1	½ - ½	3	4p	6	
	2	-2, -1, 0, +1, +2	½ - ½	5	4d	10	
	3	-3, -2, -1, 0, +1, +2, +3	½ - ½	7	4f	14	

Magnetic Quantum Number

The splitting of the fine spectral lines under the influence of magnetic field can be explained on the basis of magnetic quantum number. It is also called orientation quantum number and it is denoted by m. Its possible values are from

-l to +l it means

m = ...-3,-2,-1,0,+1,+2,+3,...

For s-orbital the value of l is equal to zero so it has only one value for magnetic quantum number that is also zero. It means that under the influence of magnetic field s-orbital remains spherically symmetrical.

For p orbital the value of l=1

So it has three values of magnetic quantum number i.e. +1, 0 and -1. These three values show that the P orbital splits into three degenerate orbitals that are p_x, p_y and p_z, which are oriented in space on x, y and z axis respectively.

Similarly for d-orbital (l = 2) there are five values of magnetic quantum numbers. i.e.

-2, -1, 0, +1, +2. Which represent five orbitals oriented at different positions in space around the nucleus. These orbitals are named as d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and d_{z^2}.

f-orbitals are seven in number and has magnetic quantum number values from -3 to +3.

3. Spin Quantum Number

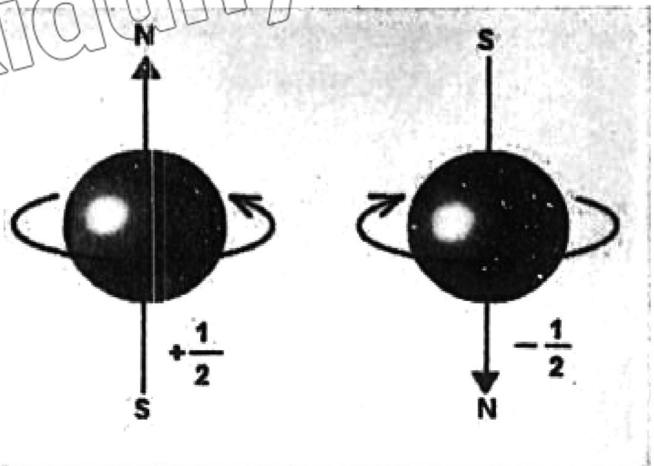


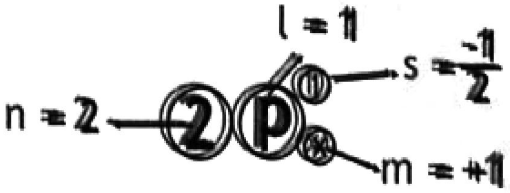
Figure 2.5: Spin Quantum Number

Maximum two electrons can reside in one orbital formed by magnetic quantum number. These two electrons should also have different identification. Actually, two electrons in one orbital must have opposite spin, if one spins clockwise the other's spin will be anti-clockwise.

Spin quantum number describe spin of an electron. Goudsmit in 1925 proved that electron also spins about its axis, it may be called self-rotation and it causes spin magnetic field around it. To reside in one orbital two electrons must cancel spin magnetic field of each other, for this purpose they have opposite spins. Clockwise spin is represented by +1/2 and is symbolised by ↑ And anticlockwise spin is represented by value -1/2 and it's symbol is ↓.

2.2.1 Quantum numbers and electronic configuration

Electronic configuration means the distribution of electrons around the nucleus in orbits and in turn in orbitals. A complete electronic configuration must clearly represent all the four quantum numbers or with the help of four quantum numbers one should be able to write the complete configuration.



2.2.2 Emission Spectrum and electronic Configuration of Elements

The concept of emission spectra is used to determine the electronic configuration of elements. When atoms absorb energy, such as through heat or electricity, electrons move to a higher energy level. When these electrons return to their lower energy levels, they release the absorbed energy in the form of light. The emitted light can be analyzed to reveal the unique spectral lines or patterns of each element. This process is essential in spectroscopy and is widely used to identify and understand the electronic structure of atoms.

The emission spectra are used to infer the electronic configuration of elements as follows:

1. Line spectrum analysis:

Each element has a characteristic line spectrum consisting of certain wavelengths of light that is emitted when electrons move between energy levels.

By analysing spectral lines in the emission spectrum, one can infer the energy levels and transitions that electrons undergo in an atom.

2. Quantized Energy Levels:

The observation of distinct lines supports the Bohr`s idea that electrons occupy specific, quantized energy levels (shells).

3. Electronic Configuration Deduction:

The number and position of the lines in the spectrum can be used to determine the number of shell electrons and the distribution of the shell electrons. For instance, the number and arrangement of lines in the spectrum indicates the number of major energy levels or shell electrons.

For example, a hydrogen atom is a classic example of an emission spectrum. Its emission spectrum is composed of distinct lines that represent the electron transitions in the hydrogen atom. It helps to determine the energy levels of hydrogen and its electronic configuration. Another example is a sodium atom. Sodium has a characteristic yellow emission line. Analyzing this line helps to determine sodium's electronic configuration, including the distribution of electrons in the energy levels of sodium.

Concept Assessment Exercise 2.3

1. Explain the role of the principal quantum number (n) in describing the energy levels of electrons within an atom.
2. When the principal quantum number (n) is 3, how many different possible values can the azimuthal quantum number (l) take?
3. Describe the significance of the magnetic quantum number (m) in relation to the arrangement of electrons within an atom.

2.3 RULES OF ELECTRONIC CONFIGURATION

1. Auf Bau principle

Electrons are distributed in orbitals / subshells in order of increasing energy. Firstly, low energy orbitals are filled then electrons are filled in high energy orbitals.

The energies of orbitals are calculated using quantum mechanical principles. This calculation provides information about the allowed energy levels and spatial distribution of electrons in atom.

The increasing energy order of orbitals is

$$1s < 2s < 2p < 3s < 3p < 4s < 3d \ldots..$$

It is apparent that sometimes the electron is filled first in higher shell(n) and then in lower shell. This can be explained on the basis of n+l rule.

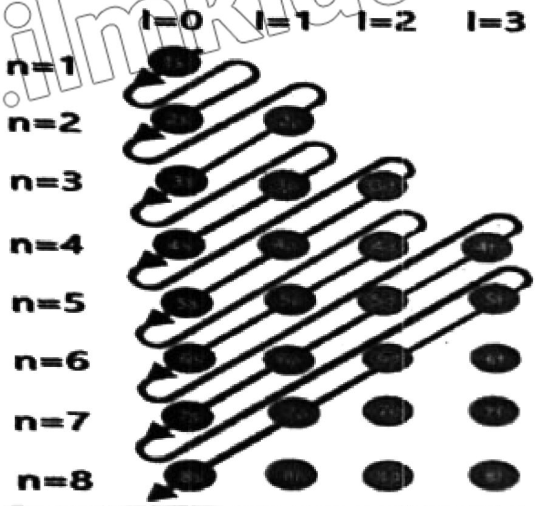


Figure 2.6: Filling order of atomic orbital

Concept Assessment Exercise 2.4

1. In which orbital of the atom the 11th electron will be configurated?
2. Place these orbitals in increasing energy order.
   5s, 4p, 4s, 3d

2. n+l Rule

Higher the n + l value higher will be the energy of the orbital.

e.g.n+l value for 4s orbital is

4 + 0 = 4 and that of 3d orbital is 3+2=5 so the energy of 3d orbital is greater than 4s orbital.

Concept Assessment Exercise 2.5

Which of the following orbitals have greater energy?

3. 5f or 6p
4. 5s or 4d

3. Pauli Exclusion principle

No two electrons in an atom can have the same values of all the four quantum numbers at least the spin quantum number will be different.

If two electrons are present in the same orbital (n,l and m are same) their spin will be opposite for both. If one is clockwise(s=+1/2) ↑ the other will be anticlockwise(s=-1/2) ↓.

e.g., two electrons in 3px orbital have following sets of quantum numbers

Electron A	Electron B
n = 3	n =3
l =1	l = 1
m =-1	m = -1
s = +1/2	s = -1/2

4. Hund's rule

According to this rule if degenerate orbitals (orbitals with equal energy) are available the electrons will tend to reside separately with same spin, instead of pairing up in the same orbital with opposite spin.

For example, if two electrons are to be filled in p orbitals its configuration will be

$$p_x^{\uparrow}\ p_y^{\uparrow}$$

If three electrons are to be filled in p orbital.

$$p_x^{\uparrow}\ p_y^{\uparrow}\ p_z^{\uparrow}$$

Energy of orbital is also related with the number of electrons present in it. Half-filled and completely filled orbitals are more stable with less energy as it is obvious in the configuration of many elements like chromium (Cr) and copper (Cu).

2.4 DETERMINATION OF ELECTRONIC CONFIGURATION OF ATOMS AND IONS WITH PROTON OR ELECTRON NUMBER AND CHARGE

To determine the electronic configuration of atoms and ions, you need to consider the number of protons and electrons in the atom or ion. Note that in a neutral atom, proton number or atomic number (z) is equal to the number of electrons in the atom. The electronic configuration can be determined by following three steps:

1. Identify the neutral atom's electron configuration:

Each neutral atom has a specific number of electrons, which can be found in the Periodic Table of Elements. For example, a neutral fluorine atom has nine electrons.

2. Determine the charge of the ion:

Ions can be positively or negatively charged, depending on whether they have gained or lost electrons. Positive ions (cations) have a deficit of electrons, while negative ions (anions) have an excess of electrons.

3. Write the electron configuration for the ion:

For cations, start with the neutral atom's electron configuration and remove electrons equal to the magnitude of positive charge from outermost shell to create the ion's configuration. For anions, start with the neutral atom's electron configuration and add electrons equal to the magnitude of negative charge in the outermost shell to create the ion's configuration.

For example, the electronic configuration of fluorine is $1s^2\ 2s^2\ 2p^5$.

Now consider a fluoride (F^-) ion with a -1 charge (anion):

Neutral fluorine atom: 9 electrons

Fluoride (F^-) anion: 9 electrons + 1 electron (added) = 10 electrons

The electronic configuration for a fluoride anion (F^-) is $1s^2\ 2s^2\ 2p^6$.

Similarly, the electronic configuration of Na is $1s^2\ 2s^2\ 2p^6\ 3s^1$ which has 11 electrons, now in Na^+ ion one electron will be removed from the valance orbital (11-1=10) so its configuration will be

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$.

Explanation of electronic configuration in terms of energy of electrons and inter-electron repulsion

The relationship between inter-electron repulsion and electronic configuration is that electrons tend to minimize repulsion by occupying their own separate orbital, rather than sharing an orbital with another electron. This is because electrons repel each other due to their identical charges, and this repulsion is minimized when electrons occupy separate orbitals in the same subshell. The repulsion between electrons increases with the increase in the number of electrons in the same orbital, leading to a higher energy for larger orbitals.

Orbital energy

The energy of an orbital depends on its distance from the nucleus and the electron-electron repulsion it experiences. Orbitals with lower energies are filled before those with higher energies.

Spin pairing repulsion

Electrons with similar spin repel each other. This is called spin pair repulsion. Electron therefore occupy separate orbitals in the same degenerate sub-shell to minimize this repulsion and have their spin same (Hund's rule).

Writing the electronic configuration

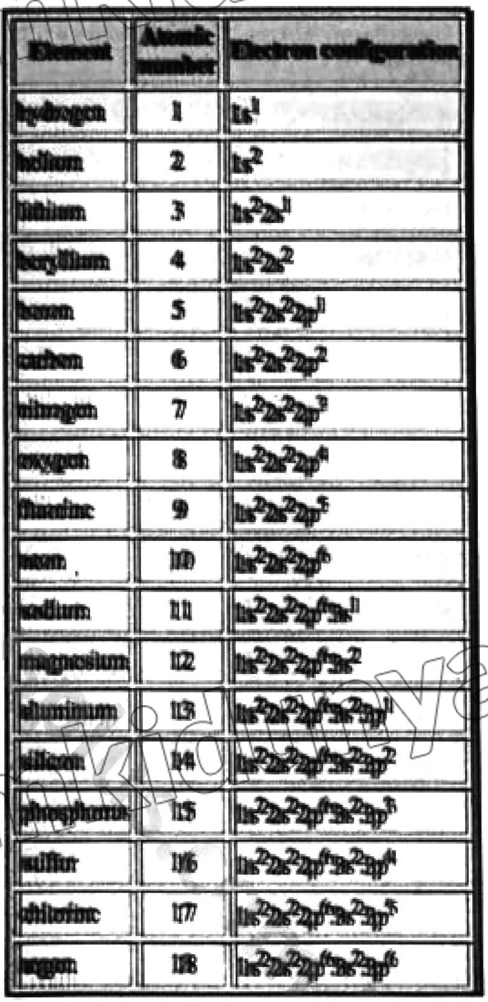
Electronic configuration of elements can be done by filling of the electrons from lower energy levels to high energy levels

The table below only represents the electronic configuration in principal quantum number and Azimuthal quantum number. Magnetic quantum number and spin quantum numbers are not being shown in this configuration. For example, the configuration $3p^6$ will mean $3p_x^2$, $3p_y^2$, $3P_z^2$, again the two electrons should be written as having clockwise and anti-clockwise spins.

If an element is having atomic number 25 its electronic configuration will be written as *follows*.

$1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^2, 3s^2, 3p_x^2, 3p_y^2, 3p_z^2, 4s^2, 3d_{xy}\uparrow, 3d_{yz}\uparrow, 3d_{zx}\uparrow, 3d_{x^2-y^2}\uparrow, 3d_{z^2}\uparrow$

Table: The Electronic configuration of first eighteen elements



Element	Atomic number	Electron configuration
hydrogen	1	$1s^1$
helium	2	$1s^2$
lithium	3	$1s^2 2s^1$
beryllium	4	$1s^2 2s^2$
boron	5	$1s^2 2s^2 2p^1$
carbon	6	$1s^2 2s^2 2p^2$
nitrogen	7	$1s^2 2s^2 2p^3$
oxygen	8	$1s^2 2s^2 2p^4$
fluorine	9	$1s^2 2s^2 2p^5$
neon	10	$1s^2 2s^2 2p^6$
sodium	11	$1s^2 2s^2 2p^6 3s^1$
magnesium	12	$1s^2 2s^2 2p^6 3s^2$
aluminum	13	$1s^2 2s^2 2p^6 3s^2 3p^1$
silicon	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
phosphorus	15	$1s^2 2s^2 2p^6 3s^2 3p^3$
sulfur	16	$1s^2 2s^2 2p^6 3s^2 3p^4$
chlorine	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
argon	18	$1s^2 2s^2 2p^6 3s^2 3p^6$

Concept Assessment Exercise 2.5

1. Write down the electronic configuration of the following elements representing all the four quantum numbers.
   a. $_{21}Sc$
   b. $_{24}Cr$
   c. $_{25}Mn$
   d. $_{30}Zn$
2. Write down the electronic configuration of the following ions.
   a. Na^+
   b. Cl^-
   c. Ca^{+2}

2.5 SHAPES OF ORBITALS

Orbital is the region in space where the probability of finding an electron is maximum. Different orbitals have different shapes in three-dimensional space. p-orbital has two lobes, d-orbital has

4 lobes except $d_z{}^2$ and s orbital is spherically symmetrical. The shapes of these orbitals or shown in figure 2.7.

s-orbital: s orbital is a spherical.

p-orbital: P orbital is dumbbell shaped

d-orbital: d orbital is cloverleaf shaped.

f-orbitals: They have complicated shapes.

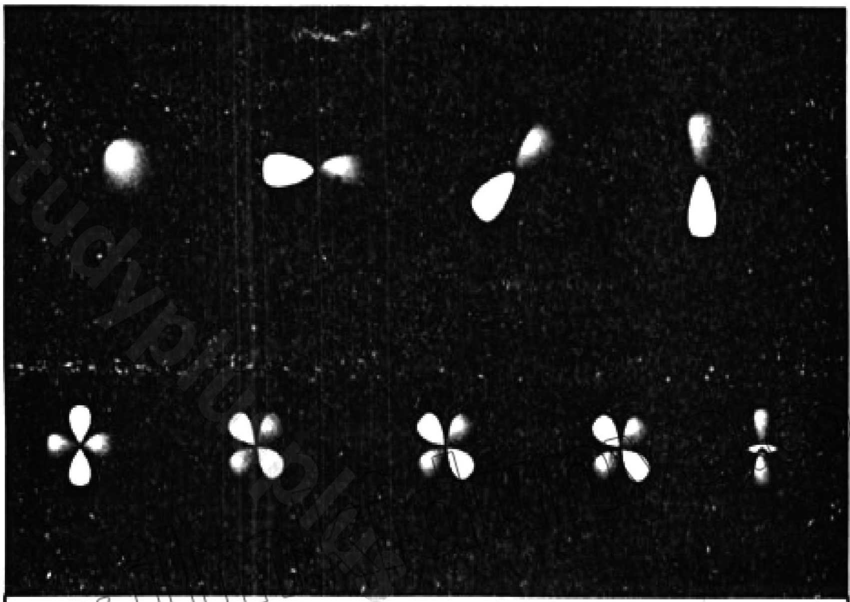


Figure 2.7: Shapes of orbitals

Free Radicals

A free radicals is an atom or molecule with an unpaired electron or electrons in its outer shell. This makes it highly reactive and capable of immediate reactions. They are activated atoms or molecules. The electronic configuration of free radicals is the same as those of atoms.

For example: $Cl^{\cdot}$, $\dot{C}H_3$, $Br^{\cdot}$

For example, the electronic configuration of chloride free radical is the same as that of chlorine atom, but they are shown by a dot on them.

2.6 IONIZATION ENERGY

The minimum energy needed to remove the outermost electron (most loosely bonded electron) from the gaseous isolated atom.

$$Na_{(g)} \longrightarrow Na^{+}{}_{(g)} + 1e \quad I.E = 496kJ/mol$$

$$Mg_{(g)} \longrightarrow Mg^{+}{}_{(g)} + 1e \quad I.E = 738kJ/mol$$

Atom is needed to be in the gaseous state to avoid the influence of other factors like heat of fusion, bond dissociation energy, and heat of the vaporization.

2.6.1 Periodic trends of ionization energy

Ionization energies generally increase from left to right in a periodic table with slight anomalies. This is due to increase number of protons in each step which strengthen the attraction of nucleus on the electrons. Electronic configuration also effects the ionization energy. In group number IIIA less ionization energies are observed as there is only one electron in p orbital which is an unstable configuration. Instead in group VA greater ionization energy values are observed this is due to the half-filled p orbitals. From left to right in main group elements shielding effect remains constant, so there is no effect on the ionization energy values in this respect. Atomic radius decreases from left to right which brings the electrons near to the nucleus thus the attraction is increased and so does the ionization energy. In a group from top to bottom the ionization energy decreases. As the atom becomes bigger and the valence electrons go away from the nucleus, the shielding effect keeps on increasing so it is easier to remove the valance electron.

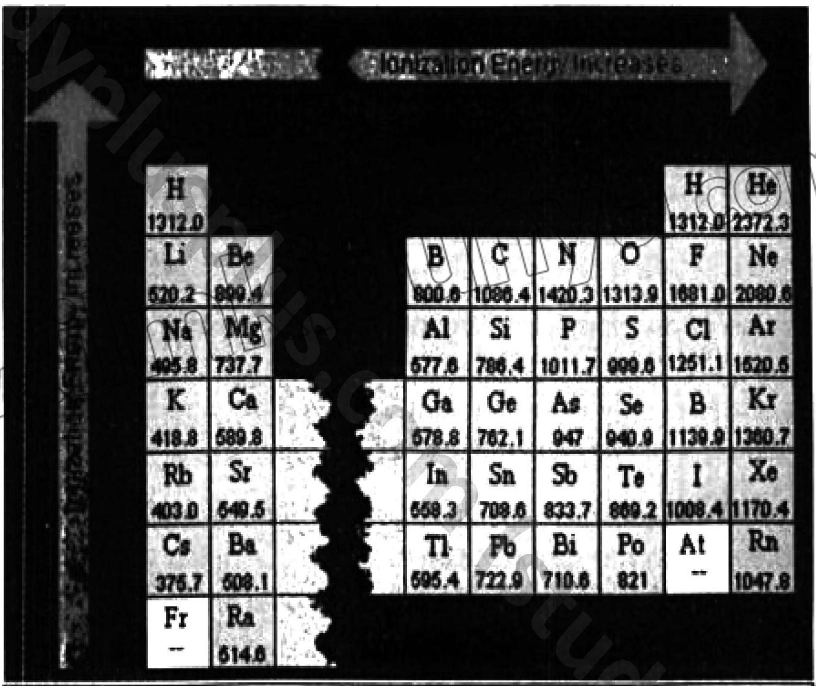


Figure 2.8: Ionization Energies

In the above table ionization energies are mentioned in kJ/mol units.

2.6.2 Factors influencing the ionization energy.

1. **Nuclear charge**

   As the nuclear charge increases moving from left to right in the periodic table the attraction on the outermost electrons also increase which in turn will increase the ionization energy. This is just according to the Coulomb's law.

2. **Atomic radii**

   Moving from left to right in the periodic table decreases the radii, which strengthens the attraction of nucleus on electrons, increasing the ionization energy. From top to bottom size increases and ionization energy decrease.

3. Shielding effect

The shielding effect plays a significant role in influencing ionization energy. As you move down a group, the number of electron shells increases. The inner electron shells act as a shield, reducing the effective nuclear charge felt by the outer electrons. This shielding effect makes it easier to remove outer electrons, leading to a decrease in ionization energy down a group. From left to right shielding effect remains constant and poses no effect on ionization energy.

4. Spin pair repulsion

When electrons are paired in half filled p orbital there is electron pair repulsion which causes the energy of the electron to increase. Increased energy makes the electron easier to remove and therefore the ionization energy decreases. For example, there is slight decrease in ionization energy in going from nitrogen to oxygen in the second period.

As you move across a period, the effective nuclear charge increases, drawing electrons closer to the nucleus. But spin pair repulsion counter acts the increased nuclear attraction, making it slightly easier to remove electron.

2.6.3 Deduction of position of an element in the periodic table by using ionization energy data

To deduce the position of an element in the periodic table using successive ionization energy data, we can analyse the trends in ionization energies and compare them with the known periodic table. Ionization energy is the amount of energy required to remove an electron from a neutral atom, resulting in a positively charged ion

Here are some key points to consider when using successive ionization energy data to determine the position of an element in the periodic table:

1. Trends in ionization energy

Ionization energy generally decreases from top to bottom in groups and increases from left to right across a period, with few exceptions like the first ionization energy decreases from beryllium to boron and from magnesium to aluminium.

2. Periodic table organization

The periodic table is organized in such a way that elements with similar ionization energies are grouped together in the same column. This organization is based on the electronic arrangement of the elements, which determines their chemical properties.

3. Comparing ionization energies

To determine the position of an element in the periodic table, we can compare its ionization energies with the known periodic table. If the element's ionization energies match the expected values for its position in the periodic table, we can confirm its position.

For example, let's consider the element with the symbol "X". This element will be located sequentially between its higher value and its lower value, keeping the lower value element on its left and higher value on its right. For example, if the I.E of an element x is 1251kJ/mol it will be placed between S and Ar which have I.E values 1000kJ/mol and 1520kJ/mol respectively. Similarly from top to bottom if an element y has I.E 738kJ/mol it can be placed between beryllium and calcium whose I.E values are 899kJ/mol and 590kJ/mol respectively.

By comparing the element's ionization energies with the periodic table, we can deduce its position in the periodic table. This method is not always accurate, as there may be some fluctuations in the ionization energies due to the nature of the element and its electronic arrangement.

2.6.4 Electronic configuration and position in periodic table by using successive ionization energy data

Moreover, the successive ionization energy values is an index of the valence of an atom. Big gapes show that the next electron is being removed from the lower shell. For example, in the case of sodium there is a big gap of first and second ionization energy.

First ionization energy: 495 kJ/mol

Second ionization energy: 4560 kJ/mol

This indicate that there is only one electron present in the valence shell, and this element must be a part of group number 1.

Similarly in case of magnesium there is small gap between first and second values of ionization energy but between the second and third value of ionization energy there is a very large gap.

The first, second, and third ionization energy values of magnesium in kJ/mol are as follows:

First ionization energy: 735 kJ/mol

Second ionization energy: 1445 kJ/mol

Third ionization energy: 7730 kJ/mol

This indicates that the third electron is being removed from the inner shell. It indicates that there are only two electrons in the valence shell which are removed easily so this element should be a part of group number 2.

Successive Ionization Energies in Kilojoules per Mole for the Elements in Period 3

General increase →

General decrease ↑

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495	4560					
Mg	735	1445	7730	Core electrons*			
Al	580	1815	2740	11,600			
Si	780	1575	3220	4350	16,100		
P	1060	1890	2905	4950	6270	21,200	
S	1005	2260	3375	4565	6950	8490	27,000
Cl	1255	2295	3850	5160	6560	9360	11,000
Ar	1527	2665	3945	5770	7230	8780	12,000

Concept Assessment Exercise 2.6

1. How does the trend in ionization energy across a period of the periodic table reflect changes in atomic structure and effective nuclear charge?
2. What factors contribute to the general decrease in ionization energy down a group?
3. In terms of ionization energy, why do noble gases possess the highest values among their respective periods, and how does this relate to their chemical reactivity?

2.7 MASS SPECTROMETRY

Mass spectrometry is a powerful analytical technique used to determine the molecular composition and structure of a sample by measuring the mass-to-charge ratio of ions. It's widely used in various scientific fields such as chemistry, biology, and physics.

2.7.1 Principle of Mass Spectrometry

Mass spectrometry involves three fundamental steps: ionization, mass analysis, and detection. The sample is first ionized, converting its molecules or atoms into charged ions. These ions are then separated based on their mass-to-charge ratio (m/z) and detected to generate a mass spectrum, which provides information about the composition and abundance of the sample's molecule or isotopic composition of element.

2.7.2 Working

The working of a mass spectrometer can be broken down into the following steps:

Ionization:

The sample is introduced into the ion source where it is ionized. This process can involve bombarding the sample with high-energy electrons (EI), introducing it to a high-voltage field (ESI), or using a laser to vaporize it Matrix Assisted Laser Desorption/Ionization (MALDI).

Ion Separation:

The resulting ions are then accelerated and directed into the mass analyzer. The mass analyzer separates ions based on their m/z ratio, allowing ions of different masses to be focused and detected at different times.

Detection:

As the ions exit the mass analyzer, they hit the detector. The detector records the time it takes for each ion to reach it, and this data is used to calculate the m/z ratio of each ion.

Data Analysis:

The information collected from the detector is used to construct a mass spectrum. The x-axis of the spectrum represents the m/z ratio, while the y-axis represents the abundance of ions at each m/z ratio. Peaks in the spectrum correspond to different ions present in the sample, with their positions revealing their masses.

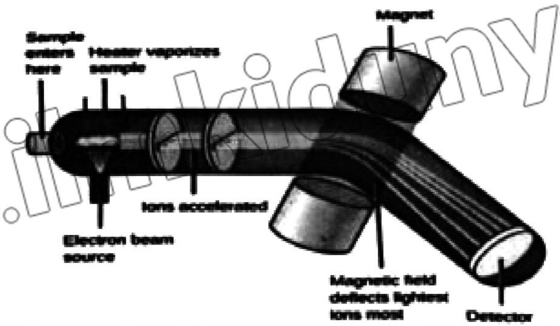


Figure 2.9: Mass Spectrometer

2.7.3 Applications:

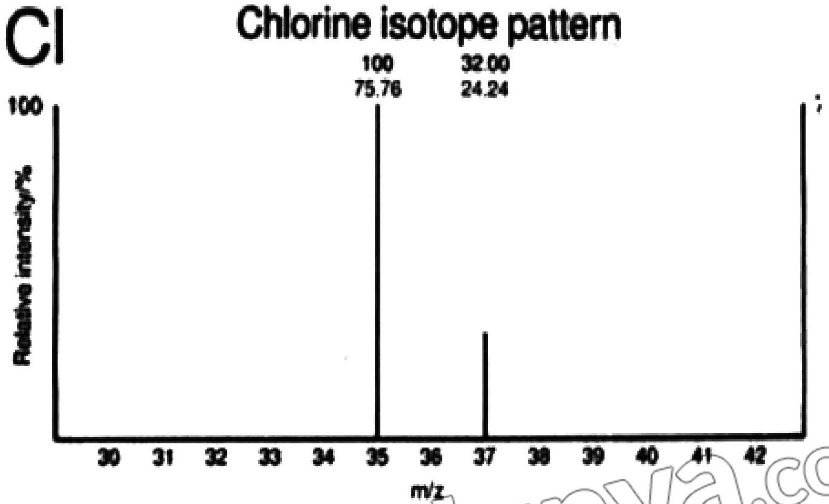
Mass spectrometry has a wide range of applications, including relative abundance of isotopes of an element, identifying unknown compounds, quantifying the amounts of specific substances, elucidating molecular structures, and studying biomolecules like proteins and nucleic acids.

The average atomic mass of an element can be calculated by using the following formula taking in account the relative abundance of all isotopes.

$$\text{Average atomic mass} = \frac{(\text{Mass No. x relative abundance}) + (\text{Mass No. x relative abundance}) + \ldots}{100}$$

Non integer relative atomic masses

Usually, the atomic masses written in the periodic table are not in integral number, these non-integer atomic masses are the result of the inclusion of relative abundance of different isotopes of an element. Relative abundance is usually taken in percentage units. They are multiplied with the mass numbers. Its summation is divided by 100.



Chlorine has two isotopes, chlorine-35 and chlorine-37, with abundances of 75.76% and 24.24%, respectively. To calculate the relative atomic mass of chlorine, we use the formula

$$\text{atomic mass (avg.)} = \frac{(35 \times 75.76) + (37 \times 24.24)}{100} = 35.48 \text{ amu}$$

Therefore, the relative atomic mass of chlorine is 35.48 amu

Concept Assessment Exercise 2.7

Calculate the average atomic mass of Mg using the following mass spectrogram.

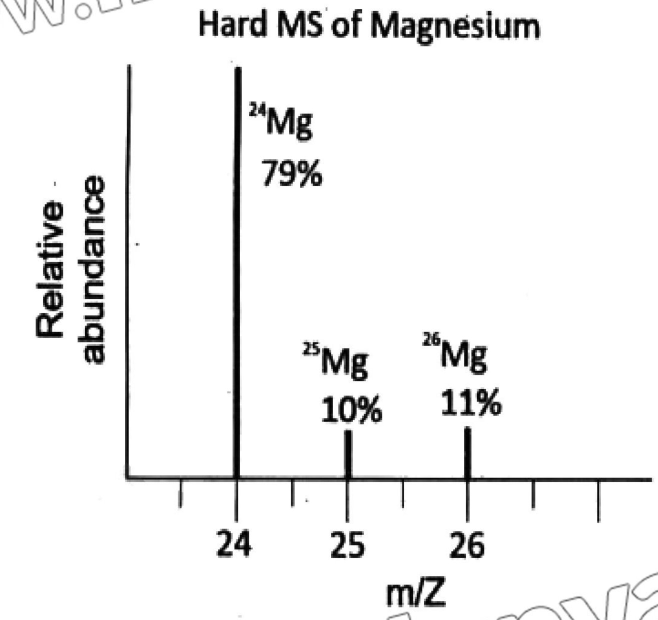


Figure 2.10: Mass Spectrograph of magnesium

2.8 ELECTRONIC CONFIGURATION OF MODERN ELECTRONIC MATERIALS

Semi-conductors are materials that possess electrical conductivity between that of conductors (like metals) and insulators (like non-metals). Their electronic configuration plays a crucial role in determining their behaviour. Let's consider silicon (Si) as an example.

Silicon has an atomic number of 14, meaning it has 14 protons and 14 electrons. The electronic configuration of an element describes how these electrons are distributed in different energy levels or electron shells.

For silicon:

- The first energy level can hold up to 2 electrons ($1s^2$).
- The second energy level can hold up to 8 electrons ($2s^2\ 2p^6$)
- The third energy level can hold up to 4 electrons ($3s^2\ 3p^2$).

Role of Electronic Configuration in determination of type of semi-conductor

In silicon, the outermost energy level is the third energy level. The 3s and 3p sublevels together can hold a maximum of 8 electrons. However, in its ground state, silicon has only 4 valence electrons, which are the electrons in the outermost energy level. This configuration gives silicon unique properties that make it a suitable material for semiconductors.

The arrangement of silicon's electrons creates a band structure. In the valence band, electrons are tightly bound to atoms and cannot move freely. In the conduction band, there are no electrons in the ground state. However, due to the relatively small energy gap between the valence and conduction bands (referred to as the band gap), electrons can be promoted from the valence band to the conduction band, creating electron-hole pairs. This process is called excitation.

Semi-conductors can be intrinsic or extrinsic. Intrinsic semiconductors are pure materials like silicon or germanium, while extrinsic semiconductors have controlled impurities intentionally added. These impurities are called dopants and can either introduce extra electrons (n-type) or create "holes" that behave like positive charge carriers (p-type). This process is known as doping and is achieved by substituting some silicon atoms with other elements like phosphorus (for n-type) or boron (for p-type). The special electronic configuration of silicon makes it able to either accept or lose the electron, so silicon can work as n-type or p-type semi-conductor depending on the doping agent. For example, if Si is doped with P, silicon will be n-type (electron accepter) while doping with elements like Boron makes Silicon p-type (electron donor) semi-conductor.

In n-type semiconductors, dopants introduce excess electrons that can move freely in the conduction band, improving electrical conductivity. In p-type semiconductors, dopants create holes in the valence band that can move, effectively behaving as positive charge carriers.

By strategically combining n-type and p-type materials, engineers can create diodes, transistors, and other electronic components that exploit the unique properties of semiconductors to control the flow of electrical current. This forms the basis of modern electronics and technology.

Concept Assessment Exercise 2.8

1. What is the key characteristic that defines a material as a semiconductor?
2. Can you name two commonly used semiconductor materials in electronic devices?

Key Points

- Neil Bohr formed the basis of modern atomic structure.
- Atom is composed of three fundamental particles electron protons and neutrons; electron is negatively charged proton is positively charged and neutron is neutral.
- Atomic radius is the average distance between the nucleus and valence and electrons, atomic radius increases from top to bottom and decreases from left to right.
- Quantum numbers are set of four numerals which tell complete address of an electron in an atom. Principal quantum Number tells about the shell number, azimuthal quantum number tells about the subshells or orbitals, magnetic quantum number deals with the degenerate orbitals and spin quantum number tells us about the clockwise and anti-clockwise spin of electron.
- Hydrogen spectrum is composed of five series of spectral lines named as Lyman series,

Balmer series, Paschen series, Bracket series, and p fund series.

- Electronic configuration is the method of distributing electrons in different orbitals using Auf Bau principle, Pauli's exclusion principle, Hund's rule and role and n + l rule.
- The minimum energy required to remove the valance electron from isolated gaseous atom is called ionization energy.

[illegible]

1. **Choose the correct answer**

(i) What does the electron configuration $1s^2\ 2s^2\ 2p^6$ represent?

a) Carbon (C) b) Oxygen (O)

c) Neon (Ne) d) Helium (He)

(ii) Which subshell can hold a maximum of 10 electrons?

a) s b) p

c) d d) f

(iii) How many unpaired electrons are there in the electron configuration $3d^5$?

a) 0 b) 1

c) 2 d) 5

(iv) Which element has the electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$?

a) Iron (Fe) b) Zinc (Zn)

c) Nickel (Ni) d) Copper (Cu)

(v) What is the electron configuration of a chlorine ion (Cl^-)?

a) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ b) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

c) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^7$ d) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^8$

(vi) Magnesium has how many isotopes?

a) 1 b) 2

c) 3 d) 4

(vii) What is the basis on which molecular ions are splitted in mass spectrometry?

a) electric field b) magnetic field

c) velocity of ions d) grid strength

(viii) Which orbital is sausage shaped?

a) s b) p

c) d d) f

(ix) Electrons tend to reside separately in the degenerate orbitals this is called:

a) Auf Bau principle b) Pauli exclusion principle

c) Hund's rule d) Fajan's rule

(x) Which quantum number explain the splitting of orbitals in three dimensional space.

a) principal quantum number b) azimuthal quantum number

c) magnetic quantum number d) spin quantum number

2. Give short answer.

(i) What is the importance of Bohr's Atomic model in modern atomic structure?

(ii) Explain the charge and mass of fundamental sub-atomic particles.

(iii) Explain the periodic trends of atomic radius with justification.

(iv) How does shielding effect change the radius of an atom in a group from top to bottom?

(v) Why is the cation always smaller than the parent atom, and anion is bigger than the parent atom?

(vi) Explain how does different spectral series originate in hydrogen spectrum?

(vii) Explain magnetic quantum number in detail. Why do s orbital have only one value of the magnetic quantum number?

(viii) Why it is so that two electrons with same spin cannot reside in an orbital.?

(ix) Why 3d orbital has greater energy than 4S orbital? Explain (n + l) rule.

(x) Calculate the average atomic mass of magnesium keeping in view the relative abundance of its isotopes.

(xi) What is effective nuclear charge?

(xii) What is the importance of electronic configuration in semiconductor materials?

(xiii) Why is there a large I.E gape between second and third values in Mg atoms?

3. Explain quantum numbers in detail.

4. What is mass spectrometry explain its working and tell how the data is analysed?

5. Describe different rules adopted for electronic configuration of elements.

6. Explain ionization energy trends in the periodic table with justifications of these trends and anomalies.

7. Explore the practical applications of atomic emission spectroscopy.
8. Explore the impact of isotopes on atomic mass calculation.

Project

1. Express the atomic structure through art.
2. With the help of clay try to form shapes of 5 d orbitals.
3. Draw the electronic configuration of all elements till Xe.