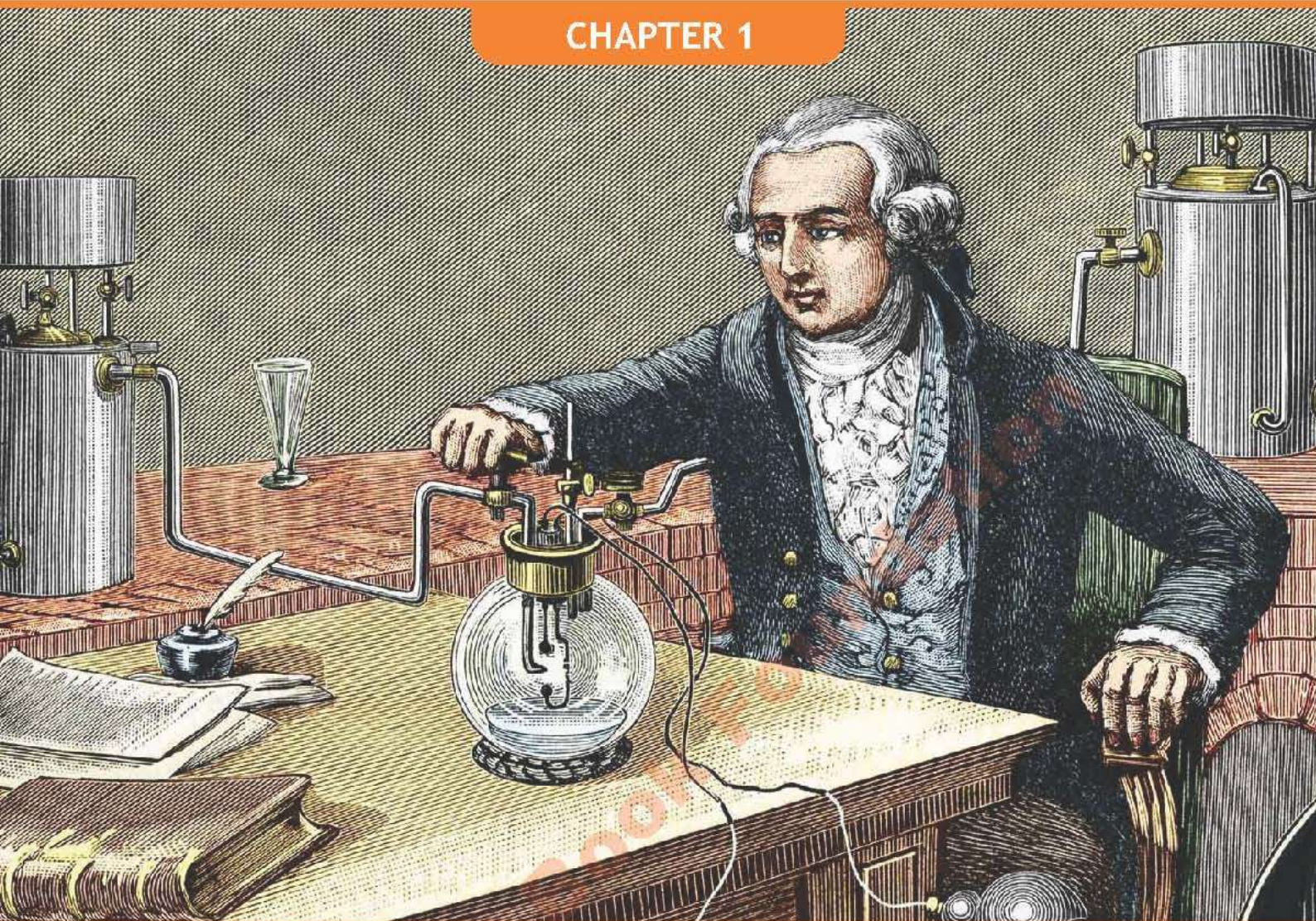


CHAPTER 1



NATURE OF SCIENCE CHEMISTRY

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

1. Describe how Al-Ghazali's burning cotton thought experiment highlight the challenges of inductive reasoning. Examples of deductive reasoning with respect to chemistry.

THOUGHT EXPERIMENTS

The experiment that is performed in the laboratory of human mind is called thought experiment. We study a specific situation, then observe what happens in that situation and finally reach at some conclusion. The difference between thought experiment and real experiment is that the former is done in mind whereas the later one in real world. Thought experiments play vital role in developing scientific theories and principles. We discuss three famous thought experiments in this textbook.

1.1 THE DISCOVERY OF ATOM

In 500 BCE, a Greek philosopher, Leucippus was the first to think about atom so he is known as the father of atomic philosophy. In 430 BCE, another Greek philosopher named Democritus, a student of Leucippus, was the first who thought that matter is made of uniform and indivisible particles called “atomos” (a Greek word meaning uncuttable). This is the first thought experiment about atom in the visible history.

Democritus further thought that atoms also existed for feelings and human soul. He held the shape and size of atoms responsible for properties of matter. He thought that sour taste of substances is due to needle shaped atom while the white colour of matter is due to smooth shaped atoms.

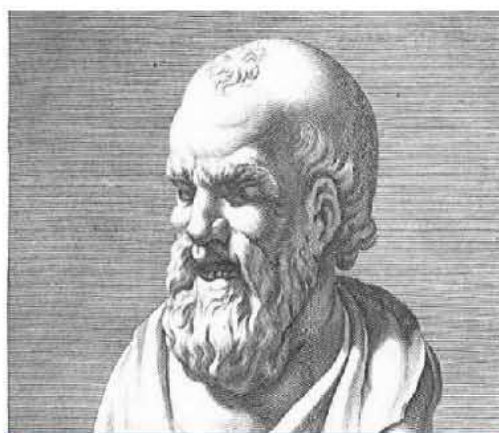
The word atom is combination of two Greek words “a” which means not and “tomos” which means to cut.

Before Democritus thought experiment, there were two Greek philosophies about changes in matter, one was that change in matter is just illusion whereas the other was that change in matter is a

reality. Democritus argued that changes in matter were due to combination and separation of indivisible particle in matter.



Leucippus



Democritus

Experimental Background of Atomic Chemistry

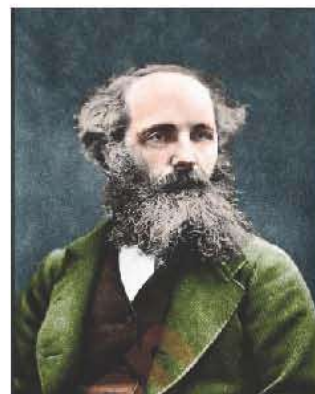
In 1808, an English chemist, John Dalton was the first who converted the Democritus thought experiment about atom into scientific theory called Dalton’s atomic theory. He wrote a book named a new system of chemical philosophy and presented an experimental picture of the formation of compounds from elements. Later on, two other chemists, Gay-Lussac and Amedeo Avogadro supported Dalton’s atomic theory and thus the experimental foundation of atomic chemistry was laid down. In this way, the thought experiment of Democritus was converted to real experiment and the atomic philosophy to atomic chemistry.

1.2 The Maxwell's Demon Experiment

In 1867, a Scottish scientist, James Clerk Maxwell devised a thought experiment on gases. He imagined two containers, say container A and container B, filled with same gases at the same temperature. The two containers shared a small frictionless molecular-sized window in the partitioning wall.

There was a little demon (invisible spirit) on the window who was smart enough to guard the window and detect speed of gas molecules in the two containers.

The demon would selectively allow fast-moving molecules to shift from container A to container B and slow-moving molecules from container B to container A. In this way, all high kinetic energy gas molecules will fill container B and low kinetic energy molecules will stay in container A. Theoretically, this will create temperature difference between the two containers, the container A will get hotter while container B colder without the expense of energy. However, this cannot happen without the cost of energy and is against the second law of thermodynamics.



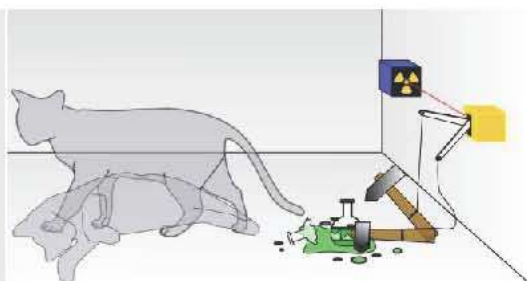
Solution to Maxwell's Demon

The Maxwell's demon thought experiment was a clear violation of second law of thermodynamics which says that heat flows naturally from hotter body to colder body which results in increased entropy of the system. The problem with Maxwell's demon was that the demon was ideally considered to be requiring no energy for the action of opening and closing the window. In fact, the demon's action was not possible without the use of energy hence increase in entropy.

If the demon is considered to be using energy for opening and closing the window, then energy will be used and entropy of the system increased which follows the second law of thermodynamics. In this way, the Maxwell's demon experiment plays role in considering all factors while studying the behaviour of physical systems in physical chemistry.

1.3 THE SCHRODINGER'S CAT EXPERIMENT

Erwin Schrodinger (1887-1961) was an Austrian scientist. He explained his cat experiment picture in a discussion with Einstein while addressing the problems in quantum mechanics. This is why one can safely assume that his cat experiment played an essential role in the development of quantum mechanics.



He imagined to keep a cat enclosed in an opaque box having poison, Geiger counter and a radioactive material. He added that an outside observer would say that the cat is in two states,

both alive and dead at the same time. The actual reason behind these two states of cat is that the radioactive material is also in two states, it decays and does not decay at the same time.

He thought that when the radioactive material decayed, the Geiger counter received radiations emitted from that material and pushed the hammer of the container having poison. As a result, the container opened and poison came out which killed the cat.

If the radioactive material did not decay, then the cat would remain alive. It means that one cannot say from outside the box whether the radioactive material decays or not, and the cat is alive or dead until the box is opened or the material and cat interact with the real world.

The Schrodinger's paradoxical thought experiment can be related with his equation that laid the foundation of quantum mechanics hence quantum chemistry. The equation gives the idea that atoms and sub-atomic particles exist in two states (particle and wave) simultaneously. The two states become one state when they are observed and measured.

When the box is not opened, the system is in superposition of two states, one is the decayed material-dead cat and the other is undecayed material-alive cat.

The cat is in two states, both alive and dead at the same time. Similarly, the radioactive material is in two states, it emits and does not emit radiations at the same time.

1.4 IMAM AL-GHAZALI - HISTORICAL BACKGROUND

Abu Hamid Al-Ghazali was a Muslim theologian and mystic. He was born in 1058 AD in Iran and died in 1111 AD. After completing his education, he moved to Iraq where his teaching and debating received unanimous approval and he got the name of Imam of Iraq. Then he turned away from his worldly status and rank and started seeing things in life with different perspective. He left Baghdad and went Damascus for a short time, then Jerusalem. From there he wrote a famous book "The Revival of Religious Science". He started working on disciplining his soul and improving his nature.



He is considered one of the most influential philosophers of the world and the most prominent Islamic philosopher. His famous work "Tahafut al-Falsafa" (the incoherence of the philosophers) is considered a breakthrough in the history of philosophical thinking of that time. He challenged the philosophical thought of Neoplatonic thinkers, who believed that perfection can be attained in this world, with logic and reason.

1.4.1 Al-Ghazali's Burning Cotton Experiment

Al-Ghazali put forward an idea of necessary causality which says that link between cause and effect is necessary and always true. As an example, Al-Ghazali argued that when a piece of cotton is placed near a burning flame, the cotton will burn. He further added that if another similar cotton piece is brought very close to a similar burning flame, the cotton will burn again.

He thought that the burning flame was the cause to burn cotton piece so there is casual link between burning flame and piece of cotton. He concluded a burning flame necessarily burns the nearby piece of cotton so this theory is called necessary causation.

The necessary causation means one thing is necessarily the cause of another thing. For example, clouds are the cause of rain fall. We can never witness rainfall without clouds.

1.4.2 Al Ghazali's Departure from Necessary Causation

Al-Ghazali performed an experiment in which he brought a cotton piece close to a burning flame. After sometime, the piece of cotton burnt. To him, that meant that the burning flame was the cause of burning cotton.

Do You Know?

Pulling trigger of a gun may cause any event to happen, as the idea of necessary causation is invalid.

He gave another example of a person who couldn't open his eyes. One day, miraculously, the person became able to open his eyelids and see the beauty of world, but he thought the opening of eyelids to be the cause of seeing things around him.

Al-Ghazali, at some stage in his life, departed from his previous point of view. He imagined that what we observe around is the continuation of events, not a kind of direct causation. He said that sticking to the theory of necessary causation would reject the concept of God's will. He put forward the logic that all things have a nature and act in habitual way because nature follows some specific principles. He further added that God created the universe (nature) and He can suspend the habitual succession of events according to His wish.

Interesting Information

God shows miracles by suspending the causal link and habitual course of events.

He argued that the blind man couldn't understand that those were the rays of light striking his eyes and made him able to see around. Actually, the blind man confused the succession of events with causation.

David Hume, another philosopher, supported the Al-Ghazali's approach of continuation of events. He added that there is no natural glue (causal link) that can hold the events around us together, rather they occur one after the another.

1.4.3 Al-Ghazali' Thought Experiment- A Challenge to Inductive Reasoning

Al-Ghazali's thought experiment has the following inductive reasoning.

1. The flame burns a piece of cotton.
2. The piece of cotton burns when kept near the flame.
3. The burning flame is the cause of burning piece of cotton.

The burning cotton experiment of Al-Ghazali proved a challenge to inductive reasoning. He concluded that when a cotton piece is kept near burning flame, it must always burn. This conclusion questions the inductive argument and tells us that repeated observation cannot be always true. He had missed some important factors in data collection, like moisture, chemical

reactions, flow of air and composition of cotton piece etc. This thought experiment hurt our dependence on inductive reasoning and underscores the importance of deductive reasoning.

1.5 REASONING

According to Garrett, “reasoning is a stepwise thinking with a purpose and goal in mind”. It means that reasoning is a specialized thinking that enables a person to mentally understand the link between cause and effect of an event. This is also reasoning that makes somebody able to solve a problem in systematic way on the basis of past experiences and present observation. There are two types of reasoning.

1.5.1 Inductive Reasoning.

In inductive reasoning, generalized conclusions are taken from specific observation. In general, we may encounter difficulties while deriving a set of conditions or situation from a specific statement so inductive logic may involve some uncertainty. In order to reduce that ambiguity, we may go beyond the given information and we must work with impartial mind.

Concept Assessment Exercise 1.1

Make inductive reasoning on the reactivity of halogens in periodic table.

1.5.2 Deductive Reasoning.

The deductive reasoning is a research approach that involves testing of hypothesis. It uses general statement to make specific conclusions. Deductive reasoning is also called top-down logic. It tells us that if the given general statement is true then the specific conclusion coming out of it must be true. The following examples, with reference to chemistry, will make deductive reasoning clear.

a. Stability of Chlorine Element

Chlorine is an element that belongs to halogen group (Group VII). We can apply deductive reasoning on it in the following way.

1. The elements that obey octet rule can exist freely.
2. The chlorine element (Cl_2) follows octet rule.
3. The chlorine element (Cl_2) has independent existence.

b. Balancing Chemical Equations

Consider a chemical reaction in which hydrogen gas reacts with oxygen gas to form water.

The deductive reasoning tool for making a balanced chemical equation under the law of conservation of mass can be broken as follows.

1. A balanced chemical equation follows the law of conservation of mass.
2. The following chemical equation is balanced.



Science Titbit

Inductive reasoning tells us the possibility of a conclusion while deductive reasoning refers the outcome of general statement.

3. The given chemical equation obeys the law of conservation of mass.

c. Chemical Properties of elements

We can relate deductive reasoning process with chemical properties of elements in the following way.

1. All elements belonging to same group have similar chemical properties.
2. Sodium and potassium lie in the same group (group I).
3. Sodium and potassium have similar chemical properties.

Concept Assessment Exercise 1.2

Apply deductive reasoning on the trends in atomic radius along a period in periodic table.

Key Points

- A thought experiment is done in the laboratory of mind, not in your college chemistry laboratory.
- Leucippus (500 BCE) , the Greek philosopher, was the father of the theory of atomism because he originated it.
- Democritus (430 BCE) was the student of Leucippus. He was the first to think that matter is made of small indivisible particles called atoms.
- James Clerk Maxwell presented his thought experiment in 1867 and believed that heat transfers from hot body to cold body without increase in entropy.
- Entropy is the disorder of a system.
- Erwin Schrodinger thought to have a cat in a box may be live and dead at the same time. This thought experiment played a role in the evolution of quantum mechanics.
- Al-Ghazali gave the idea of necessary causation by saying that a piece of cotton kept close to a burning flame must burn. The flame is necessary cause of burning piece of cotton. Later on, he thought that God's will can reject the theory of necessary causation because all natural forces are under control of God.
- David Hume supported the concept of continuation of events, not necessary causation. He thought that there is no causal relationship between cause and event, rather one event is followed by another one.
- Inductive reasoning goes from specific conclusion to general statement.
- Deductive reasoning concludes result from general statement. It is also called top-down approach to research.

References for Further Information

- Thought Experiment - Oxford Bibliographies.
- Al-Ghazali experiment - Prof Riker (Ghazali on necessary causation)
- Al-Ghazali on science, Routledge (Page 939)
- Translation of Al-Ghazali treatises- Concerning Divine Wisdom in the Creation of Man

- The Britanica
- Schrodinger's thought experiment - the magazine "Discover"
- Reasoning -ScienceDirect.com by Kirsty Williamson (Research Method for Student-2nd Edition).

Exercise

1. Choose the correct answer

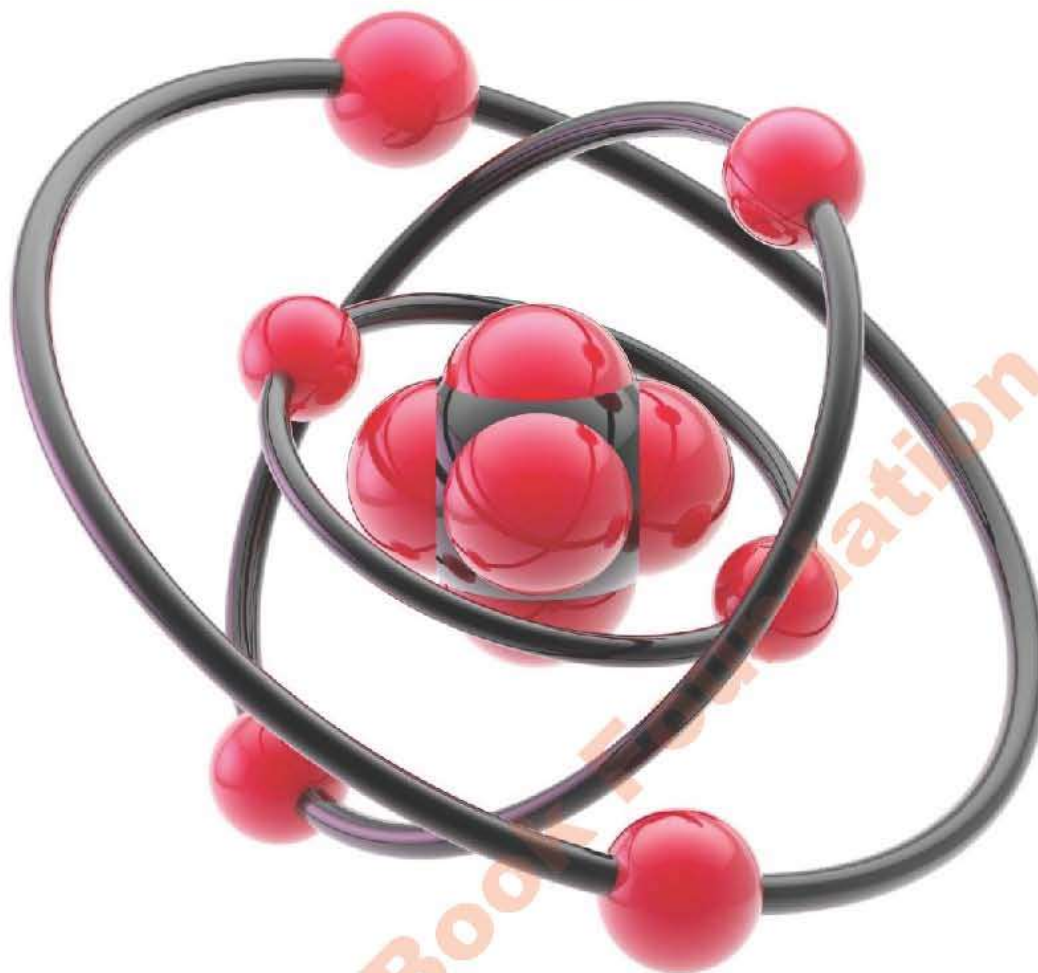
- The word atom comes from Greek language which means
 - beautiful
 - indivisible
 - smooth
 - sharp
- Leucippus is known to be the mentor of Democritus and the father of atomic philosophy. Who was the first to use the word atom?
 - Leucippus
 - James Clerk Maxwell
 - Democritus
 - Erwin Schrodinger
- Who put forward the atomic theory?
 - Dalton
 - J C Maxwell
 - Al Ghazali
 - E Schrodinger
- Who observed the movement of molecules from one container to the other in Maxwell's thought experiment?
 - Maxwell
 - the demon
 - Maxwell's students
 - Maxwell's mentor
- The Maxwell's demon experiment violates which of the following law?
 - law of conservation of mass
 - the Boyle's law
 - first law of thermodynamics
 - second law of thermodynamics
- The Schrodinger's thought experiment is believed to have contributed to evolving the well-known field of physics called
 - plasma physics
 - particle physics
 - statistical mechanics
 - quantum mechanics
- What were the findings for an outside observer in Schrodinger's cat thought experiment?
 - the cat was dead
 - the cat was alive
 - the cat was both alive and dead simultaneously

- D. the cat was neither alive nor dead
- viii. The famous book of Al-Ghazali, "Tahafut-al-Falsafa" challenged the philosophical thought of Neoplatonic thinkers which believed that
- perfection and happiness are achievable in this world
 - no happiness and perfection exist in this world
 - there is life hereafter
 - man is mortal
- ix. Al-Ghazali thought experiment was based on burning
- paper
 - cotton
 - wood
 - coal
- x. What is correct statement about Al-Ghazali's approach?
- he thought that every event must have a cause
 - he thought that there is succession of events, not causation
 - he thought that God can suspend the habitual continuation of events
- I & II only
 - II & III only
 - III only
 - I, II & III

2. Give short answer.

- What was an atom to Democritus?
 - How did Democritus connect atoms to feelings and properties of matter?
 - What was the link of life of the cat with radioactive material?
 - How can we relate Schrodinger's cat experiment with quantum mechanics?
 - Define theory of necessary causation. How did Al-Ghazali prove it?
 - Define inductive and deductive reasoning.
- Explain thought experiment of J C Maxwell.
 - Explain the experimental background of atomic theory.
 - Describe what conclusions were drawn by Schrodinger from his thought experiment.
 - How did Al-Ghazali conclude from a piece of burning cotton? Also relate his conclusions with his concept of God involvement in all natural laws.
 - Explain that Al-Ghazali's thought experiment was a challenge to inductive reasoning.
 - Take some examples from chemistry and apply them on inductive and deductive reasoning separately.

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

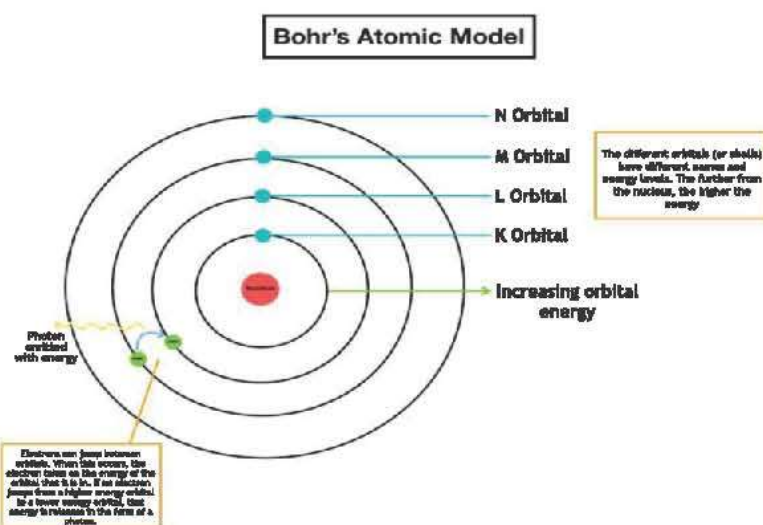


Figure 2.1: Bohr's Atomic Model

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. Its 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.

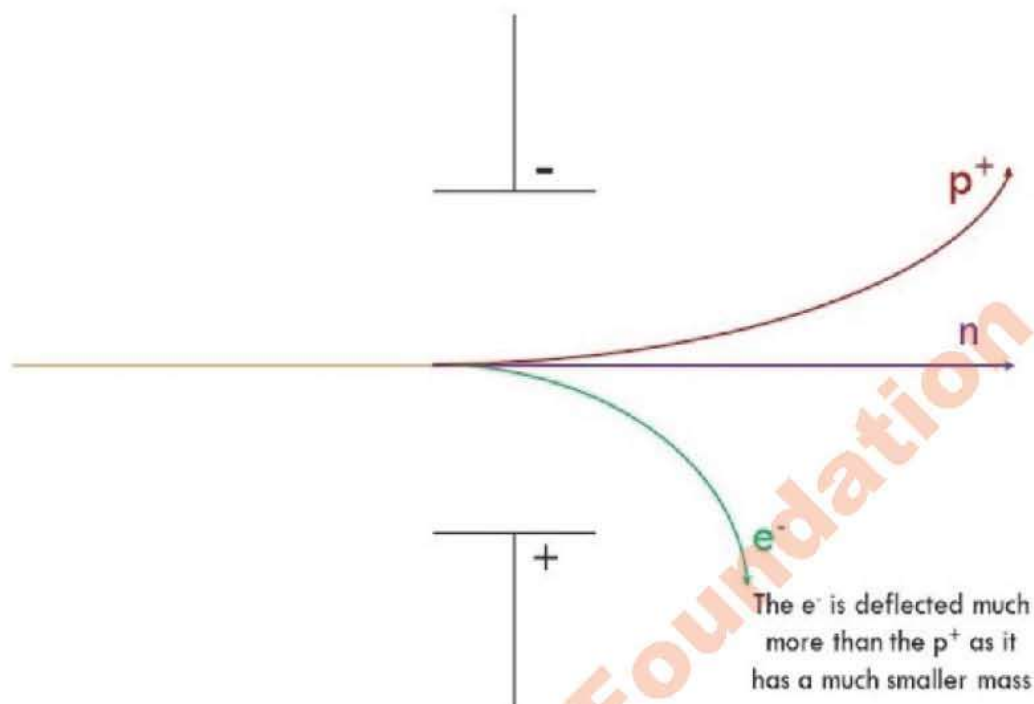


Figure 2.2: Path of positively and negatively charged particles through the uniform electric field.

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.

$$\text{Atomic number} + \text{Number of neutrons} = \text{Mass number}$$

$$(P + N = A)$$

$$\text{Number of Protons} = \text{Number of electrons (in a neutral atom)}.$$

$$\text{Number of electrons in a cation} = \text{Atomic number} - \text{magnitude of charge on cation}$$

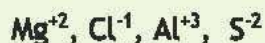
$$\text{Number of electrons in an anion} = \text{Atomic number} + \text{magnitude of charge on anion}.$$

Concept Assessment Exercise 2.1

- How many electrons are present in the following species:



2. Find out number of electrons protons and neutrons of the following species using the atomic number. (Use periodic table).

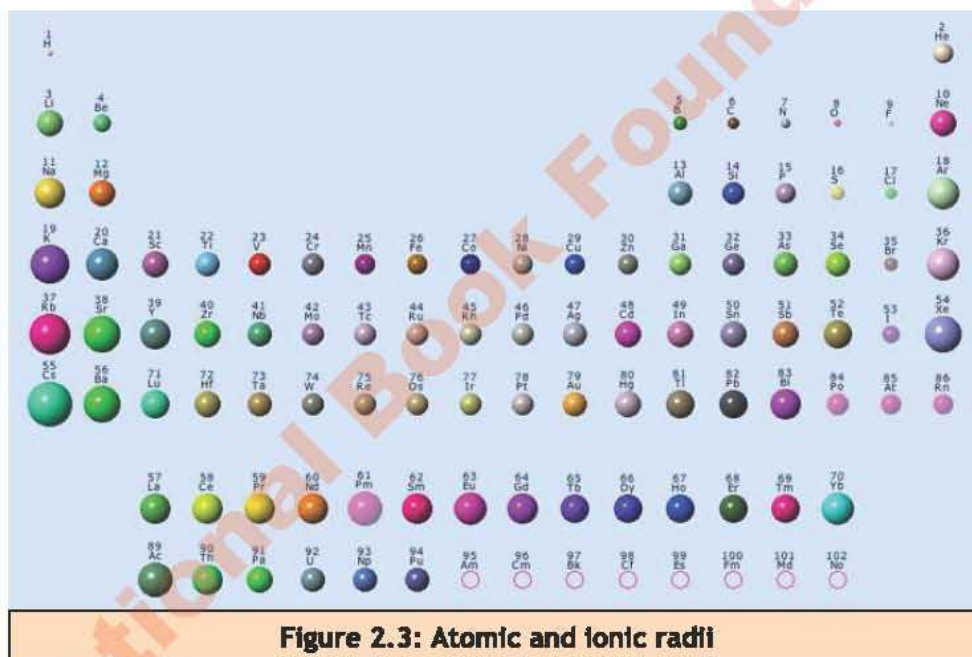


2.1.4 Atomic and Ionic Radius

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

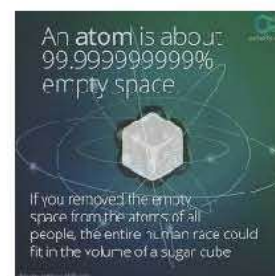
Across the period from left to right in main groups the atomic and ionic radius decrease as the nuclear charge increases. From left to right the shielding effect remains constant. However, in transition metal series it increases as the electrons are configured in the inner shell d-orbitals.



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.

1 H 1.38 1.06 0.00 —																	2 He — 0.62 0.53 0.00
3 Li 3.33 2.69 0.39 0.35	4 Be — 1.79 1.59 0.29																
		atomic number → 6 C ← atomic symbol															
		radius of C ⁻ → 1.91															
		→ 1.49 ← radius of C															
		radius of C ⁺ → 1.25															
		→ 0.95 ← radius of C ²⁺															
11 Na 3.57 2.91 0.71 0.66	12 Mg — 2.18 1.96 0.60																
19 K 4.36 3.59 1.11 1.06	20 Ca — 2.81 2.55 0.98	21 Sc 2.57	22 Ti 2.42	23 V 2.30 1.94 1.46	24 Cr 2.38 1.72 1.41	25 Mn 2.11 1.97 1.30	26 Fe 2.09 1.91 1.28	27 Co 2.05 1.48 1.21	28 Ni 2.00 1.45 1.17	29 Cu 2.77 2.24 1.38 1.14	30 Zn 1.93 1.75 1.09	31 Ga 3.70 2.64 1.56 1.49	32 Ge 2.64 2.21 1.94 1.38	33 As 2.33 1.97 1.76 1.62	34 Se 1.97 1.82 1.60 1.50	35 Br 1.72 1.62 1.53 1.39	36 Kr — 1.47 1.40 1.34
37 Rb 4.65 3.84 1.29 1.25	38 Sr — 3.08 2.80 1.16	39 Y 2.94	40 Zr 2.55	41 Nb 2.58 2.41 2.10 1.89	42 Mo 2.43 1.88 2.10 1.75	43 Tc 2.20 1.67 2.10 1.53	44 Ru 2.43 1.67 1.48	45 Rh 2.45 1.57 1.39	46 Pd 1.81 1.51 1.33	47 Ag 2.46 1.42 1.28	48 Cd 2.14 1.95 1.22	49 In 3.71 2.81 1.80 1.70	50 Sn 3.23 2.58 2.44 1.60	51 Sb 2.33 2.17 2.00 1.86	52 Te 1.97 2.07 1.85 1.74	53 I 1.72 1.87 1.78 1.64	54 Xe — 1.71 1.64 1.55

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

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

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 $n - 1$.

$$\text{Possible values: } l=0,1,2,3\dots$$

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	$\frac{1}{2}$ $-\frac{1}{2}$	1	1s	2	2
2 (L Shell)	0	0	$\frac{1}{2}$ $-\frac{1}{2}$	1	2s	2	8
	1	-1, 0, +1	$\frac{1}{2}$ $-\frac{1}{2}$	3	2p	6	
3 (M-shell)	0	0	$\frac{1}{2}$ $-\frac{1}{2}$	1	3s	2	18
	1	-1, 0, +1	$\frac{1}{2}$ $-\frac{1}{2}$	3	3p	6	
	2	-2, -1, 0, +1, +2	$\frac{1}{2}$ $-\frac{1}{2}$	5	3d	10	
4 (L-shell)	0	0	$\frac{1}{2}$ $-\frac{1}{2}$	1	4s	2	32
	1	-1, 0, +1	$\frac{1}{2}$ $-\frac{1}{2}$	3	4p	6	
	2	-2, -1, 0, +1, +2	$\frac{1}{2}$ $-\frac{1}{2}$	5	4d	10	
	3	-3, -2, -1, 0, +1, +2, +3	$\frac{1}{2}$ $-\frac{1}{2}$	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

$$m = \dots -3, -2, -1, 0, +1, +2, +3, \dots$$

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

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 $+\frac{1}{2}$ and is symbolised by $\downarrow$ And anticlockwise spin is represented by value $-\frac{1}{2}$ and it's symbol is $\uparrow$.

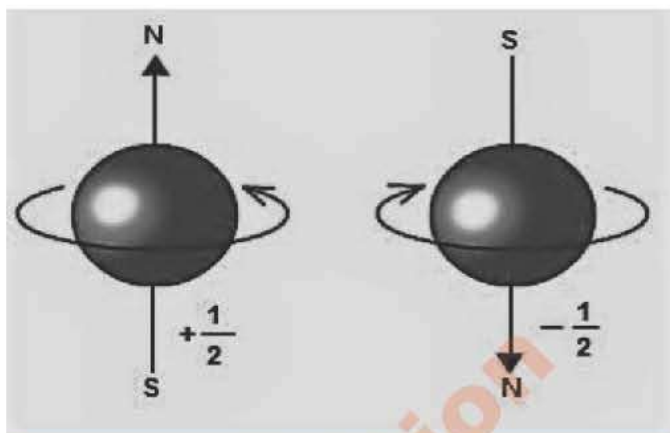
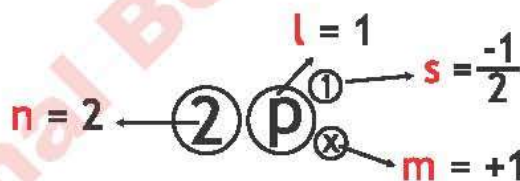


Figure 2.5: Spin Quantum Number

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

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

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.

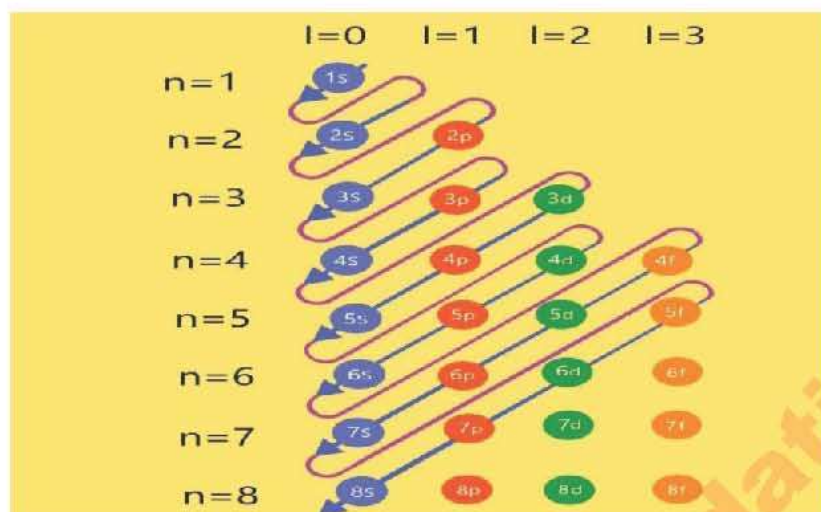


Figure 2.6: Filling order of atomic orbital

Concept Assessment Exercise 2.4

1. In which orbital of the atom the 11th electron will be configured?
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 ($s=+1/2$) $\uparrow$ the other will be anticlockwise ($s=-1/2$) $\downarrow$.

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

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

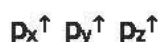
4. Hund's rule

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



If three electrons are to be filled in p orbital.



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 valence 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. Electrons therefore occupy separate orbitals in the same 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.

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

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

- Write down the electronic configuration of the following elements representing all the four quantum numbers.
 - ${}_{21}\text{Sc}$
 - ${}_{24}\text{Cr}$
 - ${}_{25}\text{Mn}$
 - ${}_{30}\text{Zn}$
- Write down the electronic configuration of the following ions.
 - Na^+
 - Cl^-
 - 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 are 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.

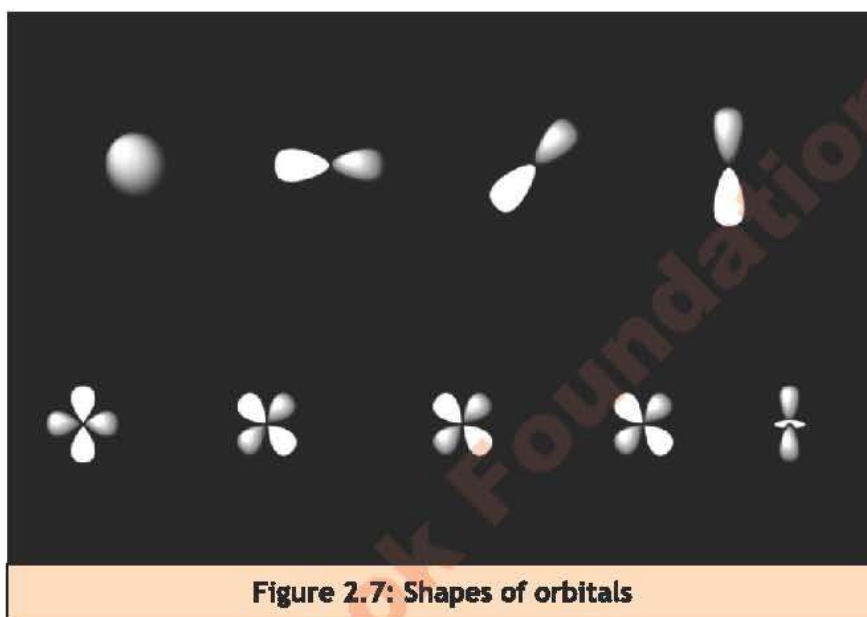


Figure 2.7: Shapes of orbitals

Free Radicals

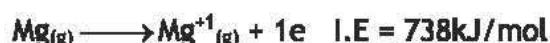
A free radical is an atom or molecule with an unpaired electron or electrons in its outer shell. This makes it highly reactive and capable of immediate reactions. They are activated atoms or molecules. The electronic configuration of free radicals is the same as those of atoms.

For example: $\text{Cl}^\cdot$, $\cdot\text{CH}_3$, $\text{Br}^\cdot$

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.



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 affects 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.

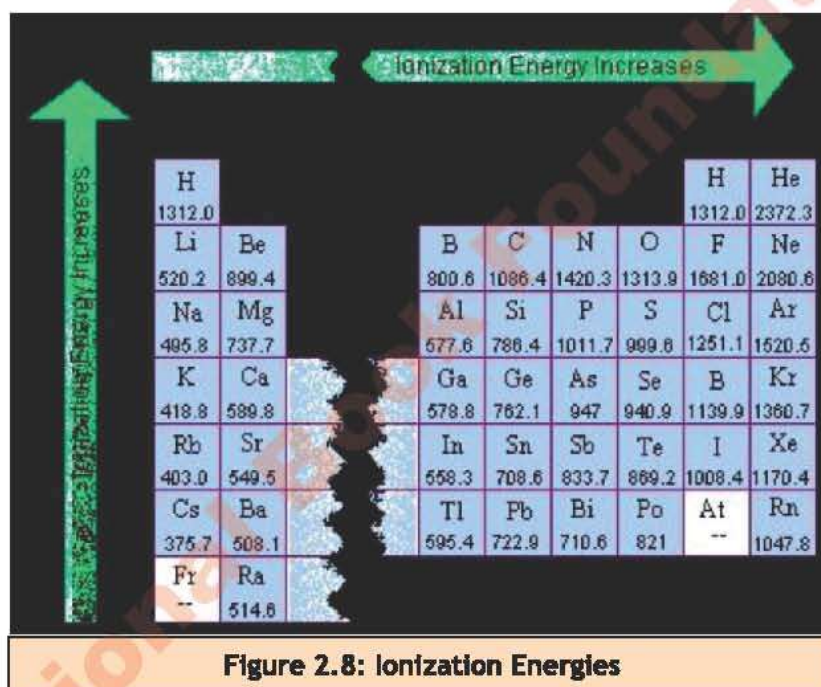


Figure 2.8: Ionization Energies

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 gaps 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 →							
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

↑ General decrease

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.

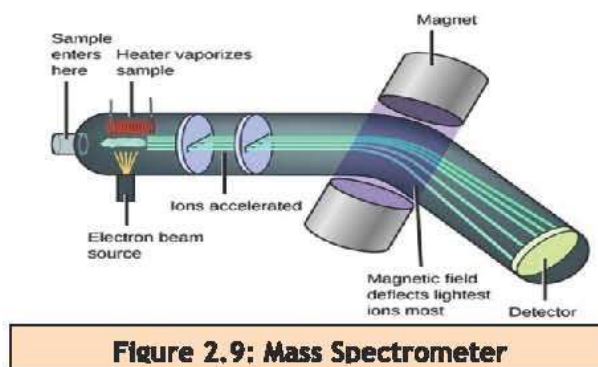


Figure 2.9: Mass Spectrometer

2.7.3 Applications:

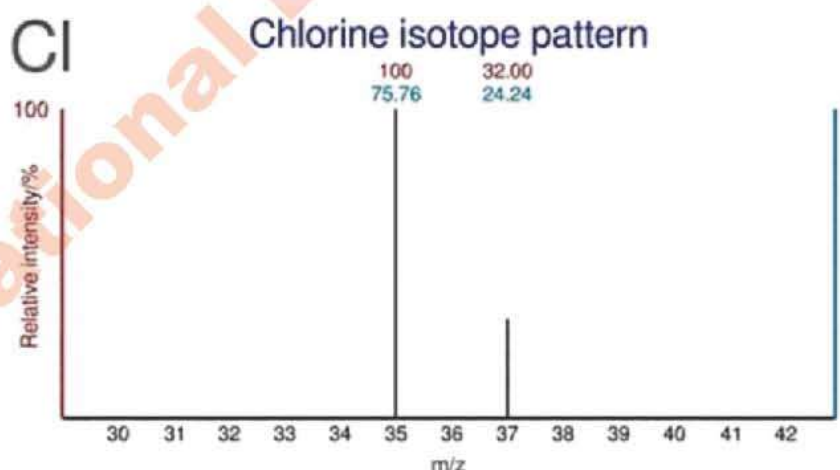
Mass spectrometry has a wide range of applications, including relative abundance of isotopes of an element, identifying unknown compounds, quantifying the amounts of specific substances, elucidating molecular structures, and studying biomolecules like proteins and nucleic acids.

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

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

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

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

Therefore, the relative atomic mass of chlorine is 35.48 amu

Concept Assessment Exercise 2.7

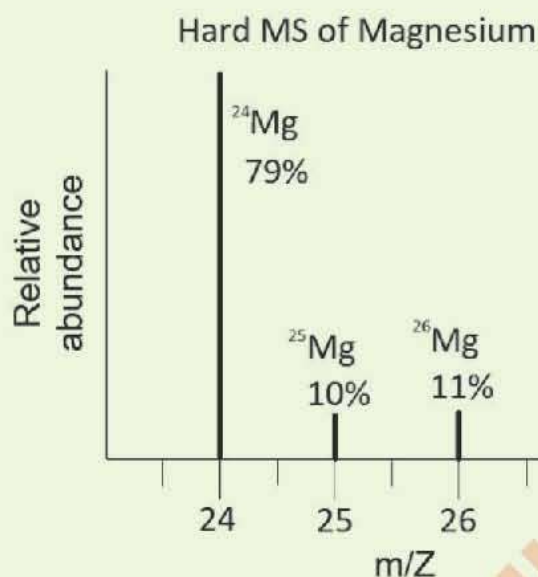


Figure 2.10: Mass Spectrograph of magnesium

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

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 acceptor) 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.

Exercise

1. Choose the correct answer

- What does the electron configuration $1s^2 2s^2 2p^6$ represent?
 - Carbon (C)
 - Oxygen (O)
 - Neon (Ne)
 - Helium (He)
- Which subshell can hold a maximum of 10 electrons?
 - s
 - p
 - d
 - f
- How many unpaired electrons are there in the electron configuration $3d^5$?
 - 0
 - 1
 - 2
 - 5
- Which element has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$?
 - Iron (Fe)
 - Zinc (Zn)
 - Nickel (Ni)
 - Copper (Cu)
- What is the electron configuration of a chlorine ion (Cl^-)?
 - $1s^2 2s^2 2p^6 3s^2 3p^6$
 - $1s^2 2s^2 2p^6 3s^2 3p^5$
 - $1s^2 2s^2 2p^6 3s^2 3p^7$
 - $1s^2 2s^2 2p^6 3s^2 3p^8$
- Magnesium has how many isotopes?
 - 1
 - 2
 - 3
 - 4
- What is the basis on which molecular ions are splitted in mass spectrometry?
 - electric field
 - magnetic field
 - velocity of ions
 - 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 gap 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. Do the electronic configuration of all elements till Xe.

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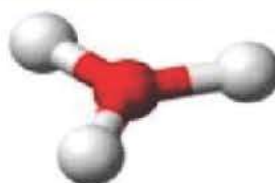
CHAPTER 3



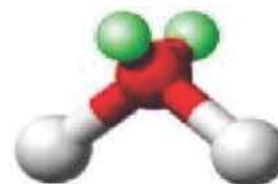
linear



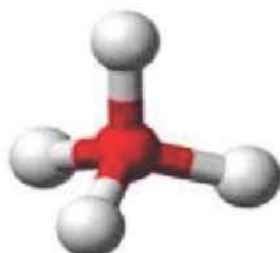
linear



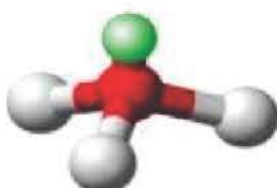
trigonal
planar



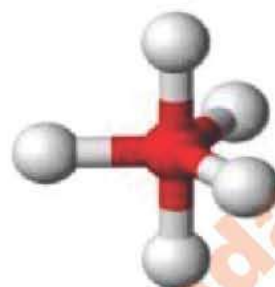
bent or
angular



tetrahedral



trigonal
pyramidal



trigonal
bipyramidal



octahedral

CHEMICAL BONDING

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

1. DEFINE ELECTRONEGATIVITY as the power of an atom to attract electrons to itself.
2. Explain the factors influencing the electronegativities of elements in terms of nuclear charge, shielding by inner shells and subshells.
3. Explain the trends in electronegativity across a period and down a group of the periodic table.
4. Use the differences in Pauling electronegativity values to predict the formation of ionic and covalent bonds.
5. Describe covalent bonding in molecules using the concept of hybridization to describe sp , sp^2 , and sp^3 orbitals.
6. Use bond energy values and the concept of bond length to compare the reactivity of covalent molecules.
7. Describe the shapes and bond angles in molecules using VSEPR theory (including describing sketching).
8. Predict the shapes, and bond angles in molecules and ions.
9. Explain hybridization and types of hybridization.
10. Explain valence bond theory.
11. Explain the importance of VSEPR theory in the field of drug design by discussing how the shape and bond angles of the molecules help chemist predict their interactions in the body.
12. Explain the salient features of molecular orbital theory.
13. Explain the paramagnetic nature of oxygen molecule in the light of MOT.
14. Calculate bond order of N_2 , O_2 , F_2 , and He
15. Describe the types of Van der Waals' forces.
16. Describe hydrogen bonding limited to molecules including ammonia and water.
17. Use the concept of hydrogen bonding to explain the anomalous properties of water.
18. Use the concept of electronegativity to explain bond polarity and dipole moments of molecules.
19. State that, in general, ionic, covalent, and metallic bonding are stronger than intermolecular forces.
20. Recognize that molecular ions/polyatomic ions can have expanded octets e.g. sulphate and nitrate.
21. Analyze the formation of dative bond in CO , ozone and H_3O^+ ion (resonance structures are not required).

In this chapter, we will discuss how VSEPR theory explains the shapes of molecules. We will also discuss how shapes of molecules effect the polarity in a molecule. Other theories such as Valence Bond Theory and Molecular Orbital Theory have also been discussed, which explain the orbital overlapping and paramagnetism in a molecule. These theories can also be used to explain the chemical and physical properties of molecules.

3.1 ELECTRONEGATIVITY

It is the power of a covalently bonded atom to attract shared pair of electrons towards itself in a molecule.

It is a dimensionless property and has no unit because it is only a tendency. It basically indicates the net result of the tendencies of atoms in different elements to attract the bond-forming electron pairs. We measure electronegativity on several scales. The most commonly used scale was designed by Linus Pauling.

3.1.1 Factors affecting Electronegativity.

Electronegativity depends upon the following factors.

- Size of atom
- Nuclear charge
- Screening by inner electrons

As the number of protons in nucleus increases, the nuclear charge increases. Hence the size of atom decreases causing the attraction of bonded electrons with the nucleus to decreases, resulting in increase of electronegativity. When the number of inner shell electrons increases, the distance between the nucleus and valence electrons increases. So, attraction of bonded electron with the nucleus decreases causing decrease in electronegativity. Table 3.1 represents electronegativity of elements in the periodic table.

Table 3.1: Electronegativity of elements in the periodic table

1 H 2.20																
3 Li 0.98	4 Be 1.57											5 B 2.04	6 C 2.55	7 N 3.04	8 O 3.44	9 F 3.98
11 Na 0.93	12 Mg 1.31											13 Al 1.61	14 Si 1.90	15 P 2.19	16 S 2.58	17 Cl 3.16
19 K 0.82	20 Ca 1.00	21 Sc 1.36	22 Ti 1.54	23 V 1.63	24 Cr 1.66	25 Mn 1.55	26 Fe 1.83	27 Co 1.88	28 Ni 1.91	29 Cu 1.90	30 Zn 1.65	31 Ga 1.81	32 Ge 2.01	33 As 2.18	34 Se 2.55	35 Br 2.96
37 Rb 0.82	38 Sr 0.95	39 Y 1.22	40 Zr 1.33	41 Nb 1.6	42 Mo 2.16	43 Tc 1.9	44 Ru 2.2	45 Rh 2.28	46 Pd 2.20	47 Ag 1.93	48 Cd 1.69	49 In 1.78	50 Sn 1.96	51 Sb 2.05	52 Te 2.1	53 I 2.66
55 Cs 0.79	56 Ba 0.89	57 La 1.1	72 Hf 1.3	73 Ta 1.5	74 W 2.36	75 Re 1.9	76 Os 2.2	77 Ir 2.20	78 Pt 2.28	79 Au 2.54	80 Hg 2.00	81 Tl 1.62	82 Pb 2.33	83 Bi 2.02	84 Po 2.0	85 At 2.2
87 Fr 0.7	88 Ra 0.9															

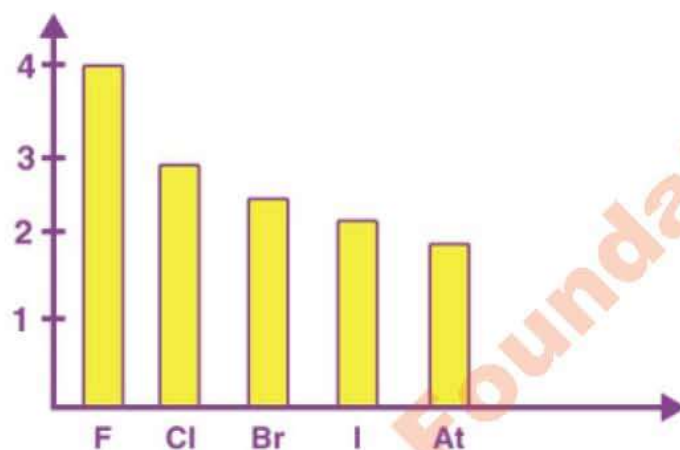
Pauling Electronegativity Values

5 B 2.04	6 C 2.55	7 N 3.04	8 O 3.44	9 F 3.98
13 Al 1.61	14 Si 1.90	15 P 2.19	16 S 2.58	17 Cl 3.16

3.1.2 Trend of Electronegativity in the Periodic Table.

Electronegativity decreases from top to bottom in groups. There is an increase in the atomic number as we move down the group in the modern periodic table. The nuclear charge also increases but the effect of the increase in nuclear charge is overcome by the addition of an extra shell (increase in shielding effect). The attraction of shared electrons with the nucleus decreases. Hence, the value of electronegativity decreases.

For example, in the halogen group as we move down the group from fluorine to astatine the electronegativity value decreases, and it is shown in the figure 3.1.

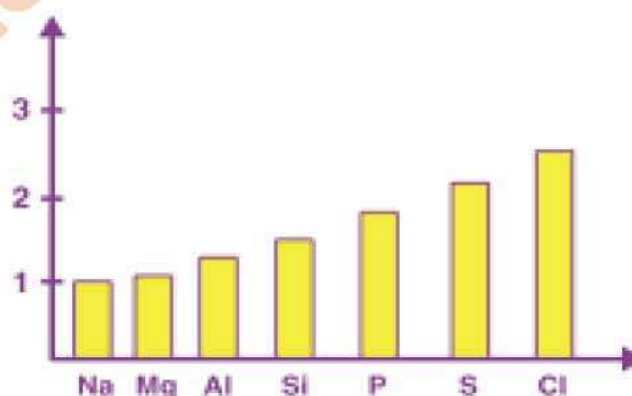


Electronegativity Trend – Down the Group

Figure 3.1: Trend of Electronegativity of Halogen down the group.

Electronegativity increases from left to right across a period. When we move from left to right in periods effective nuclear charge increases. Shielding effect remains constant. Hence, the size of atom decreases. The power of atoms to attract shared pair of electron increases.

For example, in the third period from sodium to chlorine the electronegativity value increases, and it is shown in the figure 3.2.



Electronegativity Trend – Across the Period

Figure 3.2: Trend of Electronegativity of third period elements.

3.1.3 Nature of Bond in terms of Pauling Electronegativity Values

In ionic bonds, the differences in electronegativity between two atoms is higher than 1.8. Polar-covalent bonds have differences in electronegativity between 1.8 and 0.4. Nonpolar Covalent bonds have differences in electronegativity of 0.4 or lower. In case the electronegativity of both atoms is the same, the pair of electrons will be shared equally.

Example 3.1: Consider the following substances and determine their bond types.

- (i) Oxygen molecule ($O=O$)
- (ii) Potassium Chloride (KCl)
- (iii) Hydrogen Chloride (HCl)

(i) This molecule consists of two oxygen atoms. Oxygen has an electronegativity value of 3.44. So each atom in this molecule has an electronegativity of 3.44.

The difference in electronegativity is 0, which means that none of the two atoms in the molecule pulls the electrons to itself more strongly than the other. This means that this molecule has a covalent bond.

(ii) This compound has a potassium atom with an electronegativity of 0.82 and a chlorine atom with an electronegativity of 3.16.

There is a difference in electronegativity of 2.34 which is greater than 1.8, hence the bond will be ionic.

(iii) This molecule consists of a hydrogen atom with an electronegativity of 2.20 and a chlorine atom with an electronegativity of 3.16.

In this molecule, Chlorine is more electronegative than hydrogen. This means that Chlorine pulls the electrons more closely to itself than the hydrogen atom. The difference between their electronegativities is 0.96 which is between 1.8 and 0.4. Hence the bond will be Polar Covalent Bond.

3.1.4 Covalent character in a compound

Covalent character in a molecule depends upon the polarising power of cation which in turn depends on the oxidation state of cation. Higher the polarising power of cation, more will be the covalent character. That is why when we move from left to right in periods covalent character increases.

For example, Aluminium chloride is more covalent in nature as compared to magnesium chloride. In Aluminium chloride oxidation state of aluminium atom is +3 while in Magnesium chloride oxidation state of magnesium is +2. Because of high polarizing power of Al, it can polarise the anion causing electrons to be shared between the two ions. Hence, covalent character will be developed in the compound.

3.2 DIPOLE MOMENT

It is the product of the magnitude of positive or negative charges and the distance between them. Mathematically it can be written as

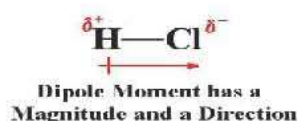
$$\mu = q \cdot r$$

Dipole Charge Separation
moment distance

SI unit of dipole moment is debye. 1 Debye is equal to 3.335×10^{-30} Cm.

(Cm is coulomb meter).

The difference between the electronegativity of two atoms in a compound determines the overall dipole moment and overall polarity of the compound.

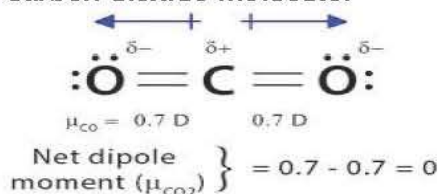


Electronegativity difference between two atoms determines the bond polarity of the molecule. Greater the electronegativity difference between two atoms, more will be the bond polar (more ionic nature). But a small difference in electronegativity of two bonded atoms will make bond less polar or more covalent in nature.

3.3 POLAR AND NONPOLAR COVALENT BOND

In polar covalent bond, due to electronegativity difference, one atom which is more electronegative will attract shared electron to itself and bear partial negative charge and other bears partial positive charge. Such molecules are called polar molecules. Polar molecules have dipoles, electric charges of equal magnitude and opposite sign.

Symmetrical polyatomic molecules are non-polar molecules having shape of Linear, Trigonal Planar and Tetrahedral. In these molecules dipole of bond exerts equal and opposite effects and hence cancels the charges. Non-polar molecules have no overall charge. Following diagram represents dipole moment of Carbon dioxide molecule.



Due to electronegativity difference between Carbon and Oxygen C=O bond in CO₂ is polar, but CO₂ is nonpolar because dipole gets canceled with each other.

Concept Assessment Exercise 3.1

1. Are the following molecules polar or non-polar? In each case give a reason for your answer.
(Electronegativity values: F = 4.0, Cl = 3.0, Br = 2.8, S = 2.5, C = 2.5, H = 2.1)

- a. Chlorine, Cl₂ b. Hydrogen fluoride, HF c. The V-shaped molecule, sulfur dichloride, SCl₂ d. The tetrahedral molecule, chloromethane, CH₃Cl
e. The tetrahedral molecule tetrabromomethane, CBr₄.

3.4 BOND ENERGY (BOND ENTHALPY)

Energy which is required to break the bond of the same type in one mole of a substance is known as bond energy. Its unit is kJ mol^{-1} . Bond energy depends upon the following factors:

- (i) Electronegativity difference between two bonded atoms
- (ii) Size of atom
- (iii) Bond order
- (iv) Bond length

The greater the electronegativity difference between two bonded atoms, the more polar will be the bond and the greater will be the bond energy.

Table 3.2: Following table represents the bond energy of hydrogen halide (Hydride of group VII).

Bond	Bond Energy (kJ mol^{-1})	Electronegativity difference between bonded atoms
H–F	562	1.8
H–Cl	431	0.9
H–Br	366	0.7
H–I	299	0.4

From the above data we conclude that greater the electronegativity difference, higher will be the value of bond energy, for example HF has greater value of bond energy. Figure 3.3 represents bond enthalpy of HX from HF to HI.

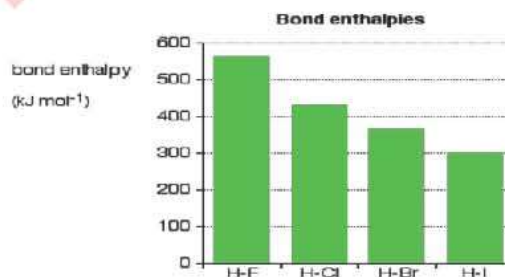


Figure 3.3: Bond enthalpy of Hydrogen halide from HF to HI

Bond Length:

Bond length is the distance between the nuclei of two covalently bonded atoms. It is measured in $\text{\AA}$ or picometer (Pm). $1\text{ pm} = 10^{-12}\text{ m}$. Bond length depends upon the size of atom. Smaller the size of atoms, the greater the bond energy due to shorter bond length.

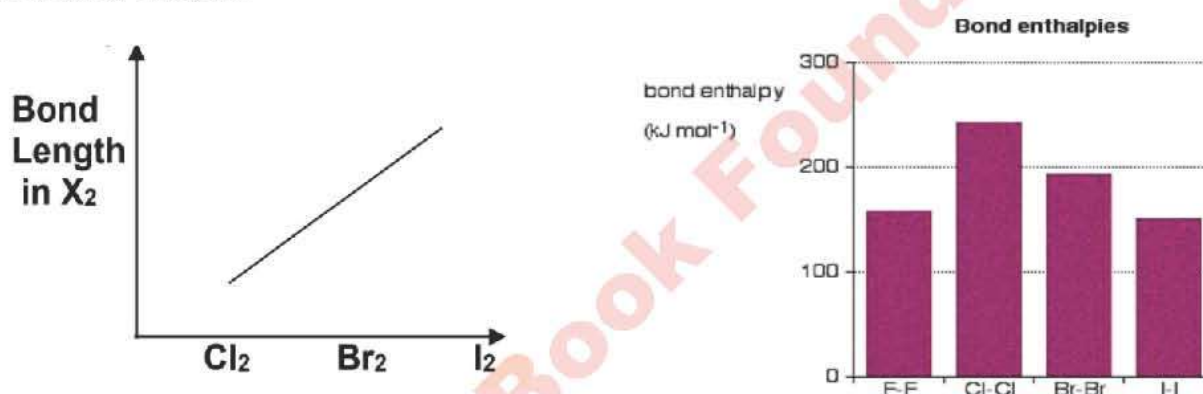
Bond energy of H-H is 436 kJ mol^{-1} and that of H-Br is 366 kJ mol^{-1} . It is due to the shorter bond length of hydrogen molecule compared to HBr. (Size of Br is greater than hydrogen).

Table 3.3: Following table represents the bond energy and bond length of Halogens.

Bond	Bond Energy (kJ mol^{-1})	Bond length (pm)
F–F	158	149
Cl–Cl	242	199
Br–Br	193	228
I–I	151	266

The atomic radius increases from fluorine to iodine. Bond energy decreases from chlorine to iodine molecule, but fluorine molecule has lower value of bond energy than chlorine. It is because of the smaller size of fluorine atoms that their lone pairs repel each other, hence less amount of energy is required to break the bond between fluorine atoms.

Bond energy is also used to predict the reactivity of covalent molecules. Greater the bond energy stronger will be the bond and that molecule will be stable and less reactive. For example, In alkyl halides, alkyl fluorides are less reactive than alkyl chlorides (as bond energy of C-F is greater than C-Cl). Trend of bond length and bond energy of halogen is shown in the following diagram.

**Figure 3.4:** (a) Bond length of Halogen from Cl_2 to I_2 (b) Bond enthalpy of Halogen from F_2 to I_2 .

3.5 SHAPES OF MOLECULES

Valence Shell Electron Pair Repulsion Theory

This theory is used to determine the shape and bond angle in the molecule.

As electrons are negatively charged particles, they repel each other when close together. So, a pair of electrons in the bonds surrounding the central atom in a molecule will repel other electron pairs. These repulsions between electron pairs force apart until the repulsive forces are minimised.

The shape and bond angles of a covalently bonded molecule depends on the number of pairs of electrons around each atom, whether these pairs are lone pairs or bonding pairs. Lone pairs of electrons have a more concentrated electron charge cloud than bonding pairs of electrons. Their cloud charges are wider and slightly closer to the nucleus of the central atom. This results in a different amount of repulsion between different types of electron pairs.

The order of repulsion is lone pair-lone pair (most repulsion) > lone pair-bond pair > bond pair-bond pair (least repulsion).

3.5.1 Shapes of Molecule containing two Electron Pairs

Those molecules where central atom is surrounded by two electron pairs and no lone pairs are linear in shape and of 180° angle.

AX_2 : BeF_2

The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is



In BeF_2 there are two electron pairs around the central beryllium atom. We see from the above figure that the arrangement that minimizes repulsions places the groups 180° apart.

3.5.2 Shapes of Molecule containing three Electron Pairs

Those molecules where central atom is surrounded by three electron pairs and no lone pair are Trigonal in shape and angle will be 120° .

Three Bonding Pairs

AX_3 : BCl_3

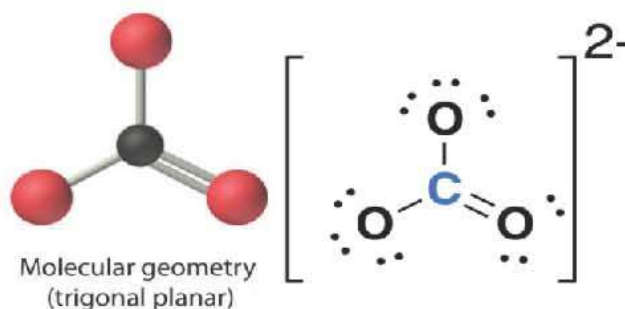
The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure and shape of BCl_3 is shown below:



There are three electron pairs around the central atom. To minimize repulsions, the groups are placed 120° apart and geometry is trigonal planar.

AX_3 : CO_3^{2-}

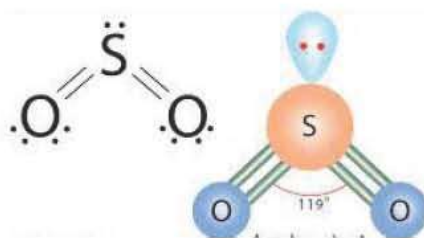
In Carbonate ion, CO_3^{2-} , the central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. There are three bonding pairs around the carbon atom. The molecular geometry of CO_3^{2-} is trigonal planar.



Two Bonding Pairs and one Lone Pair

AX₂E: SO₂

The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. The Lewis electron structure and shape of SO₂ is shown in the right side.



There are three electron pairs around the central atom, two double bonds and one lone pair. There are two bonding pairs and one lone pair, so the structure is designated as AX₂E.

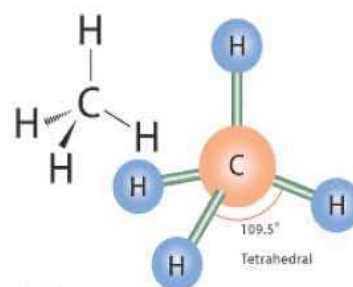
Because a lone pair occupies more space near the central atom than a bonding pair. Thus, bonding pairs and lone pairs repel each other. In SO₂, we have one BP-BP interaction and two LP-BP interactions. Thus, the shape is bent or V shaped and the angle will be less than 120°.

3.5.3 Shapes of Molecule containing four Electron Pairs

Four Bonding Pairs

AX₄ : CH₄

Those molecules where the central atom is surrounded by four electron pairs and no lone pair are tetrahedral in shape with bond angle of 109.5°. For example, In CH₄ carbon atom is surrounded by four electron pairs which are bonding pairs.

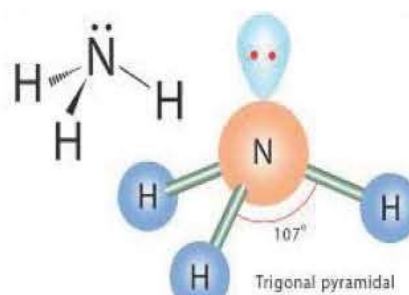


Three Bonding Pairs and one Lone Pair

AX₃E: NH₃

Those molecules where the central atom is surrounded by four electron pairs, three bonding pairs and one lone pair are Trigonal pyramidal in shape.

For example in ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron. In ammonia NH₃, nitrogen atom is surrounded by four electron pairs out of which three are bonding pairs and one lone pair. With three bonding pairs and one lone pair, the structure is designated as AX₃E.

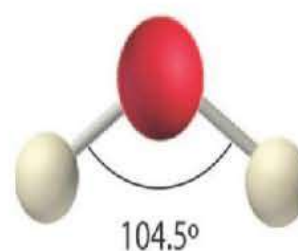


There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. However, the H-N-H bond angles are less than the ideal angle of 109.5° because of Lone Pair-Bond Pair repulsions.

Two Bonding Pairs and Two Lone Pair

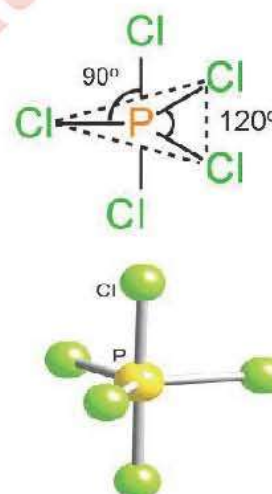
AX_2E_2 : H_2O

Those molecules where the central atom is surrounded by four electron pairs, two bonding pairs and two lone pairs are Bent in shape. With two bonding pairs and two lone pairs, the structure is designated as AX_2E_2 with a total of four electron pairs. Due to LP-LP, LP-BP, and BP-BP interactions, we expect a significant deviation from idealized tetrahedral angles. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two nuclei about the central atom, so the molecular shape is bent, or V shaped, with an H-O-H angle that is even less than the H-N-H angles in NH_3 , as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one.



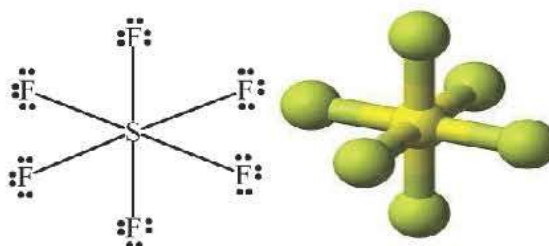
3.5.4 Shapes of Molecule containing five Electron Pairs

There are some cases in which the electrons around a central atom may not have a noble gas configuration. Those molecules where central atom is surrounded by five electron pairs and no lone pair are trigonal bipyramidal in shape. For example, PCl_5 which has five bonding pairs of electrons and no lone pairs. The repulsion between the electron pairs results in the most stable structure being a trigonal bipyramid. Three of the chlorine atoms lie in the same plane as the phosphorous atom. The bond angles $ClPCl$ within this plane are 120° . Two of the chlorine atoms lie above and below this plane at 90° to it.



3.5.5 Shapes of Molecule containing six Electron Pairs

Those molecules where central atom is surrounded by six electron pairs and no lone pair are octahedral in shape. All angles are 90° . Sulphur hexafluoride, SF_6 , has twelve electrons around the central Sulphur atom. We say that the Sulphur atom has an 'expanded octet'.



3.5.6 Expanded Octet/Hypervalency

The octet rule applies well to atoms in the second row of the periodic table, where a full valence shell includes eight electrons with an electron configuration of s^2p^6 . Even elements in the third and fourth row are known to follow this rule sometimes, but not always. In larger atoms of 3rd period onwards the valence shell contains additional subshells, d, f and g subshells.

Therefore, atoms of 3rd, 4th ... period elements can have higher valence shell counts by "expanding" into these additional subshells. When atoms contain more than eight electrons in their valence shell, they are said to be hypervalent. This is also called expanded octet. Figure 3.5 represents the molecular ions with expanded octet.

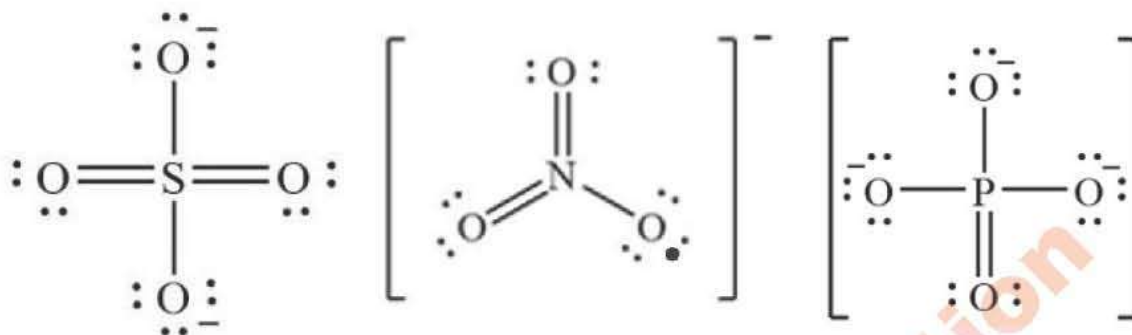


Figure 3.5: Indicates the ions with expanded octet.

Table 3.4: Shapes of Molecules

Summary of Shapes of Molecules						
Number of valence electrons	Number of bonding pairs of electrons	Number of lone pairs of electrons	Total number of electron pairs	Arrangement of orbitals	Arrangement of atoms / Angle	Examples
4	2	0	2	Linear	Linear 180°	BeCl ₂ , HCN, CO ₂
6	3	0	3	Trigonal planar	Trigonal planar 120°	BF ₃ , AlCl ₃ , NO ₃ ¹⁻
8	2	1	3	Tetrahedral	Bent 118°	SnCl ₂
	4	0	4		Tetrahedral 109.5°	CH ₄ , SiCl ₄ , SO ₄ ²⁻ , NH ₄ ¹⁺
10	3	1	4	Trigonal bipyramid	Trigonal Pyramid 107°	NH ₃ , PCl ₃ , ClO ₃ ¹⁻
	5	0	5		Bent 104.5°	H ₂ O, H ₂ S
12	6	0	6	Octahedral	Trigonal bipyramid 90° and 120°	PCl ₅ , PI ₅
					Octahedral 90°	SF ₆

3.5.7 Working out the shapes of Molecules

Add together the number of valence electrons from the central atom, and the number of electrons contributed to bonding by surrounding atoms. Include the ion charge if there is one.

Divide the total electrons by 2. This gives the number of electron pairs distributed around the central atom.

Example 1	Example 2
Predict the Geometry of NH_3 Valence electrons of nitrogen = 5 Electron from 3 chlorine atoms = 3 Total number of electrons = 8 Number of electron pairs = 4 So, the electron pairs are arranged tetrahedrally. Number of atoms surround the central atom = 3 Number of bonding pairs = 3 Number of lone pairs = 1 The molecule is trigonal pyramidal.	Predict the Geometry of NH_4^{1+} Valence electrons of nitrogen = 5 Electron from 4 hydrogen atoms = 4 Electron from molecular charge = 1+ Total number of electrons = 8 Number of electron pairs = 4 So, the electron pairs are arranged tetrahedrally. Number of atoms surround the central atom = 4 Number of bonding pairs = 4 Number of lone pairs = 0 The molecule is tetrahedral.

3.5.8 Importance of VSEPR Theory in the Field of Drug

By predicting molecular shapes and bond angles, VSEPR aids Medicinal chemists in understanding how drug molecules interact in the body.

Shape and dimensions of the molecules being used as drugs also depends upon the length and angles of the bonds between their atoms. Any change in bond angles affect the overall 3D shape of molecules thus affecting their binding ability or permeability through membranes of target cell.

Molecular Shape and Enzymatic Reactions

Enzymes recognize and bind to drug substrates based on their molecular shape. VSEPR helps predict this 3D structure, allowing designers to tailor molecules for optimal interaction with enzyme active sites. Understanding the molecular geometry through VSEPR aids in creating drugs with enhanced substrate recognition, facilitating targeted interactions in enzymatic reactions.

Enzyme-Substrate Interaction in Drug Design

Consider the interaction between a drug and the enzyme acetylcholinesterase in neuropharmacology. VSEPR guides the design of drugs with shapes that fit precisely into the enzyme's active site, enhancing efficacy and specificity.

Molecular Geometry in Drug Delivery Systems

VSEPR theory, which predicts molecular shapes and plays a vital role in designing effective drug Carriers. Liposomes, spherical lipid-based vesicles, are extensively used as drug carriers due to their biocompatibility and versatility. VSEPR informs the design of liposomal carriers by predicting the optimal arrangement of electron pairs, influencing their three-dimensional structure. For instance, tailoring liposomes into specific shapes, such as elongated or targeted geometries, enhances their ability to navigate biological barriers and efficiently deliver drugs to the desired tissues.

Now, imagine a drug molecule designed to interact with a specific enzyme. The VSEPR-derived geometry of this drug molecule needs to be considered to ensure optimal binding. If the enzyme's active site has a pocket with a tetrahedral arrangement of binding sites, a drug with a complementary tetrahedral geometry might fit more effectively.

Understanding molecular geometry also helps scientists to understand the shapes of more complex molecules such as proteins and DNA. The shapes of these molecules play incredibly important roles in determining the jobs performed by these molecules in our bodies.

Cisplatin is a neutral complex, $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, has square planar structure. Cisplatin is one of the most effective anticancer agents widely used in the treatment of solid tumors. It is generally considered as a cytotoxic drug which kills cancer cells by damaging DNA and inhibiting DNA synthesis. Cisplatin-induced DNA damage activates the various signaling pathways to prevent or to promote cell death.

Concept Assessment Exercise 3.2

1. a Predict the shapes of the following molecules.
 - i tetrachloromethane, CCl_4
 - ii beryllium chloride, BeCl_2
 - iii phosphorus (III) chloride.
- b Draw dot-and-cross diagrams for the following molecules and then predict their shapes:
 - i hydrogen sulphide, H_2S
 - ii phosphine, PH_3 .
2. a Draw a dot-and-cross diagram for a molecule of selenium hexafluoride, SeF_6 .
- b Predict the shape of selenium hexafluoride.
- c Draw the shape of the phosphorus(V) chloride molecule

3.6 VALENCE BOND THEORY

This theory was proposed by Heitler and London (1927) and later developed by Pauling. It has successfully explained bond energies, bond lengths and shapes of the covalent molecules.

According to Valence Bond Theory, covalent bonds are formed by the overlapping of partially filled atomic orbital of one atom with a partially filled atomic orbital of the other. Their identity was retained by the two overlapping atomic orbitals. The term overlap means that the two orbitals share the same common region in space.

Main points of VBT

1. A bond between two atoms is formed by the overlap of half-filled atomic orbitals of two atoms. These atomic orbitals retain their identity.
2. Electrons of overlapping orbitals have opposite spin.
3. The number of bonds formed is equal to the number of unpaired electrons present in the outermost shell of the atom.
4. By the overlapping of two orbitals overlap, a single bond which is sigma bond is formed. By the overlapping of additional orbitals, multiple bonds are formed (double and triple).
5. In order to form a bond, the overlapping orbitals must have the same symmetry with respect to the bond axis.

“A line joining the nuclei of two bonded atoms is called bond axis”.

6. Energy is released by the overlapping of orbitals. The greater the overlap between the orbitals, the greater is the energy released and the stronger will be the bond formed.

Types of Overlapping and Nature of Covalent Bonds

The two main types of covalent bonds obtained by overlapping are as follows:

- Sigma bond (σ)
- Pi Bond (π)

Sigma Bond

When there is a single bond between two atoms, the bond will be sigma bond. Sigma bond is formed by the head on overlapping of atomic orbital. It is formed between s-s, s-px, s-py, s-pz, px-px overlap.

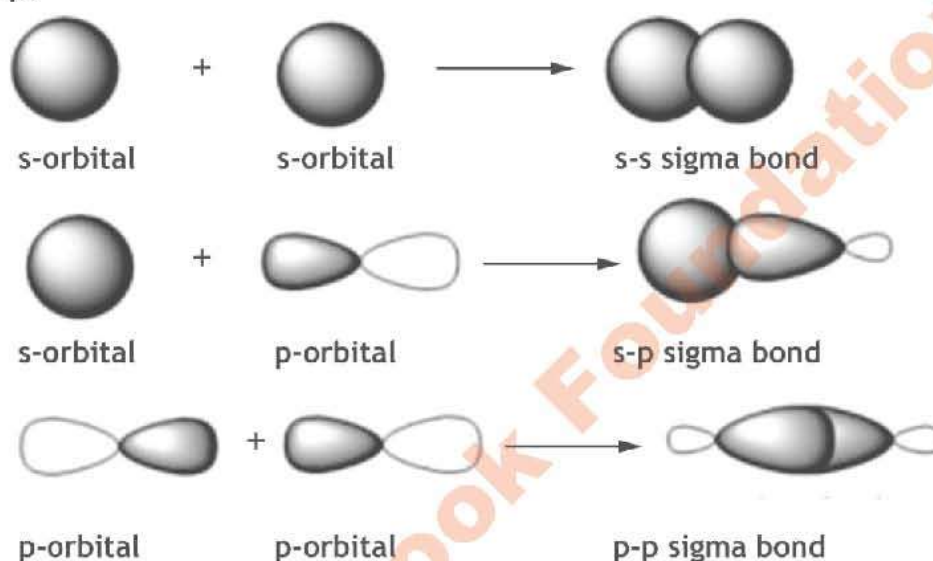


Figure 3.6: Formation of sigma bond due to (a) The s-s overlap (b) the s-p overlap (c) The p-p overlap.

Pi Bond

Pi bond is formed by the parallel overlapping of P orbitals. (Between P_y – P_y and P_z – P_z)

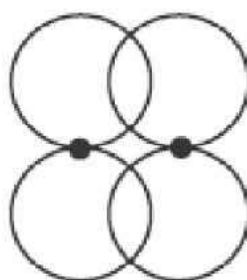


Figure 3.7: Parallel Overlapping of Orbitals (Formation of π Bond)

When there is double bond between two atoms, one should be sigma and the other should be Pi bond. When there is triple bond between two atoms, there is one sigma and two Pi bonds.

Structure of Ethene

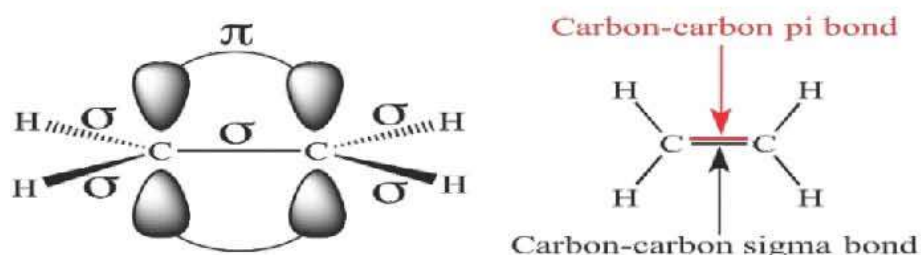


Figure 3.8: Structure of Ethene

Strength of Sigma and Pi Bond

Sigma bond is stronger than Pi bond because in sigma bond electron density is in between the line joining the two nuclei while in pi bond electron density is above and below the plane. Hence it is more diffuse bond and less amount of energy is required to break this bond.

3.6.1 Applications of Valence Bond Theory

Single Bond Formation

a) Formation of H_2 Molecule

Electron configuration of hydrogen atom is $1s^1$. Each half-filled s orbital of hydrogen atoms overlaps to form H-H bond where electron density is in between the line joining the two nuclei so bond formed is a sigma (σ) bond.

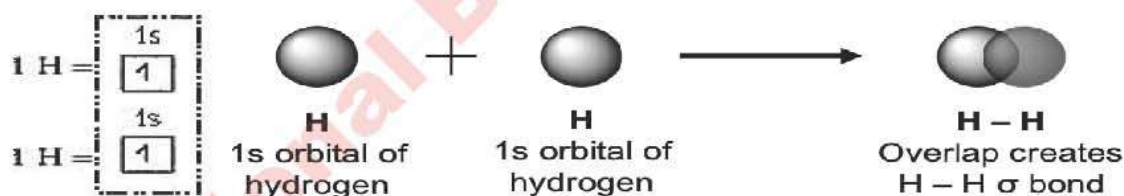


Figure 3.9: Orbital Diagram of H_2 Molecule

b) Formation of F_2 Molecule

The electronic configuration of fluorine is $1s^2 2s^2 2p^5$. Half-filled $2p_z$ orbital of each fluorine atom head on overlap to form F-F bond which is sigma bond.

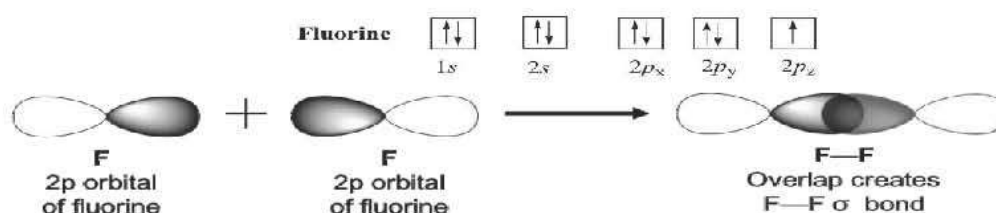
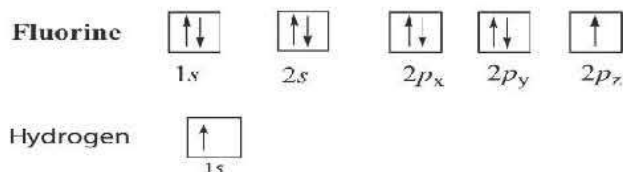


Figure 3.10: Orbital Diagram of F-F Molecule

c) Formation of HF Molecule

The electronic configurations of F and H atoms are:



In the formation of HF molecule, the half-filled $1s$ orbital of H atom overlaps with the half-filled $2p_z$ orbital of F to form H-F σ bond.



Figure 3.11: Orbital Diagram of H-F Molecule

d) Formation of O_2 Molecule

In Oxygen molecule, each oxygen atom contains two half-filled $2p_y$ and $2p_z$ orbitals so according to Valence Bond Theory two bonds are formed. One due to head on overlap of two half-filled p orbitals which is sigma bond and the other bond is formed due to parallel overlap of half-filled p orbitals which is pi bond. Electronic configuration of an oxygen atom and orbital overlapping in O_2 molecule is shown in figure 3.12.

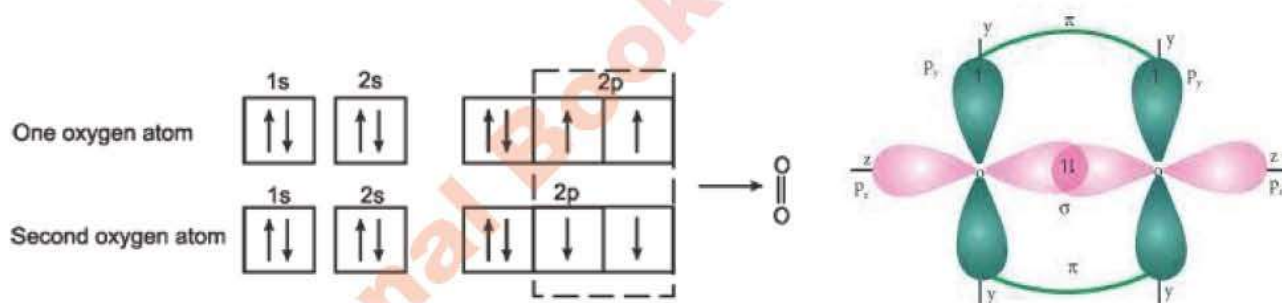


Figure 3.12: Formation of σ and π bonds in O_2 Molecule

e) Formation of N_2 Molecule

Nitrogen molecule contains two nitrogen atoms. Each nitrogen atom contains three half-filled p orbitals. According to VBT three bonds are formed. Half-filled $2p_x$ orbitals of nitrogen atoms head on overlap with each other and sigma bond is formed, while half-filled orbitals of $2p_y$ and $2p_z$ of each nitrogen atom parallel overlap with each other so two pi bonds are formed. Hence triple bond is formed between two nitrogen atoms.

The electronic configuration of N atom and orbital overlapping in nitrogen molecule is shown figure 3.13.

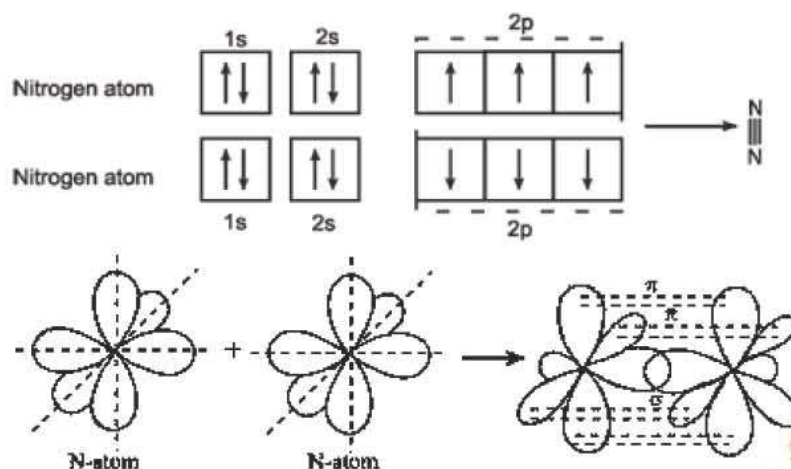


Figure 3.13: Orbital Diagram of N_2 Molecule

3.7 HYBRIDIZATION

Hybridization is the concept of mixing of atomic orbitals of different energies and different shapes to produce a new set of orbitals of the same energies and same shape called new hybrid orbitals and this process is known as hybridization.

During the process of hybridization, the electrons which are present in the ground state structure are promoted to the excited state due to which number of unpaired electrons increases. Energy which is required for the excitation of electron is compensated by the amount of energy which is released during the bond formation. There is number of types of hybridization depending upon the nature of different atomic orbitals i.e s, p d and f. Hybrid orbitals are very useful in the explanation of molecular geometry and atomic bonding properties.

Types of Hybridization

There are many types of hybridization.

For example, sp , sp^2 , sp^3 , dsp^2 , dsp^3 , d^2sp^3 , d^3sp^3 hybridization. We will discuss only three types of hybridization.

3.7.1 sp Hybridization

Intermixing of one s and one p orbital of different energies and different shapes to produce two new sets of hybrid orbitals of the same energies and same shapes is known as sp hybridization. sp -hybridized orbital has 50% s-character and 50% p-character. The sp -hybrid orbitals can form only sigma bonds by overlapping with other atomic orbitals.

Examples of sp Hybridization

1. Beryllium Chloride (BeCl_2)

The electronic configuration of Be in ground state is $1s^2 2s^2$. Since there are no unpaired electrons, it undergoes excitation by promoting one of its 2s electrons into an empty 2p orbital. Thus, in the excited state, the electronic configuration of Be is $1s^2 2s^1 2p^1$. In the excited state, the beryllium atom undergoes 'sp' hybridization by mixing a 2s and one 2p orbitals. One electron from 2s orbital is promoted to 2p to form two new hybridized orbitals which are arranged linearly.

When the two beryllium sp hybrid orbitals overlap with p orbitals of chlorine atoms, the bonding is as shown in figure 3.12. Thus, BeCl_2 is linear in shape with the bond angle of 180° .

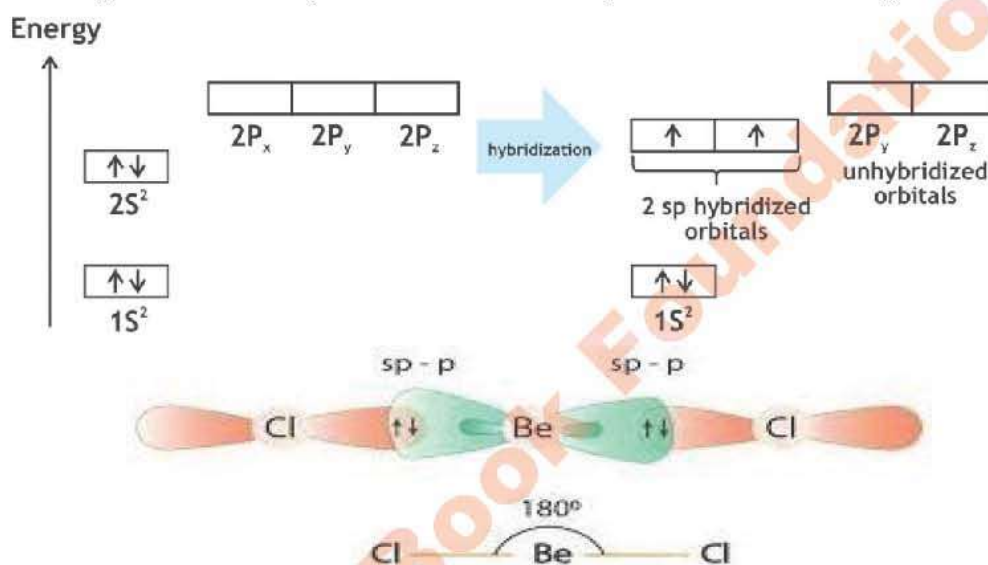
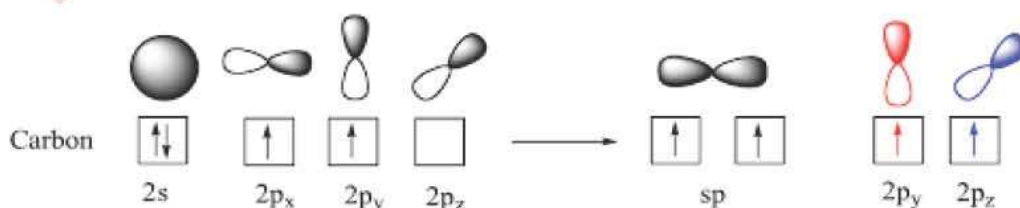


Figure 3.14: Hybridization in BeCl_2 , a Linear Molecule

2. Acetylene (C_2H_2)

In acetylene the central atom is carbon. The ground state electronic configuration of 'C' is $1s^2 2s^2 2p_x^1 2p_y^1$. There are only two unpaired electrons in the ground state. However, the valency of carbon is four i.e., it forms 4 bonds. To form four bonds, there must be four unpaired electrons. Hence carbon promotes one of its 2s electrons into the empty $2p_z$ orbital in the excited state. Thus, in the excited state, the electronic configuration of carbon is $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$.



Each carbon atom undergoes 'sp' hybridization by using a 2s and one 2p orbitals in the excited state to give two half filled 'sp' orbitals, which are arranged linearly. The two carbon atoms

form a σ sp-sp bond with each other by using sp-orbitals. However, there are also two unhybridized p orbitals i.e, $2p_y$ and $2p_z$ on each carbon atom which are perpendicular to the sp hybrid orbitals. These orbitals form two π bonds between the two carbon atoms.

Thus, a triple bond (including one σ sp-sp bond and two π bonds) is formed between carbon atoms. Each carbon atom formed a sigma bond with the hydrogen atom by the overlapping of sp-s. Thus, acetylene molecule is linear with 180° of bond angle.

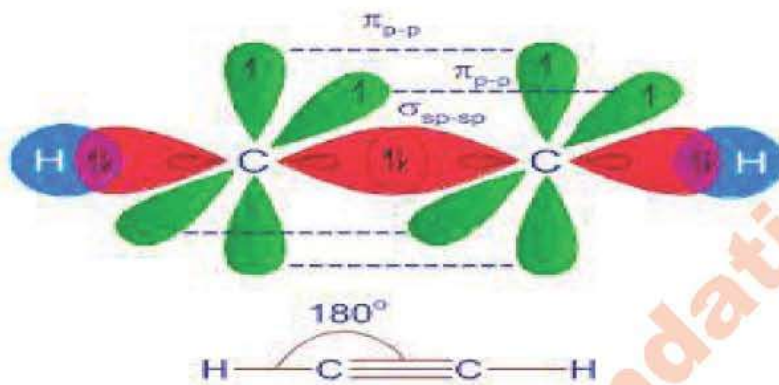


Figure 3.15: Hybridized Orbital Diagram and Linear structure of Acetylene Molecule.

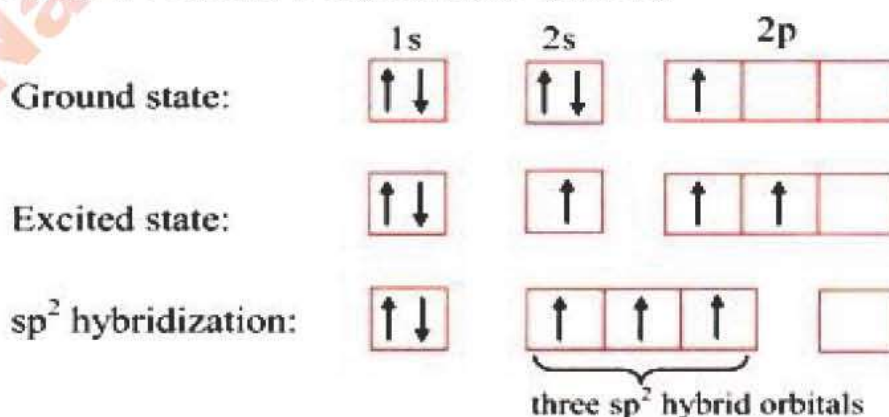
3.7.2 sp^2 Hybridization

It is the intermixing of one s and two p orbitals having different energy and different shape to produce three hybridized orbitals of the same energy and same shape and this phenomenon is known as sp^2 hybridization.

Examples of sp^2 Hybridization.

1. Boron trichloride (BCl_3)

The electronic configuration of 'B' in ground state is $1s^2 2s^2 2p^1$ with only one unpaired electron. Since the formation of three bonds with chlorine atoms require three unpaired electrons, there is promotion of one of 2s electron into the $2p_z$ orbital by absorbing energy. Excited state electronic configuration of boron after absorbing energy is $1s^2 2s^1 2p_x^1 2p_y^1$. In the excited state, Boron undergoes sp^2 hybridization by using a 2s and two 2p orbitals to give three half-filled sp^2 hybrid orbitals which are oriented in trigonal planar symmetry.



In BCl_3 , three sp^2 hybridized orbitals of boron atom overlap with three p orbitals of three chlorine atoms and forms three σ sp^2 -p bonds. Thus, the shape of BCl_3 is trigonal planar with bond angles equal to 120° .

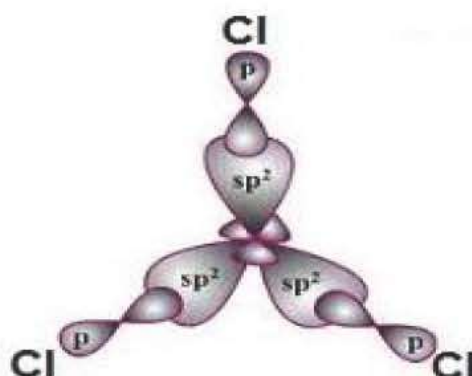
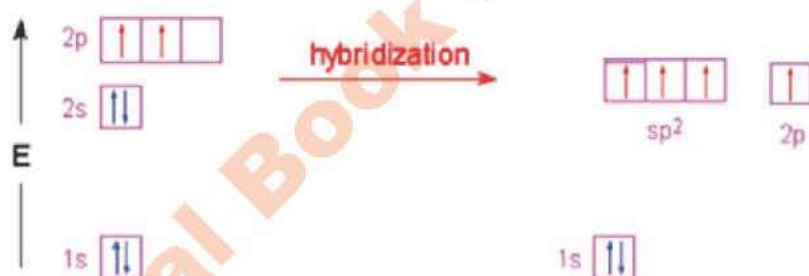


Figure 3.16: BCl_3 , Trigonal Planar Molecule.

2. Ethylene (C_2H_4)

During the formation of ethylene molecule, each carbon atom undergoes sp^2 hybridization in its excited state by mixing 2s and two 2p orbitals to give three half-filled sp^2 hybrid orbitals oriented in trigonal planar symmetry. There is also one half filled unhybridized 2p orbital on each carbon perpendicular to the plane of sp^2 hybrid orbitals.



The carbon atoms form a σ bond with each other by using sp^2 hybrid orbitals. A π bond is also formed between them due to the parallel overlapping of unhybridized $2p_z$ orbitals. Thus, there is a double bond (σ and π) between two carbon atoms. Each carbon atom also forms two σ bonds between sp^2 orbital of carbon atom and s orbitals of two hydrogen atoms.

Thus, ethylene molecule is planar with HCH and HCC bond angles equal to 120° . All the atoms are present in one plane.

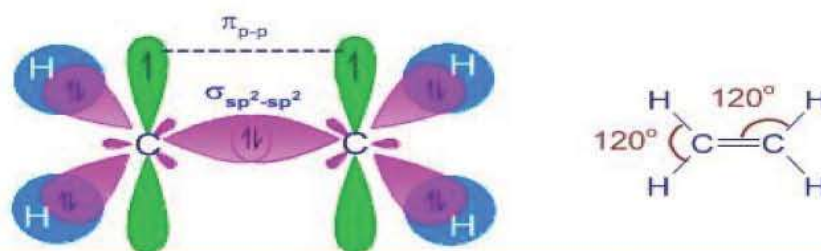
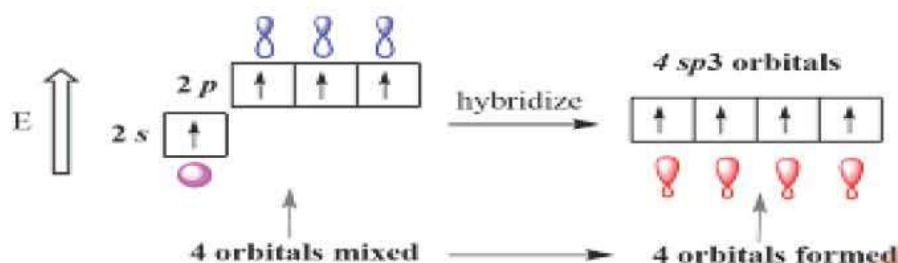


Figure 3.17: C_2H_4 , Trigonal Planar Molecule

3.7.3 sp^3 Hybridization

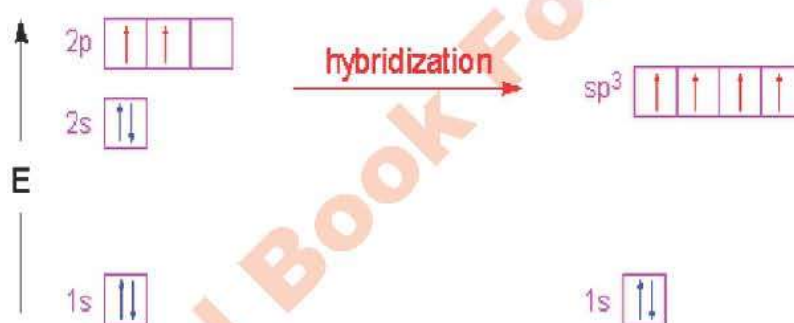
It is the intermixing of one s and three p orbitals having different energy and different shape to produce four hybridized orbitals of the same energy and same shape and this phenomenon is known as sp^3 hybridization.



Examples of sp^3 Hybridization

1. Methane (CH_4)

During the formation of methane molecule, the carbon atom undergoes sp^3 hybridization. In the excited state by mixing one ' $2s$ ' and three $2p$ ' orbitals, four half-filled sp^3 hybrid orbitals are formed which are oriented in tetrahedral symmetry in space around the carbon atom.



Each of these sp^3 hybrid orbitals forms form sigma bond with s orbital of hydrogen atom. Thus, carbon forms four σ sp^3 - s bonds with four hydrogen atoms. Methane molecule is tetrahedral in shape with $109^\circ.5'$ bond angle.

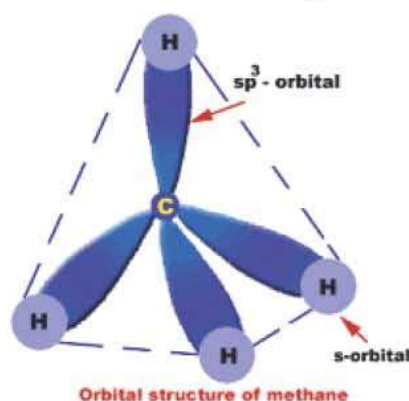


Figure 3.18: CH_4 , a Tetrahedral Molecule

2. Ethane (C_2H_6)

Just as in methane molecules, each carbon atom undergoes sp^3 hybridization in the excited state to give four sp^3 hybrid orbitals in tetrahedral geometry. The two carbon atoms form a σ sp^3-sp^3 bond with each other due to overlapping of sp^3 hybrid orbitals along the inter-nuclear axis. While the six carbon-hydrogen bonds are formed from overlaps between the remaining sp^3 orbitals on the two carbons and the $1s$ orbitals of hydrogen atoms. All of these are sigma bonds.

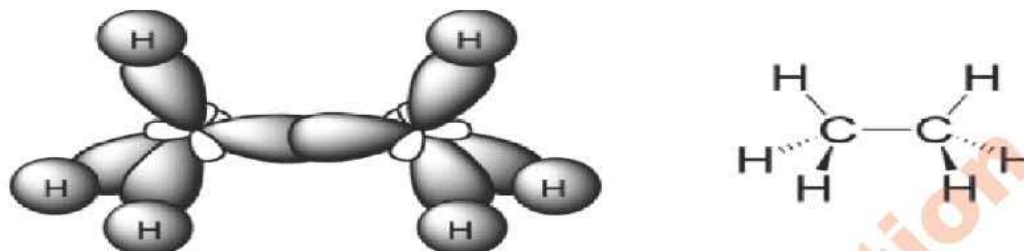


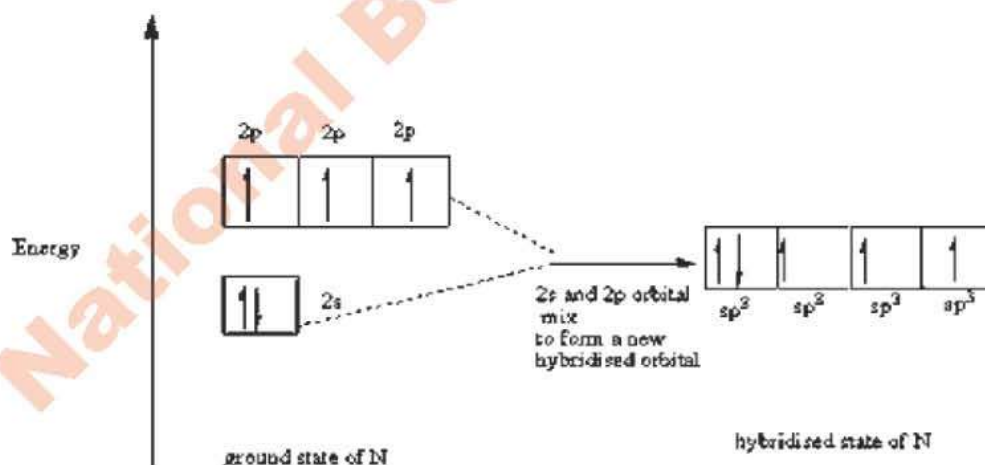
Figure 3.19: C_2H_6 , Tetrahedral Molecule

3. Ammonia (NH_3)

The ground state electronic configuration of nitrogen atom is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$. Since there are three unpaired electrons in the $2p$ sublevel, the nitrogen atom can form three bonds with three hydrogen atoms.

In ammonia, nitrogen atom undergoes sp^3 hybridization of a $2s$ and three $2p$ orbitals to give four sp^3 orbitals, which are arranged in tetrahedral symmetry. This arrangement will give more stability to the molecule due to minimization of repulsions.

Among them three are half filled and one is full filled.



3 sp^3 orbital of Nitrogen atom overlap with s orbital of three hydrogen atoms by using three half-filled sp^3 hybrid orbitals. There is also a lone pair on nitrogen atom belonging to the full filled sp^3 hybrid orbital. It occupied more space than the bond pairs. However, the HNH bond angle is not equal to normal tetrahedral angle i.e. 109.5° . The reported bond angle is 107° . The

observed decrease in the bond angle is due to the repulsion caused by the lone pair over the bond pairs. That is why ammonia molecule is trigonal pyramidal in shape.

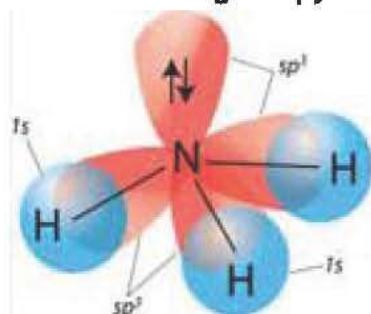


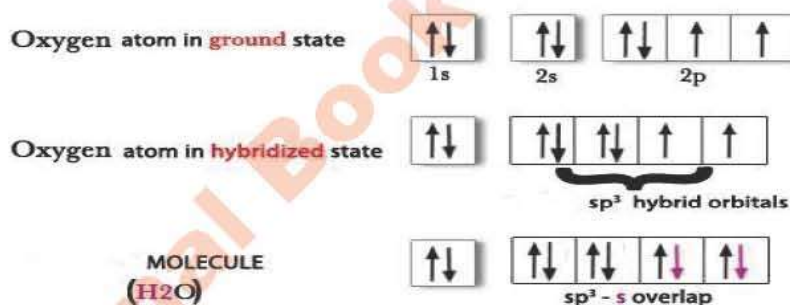
Figure 3.20: NH_3 , Trigonal Pyramidal Molecule

4. Water Molecule (H_2O)

The electronic configuration of oxygen is $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$. There are two unpaired electrons in oxygen atom which may form bonds with hydrogen atoms. The experimental bond angles reported were equal to 104.5° . To account this, sp^3 hybridization before the bond formation was proposed.

During the formation of water molecule, the oxygen atom undergoes sp^3 hybridization by mixing a $2s$ and three $2p$ orbitals to furnish four sp^3 hybrid orbitals oriented in tetrahedral geometry.

Among them, two are half filled and the remaining two are completely filled.



Now the oxygen atom forms two σ sp^3 - s bonds with hydrogen atoms by using half-filled hybrid orbitals. Bond angle between HOH in water molecule is 104.5° . It is again due to repulsions caused by two lone pairs on the bond pairs. Thus, water molecule gets angular shape (V shape).

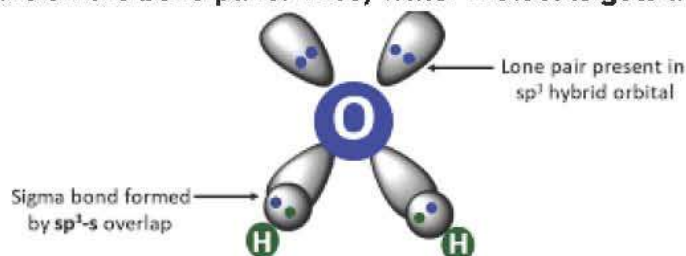


Figure 3.21: Hybridization in H_2O Molecule

3.8 CO-ORDINATE COVALENT BOND

A Co-ordinate Covalent Bond (or dative covalent bond) is formed when one atom provides both the electrons needed for a covalent bond or shared paired of electron is donated by one atom only. For dative covalent bonding we need:

One atom having a lone pair of electron and the second atom having an unfilled empty orbital to accept the lone pair (an electron-deficient atom/molecule).

During the formation of hydronium ion, water containing lone pair of electrons donate a pair of electrons and form dative bond with the electron deficient hydrogen ion.

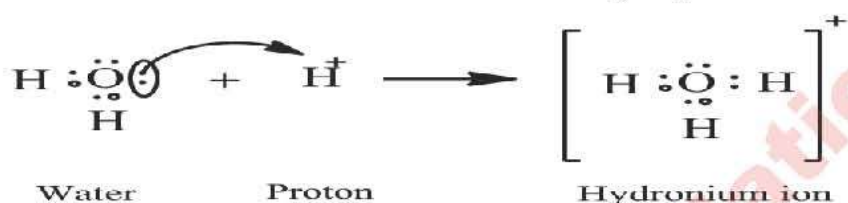
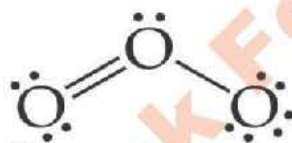
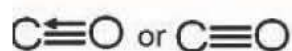
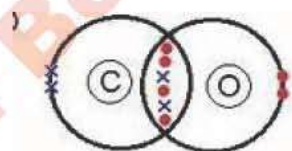


Figure 3.22: Formation of Coordinate Covalent Bond in Hydronium ion

In Ozone (O_3) molecule, central oxygen atom donates its electron pair with other oxygen atom and form dative bond.



Coordinate covalent bond is also present in carbon monoxide molecule.



In this molecule oxygen atom form coordinate covalent bond with carbon atom.

Concept Assessment Exercise 3.3

- Draw dot-and-cross diagrams to show the formation of a co-ordinate bond between the following:
 - boron trifluoride, BCl_3 , and ammonia, NH_3 , to form the compound Cl_3BNH_3
 - phosphine, PH_3 , and a hydrogen ion, H^+ , to form the ion PH_4^+
- Draw the displayed formulae of the products formed in part a. Show the co-ordinate bond by an arrow.

3.9 INTERMOLECULAR FORCES (FORCES BETWEEN MOLECULES)

Intermolecular forces are those forces which are present between the Covalent molecules. Physical properties such as melting point, boiling point, density etc can be explained on the basis of intermolecular forces.

3.9.1 Types of Intermolecular Forces.

There are three types of intermolecular forces

- Permanent Dipole-Dipole forces
- Instantaneous dipole induced dipole forces
- Hydrogen bonding

1. Permanent dipole-dipole Forces

These forces are present between polar molecules. Polar molecules are those molecules where due to electronegativity difference one atom bears partial positive charge and the other, which is more electronegative, bears partial negative charge.

Some molecules with polar bonds have an overall dipole (e.g. $\text{H}^{\delta+}-\text{Cl}^{\delta-}$), Although not all do e.g. In CCl_4 the individual dipoles cancel each other out, so CCl_4 is non polar molecule. There are attractions between these permanent dipoles in neighboring molecules e.g. between H-Cl molecules. $\text{H}^{\delta+}-\text{Cl}^{\delta-} \cdots \text{H}^{\delta+}-\text{Cl}^{\delta-}$

Stronger the dipole-dipole forces, higher will be the value of melting point, boiling point, heat of vaporization and heat of sublimation of particular compound.

2. Instantaneous Dipole induced Dipole Forces

Those forces which are present between nonpolar molecules are called Instantaneous dipole induced dipole forces.

Even in molecules with no polar bonds, there are temporary dipoles. It is because of uneven electron distribution due to the constant movement of electrons. This induces a temporary dipole in a neighboring molecule, producing a temporary dipole induced dipole forces of attraction.

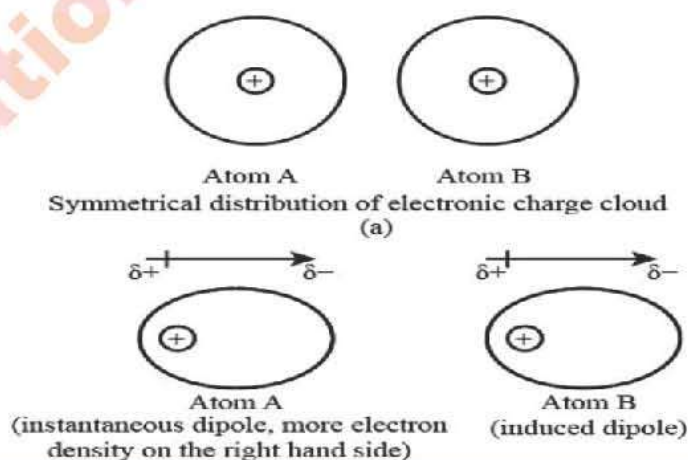


Figure 3.23: Instantaneous Dipole induced Dipole Forces.

Strength of Permanent dipole-dipole forces and Instantaneous dipole induced dipole forces (Vander waal,s forces) depends upon the following factors.

- Molecular size
- Atomic size
- Molecular mass
- No of electron in the molecule

The bigger the molecule i.e., more the electrons, larger the size or higher the relative molecular mass, greater will be the van der Waals' forces. The following table represents the boiling point of Alkanes.

Table 3.5: Boiling point of first four members of alkane

Name	Molecular formula	Boiling point (°C)
Methane	CH ₄	-164
Ethane	C ₂ H ₆	-89
Propane	C ₃ H ₈	-42
Butane	C ₄ H ₁₀	-1

For example, the above table shows that the boiling point of propane (C₃H₈) is greater than that of ethane (C₂H₆). It is because molecular mass of C₃H₈ is 44 which is greater than Mr of C₂H₆ which is 30.

3. Hydrogen Bonding

This is a special case of permanent dipole-dipole forces - It is present between those molecules where hydrogen is covalently bonded with higher electronegative elements such as F, N and O. There is a strong attraction from the lone pair on the N, O or F of one molecule to the exposed Hydrogen nucleus of another molecule. This is simply a strong intermolecular force - it is **NOT** a bond. Those covalent compounds which form hydrogen bonding with water molecules are water soluble. For example, ammonia is soluble in water. Figure 3.24 is represents the hydrogen bonding between ammonia and water molecules.

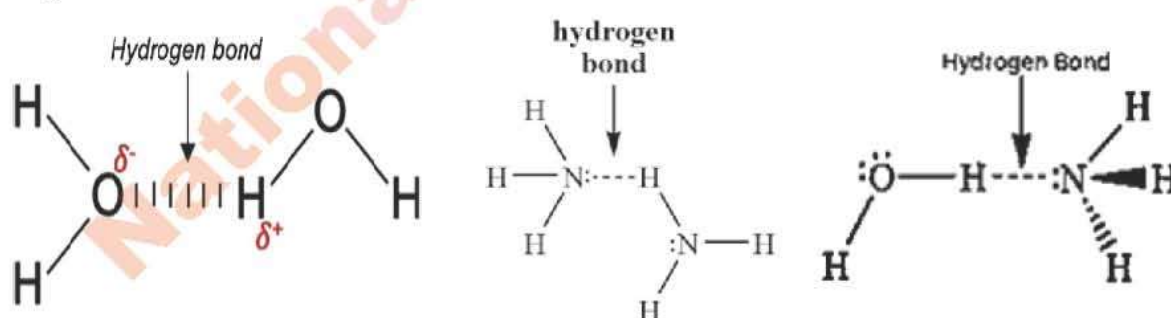


Figure 3.24: Hydrogen Bonding between Ammonia and Water Molecules.

3.9.2 Peculiar Behaviour of Hydrogen Bonding

Ice is less dense than water.

Most of the solids are denser than their liquids. This is because in solid state, the molecules are more closely packed. But this is not true of water. In ice, there is a three-dimensional hydrogen bonded network of water molecules. This produces a rigid lattice in which each oxygen atom is surrounded by a tetrahedron of hydrogen atoms. This 'more open' arrangement, due to the relatively long hydrogen bonds, allows the water molecules to be slightly farther apart than in the liquid (Figure 3.25). Hence water in solid state occupy more space. So, the density of ice is less than that of liquid water. That is why ice floats on water.



Figure 3.25: A model of ice. Oxygen Atoms are Red, Hydrogen atoms are white, Hydrogen Bonds are Lilac. This Hydrogen Bonded arrangement makes ice less dense than Water

The strength of intermolecular forces

H-bonding > permanent dipole-dipole > Instantaneous dipole induced dipole forces

Table 3.6: Comparison of boiling point of different compounds

Molecule	CH ₄	HCl	H ₂ O
Boiling Points (°C)	−162	−85	100
Intermolecular forces	Instantaneous dipole induce dipole forces	Permanent dipole dipole forces	Hydrogen bonding

Melting and boiling points of covalent molecules depend upon the intermolecular forces not on the covalent bonds in the molecule. Covalent bonds are very strong (values in hundreds of kJ mol^{−1}). The forces between molecules are much weaker than covalent bond. Figure 3.26 represents boiling points of hydrides of Groups 4, 5, 6 and 7.

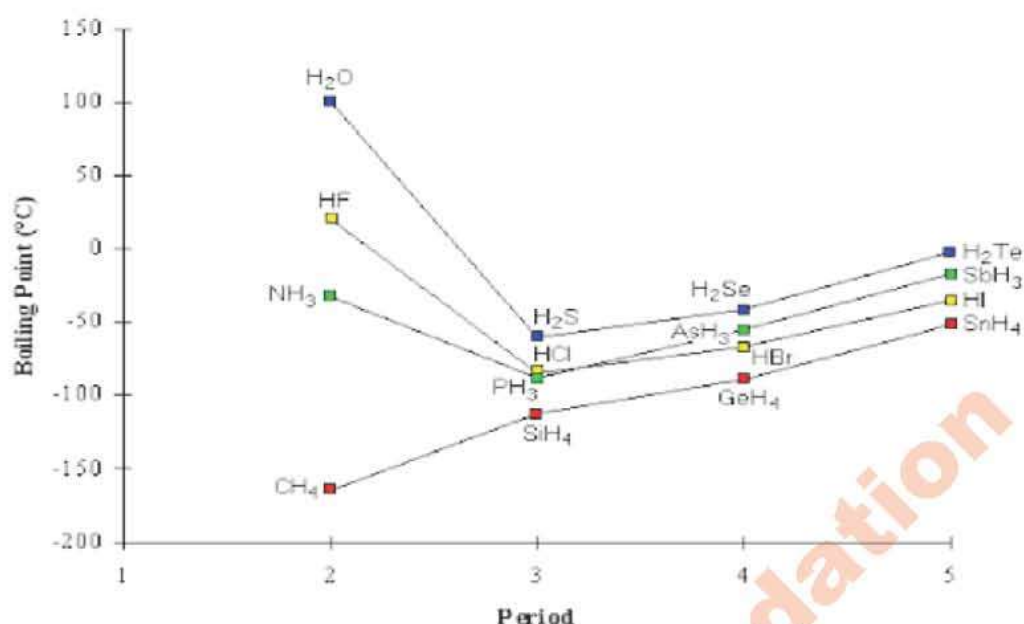


Figure 3.26: Boiling Points of Hydrides of Group 4, 5, 6 and 7 Elements

Concept Assessment Exercise 3.4

1 a The boiling points of the halogens are

Fluorine	-188°C	Chlorine	-35°C
Bromine	+59°C	Iodine	+184°C

Explain the trend in these boiling points.

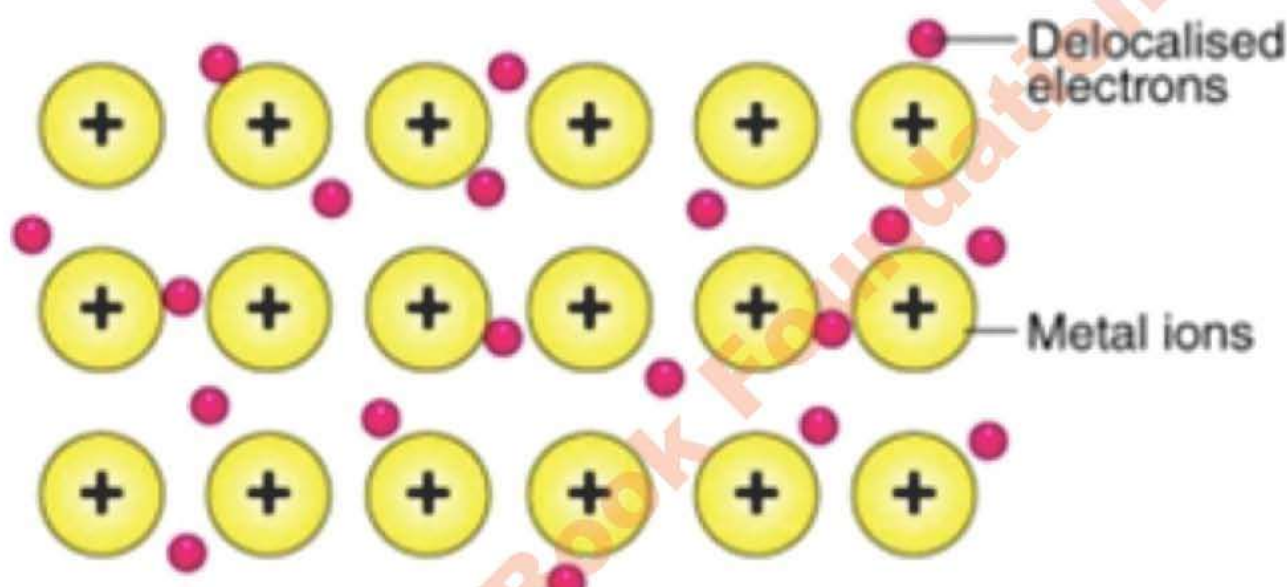
b The table lists the formulae and boiling points of some alkanes. Explain this trend.

	Structural formula	Boiling point / °C
Methane	CH ₄	-164
Ethane	CH ₃ CH ₃	-88
Propane	CH ₃ CH ₂ CH ₃	-42
Butane	CH ₃ CH ₂ CH ₂ CH ₃	0

- Bromine, Br₂, and iodine monochloride, ICl, have the same number of electrons. But the boiling point of iodine monochloride is nearly 40°C higher than the boiling point of bromine. Explain this difference.
- Draw diagrams to show hydrogen bonding between the following molecules:
a Ethanol and water b Ammonia and water c Two HF molecules

3.9.3 Comparison of strength of Ionic, Covalent, metallic bonding and intermolecular forces

The strength of a bond depends on the specific elements involved. Ionic bonds contain strong electrostatic forces of attraction between positive and negative ions. Metallic bonds occur between atoms within a metal, where electrons are shared and free to move throughout the material. This creates a "sea" of delocalized electrons that hold the metal atoms together. Covalent bonds are formed by sharing of electrons. This sharing of electrons results in the formation of a strong bond between the atoms. The electrons are held in the region between the nuclei of the bonded atoms and the positive nuclei are attracted to these shared electrons. This leads to a stable and strong bonding interaction.



Intermolecular forces are weaker than ionic, covalent and metallic bonding and occur between molecules, not within a single molecule. These forces are responsible for holding molecules together in a substance but are much weaker as compared to the forces within a molecule (covalent bonds).

Table 3.7: Following table represents mp/bp of ionic, simple covalent, giant covalent and metallic substances.

Substance	Bonding / structure	Melting point/°C	Boiling Point/°C
Sodium Chloride	Ionic (Electrostatic forces)	801	1465
Diamond	Giant Covalent (Covalent bond)	4000	4830
Iron	Metallic (electrostatic forces)	1538	2862
Methane	Simple Covalent (Intermolecular forces)	-182	-161.6

It is obvious from the above table that the melting point/boiling point of methane is lower than that of other substances because it contains weak intermolecular force which requires less amount of energy to break.

3.10 Molecular Orbital Theory

The molecular orbital theory was proposed by Hund and Mullikan in 1932. According to this theory, linear combination of atomic orbitals form new orbitals called molecular orbitals which are characteristics of the whole molecule. During this process identity of both atomic orbitals is lost. After the combination of atomic orbitals different types of molecular orbitals are formed which differ in energy. One of lower energy, is called bonding molecular orbital (BMO) while other of high energy is called anti-bonding molecular orbital (ABMO).

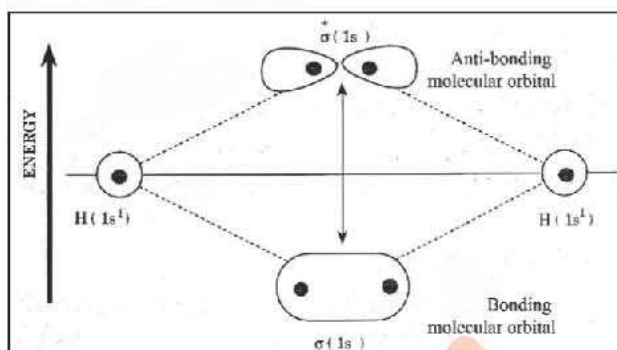


Figure 3.27: Energy diagram of bonding and anti-bonding molecular orbitals

Paramagnetic or diamagnetic nature of the molecule can be explained on the basis of molecular orbital theory as given below.

- Molecules having unpaired electrons in the molecular orbitals are paramagnetic in nature and can be attracted by magnetic field.
- Molecules having no unpaired electrons in the molecular orbitals are diamagnetic in nature and cannot be attracted by magnetic field. They repel magnetic field.

3.10.1 Bonding and Antibonding Molecular Orbitals

A bonding molecular orbital (BMO) is formed by the overlap of atomic orbitals. BMO has high electron density in the region between the two nuclei which is responsible for the stability of bond. Each electron in the BMO contributes to attraction between the two atoms. They are designated as σ and π BMO.

An antibonding molecular orbital (ABMO) is formed by the subtraction overlap of atomic orbitals. It has zero electron density in between two nuclei and the concentration of electron density is on the opposite side. Each electron in ABMO contributes to repulsion between two atoms. They are designated as σ^* and π^* ABMO.

The number of Molecular orbitals formed is equal to the number of atomic orbitals that are combined. Electrons in the molecular orbitals are influenced by all nuclei but in atomic orbital an electron is influenced by one nucleus.

The filling of electrons into the molecular orbitals occur according to

- Aufbau Principle
- Pauli's Exclusion Principle
- Hund's Rule

There are two types of overlapping in molecular orbital theory.

- i. Head on approach (linear overlapping) or linear combination
- ii. Sideways approach (parallel overlapping)

Head on approach or linear overlapping takes place by the combination of s-s, s-p and p_x-p_x

Orbitals. When “s” atomic orbitals overlap with each other two molecular orbitals σ_s of low energy and σ*_s of high energy molecular orbital is formed.

Sideways approach or parallel overlapping of atomic orbital takes place between p_y-p_y and p_z-p_z orbitals. When two p orbitals p_y or p_z atomic orbitals overlap with each other two molecular orbitals π_{py} = π_{pz} of low energy and π*_{py} = π*_{py} of high energy molecular orbital is formed.

When three 2p atomic orbitals (p_x, p_y and p_z) of one atom overlap with three 2p atomic orbitals of other atom, six molecular orbitals (three bonding and three anti-bonding) are formed. These molecular orbitals according to the energy are

$$\sigma 2p_x > \pi 2p_y = \pi 2p_z > \pi^* 2p_y = \pi^* 2p_z > \sigma^* 2p_x$$

3.10.2 Bond Order (No. of Bonds)

It is the total number of bonds formed when two atoms of atomic orbitals overlap with each other. It half of the difference between the number of bonding electrons and anti-bonding electrons.

$$\text{Bond order} = \frac{\text{No. of electrons in BMOs} - \text{No. of electrons in ABMOs}}{2}$$

The number of bonds formed in hydrogen molecule may be calculated as follows.

$$\text{No. of electrons in the Bonding orbitals} = 2$$

$$\text{No. of electrons in the anti-bonding orbitals} = 0$$

$$\text{Bond order} = \frac{2-0}{2} = 1$$

If bond order is zero, the molecule is unstable, and it does not exist. A positive value of order reveals that the molecule exists and is stable.

3.10.3 Relative Energies of the Molecular Orbitals

Spectroscopic measurements determine the relative energies of the molecular orbitals formed from 2s and 2p atomic orbitals.

- a) The following increasing order of energy shows the molecular orbitals of diatomic molecules such as O₂, F₂ and their positive and negative ions.

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_x < \pi 2p_y = \pi 2p_z < \pi^* 2p_y = \pi^* 2p_z < \sigma^* 2p_x$$

- b) The diatomic molecule such as H₂, He₂, B₂, C₂, and N₂ (lighter molecules) show slightly different energy order.

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p_y = \pi 2p_z < \sigma 2p_x < \pi^* 2p_y = \pi^* 2p_z < \sigma^* 2p_x$$

Elements of second period having atomic number 3 to 7 (prior to oxygen) have a relatively small difference in energy between the 2s and 2p orbitals. As the energy difference between 2s and 2p atomic orbitals is small, as a result, σ_{2s} and σ^*_{2s} MO do not retain pure s-character (hybridization of A.O.). Mixing of 2s and 2p orbitals is the primary cause of the difference in the molecular orbitals of nitrogen and oxygen, which is influenced by the initial atomic orbital energies. Hence energy of σ_{2p_x} is greater than π_{2p_y} and π_{2p_z} .

3.10.4 Molecular Orbital Diagram of Homo Nuclear Diatomic Molecules

After having discussed the basic principles of molecular orbital theory, we are now able to take up the electronic structures and bonding properties of some homo-nuclear diatomic molecules.

1. Hydrogen Molecule H_2

Hydrogen molecule is formed from the overlap of 1s atomic orbitals of two hydrogen atoms. They give rise to two molecular orbitals σ_{1s} and σ^*_{1s} . The molecule has two electrons which occupy the lower energy σ_{1s} orbital as shown in the figure 3.28.

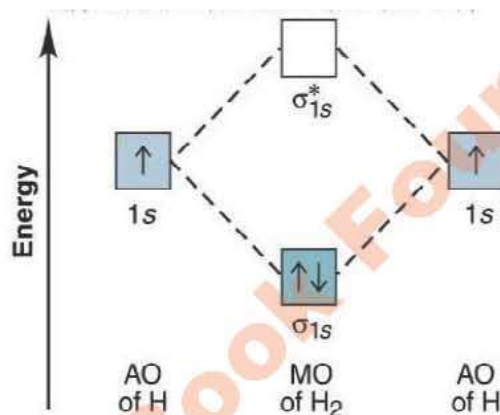


Figure 3.28: Energy Diagram of BMO and ABMO of H_2

Total number of electrons = 2

Electronic configuration of hydrogen atom is $1s^1$

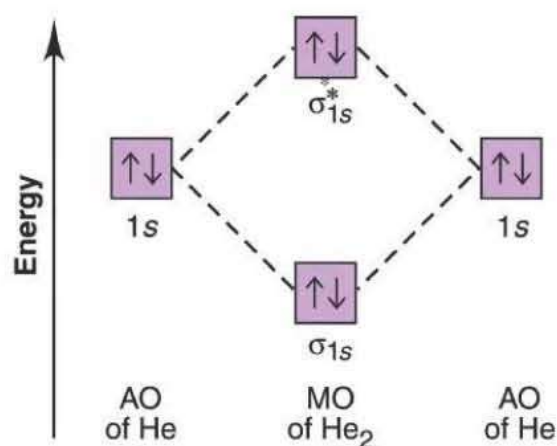
$H_2 = \sigma_{1s}^2, \sigma^*_{1s}^0$

Bond order = $\frac{2-0}{2} = 1$

Magnetic character = Diamagnetic (having no unpaired electron)

2. Helium Molecule (Hypothetical) He_2

The energy level diagram for He_2 is similar to that of H_2 except that it has two more electrons occupying the anti-bonding σ^*_{1s} orbital as shown in the figure 3.29.

Figure 3.29: Energy Diagram of BMO and ABMO He₂

Total number of electrons = 4

Electronic configuration of helium is $1s^2$

$\text{He}_2 = \sigma 1s^2, \sigma^* 1s^2$

Bond order = $\frac{2-2}{2} = 0$

Magnetic character: As there is no unpaired electron in the molecular orbitals of He₂ molecule, it is diamagnetic.

As bond order of He₂ is zero so molecule is unstable, and it does not exist. Helium exist only as mono-atomic molecules.

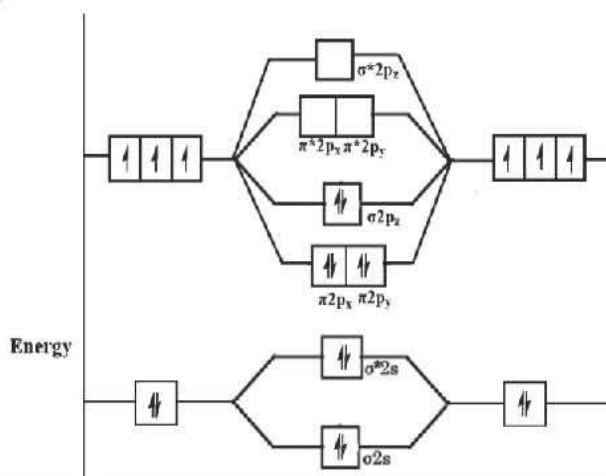
3. Nitrogen Molecule N₂

Nitrogen contains three unpaired electrons in 2p orbitals.

Electronic configuration of nitrogen is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$

Total number of electrons in N₂ molecule = 14

The following diagram represents the molecular orbitals of nitrogen molecule.

Figure 3.30: Energy Diagram of BMO and ABMO of N₂

Distribution of electrons in the molecular orbitals of nitrogen molecule is.

$$N_2 = (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_y)^2 = (\pi 2p_z)^2 (\sigma 2p_x)^2$$

$$\text{Bond order} = \frac{10-4}{2} = 3$$

Magnetic character: As there is no unpaired electron in the molecular orbitals of N_2 molecule, it is diamagnetic.

Bond order of N_2 is three. Two N-atoms are bonded through triple bond. N_2 molecule is very stable molecule and has a very high bond energy 946 kJ mol^{-1} . It is diamagnetic in nature and possesses a very short bond length.

4. Oxygen Molecule O_2

Electronic configuration of oxygen is $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$

Oxygen contains two unpaired electrons in 2p orbitals i.e. $2p_y$ and $2p_z$.

Total number of electrons in O_2 molecule = 16

The following diagram represents the molecular orbitals of oxygen molecule.

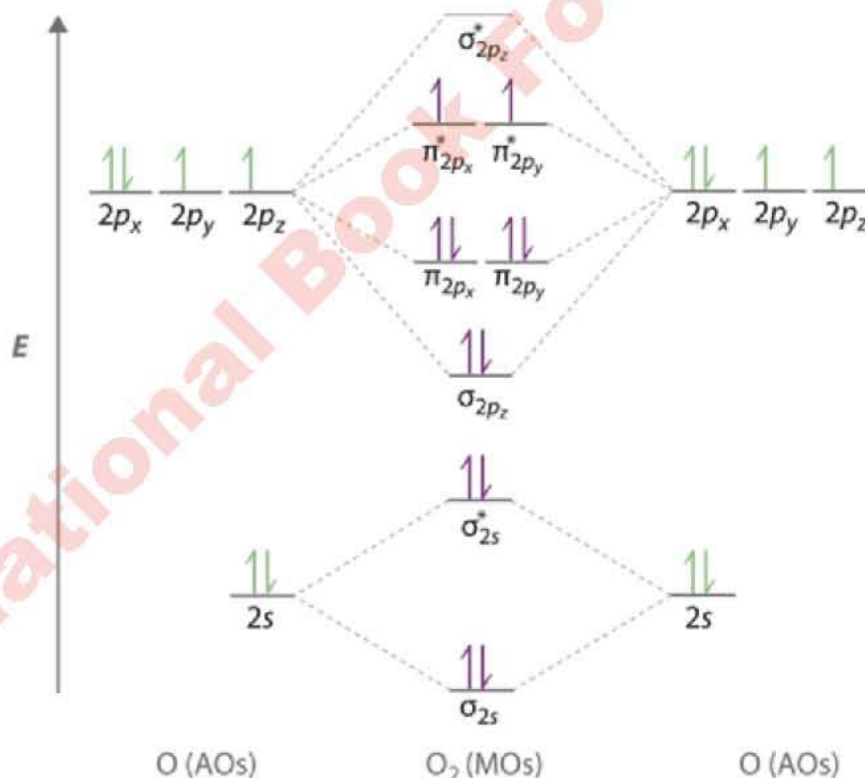


Figure 3.31: Energy Diagram of BMO and ABMO of O_2

$$O_2 = (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_x)^2 (\pi 2p_y)^2 = (\pi 2p_z)^2 (\pi^* 2p_y)^1 = (\pi^* 2p_z)^1$$

$$\text{Bond order} = \frac{10-6}{2} = 2$$

Paramagnetic Nature of Oxygen molecule

It is found from molecular orbital diagram of oxygen molecule that the electrons present in the two π^* orbitals are unpaired. The two unpaired electrons reside in the degenerate anti-bonding orbitals π^*2p_y and π^*2p_z . These unpaired electrons not only go around the atom in their orbitals, but they also spin, which creates a magnetic field. Unpaired electrons spin in the same direction as each other which increases the magnetic field effect. Due to the presence of these unpaired electrons, O_2 is found to be paramagnetic in nature.

Paramagnetic behavior of O_2 molecule is not explained by Valance Bond Theory. It is obvious that the two oxygen atoms are bonded through a double bond. So, we conclude that the molecule should be very stable as it possesses high bond energy i.e. 498 kJ mol^{-1} with bond length $1.21 \text{ \AA}$.

5. Fluorine Molecule F_2

Electronic configuration of Fluorine is $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$

Total number of electrons in F_2 molecule = 18

The following diagram represents the molecular orbitals of fluorine molecule.

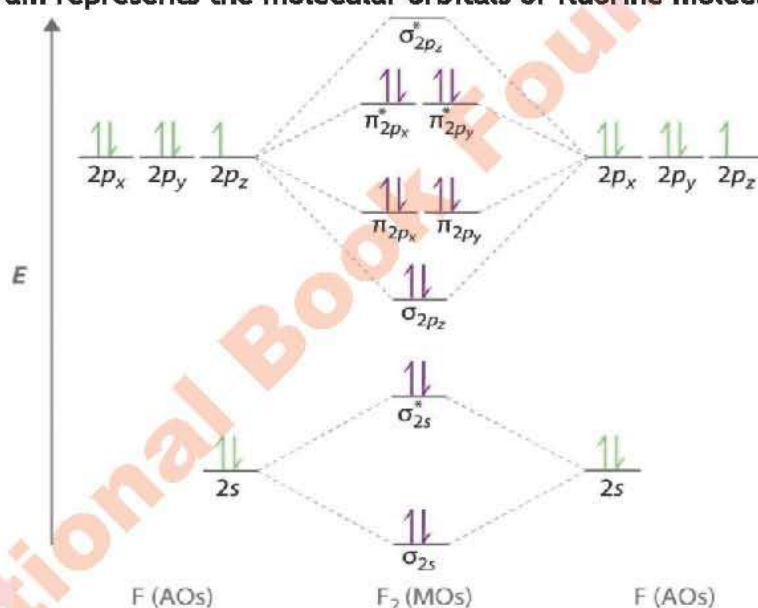


Figure 3.32: Energy Diagram of BMO and ABMO of F_2

$$F_2 = (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_x)^2 (\pi 2p_y)^2 = (\pi 2p_z)^2 (\pi^* 2p_y)^2 = (\pi^* 2p_z)^2$$

$$\text{Bond order} = \frac{10 - 8}{2} = 1$$

Magnetic character: As there is paired electron in the molecular orbitals of F_2 molecule, it is diamagnetic.

Bond order of F_2 is one. Two F-atoms are bonded through a single bond. The F-F bond distance is longer ($1.43 \text{ \AA}$) than the bond distance for O_2 ($1.21 \text{ \AA}$) and N_2 ($1.09 \text{ \AA}$) molecules. The bond energy of F_2 molecule is quite low (159 kJ mol^{-1}). It is diamagnetic in nature because it has no unpaired electrons.

Key Points

- Electronegativity is the power of an atom to attract shared paired of electron to itself in a molecule. Nonmetals have higher value of electronegativity compared to metals.
- Valence shell electron repulsion theory is used to predict the geometry of molecules.
- Valence bond theory based on the overlapping of atomic orbitals in order to form a chemical bond.
- By predicting molecular shapes and bond angles, VSEPR aids Medicinal chemists in understanding how drug molecules interact in the body.
- According to Molecular orbital theory the number of molecular orbitals produced is always equal to the number of atomic orbitals of atoms in the molecules that have combined. In these molecular orbitals bonding molecular orbitals are lower in energy from their parent atomic orbitals, and the antibonding molecular orbitals are higher in energy. This theory is used to explain the paramagnetic character of the molecule.
- Intermolecular forces are present between the molecules while intramolecular forces are present within the molecules i.e. covalent bonds.
- Hydrogen bonding is the strongest dipole dipole forces. Covalent compounds which form hydrogen bonding with water molecules are soluble in water.
- Vander Waals forces depends on the molecular mass, no of electrons present in the molecule and molecular size.
- Bond energy is the amount of energy required to break the bond of same type in one mole of bonds. It depends upon the electronegativity difference between two bonded atoms and bond length.
- Dipole moment is the product of the magnitude of charges and distance between them.

References for Further Information

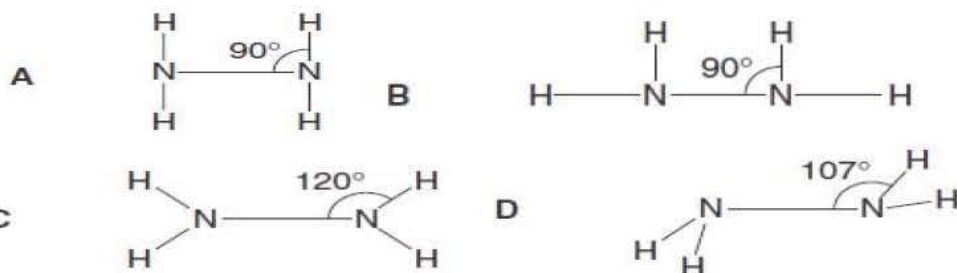
- Physical Chemistry by Peter Atkins and Julio de Paula
- Intermolecular interaction by Gunnar Karlstrom and Bo Jonsson
- Molecular geometries and covalent bonding theories by Prof. Geiger, Michigan State University
- Kortagere, S., Krasowski, M.D. and Ekins, S. (2009) 'The importance of discerning shape in molecular pharmacology', Trends in Pharmacological Sciences, 30(3), pp. 138-147. doi:10.1016/j.tips.2008.12.001.
- Nikolova, M.P., Kumar, E.M. and Chavali, M.S. (2022) 'Updates on responsive drug delivery based on liposome vehicles for cancer treatment', Pharmaceutics, 14(10), p. 2195. doi:10.3390/pharmaceutics14102195.

Exercise

1. Choose the correct answer

- (i) Which of the following molecules is nonpolar?
- | | |
|-----------------------------|------------------------------------|
| a. CCl_2F_2 | b. CHCl_3 |
| c. C_2Cl_4 | d. $\text{C}_2\text{H}_5\text{Cl}$ |

- (ii) Which is the most likely shape of hydrazine, N_2H_4 ?



- (iii) Which molecule contains only six bonding electrons?

- a. C_2H_4
b. C_2F_6
c. H_2O
d. NF_3

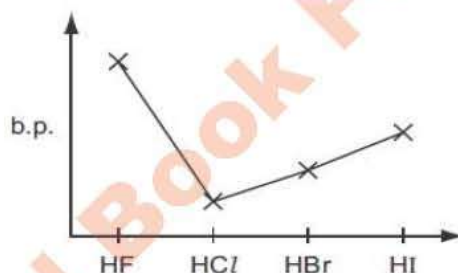
- (iv) Which molecule is trigonal planar in shape?

- a. NF_3
c. C_3H_6

- (v) Which of the following orbitals overlap with each other in the PH_3 molecule?

- a. $sp^2 - s$
b. $sp - s$
c. $sp^3 - p$
d. $sp^3 - s$

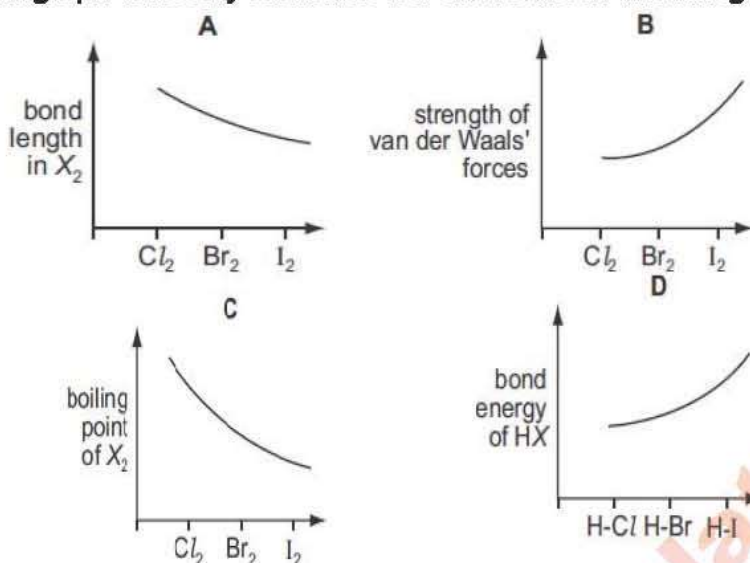
- (vi) The diagram shows the variation of the boiling points of the hydrogen halides.



What explains the higher boiling point of hydrogen fluoride?

- The bond energy of HF molecules is greater than in other hydrogen halides.
- The effect of nuclear shielding is much reduced in fluorine which polarizes the HF molecule.
- The electronegativity of fluorine is much higher than for other elements in the group.
- There is hydrogen bonding between HF molecules.

(vii) Which graph correctly describes a trend found in the halogen group?



(viii) Sp^3 hybridization is not important in describing the bonding in;

- a. NH_4^+ b. CCl_4
c. H_2O d. AgCl

(ix) In the formulation of N_2^+ from N_2 , the electron is removed from;

- a. $\sigma 2p_x$ orbital b. $\sigma^* 2p_x$ orbital
c. $\pi 2p_y$ orbital d. $\pi^* 2p_y$ orbital

(x) In which process are hydrogen bonds broken?

- a. $\text{H}_2(\text{l}) \rightarrow \text{H}_2(\text{g})$
c. $2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$
- b. $\text{NH}_3(\text{l}) \rightarrow \text{NH}_3(\text{g})$
d. $\text{CH}_4(\text{g}) \rightarrow \text{C}(\text{g}) + 4\text{H}(\text{g})$

(xi) The CN^- ion is widely used in the synthesis of organic compounds.

What is the pattern of electron pairs in this ion?

	bonding pairs of electrons	lone pairs on carbon atom	lone pairs on nitrogen atom
A	2	1	1
B	2	2	1
C	3	1	1
D	3	1	2

(xii) Which chlorine compound has bonding that can be described as ionic with some covalent character?

- a. NaCl
c. AlCl₃
- b. MgCl₂
d. SiCl₄

(xiii) Gaseous nitrogen is less reactive than gaseous fluorine. What is the reason for this difference in reactivity?

- The boiling point of nitrogen is lower than that of fluorine.
- The relative molecular mass of nitrogen is lower than that of fluorine.
- The atomic radius of nitrogen is greater than that of fluorine.
- The bond strength in the molecule is greater in nitrogen than in fluorine.

2. The table shows the atomic number and boiling points of some noble gases.

Gas	helium	neon	argon	krypton	Xenon
Atomic number	-12	-110	-118	-136	-154
Boiling point / °C	-253	-246	-186	-152	-107

a Explain this trend in boiling points. b Xenon forms a number of covalently bonded compounds with fluorine. i Draw a dot-and-cross diagram for xenon tetrafluoride, XeF_4 .

iii Suggest a shape for XeF_4 . Explain why you chose this shape.

3. Aluminium chloride, AlCl_3 , and ammonia, NH_3 , are both covalent molecules.

A Draw a diagram of an ammonia molecule, showing its shape. Show any lone pairs of electrons. Also State the bond angle HNH in the ammonia molecule.

b What type of forces are present in ammonia molecule. Draw diagram to show forces between ammonia molecules.

c An ammonia molecule and an aluminium chloride molecule can join together by forming a co-ordinate bond. i Explain how a co-ordinate bond is formed.

ii Draw a dot-and-cross diagram to show the bonding in the compound formed between ammonia and Aluminium chloride, H_3NAlCl_3 .

4. Electronegativity values can be used to predict the polarity of bonds.

a Explain the term electronegativity.

b The electronegativity values for some atoms are given below: H = 2.1, C = 2.5, F = 4.0, Cl = 3.0, I = 2.5 Use these values to predict the polarity of each of the following bonds by copying the bonded atoms shown below and adding δ^+ or δ^- above each atom.

i H—I

ii F—I

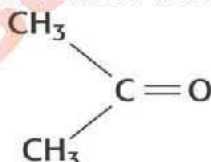
iii C—Cl

c Describe the shape of this ICl_3 molecule. Also mention bond angle in it.

d The boiling points of the hydrogen halides are shown in the table.

Hydrogen halide	HF	HCl	HBr	HI
Boiling point / °C	+20	-85	-67	-35

- i Explain the trend in boiling points from HCl to HI.
 - ii Explain why the boiling point of HF is so much higher than the boiling point of HCl.
 - e Tetrachloromethane, CCl_4 , is a non-polar molecule. Draw a diagram to show the shape of this molecule. Explain why this molecule is non-polar.
- 5.
- a. Hydrogen sulphide, H_2S , is a covalent compound. Explain the type of hybridization also write bond angle in HSH . Also show on your diagram the partial charges on each atom as δ^+ or δ^- and an arrow showing the exact direction of the dipole in the molecule as a whole.
 - b. Oxygen, O, sulphur, S, and selenium, Se, are in the same group in the Periodic Table.
 - i Explain why hydrogen selenide, H_2Se , has a higher boiling point than hydrogen sulphide, H_2S .
 - ii Explain why the boiling point of water is so much higher than the boiling point of hydrogen sulphide.
- 6.
- a. Describe the shape of the carbon dioxide molecule.
 - b. Bromine is a liquid at room temperature. Weak van der Waals' forces hold the bromine molecules together. Describe how van der Waals' forces arise.
7. Water is extensively hydrogen bonded. This gives it anomalous (peculiar) properties.
- a Explain why ice is less dense than liquid water. Also State two other anomalous properties of water.
 - b Propanone has the structure shown below.



When propanone dissolves in water, it forms a hydrogen bond with water. Draw a diagram to show a propanone molecule and a water molecule forming a hydrogen bond.

- c (i) Propanone has a double bond. One of the bonds is a σ bond (sigma bond). The other is a π bond (pi bond). Explain the difference between a σ bond and a π bond in terms of how they are formed.
- ii Copy the diagram, then complete it to show the shapes of the electron clouds in the σ bond and the π bond between the carbon atoms in ethene. Label your diagram.



8. Energies of orbitals can be explained by molecular orbital theory. It has been observed that in case of Nitrogen molecule σ_{2p_x} is higher in energy than π_{2p_y} and π_{2p_z}
- Draw molecular orbital energy diagram for nitrogen molecule.
 - Give reason why the σ_{2p_x} energy is greater than π_{2p_y} and π_{2p_z} .
9. Carbon can make a bond with hydrogen to form ethyne. Bond energy of C-H is same although 2s and 2p orbitals are involved which have difference in energies. Explain the formation of ethyne molecule on the basis of hybridization with the help of diagram.
10. Explain the magnetic properties of O_2 , O_2^+ and N_2 by applying molecular orbital theory.
11. Differentiate between a sigma bond and a pi bond.

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CHAPTER 4



STOICHIOMETRY

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

1. Express balanced chemical equations in terms of moles, representative particles, masses, and volumes of gases at STP.
2. Explain the concept of limiting reagents.
3. Calculate the maximum amount of product and amount of any unreacted excess reagent.
4. Calculate theoretical yield, actual yield, and percentage yield when given appropriate information.
5. State the volume of one mole of a gas at STP.
6. Use the volume of one mole of gas at STP to solve mole-volume problems.
7. Calculate the gram molecular mass of a gas from density measurements at STP.
8. Derive measurements of mass, volume, and number of particles using moles.
9. Calculate the quantities of reactants and products involved in a chemical reaction using stoichiometric principles. (Some examples include calculations involving reacting masses, volumes of gasses, volumes, and concentrations of solutions, limiting reagent and excess reagent, percentage yield calculations).
10. Explain with examples, the importance of stoichiometry in the production and dosage of medicine.

What does a chemical equation indicate? The elements and compounds react together in definite proportions. The study of the relationships between the amounts of the reactants and the products is referred to as stoichiometry. The word stoichiometry is derived from Greek words, stoicheion means element, and metron, means measurement. Such a study is essential when quantitative information about a chemical reaction is required. Moreover, it is important to predict the yields of products in chemical reactions.

4.1 MOLE

Remember that chemists use the mole as the SI unit to weigh and count atoms, molecules, and ions. A mole is the amount of substance that contains 6.023×10^{23} representative particles. This experimentally determined number is called Avogadro's number. Just as a dozen represents 12 identical things, a mole represents 6.023×10^{23} particles of a substance. For example, a mole of carbon is 6.023×10^{23} carbon atoms. A mole of sodium is 6.023×10^{23} Na atoms. One mole of water is 6.023×10^{23} H₂O molecules. The terms for particles are atoms, molecules or ions. This relationship allows us to convert moles into representative particles and vice versa.

The atomic mass, formula mass and molecular weight of a substance in grams are equal to one mole of the substance. This relationship allows us to convert the mass of a substance to moles and vice versa. For example,

One mole of O atoms = 16 g One mole of O₂ molecules = 32 g

One mole of H₂O molecules = 18 g One mole of Na⁺ ions = 23 g

One mole of NaCl formula units = 58.5 g

4.1.1 Molar Volume (V_m)

One mole of any gas at STP (standard temperature and pressure) occupies a volume of 22.414 dm³. This volume is called Molar volume. With the help of this relationship, we can convert the mass of a gas at STP into its volume and vice versa.

22.414 dm³ of any gas at STP = 1 mole = 6.02×10^{23} molecules.

22.414 dm³ of H₂ gas at STP = 2g = 6.02×10^{23} molecules.

22.414 dm³ of NH₃ gas at STP = 17g = 6.02×10^{23} molecules.

Example 4.1:

Determine the volume of 2.5 moles of chlorine molecules at STP.

Solution:

We know that

22.414 dm³ of Cl₂ at STP = 1 mole

Or 1 mole of Cl₂ occupies a volume of 22.414 dm³ at STP.

2.5 mole of Cl₂ occupy a volume of $22.414 \text{ dm}^3 \times 2.5 = 56.035 \text{ dm}^3$

4.1.2 Molar mass and density of gases

Density is defined as the mass per unit volume of a substance. As molar mass of all the gases occupies same volume at STP. Therefore, density of a gas is depended on its molar mass. A gas having higher molar mass will have higher density and vice versa. So, density of a gas can be calculated from its molar mass and molar volume. If the density of gas at STP is determined, its molar mass can be calculated.

Example 4.2:

Calculate the gram molecular mass of a gas which has density of 1.43 g/dm^3 at STP.

Solution:

$$\begin{aligned} 1 \text{ dm}^3 \text{ of gas at STP} &= 1.43\text{g} \\ 22.4 \text{ dm}^3 \text{ of gas at STP} &= 1.43 \times 22.4 \\ &= 32.032\text{g} \end{aligned}$$

As 22.4 dm^3 of a gas at STP = molar mass

Therefore, gram molecular mass of gas is 32.032 amu.

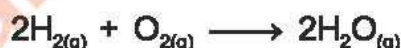
Concept Assessment Exercise 4.1

1. How many moles of oxygen molecule are there in 20.0 dm^3 of oxygen gas at STP?
2. What volume does 0.6 mole of H_2 gas occupy at STP?

4.1.3 Stoichiometric Calculations and Mole Ratio

What does a balanced chemical equation tell us?

Consider the following reaction,

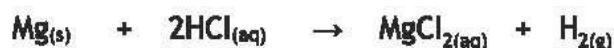


We get the following information from this chemical equation.

- 2 moles of H_2 combine with 1 mole of O_2 to produce 2 moles of H_2O
- $2 \times 6.02 \times 10^{23}$ molecules of hydrogen react with 6.02×10^{23} molecules of oxygen to produce $2 \times 6.02 \times 10^{23}$ molecules of water vapour.
- 4g (2 moles) of H_2 combine with 32g (1 mole) of O_2 to produce 36g (2 moles) of H_2O
- At STP, $2 \times 22.414 \text{ dm}^3$ of H_2 combine with $1 \times 22.414 \text{ dm}^3$ of O_2 to produce $2 \times 22.414 \text{ dm}^3$ of H_2O vapour.

Example 4.3:

When 100g of magnesium is treated with dilute hydrochloric acid. What volume of hydrogen can be collected at STP?



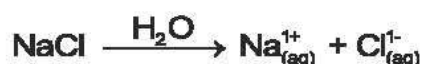
Solution:

$$\text{Moles of Mg} = \frac{100}{24} = 4.17$$

1 mol of Mg produces = 1 mol of H₂ at STP

1 mol of Mg produces = 1 x 22.4 dm³ of H₂ at STP

So, 4.17 mol Mg will produce = 22.4 dm³ x 4.17 = 93.408 dm³ of H₂ at STP

Example 4.4:

- The chemical equation shows that 1 mole of NaCl when dissolved in water gives 1 mole of Na¹⁺ ions and 1 mole of Cl¹⁻ ions.
- When 6.02×10^{23} formula units of NaCl are dissolved in water, they produce 6.02×10^{23} Na¹⁺ and 6.02×10^{23} Cl¹⁻ ions.
- 58.5g of NaCl dissolved in water gives 23g of Na¹⁺ ions and 35.5g of Cl¹⁻ ion

Concept Assessment Exercise 4.2

- What quantitative information do you get from the following chemical equation.



- Compare and contrast the terms, molecular mass and molar mass
- What mass of Zn is needed to produce 100 cm³ of H₂ at STP



Using mole as unit of quantity we can calculate mass, volume, molecules etc. particles used in calculations.

4.1.4 Mole -mole calculation

In a balanced chemical equation, the coefficient used are taken as mole that indicate the proportion to the next chemical in equation e.g.,



The reaction indicates that for complete burning of one mole of CH₄ require 2 mole of O₂ or 1 mole of methane can produced 2 moles of water and 1 mole of CO₂.

Example 4.5:

How much MgO formed when 4 moles of magnesium react with excess of O₂. Also calculate moles of O₂ required?

Solution:

2 moles of Mg produce MgO = 2 moles

1 moles of Mg produces MgO = 2/2

4 moles of Mg produce MgO = $2/2 \times 4 = 4$ moles of MgO

So 4 moles of Mg give 4 moles of MgO

Similarly

2 moles of Mg required $\text{O}_2 = 1$ mole

1 moles of Mg required $\text{O}_2 = 1/2$ mole

4 moles of Mg required $\text{O}_2 = 1/2 \times 4 = 2$ moles of O_2

Hence 4 moles of Mg needed 2 mole of O_2

4.1.5 Mole - mass calculations:**Example 4.6**

Potassium chlorate is used in making matches and dyes, on decomposition, it produces KCl and oxygen gas.

If 25 g KClO_3 is decomposed, calculate the quantities of the following:

- How many moles of O_2 are produced.
- How much mass in gram of O_2 is produced.

Solution:

Given mass of $\text{KClO}_3 = 25\text{g}$

Molar mass of $\text{KClO}_3 = 39 + 35.5 + 16 \times 3 = 122.5\text{g/mole}$

Moles of $\text{KClO}_3 = 25/122.5 = 0.204$ moles

2 moles of KClO_3 give oxygen = 3 moles

0.204 moles of KClO_3 give oxygen = $3/2 \times 0.204 = 0.306$ moles of O_2

b) Mass of $\text{O}_2 = \text{moles} \times \text{molar mass}$

$= 0.306 \times 32 = 9.796$ grams

Do You Know?**What is the Mole Day?**

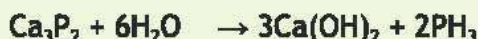
The mole day is a sort of funny celebration day for chemists, which takes place on October 23 between 6:02 am and 6:02 pm. This makes the date to be 6:02 10²³. This celebrates basically Avogadro constant, which is roughly $6.02 \cdot 10^{23}$.

Concept Assessment Exercise 4.3

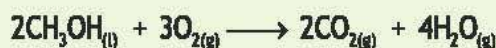
- CO can reduce iron (III) oxide into iron metal. How many moles of CO are needed to reduce 5 moles of Fe_2O_3 .



2. Calculate amount of phosphine (PH_3) that can be prepared when 1 mole of calcium phosphide (Ca_3P_2) reacts with excess of H_2O .



3. Methanol burns according to the following equation.



If 3.50 moles of methanol are burnt in oxygen, calculate

- How many moles of oxygen are used?
 - How many moles of water are produced?
4. Calculate the no. of molecules and volume of O_2 at STP produced by thermal decomposition of 490 grams of KClO_3

Example 4.7

20g of H_2SO_4 on dissolving in water ionizes completely. Calculate

- No. of H_2SO_4 molecules
- No. of H^+ and SO_4^{2-}
- Mass of individual ions

Solution

$$\begin{aligned} \text{a. Mass of } \text{H}_2\text{SO}_4 &= 20\text{g} \\ \text{Molar Mass of } \text{H}_2\text{SO}_4 &= 98.016\text{g mole}^{-1} \\ \text{No of molecules of } \text{H}_2\text{SO}_4 &= \frac{\text{Mass of } \text{H}_2\text{SO}_4}{\text{Molar Mass of } \text{H}_2\text{SO}_4} \times 6.02 \times 10^{23} \\ &= \frac{20}{98.016} \times 6.02 \times 10^{23} \\ &= 1.228 \times 10^{23} \end{aligned}$$

- b. H_2SO_4 dissolves in water as follows:



According to equation

$$1 \text{ molecule of } \text{H}_2\text{SO}_4 = 2\text{H}^+ \text{ ions}$$

$$\begin{aligned} 1.228 \times 10^{23} \text{ molecules of } \text{H}_2\text{SO}_4 &= 2 \times 1.228 \times 10^{23} \text{ H}^+ \text{ ions} \\ &= 2.456 \times 10^{23} \text{ H}^+ \text{ ions} \end{aligned}$$

$$\text{As } 1 \text{ molecule of } \text{H}_2\text{SO}_4 = 1 \text{ SO}_4^{2-} \text{ ion}$$

$$\text{So, } 1.228 \times 10^{23} \text{ molecule of } \text{H}_2\text{SO}_4 = 1.228 \times 10^{23} \text{ SO}_4^{2-} \text{ ions}$$

c. Mass of individual ions

$$= \frac{\text{No. of ions}}{6.02 \times 10^{23}} \times \text{Molar mass of an ion}$$

$$\begin{aligned} \text{Mass of H}^+ &= \frac{2.456 \times 10^{23}}{6.02 \times 10^{23}} \times 1.008 \\ &= 0.411\text{g} \end{aligned}$$

$$\begin{aligned} \text{Mass of SO}_4^{2-} &= \frac{1.228 \times 10^{23}}{6.02 \times 10^{23}} \times 96 \\ &= 19.58\text{g} \end{aligned}$$

4.1.6 Solution Stoichiometry

In solutions the most common concentration unit is molarity. The molarity of a solution is simply the numerical value of its concentration in mol/dm³.

If you read label on the bottle of concentrated H₂SO₄ you will notice 98% H₂SO₄ by mass and also 18M H₂SO₄. What does 18M stand for? This means there are 18 moles of H₂SO₄ in each dm³ of solution. Similarly, conc. HCl is 37% and 12.1 M HCl. This means there are 12.1 moles of HCl in each dm³ of solution. We can express the concentration in terms of moles of solute in the given volume of solution.

Molarity is the concentration unit in which amount of solute is expressed in moles and quantity of solution in dm³.

"Molarity is defined as the number of moles of solute dissolved per dm³ of solution".

Mathematically,

$$M = \frac{\text{mole of solute}}{\text{dm}^3 \text{ of solution}}$$

Example 4.8

Urea (NH₂CONH₂) is a white solid used as fertilizer and starting material for synthetic plastic. A solution contains 40g urea dissolved in 500cm³ of solution. Calculate the molarity of this solution.

Solution

$$\begin{aligned} \text{Mass of urea} &= 40\text{g} \\ \text{Molar Mass of urea (NH}_2\text{CONH}_2) &= 14 + 1 \times 2 + 12 + 16 + 14 + 1 \times 2 \\ &= 60\text{g/mol} \\ \text{Moles of urea} &= \frac{40\text{g}}{60\text{g/mol}} = 0.667\text{mol} \\ \text{Volume of solution} &= \frac{500}{1000} = 0.5\text{dm}^3 \end{aligned}$$

Now

$$\text{Molarity} = \frac{\text{mole of solute}}{\text{dm}^3 \text{ of solution}}$$

$$\text{Molarity} = \frac{0.667 \text{ mol}}{0.5 \text{ dm}^3}$$

$$= 1.334 \text{ M}$$

In solution stoichiometry we use volumes of solutions of known concentration instead of masses of reactants and products and their molarity is used to determine its moles.

Example 4.9

When 250 cm³ of 0.1 M AgNO₃ solution is added to an excess of NaCl solution. What mass of AgCl will be formed.

Solution



Find the moles of silver nitrate present in the solution.

As the solution is 0.1 M

$$1000 \text{ cm}^3 \text{ of solution contain} = 0.1 \text{ mol of AgNO}_3$$

$$250 \text{ cm}^3 \text{ of solution contain} = \frac{0.1 \times 250}{1000} = 0.025 \text{ mol of AgNO}_3$$

Now

$$1 \text{ mol of AgNO}_3 \text{ produces} = 1 \text{ mol of AgCl}$$

$$0.025 \text{ mol of AgNO}_3 \text{ will produce} = 0.025 \text{ mol of AgCl}$$

$$\text{Mass of AgCl produced} = \text{moles} \times \text{molar mass}$$

$$= 0.025 \times 143.5$$

$$= 3.59 \text{ g}$$

When two solutions are mixed, we proceed as follows.

$$\text{Moles of reactant 1} = M_1 V_1 \quad \text{and} \quad \text{Moles of reactant 2} = M_2 V_2$$

The ratio between moles of reactants is the same as given by the balanced chemical equation.

$$M_1 V_1 : M_2 V_2 = n_1 : n_2$$

Where n_1 and n_2 are moles of reactants in the chemical reaction.

$$\frac{M_1 V_1}{M_2 V_2} = \frac{n_1}{n_2}$$

In this expression the ratio of two volumes remains the same whether you used volumes in dm³ or cm³

$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

Example 4.10

What volume of 0.5M sodium sulphate will react with 275cm³ of 0.25M barium chloride solution to completely precipitate Ba²⁺ in solution.

Solution

$$V_1 = ?$$

$$V_2 = 275\text{cm}^3$$

$$M_1 = 0.5\text{M}$$

$$M_2 = 0.25\text{M}$$

$$n_1 = 1$$

$$n_2 = 1$$

$$\begin{aligned} \frac{M_1 V_1}{n_1} &= \frac{M_2 V_2}{n_2} \\ \frac{0.5 \times V_1}{1} &= \frac{0.25 \times 275}{1} \\ V_1 &= \frac{0.25 \times 275}{0.5} \\ V_1 &= 137.5\text{cm}^3 \end{aligned}$$

Concept Assessment Exercise 4.4

1. Potassium chlorate (KClO₃) is a white solid. It is used in making matches and dyes.

Calculate the molarity of solution that contains. (a) 1.5 moles of this compound dissolved in 250cm³ of solution (b) 75g of this compound dissolved to produce 1.25dm³ of solution. (c) What is the molarity of a 50cm³ sample of potassium chlorate solution that yields 0.25g residue after evaporation of the water.

2. What volume of 0.25M LiOH will completely react with 0.500dm³ of 0.25M H₂SO₄.



3. How many grams of NaOH are required to neutralize 40cm³ of 0.5M HCl solution.

**4.2 LIMITING AND NON LIMITING REACTANTS**

When two reactants are mixed for a reaction, usually one of them reacts completely and other reactant does not react completely. The reactant that is completely consumed in the reaction and limits the amounts of product formed is called limiting reactant and reactant that is left unreacted after the completion of reaction is called non limiting or excess reactant.

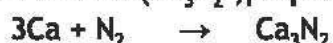
To understand this concept, consider the following reaction



When 1 mole of O_2 and 1 mole of H_2 are mixed, all the H_2 will react completely and O_2 will be left unreacted because for 1 mole of H_2 , $\frac{1}{2}$ mole of O_2 is required, which is available but for complete reaction of 1 mole of O_2 , 2 moles of H_2 are required which are not available that's why H_2 is limiting reactant, and O_2 is non-limiting or excess reactant.

Example 4.11:

Calculate the mass of calcium nitride (Ca_3N_2) prepared from 54.9 grams of Ca and 43.2 grams of N_2



Solution:

Moles of Ca = $54.9/40 = 1.37$ moles

Moles of N_2 = $43.2/28 = 1.54$ moles

3 moles of Ca produce = 1 mole of Ca_3N_2

1 moles of Ca produce = $1/3$ moles of Ca_3N_2

1.37 moles of Ca produce = $1/3 \times 1.37 = 0.457$ moles of Ca_3N_2

1 mole of N_2 produces = 1 mole of Ca_3N_2

1.54 moles N_2 produce = 1.54 moles of Ca_3N_2

Ca produced least amount (0.457 moles of Ca_3N_2) so it is limiting react

Concept Assessment Exercise 4.5

1. How much volume is occupied by marsh gas (CH_4) at STP containing 4.8×10^{24} molecules.
2. Calculate the molecular weight of a gas with the density of 1.25g/dm^3 .
3. Calculate molecules of H_2O produced by 500 molecules each of H_2 and O_2 . Which one is the limiting reactant? How much excess reactant is left unreacted? What would happen if molecules of O_2 were doubled?
4. Excess of AgNO_3 was added to FeCl_3 and 2.02g of AgCl was produced. Calculate amount of FeCl_3 produced in the reaction.

4.3 THEORETICAL YIELD, ACTUAL YIELD AND PERCENT YIELD

We adopted an optimistic approach to the amount of product resulting from the chemical reaction. We assume that 100% of the limiting reactant becomes product. The amount of product as calculated from the balanced chemical equation is called the theoretical yield. In reality, the amount of products during chemical reactions does not match what the chemical equation shows because some side reactions produce alternative products, some of the product may remain in solution, the reaction may be stopped before completion, etc. Whatever the

reason, the fact is that the reaction produces less product than the calculated amount. Quantity of product produced experimentally in a chemical reaction is called the actual yield, and the percentage yield is 100 times the ratio of the actual yield to the theoretical yield.

$$\text{Percent yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

Example 4.12:

Calculate the percent yield of Ozone that could be produced by 10g of O_2 .

Actual yield of O_3 1.05g .

Solution:



Molar mass of O_3 = 48 g/mol

Mass of O_2 = 10g

Molar mass of O_2 = 32g/mol

$$\text{Moles of } O_2 = \frac{10}{32} = 0.3125$$

3 mol of O_2 give = 2 mol of O_3

1 mol of O_2 gives = $\frac{2}{3}$ mol of O_3

$$0.3125 \text{ mol of } O_2 \text{ will give} = \frac{10}{32} \times 0.3125 = 0.208 \text{ mol of } O_3$$

Mass of O_3 produced = $0.208 \times 48 = 10g$

Actual yield = 1.05g of O_3

Percent yield = $1.05/10 \times 100 = 10.5 \%$

Concept Assessment Exercise 4.6

- Determine the amount of Ferric Chloride produced by the reaction of $KMnO_4$, 10 moles of $FeCl_2$ and 22 moles of HCl .

$$KMnO_4 + 5FeCl_2 + 8HCl \rightarrow MnCl_2 + KCl + 5FeCl_3 + 4H_2O$$
- Baking soda is commercially prepared by passing ammonia and carbon dioxide through saturated solution of $NaCl$. If 20g NH_3 and 30g CO_2 produced 40g baking soda then calculate percentage yield of baking soda taking $NaCl$ and H_2O in excess?

$$NaCl + H_2O + CO_2 + NH_3 \rightarrow NaHCO_3 + NH_4Cl$$

4.4 Importance of stoichiometry in the production and dosage of medicine

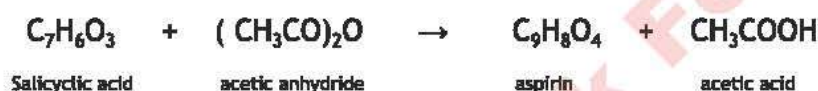
In the production of medicines the amount of active ingredient is essential to produce desired effects. Stoichiometry ensures the accuracy of drug synthesis. Any deviation can result in incomplete reaction or contamination with un-reacted reactants or by-products. Stoichiometry allows chemists to precisely control chemical reactions to produce drugs, to ensure its efficiency, effectiveness and safe use. For examples;

- In the preparation of antibiotics, the stoichiometry ensures that each dose matches the active ingredient and target bacteria.
- Use of insulin relies on the stoichiometry to precise control of blood sugar levels.
- Stoichiometry determines the concentration of viral antigens in the preparation of vaccine for effective results.

Activity: Synthesis of aspirin

Materials required: Salicylic acid, acetic anhydride, sulphuric acid, sodium hydrogen carbonate, ice bath, water, filtration set up.

Chemical reaction



Steps:

- Mix reactants in stoichiometrically calculated amounts (one mole of each reactants) in a flask and add few drops of sulphuric acid to catalyse the reaction.
- Place the flask in ice bath.
- Stir the mixture with a glass rod.
- The flask will be filled with insoluble aspirin.
- When the reaction is over, add sodium hydrogen carbonate solution to neutralize excess acid.
- Filter the aspirin, wash and dry aspirin crystals.
- Calculate the amount of aspirin formed.
- Calculate theoretical yield using stoichiometry.
- Compare the actual yield obtained experimentally with the theoretical yield and assess the efficiency of the synthesis.

This activity helps you to understand how stoichiometry influences production and dosage of medicine.

Key Points

- A mole is the amount of substance that contains 6.023×10^{23} representative particles.
- One mole of any gas at STP (standard temperature and pressure) occupies a volume of 22.414 dm^3 . This volume is called Molar volume.

- The reactant that completely reacts in the reaction and limits the amounts of product formed is called limiting reactant
- Percent yield = Actual yield / theoretical yield $\times$ 100.

References for Further Information

- James Brady and John R. Holum, Chemistry, The studies of matter and its changes.
- Theodore L. Brown, H. Eugene LeMay Jr and Bruce E. Bursten, Chemistry, The central Science.
- Rose Marie Gallagher and Paul Ingram, Complete chemistry.
- Graham Hill and John Holman, Chemistry in Context
- E. N. Ramesden, Calculations for A-Level chemistry.

Exercise

1. Choose the correct answer

- (i) Which sample produces most hydrogen by reaction with excess of HCl?
- (a) 0.25mol Ca (b) 0.25mol Al
(c) 0.25mol Zn (d) 0.25 Na
- (ii) A flask contains 500 cm³ of SO₂ at STP. The flask contains SO₂
- (a) 40 g (b) 100 g
(c) 50 g (d) 1.42 g
- (iii) When 1 mole of each of the following is completely burnt in oxygen, which will give the greater mass of CO₂?
- (a) CO (b) Diamond
(c) Ethane (d) Methane
- (iv) Which one occupies more volume at STP.
- (a) 1g O₂ (b) 1g H₂
(c) 1g CH₄ (d) 1g NO₂
- (v) 0.2 moles of Na₂SO₄, when completely ionized produce Na⁺ ions.
- (a) 2.4×10^{22} (b) 2.4×10^{23}
(c) 1.204×10^{23} (d) 0.12×10^{23}
- (vi) How much volume of NH₃ gas produced when 3g H₂ react with excess of N₂ at STP.
- (a) 24 dm³ (b) 2.24dm³
(c) 2.4 dm³ (d) 1.2dm³

- (vii) When equal volumes of SO_2 and O_2 taken for the formation of SO_3 , which one will be Left unreacted.
- (a) SO_2 (b) O_2
(c) Both (d) Not possible
- (viii) 0.1 moles of laughing gas (N_2O) consist of.
- (a) 6.022×10^{22} molecules (b) 1.806×10^{23} atoms
(c) 1.204×10^{23} atoms of N (d) All
- (ix) Which pair contains equal quantities?
- (a) Volume of 28g N_2 and 8g CH_4 at STP
(b) Molecules in 0.1 mole NH_3 and $2.2414 \text{ dm}^3 \text{ O}_2$ at STP
(c) Mass of 1.204×10^{24} molecules of CO_2 and 4.8×10^{24} atoms of NH_3
(d) Bonds in 56g N_2 and 2 mole CH_4
- (x) $2\text{X} + 3\text{y} \rightarrow 1\text{Z}$
When 12 moles of y react with excess of X and give 3 moles of Z, its percentage yield is?
- (a) 25% (b) 33.33%
(c) 66% (d) 75%

2. Give short answer.

- (i) 49 g each of H_2SO_4 and H_3PO_4 have same number of molecules but having different number of atoms.
- (ii) Different gases having different masses occupy equal volume at STP.
- (iii) One mole of Na and Al has equal No. of atoms but size of atoms are different.
- (iv) Limiting reactant is always in lesser quantity in reaction mixture or not.
- (v) Amount of product obtained through balance chemical equation is greater than the amount obtained experimentally.
- (vi) What are the basic assumption in Stoichiometric calculations?
- (vii) 18g of steam has Avogadro's No of molecules but 58.5g of NaCl has not.
- (viii) Why 2moles of Na react with 1mole of chlorine gas to produce 1mole of NaCl?

3. Calculate each of the following quantities.

- (i) Mass in gram of 0.74 mol KMnO_4 .
- (ii) Moles of O atoms in 9.22g $\text{Mg}(\text{NO}_3)_2$.
- (iii) Number of O atoms in 0.037g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

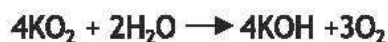
- (iv) Mass in kg of 2.6×10^{20} molecules of SO_3
- (v) Total number of ions in 14.3 g CaBr_2 .
- (vi) Mass in mg of 0.45 mole of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.
- (vii) Mass in grams of 2.78×10^{21} molecules of N_2O_4 .
- (viii) Volume of SO_2 at STP of 4.8×10^{23} molecules of SO_2 .
- (ix) Mass in gram of $\text{Ca}(\text{NO}_3)_2$ having 2×10^{21} ions of Nitrate
- (x) Covalent bonds in 22 gram of dry ice.

4. Calcium ion can be precipitated from solution by sodium oxalate.



Is 15 g Ca^{2+} can be completely precipitated by 15 g of sodium oxalate. If Ca^{2+} ions are left in the solution, calculate how much Ca^{2+} ions are left in the solution?

5. 0.05 mol of potassium chlorate heated for a time and its 0.015 mol left. How much KCl produced, also calculate molecules of O_2 produced? $2\text{KClO}_3 \rightarrow 2\text{KCl} + 3\text{O}_2$.
6. Calculate No. of moles of water produce by 5×10^{24} molecules of H_2SO_4 and 20g of NaOH.
7. Formalin is an aqueous solution of formaldehyde (HCHO), used as a preservative for biological specimens. A biologist wants to prepare 1dm^3 of 11.5M formalin. What mass of formaldehyde he requires?
8. What mass of CaCO_3 , would you add to 100cm^3 of 0.5M HCl to completely neutralize acid?
- $$\text{CaCO}_{3(s)} + 2\text{HCl}_{(aq)} \rightarrow \text{CaCl}_{2(aq)} + \text{CO}_{2(g)} + \text{H}_2\text{O}_{(l)}$$
9. Calculate mass of oxygen required for complete combustion of 1 mole of gasoline (C_8H_{18}).
10. Graphite is the crystalline form of carbon used in "lead" pencil.
- a) How many moles are present in 315mg graphite?
 - b) How many carbon atoms are in it?
11. Manganese is transition metal essential for the growth of strong bones, Calculate mass of 3.22×10^{20} atoms of manganese found in 1 kilogram of bone?
12. How much mass of excess reactant left after 40.5g of Aluminum metal reacts with 196g of H_2SO_4 .
13. Calculate mass of SO_2 that will be produced with 155g of Cu from the roasting of CuS.
- $$\text{CuS} + \text{O}_2 \rightarrow \text{Cu} + \text{SO}_2$$
14. SO_2 is air pollutant it contributes to acid rain. Its emission is controlled by absorbing it into a base (NaOH). Calculate mass of SO_2 absorbed by 33g of NaOH.
- $$\text{SO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O}$$
15. Potassium super oxide (KO_2) is used as source of oxygen in re-breathing mask.



Identify limiting reactant in each of following reactant mixtures.

- i) 6.4 moles KO_2 and 2.1 moles of H_2O .
 - ii) 8.4 moles of KO_2 and 1.5 moles of H_2O .
16. Critically evaluate the importance of the mole concept in understanding chemical reactions.
 17. Analyze the relationship between molar volume and Avogadro's number.
 18. Compare and contrast the molar volumes of different gases under the same condition of temperature and pressure.

Project:

Develop a series of conversation problems that involve moles, grams, and molecules. Ask students to create step-by-step guide or tutorial explaining how to convert between these units.

CHAPTER 5



STATES AND PHASES OF MATTER

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

1. Describe simple properties of liquids e.g., diffusion, compression, expansion, motion of molecules, spaces between them, intermolecular forces and kinetic energy based on kinetic molecular theory.
2. Describe types of intermolecular forces.
3. Explain the strength and applications of dipole-dipole forces, hydrogen bonding and London forces.
4. Describe physical properties of liquids such as evaporation, vapor pressure, boiling point, viscosity and surface tension.
5. Apply the concept of hydrogen bonding to explain the properties of water (specifically high surface tension, high specific heat, low vapor pressure, high heat of vaporization, and high boiling point).
6. Define molar heat of fusion and molar heat of vaporization.
7. Describe how heat of fusion and heat of vaporization affect the particles that make up matter.
8. Outline the importance of heat of fusion in the study of glaciers and ice sheets (particularly while studying polar ice caps).
9. Describe the physical properties of gases (including compressibility, expandability, and pressure exerted by gases).
10. Describe liquid crystals and give their uses in daily life.
11. Differentiate liquid crystals from pure liquids and crystalline solids.
12. Describe simple properties of solids e.g., compression, expansion, motion of molecules inter particle space, intermolecular forces and kinetic energy based on kinetic molecular theory.
13. Differentiate between amorphous and crystalline solids.
14. Describe properties of crystalline solids like geometrical shape, melting point, habit of a crystal, cleavage, and crystal growth.

Phases within a system exist as gas, liquid or solid. The matter within a system contains only a single phase of gaseous phase, but it may have one or more liquid or solid phases. All the phases of matter are made up of microscopic particles which differ in their behaviour in the three phases.

5.1 KINETIC MOLECULAR INTERPRETATION OF LIQUIDS

The postulates of the kinetic molecular theory of liquids are given below:

- A liquid consists of molecules in contact with each other.
- Molecules within a liquid are in constant motion, but the motion of the molecules is limited by their close packing.
- The attractive forces of liquid molecules are greater than the attractive forces of gas molecules. However, these attractive forces are not sufficient to hold the molecules in a fixed position. Liquid molecules can slide past each other.
- The average kinetic energy of liquid molecules is directly proportional to the absolute temperature.
- At constant temperature, the average KE of the molecules is equal to the K.E of the vapours of the liquids.

5.1.1 Properties of Liquids

There are some common properties of liquids, which can be explained by the Kinetic Molecular Theory.

1. Diffusion

Diffusion in liquids occurs because molecules move from one place to another. Restricted movement of a molecule reduces the rate of diffusion, e.g. an ink drop added to water slowly spreads due to the relatively small spaces between the molecules. Diffusion between molecules in densely packed liquids is slow because there are fewer collisions between them.

2. Compression (effect of pressure)

By raising the pressure, the liquid cannot be significantly compressed, because the molecules are already in close contact with each other, e.g., an increase in pressure from one to two atmospheres reduces the volume of water to 0.0045 per cent, which is negligible. However, the same pressure reduces the gas volume by up to 50 percent.

3. Expansion (effect of temperature)

Liquids expand when heated because the intermolecular forces between them decrease. In addition, an increase in temperature increases effective collisions between molecules. As the temperature drops, the volume decreases.

4. Motion of molecules

The molecules move with lesser speed due to larger forces of attraction among them, as a result they have lesser kinetic energy. However, the kinetic energy increases with the increase in temperature.

5. Spaces between them

The molecules that make up liquid states are quite close to each other. There is very little spaces between them. As a result, the rate of intermolecular collisions is moderate. Therefore, the average kinetic energy is also moderate.

6. Intermolecular forces

The forces of attraction between individual particles of matter are called intermolecular forces. The physical properties of liquids, such as boiling point, vapor pressure, surface tension, viscosity, and heat of vaporization, depend on the strength of attractive forces between molecules.

7. Kinetic Energy based on Kinetic Molecular Theory

According to kinetic molecular theory, molecular movements and collisions caused by strong intermolecular attraction are minimal. Let's look at the example of water, because the molecules are closer together and have a strong attraction due to hydrogen bonding, so they have low kinetic energy

5.2 PHYSICAL PROPERTIES OF LIQUIDS

5.2.1 Vapour Pressure and Boiling Point

When a liquid is heated, its vapour pressure increases with increasing temperature due to the decrease of intermolecular forces. As a result, more and more vapor are released into the air. A stage is reached where the liquid begins to boil. So the temperature at which the vapour pressure of a liquid is equal to the atmospheric pressure or some external pressure is called the boiling point of the liquid.

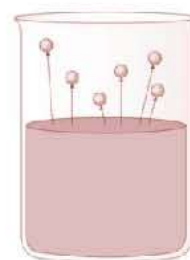
e.g. Boiling Point of water at 760mmHg = 100 °C

Boiling Point of water at 23.7mmHg = 25 °C

5.2.2 Evaporation

The molecules in liquids are in motion and move within the liquid volume. The energy of molecules is not equally distributed. The molecules having high kinetic energy move faster while other molecules having low kinetic energy move slowly. When the high speed molecules reach the surface of the liquid it may escape the attraction of its side or neighbouring molecules and leave the surface of the liquid.

The spontaneous change of a liquid into its vapour at the surface of liquid at given temperature is called evaporation. Evaporation takes place at all temperatures. Evaporation causes cooling. When the high energy molecules leave the liquid during evaporation, low energy molecules are left behind, the average kinetic energy of molecules of liquid decreases and temperature of the liquid falls so heat moves from surrounding to the liquid and temperature of surrounding falls.



Evaporation is controlled by different factors. When surface area of a liquid increases, evaporation increases because evaporation takes place from liquid surface. When liquid surface increases then more molecules can escape and rate of evaporation increases. Intermolecular forces is another factor which affect evaporation. When intermolecular forces are strong molecules of liquid cannot leave the liquid surface easily and evaporation decreases. Rate of evaporation is slow when intermolecular forces are strong and when intermolecular forces are weak, the rate of evaporation is faster. At high temperature molecules have greater energy and rate of evaporation increases. Gasoline and ethyl alcohol whose molecules have weaker intermolecular forces (London forces of attraction) evaporation is much faster than water. Where molecules of water have strong intermolecular forces (Hydrogen bonding).

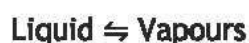
Do You Know?

Why Does High Air Humidity Make it Feel Hotter?

The natural mechanism of our body to cool itself down is sweating. Evaporation of sweat from our skin takes up energy from our bodies, cooling ourselves down. The more water there is already in the air (higher humidity), the more difficult this evaporation process take place. Therefore, higher concentration of water on air, makes us feel hotter because we cannot cool down efficiently.

5.2.3 Vapour pressure:

The liquid molecules having high kinetic energy leave the liquid surface and escape out of liquid and this process is called evaporation. When the surface of liquid is open the liquid molecules mixed up with air above the liquid and the molecules leave the surface and go away. If the surface of liquid is covered and the system is closed the molecules of liquid evaporate and start gathering above the surface of liquid. These evaporated molecules collide with surface of liquid and also with walls of the container. These molecules are captured by surface of the liquid. This coming back of vapours to liquid and captured by liquid surface is called condensation. Both the processes evaporation and condensation continue till a time reaches when the rate of evaporation is equal to the rate of condensation. This state is called the state of dynamic equilibrium.



Vapour pressure of a liquid is the pressure exerted by vapour of the liquid in equilibrium with the liquid at a given temperature. At a constant temperature the number of molecules leaving the surface of liquid is equal to the number of molecules coming back into liquid. At one moment the molecules of liquid are in liquid state may be in vapour state in next moment during evaporation. The vapour pressure is independent of the amount of liquid or volume of container. The surface area has no effect on vapour pressure. Larger surface area has larger target for evaporation and for returning the molecules.

The vapour pressure of liquid depends on nature of the given liquid (intermolecular forces between its molecules, size of molecules whether small or large molecules) and the other important factor is temperature. Increasing temperature increases the kinetic energy of molecules. At high temperature molecules of liquid have high kinetic energy and capacity of

molecules to break the intermolecular forces and escape to leave the liquid surface also increases and as a result the rate of evaporation increases this causes the increase of vapour pressure. Water shows increase of vapour pressure from 4.579 torr at 0°C to 9.209 torr at 10°C , 527.8 torr at 90°C and 760 torr at 100°C .

Intermolecular forces are also a factor which decides increase or decrease in vapour pressure of a liquid. At a particular temperature stronger the intermolecular forces lower the vapour pressure and weaker the intermolecular forces higher the vapour pressure. At the same temperature different liquids have different vapour pressure. At 20°C Glycerol has 0.00016 torr and Isopentane 580 torr vapour pressure.

Table 5.1: Vapour pressure of some liquids at 20°C .

Name of compound	Vapour pressure at 20°C (torr)
Glycerol	0.00016
Mercury	0.012
Water	43.9
Carbon Tetrachloride	87
Chloroform	170
Ethyl ether	442.2
Isopentane	580

Water boils at 100°C at 760 torr pressure at sea level and boils at 120°C at 1489 torr pressure. While boils at 25°C at 23.7 torr pressure. At Murree hills where external pressure is 700 torr water boils at 98°C while water boils at 69°C at the top of Mount Everest where external pressure at 323 torr.

When the external pressure increases artificially the boiling temperature increases as in pressure cooker. A pressure cooker is a closed container from which water vapor cannot escape and pressure is created and the boiling temperature rises, therefore food is cooked quickly.

In vacuum distillation liquid boils at low temperature which requires less amount of heat. Under this process boiling point of liquid is decreased and liquids like glycerine having boiling point 290°C at 760 torr pressure can decompose at this temperature and cannot be distilled at this temperature. By vacuum the boiling point of glycerine decreases to 210°C at 50 torr and is distilled without decomposition.

The liquid reach to their boiling point when their vapour pressure become equal to atmospheric pressure at sea level 760 torr. When different liquids are heated, due to the difference in their intermolecular forces they show different vapour pressure and so their boiling point is different.

5.2.4 Boiling point

By heating the liquid, its vapour pressure increases. When heating is continued a stage will reach when the vapour pressure of the liquid becomes equal to external pressure or atmosphere pressure. The temperature at which the vapour pressure of a liquid becomes equal to external

pressure or atmospheric pressure is called boiling point or boiling temperature. At this temperature boiling starts. The kinetic energy of molecules increases by heating and temperature of the liquid also increases. When the kinetic energy of the liquid molecules become maximum then further heat supplied will not increase the temperature (temperature remains constant at boiling point) because the further heating will break the intermolecular forces and the liquid is converted into vapours. The amount of heat required to convert one mole of liquid into vapours at its boiling point is called, its molar heat of vaporization. For water the molar heat of vaporization is 40.6 kJ/mole.

5.2.5 Boiling point and atmospheric pressure

Boiling point of liquid depends on intermolecular forces. Greater the intermolecular forces high is the boiling temperature and vice versa. Boiling point depends on external pressure or atmospheric pressure. Boiling point is the temperature at which vapour pressure of a liquid becomes equal to external pressure or atmospheric pressure. When external pressure is high then larger amount of heat is required to produce vapour pressure equal to external pressure and liquid boils at high temperature hence boiling point is high. Likewise, at lower external pressure liquid boils at lower temperature as liquid requires less amount of heat to boil and boiling point is low.

5.2.6 Viscosity

A common observation is that water can be poured from one container to another very quickly compared to honey and glycerine. The resistance to flow of a liquid is called viscosity. The higher the viscosity, the slower the liquid flows. Viscosity measures how easily molecules slide past each other. To understand viscosity, think of a fluid flowing in a pipe as consisting of a series of concentric circular layers. Resistance is caused by internal friction between layers of molecules. The layer next to the walls have the lowest speed. Each layer attracts the other and thus causes resistance to flow.

Units:

SI units of viscosity is Pascal Second (Pa.s). Non-SI unit of viscosity is poise.

$$1 \text{ poise} = 0.1 \text{ kg m}^{-1}\text{s}^{-1} \text{ or gcm}^{-1}\text{s}^{-1}$$

$$1 \text{ Pa.s} = 1 \text{ kgm}^{-1}\text{s}^{-1} = 10 \text{ poise}$$

The size and shape of the molecule strongly influence viscosity. Liquids such as water, acetone, benzene and methanol, whose molecules are small and compact, have a low viscosity. In liquids with large and irregular molecules, such as honey, glycerine tends to tangle with each other. This hinders the flow of molecules and leads to high viscosity. The stronger the intermolecular force, the higher the viscosity. Liquids whose molecules form hydrogen bonds are more viscous than others without hydrogen bonds. For example, water is more viscous than methanol mainly due to extensive hydrogen bonding. Molecules move faster when the temperature rises. This is because; an increase in temperature decreases intermolecular forces. This dependence is quite visible for very viscous liquids such as honey and syrup. These liquids are easier to pour when hot than cold.

5.2.7 Surface Tension

Surface tension is the property of the surface of liquids to behave as if a membrane were stretched over it. All molecules below the surface of a liquid are surrounded by other molecules in all directions. Thus, the force exerted by such molecules is balanced in all directions, while at the surface of a liquid there are molecules beside and below but none above it. This results in an unbalanced force that pulls the surface molecules inward. Molecules on the surface therefore feel an inward pull, creating surface tension. "A force in dynes acting at right angles to a unit length of liquid surface is called surface tension." For a molecule to reach the surface, it must overcome the downward force of attraction. This means that work must be done to bring it to the surface. Therefore, increasing the surface area of the liquid requires input energy. Surface tension can also be defined as the amount of energy required to expand the surface of a liquid per unit area. Molecules on the surface of a liquid are less stable than inside it, so a liquid is stable if it has the fewest molecules on its surface. This happens when the surface of the liquid is the smallest. Spheres have less surface area per unit volume than anything else. Therefore, small liquid droplets are usually spherical.

The surface tension of a liquid directly depends on the strength of the intermolecular forces. The stronger the intermolecular forces between the liquid molecules, the higher the surface tension and vice versa. For example, water has a higher surface tension than many other liquids, such as alcohols, ethers, benzene, etc. This is due to the strong hydrogen bonding between water molecules. The surface tension of a liquid decreases with increasing temperature. This is because the increased kinetic energy of the molecules reduces the strength of the intermolecular forces. It is different for different liquids because of different types of intermolecular forces.

Units

SI unit of surface tension is joule per square meter, Jm^{-2} or Newton per meter, Nm^{-1} .

5.2.8 Concept of Hydrogen Bonding to Explain the Properties of Water

Hydrogen bonding in water contributes to its unique properties, which are as follows.

- Surface tension is affected by strong intermolecular attractive forces. Water has hydrogen bonding which is strong intermolecular force. This creates a high surface tension.

Solvent	Surface tension ($\gamma \times 10^{-2}$) (Nm^{-1})
Water	7.275
Methanol	2.26
Ethanol	2.28
Benzene	2.888

Hexane	1.84
CCl ₄	2.70

- ii. Vapour pressure: vapour pressure of a liquid is affected by intermolecular attractive forces. Strong forces of attraction make the evaporation slow. Due to hydrogen bonding in water which is strong intermolecular attractive force decreases evaporation and so water has low vapour pressure.
- iii. High heat of vaporization of water: Heat of vaporization of water compared to other liquids is high because of strong intermolecular forces of hydrogen bonding in water. More heat is required to overcome these attractive forces to vaporize water and as a result water show high heat of vaporization than other liquids.
- iv. High heat of vaporization of water results in high boiling point. Due to strong hydrogen bonding water has low vapor pressure. So, more heat is required to enhance evaporation and produce vapour pressure equal to external pressure. As a result water has high B.P.

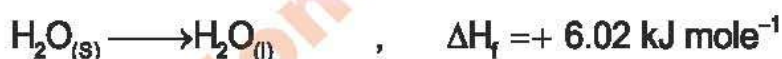
5.3 ENERGETIC OF PHASE CHANGES

Physical and chemical changes are accompanied by a change in energy in the form of heat. Physical energy change is a quantitative measurement of the strength of intermolecular forces. The change in energy at constant pressure is called the change in enthalpy, denoted by ΔH . It is expressed in kJ mol^{-1} . When a substance undergoes a phase change (change of state), its temperature remains constant even when heat is added.

5.3.1 Molar Heat of Fusion and Molar Heat of Vaporization

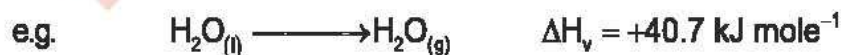
Molar heat of fusion (ΔH_f) is the amount of heat required to convert one mole of a solid into its liquid state at its melting point is called molar heat of fusion (ΔH_f)

e.g. Molar heat of fusion for ice is $+6.02 \text{ kJ mole}^{-1}$



Molar heat of vaporization (ΔH_v)

The amount of heat required to convert one mole of a liquid into its vapours at its boiling point is called molar heat of vaporization.



5.3.2 Energy Changes and Intermolecular Forces:

As a result of melting of a solid, a small change in intermolecular distance and potential energy takes place in atoms, molecules or ions. On the other hand on evaporation of a liquid atoms, molecules or ions undergo large changes in their intermolecular distance and potential energy. Therefore, heat of vaporisation is much greater than that heat of fusion.

5.3.3 Liquid Crystals and Their uses in Daily Life

Pure liquids have sharp melting points and at its melting point the temperature remains constant. Generally, when solids are heated, they are converted into liquids. In 1888 Fredesick Reimitaz discovered a universal property during study of cholesteryl benzoate an organic compound. When this compound is heated it turns milky liquid at 145°C and turns into clear liquid at 179°C. When cooled the reverse occurs. The turbid liquid state is called liquid crystals.

There are many crystalline solids which melt to turbid liquid and then clear liquid phase. Turbid liquid phase can flow and have properties of liquids like viscosity. Surface tension etc. It is to be noted that molecules of this turbid liquids have some degree of order and resemble crystals in properties like optical properties.

The liquid crystalline state between melting temperature and clearing temperature is called liquid crystals. Liquids crystals are always isotropic while crystalline solid may be isotropic or anisotropic.



Long rod like molecular substance make these type of liquid crystals. These molecules oriented in random direction in normal liquid phase and in liquid crystal form they are in order. On basis of order of molecules the liquid crystals are nematic, smectic and cholestrinic.

The liquid crystal is intermediate between solid crystal and clear liquid its properties are also between crystals properties and those of isotropic liquids. Liquid crystals have property of crystals like optical property and have fluidity of liquids.

5.3.4 Uses of liquid crystals

1. Liquid crystals are used in the display of electrical devices like digital watches, laptops computers, calculators etc.
2. Due to electromagnetic optic characteristic and photoelectric properties of nematic and cholesteric types liquid crystals were used in different laboratories, universities and industries began to focus on their applications.
3. Cholesteric liquid crystals applied to skin are used to locate veins, arteries, infections, tumours etc. which are warmer than other tissue.
4. Nematic liquid crystals are used in magnetic resonance. Molecules dissolved in nematic crystal liquid solvents show resolved NMR spectrum. Intermolecular Dipole-Dipole fine structures are obtained.
5. Liquid crystals are used in chromatographic separation to study molecular arrangements, kinetics and as anisotropic fluid for visible, UV and IR spectroscopy.
6. Liquid crystals are used in Oscillography system, television displays, liquid crystal screens have also been developed.
7. Liquid crystals polymers are used in industries. Polyester liquid crystals were developed for fire resistant and used as coating for multifibre, optical cables etc.

5.3.5 Differentiation of liquid crystals from pure liquid and crystalline solids

In liquid crystals, the molecules are arranged as in a crystal, but with certain degrees of freedom, so that they can flow like liquids. They have both fluidity and some long-range molecular order. They have the ability to change their molecular structure in response to external factors such as temperature, electric field or pressure.

Pure liquids have a random arrangement of molecules with no long-range order. They can flow freely and take the form of a vessel. Pure liquids show no significant changes in molecular arrangement in response to external stimuli, other than changes in temperature or pressure.

In solids molecules or atoms have a well-ordered and repeating three-dimensional arrangement. A solid maintains a certain shape and volume. Some crystalline solids can change phase under the influence of temperature.

5.3.6 Glaciers and ice caps

- The study of glaciers, particularly polar ice sheets, heavily relies on understanding the significant role that heat of fusion plays in their behaviour.
- The melting and freezing of ice are closely tied to the heat of fusion. Hence, it holds great significance to anticipate the response of glaciers and ice sheets to fluctuations in temperature.
- The increasing global temperatures caused by global warming will necessitate the consideration of heat of fusion as a crucial element in evaluating the susceptibility of polar ice sheets. By utilizing this information, scientists are able to make predictions regarding the extent of ice melting and its impact on sea levels as well as other environmental transformations.
- The quantity of water released during the melting of ice is directly proportional to the heat of fusion. Through the analysis of the heat absorbed during the melting process of ice cores, researchers are able to obtain valuable information about previous climatic conditions.

5.4 GENERAL PROPERTIES OF GASES

1. Gases do not have definite shape and volume. Gas molecules are free to move. Molecules of gas are in random motion. Volume of the gas is the volume of its container. Similarly, the gases have no definite shape and acquire the shape of the container.
2. Intermolecular space in gas molecules is more due to which gases show low densities. Gases bubble and rise up through liquid due to its low densities than liquids and solids.
3. Intermolecular spaces in gases are more enough to accommodate other gases molecules and show properties of diffusion and effusion.
4. When gases are heated the velocity of molecules increases and volume of gases increases. Similarly, if volume is available then gases can expand and occupy the available volume.

5. Gas molecules are in random motion and collide with each other and with the walls of the container. Gases exert pressure due to the number of collisions.
6. Gases have some common physical properties. According to kinetic molecular theory the space between gas molecules is more than solids and molecules of gas are free to move. The kinetic energy of molecules of a gas depends on temperature. Gases are free to flow and fill the available volume or container.

1. Compressibility:

Gases are highly compressible because the particles in gases are far apart and large spaces exist between them. So gases can be compressed into small volume by applying pressure. Due to this property of gases large volume of a gas can be placed in small cylinder by compression. For example oxygen gas in cylinders are supplied to hospitals. Compressed Natural gas (CNG) is used in vehicles liquid petroleum Gas (LPG) is used for cooking in kitchen.

The state of a substance is determined by the balance between kinetic energy of individual particles atoms or molecules and the intermolecular forces between them. The kinetic energy keeps the particles apart and moving around and determines the temperature of the substance while intermolecular forces draw molecules together.

In gases average kinetic energy of molecules is larger than average energy of attraction between particles or molecules of the gas.

2. Expandability:

Gases expand to fill its container. Expandability of gases is spontaneous and gases occupy the available volume. The gas molecules are in random motion having kinetic energy and there is empty space between gas molecules. The air contained in a balloon fills up the whole balloon. If the gas in balloon is let into the room it will spread in the room. In balloon gas has high pressure and, in the room, gas has low pressure. Compressed gas can also expand if volume is available. Compression and expansion of gases is also used in liquefaction of gases.

3. Pressure exerted by the Gases:

Molecules of a gas are in constant random motion and collide against walls of the container. Due to collisions with the walls of the container the walls experience a continuous force. Due to this force gases exert pressure. Pressure is force per unit area.

5.5 GENERAL PROPERTIES OF SOLIDS:

- Solids have definite mass, volume and shape. It has a compact arrangement of constituent particles. There is short distance between molecules and forces of attraction between its particles is very strong. Due to this reason solids are non-compressible and they cannot diffuse into each other. Solid particles only have vibrational motion.
- Solids are a collection of atoms or molecules held together in a definite shape under constant conditions. Substances which are rigid, hard, cannot flow and have definite volume under constant conditions.
- They have definite size under constant conditions, because of strong forces of attraction

between its atoms or molecules. Its constituent particles (atoms, molecules or ions) cannot move randomly. Particles only show vibrational motion.

- Solid particles are held together by strong cohesive forces.
- Its constituent particles (atoms, molecules or ions) are closely packed with each other. There exists a well ordered arrangement in solids.

5.5.1 Kinetic molecular interpretation of solids:

Solids show maximum attractive forces among their particles (atoms, molecules or ions) due to very close packing of arrangement.

The particles of solids are closely packed as a result they occupy minimum volume and show high density.

Solid particles do not show translational motion therefore there is no collision between the molecules.

- The particles of solid can only vibrate and possess only vibrational kinetic energy.
- Crystalline solids have definite, distinctive geometric shape due to orderly arrangement of particles (atoms, molecules or ions) in three dimensional shape.

5.5.2 Properties of solids based on kinetic molecular theory

1. Diffusion:

Diffusion depends on velocity of molecules. Movement of molecules in solids is vibration only and show negligible diffusion.

2. Motion of molecules:

Particles of solids (atoms, molecules or ions) are closely packed with each other and show only vibrational motion. Particles can only vibrate about their mean position.

3. Inter molecular forces:

Intermolecular forces are maximum in solids. Molecules of solids are held together in fixed position by strong forces of attraction and can vibrate about their fixed position.

4. Compression:

The particles of solids are closely packed and have no space between them. There is minimum or no effect of pressure on solids.

5. Expansion:

Solids expand when heated (volume increases). This is due to the fact that increase in temperature decreases intermolecular attractive forces and space is created between the molecules and volume increases.

5.5.3 Types of solids

Solids are classified on the basis of regular arrangements of its particles (atoms, ions or molecules). There are two types of solids accordingly.

1. Crystalline solids:

The solids which have definite regular and three-dimensional geometric shapes are called crystalline solids e.g., NaCl, diamond, ice, glucose ZnSO_4 etc. In these solids the arrangement of atoms ions or molecules are in a definite three-dimensional pattern. this recurring geometrical pattern of structure extends in three dimensions.

2. Amorphous solids:

Amorphous solids are those whose constituent particles (atoms, ions or molecules) do not possess arrangement in regular orderly manner. These solids have no definite Geometric shapes are called amorphous solids for example glass, plastic, rubber, etc. These solids have solids state properties but do not have in ordered crystalline state. The crystalline solids can be converted into amorphous solids by melting and cooling the molten mass rapidly. So, the particles do not find time to arrange themselves. The amorphous solids can have some small regions of orderly arrangement. These crystalline parts of amorphous solids are known as crystallites. Amorphous solids have no sharp melting points. The particles of glass soften over high temperature and can be molded.

5.5.4 Properties of crystalline solids**1. Geometrical shape:**

Crystals have a geometric shape. The particles of solids (ions, atoms or molecules) are arranged in three-dimensional space. The internal angles of a crystal (where surfaces intersect) are always the same, no matter in what form they are grown.

2. Melting point:

Crystalline solids have sharp melting points. When a solid is heated, its particles start vibrating at higher temperature and transfer their kinetic energy throughout the solid. At the melting point, their vibration energies become so high that they start leaving fixed positions simultaneously and the solid turn into a liquid.

3. Cleavage planes:

Crystalline solids break up along certain planes called cleavage planes. When pressure is applied to it along the cleavage plane, it changes into small crystals of the same size and shape as that of the original crystal. For a given crystalline solid, the cleavage planes are bent towards each other. The angles between them vary from one crystalline solid to another.

4. Habits of a crystal

Crystals slowly form when a saturated solution is cooled. With slow cooling, liquid crystals are formed. Crystals form by growing in different directions. If the growth conditions remain the same, crystals of the same shape will form. The shape of a crystal in which it usually grows is called habit of a crystal. For example, cubic crystals of sodium chloride are obtained from its aqueous solution. But if the conditions are changed, the shape of crystals also changes. For example, if 10% urea is present in aqueous solution of sodium chloride, octahedral crystals of sodium chloride are obtained.

Key Points

- Forces of attraction between molecules of a substance in any phase are called intermolecular forces.
- The forces of attraction between positive end of one molecule and the negative end of other molecule are called Dipole-Dipole forces.
- The attractive forces between dipoles and induced dipole are called Dipole induced dipole forces or as Debye forces
- The momentary forces of attraction created between instantaneous dipole and induced dipole called instantaneous dipole induced Dipole forces or London Forces.
- The spontaneous change of a liquid into its vapour at the surface of liquid at given temperature is called evaporation.
- Vapour pressure of a liquid is the pressure exerted by vapour of the liquid in equilibrium with the liquid at a given temperature.
- The temperature at which the vapour pressure of a liquid becomes equal to external pressure or atmospheric pressure is called boiling point or boiling temperature.
- The resistance to flow of a liquid is called viscosity.
- A dyne force acting at right angles to a unit length of liquid surface is called surface tension
- Molar heat of fusion (ΔH_f) is the amount of heat required to convert one mole of a solid into its liquid state at its melting point is called molar heat of fusion
- The amount of heat required to convert one mole of a liquid into its vapours at its boiling point is called molar heat of vaporization
- The liquid crystalline state between melting temperature and clearing temperature is called liquid crystals.
- Crystalline solids have definite, distinctive geometric shape due to orderly arrangement of particles (atoms, molecules or ions) in three-dimensional shape.
- The breaking of crystalline solids takes place along definite planes which are called cleavage planes.

References for Further information:

- Holderness & Lambert, A New Certificate Chemistry.
- John Olmsted III and Gregory M. Williams, Chemistry, The Molecular Science.
- Osei Yaw Ababio, New School Chemistry.
- George M. Bodner and Harry L. Pardue, Chemistry, an experimental Science.

Exercise

1. Choose the Correct Answer

- Van Der Waal's forces are effective;

(a) At long distance	(b) Both at long as well as short distance
(c) Only at short distance	(d) Independent of distance

- ii. Which one of the following forces are also called London forces?
(a) Ion-dipole forces (b) Dipole-induced dipole forces
(c) Dipole-dipole forces (d) Dispersion forces
- iii. Which of the following two halogens are gases at room temperature?
(a) Fluorine and Iodine (b) Chlorine and Bromine
(c) Fluorine and Chlorine (d) Iodine and Bromine
- iv. The intermolecular forces are of;
(a) Two types (b) Three types
(c) Four types (d) Five types
- v. Thermostat is an instrument which;
(a) Increases the temperature (b) Decreases the temperature
(c) Maintains the temperature (d) Fluctuate the temperature
- vi. The scientist who discussed the phenomenon of viscosity are;
(a) Poissuelle (b) Newton
(c) Fritz (d) Vander Wall
- vii. The distillation under reduced pressure is called;
(a) Fractional distillation (b) Vacuum distillation
(c) Steam distillation (d) Pressure distillation
- viii. The unit of surface tension is;
(a) Newton per metre (b) Newton per metre square
(c) 760mmHg (d) Newton square per metre
- ix. The intermediate phase lying between the solid phase and the normal liquid phase is called;
(a) Crystalline solid (b) liquid crystals
(c) Mesogens (d) Crystal lattice
- x. In which of the following are the particles the most disordered?
(a) Water at 100 °C (b) Steam at 100 °C
(c) Impure water at 102 °C (d) Water at 10 °C

- xi. Which of these statement best supports the idea that matter is made up of particles?
- (a) Liquids always fill the space available to them
 - (b) Liquids are easily compressible
 - (c) 1 cm^3 of water produces nearly 1700 cm^3 of steam
 - (d) If a bottle of perfume is opened, the smell spread quickly
- xii. Which of these processes involve a weakening of the attraction between particles?
- (a) Condensation
 - (b) Freezing
 - (c) Crystallization
 - (d) Evaporation
- xiii. A liquid is thought to be pure ethanoic acid (acetic acid), which of the following is the best way to test its purity?
- (a) Measure its B.P
 - (b) React it with ethanol
 - (c) Burn it completely in oxygen
 - (d) Dehydrate it with concentrated H_2SO_4

2 Give short answer.

- i. Give the general properties of liquids as to
 - (a) Diffusion
 - (b) Compression
- ii. What are the types of intermolecular forces, give examples?
- iii. What is hydrogen bonding, give particular examples?
- iv. What are the applications of H-bonding?
- v. What are the different types of physical properties of liquids?
- vi. Define vapour pressure. What are the factors affecting the V.P?
- vii. What is
 - (a) Viscosity.
 - (b) Surface tension.
- viii. Define molar heat of fusion and molar heat of vaporization.
- ix. How will you differentiate liquid crystals from pure liquids?
- x. Why distillation under reduced pressure is often used in the purification of chemicals?

3 (a) Give the simple properties of liquids with special reference to the following:

- Diffusion
 - Compression
 - Expansion
 - Inter molecular forces
 - Kinetic energy
- (b) Explain on the basis of kinetic molecular theory. Why the boiling point of a liquid remains constant although heat is continuously supplied to the liquid?
- 4 (a) Define and explain evaporation.
- (b) What are the factors affecting evaporation?
- (c) Different liquids have different rates of evaporation. Explain with reference to ether and alcohol?
- 5 (a) Define and explain vapour pressure. How equilibrium is established between evaporation and condensation?
- (b) What are the factors affecting vapour pressure of a liquid?
- (c) Kinetically how will you explain the effect of temperature on vapour pressure?
- 6 (a) Define and explain boiling point of a liquid?
- (b) How will you explain the effect of pressure on the boiling point of a liquid?
- (c) Practically how will you explain the
- (i) Effect of increase of pressure on boiling point.
 - (ii) Effect of decrease of pressure on boiling point.
- 7 (a) Define and explain the term viscosity of a liquid? How does the resistance to the layers causes viscosity?
- (b) What are the factors affecting the viscosity of a liquid?
- (c) Use the concept of hydrogen bonding to explain the following properties of water?
- (i) High surface tension
 - (ii) High heat of vaporization
 - (iii) High boiling point
- 8 (a) Define and explain the phenomenon of surface tension?
- (b) What are the factors affecting surface tension?
- (c) Define dynamic equilibrium between two physical states?
- (d) Define?

- (i) Molar heat of fusion
 - (ii) Molar heat of vapourization
- 9 (a) Define a liquid crystal?
- (b) What are the uses of liquid crystals in daily life?
- (c) How will you differentiate liquid crystals from pure liquids and crystalline solids?
- 10 What are the energetics of phase changes?
- 11 (a) Define and explain the boiling point of a liquid?
- (b) How will you explain the two practical applications regarding the effect of pressure on the boiling point of a liquid?
- 12 How can you interpret the anomalous behaviour of water?
- 13 Evaluate the impact of temperature on surface tension of liquids.
- 14 Interpret the influence of intermolecular forces on the following properties of liquids.
- (a) Vapour pressure
 - (b) boiling point
- 15 Evaluate the importance of H-bonding in understanding physical properties of water.
- 16 Differentiate between molar heat of fusion and molar heat of vaporization.

Project:

Explore the science behind LCDs and prepare a report about it.