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Fundamentals of Engineering Chemistry

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Preface

The purpose of this book is to provide an in-depth information on fundamentals of Engineering Chemistry to the student community to improve their general understanding on the subject and designed as a textbook for the beginners in all branches of Engineering according to the recent syllabus of Swami Vivekananda University, Kolkata. The book has been divided into four Chapters.

The first Chapter is Basis of atomic theory and electronic structure of atoms, second chapter is Introduction to Chemical Bonding, third chapter is Classification of Elements and Periodicity in Properties and the fourth chapter is Acid Base Theory. All the four chapters include all the basic fundamental aspects of Chemistry.

The aim of this book is to provide an easy and simple yet logical framework for each chapter into which the readers fit themselves to understand each and every topic. Primarily this book aimed at first the fundamental topics of engineering chemistry for the first-year students.

Every attempt has been made to make this book error free and useful for the students. Each Chapter contains exercise where probable questions on the particular chapter is provided.

Any constructive suggestion and criticism regarding the improvement of this book will be acknowledged.

Dr. Arpita Sarkar Date: 16-12-2023
Associate Professor,
Swami Vivekananda University, Kolkata, West Bengal, India

Acknowledgement

I would like to express my heartfelt appreciation to Swami Vivekananda University in Kolkata, India, for their invaluable support and encouragement in the creation of this book, "Fundamentals of Engineering Chemistry" The university's unwavering dedication to fostering research and excellence in teaching has been instrumental in shaping the focus and content of this publication. The collaborative environment and extensive resources provided by Swami Vivekananda University have enabled us to thoroughly explore and present the latest developments in engineering chemistry. This supportive setting has been crucial for conducting the necessary research and ensuring that the material presented in this textbook is both current and relevant to the needs of today's engineering students. I am particularly grateful for the university's commitment to academic excellence and innovation. Their support has allowed us to create a comprehensive and accessible resource that we hope will be beneficial to both students and educators in the field of engineering. It is my sincere hope that this book, reflecting our shared commitment to knowledge, progress, and the pursuit of excellence, will serve as a valuable tool for Swami Vivekananda University as well as the broader academic community. We look forward to continuing our partnership and contributing to the advancement of education and research in Engineering Chemistry. Thank you to everyone at Swami Vivekananda University who has contributed to this endeavour. Your support and encouragement have been greatly appreciated.

Sincerely,

Dr. Arpita Sarkar
Associate Professor,
Swami Vivekananda University, Kolkata, West Bengal, India

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CHAPTER 1

ATOMIC STRUCTURE

1.1 INTRODUCTION

Chemistry is actually defined as the study of matter with respect to its structure, composition and the properties. Matter consists of atoms, and therefore an understanding of the structure of atom is very important.

In this chapter, we will basically outline some concepts fundamental to an understanding of atomic structure. In this lesson you will learn about the internal structure of an atom and the correlations between its structure and properties.

You have studied in your earlier classes that the earliest concept of atom was revived by John Dalton in the beginning of nineteenth century in terms of his atomic theory which successfully explained the laws of chemical combination. Later experiments showed that the atom is not indivisible but has an internal structure. An atom is the smallest unit quantity of an element. It is capable of existence, either alone or in chemical combination with other atoms of the same or another element.

An atom consists of central nucleus surrounded by one or more orbital of electrons which are called the fundamental particles of atoms.

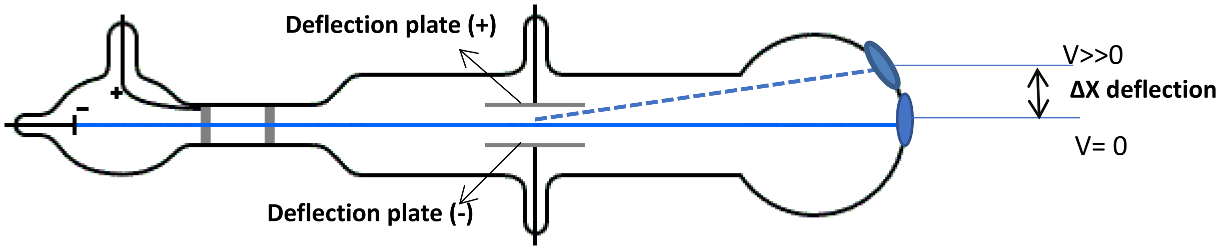
Fundamental Particles of Atom:

A) Discovery of the Electron

In 1897 J.J. Thomson discovered electron as a constituent of atom. He determined that an electron had a negative charge and had very little mass as compared to that of the atom. He also determines the charge to mass ratio. In 1906 he wins the Nobel Prize.

J. J. Thomson (1856-1940)
Won Nobel Prize in Physics
in 1906

The Experiment:



If ΔV (the voltage difference between the two deflection plates) = 0 there is no deflection, but when ΔV is large there is Δx deflection towards the positive plate.

Therefore, cathode rays = <u>negatively charged particles</u> = electrons

$\Delta x_{(-)} \propto$ $e_{(-)}$ = Charge of the negative particle
$m_{(-)}$ = Mass of the negative particle

BUT when a very large ΔV is applied a slight deflection towards the negative plate is also observed. **<u>Therefore there is also a positively charged particle!</u>**

$\Delta x_{(+)} \propto$ $e_{(+)}$ = Charge of the positive particle
$m_{(+)}$ = Mass of the positive particle

BUT $|\Delta x_{(-)}| >>> |\Delta x_{(+)}|$

Thompson suspected that the positive particle was H+ and H was the source of the negative particle. Since H is electronically neutral,

$$\text{Then } |e_{(-)}| = |e_{(+)}|$$

So,

$$\frac{|\Delta x_{(-)}|}{|\Delta x_{(+)}|} = large$$

Since the above ratio is large the ratio of masses will be large and thus $m_{(-)} >> m_{(+)}$

This negative particle from the cathode ray tubes was named the **<u>electron</u>** ($m = 9.11 \times 10^{-31}$ kg).

<u>“ATOMS ARE NOT INDIVISIBLE”!</u>

Proton was found approximately 1840 times heavier than an electron.

Thomson’s Model

On the basis of his experiments on discharge tubes, Thomson proposed that atoms can be considered as a large positively charged body with a number of small negatively charged electrons scattered throughout it. This model (Fig.1.1) was called as plum pudding model of the atom.

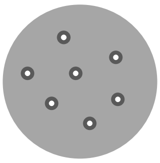


Fig. 1.1: A pictorial representation of Thomson’s plum-pudding model

The electrons represent the plums in the pudding made of positive charge. It is sometimes also called as watermelon model. In this, the juicy pulp of the watermelon represents the positive charge and the seeds represent the electrons.

B) Discovery of the Nucleus

Ernest Rutherford
(1871-1937)
Won Nobel Prize in
Chemistry in 1908

Ernest Rutherford performed an experiment called 'Gold Foil Experiment' or 'α- ray scattering experiment' to test the structure of an atom as proposed by Thomson.

- α-particles were known to be heavy, charged particles
- α-particles are helium ($_{2}He^{4}$) atoms-this was unknown in 1911.

In 1911 Rutherford tested the plum pudding model. (Experiments were done with a postdoc, Hans Geiger, and an undergraduate, E. Marsden.) In this experiment a beam of fast-moving alpha particles (positively charged helium ions) was passed through a very thin foil of gold. He expected that the alpha particles would just pass straight through the gold foil and could be detected by a photographic plate. But, the actual results of the experiment (Fig. 1.2) were quite surprising.

(Case-I): when no gold foil

Count rate = ____________________

α-particles / min

(Case-II): when gold foil is placed

Count rate =

____

α-particles / min.

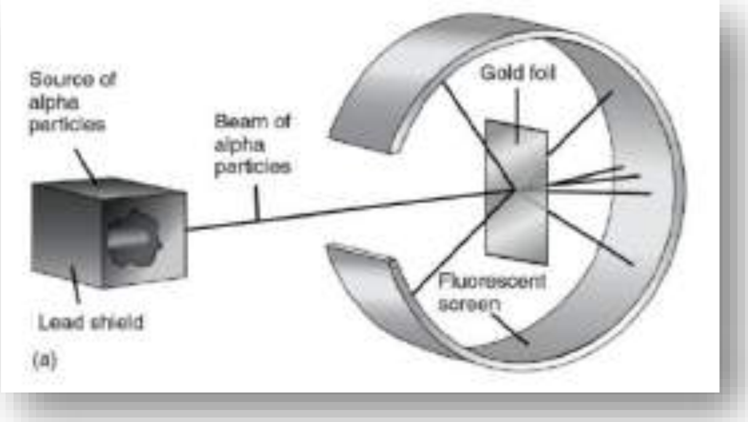


Fig 1.2: Schematic representation of Rutherford's α-ray scattering experiment

It appeared that all of the α-particles passed through the Au foil. A detector was built that could swing around to the front side and measure any potential back scattered particles.

It was observed that few particles were deflected from their path. Some of these deflected slightly while a few deflected through large angles and about 1 in 10,000 α- particles suffered a rebound

(Case-II): when backscattering occurs

Count rate = ____________________ α-particles / min, Backscattering was detected!!

These results led Rutherford to conclude that:

1. The atom contained some dense and positively charged region located at the center of the atom that he called as nucleus.
2. All the positive charge of the atom and most of its mass was contained in the nucleus.
3. The rest of the atom must be empty space which contains the much smaller and negatively charged electrons.

4. The model proposed by Rutherford explained the observation in the α-ray scattering experiments as shown below in Fig 1.3.

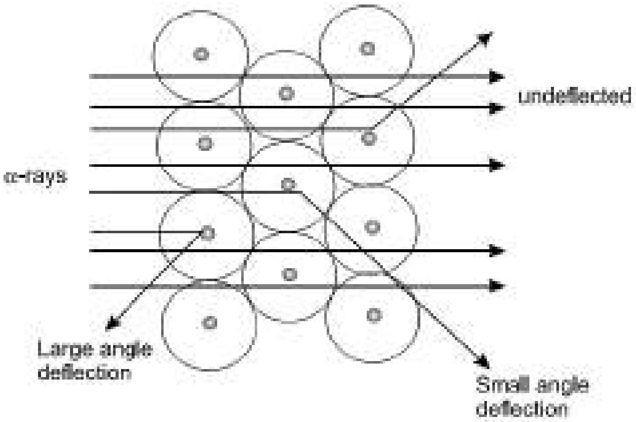


Fig 1.3: Explanation of the results of α- ray scattering model

Table 1.1: Properties of the proton, electron and neutron

	Proton	Electron	Neutron
Charge/C	+1.602 x 10^{-19}	-1.602 x 10^{-19}	0
Charge number (relative charge)	1	-1	0
Rest mass/kg	1.673 x 10^{-27}	9.109 x 10^{-31}	1.675 x 10^{-27}
Relative mass	1837	1	1839

1. A neutron and a proton have approximately the same mass and, relative to these, an electron has negligible mass (Table 1.1).

2. The charge on a proton is positive and of equal magnitude, but opposite sign, to that on a negatively charged electron; a neutron has no charge.

3. In an atom of any element, there are equal numbers of protons and electrons and so an atom is neutral.

4. The nucleus of an atom consists of protons and (with the exception of protium; see Section 9.3) neutrons, and is positively charged.

A nuclide is a particular type of atom and possesses a characteristic atomic number, Z, which is equal to the number of protons in the nucleus. Atom is electrically neutral, so, Z also equals the number of electrons. The mass number, A, of a nuclide is the number of protons and neutrons in the nucleus. A shorthand method of showing the atomic number and mass number of a nuclide along with its symbol, E, is:

$${}^{A}_{Z}E$$

Drawbacks of Rutherford's Model:

According to the Maxwell's theory of electromagnetic radiation, a charged accelerated particle would continuously emit radiation and ultimately lose energy.

Since the <u>electron in the atom is also a charged particle and is under acceleration</u>, it is expected to continuously lose energy. As a consequence, the electron moving around the nucleus would approach the nucleus by a spiralpath

(Fig. 1.4) and the <u>structure of atom would collapse</u>.

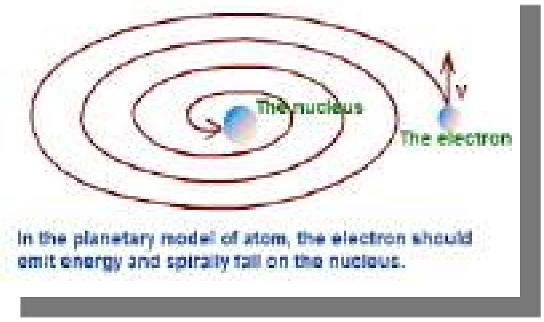


Fig. 1.4: Failure of Rutherford's scattering experiment model

But in reality it does not happen so; we can say that the Rutherford's model **<u>failed to explain thestability of the atom.</u>**

The next attempt to suggest a model for atom was made by Neils Bohr- a student of Rutherford. This model used the concept of quantisation of energy of electrons in the atom. Since this fact was suggested by line spectrum of hydrogen atom it is worthwhile to understand the meaning of a spectrum. For this we begin with the understanding of the nature of an electromagnetic radiation.

1.2 ELECTROMAGNETIC RADIATIONS

Electromagnetic radiation is a kind of energy, which is transmitted through space in the form of electric and magnetic fields. These do not require any medium to propagate. Visible light, radiant heat, radio waves, X-rays and gamma radiation are some of the examples of electromagnetic radiations. According to the Maxwell's theory, an electromagnetic radiation can be visualised as oscillating electric and magnetic fields. These travel as waves in the planes perpendicular to each other and also to the direction of propagation. (Fig. 1.5 (a)). These radiations travel with the velocity of light (3.0 × 108 m s-1).

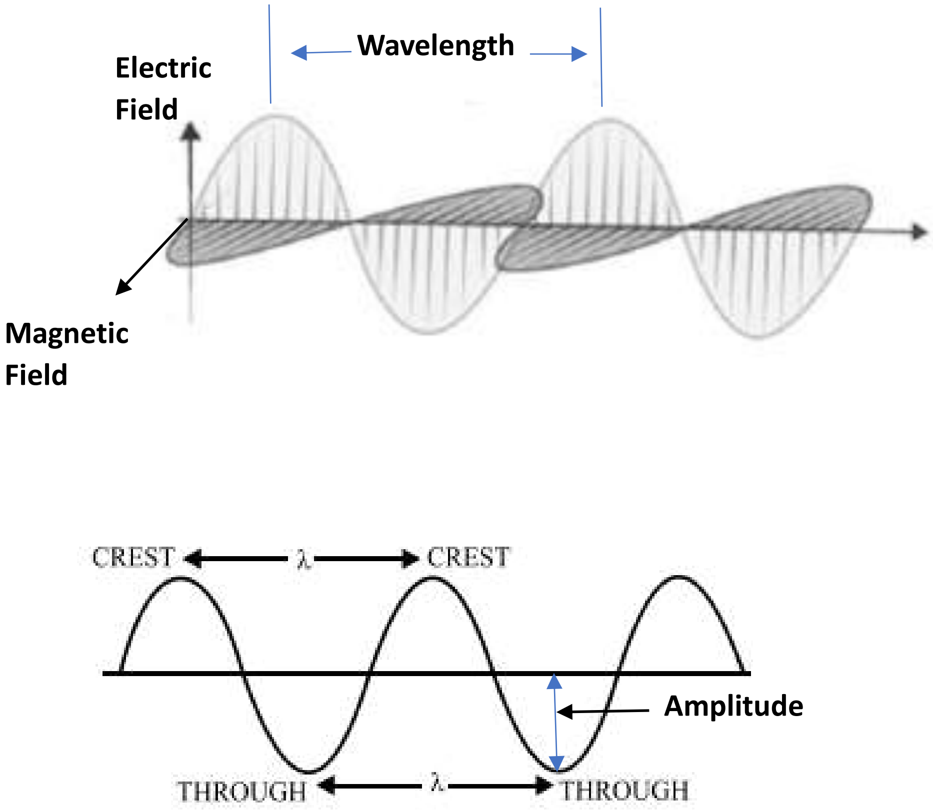


Fig. 1.5: (a) An electromagnetic wave showing electric and magnetic fields travelling in planes perpendicular to each other and also to the direction of propagation (b) Characteristics of electromagnetic wave

Characteristic Parameters of Electromagnetic Radiations

The electromagnetic radiations are characterized by a number of parameters. These are

Amplitude: This refers to the maximum height to which the wave oscillates. It equals the height of the crests or depth of the troughs.

Wavelength: It is the linear distance between two consecutive wave-crests or wave- troughs as shown in Fig. 3.6(b). It is represented by a Greek letter lambda (λ) and is expressed in terms of m, cm, nm or Angstrom (1Å = 10-10 m).

Frequency: It is defined as the number of wave crests or wave troughs that pass through a given point per second. It is represented by a Greek letter nu (ν) and is expressed in terms of s^{-1}. It is also called as Hz (Hertz).

Wave number: It equals the number of waves per unit length. It is denoted as v (nu bar) and is equal to the reciprocal of the wavelength. The SI unit of v is m–1 (meter inverse). However, sometimes it is also expressed as cm^{-1}

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

Velocity: it is defined as the linear distance travelled by the wave in one second. The velocity in meters per second can be obtained by multiplying frequency in Hertz (s^{-1}) with wavelength in meters. $c = \upsilon\lambda$ or $\upsilon = \frac{c}{\lambda}$

The velocity of a radiation depends on the medium. In vacuum the velocity is equal to 3.00×10^8 m s^{-1}. The electromagnetic radiations also show the characteristics of particles. These are called as quanta. These quanta are actually bundles of energy. A quantum of visible light is called a photon. The energy of the quantum (or photon) is proportional to the frequency of the radiation. The two are related as $E = h\upsilon$

The energy of the quantum can also be related to the wavelength or wave number as

$E = h\frac{c}{\lambda}$ or $E = hc\bar{\upsilon}$

the energy of photon can be readily calculated from these equations if we know the frequency, wavelength or wave number

Electromagnetic Spectrum

Depending on their characteristics (wavelength, frequency and wave number) electromagnetic radiations are of many types and constitute what is called as an electromagnetic spectrum. (Fig. 1.6) The part of the spectrum that we can see is called visible spectrum and is a very small part of the overall spectrum.

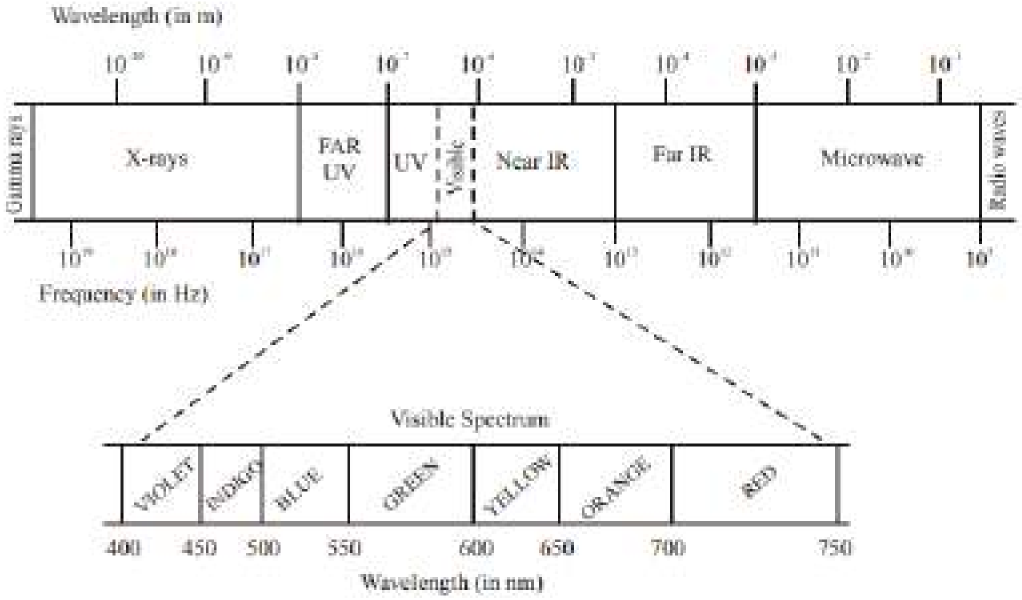


Fig. 1.6: The electromagnetic spectrum

Line Spectrum

when we pass a beam of sunlight through a prism, we get a range of colours from violet to red (VIBGYOR) in the form of a spectrum (like rainbow). This is called a continuous spectrum because the wavelengths of the light vary continuously that is without any break. Let us take another example. You are aware of the flame tests for identifying cations in the qualitative analysis. Compounds of sodium impart a bright yellow colour to the flame; copper gives a green flame while strontium gives a crimson red coloured flame. If we pass such a light through a prism, it gets separated into a set of lines. This is called as a line spectrum. Fig. 1.7 differentiates between a continuous and a line spectrum.

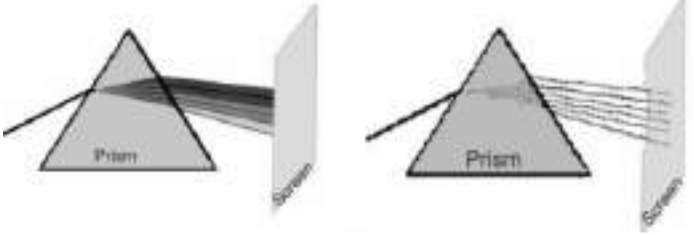
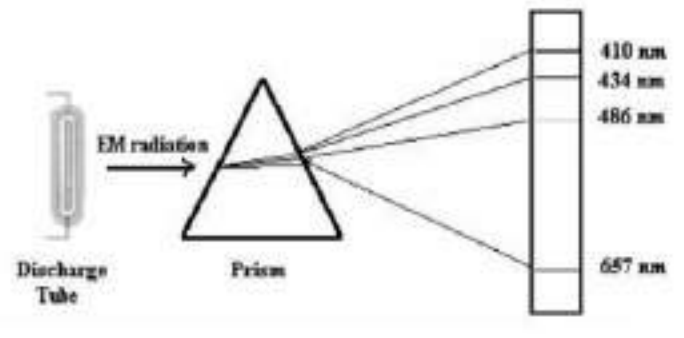


Fig. 1.7: a) a Continuous spectrum b) a Line spectrum

Line Spectrum of Hydrogen Atom

When an electric discharge is passed through a discharge tube containing hydrogengas at low pressure, it emits some light. When this light is passed through a prism itsplits up into a set of five lines. This spectrum is called the line spectrum of hydrogen(Fig. 1.8)



Johann Balmer
(1825-1898)

Fig. 1.8: A schematic diagram showing line spectrum of hydrogen in the visible range

On careful analysis of the hydrogen spectrum, it was found to consist of a few sets of linesin the ultraviolet, visible and infrared regions. These sets of lines were observed by different scientists. The hydrogen spectrum can be explained effectively using another atomic theory proposed by Niels Bohr.

1.3 BOHR THEORY AND THE ATOMIC SPECTRA OF HYDROGEN

Bohr’s Atomic Model:

In 1913, Niels Bohr (1885-1962) proposed another model of the atom where electrons move around the nucleus in circular paths. Bohr’s atomic model is built upon a set of postulates, which are as follows:

Bohr won the Nobel Prize in Physics in 1922 for his work

1. The electrons move in definite circular paths around the nucleus (Fig 3.10). These circular paths are termed as orbits and postulated that as long as the electron is in a given orbit its energy does not change (or energy remains fixed). These orbits were therefore referred to as stationary orbits or stationary states or non-radiating orbits.

2. The angular momentum of an electron of mass m_e moving in a circular orbit of radius r and velocity v is an integral multiple of h/2π.

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

Where n = positive integer (1, 2, 3…) known as the **principal quantum number**.

3. The electron can change its orbit by absorbing or releasing energy. An electron at a lower (initial) state of energy, E_i can go to a (final) higher state of energy, E_f by absorbing (Fig 1.9) a single photon of energy given by $E = h\nu = E_f - E_i$ ...(2.1a)

Figure 2.1a

Figure 2.1b

Fig. 1.9: Absorption and emission of photon causes the electron to change its energy level

Similarly, when electron changes its orbit from a higher initial state of energy E_i to a lower final state of energy E_f, a single photon of energy hν is released (Fig. 2.1b)

Thus, the appearance of discrete lines in the spectrum of atomic hydrogen can be explained in terms of jump of electrons between different selected orbits, radiation of various 'ν's are emitted thereby.

In Bohr's theory the basic Rutherford's model is maintained only an extra restriction regarding angular momentum is introduced. Hence, the condition of equilibrium between centrifugal and coulombic force still applies to these orbits.

For an electron moving in an orbit of radius r around the nucleus of Z unit positive charge, we have,

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\varepsilon_0 r^2}$$

$$\text{or, } mv^2r = \frac{Ze^2}{4\pi\varepsilon_0} \text{ ------------------------(i)}$$

At the same time Bohr condition of angular momentum requires,

$$mvr = \frac{nh}{2\pi} \qquad \text{or squaring} m^2v^2r^2 = \frac{n^2h^2}{4\pi^2} \text{--------------- (ii)}$$

Dividing (ii) by (i) to eliminate v^2

$$\text{m} = \frac{n^2h^2\varepsilon_0}{\pi Ze^2 r} \text{or,} r = \frac{n^2h^2\varepsilon_0}{\pi Ze^2 m} \text{ ---------------(iii)}$$

This is the expression for radii of permitted Bohr orbits.

Now, for n= 1, we will get the radius of first Bohr orbit which is denoted by a_0 which is actually exactly same for H atom, when Z= 1, n= 1 and r = 0.0529 nm. This is called atomic unit of length or Bohr radius. The quantity a_0 is calledthe radius of the first Bohr orbit and is a measure of the size of atoms. It isalso a measure of the domain in which quantum effects are dominant: forif an electron in a one-electron atom is regarded as being contained in abox of size a_0/Z, with kinetic energy $p^2/2m_0 = Z^2e^2/8\pi\varepsilon_0 a_o$ according toBohr's semi-classical picture, then its mean momentum p is zero (otherwiseit would not be contained in the box).

Energy of An Electron in A Bohr Orbit:

An electron in the atom possesses, kinetic energy (K.E) and potential energy (P. E)

Total Energy, E= K.E. + P.E.

Kinetic Energy, K. E. = $\frac{1}{2}mv^2$ for a particle of mass m and velocity v

Now for an electron we know,

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\varepsilon_0 r^2}$$

Therefore,

$$\frac{1}{2}mv^2 = \frac{Ze^2}{8\pi\varepsilon_0 r^2}$$

Kinetic energy of the electron = $E_{KE} = \frac{Ze^2}{8\pi\varepsilon_0 r}$

Potential Energy of an electron in an atom is calculated with reference to its position at infinity from the nucleus, at this point potential energy is zero. Potential energy is then given by the total work done in bringing the electron from infinity to its position in the orbit of radius ‘r’.

The force involved is coulombic force of attraction by the nucleus = $\frac{Ze^2}{4\pi\varepsilon_0 r^2}$

The work done, W and hence the Potential energy, $E_{PE} = \int_{r=\infty}^{r=r} \frac{Ze^2}{4\pi\varepsilon_0 r^2}dr = -\frac{Ze^2}{4\pi\varepsilon_0 r}$

So, total energy, $E = E_{KE} + E_{PE}$

$$= \frac{Ze^2}{8\pi\varepsilon_0 r} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$= -\frac{Ze^2}{8\pi\varepsilon_0 r}$$

Now we know $r = \frac{n^2h^2\varepsilon_0}{\pi Ze^2 m}$

Therefore total energy

$$\boxed{\mathrm{E} = -\frac{Z^2 e^4 m}{8\varepsilon_0^2 n^2 h^2} = = R_H \left(\frac{1}{n^2}\right)}$$

Where, $R_H = -\frac{mZ^2 e^4}{8h^2 \varepsilon_0^2}$

Where, m = mass of the electron
h = Planck’s constant
z = nuclear charge
ε_0= permitivitty of the medium

Atomic Spectra of Hydrogen

The atomic spectrum refers to the unique pattern of spectral lines emitted or absorbed by atoms when they undergo transitions between energy levels. These spectral lines are characteristic of each element and provide valuable information about the atom's structure and properties.
When an atom absorbs energy, typically through heating or exposure to electromagnetic radiation, its electrons can move to higher energy levels. Conversely, when these excited electrons return to lower energy levels, they emit energy in the form of photons with specific frequencies corresponding to the energy difference between the initial and final states. These emitted photons form the atomic spectrum of the element.
The atomic spectrum can be observed across different regions of the electromagnetic spectrum, including the visible, ultraviolet, infrared, and even X-ray and gamma-ray regions, depending on the energy transitions involved.

There are several types of atomic spectra:

Emission Spectrum: This spectrum is produced when atoms emit photons as their electrons transition from higher to lower energy levels. Each element emits a unique set of spectral lines, allowing for identification and analysis.

Absorption Spectrum: When a continuous spectrum of electromagnetic radiation passes through a cool, dilute gas, atoms absorb specific frequencies of light, resulting in dark lines superimposed on the continuous spectrum. These dark lines, known as absorption lines, correspond to the frequencies of light that the atoms have absorbed.

Fluorescence Spectrum: In fluorescence, atoms or molecules absorb photons of a particular wavelength and then re-emit them at longer wavelengths, producing a characteristic fluorescence spectrum.

X-ray Spectrum: In X-ray spectroscopy, atoms emit X-rays when electrons transition from higher to lower energy levels. X-ray spectra are used in various scientific and medical applications, including material analysis and medical imaging.

Atomic spectra are fundamental to many areas of science, including chemistry, and physics. They provide valuable information about the composition, temperature, and other properties of celestial objects, help identify elements in laboratory experiments, and contribute to our understanding of atomic and molecular structure.

The atomic spectra of hydrogen are fascinating and historically significant in the field of chemistry and physics. When the electrons in a hydrogen atom move between energy levels, they emit or absorb electromagnetic radiation, resulting in distinct spectral lines. These lines are characteristic of the elements and can be used to identify them.

The hydrogen spectrum is particularly well-known because it was one of the first to be studied extensively and provided crucial insights into atomic structure. Danish physicist Niels Bohr developed a theoretical model of the hydrogen atom in 1913, which successfully explained the observed spectral lines.

The hydrogen spectrum consists of several series of spectral lines, including the Lyman series, Balmer series, Paschen series, Brackett series, and Pfund series. Each series corresponds to transitions between specific energy levels in the hydrogen atom. The Balmer series, for example, corresponds to electron transitions to or from the second energy level (n=2), while the Lyman series involves transitions to or from the first energy level (n=1).

These spectral lines can be observed in various regions of the electromagnetic spectrum, including the visible, ultraviolet, and infrared. For example, the Balmer series includes visible spectral lines, making it particularly important for early spectroscopic studies.

The discovery and understanding of hydrogen's atomic spectra played a crucial role in the development of quantum mechanics and our modern understanding of atomic structure. Today, hydrogen spectra continue to be studied in various scientific disciplines, including physics, astronomy, and chemistry, providing valuable insights into fundamental processes at the atomic level.

Bohr obtained the following expressions for the energy of an electron in stationary states of hydrogen atom by using his postulates:

$$\boxed{\textbf{Energy of the orbit, } E_n = R_H \left(\frac{1}{n^2}\right)}$$

If*n* increases the value of the energy decreases. It means that as we go farther from the nucleus the energy of the orbit goes on increasing.Now let us consider two orbits with quantum umber n_1 and n_2 and $n_1 > n_2$. Therefore, corresponding energies are $E_2 > E_1$.

If an electron is initially excited to the higher orbit (n_2) and then allowed to return to the lower orbit (n_1) the difference of energy (E_2-E_1) will be emitted in the form of radiation and give rise to a spectral line. The frequency, ν of this line will be given by, $(E_2 - E_1) = h\nu$.

Now from the expression of energy of an electron,

$$E_1 = R_H \frac{1}{n_1^2}, \qquad E_2 = R_H \frac{1}{n_2^2}$$

$$E_2 - E_1 = R_H \left[\frac{1}{n_2^2} - \frac{1}{n_1^2}\right]$$

$$E_2 - E_1 = -R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

Putting the value of R_H we get,

$$h\nu = \frac{e^4 m}{8\varepsilon_0^2 h^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right], \text{ (here, Z= 1, in case of H atom)}$$

$$\nu = \frac{e^4 m}{8\varepsilon_0^2 h^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\bar{\upsilon} = \frac{\nu}{c} = \frac{e^4 m}{8\varepsilon_0^2 h^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\boxed{\bar{\upsilon} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right], \text{ R= Rydberg constant}}$$

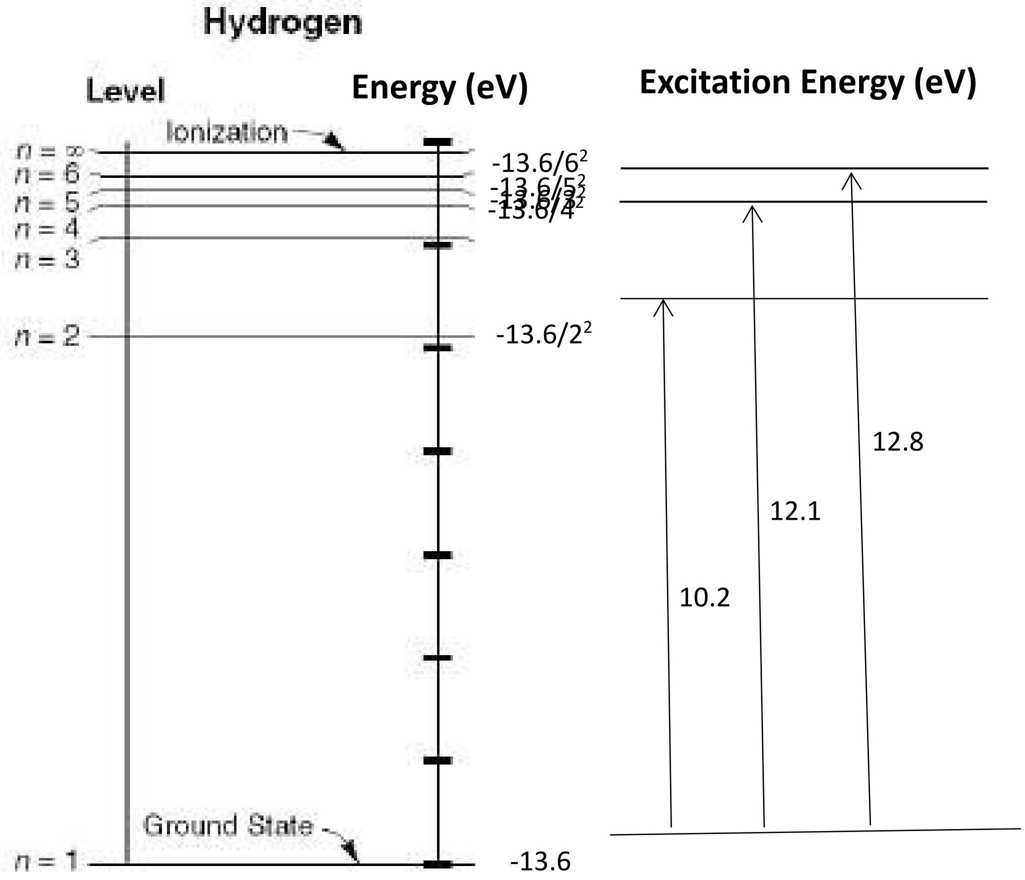
The value of R = 1.096776x 107m^{-1}

If we calculate the energy for n= 1,

$$E_1 = \frac{e^4 m}{8\varepsilon_0^2 h^3} = 13.6 \text{ eV}$$

This energy is called ground state energy of an electron within an atom.

The energy levels are indicated schematically in Figure given below. The electron energy is quantized, with only certain discrete values allowed. In the lowest energy level, known as the ground state, the electron has energy, E1= 13.6 eV. The higher states, n= 2,3,4,...with energies−3.6 eV,−1.5 eV,−0.85 eV,... are called excited states. The n is known as the principal quantum numberof the atom. It tells us which energy level will be occupied by the electron.



The **Lyman series** is a series of spectral lines in the atomic spectrum of hydrogen. It was first observed by the American physicist Theodore Lyman in 1906. The series corresponds to transitions of electrons in hydrogen atoms between higher energy levels (with principal quantum number n>1) and the lowest energy level (n=1).

In the Lyman series, electrons transition from higher energy levels to the first energy level (n=1). As these transitions occur, energy is released in the form of photons. Each photon carries energy corresponding to the energy difference between the initial and final energy levels. The frequency of the emitted photons in the Lyman series falls within the ultraviolet region of the electromagnetic spectrum.

The Lyman series is particularly important because it represents transitions to the lowest energy level in the hydrogen atom. The first line in the Lyman series, known as Lyman-α (Ly-α), corresponds to the transition of an electron from the second energy level (n=2) to the first energy level (n=1). Subsequent lines in the series represent transitions from higher energy levels to the first energy level.

The Lyman series is often used in astrophysics to study the properties of celestial objects, such as stars and galaxies, based on the absorption or emission lines observed in their spectra. It also played a crucial role in the development of quantum mechanics and our understanding of atomic structure, particularly in the early 20th century when the quantized nature of energy levels in atoms was being explored.

In spite of the successes of the Bohr model to predict the spectra of hydrogen, and hydrogen-like ions, there are several results that it cannot explain. It cannot be applied to atoms with two or more electrons since it does not take into account the Coulomb interaction between electrons. A closer look at the atomic spectral lines emitted from various gases shows that some spectral. This theory cannot be applied to multi-electron atoms. It does not provide a method to calculate relative intensities of spectral lines.

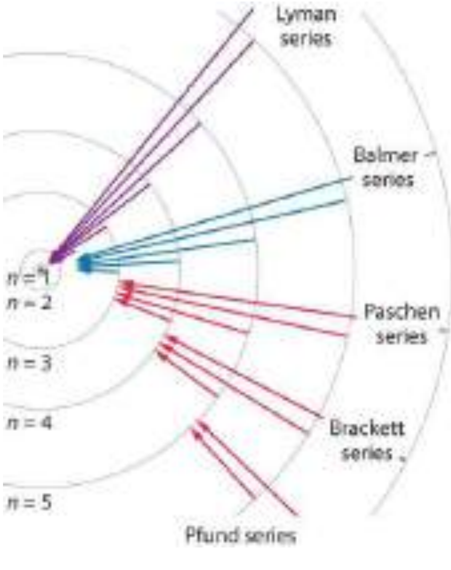
The **Balmer series** is another important spectral series in the atomic spectrum of hydrogen. It was discovered by the Swiss physicist Johann Balmer in 1885. The Balmer series corresponds to transitions of electrons in hydrogen atoms between higher energy levels (with principal quantum number ($n>2$)and the second energy level ($n=2$).

In the Balmer series, electrons transition from higher energy levels to the second energy level ($n=2$). As these transitions occur, energy is released in the form of photons. Each photon carries energy corresponding to the energy difference between the initial and final energy levels. The wavelengths of the emitted photons in the Balmer series fall within the visible region of the electromagnetic spectrum, making them observable with optical instruments.

The Balmer series is particularly significant because it includes transitions to and from the second energy level, which lies closer to the ground state ($n=1$) than higher energy levels. The first line in the Balmer series, known as H-α (Balmer-α), corresponds to the transition of an electron from the third energy level ($n=3$) to the second energy level ($n=2$). Subsequent lines in the series represent transitions from higher energy levels to the second energy level.

The Balmer series played a crucial role in the historical development of atomic theory, providing evidence for the quantized nature of energy levels in atoms. It is widely used in astronomy to study the properties of stars and other celestial objects based on the absorption or emission lines observed in their spectra. Additionally, the Balmer series has practical applications in spectroscopy and optical instrumentation.

Besides Lyman series in ultraviolet region and Balmer series in visible region there are three others in the infrared region- **Paschen, Bracket and Pfund** series. Another series called Humphreys lies in the far-infrared region.



Lyman series $\frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$, $n_1=1, n_2= 2, 3, 4….$

Balmer series $\frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$, $n_1=2, n_2= 3, 4, 5….$

Paschen series $\frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$, $n_1=3, n_2=4, 5, 6….$

Bracket series $\frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$, $n_1=4, n_2= 5, 6, 7….$

Pfund series $\frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$, $n_1=5, n_2= 6, 7, 8…$

In spite of the successes of the Bohr model to predict the spectra of hydrogen, and hydrogen-like ions, there are several results that it cannot explain. It cannot be applied to atoms with two or more electrons since it does not take into account the Coulomb interaction between electrons. A closer look at the atomic spectral lines emitted from various gases shows that some spectral. This theory cannot be applied to multi-electron atoms. It does not provide a method to calculate relative intensities of spectral lines.

The limitation of the Newtonian mechanics for atomic system led to the development of a new mechanics suitable for subatomic particles with prominent wave character and this was termed as quantum mechanics. The structure of atoms can be successfully described by the theory of quantum mechanics, and there is no doubt that in order to understand atomic structure one has to learn quantum mechanics. However, quantum mechanics came into being as the culmination of the development of earlier theories like Bohr's theory of hydrogen, based on Rutherford's nuclear atom and incorporating the ideas of Planck, which was the famous starting point for atomic structure. Bohr's semi-classical theory was not general enough to describe more than the gross features of the simplest one-electron atom, but it provided a model of an atom which is easily visualized. Because of its vividness we tend to retain Bohr's picture in the back of the mind, although we reject the classical mechanistic parts of Bohr's model as a serious explanation of atomic structure.

Quantum mechanics is the branch of physics that deals with the behaviour of matter and energy on the smallest scales, typically at the level of atoms and subatomic particles. It provides a theoretical framework for understanding the fundamental properties of particles and the interactions between them. Quantum mechanics revolutionized our understanding of nature and has led to numerous technological advancements across various fields.

1.4 KEY PRINCIPLES AND CONCEPTS OF QUANTUM MECHANICS:

Wave-Particle Duality: One of the most fundamental concepts in quantum mechanics is the idea that particles, such as electrons and photons, exhibit both wave-like and particle-like behaviour. This duality is described by wave functions, which represent the probability amplitudes of finding particles in different states.

Quantization of Energy: In quantum mechanics, energy levels are quantized, meaning they can only take on certain discrete values. This is in contrast to classical physics, where energy is continuous. The quantization of energy is evident in phenomena such as the discrete atomic spectra observed in spectroscopy.

Uncertainty Principle: Proposed by Werner Heisenberg, the uncertainty principle states that certain pairs of physical properties, such as position and momentum, cannot be precisely known simultaneously. There is a fundamental limit to the precision with which these properties can be measured.

Quantum Superposition: Quantum superposition is the principle that a quantum system can exist in multiple states simultaneously until it is measured or observed. This leads to phenomena such as interference, where the probabilities of different outcomes interfere with each other.

Quantum Entanglement: Quantum entanglement is a phenomenon where the quantum states of two or more particles become correlated in such a way that the state of one particle is dependent on the state of another, even when they are separated by large distances. This concept has profound implications for quantum information and communication.

Quantum Tunnelling: Quantum tunnelling is the phenomenon where particles can pass through potential energy barriers that would be classically forbidden. It plays a crucial role in various phenomena, including nuclear fusion in stars and the operation of semiconductor devices.

Quantum mechanics has applications in a wide range of fields, including quantum computing, cryptography, materials science, and particle physics. Its principles have reshaped our understanding of the universe and continue to drive scientific and technological progress.

1.5 DE BROGLIE MODIFICATION: MATTER AS A WAVE

1924 Louis de Broglie postulated that just as light has wave-like and particle-like properties, matter (electrons) must also be both particle-like and a wave-like.

Using Einstein's idea that the momentum of a photon
(p) = h/λ, de Broglie suggested:

Wavelength of a particle = $\lambda= h/p$,h = Planck's constant
m = mass of the particle
v = speed of the particle
mv = linear momentum (p) so,$\lambda= h/(mv)$

de Broglie wavelength for matter waves $\boxed{\lambda= h/p = h/(mv)}$

1.6 HEISENBERG'S UNCERTAINTY PRINCIPLE:

Werner Heisenberg
(1901-1976)
Heisenberg got the phys.
is Nobel prize in 1932

From an analysis of the wave particle dualism of the matter, W. Heisenberg (1927) stated that it is not possible to determine simultaneously both the position and the momentum of a body with any arbitrary desired accuracy. The product of uncertainty Δx in the position of a body at any instant and the uncertainty Δp in the momentum at the same instant will be at least of the order of h, the Planck constant. Mathematically stated

$$\Delta x \, \Delta p \geq h/4\pi$$

If the position of an object is known exactly (i.e., $\Delta x = 0$), then the uncertainty in the momentum must be infinite, meaning that we cannot say anything about the velocity. Similarly, if the velocity is known exactly, then the position would be entirely uncertain and the particle could be anywhere. It means that we cannot say anything about the position of the particle. In actual practice none of the two properties can be measured with certainty. Due to the small value of the Planck's constant, h (6.626×10^{-34} J s) this principle is not relevant while making measurements of large objects like car, bus or aeroplane etc. It is relevant, only when you are making measurements on very small objects such as electrons. Heisenberg's principle questioned the validity of Bohr's model. It is so because according to Bohr's model we can precisely calculate the radius of the orbit (i.e., the position of the electron) and the velocity of electron in it. But it is not possible according to Heisenberg's principle. It motivated many scientists to develop newer models of the atom using the dual nature of the electron. This resulted into the development of a Quantum mechanical or Wave Mechanical Model of the atom discussed in the next section.

1.7 WAVE MECHANICAL MODEL OF ATOM:

Wave Mechanical Model of atom was proposed by Erwin Schrödinger- an Austrian physicist in 1926. This model is basically a formalism or a mathematical recipe, which is based on some postulates that have no foundation in classical physics. The correctness of these postulates can be justified in terms of the correctness of the results predicted by them. According to this Model, the motion of electron inside the atom could be described in terms of a mathematical function called, wave function, ψ (Greek letter, psi). The wave functions are assumed to contain all the information about the electron and are obtained by solving a differential equation called Schrödinger wave equation (SWE). The square of the wave function ψ^2 is a measure of the probability of finding an electron in a three-dimensional space around the nucleus. On solving the SWE for hydrogen atom, we get a number of wave functions, which are characterized by three quantum numbers viz.,

- Principal quantum number, n

- Azimuthal quantum number, l
- Magnetic quantum number, m_l
- Magnetic spin quantum number, m_s

These quantum numbers arise in the process of logically solving the wave equation. Every electron in an atom has a unique (different) set of quantum numbers which help to describe the three-dimensional region where there is maximum probability of finding the electron. This region is called as atomic orbital or simply orbital.

The three quantum numbers describe the size, shape, and orientation of the atomic orbitals in space. There is an additional quantum number which does not follow from the Schrödinger wave equation but is introduced to account for electron spin. The fourth quantum number thus help in designating the electrons present in the atom. Let us understand the significance of each of these quantum numbers.

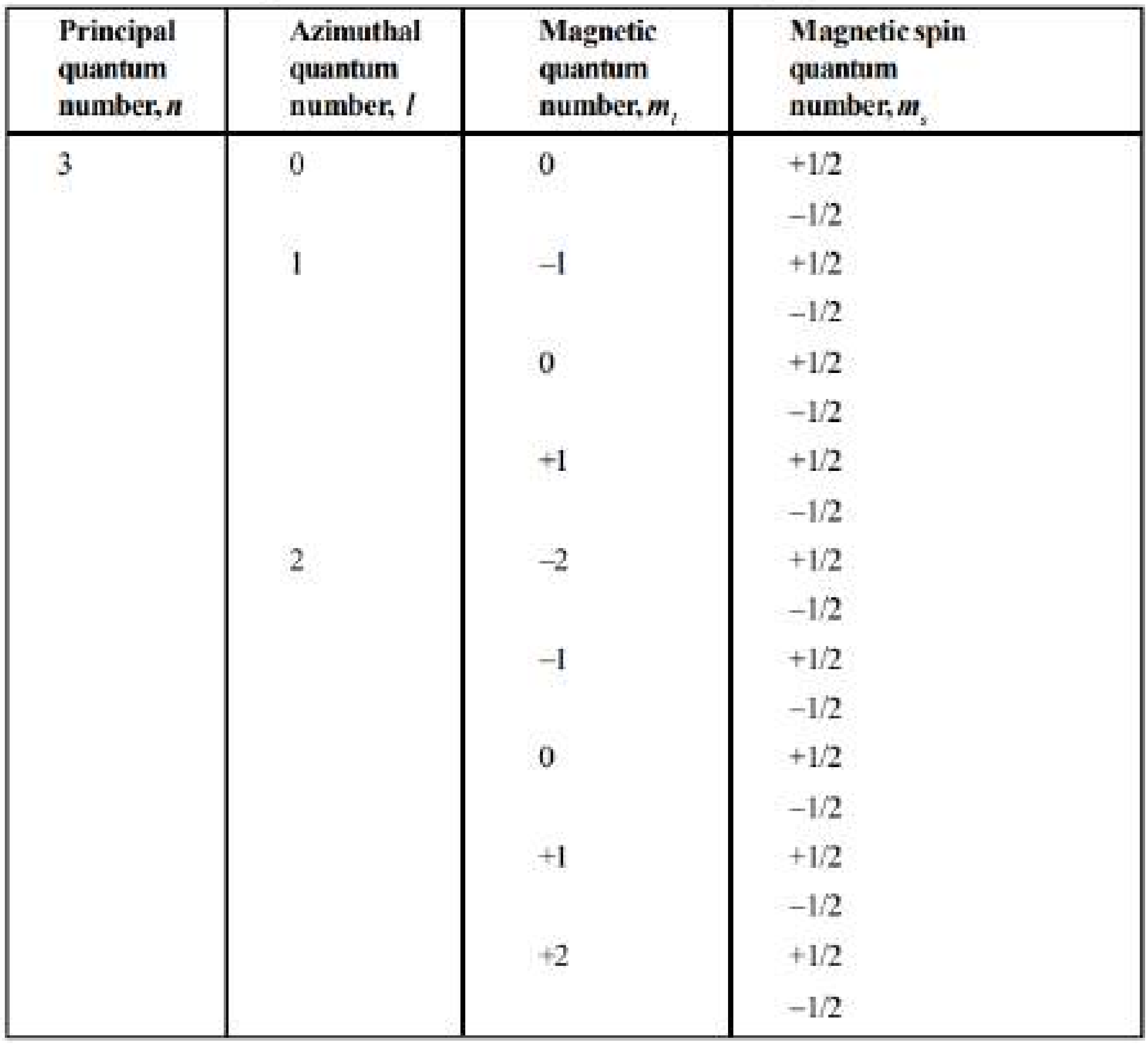
The principal quantum number, n describes the energy level (or principal shell) of the electron within the atom. n can have only positive non zero integral values (i.e., n = 1,2,3,4……). This means that in an atom, the electron can have only certain energies. Thus, we may say that n quantizes energy of the electron. The principal quantum number also determines the mean distance of the electron from the nucleus, i.e., its size. Greater the value of n farther is the electron from the nucleus. Each principal shell can accommodate a maximum of 2n 2 electrons, i.e., n =1 number of electrons: 2 n =2 number of electrons: 8 n =3 number of electrons: 18 and so on.

Azimuthal quantum number, l is related to the geometrical shape of the orbital. The value of l may be zero or a positive integer less than or equal to n–1 (n is the principal quantum number), i.e., l = 0,1,2,3…… (n–1). Different values of l correspond to different types of subshells and each subshell contains orbitals of a given shape. l = 0 , corresponds to s-subshell and contains the orbital with spherical shape called as s orbital. l = 1, corresponds to p-subshell and contains the orbitals with a dumb-bell shape called as p-orbitals. There are three p-orbitals in each p-subshell l = 2 , corresponds to d-subshell and contains the orbitals with a cloverleaf shape called as d-orbitals. l = 3 , corresponds to f-subshell and contain f orbitals. There are seven f-orbitals in each f-subshell. The shapes of s, p and d orbitals will be discussed in the next subsection.

Magnetic quantum number, m_l describes the direction or orientation of the orbital in space. The quantum number ml may have any integral value from – l to + l. For example, for l = 1; m_l can have the values as –1,0 and 1.

Magnetic spin quantum number, $m_s$describes the spin of the electron i.e., whether it is clockwise or anticlockwise. The quantum number, m_s does not arise while solving SWE. The clockwise and anticlockwise direction of electron spin has arbitrarily been assigned the values as +1/2 and –1/2 respectively. To sum up, let us take an example of an electron belonging to the third shell (n = 3). This electron can be in an s-subshell (l = 0) or a p-subshell (l = 1) or a d-subshell (l = 2). If it happens to be in a p-subshell it may be in any of the three possible p orbitals (corresponding to $m_l = -1, 0 + 1$ directed along x, y or z– axis. And within the orbital it may have clockwise ($m_s = +\frac{1}{2}$) or anti-clockwise ($m_s = -\frac{1}{2}$) direction of electron spin.

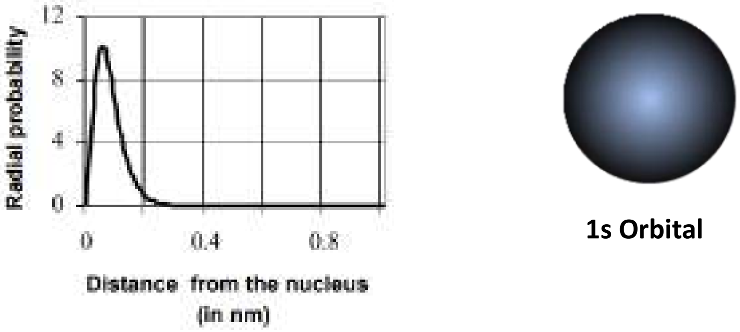
The possible values of different quantum numbers for an electron belonging to the third shell are given below:



Principal quantum number, n	Azimuthal quantum number, l	Magnetic quantum number, m_l	Magnetic spin quantum number, m_s
3	0	0	+1/2
			−1/2
	1	−1	+1/2
			−1/2
		0	+1/2
			−1/2
		+1	+1/2
			−1/2
	2	−2	+1/2
			−1/2
		−1	+1/2
			−1/2
		0	+1/2
			−1/2
		+1	+1/2
			−1/2
		+2	+1/2
			−1/2

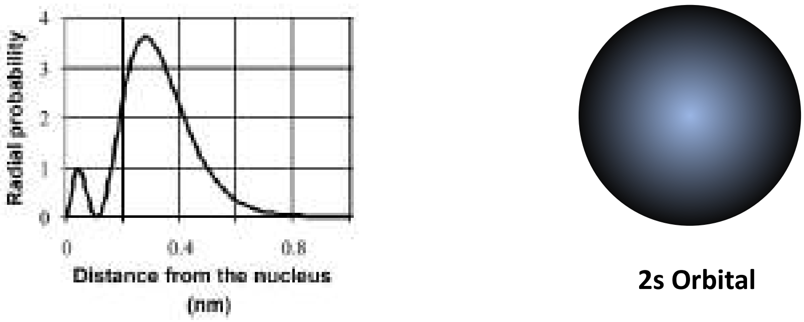
1.8 SHAPES OF ORBITALS

We have defined an orbital as “the three-dimensional region of space around the nucleus where there is maximum probability of finding the electron”. Let us try to understand the meaning of an orbital by taking the example of 1s orbital (n =1; l =0). This can be understood in terms of a radial probability curve. Such a curve gives the variation of the probability of finding the electron as a function of distance from the nucleus. For 1s orbital the radial probability curve (Fig. 1.10 (a)) shows that the probability of finding the electron in 1s orbital increases as we move away from the nucleus and reaches a maximum at a certain distance (= 0.0529 nm or 52.9 pm for hydrogen atom) and then decreases as we go further away from it and at a certain distance it becomes close to zero. The curve shows the radial probability for a given direction. Theprobability would be same for all possible directions. If we put all such curves together itwould give a spherical distribution of the electron probability. Since the radial probabilitydoes not become zero at any distance, we cannot specify the size of the sphere. Therefore,the orbital is represented as a boundary surface diagram, which may be thought as a regionof space, which contains 95 % of the probability of finding the electron, as indicated inFig.1.10(b). Thus the 1s orbital is represented as a sphere.



1s Orbital

Fig.1.10: (a) Radial probability curve for 1s orbital (b) Boundary surface diagram for 1s orbital



2s Orbital

Fig.1.11: (a) Radial probability curve for 2s orbital (b) Boundary surface diagram for 2s orbital

Similarly, the Fig 1.11 (a) gives the radial probability curve for a 2s orbital while the Fig 1.11 (b) shows the boundary surface diagram for the same. Two things can be noted here. First thing is that for a 2s orbital the boundary surface diagram is bigger as compared to a 1s orbital. Secondly, the radial probability curve shows two maxima. The probability initially increases, reaches a maximum then it decreases and comes close to zero. It increases again and decreases as we move further away from the nucleus. The region where the probability comes close to zero (before increasing again) is called a spherical node. There are n–l–1 spherical nodes in an orbital. A node is a region in space where the probability of finding the electron is close to zero.

p- orbital: Now when we draw the shape of a p orbital (n =1; l =1) we get a shape as shown in the Fig. 1.12. This picture shows the shape of one of the three possible p orbitals which is directed towards the z-axis; p_z. You may note that the probability picture for a p_z orbital consists of two lobes; one along the positive z-axis and the other along the negative z-axis. Another important feature of a p- orbital is the absence of the electron probability in the XY- plane. Such a plane is called a nodal plane. The shapes of the three p-orbitals are given in Fig. 1.12.

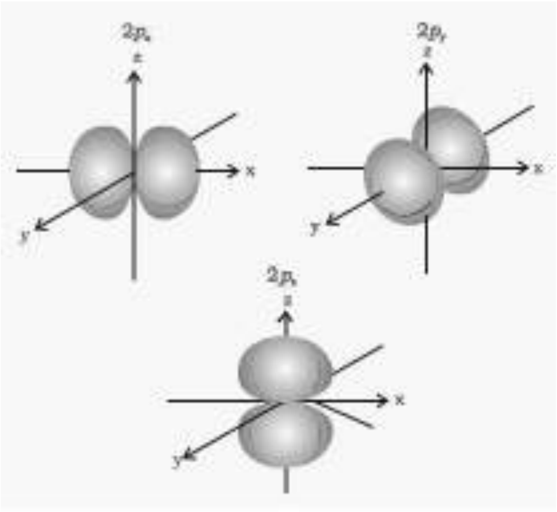


Fig. 1.12: Diagrams for 2p orbitals (2p$_x$, 2p$_y$, 2p$_z$)

The size, shape and energy of the three orbitals are identical. They differ however, in the way the lobes are oriented. Since the lobes may be considered to lie along the x, y or z axis, they are given the designations 2px, 2py, and 2pz.It should be understood, however, that there is no simple relation between the values of ml (–1, 0 and +1) and the x, y and z directions.

Like s orbitals, p orbitals increase in size and energy with increase in the principal quantum number and hence the order of the energy and size of various p orbitals is 4p > 3p > 2p.

For l = 2, the orbital is known as d-orbital and the minimum value of principal quantum number (n) has to be 3. As the value of l cannot be greater than (n–1). There are five m_l values (–2, –1, 0, +1 and +2) for l = 2 and thus there are five d orbitals. The Fig. 1.12 gives the shapes of five possible d-orbitals. The d-orbitals also contain nodal planes. The five d- orbitals have different shapes but they all have same energies i.e.,these are degenerate.

The five d-orbitals are designated as d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$and d_{z^2}. The shapes of the first four d-orbitals that is d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$are similar to each other. But d_{z^2} is different from others. The d orbitals of higher n values will have same shape but different energies and size.

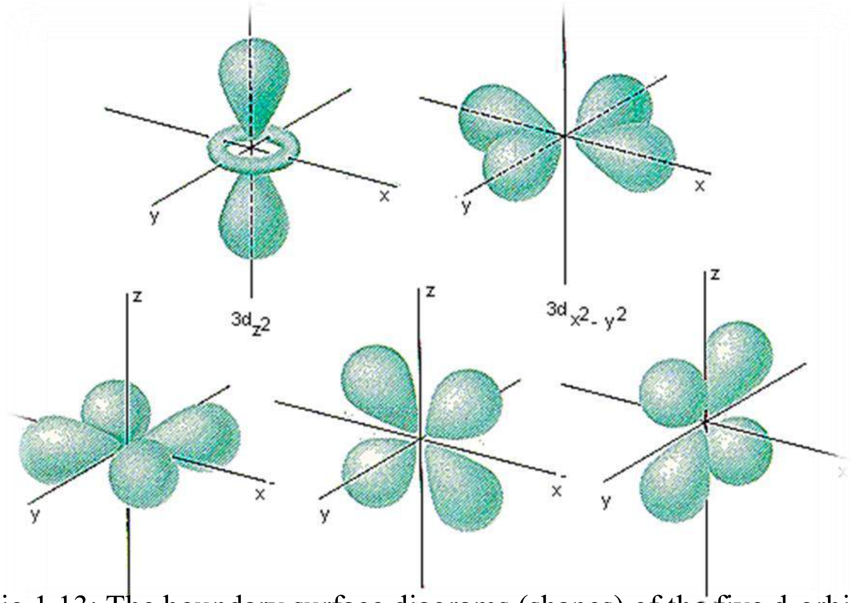


Fig.1.13: The boundary surface diagrams (shapes) of the five d-orbitals

Electronic Configuration of Elements

We have learnt so far that an atom consists of a positively charged nucleus surrounded by electrons present in orbitals of different shapes and sizes. These orbitals are part of different shells and sub-shells and are characterized by the three quantum numbers viz. n,l and m_l. Let us now take up the distribution of electrons in these shells and sub-shells. Such a distribution of electrons is called Electronic Configuration and is governed by three basic rules or principles.

One may ask what the utility of knowing the electron configuration is. The modernapproach to the chemistry dependsalmost entirely on electronic distribution tounderstand and explain the chemical behaviour.

For example, questions like why two or moreatoms combine to form molecules, why someelements are metals while others are nonmetals,why elements like helium and argonare not reactive but elements like the halogensare reactive, find simple explanation from theelectronic configuration. These questions haveno answer in the Daltonian model of atom. A detailed understanding of the electronicstructure of atom is, therefore, very essential for getting an insight into the various aspectsof modern chemical knowledge.

Aufbau Principal:

Aufbau is a german word which means building up. Here all we concern about is building up the orbitals means filling up of orbitals with electrons.

In the ground state of the atoms the orbitals are filled in order of their increasing energies. In other words electrons first occupy lower energy orbitals available to them and enter in the higher energy orbitals only after the lower energy orbitals are filled.

The order in which the energies of the orbitals increase and hence the orders in which orbitals are filled is given below,

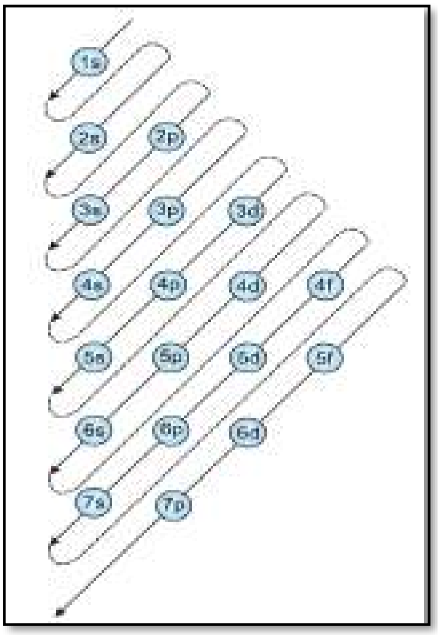
1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 4f, 5d, 6p, 7s……

Now, how does one know the increasing order of the orbital energies?

You have learnt above that the principal quantum number determines the energy of the orbitals.

Higher the value of n higher the energy is. This is true only for hydrogen atom.

For other atoms, we need to consider both n and l. This means that different sub-shells in a given shell have different energies. The order of orbital energies can be determined by the following (n + l) rules.



- **Rule 1:**An orbital with a lower value for (n + l) has lower energy. For example, the 4s orbital (n + l = 4+0=4) will fill before a 3d orbital (n + l = 3 + 2 =5).

- **Rule 2:**If the value of (n + l) is same for two orbitals then the orbital with lower value of n will be filled first. For example, the 3d orbital (n + l = 3+2=5) will fill before a 4p orbital (n + l = 4 + 1 =5).

Following these rules the increasing order of the orbital energies comes out to be

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

The order may be remembered by using the method given in the right-hand side Figure. Starting fromthe top, the direction of the arrows gives theorder of filling of orbitals that is starting fromright top to bottom left.

1.9 PAULI'S EXCLUSION PRINCIPLE:

This principle concerns the spin of electrons present in an orbital. According to the Pauli's principle, no two electrons can have all the four quantum numbers to be same.

For example, if a given electron in an atom has the set of four quantum numbers as n=2, l=1, m_l=1 and m_s= + ½ then no other electron in the atom can have the same set of quantum numbers that means other electron will have has the set of four quantum numbers as n=2, l=1, m_l=1 and m_s= - ½.

As it is known that an orbital is characterized by three quantum numbers so the electrons occupying a given orbital would have same values of these three quantum numbers.

These electrons are distinguished in terms of their spin quantum number, m_s.

Since the spin quantum number can have only two values so only two electrons can occupy a given orbital.

In fact, this fourth quantum number was introduced through Pauli's principle only.

1.10 BUILD-UP OF THE ELEMENTS: HUND'S RULE

This rule describes how the electrons will occupy a set of orbitals of the same energy, i.e. constituents of a subshell. According to this rule if a number of orbitals of the same subshell are available then the electrons distribute in such a way that each orbital is first singly occupied with same spin. For example, the six electrons in carbon distribute as$1s^2\ 2s^2\ 2p^1x\ 2p^1y2p^0z$ and not as $1s^2\ 2s^2\ 2p^2x\ 2p^0y2p^0z$.

Since electrons repel each other, they remain as far as possible from one another by occupying different orbitals.

The rules discussed above can be used to write the electronic configuration of different elements.

This rule deals with the filling of electronsinto the orbitals belonging to the samesubshell (that is, orbitals of equal energy,called degenerate orbitals). It states: pairingof electrons in the orbitals belonging tothe same subshell (*p*, *d* or *f*) does not takeplace until each orbital belonging to thatsubshell has got one electron each i.e., itis singly occupied.
Since there are three *p*, five *d* and seven *f*orbitals, therefore, the pairing of electrons willstart in the *p*, *d* and *f* orbitals with the entryof 4th, 6th and 8th electron, respectively. Ithas been observed that half-filled and fullyfilled degenerate set of orbitals acquire extra stability due to their symmetry.
There are two common ways of representing the electronic configurations. These are

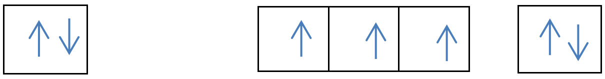
a) **Orbital notation method:**
In this method the filled orbitals are written in the order of increasing energies. The respective electrons in them are indicated as superscripts as shown in the example given below.
For example, the electronic configuration of nitrogen atom (atomic number 7) is written as $1s^2 2s^2 2p^1x\ 2p^1y2p^1z$.

b) **Orbital diagram method:**

In this method the filled orbitals are represented by circles or boxes and are written in the order of increasing energies. The respective electrons are indicated as arrows whose direction represents their spin.

For example, the electronic configuration of nitrogen in the orbital diagram notation can be written as

1s 2s 2p



The electrons in the outer shell are called **valence electrons.**

Electronic configurations can also be written in a short hand form. In this method the last completed orbital shell is represented in terms of a noble gas. For example, the electronic configuration of lithium and sodium can be written as

Li [He]$2s^1$
Na [Ne]$3s^1$

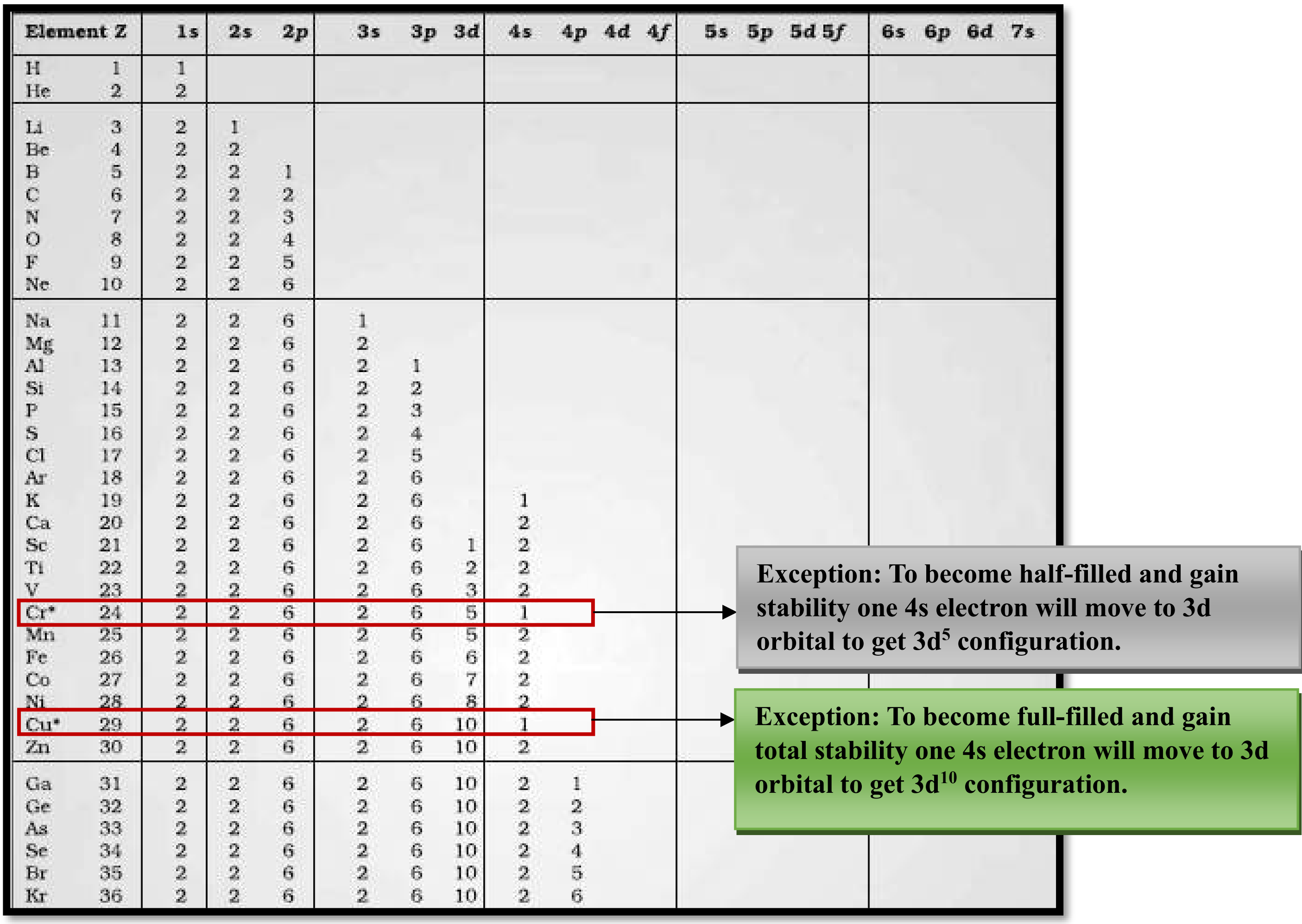
The electrons in the noble gas configuration are termed as core electrons while the ones in the outer shell are called valence electrons.

Stability of Completely Filled and Half-Filled Subshells

The ground state electronic configuration of the atom of an element always corresponds to the state of the lowest total electronic energy. The electronic configurations of most of the atoms follow the basic rules given in the previous Section.

However, in certain elements such as Cu, or Cr, where the two subshells (4s and 3d) differ slightly in their energies, an electron shifts from a lower energy (4s) to a higher energy (3d), provided such a shift results the higher energy orbitals to be either completely filled or half filled.

Electronic Configuration of the Elements upto 36 atomic number



Element	Z	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
H	1	1																	
He	2	2																	
Li	3	2	1																
Be	4	2	2																
B	5	2	2	1															
C	6	2	2	2															
N	7	2	2	3															
O	8	2	2	4															
F	9	2	2	5															
Ne	10	2	2	6															
Na	11	2	2	6	1														
Mg	12	2	2	6	2														
Al	13	2	2	6	2	1													
Si	14	2	2	6	2	2													
P	15	2	2	6	2	3													
S	16	2	2	6	2	4													
Cl	17	2	2	6	2	5													
Ar	18	2	2	6	2	6													
K	19	2	2	6	2	6		1											
Ca	20	2	2	6	2	6		2											
Sc	21	2	2	6	2	6	1	2											
Ti	22	2	2	6	2	6	2	2											
V	23	2	2	6	2	6	3	2											
Cr*	24	2	2	6	2	6	5	1											
Mn	25	2	2	6	2	6	5	2											
Fe	26	2	2	6	2	6	6	2											
Co	27	2	2	6	2	6	7	2											
Ni	28	2	2	6	2	6	8	2											
Cu*	29	2	2	6	2	6	10	1											
Zn	30	2	2	6	2	6	10	2											
Ga	31	2	2	6	2	6	10	2	1										
Ge	32	2	2	6	2	6	10	2	2										
As	33	2	2	6	2	6	10	2	3										
Se	34	2	2	6	2	6	10	2	4										
Br	35	2	2	6	2	6	10	2	5										
Kr	36	2	2	6	2	6	10	2	6										

Exception: To become half-filled and gain stability one 4s electron will move to 3d orbital to get 3d^5 configuration.

Exception: To become full-filled and gain total stability one 4s electron will move to 3d orbital to get 3d^{10} configuration.

1.11 DEVELOPMENT OF QUANTUM MECHANICS: SCHRÖDINGER WAVE EQUATION:

The Schrödinger equation is a fundamental equation in quantum mechanics that describes how the quantum state of a physical system changes over time. It's named after Austrian physicist Erwin Schrödinger, who developed it. In 1925, Erwin Schrödinger and Werner Heisenberg independently developed the new quantum theory. Schrödinger's method involves partial differential equations, whereas Heisenberg's method employs matrices; however, a year later the two methods were shown to be mathematically equivalent. Most textbooks begin with Schrödinger's equation, since it seems to have a better physical interpretation via the classical wave equation. Indeed, the Schrödinger equation can be viewed as a form of the wave equation applied to matter waves.

Starting with the expressions similar to those applicable for standing waves and applying de Broglie relationship, Schrodinger arrived at a fundamental equation for the electron wave. The time-dependent Schrödinger equation for a single non-relativistic particle of mass m in a potential V(r,t) is given by:

$$i\hbar\frac{\partial^2}{\partial x^2}\Psi(r,t) = -\frac{\hbar^2}{2m}\nabla^2\Psi(r,t) + V(r,t)\Psi(r,t)$$

Where:

- $\Psi(r,t)$ is the wave function of the particle, which is a complex-valued function of position rr and time t.
- i is the imaginary unit.
- $\hbar$ is the reduced Planck constant.
- ∇^2 is the Laplacian operator, representing the spatial second derivative.
- $V(r,t)$ is the potential energy experienced by the particle.

This equation describes how the wave function evolves in time under the influence of the potential energy. The time-independent Schrödinger equation is derived by separating the variables and assuming the potential is time-independent, resulting in an equation for the spatial part of the wave function only. This equation is widely used in quantum mechanics to predict the behaviour of quantum systems, such as atoms, molecules, and subatomic particles.

The Schrödinger Equation: Derivation:

The wave equation may be arrived at by assuming that the laws of motion representing a standing wave are equally applicable to matter waves, for example those associated with an electron in the atomic system. Necessary adjustment is then introduced into the general equation for such waves to incorporate the particle nature of the electron using de Broglie relation.

The equation applicable to a wave moving in one direction is represented by following equation,

$$\frac{d^2f(x)}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi \quad \text{--------------------(i)}$$

Extending this to a wave moving in three dimensions *f(x)* is replaced by a new function depending on three Cartesian coordinates: $\psi(x, y, z)$.

$$\frac{\partial^2\psi(x,y,z)}{\partial x^2}+\frac{\partial^2\psi(x,y,z)}{\partial y^2}+\frac{\partial^2\psi(x,y,z)}{\partial z^2} = -\frac{4\pi^2}{\lambda^2}\,\psi\text{---------------------(ii)}$$

Writing simply ψ for ψ(x, y, z) above equation transformed to

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2} = -\frac{4\pi^2}{\lambda^2}\,\psi\text{---------------(iii)}$$

The symbol ∇^2(del squared) is often used to represent the differential operator (Laplacian Operator); in Cartesian coordinates,

$$\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

So, the equation (iii) is now expressed as; $\nabla^2\psi = -\frac{4\pi^2}{\lambda^2}\psi$ ---------------(iv)

The fundamental postulate of Schrödinger is that an equation of type (i) or (iii) may be applied to all particles. The equations may be further adjusted by inserting the mass (m) and velocity (v) of the particle concerned from the de Broglie relationship. From (iv)

$$\nabla^2\psi = -\frac{4\pi^2 m^2 v^2}{h^2}\,\psi\text{ ---------------(v)}$$

The total energy E of the particle must be equal to the sum of its potential energy U and kinetic energy.

$$E = U + \frac{1}{2}mv^2 \quad\text{or,}\quad mv^2 = 2\,(E-U)\text{ ---------------(vi)}$$

Substituting in equation (v), $\nabla^2\psi = -\frac{8\pi^2 m}{h^2}(E-U)\,\psi$

Or, $$\boxed{\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E-U)\,\psi = 0}$$

This is the wave equation of Schrödinger in the time independent form. This wave equation may also be expressed as

$$-\nabla^2\psi + \frac{8\pi^2 m}{h^2}U\,\psi = \frac{8\pi^2 m}{h^2}E\,\psi$$

$$\text{or,}\quad -\frac{h^2}{8\pi^2 m}\nabla^2\psi + U\,\psi = E\,\psi$$

$$\text{or,}\quad \left[-\frac{h^2}{8\pi^2 m}\nabla^2 + U\right]\psi = E\,\psi$$

or, $\boxed{\hat{H}\,\psi = E\,\psi}$ ------------------(vi)

Here H is called **Hamiltonian or energy operator** which is equal to the expression in the bracket. The operator H on ψ enables us to obtain the total energy of the system.

Here ψ is called wave function or probability amplitude function. Selection of acceptable values of is made according to the following conditions:

- Must be single-valued because the probability of finding the electron at any point must have only one value.
- Must be continuous.
- Must be finite.
- The total probability of finding the electron over the whole space must be equal to 1, i.e, must be normalized.

$$\int_{-\infty}^{\infty} \psi^2 dxdydz = 1$$

Each acceptable value of obtained from the solution of Schrödinger equation (as applied to the electrons in an atom) represents an orbital. Each such orbital corresponds to the definite energy value of the electron.

Probability Density Function

Probability Density Function(PDF) defines the probability function representing the density of a continuous random variable lying between a specific range of values.

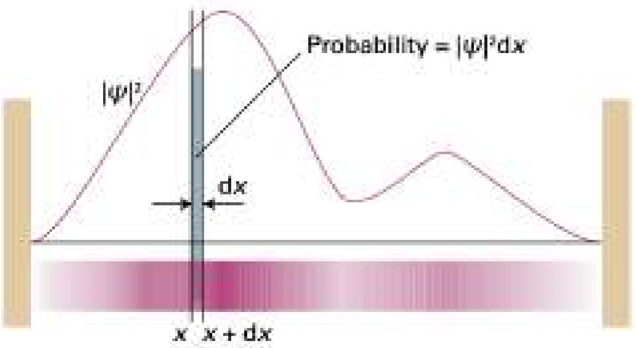
Stationary state is a state of a system whose probability density given by $|\Psi^2|$ is invariant with time. In an atom, the electron is a matter wave with quantised angular momentum, energy, etc. The movement of the electrons in their orbit is such that probability density varies only with respect to the radius and angles.The movement is akin to a stationary wave between two fixed ends and is independent of time. The wave function concept of matter waves is applied to the electrons of an atom to determine its variable properties.

Probability Density Function Graph

The probability density function is defined as an integral of the density of the variable density over a given range. It is denoted by f (x). This function is positive or non-negative at any point of the graph, and the integral, more specifically the definite integral of PDF over the entire space is always equal to one. The graph of PDFs typically resembles a bell curve, with the probability of the outcomes below the curve. The below figure depicts the graph of a probability density function for a continuous random variable x with function f(x).

The movement is akin to a stationary wave between two fixed ends and is independent of time. The wave function concept of matter waves is applied to the electrons of an atom to determine its variable properties.

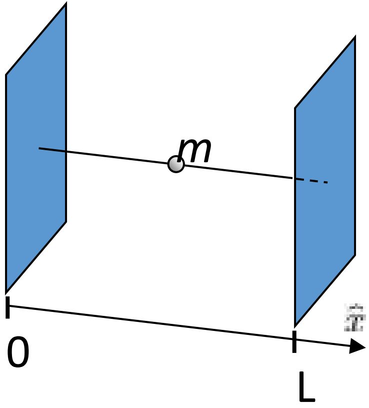
The wave function is a probability amplitude and the square of it ($\psi^*\psi$ or $|\psi^2|$) is a probability density. The probability of finding a particle in the region between x and x+dx is proportional to $|\psi^2|$dx.



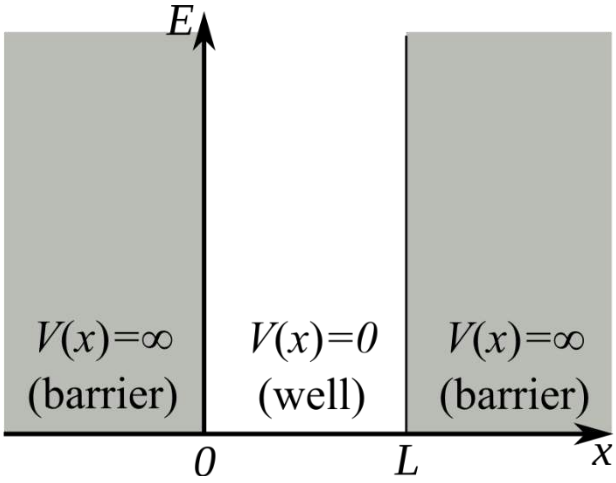
1.12 PARTICLE IN A BOX

The particle in a box problem is a common application of a quantum mechanical model to a simplified system consisting of a particle moving horizontally within an infinitely deep well from which it cannot escape. The solutions to the problem give ψ and the possible values of E and that the particle can possess. E represents allowed energy values and ψ is a wave function, which when squared gives us the probability of locating the particle at a certain position within the box at a given energy level.

Let us consider a particle trapped in a region of space in one dimension (along x axis), it is restricted to move between x = 0 and x = L by infinitely high impenetrable walls. The situation is analogous to a particle confined in a box or a square well whose walls are infinitely high. The particle does not lose energy when it collides with such walls; hence its total energy remains constant.



The potential energy U inside the box is also constant which is equal to 0 (U =0 for 0<x<L) and goes to infinity at the walls of the box (U = ∞ for x < 0 or x > L). We assume the walls have infinite potential energy to ensure that the particle has zero probability of being at the walls or outside the box. Doing so significantly simplifies our later mathematical calculations as we employ these boundary conditions when solving the Schrödinger Equation.



The time-independent Schrödinger equation for a particle of mass m moving in three directions with energy E is

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2}(\mathrm{E} - \mathrm{U})\psi = 0 \qquad , \qquad \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = \nabla^2$$

The time-independent Schrödinger equation for a particle of mass m moving in one direction in a one-dimensional box with energy E is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}\mathrm{E}\psi = 0$$

Since (U =0 for 0<x<L)

$$\frac{8\pi^2 m}{h^2}\mathrm{E}\psi = -\frac{\partial^2\psi}{\partial x^2}$$

$$\boldsymbol{\mathrm{E}\psi = -\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi}{\partial x^2}}$$

The differential equation may be written as

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{8\pi^2 m}{h^2}E\psi$$

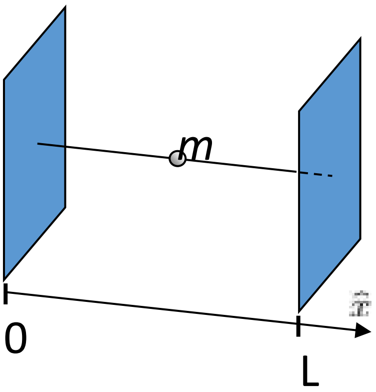
Or, $$\frac{\partial^2\psi}{\partial x^2} = -k^2\psi, \text{ where } k^2 = \frac{8\pi^2 m}{h^2}E$$

The general solution of this differential equation is

$\psi = A\ sin\ kx + B \cos kx$--------------------(vi)

where A, B, and k are constants.

We now need to apply our boundary conditions to find the solution to our particular system.According to our boundary conditions, the probability of finding the particle at x=0 or x=L is zero that is ψ is zero. When x = 0 sin(0) = 0 and cos(0)=1; therefore, B must equal 0 to fulfill this boundary condition.



$\psi = A\ sin\ kx + B \cos kx$

$$0 = A\ sin\ (0) + B\cos(0) \text{ or, } B = 0$$

The equation (vi) thus reduced to $\psi = A\ sin\ kx$

To determine A, we have to apply the boundary conditions again. **Recall that the probability of finding a particle at x = L, ψ is zero.**

Hence, putting **ψ is zero at x = L in the equation**

$\psi = A\ sin\ kx$

we will get

$$0 = A\ sin\ kL$$

Now, this is true when $kL = n\pi$ where n=1, 2, 3, ……

Or, $k = n\pi/L$ and $\psi = A\ sin\ (n\pi x/L) = A\ sin\ \frac{\sqrt{8\pi^2 mE_n}}{h}x$

For normalization, we note that the particle is confined within the region x= 0 to x= Land hence the total probability of finding the particle in this region must be equal to 1.

$$\int_0^L \psi^2\, dx = 1$$

$$\int_0^L A^2 sin^2\left(\frac{n\pi x}{L}\right) dx = 1$$

$$or,\ A^2 \int_0^L \frac{1}{2}\left(1 - cos\frac{2n\pi x}{L}\right) dx = 1$$

Simplifying we get $A = \sqrt{2/L}$. The normalized wave functions of the particle are therefore

$$\psi = \sqrt{\frac{2}{L}} sin\left(\frac{n\pi x}{L}\right)$$

Solving for E results in the allowed energies for a particle in a box:

$$\boxed{E = \frac{n^2 h^2}{8mL^2}}$$

This is a very important result; it tells us that:

1. The energy of a particle is quantized.

2. The lowest possible energy of a particle is NOT zero. This is called the zero-point energy and means the particle can never be at rest because it always has some kinetic energy.

This is also consistent with the Heisenberg Uncertainty Principle: if the particle had zero energy, we would know where it was in both space and time.

The pictorial representation of wave function and probability densities of a particle confined in a one-dimensional box with infinitely high rigid walls is shown below:

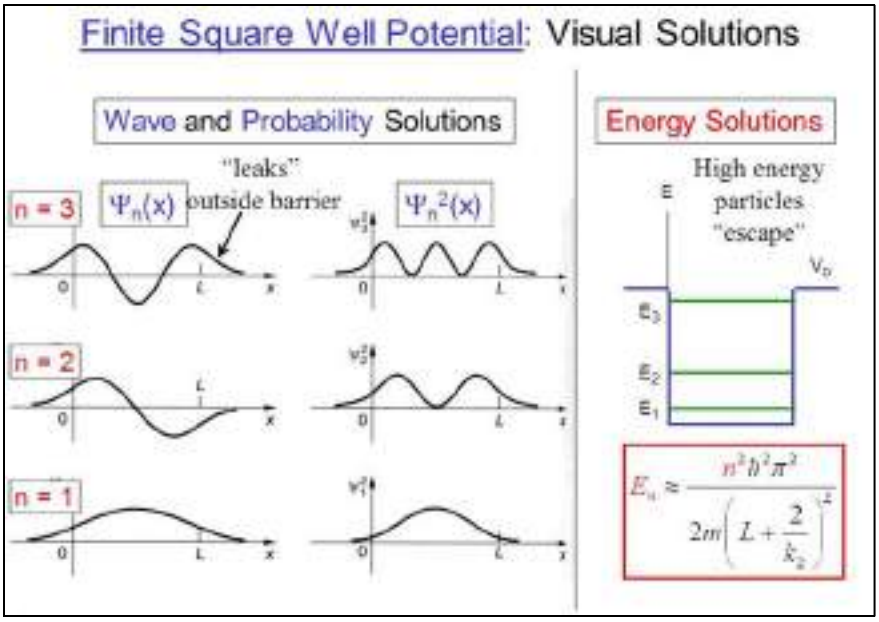


Fig. 1.14: Wave function and probability densities of a particle confined in a one-dimensional box with infinitely high rigid walls

The plots of the probability densities are also interesting. For n=1 the most probable position of the particle is at L/2; but for n=2 this point corresponds to a node and the most probable position of the particle is at L/4, for n=3 this point corresponds to a node and the most probable position of the particle is at L/6.

1.13 EXERCISE:

1. Compare the mass of an electron with that of the proton.
2. What is a fundamental particle?
3. What is the name given to neutral particles in the atom?
4. List the three constituent particles of an atom.
5. What was the aim of Rutherford’s α-rays scattering experiment?
6. Briefly describe Rutherford’s model of an atom.
7. On what basis was the Rutherford’s model rejected.
8. What is an electromagnetic radiation?
9. What is wave number? How is it related to wave length?
10. What is the difference between a ‘quantum’ and a ‘photon’?
11. What is the difference between a line spectrum and a continuous spectrum?
12. What are the main postulates of Bohr’s model?
13. How does the energy of a Bohr orbit vary with the principal quantum number ‘n’
14. What do you understand by wave-particle duality?
15. Compute the de-Broglie wavelength associated with an electron moving with a velocityof 100 km /second? (m_e= 9.1 x 10-31kg).
16. State Heisenberg’s Uncertainty Principle?
17. What do you understand by a Wave Function?
18. What is the difference between an orbit and an orbital?
19. What are quantum numbers? List different quantum numbers obtained from SchrödingerWave Equation?
20. Give the significance of the principal, azimuthal and magnetic quantum numbers?
21. What are the shapes of s,p and d orbitals?
22. Describe the shape of a 2s orbital. How is it different from that of a 1s orbital?
23. What do you understand by
    i) a spherical node?
    ii) a nodal plane?
24. How many spherical nodes will be there in 3s orbital?
25. What is the physical significance of the Schrodinger wave function?
26. What is meant by stationary state, and what is its relevance to the atom?

CHAPTER 2

INTRODUCTION TO CHEMICAL BONDING

2.1 INTRODUCTION

The constituent of any matter is one or different type of elements. Under normal conditions except the noble gases no other element exists as an independent atom in nature. However, there are a group of atoms which exist together as one species having characteristic properties and such a group of atoms is called a molecule. Obviously there must be some force which is imposed on one form of matter by another form of matter whenever they interact with each other and that force holds these constituent atoms together in the moleculesand stabilises them by causing an overall loss of energy. The attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species is called a chemical bond.Consequently, it can be recognised that the strength of the chemical bonds between its constituents is critical to the stability of the emerging compound; the stronger and more stable the chemical bonds between its constituents, the more stable the resulting molecule.

Conversely, if the chemical connection between the ingredients is weak, the resulting product lacks stability and is quickly transformed into a more stable chemical complex by another reaction (containing stronger bonds). The atoms attempt to lose their energy in order to achieve stability.

2.2 ATTAINMENT OF A STABLE CONFIGURATION:

Chemical bonding is a fundamental concept in chemistry that explains how atoms combine to form molecules or compounds. Atoms bond with each other to attain a stable electron configuration, usually by filling their outer electron shells and to achieve a lower energy state. This usually involves filling or emptying their outermost electron shells (valence shells) to mimic the electron configuration of noble gases, which are known for their stability.

2.3 TYPES OF BONDS:

Atoms can achieve this stable electron configuration through various types of bonding:

Ionic Bonding: Atoms transfer electrons to achieve a full valence shell. For example, sodium (Na) has one electron in its outer shell, while chlorine (Cl) needs one electron to complete its outer shell. So, sodium transfers its electron to chlorine, forming Na^+ and Cl^- ions, which are attracted to each other due to their opposite charges.

Covalent Bonding: Atoms share electrons to complete their outer shells. By sharing electrons, each atom can achieve a full valence shell. For example, in a molecule of hydrogen gas (H_2), two hydrogen atoms share their electrons to form a stable covalent bond.

Metallic Bonding: In metals, atoms achieve stability by sharing their valence electrons with neighbouring atoms. This creates a "sea" of delocalized electrons that move freely throughout the metal lattice, holding the positively charged metal ions together.

The stability attained through chemical bonding reduces the overall energy of the system, making it more energetically favourable. This stability is evident in the formation of molecules and compounds, where atoms bond together to minimize their energy and achieve a more favourable electron configuration.

So, depending upon the electropositive or electronegative type of the atoms involved three types of bond can be formed which are mentioned below,

Types of Atoms Involved	The Types of Bonds Formed
Electropositive element + **Electronegative element**	Ionic bond or Electrovalent bond
Electronegative element + **Electronegative element**	Covalent bond
Electropositlve element + **Electropositive element**	Metallic bond

Ionic bonding involves the complete transfer of one or more electrons from one atom to another. Covalent bonding involves the sharing of a pair of electrons between two atoms.

In metallic bonding the valence electrons are free to move throughout the whole crystal.

Before we proceed to the details of different types of chemical bonding we should have knowledge of few basic things for example Octet rule, Lewis dot structures. The next part will deal with that.

2.4 OCTET RULE:

Atoms of noble gases contain eight electrons (except He which contains two electrons) in their outermost shell. They are generally chemically inert which suggests that this eight-electron configuration or Octet is very stable. So, the atoms of other elements would also tend to achieve such a stable octet in their outermost shell. This tendency drives the atoms to combine with one another that occur through the involvement of outermost electrons. Thus each atom effectively may have eight electrons in their outermost shell. This is called rule of eight or the octet rule.

2.5 LEWIS STRUCTURES AND LEWIS SYMBOLS

Lewis structures:

In order to explain the chemical bonding in terms of electrons, a number of attempts were made, but in 1916, Kossel and Lewis independently proposed a satisfactory explanation. Lewis postulated that atoms achieve the stable octet when they are linked by chemical bonds. In the case of Na and Cl this can happen by the complete transfer of an electron from sodium to chlorine to produce Na^+ and Cl^- ions. In case of other molecules like, Cl_2, H_2, F_2 etc. the bond is formed by the sharing of a pair of electrons between the atoms and doing so each atom attains a stable eight electrons configuration in outermost shell that is they obey the octet rule.

Lewis symbols:

During bond formation only outermost shell electrons take part in chemical combination and they are known as valence electrons. G. N. Lewis introduced simple notation to represent valence electrons in an atom. These notations are called Lewis symbols. For example, Lewis symbols for few elements are given below:

2.6 IONIC BONDS:

Ionic bonds are formed when electropositive elements react with electronegative elements. Consider the ionic compound sodium chloride. A sodium atom has the electronic configuration $ls^{2}2s^{2}2p^{6}3s^{1}$. The first and second shells of electrons are full, but the third shell contains only one electron. When this atom reacts, it will do so in such a way that it attains a stable electron configuration. If the sodium atom can lose one electron from its outer shell, it will attain this configuration and in doing so the sodium acquires a net charge of +1 and is called a sodium ion Na+. The positive charge arises because the nucleus contains 11 protons, each with a positive charge, but there are now only 10 electrons. Sodium atoms tend to lose an electron in this way and so sodium is an electropositive element:

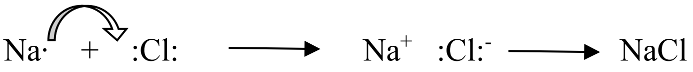
$$\underset{\text{Sodium atom}}{\mathrm{Na}} \longrightarrow \underset{\text{Sodium ion}}{\mathrm{Na+}} + \text{electron}$$

Chlorine atoms have the electronic configuration $ls^{2}2s^{2}2p^{6}3s^{2}3p^{5}$. They are only one electron short of the stable configuration to complete its octet $s^{2}2s^{2}2p^{6}3s^{2}3p^{6}$ and when chlorine atoms react, they gain an electron. Thus, chlorine is an electronegative element.

$$\underset{\text{Chlorine atom}}{Cl} + \text{electron} \longrightarrow \underset{\text{Chloride ion}}{Cl^-}$$

Through gaining an electron, an electrically neutral chlorine atom becomes a chloride ion with a net charge of -1.

When sodium and chlorine react together, the outermost electron of the sodium atoms is transferred to the chlorine atoms producing sodium ions Na+ and chloride ions Cl^-. So, there will be an electrostatic attraction between the positive and negative ions that will hold the ions together in a crystal lattice. An ionic or electrovalent bond will form between the above-mentioned ions. The process is energetically favourable as both sorts of atoms attain the stable noble gas configuration, and sodium chloride NaCl (Na+Cl−) is formed readily. This may be illustrated diagrammatically in a Lewis diagram showing the outer electrons as dots;



Electrostatic attraction

2.7 ENERGETICS OF IONIC COMPOUND FORMATION: BORN-HABER CYCLE

We have just described the formation of an ionic compound (NaCl) as a result of transfer of electrons as proposed by Kossel. You may raise a question here that when **more energy is required** (ionisation energy) to form a sodium ion from sodium atom, **than that released** (electron affinity) in the formation of chloride ion from chlorine atom then how do we say that the formation of NaCl is accompanied by a decrease in energy? Your question is quite justified but let us assure you that there is no anomaly. Let us look at the whole process somewhat closely to clarify your doubts.

The formation of NaCl from sodium and chlorine can be broken down into a number of steps as :

a) **Sublimation** of solid sodium to gaseous sodium atoms.

$$Na(s) \longrightarrow Na(g) ; \qquad \Delta H = 108.7 \text{ kJ mol}^{-1}$$

b) **Ionization** of gaseous sodium atom to give sodium ion.

$$Na(g) \longrightarrow Na^+(g) + e^- ; \qquad \Delta H = 493.8 \text{ kJ mol}^{-1}$$

c) **Dissociation** of gaseous chlorine molecule into chlorine atoms

$$\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)\ ; \qquad \Delta H = -120.9\ kJ\ mol^{-1}$$

d) Conversion of gaseous chlorine atom to chloride ion **(addition of electron)**

$$Cl(g) + e^- \longrightarrow Cl^-(g); \qquad \Delta H = -379.5\ kJ\ mol^{-1}$$

e) Formation of NaCl from sodium and chloride ions.**(Crystal or lattice formation)**.

$$Na^+(g) + Cl^-(g) \longrightarrow Na^+Cl^-(s); \qquad \Delta H = -754.8\ kJ\ mol^{-1}$$

The energy released in this step is **lattice energy**.

The net reaction would be

$$Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow Na^+Cl^-(s); \qquad \Delta H = -410.9\ kJ\ mol^{-1}$$

The overall energy change can be computed by taking the sum of all the energy changes:

$$\Delta H = (180.7 + 493.8 + 120.9 - 379.5 - 754.8) = -410.9\ kJ\ mol^{-1}$$

Thus we see that the net process of formation of NaCl from sodium and chlorine is accompanied by a large decrease in the energy. The approach we have just followed is based on the law of conservation of energy and is known as **Born-Haber cycle**.

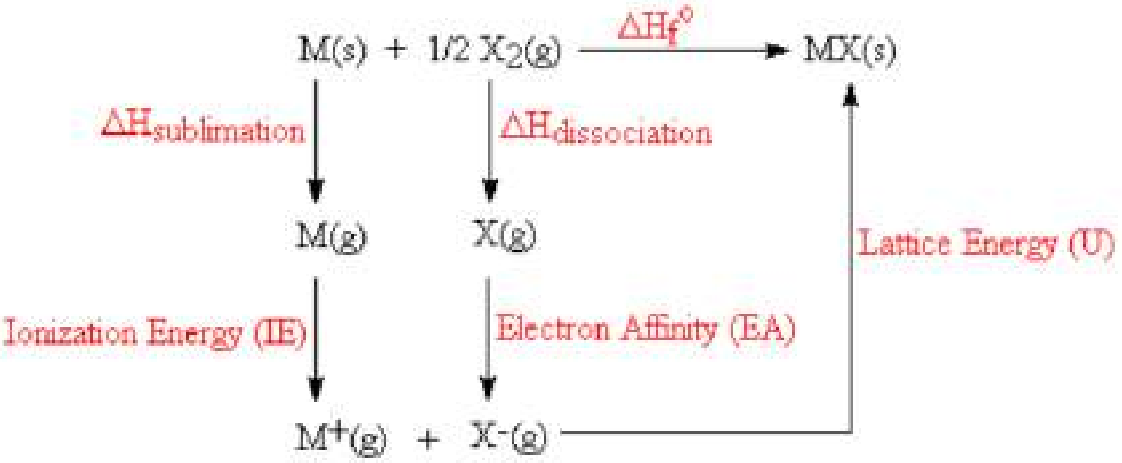
Of the five different types of energies involved, two (sublimation and dissociation energies) are generally have low values than the rest. Therefore, the three energy terms i.e., ionization energy, electron affinity and lattice energy are important in determining the formation of an ionic compound. On the basis of the above discussion we can say that the formation of an ionic compound is favoured by

i. Low ionisation energy of the metal,

ii. High electron affinity of the other element (non-metal), and

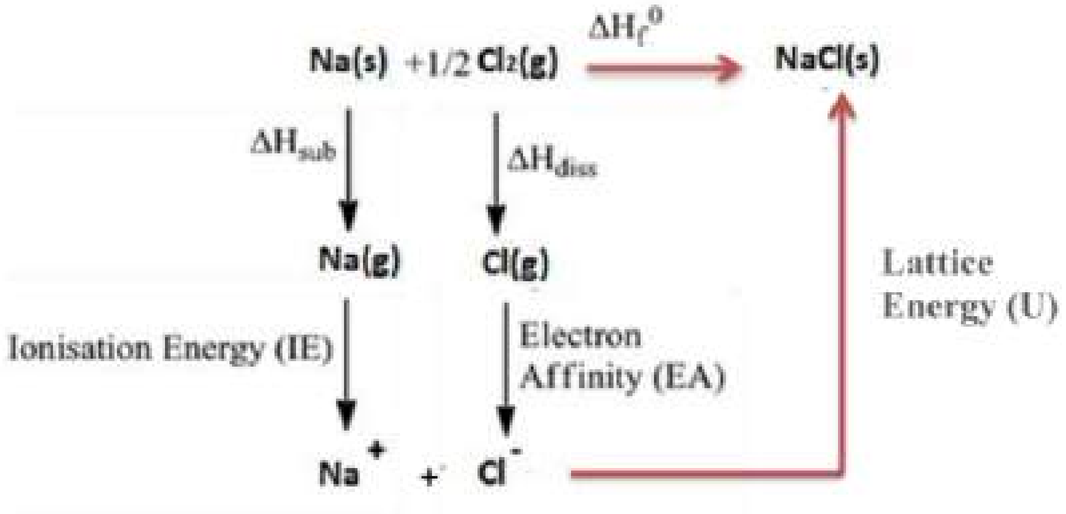
iii. High lattice energy

Born Haber Cycle General format for any MX ionic compound:



$$\Delta H_f^\circ = \Delta H_{sub} + IE + \Delta H_{diss} + EA + U$$

<u>Born Haber Cycle for Sodium Chloride (NaCl)</u>



$$\Delta H^\circ_f = \Delta H_{sub} + 1^{st}\ IE + 2^{nd}\ IE + (\Delta H_{diss}) + 1^{st}\ EA + 2^{nd}\ EA + LE$$

1. **Calculate the lattice enthalpy for lithium fluoride, given the following information:**
   1. Enthalpy of sublimation for solid lithium = 161 kJ/mol
   2. First ionization energy for lithium = 520 kJ/mol
   3. F-F bond dissocation energy = 154 kJ/mol
   4. Electron affinity for fluorine = -328 kJ/mol
   5. Enthalpy of formation for solid lithium fluoride = -617 kJ/mol

Hint: Use the concept of Born Haber Cycle and the following expression.

ΔH°_f = ΔHsub+1st IE+ 2nd IE+ ΔHdiss + 1st EA+ 2nd EA + LE

Ans:

ΔH°_f = ΔHsub+1st IE+ 2nd IE+ ΔHdiss + 1st EA+ 2nd EA + LE

-617=161+520+154-328+LE

LE = 161+520+154-328+617 = -1124

Lattice energy for LiF(s) = -1124 kJ/mol

2.8 CHARACTERISTICS OF IONIC COMPOUNDS

Ionic or electrovalent bond is formed between electropositive and electronegative element. Electropositive elements are generally metals and electronegative elements are mainly non-metals. The compounds formed by this bond are soluble in polar solvent like water; aqueous solution of these compounds can conduct electricity.

- These exist as crystalline solids in which the ions are arranged in a regular three dimensional structure. The ionic compounds are generally hard and brittle in nature.
- These compounds have high melting and boiling points due to strong electrostatic interactions between the ions.
- These are generally soluble in water and less soluble in non-polar solvents like ether, alcohol, etc.
- These conduct electricity when in molten state or in aqueous solutions.

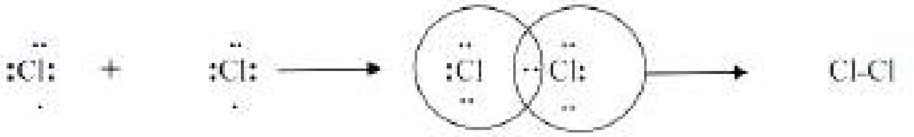
Kossel's theory explains bonding quite well but only for a small class of solids composed of electropositive elements of Group 1 and 2 with highly electronegative elements. Secondly, this theory is incapable of explaining the formation of compounds like, SO_2 or O_2, etc. For example in case of O_2, there is no reason to expect that one atom of oxygen would lose two electrons while the other accepts them. The problem was solved by Lewis theory of covalent bonding.

2.9 COVALENT BOND

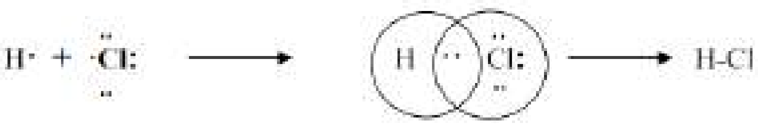
When two electronegative atoms react together, both atoms have atendency to gain electrons, but neither atom has any tendency to loseelectrons. In such cases the atoms share electrons so as to attain a noble gasconfiguration.Generally, atoms of non-metals combine to get a stable structure by sharing a pair of electrons between themselves and thus a molecule of a compound is formed. The bond formed in this case is called covalent bond and the compound is called covalent compound.

Examples: Cl_2, HCl, CH_4

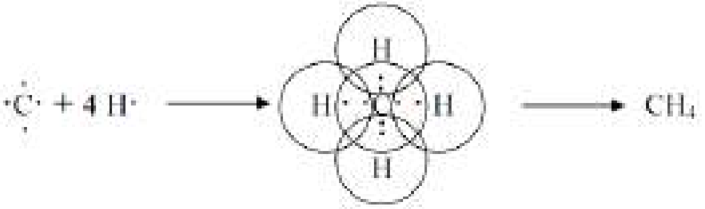
(i) Cl_2



(ii) HCl



(iii) CH_4



Characteristics: Covalent bonds are formed between two electronegative elements. Covalent compounds are volatile, insoluble in polar solvent but soluble in nonpolar solvent like organic solvents. They do not conduct electricity and have low boiling and melting point.

2.10 POLAR COVALENT BOND

You may have noticed that in the process of bond formation, the elements of second period acquire eight electrons in their valence shell. This is called **'Octet rule'**. You may also note that in case of H_2 and Cl_2 the atoms are linked by a single line while in case of O_2 the atoms are linked by two lines. These lines represent bonds. When two atoms are bound by sharing a single pair of electron, they are said to be joined by a single bond. And when, two pairs of electrons are shared (as in case of O_2), the two atoms are said to be bound by a double bond. In nitrogen (N_2) the two atoms are joined by a triple bond as they share three pairs of electrons.

In a Lewis representation the electrons shown to be involved in the bond formation are called bonding electrons; the pair of electrons is called *'bond pair'* and the pairs of electrons not involved in the bonding process are called *'lone pairs'*. The nature of the electron pair plays an important role in determining the shapes of the molecules. This

In a chemical bond the shared electron pair is attracted by the nuclei of both the atoms. When we write the electron dot formula for a given molecule this shared electron pair is generally shown in the middle of the two atoms indicating that the two atoms attract it equally. However, actually different kinds of atoms exert different degrees of attraction on the shared pair of electrons. A more electronegative atom has greater attraction for the shared pair of electrons in a molecule. As a consequence in most cases the sharing is not equal and the shared electron pair lies more towards the atom with a higher electronegativity. For example, in HCl, the shared pair of electron is attracted more towards more electronegative chlorine atom. As a result of this unequal sharing of the electron pair , the bond acquires polarity or partial ionic character.

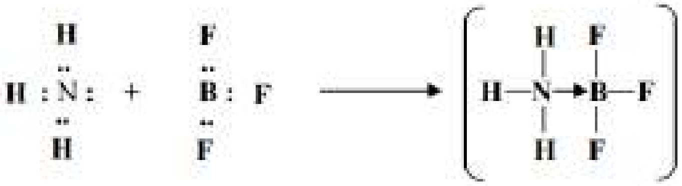
$$H \; : \overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}} : \qquad H^{\delta+} - Cl^{\delta-}$$

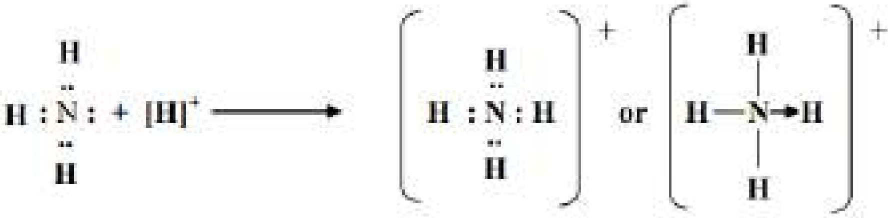
In an extreme case, the difference in the electronegativity may be so high that the electron pair is practically under the influence of a single atom. In other words the polarization of the bond is complete i.e., we have a case of ionic bonding. Thus , though the Lewis theory talks about covalent bonding it can account for the formation of ionic compounds also.

2.11 COORDINATE BOND

A covalent bond results from the sharing of a pair of electrons between two atoms, where each atom contributes, one electron to the bond. It is also possible to have an electron pair bond where both electrons originate from one atom and none from the other. Such bonds are called coordinate bonds or dative bonds. Since, in coordinate bonds, two electrons are shared by two atoms, they differ from normal covalent bonds only in the way they are formed, and once formed they are identical to normal covalent bonds.

Even though the ammonia molecule has a stable electron configuration, it can react with a hydrogen ion H^+ by donating a share in the lone pair of electrons, forming the ammonium ion NH_4^+.





Covalent bonds are usually shown as straight lines joining the two atoms, and coordinate bonds as arrows indicating which atom is donating the electrons. Similarly ammonia may donate its lone pair to boron trifluoride, and by this means the boron atom attains a share in eight electrons:

2.12 CHARACTERISTIC PROPERTIES OF COVALENT COMPOUNDS

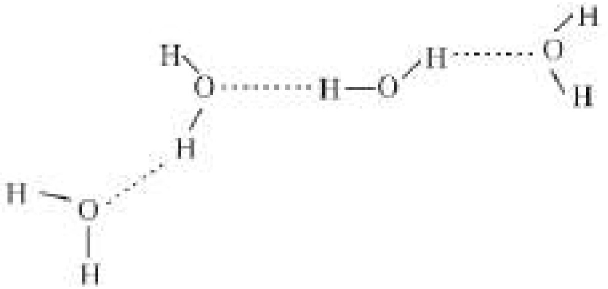
- The covalent compounds have low melting and boiling points due to weak forces of interaction between the molecules.
- The covalent compounds are poor conductors of electricity as these lack ionic species.
- The covalent compounds are generally insoluble in water and dissolve in nonpolar solvents like benzene, carbon tetrachloride etc.

2.13 HYDROGEN BOND:

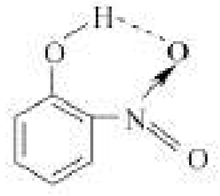
Hydrogen bonding is an electrostatic attractive force between covalently bonded hydrogen atom attached with a strong electronegative element (like F, O, and N) and an atom of highly electronegative element of the same or different molecule.

When H atom is covalently bonded to a strongly electronegative and small size atom (like F, O, N) the shared electron pair between the H-atom and the strongly electronegative atom will be shifted much more nearer to the electronegative atom. As a result ionic character in the covalent bond is developed and H atom becomes partially positively charged and the electronegative atom becomes partially negatively charged and the molecule behaves as a dipole.

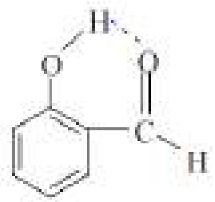
atom (like nitrogen, oxygen or fluorine) and the unshared pair of electrons on another electronegative atom. Hydrogen bond is a weak bond, the strength being just about 4-25 kJ mol–1. It is quite small as compared to the covalent bond, which needs a few hundreds of kJ mol–1 of energy to break. However, it is strong enough to be responsible for the high boiling points of H2O and HF etc. In fact it is due to hydrogen bonding only that water exists as a liquid. The low density of ice also can be explained in terms of hydrogen bonding.



Due to the difference in the electronegativity between hydrogen and the other electronegative atom, the bond connecting them becomes polar. The hydrogen atom acquires a positive charge while the electronegative atom bears the negative charge. Hydrogen bonding results from the electrostatic interaction between the positively charged hydrogen atom and the negatively charged electronegative atom. The second electronegative atom may be a part of the same molecule or it may belong to a different molecule. Accordingly, there are two types of hydrogen bonds. If the hydrogen bond is formed between two different molecules it is called **intermolecular hydrogen bond**. When the hydrogen bond exists within the same molecule, it is called **intramolecular hydrogen bonding.** Salicyldehyde and o-nitrophenol are two common examples of the molecules showing intramolecular hydrogen bonding whereas in water, intermolecular hydrogen bonding exists.



o-nitrophenol



Salicyldehyde

Hydrogen bonding plays an important role in the structure and function of many biomolecules like proteins and nucleic acids.

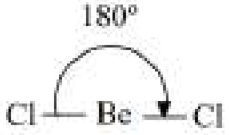
2.14 VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

In a molecule the constituent atoms have definite positions relative to one another i.e., the molecules have a definite shape. The theories of bonding that we have discussed so far do not say anything about the shape of the molecules. A simple theory called VSEPR theory was put forth by Sidgwick and Powell in 1940 to explain the shapes of molecules. It was later refined and extended by Nyholm and Gillespie in1957. This theory focuses on the electron pairs present in the valence shell of the central atom of the molecule and can be stated in terms of two postulates:

POSTULATE 1

The electron pairs (both bonding and non-bonding) around the central atom in a molecule arrange themselves in space in such a way that they minimize their mutual repulsion. In other words, the chemical bonds in the molecule will be energetically most stable when they are as far apart from each other as possible. Let us take up some examples.

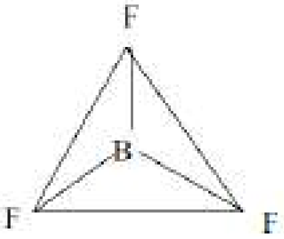
$BeCl_2$ is one of the simple triatomic molecules. In this molecule, the central atom, beryllium has an electronic configuration of $1s^2\ 2s^2$. That is it has two electrons in its valence shell. In the process of covalent bond formation with two chlorine atoms two more electrons are contributed (one by each chlorine atom) to the valence shell. Thus there are a total of 4 valence electrons or two pairs of valence electrons. According to the postulate given above, these electron pairs would try to keep as far away as possible. It makes the two electron pairs to be at an angle of 180° which gives the molecule a linear shape.



Cl — Be — Cl

linear molecule

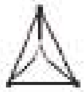
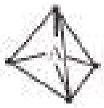
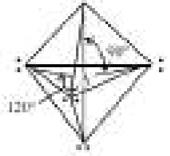
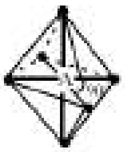
BF_3 : In boron trifluoride, the central atom, boron has an electronic configuration of $1s^2$ $2s^2$ $2p^1$. That is, it has three electrons in its valence shell. In the process of covalent bond formation with three fluorine atoms three more electrons are contributed (one by each fluorine atom) to the valence shell. Thus there are a total of 6 valence electrons or three pairs of valence electrons. According to the VSEPR postulate, these electron pairs would try to keep as far apart as possible. It makes the three electron pairs to be located at an angle of 120° which gives the molecule a planar trigonal shape.



Planar trigonal shape

Thus different molecules would have different shapes depending on the number of valence shell electrons involved. The geometric shapes associated with various numbers of electron

Table 2.1: Geometric arrangements of electron pairs around central atom

Molecule Type	Number of electron pairs	Predicted geometry	Representative structure	Examples
AX_2	2	Linear		$HgCl_2$, BeH_2
AX_3	3	Planer trigonal		BF_3, BCl_3
AX_4	4	Tetrahedral		CCl_4, CH_4, $SiCl_4$
AX_5	5	Trigonal bipyramidal		PCl_5, PF_5
AX_6	6	Octahedral		SF_6, PF_6^-

POSTULATE 2

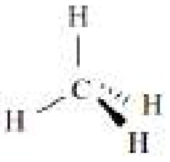
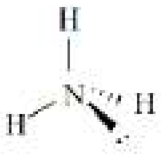
The repulsion of a lone pair of electrons for another lone pair is greater than that between a bond pair and a lone pair which in turn is greater than that between two bond pairs The order of repulsive force between different possibilities is as under.

lone pair - lone pair > lone pair - bond pair > bond pair - bond pair

The shapes of the molecules given in Table 5.1. correspond to the molecules containing only bond pair electrons. The shapes of molecules containing a combination of lone pairs and bond pairs would be distorted from the above mentioned shapes.

Let us take an example of three molecules namely, methane, ammonia and water. All the three contain a total of 4 electron pairs around their central atom. But the nature of these is different in the three cases. In methane molecule the central carbon atom has 4 valence electrons and it shares 4 electrons with four hydrogen atoms. So there are a total of 4 bond pairs and according to Table 5.1 it should have a tetrahedral shape. In case of ammonia also there are four pairs of electrons but their nature is different. Three of these are bond pairs while one is a lone pair. Similarly, in case of water again there are four pairs of electrons ; two are bond pairs while two are lone pairs. Due to the differences in the mutual repulsion between bond pair - bond pair and lone pair - bond pair the molecular shape would be slightly distorted from the expected tetrahedral shape. The number and nature of electron pairs and the geometries of these three molecules are given in

of lone pairs and bond pairs.

Molecule	Number of bond pairs	Number of lone pairs	Molecular geometry	Molecular Shape	Bond angle (in degrees)
CH_4	4	0	tetrahedral		109.5
NH_3	3	1	trigonal pyramidal		107
H_2O	2	2	angular or bent		104.5

We have so far learnt that a chemical bond formation between two atoms can occur by transfer (ionic bonding) or sharing (covalent bonding) of electrons. The processes of bond formation and the bonding in simple molecules can be conveniently represented in terms of electron – dot structures. Further, the VSEPR theory provides a good idea of the shapes of the molecules. But! have you noticed that we have been representing electrons as well defined dots i.e., localized particles. This is in contradiction with the probabilistic (orbital) representation of the electron that you have learnt in lesson 3. Let us learn how do we explain the process of bond formation in terms of modern theories that incorporate the wave mechanical representation of atom.

2.15 MODERN THEORIES OF CHEMICAL BONDING:

The theories of chemical bonding proposed (in 1916) by Kossel and Lewis are called as classical theories of bonding. These do not take into account the wave mechanical or quantum mechanical principles. After the development of quantum mechanical description of atomic structure two more theories were proposed to explain the bonding between atoms. These are called modern theories of chemical bonding. These are Valence Bond Theory (VBT) and Molecular Orbital Theory (MOT). Let us discuss these theories in brief.

2.16 VALENCE BOND THEORY

Valence bond theory was proposed by Heitler and London in 1927, to describe the formation of hydrogen molecule from its atoms. Linus Pauling and others further developed it. In this approach the process of chemical bond formation can be visualised as the overlapping of atomic orbitals of the two atoms as they approach each other. The strength of the bond depends on the effectiveness or extent of the overlapping. Greater the overlapping of the orbitals, stronger is the bond formed. Let us take the example of bonding in hydrogen molecule to understand the VB approach.

Suppose that the two hydrogen atoms are at infinite distance from each other. Their electrons are in their respective 1s orbitals and are under the influence of the corresponding nuclei. As the two atoms approach each other their 1s orbitals begin to overlap which lead maximum and the energy is minimum. The overlapping can be equated to the sharing of electrons between the atoms. The electrons occupying the shared region of orbitals are under the influence of both the nuclei.

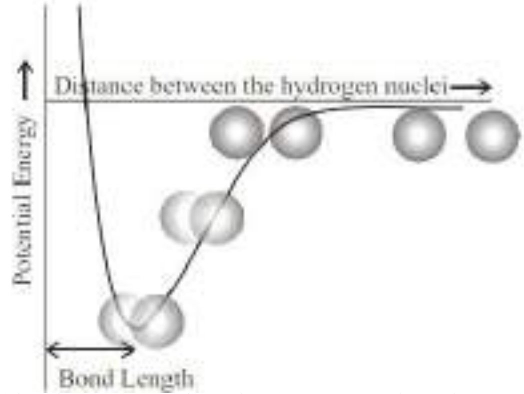
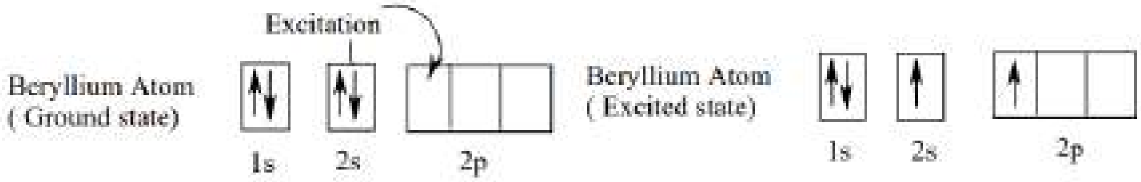


Fig. 2.1: Formation of hydrogen molecule from overlapping of two hydrogen atoms

This simple approach can be used to explain the bonding in simple diatomic molecules like HF,F_2 etc.. However, to explain bonding in molecules containing more than two atoms some additional concepts like excitation and hybridisation need to be used.

Hybridisation

Let us take up the example of bonding in a triatomic molecule; say beryllium hydride (BeH_2) to understand the concept of hybridisation of orbitals and the need for the same. The atomic number of beryllium is 4. Its electronic configuration is $1s^2$ $2s^2$. In order to form bonds with two hydrogen atoms the valence electrons ($2s^2$) of beryllium atom must overlap with the 1s electrons of the two hydrogen atoms. Since the valence shell of beryllium atom contains both the electrons in the same orbital (i.e., 2s) it cannot overlap with the 1s orbital of hydrogen atoms containing one electron.[You know that an orbital can contain a maximum of two electrons with opposite spin]. Pauling got over this problem by suggesting that in the process of bond formation an electron from the 2s orbital of beryllium atom gets momentarily excited to the empty 2p orbital as shown below.



Now the two valence electrons are in two singly occupied orbitals which can overlap with the 1s orbitals of the two hydrogen atoms and form two bonds. The problem is still not over. The two bonds formed by these overlaps would be of different nature. One of these would involve overlapping of 2*s* orbital of beryllium with 1*s* orbital of hydrogen while the other would involve overlapping of 2*p* orbital of beryllium with 1*s* orbital of hydrogen. However, experimentally the two bonds are found to be equivalent.

This problem is solved with the help of a concept called **hybridisation** of orbitals. According to this two or more than two non equivalent orbitals (having different energies and shapes) of comparable energies mix or hybridize and give rise to an equal number of equivalent (same energies and shapes) hybrid orbitals.

In case of $BeCl_2$ the two singly occupied orbitals (2s and 2p) hybridize to give two sp-hybrid orbitals. This is called **sp- hybridisation**. These hybrid orbitals lie along the z-direction and point in opposite directions.

These hybrid orbitals can now overlap with the 1s orbitals of hydrogen atoms to give the linear molecule of $BeCl_2$. as shown below, Fig. 2.2. The concept of hybridisation as illustrated above can be used to describe the bonding and shapes of different molecules by considering hybridisation of suitable orbitals. Let us take up some more cases involving hybridisation of s and p orbitals.

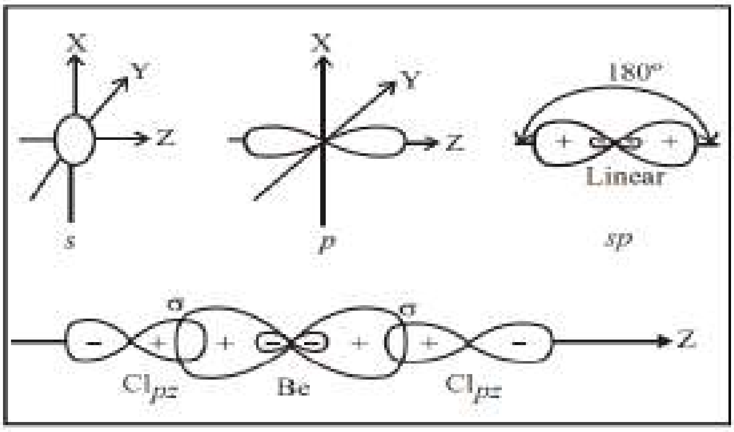
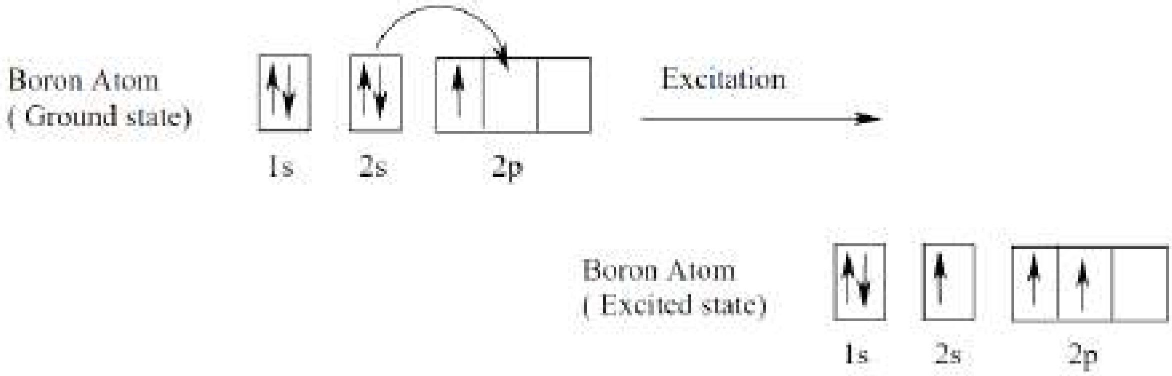
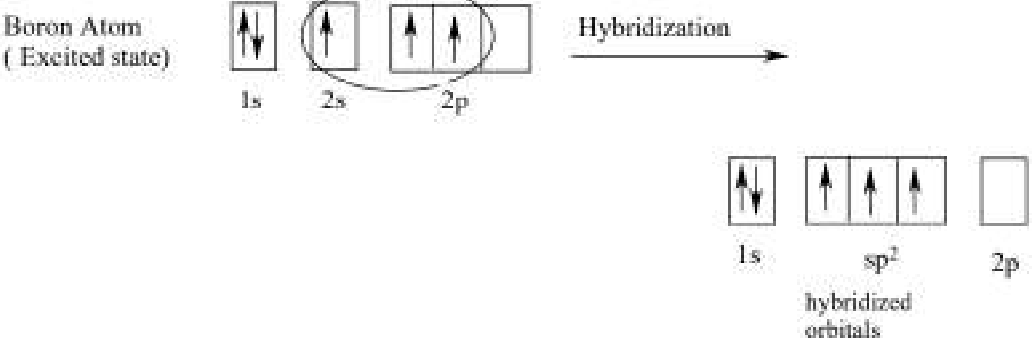


Fig. 2.2: Formation of $BeCl_2$; sp hybridisation

Boron trichloride (sp^2 hybridisation) : In boron there are five electrons and the electronic configuration is $1s^2, 2s^2, 2p^1$. There are three electrons in the valence shell of boron atom. In order to form bonds with three chlorine atoms one of the electrons from the 2s orbital of boron atom is excited to its 2p orbital.



One 2s orbital and two 2p orbitals hybridise to give three sp^2 hybridized orbitals. This is called **sp^2 - hybridisation**.



The three hybridized orbitals are coplanar and directed towards the corners of an equilateral triangle. These hybrid orbitals then form bonds with the p –orbitals of chlorine atoms as shown below, Fig. 2.3.

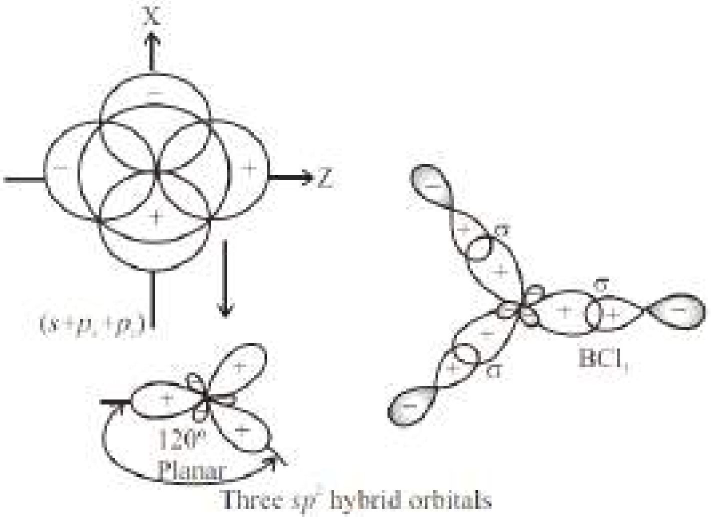
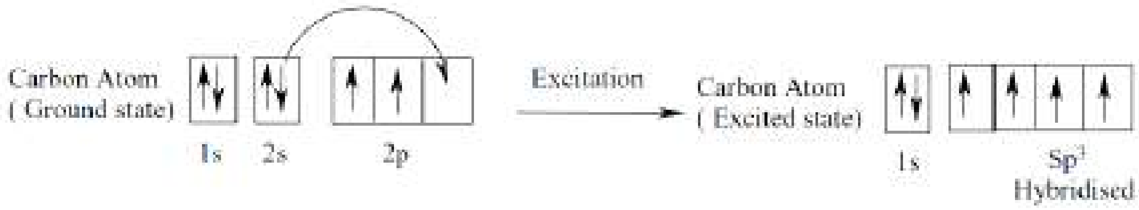


Fig. 2.3: Formation of BCl_3; sp^2 hybridisation.

Bonding in Methane (sp^3 hybridisation) : In case of methane the central atom, carbon, has an electronic configuration of $1s^2$, $2s^2$, $2p^2$. In order to form bonds with four hydrogen atoms one of the electrons from the 2s orbital of carbon atom is excited to the 2p orbital.

One 2s orbital and three 2p orbitals of the carbon atom then hybridize to give four sp^3 hybridized orbitals. This is called **sp^3- hybridisation.**



These four sp^3 hybrid orbitals are directed towards the corners of a regular tetrahedron. These hybrid orbitals then form bonds with the 1s orbitals of hydrogen atoms to give a methane molecule as shown below, Fig. 2.4.

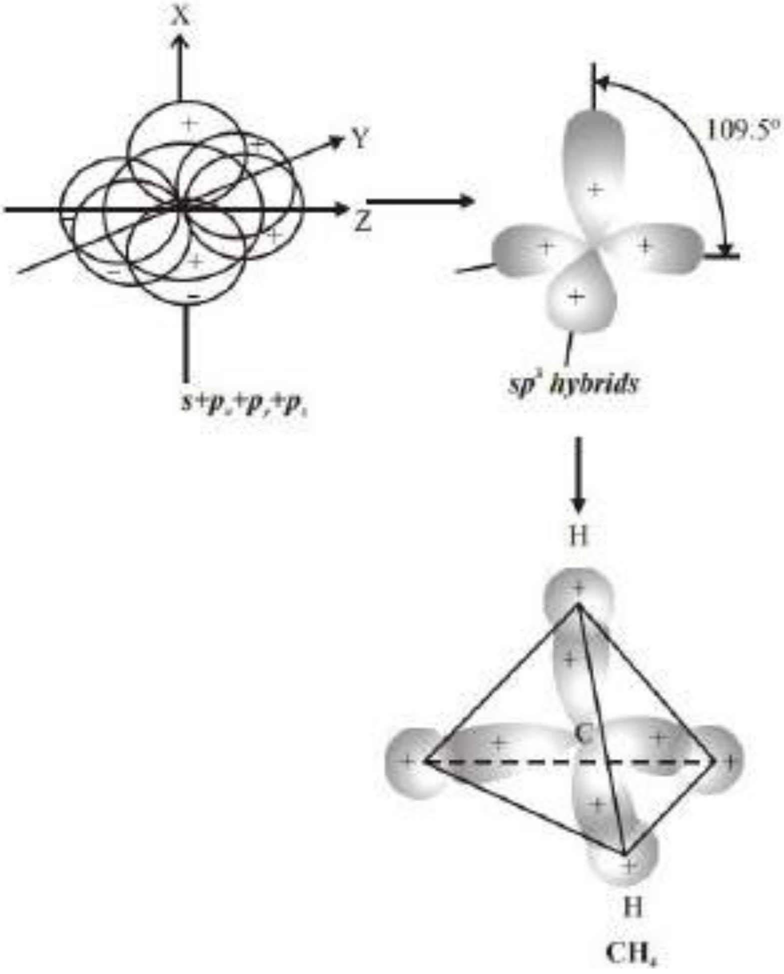
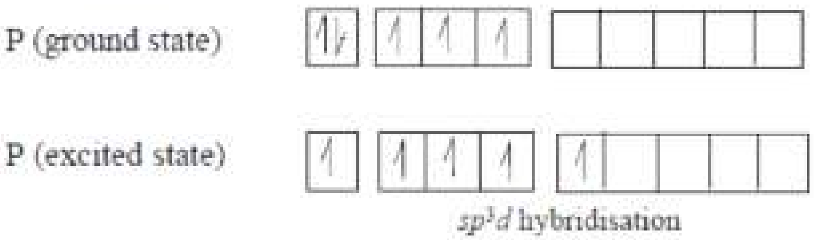


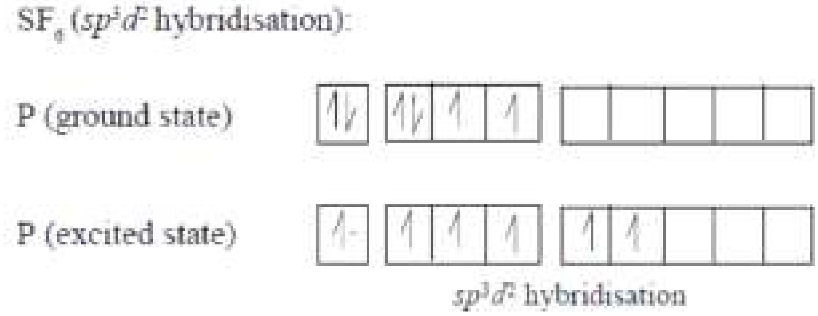
Fig. 2.4 : Formation of CH_4 ; sp^3 hybridisation.

Phosphorus pentachloride (sp^3d hybridisation):



Five sp3d hybrid orbitals are formed which are directed towards the corners of a trigonal bipyramidal (Fig. 2.5a). These orbitals overlap with singly filled p-orbitals of five chlorine bonds are formed. Thus PCl5σatoms and five molecule has a trigonal bipyramidal geometry.

Three P–Cl bonds (equatorial) make an angle of 120º with each other and lie in one plane. The other two P–Cl bonds (axial) are at 90º to the equatorial plane, one lying above and the other lying below the plane.



Six sp^{3}d^2 hybrid orbitals are formed which are directed towards the corners of a regular σoctahedron. These orbitals overlap with singly filled orbitals of six F atoms and form bonds giving a regular octahedral geometry (Fig. 2.5 b)

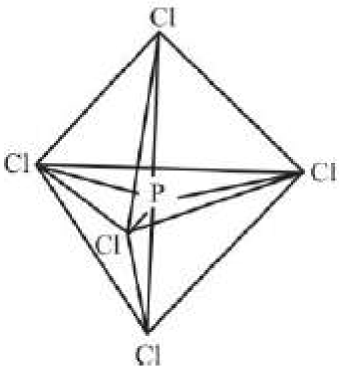


Fig. 2.5 (a) : Trigonal bipyramidal geometry molecule

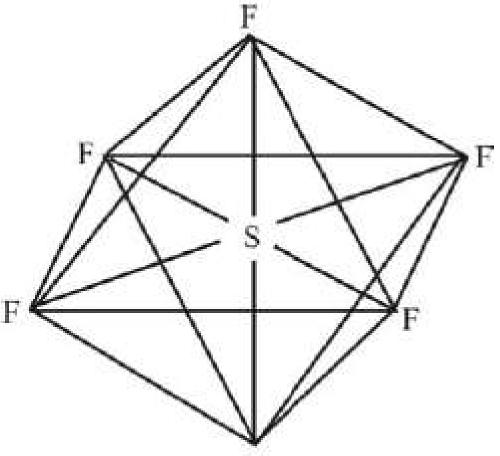


Fig. 2.5 (b): Octahedral geometry of SF$_6$ of PCl$_5$ molecule.

Hybridisation And Multiple Bonds

So far we have discussed the bonding in those molecules in which the orbitals on a single central atom are hybridized. Let us see how does the concept of hybridisation help us in understanding bonding between pairs of such atoms. In the case of bonding in ethane (C_2H_6), two carbon atoms are bonded to each other and each carbon atom is bonded to three hydrogen atoms. You would recall that in the case of methane the valence orbitals of carbon atom undergo sp^3 hybridisation. In ethane each carbon atom undergoes sp^3 hybridisation to give four *sp^3* hybridized orbitals. The two carbon atoms form a carbon – carbon bond by sp^3 - sp^3 overlapping. The remaining six *sp^3 hybridized* orbitals overlap with 1*s* orbitals of hydrogen atoms to give a molecule of *ethane*, C_2H_6 as shown in fig. 1.

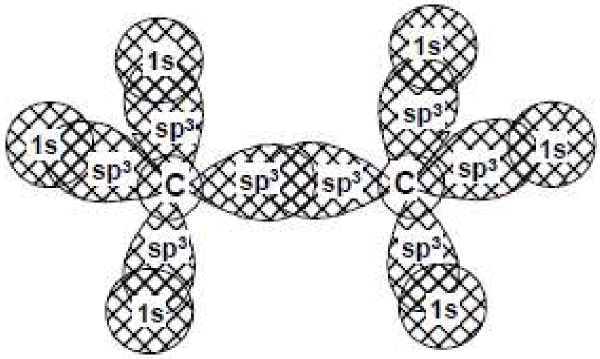


Fig. 2.6: Formation of ethane molecule

Bonding in ethene: In case of ethene, the relevant orbitals of the carbon atoms undergo *sp^2* hybridisation. Here, only two of the three *p* orbitals of the carbon atoms hybridize with the *2s* orbital to form three *sp^2* hybrid orbitals each. The remaining p-orbitals (one on each carbon atom) do not take part in hybridization. A carbon – carbon bond is formed by overlapping of *sp^2* orbital on the two carbon atoms [Fig 2.7(a)]. The remaining four *sp^2* hybridized orbitals overlap with the 1*s* orbitals of hydrogen atoms to give the basic skeleton of the molecule. This leaves an un-hybridized p orbital each on both the carbon atoms [Fig 2.7(b)]. These are perpendicular to the molecular plane and undergo sideways overlap to give an electron cloud in the plane above and below the molecule [Fig 2.7(b and c)]. This is called a π- bond. In ethene there are two bonds between the carbon atoms (one sigma and one pi bond).

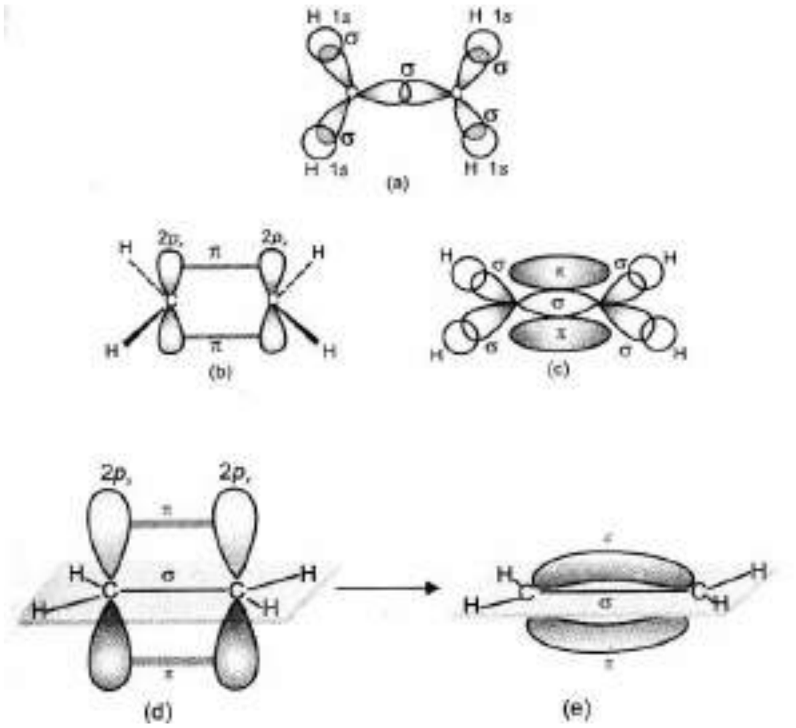


Fig. 2.7 : Formation of ethylene molecule: a) formation of the basic skeleton of the molecule b) sideways overlapping of the un-hybridized p orbitals and c) a π- bond (d) and (e) complete picture of ethylene molecule.

Bonding in ethyne (acetylene): In case of acetylene the bonding can be explained in terms of sp-hybridisation in carbon atoms. One 2s and one 2p orbitals hybridize to give two sp-hybridized orbitals. This leaves two mutually perpendicular unhybridised *p* orbitals each on both the carbon atoms. The carbon–carbon bond is formed by sp - sp overlapping with each other. The remaining sp orbital on each carbon overlaps with the 1s orbital of hydrogen to give C-H bonds (Fig. 2.8). The unhybridised *p* orbital each on both the carbon atoms overlap sideways to give two π-bonds.

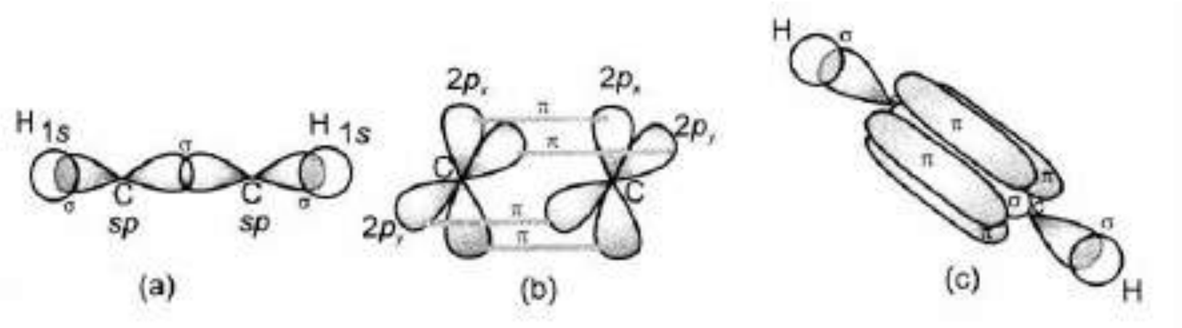


Fig. 2.8 : Formation of acetylene molecule : a) formation of the basic skeleton of the molecule b) sideways overlapping of two pairs of un-hybridized p orbitals and c) two mutually perpendicular π- bonds.

2.17 METALLIC BONDS AND METALLIC STRUCTURES

In the early 1900's, Paul Drüde came up with the "sea of electrons" metallic bonding theory by modeling metals as a mixture of atomic cores (atomic cores = positive nuclei + inner shell of electrons) and valence electrons. Metallic bonds occur among metal atoms. Whereas ionic bonds join metals to non-metals, metallic bonding joins a bulk of metal atoms. A sheet of aluminum foil and a copper wire are both places where you can see metallic bonding in action.

Metals tend to have high melting points and boiling points suggesting strong bonds between the atoms. Even a soft metal like sodium (melting point 97.8°C) melts at a considerably higher temperature than the element (neon) which precedes it in the Periodic Table. Sodium has the electronic structure $1s^2 2s^2 2p^6 3s^1$. When sodium atoms come together, the electron in the 3s atomic orbital of one sodium atom shares space with the corresponding electron on a neighboring atom to form a molecular orbital - in much the same sort of way that a covalent bond is formed.

The difference, however, is that each sodium atom is being touched by eight other sodium atoms and the sharing occurs between the central atom and the 3s orbital on all of the eight other atoms. Each of these eight is in turn being touched by eight sodium atoms, which in turn are touched by eight atoms - and so on and so on, until you have taken in all the atoms in that lump of sodium. All of the 3s orbital on all of the atoms overlap to give a vast number of molecular orbital that extend over the whole piece of metal. There have to be huge numbers of molecular orbital, of course, because any orbital can only hold two electrons.

The electrons can move freely within these molecular orbital, and so each electron becomes detached from its parent atom. The electrons are said to be delocalized. The metal is held together by the strong forces of attraction between the positive nuclei and the delocalized electrons.

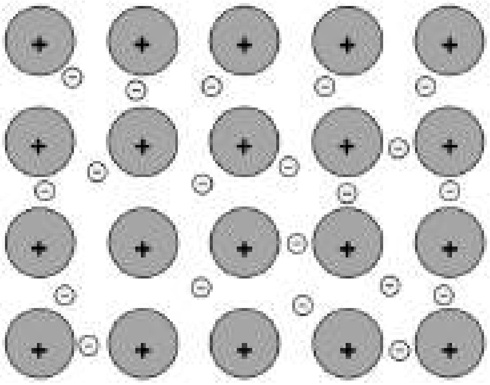


Fig. 2.9 : Metallic Bonding: The Electron Sea Model: Positive atomic nuclei (orange circles) surrounded by a sea of delocalized electrons (small circles).

This is sometimes described as "an array of positive ions in a sea of electrons". If you are going to use this view, beware! Is a metal made up of atoms or ions? It is made of atoms. Each positive center in the diagram represents all the rest of the atom apart from the outer electron, but that electron has not been lost - it may no longer have an attachment to a particular atom, but it's still there in the structure. Sodium metal is therefore written as Na, not Na^+.

Properties of metallic structures

The properties of metals can be explained using metallic bonding.

- Metals have high melting and boiling points. The metallic bonds found throughout the whole metallic lattice structure are very strong. Melting the metal would require the breaking of these bonds which would take lots of energy due to their strength and number
- Metals are hard, strong and have a high density. The metal ions in the metallic lattice are closely packed together with only very small gaps between them. This, along with the strength of the metallic bonds, makes the structure very hard, dense and strong and makes them suitable for a range of uses such as making bridges and vehicles
- Metals are good conductors of electricity. For example, copper is used in electrical wiring as it is a good conductor of electricity. Metals are able to conduct electricity due

to the delocalized electrons which are free to move and carry charge throughout the metallic lattice structure.

- Metals are malleable and ductile. Malleable means that the metal can be moulded into a variety of different shapes. Ductile means that the metal can be stretched out into thin wires without breaking.

The metal ions in a metallic lattice are arranged in layers which are able to slide and move over each other. If heat is applied to a metallic lattice, the forces of attraction holding the layers of ions in place are overcome and the layers can slide over each other. By applying force to a metallic lattice, we can also move the layers of atoms over each other into new positions. This means that we can use a combination of heat and force to force the layers of ions to move and change the shape of the metal. This is very useful in manufacturing as these metallic structures can be changed into whatever shape is needed and they will still be strong.

2.18 EXERCISE:

1. Define electrovalent bond.

2. Show the formation of a nitrogen molecule from two nitrogen atoms in terms of Lewis theory.

3. What do you understand by a polar covalent bond? Give two examples.

4. What is a coordinate covalent bond? How is it different from a covalent bond?

5. What are the basic postulates of VSEPR theory?

6. Predict the shape of methane (CH_4) on the basis of VSEPR theory.

7. What do you understand by the term, ‘hybridisation’?

8. How would you explain the shape of ammonia molecule on the basis of hybridisation?

9. What do you understand by a chemical bond?

10. Explain the process of bond formation as a decrease in energy.

11. What do you understand by the term, ‘bond length’?

12. What are Lewis electron-dot symbols? Show the formation of $MgCl_2$ in terms of Lewis symbols.

13. Define a coordinate bond and give some examples.

14. What is VSEPR theory? Predict the shape of SF_6 molecule using this theory.

15. Why do we need the concept of hybridisation? How does it help in explaining the shape of methane?

16. Write a short note on metallic bond and metallic structures.

CHAPTER 3

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

3.1 INTRODUCTION

The periodic table is an ordered arrangement of the chemical elements into rows and columns and is also known as the periodic table of the elements. The Periodic Table is arguably the most important concept in chemistry, both in principle and in practice. In this chapter 3 we will study the historical development of the Periodic Table.

3.2 IMPORTANCE OF THE CLASSIFICATION OF THE ELEMENTS

It is well known that the elements are the basic units of all types of matter. However, in 1800, only 31 elements were known. By 1865, the number of identified elements had increased upto 63. Till now, 114 elements are known and the recently discovered elements among them are mostly man-made. The efforts to synthesize new elements are still continuing. The number of such elements is large and so, it is very difficult to study individually the chemistry of all these elements and their innumerable compounds individually. To overcome this problem, scientists searched for a systematic way to organize their knowledge by classifying the elements. This not only would rationalize known chemical facts about elements, but also will be able to predict new ones for undertaking further study.

3.3 ORIGIN OF PERIODIC CLASSIFICATION

Classification of elements into groups and development of Periodic Law and Periodic Table are the consequences of systematizing the knowledge gained by a number of scientists through their observations and experiments. The German chemist, Johann Dobereiner in early 1800's was the first to consider the idea of trends among properties of elements. By 1829 he noted a similarity among the physical and chemical properties of several groups of three elements (Triads). In each case, he noticed that the middle element of each of the Triads had an atomic weight about half way between the atomic weights of the other two (Table 3.1).

The early years of the 19th century witnessed a rapid development in analytical chemistry—the art of distinguishing different chemical substances—and the consequent building up of a vast body of knowledge of the chemical and physical properties of both elements and compounds. This rapid expansion of chemical knowledge soon necessitated classification.

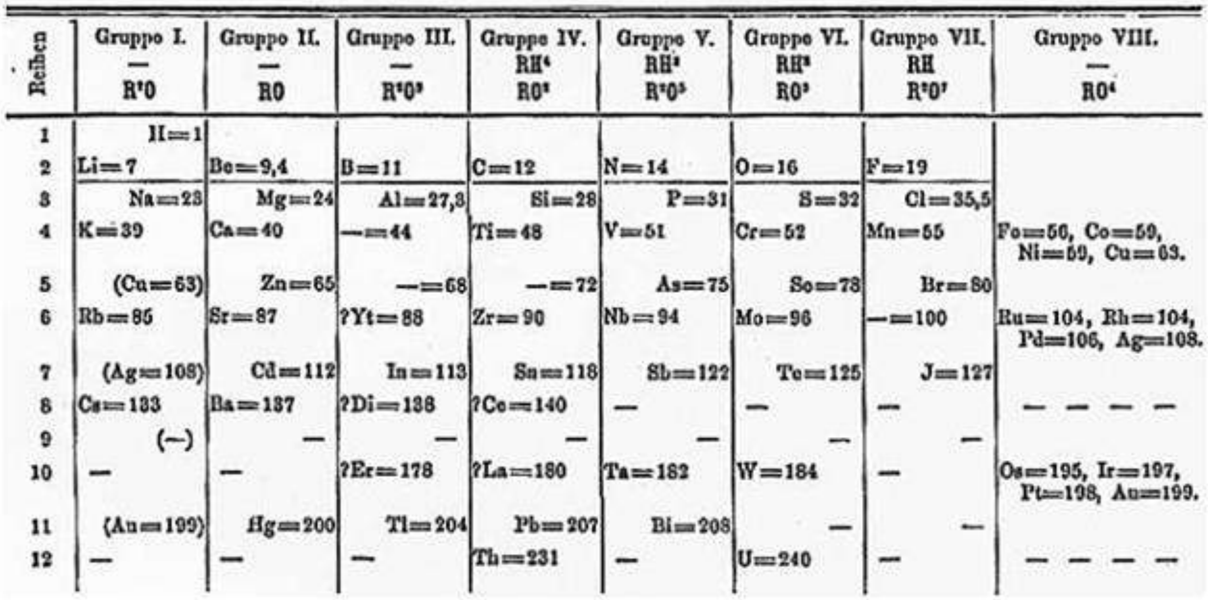
3.4 DEVELOPMENT OF THE PERIODIC TABLE

The modern periodic table was developed by the Russian chemist Dmitri Mendeleev and the German chemist Lothar Meyer. Around 1869 Mendeleev recognized the periodicity of the elements. Although scientists previously classified the elements, Mendeleev succeeded in interpreting the principles in an adequate way. Mendeleev arranges the elements according to their atomic mass in his periodic table.

Mendeleev arranged elements in horizontal rows and vertical columns of a table in orderof their increasing atomic weights in such a way that the elements with similar properties occupied the same vertical column or group. Mendeleev's system of classifying elements was more elaborate than that of Lothar Meyer's. He fully recognized the significance of periodicity and used broader range of physical and chemical properties to classify the elements. In particular, Mendeleev relied on the similarities in the empirical formulas and properties of the compounds formed by the elements. He realized that some of the elements did not fit in with his scheme of classification if the order of atomic weight was strictly followed.

Mendeleev's Periodic law: The physical and chemical properties of elements are a periodic function of their atomic weights. If the elements are arranged in order of their increasing atomic weights, after a regular interval elements with similar properties are repeated. On the basis of his law, Mendeleev proposed a periodic table for classification of elements which is known as Mendeleev's Periodic Table.

Table. Mendeleev periodic table*:



Reihen	Gruppo I. — R^2O	Gruppo II. — RO	Gruppo III. — R^2O^3	Gruppe IV. RH^4 RO^2	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^2 RO^3	Gruppe VII. RH R^2O^7	Gruppo VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

*http://en.wikipedia.org/wiki/Dmitri_Mendeleev

Merits and limitations of the Mendeleev periodic table:

Merits:

In Mendeleev periodic table, elements were arranged according to their similarities in physical and chemical properties. Therefore, it makes easier for studying and remembering the properties of huge numbers of elements just knowing the properties of the group . Furthermore, based on the periodic table the properties of some unknown elements can be predicted. This was a great achievement.

Limitations:

Hydrogen was placed in Group I, although, its properties resembled the Group I elements (the alkali metals) as well as the group VII elements (the halogens). Hence, in the periodic table the position of hydrogen was not justified.

In some cases Mendeleev placed elements according to their similarities in properties and not in increasing order of their atomic masses, while some dissimilar elements were grouped together. Thus, the position of these elements was not justified. For example, cobalt (at. mass 58.9) was placed before nickel (at. mass 58.6); copper and mercury are similar in their properties but were placed separately. Copper was placed in group I although it did not resemble the elements of this group.

Novel metals, *e .g* . Cu, Ag, Au were placed in Group I with chemically dissimilar alkaline earth metals. Moreover, Mn has been placed with halogens.

Same element with different atomic mass but same in atomic number is known as isotope of the element. In Mendeleev periodic table isotopes should have different place, but there was no province for the positions of isotopes.

In certain pairs of elements like, Ar (40) and K (39); Co (58.9) and Ni (58.6); Te (127.6) and I (126.9) the arrangement was not justified, *e .g* .Ar was placed before K.

Valences states or the elements have not been considered for their placement in a group.

Fourteen elements that follow lanthanum called lanthanides and fourteen elements following actinium called actinides were not given proper places in Mendeleev's periodic table, rather they have been provide two rows at the bottom of the table.

3.5 MODERN PERIODIC LAW AND THE PRESENT FORM OF THE PERIODIC TABLE

Earlier scientists assumed that the properties of elements are periodic functions of their atomic masses. On the basis of this assumption, Mendeleev placed 63 elements in a vertical column called groups and in horizontal rows called periods.

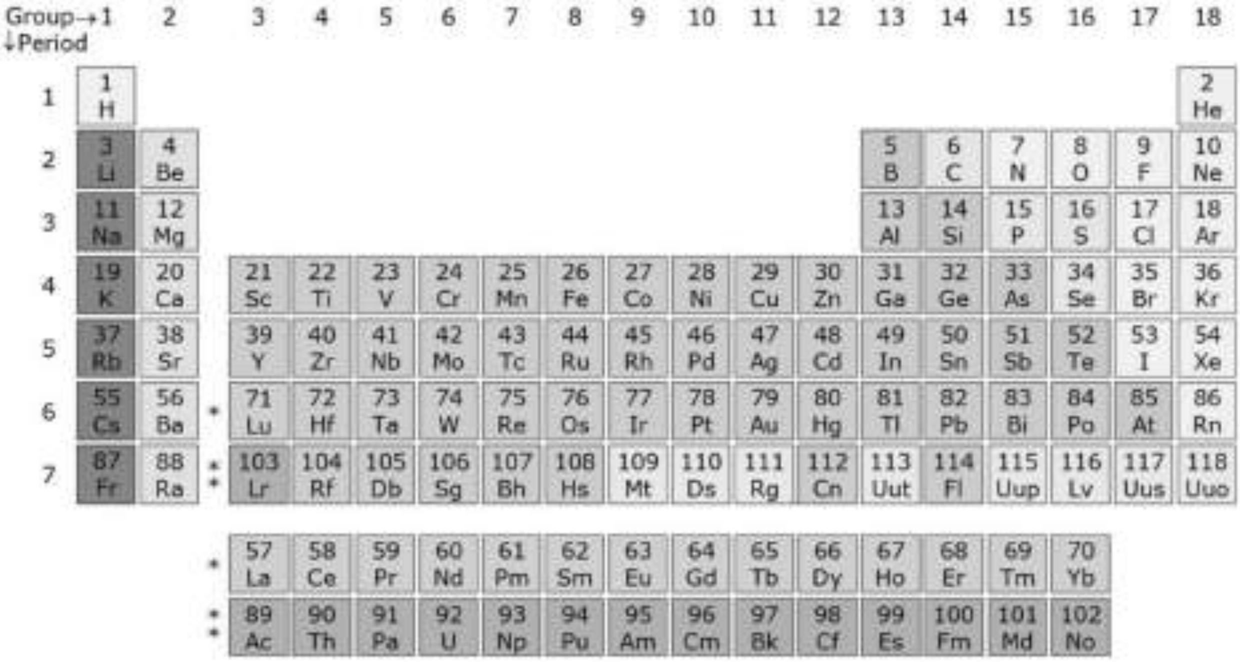
This method was rejected as it could not explain the position of certain elements, rare earth metals, and isotopes. A scientist named Henry Moseley removed these defects and put forward the modern periodic table with the modern periodic law.

Moseleys Periodic Law:

He stated that the properties of elements are periodic functions of their atomic number.

Modern Periodic Table:

A tabular arrangement of elements in groups and periods which highlights the regular trends in properties of elements is defined as the periodic table.



Group→ ↓Period	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
			**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Features of Modern Periodic Table

There are eighteen vertical columns known as groups in the modern periodic table which are arranged from left to right and seven horizontal rows which are known as periods. **Group number**	**Group name**	**Property**
Group 1 or IA	Alkali metals	They form strong alkalis with water
Group 2 or IIA	Alkaline earth metals	They also form alkalis but weaker than group 1 elements
Group 13 or IIIA	Boron family	Boron is the first member of this family
Group 14 or IVA	Carbon family	Carbon is the first member of this property
Group 15 or VA	Nitrogen family	This group has non-metals and metalloids
Group 16 or VIA	Oxygen family	They are also known as chalcogens
Group 17 or VIIA	Halogen family	The elements of this group form salts.

Group 18	Zero group	They are noble gases and under normal conditions they are inert.

Classifications of Elements in the Periodic Table

The elements of group 1, 2, 13, 14, 15, 16, and 17 are known as the main group elements or normal elements. The elements of groups 3, 4, 5, 6, 7, 8, 9, 11 and 12 are known as the transition elements. Group 18 is called **noble gases** or **inert gases**. Their outermost shell is completely filled. Due to this stable electronic configuration, they generally don't react with the other elements.

When we talk about the periods of a modern periodic table, one should keep in mind that the number of shells present in an atom determines its period number. The elements of period one will have only one shell, elements of period two will have two shells and so on. The first period of the modern periodic table is the shortest period as it contains only two elements. The period number two and three consists of eight elements each and is known as short groups. Period four and five have eighteen elements and are known as the long group. In the modern periodic table, group number 3 of period six contains the lanthanide series which are the rare earth elements. We have radioactive elements (actinides) present in group 3 of period seven.

3.6 NOMENCLATURE OF ELEMENTS WITH ATOMIC NUMBERS > 100

It is a generally accepted convention that the discoverer of an element has the honour of naming it. The inspiration often comes from origin, mythical characters, place, physical or chemical properties, and more recently to commemorate the names of eminent scientists. Of course, the suggestion has to be ratified by the International Union of Pure and Applied Chemistry (IUPAC). Newly discovered or undiscovered superheavy elements are often referred to in the scientific literature but until they have received permanent names and symbols from IUPAC, temporary designators are required. In 1978 IUPAC Commission on the Nomenclature of Inorganic Chemistry decided that it is necessary to have a systematic naming for the elements with atomic number greater than 100 (Z > 100), even for those which had not been discovered. The Commission decided that these elements would be best named systematically and that names should accord with the following rules:

The name is derived directly from the atomic number of the element using the following Latin numerical roots.

Number	**Root**
0	nil
1	un
2	bi
3	tri
4	quad

5	pent
6	hex
7	sept
8	oct
9	enn

1. The roots are put together in the order of the digits which make up the atomic number and terminated by 'ium' to spell out the name. The final 'n' of 'enn' is elided when it occurs before 'nil', and the final 'i' of 'bi' and of 'tri' when it occurs before 'ium'.

2. The symbol of the element is composed of the initial letters of the numerical roots which make up the name.

3. The root 'un' is pronounced with a long 'u', to rhyme with 'moon'. In the element names each root is to be pronounced separately.

Here are a few examples of the names generated for elements with atomic numbers 101 to 900.

Atomic number	**Name**	**Symbol**
101	Unnilunium	Unu
102	Unnilbium	Unb
103	Unniltrium	Unt
104	Unnilquadium	Unq
105	Unnilpentium	Unp
106	Unnilhexium	Unh
107	Unnilseptium	Uns
108	Unniloctium	Uno
109	Unnilennium	Une
110	Ununnilium	Uun
111	Unununium	Uuu

112	Ununbium	Uub
113	Ununtrium	Uut
114	Ununquadium	Uuq
115	Ununpentium	Uup
116	Ununhexium	Uuh
117	Ununseptium	Uus
118	Ununoctium	Uuo
119	Ununennium	Uue
120	Unbinilium	Ubn
121	Unbiunium	Ubu
130	Untrinilium	Utn
140	Unquadnilium	Uqn
150	Unpentnilium	Upn
160	Unhexnilium	Uhn
170	Unseptnilium	Usn
180	Unoctnilium	Uon
190	Unennilium	Uen
200	Binilnilium	Bnn
201	Biniluniium	Bnu
202	Binilbium	Bnb
300	Trinilnilium	Tnn
400	Quadnilnilium	Qnn

500	Pentnilnilium	Pnn

3.7 SHIELDING AND EFFECTIVE NUCLEAR CHARGE

For an atom or an ion with only a single electron, we can calculate the potential energy by considering only the electrostatic attraction between the positively charged nucleus and the negatively charged electron. When more than one electron is present, however, the total energy of the atom or the ion depends not only on attractive electron-nucleus interactions but also on repulsive electron-electron interactions. When there are two electrons, the repulsive interactions depend on the positions of *both* electrons at a given instant, but because we cannot specify the exact positions of the electrons, it is impossible to exactly calculate the repulsive interactions. Consequently, we must use approximate methods to deal with the effect of electron-electron repulsions on orbital energies.

Electron Shielding and Effective Nuclear Charge

If an electron is far from the nucleus (i.e., if the distance rr between the nucleus and the electron is large), then at any given moment, many of the other electrons will be *between* that electron and the nucleus (Below Figure). Hence the electrons will cancel a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between it and the electron farther away. As a result, the electron farther away experiences an effective nuclear charge (Zeff) that is less than the actual nuclear charge Z. This effect is called electron shielding.

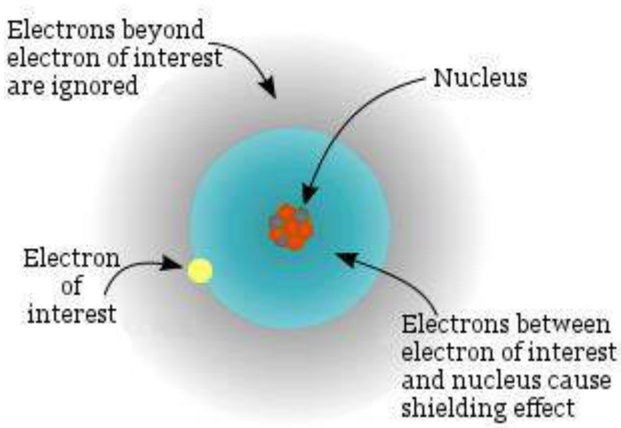


Figure: This image shows how inner electrons can shield outer electrons from the nuclear charge.

As the distance between an electron and the nucleus approaches infinity, Zeff approaches a value of 1 because all the other $(Z-1)$ electrons in the neutral atom are, on the average, between it and the nucleus. If, on the other hand, an electron is very close to the nucleus, then at any given moment most of the other electrons are farther from the nucleus and do not shield the nuclear charge. At $r \approx 0$, the positive charge experienced by an electron is approximately the full nuclear charge, or $Z_{eff} \approx Z$. At intermediate values of r, the effective nuclear charge is somewhere between 1 and Z:

$1 \leq Z_{eff} \leq Z$.

Notice that $Z_{eff} = Z$ only for hydrogen and only for helium are Z_{eff} and Z comparable in magnitude

Shielding

Shielding refers to the core electrons repelling the outer electrons, which lowers the effective charge of the nucleus on the outer electrons. Hence, the nucleus has "less grip" on the outer electrons insofar as it is shielded from them.

Zeff can be calculated by subtracting the magnitude of shielding from the total nuclear charge and the effective nuclear charge of an atom is given by the equation:

$Z_{eff}=Z-S$

where Z is the atomic number (number of protons in nucleus) and SS is the shielding constant. The value of Z_{eff} will provide information on how much of a charge an electron actually experiences.

We can see from the above equation that the effective nuclear charge of an atom increases as the number of protons in an atom increases. Therefore as we go from left to right on the periodic table the effective nuclear charge of an atom increases in strength and holds the outer electrons closer and tighter to the nucleus. As we will discuss later on in the chapter, this phenomenon can explain the decrease in atomic radii we see as we go across the periodic table as electrons are held closer to the nucleus due to increase in number of protons and increase in effective nuclear charge.

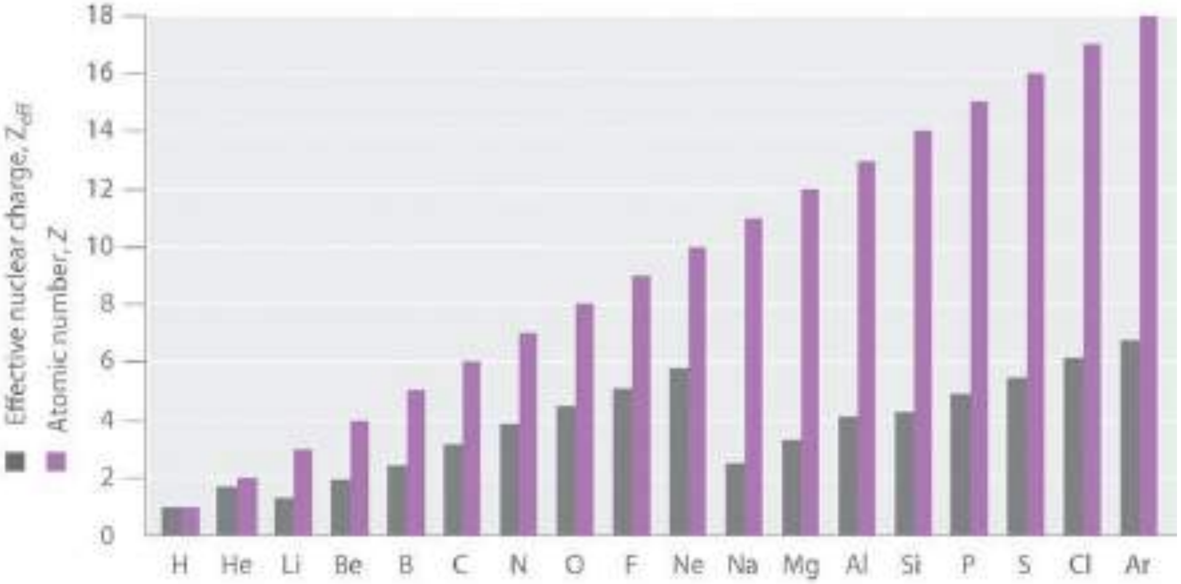


Figure : Relationship between the Effective Nuclear Charge Zeff and the Atomic Number *Z* for the Outer Electrons of the Elements of the First Three Rows of the Periodic Table. Except for hydrogen, (Z_{eff} is always less than Z, and (Z_{eff} increases from left to right as you go across a row.

Electrons that are shielded from the full charge of the nucleus experience an *effective nuclear charge (*Z_{eff}) of the nucleus, which is some degree less than the full nuclear charge an electron would feel in a hydrogen atom or hydrogenlike ion.

3.8 SLATER'S RULES

We have previously described the concepts of electron shielding, orbital penetration and effective nuclear charge, but we did so in a qualitative manner. In this section, we explore one model for quantitatively estimating the impact of electron shielding, and then use that to calculate the effective nuclear charge experienced by an electron in an atom. The model we will use is known as Slater's Rules (J.C. Slater, *Phys Rev* **1930**, *36*, 57).

The general principle behind Slater's Rule is that the actual charge felt by an electron is equal to what you'd expect the charge to be from a certain number of protons, but minus a certain amount of charge from other electrons. Slater's rules allow you to estimate the effective nuclear charge Zeff from the real number of protons in the nucleus and the effective shielding of electrons in each orbital "shell" (e.g., to compare the effective nuclear charge and shielding 3d and 4s in transition metals). Slater's rules are fairly simple and produce fairly accurate predictions of things like the electron configurations and ionization energies.

Slater's Rules

- **Step 1**: Write the electron configuration of the atom in the following form:

(1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p) . . .

- **Step 2**: Identify the electron of interest, and ignore all electrons in higher groups (to the right in the list from Step 1). These do not shield electrons in lower groups

- **Step 3**: Slater's Rules is now broken into two cases:

o the shielding experienced by an s- or p- electron,

- electrons within same group shield **0.35**, except the 1*s* which shield **0.30**

- electrons within the n-1 group shield **0.85**

- electrons within the n-2 or lower groups shield **1.00**

o the shielding experienced by n*d* or n*f* valence electrons

- electrons within same group shield **0.35**

- electrons within the lower groups shield **1.00**

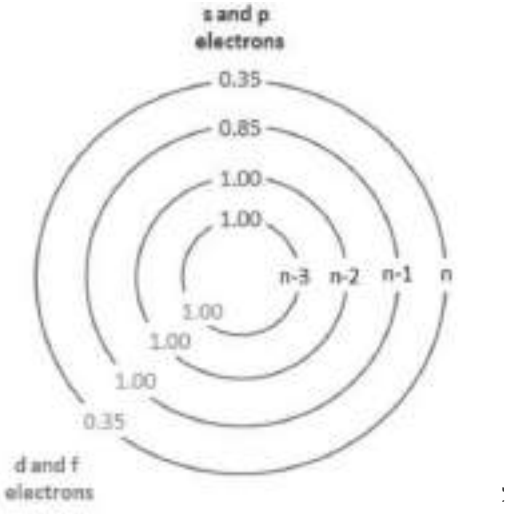


Figure: Graphical onstants indicated.

Shielding happens when electrons in lower valence shells (or the same valence shell) provide a repulsive force to valence electrons, thereby "negating" some of the attractive force from the positive nucleus. Electrons really close to the atom (n-2 or lower) pretty much just look like protons, so they completely negate. As electrons get closer to the electron of interest, some more complex interactions happen that reduce this shielding.

EXAMPLE: The Shielding of 2p Electrons of Nitrogen Atoms

What is the shielding constant experienced by a 2p electron in the bromine atom?

Given: Nitrogen (N)

Asked for: S, the shielding constant, for a 2p electron

Strategy:

A. Determine the electron configuration of nitrogen, then write it in the appropriate form.

B. Use the appropriate Slater Rule to calculate the shielding constant for the electron.

Solution A N: 1s2 2s2 2p3

N: (1s2)(2s2,2p3)

Solution B

S[2p] = (0.85*2) + (0.35*4) = 3.10

- the 1s electrons shield the other 2p electron to 0.85 "charges".
- the 2s and 2p electrons shield the other 2p electron equally at 0.35 "charges".

EXAMPLE: The Shielding of 3d Electrons of Bromine Atoms

What is the shielding constant experienced by a 3*d* electron in the bromine atom?

Given: Bromine (Br)

Asked for: *S*, the shielding constant, for a 3*d* electron

Strategy:

Determine the electron configuration of bromine, then write it in the appropriate form.

Use the appropriate Slater Rule to calculate the shielding constant for the electron.

Solution A Br: 1s2 2s2 2p6 3s2 3p6 4s2 3d10 4p5

Br: (1s2)(2s2,2p6)(3s2,3p6)(3d10)(4s2,4p5)

Ignore the group to the right of the 3d electrons. These do not contribute to the shielding constant.

Solution B *S*[3d] = (1.00*18) + (0.35*9) = 21.15

Calculating Zeff

As discussed previously, Zeff can be calculated by subtracting the magnitude of shielding from the total nuclear charge and the effective nuclear charge of an atom is given by the equation:

Zeff = Z−S

EXAMPLE: What is the effective nuclear charge experienced by a valence p- electron in boron?

Given: Boron (B)

Asked for: Zeff for a valence p- electron

Strategy:

A. Determine the electron configuration of boron and identify the electron of interest.

B. Use the appropriate Slater Rule to calculate the shielding constant for the electron.

C. Use the Periodic Table to determine the actual nuclear charge for boron.

D. Determine the effective nuclear constant.

Solution:

A B: 1*s*2 2*s*2 2*p*1 . The valence p- electron in boron resides in the 2*p* subshell.

B: (1*s*2)(2*s*2,2*p*1)

B *S*[2*p*] = 1.00(0) + 0.85(2) + 0.35(2) = 2.40

C Z = 5

D Zeff = 2.60

3.9 PERIODIC TRENDS IN PROPERTIES OF ELEMENTS

Atomic Radii

Atomic radii is useful for determining many aspects of chemistry such as various physical and chemical properties. The periodic table greatly assists in determining atomic radius and presents a number of trends.

Definition

Atomic radius is generally stated as being the total distance from an atom’s nucleus to the outermost orbital of electron. In simpler terms, it can be defined as something similar to the radius of a circle, where the center of the circle is the nucleus and the outer edge of the circle is the outermost orbital of electron. As you begin to move across or down the periodic table, trends emerge that help explain how atomic radii change.

The effective nuclear charge (Zeff) of an atom is the net positive charge felt by the valence electron. Some positive charge is shielded by the core electrons therefore the total positive charge is not felt by the valence electron. A detailed description of shielding and effective nuclear charge can be found here. Zeff greatly affects the atomic size of an atom. So as the Zeff decreases, the atomic radius will grow as a result because there is more screening of the electrons from the nucleus, which decreases the attraction between the nucleus and the electron. Since Zeff decreases going down a group and right to left across the periodic table, the atomic radius will *increase* going down a group and right to left across the periodic table.

Types of Radius with Respect to Types of Bonds

Determining the atomic radii is rather difficult because there is an uncertainty in the position of the outermost electron – we do not know exactly where the electron is. This phenomenon can be explained by the Heisenberg Uncertainty Principle. To get a precise measurement of the radius, but still not an entirely correct measurement, we determine the radius based on the distance between the nuclei of two bonded atoms. The radii of atoms are therefore determined by the bonds they form. An atom will have different radii depending on the bond it forms; so there is no fixed radius of an atom.

Covalent Radius

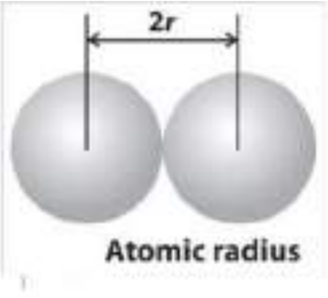
When a covalent bond is present between two atoms, the covalent radius can be determined. When two atoms of the same element are covalently bonded, the radius of each atom will be half the distance between the two nuclei because they equally attract the electrons. The distance between two nuclei will give the diameter of an atom, but you want the radius which is half the diameter.

Covalent radii will increase in the same pattern as atomic radii. The reason for this trend is that the bigger the radii, the further the distance between the two nuclei. See explanation for Zeff for more details.

The covalent radius depicted below in Figure will be the same for both atoms because they are of the same element as shown by X.

Periodic trends in Atomic and Ionic Radii:

Atomic radius or size of an atom (distance from nucleus to outermost electron). The atomic size is defined as the value of r below which 90% of electron density is contained



- Along a period left to right atomic radius decreases because as we go from left to right principle quantum number “n” remain same. So, electrons are put into the same level and as number of electrons increases number of protons also increases in nucleus. So, attraction of nucleus on the outermost electrons increases as a result atomic size decreases since electrons are pulled more tightly towards the nucleus. While as we go down, electrons are filled into orbitals (energy levels) that are farther away from the nucleus (attraction not as strong) and so along a group (down a column), atomic radius increases.

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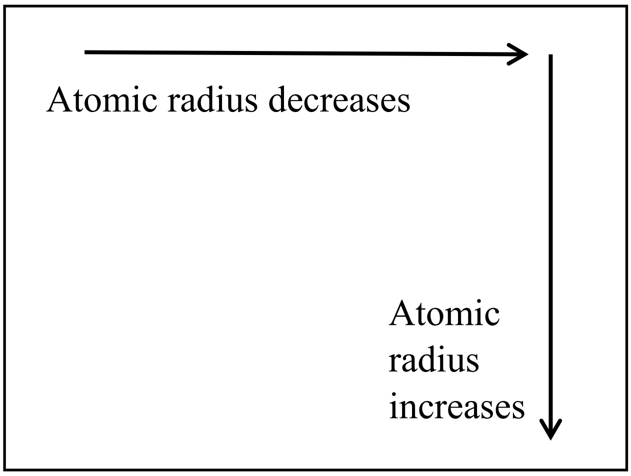
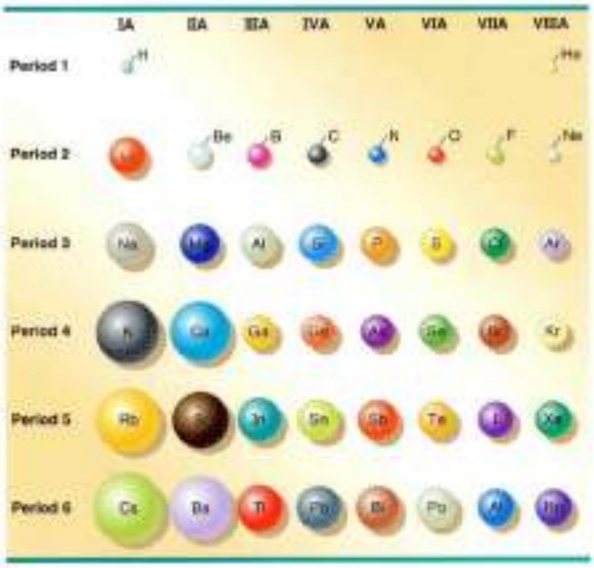




Shielding and its Effects on Atomic Radius

The Lanthanide Contraction is the result of a poor shielding effect of the 4f electrons. The shielding effect is described as the phenomenon by which the inner-shell electrons shield the outer-shell electrons so they are not effected by nuclear charge. So when the shielding is not as good, this would mean that the positively charged nucleus has a greater attraction to the electrons, thus decreasing the atomic radius as the atomic number increases. The s orbital has the greatest shielding while f has the least and p and d in between the two with p being greater than d.

The Lanthanide Contraction can be seen by comparing the elements with f electrons and those without f electrons in the d block orbital. Pd and Pt are such elements. Pd has 4d electrons while Pt has 5d and 4f electrons. These 2 elements have roughly the same atomic radius. This is due to Lanthanide Contraction and shielding. While we would expect Pt to have a significantly larger radius because more electrons and protons are added, it does not because the 4f electrons are poor at shielding. When the shielding is not good there will be a greater nuclear charge, thus pulling the electrons in closer, resulting in a smaller than expected radius.

Ionic Radius:

The radius of each atom in an ionic bond will be different than that in a covalent bond. This is an important concept. The reason for the variability in radius is due to the fact that the atoms in an ionic bond are of greatly different size. One of the atoms is a cation, which is smaller in size, and the other atom is an anion which is a lot larger in size. So in order to account for this difference, one most get the total distance between the two nuclei and divide the distance according to atomic size. The bigger the atomic size, the larger radius it will have. This is depicted in Figure 2 as shown below where the cation is displayed on the left as X^+, and clearly has a smaller radius than the anion, which is depicted as Y- on the right.

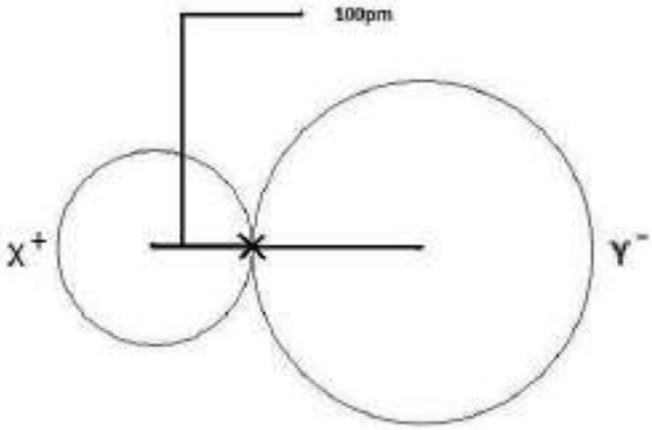
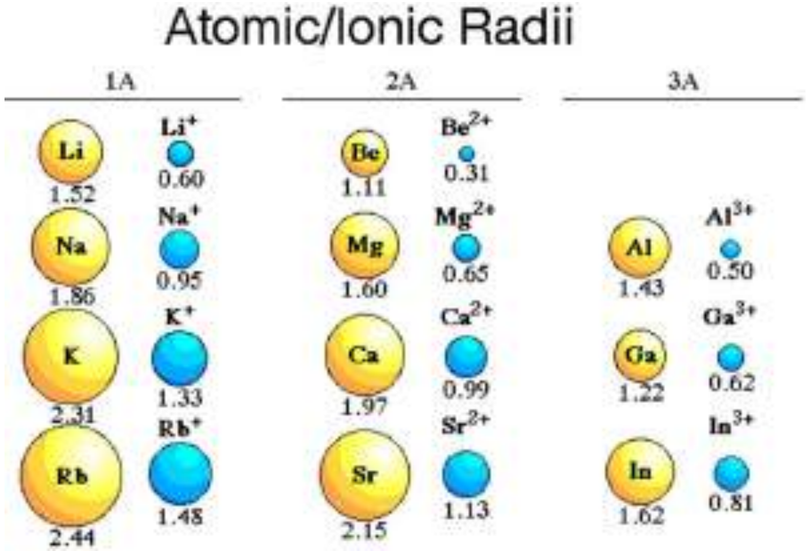


Figure: *Ionic radii*

Ionic radius is the size of an atom when it is an ion and so it will follow similar trend. In case of ions, metals lose electron which means more protons than electron so more attraction. As a result ionic radius < neutral atomic radius e.g, $Na^+ < Na$, $K^+ < K$, $Li^+ < Li$

For nonmetals they try to gain electrons to produce ions, which mean more electron than protons. So, attraction is less compare to neutral atom. So, ionic radius> neutral atomic radius.

$C^- > Cl$, $O^- > O$, $Br^- > Br$

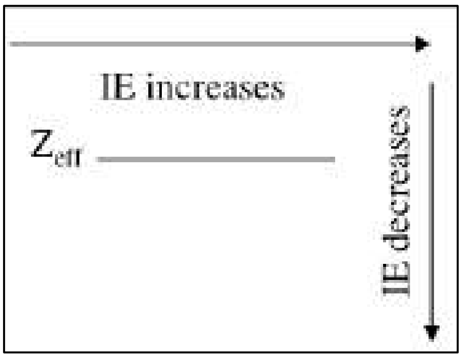


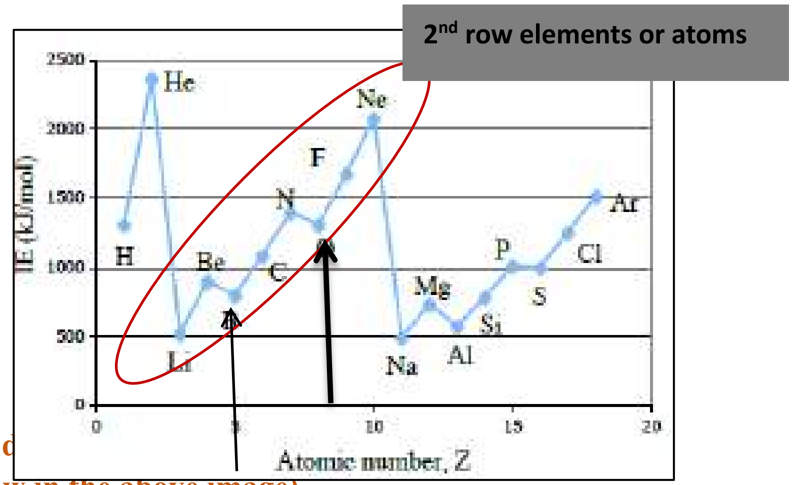
Periodic trends in ionization energy:

Across a row, IE will increase. Z increases, but n (the shell) stays constant. The outermost e^- is bound more tightly to the nucleus and requires more E to be ejected.

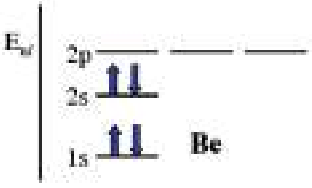
Down a column, IE will decrease. Although Z increases as you go down a column, so does n. Shells are well-separated in space, so electrons in larger n are farther away from the nucleus. A large distance from the nucleus dominates over the increased Z, making electrons less strongly bound and therefore decreasing IE.

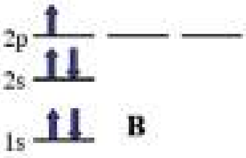
General trends

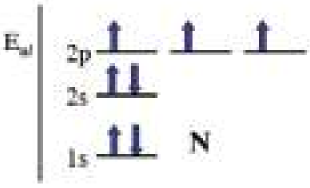


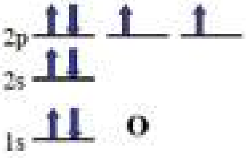


- **Some “glitches” in the trend occur c** **IE_B and IE_N -IE_O (indicated by arrow in the above image)**









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

$1s^2 2s^2 2p^4$

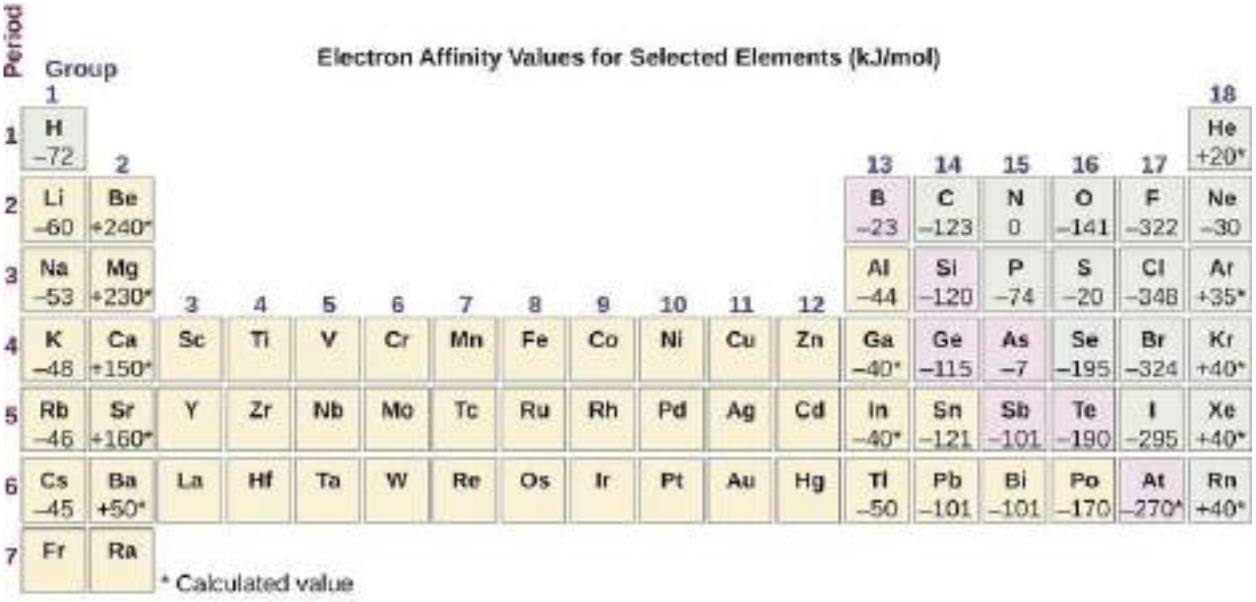
In case of Boron, removal of 2p electron is easier compare to 2s electron of Be. Because after removal of one 2p electron from B it will get stable electronic configuration like Be. That is why Ionization energy of B< Ionization energy of Be. Similarly if we compare N and O, O has an extra 2p electron which can be easily removed due to the internal electron-electron repulsion and so removal of extra electron from O is easier compare to N’s stable $2p^3$configuration.So, Ionization energy of O< Ionization energy of N.

Variation in Electron Affinities

The electron affinity [EA] is the energy change for the process of adding an electron to a gaseous atom to form an anion (negative ion).

$X(g) + e^{-} \quad X^{-}(g) \quad EA_1$

This process can be either endothermic or exothermic, depending on the element. The EA of some of the elements is given in Figure . You can see that many of these elements have negative values of EA, which means that energy is released when the gaseous atom accepts an electron. However, for some elements, energy is required for the atom to become negatively charged and the value of their EA is positive. Just as with ionization energy, subsequent EA values are associated with forming ions with more charge. The second EA is the energy associated with adding an electron to an anion to form a –2 ion, and so on.



Electron Affinity Values for Selected Elements (kJ/mol)

Period \ Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H –72																	He +20*
2	Li –60	Be +240*											B –23	C –123	N 0	O –141	F –322	Ne –30
3	Na –53	Mg +230*											Al –44	Si –120	P –74	S –20	Cl –348	Ar +35*
4	K –48	Ca +150*	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga –40*	Ge –115	As –7	Se –195	Br –324	Kr +40*
5	Rb –46	Sr +160*	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In –40*	Sn –121	Sb –101	Te –190	I –295	Xe +40*
6	Cs –45	Ba +50*	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl –50	Pb –101	Bi –101	Po –170	At –270*	Rn +40*
7	Fr	Ra																

* Calculated value

Figure: This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.:

As we might predict, it becomes easier to add an electron across a series of atoms as the effective nuclear charge of the atoms increases. We find, as we go from left to right across a period, EAs tend to become more negative. The exceptions found among the elements of group 2 (2A), group 15 (5A), and group 18 (8A) can be understood based on the electronic structure of these groups. The noble gases, group 18 (8A), have a completely filled shell and the incoming electron must be added to a higher *n* level, which is more difficult to do. Group 2 (2A) has a filled *ns* subshell, and so the next electron added goes into the higher energy *np*, so, again, the observed EA value is not as the trend would predict. Finally, group 15 (5A) has a half-filled *np* subshell and the next electron must be paired with an existing *np* electron. In all of these cases, the initial relative stability of the electron configuration disrupts the trend in EA.

We also might expect the atom at the top of each group to have the largest EA; their first ionization potentials suggest that these atoms have the largest effective nuclear charges. However, as we move down a group, we see that the second element in the group most often has the greatest EA. The reduction of the EA of the first member can be attributed to the small size of the n = 2 shell and the resulting large electron–electron repulsions. For example, chlorine, with an EA value of –348 kJ/mol, has the highest value of any element in the periodic table. The EA of fluorine is –322 kJ/mol. When we add an electron to a fluorine atom to form a fluoride anion (F–), we add an electron to the *n* = 2 shell. The electron is attracted to the nucleus, but there is also significant repulsion from the other electrons already present in this small valence shell. The chlorine atom has the same electron configuration in the valence shell, but because the entering electron is going into the *n* = 3 shell, it occupies a considerably larger region of space and the electron–electron repulsions are reduced. The entering electron does not experience as much repulsion and the chlorine atom accepts an additional electron more readily.

The properties discussed in this section (size of atoms and ions, effective nuclear charge, ionization energies, and electron affinities) are central to understanding chemical reactivity. For example, because fluorine has an energetically favourable EA and a large energy barrier to ionization (IE), it is much easier to form fluorine anions than cations. Metallic properties including conductivity and malleability (the ability to be formed into sheets) depend on having electrons that can be removed easily. Thus, metallic character increases as we move down a group and decreases across a period in the same trend observed for atomic size because it is easier to remove an electron that is farther away from the nucleus.

Electronegativity

Valence electrons of both atoms are always involved when those two atoms come together to form a chemical bond. Chemical bonds are the basis for how elements combine with one another to form compounds. When these chemical bonds form, atoms of some elements have a greater ability to attract the valence electrons involved in the bond than other elements.

Electronegativity is a measure of the ability of an atom to attract the electrons when the atom is part of a compound. Electronegativity differs from electron affinity because electron affinity is the actual energy released when an atom gains an electron. Electronegativity is not measured in energy units, but is rather a relative scale. All elements are compared to one another, with the most electronegative element, fluorine, being assigned an electronegativity value of 3.98. Fluorine attracts electrons better than any other element. The table below shows the electronegativity values for the elements.

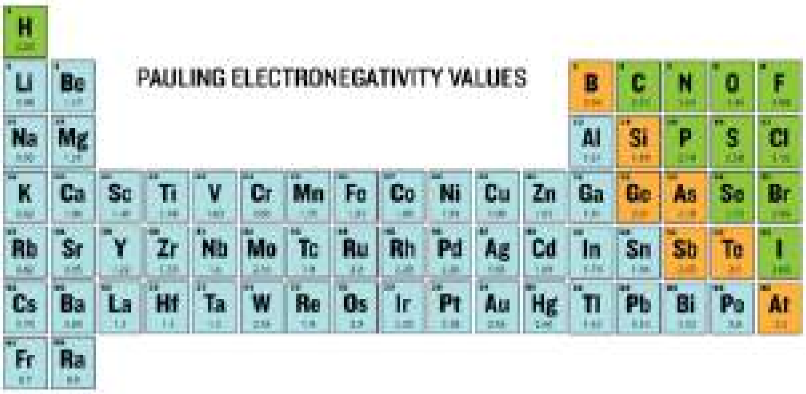


Figure: The electronegativity scale was developed by Nobel Prize winning American chemist Linus Pauling. The largest electronegativity (3.98) is assigned to fluorine and all other electronegativity measurements are on a relative scale.

Since metals have few valence electrons, they tend to increase their stability by losing electrons to become cations. Consequently, the electronegativities of metals are generally low. Nonmetals have more valence electrons and increase their stability by gaining electrons to become anions. The electronegativities of nonmetals are generally high.

Trends

Electronegativities generally increase from left to right across a period. This is due to an increase in nuclear charge. Alkali metals have the lowest electronegativities, while halogens have the highest. Because most noble gases do not form compounds, they do not have electronegativities. Note that there is little variation among the transition metals. Electronegativities generally decrease from top to bottom within a group due to the larger atomic size.

Of the main group elements, fluorine has the highest electronegativity (EN =4.0) and cesium the lowest (EN =0.79). This indicates that fluorine has a high tendency to gain electrons from other elements with lower electronegativities. We can use these values to predict what happens when certain elements combine.

When the difference between electronegativities is greater than ~1.7, then a complete exchange of electrons occurs. Typically this exchange is between a metal and a nonmetal. For instance, sodium and chlorine will typically combine to form a new compound and each ion becomes isoelectronic with its nearest noble gas. When we compare the EN values, we see that the electronegativity for Na is 0.93 and the value for Cl is 3.2. The absolute difference between ENs is $|0.93-3.2|=2.27$. This value is greater than 1.7, and therefore indicates a complete electron exchange occurs.

Pauling Scale of Electronegativity

Linus Pauling was the original scientist to describe the phenomena of electronegativity. The best way to describe his method is to look at a hypothetical molecule that we will call XY. By comparing the measured X-Y bond energy with the theoretical X-Y bond energy (computed as the average of the X-X bond energy and the Y-Y bond energy), we can describe the relative affinities of these two atoms with respect to each other.

Δ Bond Energies = (X-Y)measured – (X-Y)expected

If the electonegativities of X and Y are the same, then we would expect the measured bond energy to equal the theoretical (expected) bond energy and therefore the Δ bond energies would be zero. If the electronegativities of these atoms are not the same, we would see a polar molecule where one atom would start to pull electron density toward itself, causing it to become partially negative.

By doing some careful experiments and calculations, Pauling came up with a slightly more sophisticated equation for the relative electronegativities of two atoms in a molecule: EN(X) - EN(Y) = 0.102 (Δ1/2). In that equation, the factor 0.102 is simply a conversion factor between kJ and eV to keep the units consistent with bond energies.

By assigning a value of 4.0 to Fluorine (the most electronegative element), Pauling was able to set up relative values for all of the elements. This was when he first noticed the trend that the electronegativity of an atom was determined by it's position on the periodic table and that the electronegativity tended to increase as you moved left to right and bottom to top along the table. The range of values for Pauling's scale of electronegativity ranges from Fluorine (most electronegative = 4.0) to Francium (least electronegative = 0.7). Furthermore, if the electronegativity difference between two atoms is very large, then the bond type tends to be more ionic, however if the difference in electronegativity is small then it is a nonpolar covalent bond.

The major drawback of this method is that it is not possible often to have values of X-X bond energy and the Y-Y bond energy by simple thermochemical calculation.

Mulliken Electronegativity

A method for estimating electronegativity was developed by Robert Mulliken (1896–1986; Nobel Prize in Chemistry 1966) who noticed that elements with large first ionization energies tend to have very negative electron affinities and gain electrons in chemical reactions. Conversely, elements with small first ionization energies tend to have slightly negative (or even positive) electron affinities and lose electrons in chemical reactions. Mulliken recognized that an atom’s tendency to gain or lose electrons could therefore be described quantitatively by the average of the values of its first ionization energy and the absolute value of its electron affinity.

Robert S. Mulliken proposed that the arithmetic mean of the first ionization energy (EI1) and the electron affinity (Eea) should be a measure of the tendency of an atom to attract electrons. As this definition is not dependent on an arbitrary relative scale, it has also been termed *absolute electronegativity.* Using our definition of electron affinity, we can write Mulliken’s original expression for electronegativity as follows:Mulliken’s definition used the magnitude of the ionization energy and the electron affinity. By definition, the magnitude of a quantity is a positive number. Our definition of electron affinity produces negative values for the electron affinity for most elements, so vertical lines indicating absolute value are needed in the Equation to make sure that we are adding two positive numbers in the numerator.

$\chi = |E_{I1} + E_{ea}|/2$

Elements with a large first ionization energy and a very negative electron affinity have a large positive value in the numerator of Equation , so their electronegativity is high. Elements with small first ionization energy and a small electron affinity have a small positive value for the numerator in Equation, so they have a low electronegativity. Inserting the appropriate data into Equation gives a Mulliken electronegativity value for fluorine of 1004.6 kJ/mol. To compare Mulliken’s electronegativity values with those obtained by Pauling, Mulliken’s values are divided by 252.4 kJ/mol, which gives Pauling’s value (3.98).

However, it is more usual to use a linear transformation to transform these absolute values into values that resemble the more familiar Pauling values. For ionization energies and electron affinities in electronvolts:

$\chi_{\text{Mulliken}} = 0.187(E_{I1} + E_{ea}) + 0.17$

and for energies in kJ/mol,

$\chi_{Mulliken} = (1.97\times10-3)(E_{I1}+E_{ea})+0.19$

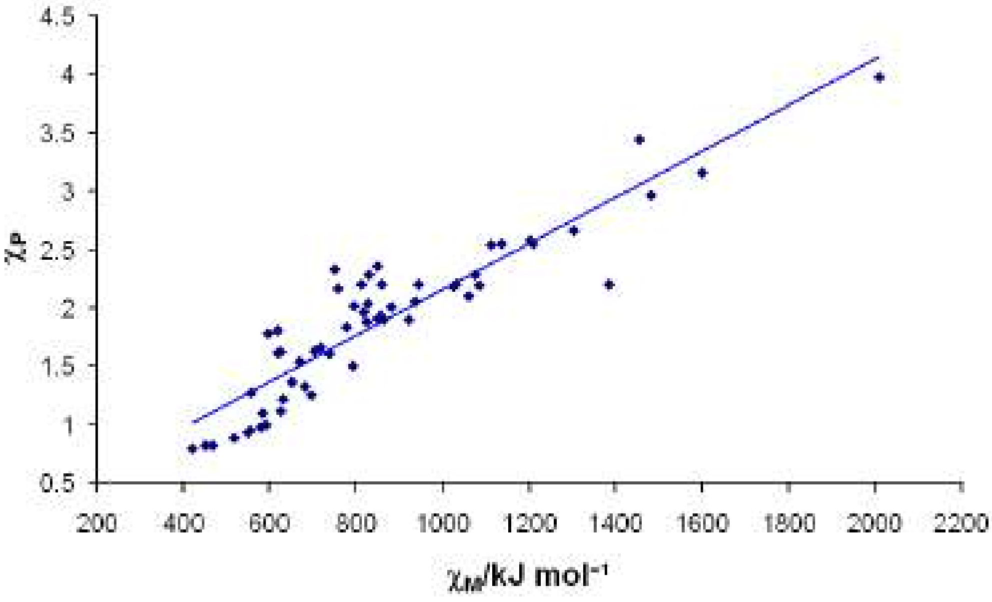
The Mulliken electronegativity can only be calculated for an element for which the electron affinity is known, fifty-seven elements as of 2006. The Mulliken electronegativity of an atom is sometimes said to be the negative of the chemical potential. By inserting the energetic definitions of the ionization potential and electron affinity into the Mulliken electronegativity, it is possible to show that the Mulliken chemical potential is a finite difference approximation of the electronic energy with respect to the number of electrons., i.e.,

$\mu_{Mulliken} = -\chi_{Mulliken} = -E_{I1}+E_{ea2}$

All electronegativity scales give essentially the same results for one element relative to another. Even though the Mulliken scale is based on the properties of individual *atoms* and the Pauling scale is based on the properties of atoms in *molecules*, they both apparently measure the same basic property of an element. In the following discussion, we will focus on the relationship between electronegativity and the tendency of *atoms* to form positive or negative ions. We will therefore be implicitly using the Mulliken definition of electronegativity. Because of the parallels between the Mulliken and Pauling definitions, however, the conclusions are likely to apply to atoms in molecules as well.

Significance

Despite being developed from a very different set of principles than Pauling Electronegativity, which is based on bond dissociation energies, there is a good correlation between Mulliken and Pauling Electronegativities for the atoms, as shown in the plot below.



Although Pauling electronegativities are usually what are found in textbooks, the Mulliken electronegativity more intuitively corresponds to the "ability of an atom to draw electrons toward itself in bonding," and is probably a better indicator of that property. However, because of the good correlation between the two scales, using the Pauling scale is sufficient for most purposes.

Allred-Rochow Electronegativity

Allred-Rochow Electronegativity is a measure that determines the values of the electrostatic force exerted by the effective nuclear charge on the valence electrons. The value of the effective nuclear charges is estimated from Slater's rules. The higher charge, the more likely it will attract electrons. Although, Slater's rule are partly empirical. So the Allred-Rochow electronegativity is no more rigid than the Pauling Electronegativity.

Slater's rules

Slater's rules are rules that provides the values for the effective nuclear charge concept, or Zeff. These rules are based on experimental data for electron promotion and ionization energies, and Zeff is determined from this equation:

$Zeff=Z-S$

Where

- Z is the nuclear charge,
- Zeff is the effective nuclear charge, and
- S is the shielding constant

Through this equation, this tells us that electron may get reduced nuclear charge due to high shielding. Allred and Rochow used Zeff because it is accurate due to the involvement of shielding that prevents electron to reach its true nuclear charge: Z. When an atom with filled s-shell attracts electrons, those electrons will go to the unfilled p-orbital. Since the electrons have the same negative charge, they will not only repel each other, but also repel the electrons from the filled s-shell. This creates a shielding effect where the inner core electrons will shield the outer core electrons from the nucleus. Not only would the outer core electrons experience effective nuclear charge, but it will make them easily removed from the outer shell. Thus, It is easier for outer electrons to penetrate the p shell, which has little likelihood of being near the nuclear, rather than the s shell. Consider this, each of the outer electron in the (ns, np) group contributes S = 0.35, S = 0.85 in the (n - 1) shell, and S = 1.00 in the (n - 2) or lower shells.

Allred and Rochow were two chemists who came up with the Allred-Rochow Electronegativity values by taking the electrostatic force exerted by effective nuclear charge, Zeff, on the valence electron. To do so, they came up with an equation:

$\chi_{AR}=[(3590\times Zeff)/r^2cov)+0.744$

At the time, the values for the covalent radius, rcov, were inaccurate. Allred and Rochow added certain perimeters so that it would more closely correspond to Pauling's electronegativity scale.

According to this scale, the electronegativities increases from left to right just like Pauling's scale because the Z is increasing. As we go down the group, it decreases because of the larger atomic size that increases the distance between the electrons and nucleus.

3.10 EXERCISE:

1. Explain why the electron gain enthalpy of fluorine is less negative than that of chlorine.
2. All transition elements are d-block elements, but all d-block elements are not transition elements. Explain.
3. Identify the group and valency of the element having atomic number 119. Also predict the outermost electronic configuration and write the general formula of its oxide.
4. Among the elements B, Al, C and Si, (i) which element has the highest first ionisation enthalpy? (ii) which element has the most metallic character? Justify your answer in each case.
5. Write four characteristic properties of p-block elements.
6. Explain the following: (a) Electronegativity of elements increase on moving from left to right in the periodic table. (b) Ionisation enthalpy decrease in a group from top to bottom?
7. Discuss the factors affecting electron gain enthalpy and the trend in its variation in the periodic table.
8. Define ionisation enthalpy. Discuss the factors affecting ionisation enthalpy of the elements and its trends in the periodic table.
9. Justify the given statement with suitable examples— "the Properties of the elements are a periodic function of their atomic numbers".
10. Write down the outermost electronic configuration of alkali metals. How will you justify their placement in group 1 of the periodic table?
11. Write the drawbacks in Mendeleev's periodic table that led to its modification.
12. In what manner is the long form of periodic table better than Mendeleev's periodic table? Explain with examples.
13. Discuss and compare the trend in ionisation enthalpy of the elements of group1 with those of group17 elements.

CHAPTER 4

ACID BASE THEORIES

4.1 INTRODUCTION

In our daily lives we use several acidic and basic chemicals. Some of the acidic chemicals are naturally derived like citric acid in fruits and some are synthetically derived like sulphuric acid. Acids and bases are typical substances that react to produce salt and water when they come into contact with each other. The Latin word acere, which meaning sour, is the source of the word acid.

This is already know that acids are sour in taste and change the colour of blue litmus to red, whereas, bases are bitter and change the colour of the red litmus to blue. Litmus is a natural indicator, turmeric is another such indicator. Have you noticed that a stain of curry on a white cloth becomes reddish-brown when soap (which is basic in nature) is scrubbed on it? It turns yellow again when the cloth is washed with plenty of water. You can also use synthetic indicators such as methyl orange and phenolphthalein to test for acids and bases.

In this Chapter, we will study the reactions of acids and bases, how acids and bases cancel out each other's effects and many more interesting things that we use and see in our day-to-day life.

4.2 ACIDS AND BASES

The acid definition is given as any hydrogen that contains a substance capable of donating a proton (a hydrogen ion) to the other substance. A base is an ion or molecule that is able to accept a hydrogen ion from an acid.

Usually, the acidic substances are identified with their sour taste. Basically, an acid is a molecule that can donate an H^+ ion and also can remain energetically favorable after a loss of H^+ ion. Acids are much known to turn blue litmus into the red.

On the other side, bases are characterized by a slippery texture and a bitter taste. A base that is dissolved in water is known as an alkali. When these substances react chemically with acids, they further yield salts. Besides, the bases are much known to turn red litmus into blue.

4.3 ACID-BASE THEORIES: CONCEPT OF ARRHENIUS, LOWRY BRONSTED AND LEWIS THEORY FOR ACID AND BASE

To define acids and bases, three alternative hypotheses have been proposed. The Arrhenius theory, the Bronsted-Lowry theory, and the Lewis theory of acids and bases are among these hypotheses. This subsection provides a brief overview of each of these theories. There are three hypotheses that can be used to define acids and bases.

1. An acid generates H^+ ions in a solution, whereas a base generates an OH^- ion in its solution," according to the Arrhenius theory of acids and bases.
2. "An acid is a proton donor, while a base is a proton acceptor," according to the Bronsted-Lowry theory.
3. Finally, the Lewis definition of acids and bases depicts acids and bases as "electron-pair acceptors" and "electron-pair donors," respectively.

Arrhenius Theory of Acids and Bases

According to the Arrhenius theory, acid is a chemical that when dissolved in water produces the H^+ ion. It raises the H^+ ion concentration in the solution. The base is a chemical that dissolves in an aqueous solution and ionises the OH^- ion. Thus the solution contains a high concentration of OH^- ions.

In an aqueous solution, Arrhenius acid increases the concentration of protons or H^+ ions.

Arrhenius Acids

Definition of acids according to Arrhenius: Svante Arrhenius, a Swedish chemist, first presented the Arrhenius hypothesis of acids and bases in 1884. He proposed categorising certain substances as acids or bases depending on the type of ions generated when they were combined with water.

Hydrochloric acid in the water, for example. As stated below, HCl undergoes a dissociation reaction to produce H+ and Cl– ions. The formation of hydronium ions raises the concentration of H^+ ions.

$HCl\ (aq) \rightarrow H^+(aq) + Cl^-(aq)$

$HCl\ (aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

Arrhenius Base

A substrate called an Arrhenius base raises the concentration of hydroxide ions in an aqueous solution. The extremely soluble sodium hydroxide molecule in water, which dissociates to generate sodium ion and hydroxide ion, is an Arrhenius base example.

To increase the concentration of hydroxide ions in an aqueous solution, NaOH entirely dissolves to give hydroxide ions and sodium ions.

$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$.

Bronsted Theory of Acids and Bases

Bronsted Lowry Acid

An acid is defined as a donor of protons by the Bronsted-Lowry theory.

According to this hypothesis, a base is a proton acceptor (or an H^+ ion acceptor).

Bronsted acids dissociate to release protons, resulting in a higher concentration of H^+ ions in the solution.

Acid ⇌ Proton + Conjugate base

Bronsted Lowry Base

Bronsted bases, on the other hand, take protons from the solvent water to produce hydroxide ions.

The capacity to explain the acidic or basic character of ionic species is one advantage of the Bronsted-Lowry definition of acids and bases.

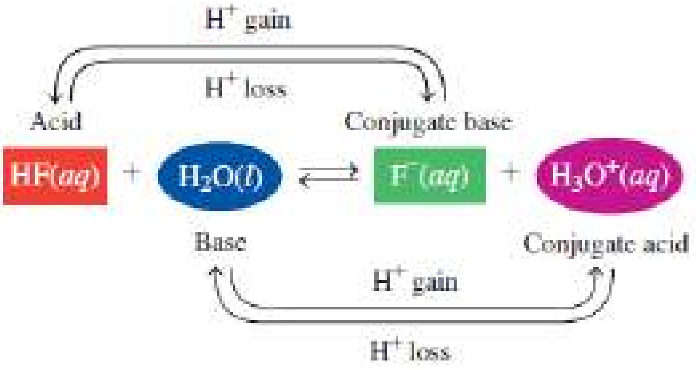
This theory has a significant flaw in that it does not explain how chemicals that lack hydrogen, such as BF_3 and $AlCl_3$, display acidic characteristics.

Base + Proton ⇌ Conjugate acid

Strong Bronsted-Lowry acids are those that have a strong inclination to donate a proton but have a weak conjugate base.

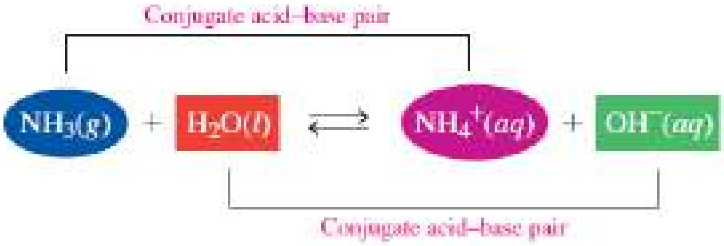
Weak Bronsted-Lowry acids have a slight tendency to give a proton, while their conjugate base is strong.

Conjugate Acid–Base Pairs According to the Brønsted–Lowry theory, a conjugate acid–base pair consists of molecules or ions related by the loss of one H^+ by an acid, and the gain of one H^+ by a base. Every acid–base reaction contains two conjugate acid–base pairs because an H^+ is transferred in both the forward and reverse directions. When an acid such as HF loses one H^+, the conjugate base F^- is formed. When the base H_2O gains an H^+, its conjugate acid, H_3O^+, is formed. Because the overall reaction of HF is reversible, the conjugate acid H3O+ can donate H+ to the conjugate base F^- and re-form the acid HF and the base H_2O. Using the relationship of loss and gain of one H+, we can now identify the conjugate acid–base pairs as HF/F^- along with H_3O^+ /H_2O.



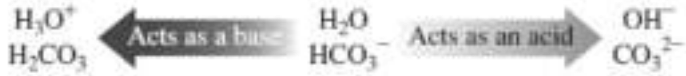
HF, an acid, loses one H^+ to form its conjugate base F^-. Water acts as a base by gaining one H^+ to form its conjugate acid H_3O^+.

In another reaction, ammonia (NH_3) accepts H^+ from H_2O to form the conjugate acid NH_4^+ and conjugate base OH^-. Each of these conjugate acid–base pairs, NH_4^+/NH_3 and H_2O/OH^-, is related by the loss and gain of one H^+.



Ammonia, NH_3, acts as a base when it gains one H^+ to form its conjugate acid NH_4^+. Water acts as an acid by losing one H^+ to form its conjugate base OH^-.

In these two examples, we see that water can act as an acid when it donates H^+ or as a base when it accepts H^+. Substances that can act as both acids and bases are **amphoteric** or *amphiprotic*. For water, the most common amphoteric substance, the acidic or basic behavior depends on the other reactant. Water donates H^+ when it reacts with a stronger base, and it accepts H^+ when it reacts with a stronger acid. Another example of an amphoteric substance is bicarbonate (HCO_3^-). With a base, HCO_3^- acts as an acid and donates one H^+ to give CO_3^{2-}. However, when HCO_3^- reacts with an acid, it acts as a base and accepts one H^+ to form H_2CO_3.



Amphoteric substances act as both acids and bases.

Lewis Concept of Acids and Bases

Lewis acid: An acid, according to Lewis' definition, is a species with an empty orbital and hence the ability to take an electron pair.

A Lewis base is a species that has a single pair of electrons and hence can operate as an electron donor.\

The hydrogen atom is not included in this theory's description of acids and bases.

Lewis acids have electrophilic properties, while Lewis bases have nucleophilic properties.

Cu^{2+}, BF_3, and Fe^{3+} are examples of Lewis acids. F^-, NH_3, and C_2H_4 are examples of Lewis bases (ethylene).

A Lewis acid absorbs an electron pair from a Lewis base, resulting in the formation of a coordinate covalent bond. Lewis adduct is the name given to the resultant chemical.

This notion has the advantage of allowing various substances to be classified as acids or bases. However, it provides little information about the acid and base's strength.

One of the theory's flaws is that it doesn't account for acid-base reactions that don't involve the development of a coordinate covalent bond.

4.4 pH OF ACIDS AND BASES

To find the numeric value of the acidity or basicity level of a substance, the pH scale (pH stands for 'potential of hydrogen') can be used. Here, the pH scale is the most common and trusted procedure to measure how acidic or basic a substance is. Also, a pH scale measure can differ from 0 to 14, where 14 is the most basic, and 0 is the most acidic a substance can be.

The other way to check if a substance is acidic or basic is by using a litmus paper. There exist two types of litmus paper available, used to identify the acids and bases. They are the red litmus paper and the blue litmus paper. The blue litmus paper changes red under acidic conditions, whereas the red litmus paper turns blue under alkaline or basic conditions.

4.5 PROPERTIES OF ACIDS AND BASES

Properties of Acids

- Acids are good conductors of electricity.
- They are corrosive in nature.
- When reacted with metals, acid substances produce hydrogen gas.
- Always, their pH values are less than 7.
- Acids are sour-tasting substances.
- Examples of acids are Hydrochloric acid HClHCl, Sulfuric acid [H_2SO_4], Acetic acid [CH_3COOH], and more.

Properties of Bases

Some of the properties, such as a bitter taste, are owned by all bases. The bases also feel slippery. You can dream about what slippery soap looks like, and this is a foundation. Also, bases conduct electricity when immersed in water because they consist of charged particles in the solution.

- Bases are found to have a soapy texture when we touch them.
- When dissolved in water, these substances release hydroxide ions (OH^- ions)

- Bases act as good conductors of electricity in their aqueous solutions
- Always, the pH values corresponding to the bases are greater than 7.
- Bases are bitter-tasting substances, having the ability to turn red litmus paper into blue.
- Examples can be given as milk of magnesia [$Mg(OH)_2$], Sodium Hydroxide NaOH, Calcium Hydroxide [$Ca(OH)_2$], and more.

Neutral Substances

These are the substances, which have no properties of either acid or base, which has a similar amount of hydroxyl ions and hydrogen ions, and they do not modify the color of the litmus surface.

- Neutral substances do not display any acidic or basic characteristics.
- Their pH values approximately 7.
- Neutral substances have no effect on blue or red litmus paper.
- pH of pure water is exactly 7.
- Examples are Common salt (NaCl), Water, and more
-

4.6 USES OF ACIDS AND BASES

Various uses of acids and bases can be listed as follows:

Uses of Acids

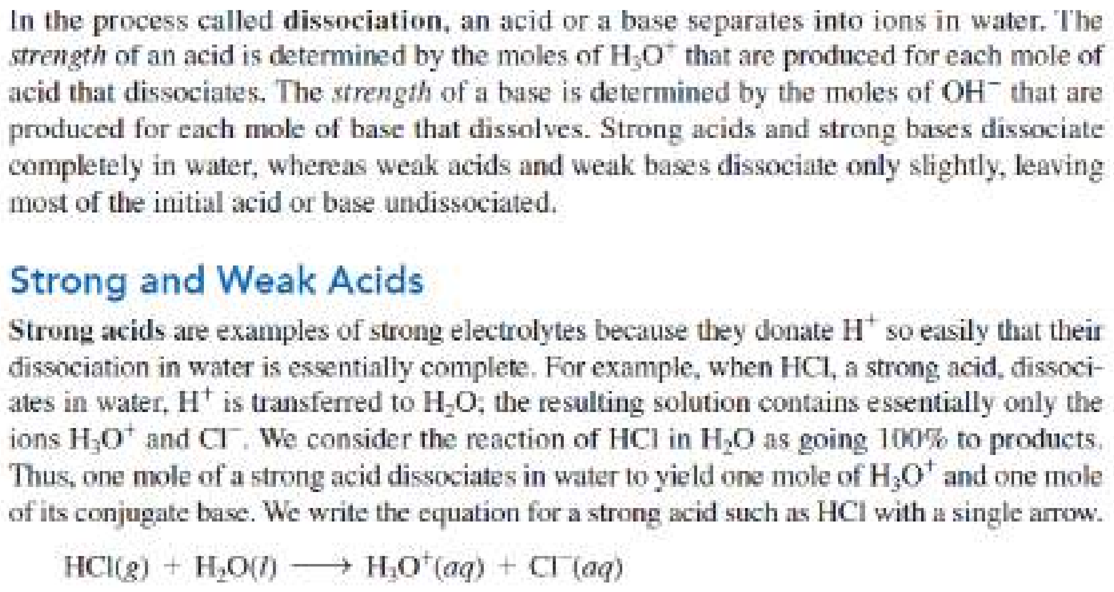
- Vinegar, which is a diluted solution of acetic acid, has different household applications. It is used primarily as a food preservative.
- Citric acid is an integral part of orange juice and lemon juice. It is also used as a food preservative.
- Sulfuric acid is more widely used in batteries. Commonly, the batteries used to start automobile engines contain this acid.
- The industrial production of dyes, explosives, paints, and fertilizers involves the use of nitric acid and sulfuric acid.
- Phosphoric acid is a primary ingredient in various soft drinks.

Uses of Bases

- The manufacturing of paper and soap involves the use of sodium hydroxide. Also, NaOH is used in the manufacturing of rayon.

- $Ca(OH)_2$, which is also called calcium hydroxide or slaked lime, is used to manufacture the bleaching powder.
- Dry mixes used in decoration or painting are made using a limited amount of calcium hydroxide.
- Magnesium hydroxide, also called the milk of magnesia, is most commonly used as a laxative. It also reduces if there is any excess acidity in the human stomach and is, thus, used as an antacid substance.
- Ammonium hydroxide is an important reagent that is used in laboratories.
- Any excess acidity in soils is neutralized by employing the slaked lime.

4.7 STRENGTHS OF ACIDS AND BASES

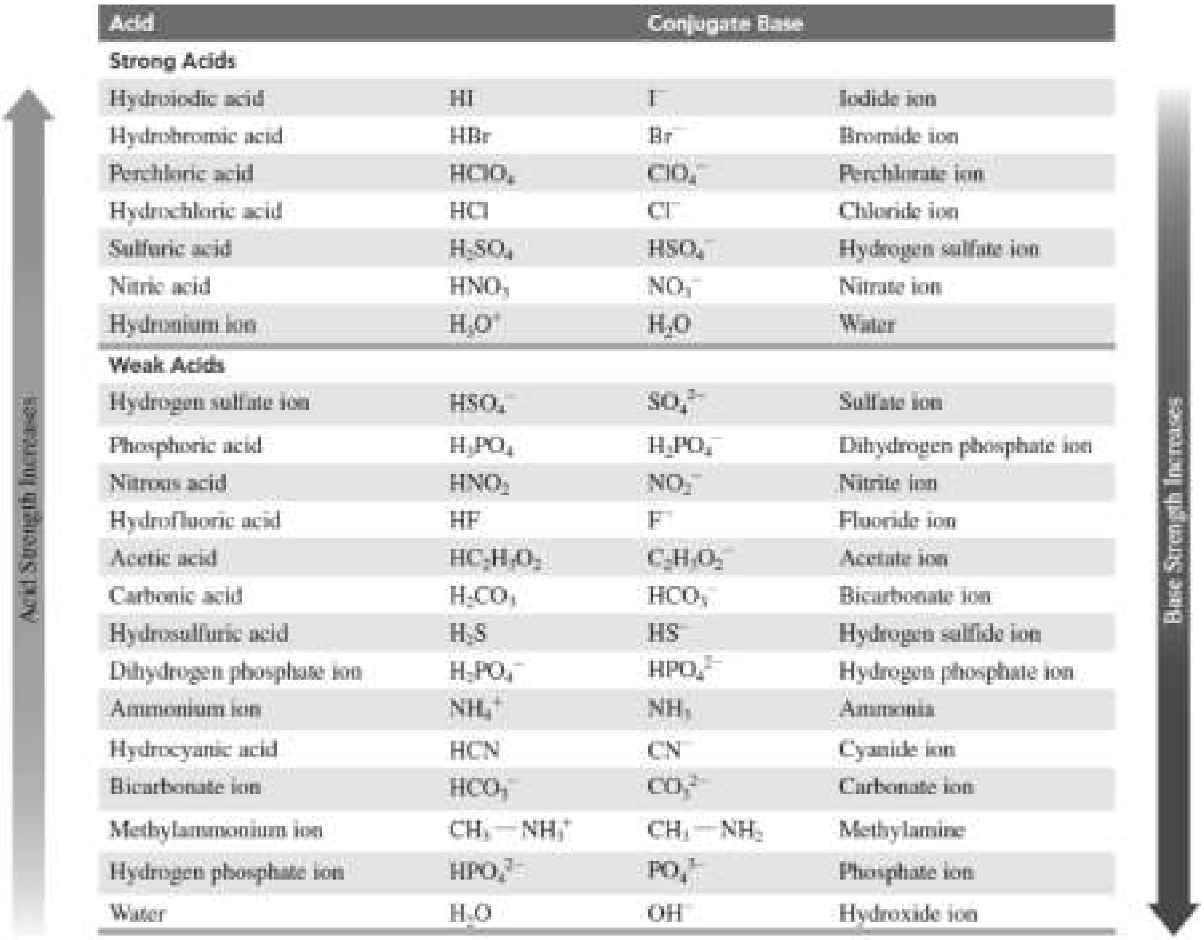


In the process called **dissociation,** an acid or a base separates into ions in water. The *strength* of an acid is determined by the moles of H_3O^+ that are produced for each mole of acid that dissociates. The *strength* of a base is determined by the moles of OH^- that are produced for each mole of base that dissolves. Strong acids and strong bases dissociate completely in water, whereas weak acids and weak bases dissociate only slightly, leaving most of the initial acid or base undissociated.

Strong and Weak Acids

Strong acids are examples of strong electrolytes because they donate H^+ so easily that their dissociation in water is essentially complete. For example, when HCl, a strong acid, dissociates in water, H^+ is transferred to H_2O; the resulting solution contains essentially only the ions H_3O^+ and Cl^-. We consider the reaction of HCl in H_2O as going 100% to products. Thus, one mole of a strong acid dissociates in water to yield one mole of H_3O^+ and one mole of its conjugate base. We write the equation for a strong acid such as HCl with a single arrow.

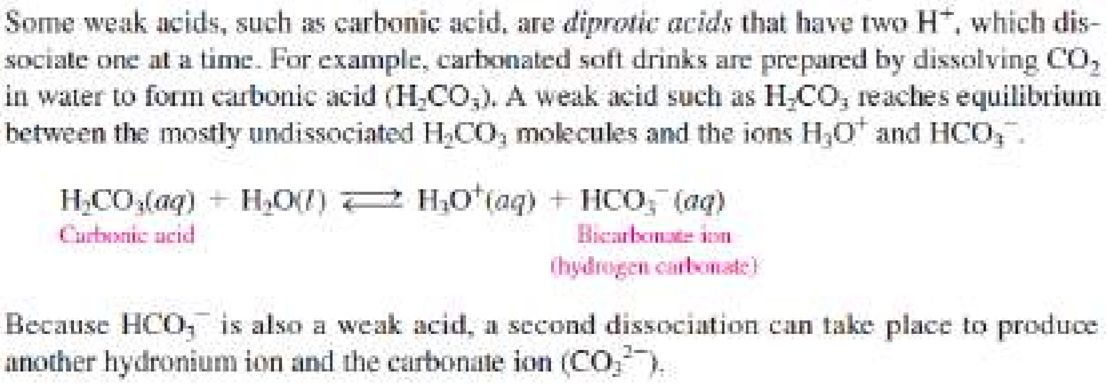
$$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$



Acid		Conjugate Base	
Strong Acids			
Hydroiodic acid	HI	I^-	Iodide ion
Hydrobromic acid	HBr	Br^-	Bromide ion
Perchloric acid	$HClO_4$	ClO_4^-	Perchlorate ion
Hydrochloric acid	HCl	Cl^-	Chloride ion
Sulfuric acid	H_2SO_4	HSO_4^-	Hydrogen sulfate ion
Nitric acid	HNO_3	NO_3^-	Nitrate ion
Hydronium ion	H_3O^+	H_2O	Water
Weak Acids			
Hydrogen sulfate ion	HSO_4^-	SO_4^{2-}	Sulfate ion
Phosphoric acid	H_3PO_4	$H_2PO_4^-$	Dihydrogen phosphate ion
Nitrous acid	HNO_2	NO_2^-	Nitrite ion
Hydrofluoric acid	HF	F^-	Fluoride ion
Acetic acid	$HC_2H_3O_2$	$C_2H_3O_2^-$	Acetate ion
Carbonic acid	H_2CO_3	HCO_3^-	Bicarbonate ion
Hydrosulfuric acid	H_2S	HS^-	Hydrogen sulfide ion
Dihydrogen phosphate ion	$H_2PO_4^-$	HPO_4^{2-}	Hydrogen phosphate ion
Ammonium ion	NH_4^+	NH_3	Ammonia
Hydrocyanic acid	HCN	CN^-	Cyanide ion
Bicarbonate ion	HCO_3^-	CO_3^{2-}	Carbonate ion
Methylammonium ion	$CH_3-NH_3^+$	CH_3-NH_2	Methylamine
Hydrogen phosphate ion	HPO_4^{2-}	PO_4^{3-}	Phosphate ion
Water	H_2O	OH^-	Hydroxide ion

Acids are weak electrolytes because they dissociate slightly in water, forming only a small amount of H_3O^+ ions. A weak acid has a strong conjugate base, which is why the reverse reaction is more prevalent. Even at high concentrations, weak acids produce low concentrations of H_3O^+ ions

Diprotic Acids



Some weak acids, such as carbonic acid, are *diprotic acids* that have two H^+, which dissociate one at a time. For example, carbonated soft drinks are prepared by dissolving CO_2 in water to form carbonic acid (H_2CO_3). A weak acid such as H_2CO_3 reaches equilibrium between the mostly undissociated H_2CO_3 molecules and the ions H_3O^+ and HCO_3^-.

$$\underset{\text{Carbonic acid}}{H_2CO_3(aq)} + H_2O(l) \rightleftharpoons H_3O^+(aq) + \underset{\substack{\text{Bicarbonate ion}\\ \text{(hydrogen carbonate)}}}{HCO_3^-(aq)}$$

Because HCO_3^- is also a weak acid, a second dissociation can take place to produce another hydronium ion and the carbonate ion (CO_3^{2-}).

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

Bicarbonate ion (hydrogen carbonate) — Carbonate ion

Carbonic acid, a weak acid, loses one H^+ to form hydrogen carbonate ion, which loses a second H^+ to form carbonate ion.

Sulfuric acid (H_2SO_4) is also a diprotic acid. However, its first dissociation is complete (100%), which means H_2SO_4 is a strong acid. The product, hydrogen sulfate (HSO_4^-) can dissociate again but only slightly, which means that the hydrogen sulfate ion is a weak acid.

$$H_2SO_4(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + HSO_4^-(aq)$$

Sulfuric acid — Bisulfate ion (hydrogen sulfate)

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$$

Bisulfate ion (hydrogen sulfate) — Sulfate ion

In summary, a strong acid such as HI in water dissociates completely to form an aqueous solution of the ions H_3O^+ and I^-. A weak acid such as HF dissociates only slightly in water to form an aqueous solution that consists mostly of HF molecules and a few H_3O^+ and F^- ions (see **FIGURE 14.2**).

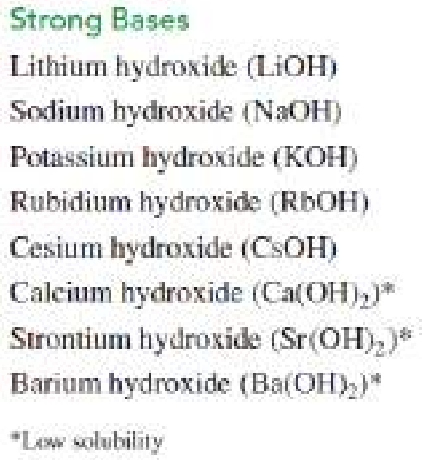
Strong acid: $HI(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + I^-(aq)$ Completely dissociated

Weak acid: $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$ Slightly dissociated

Strong and Weak Bases

As strong electrolytes, **strong bases** dissociate completely in water. Because these strong bases are ionic compounds, they dissociate in water to give an aqueous solution of metal ions and hydroxide ions. The Group 1A (1) hydroxides are very soluble in water, which can give high concentrations of OH^- ions. A few strong bases are less soluble in water, but what does dissolve dissociates completely as ions. For example, when KOH forms a KOH solution, it contains only the ions K^+ and OH^-.

$$KOH(s) \xrightarrow{H_2O} K^+(aq) + OH^-(aq)$$



Strong Bases

Lithium hydroxide (LiOH)

Sodium hydroxide (NaOH)

Potassium hydroxide (KOH)

Rubidium hydroxide (RbOH)

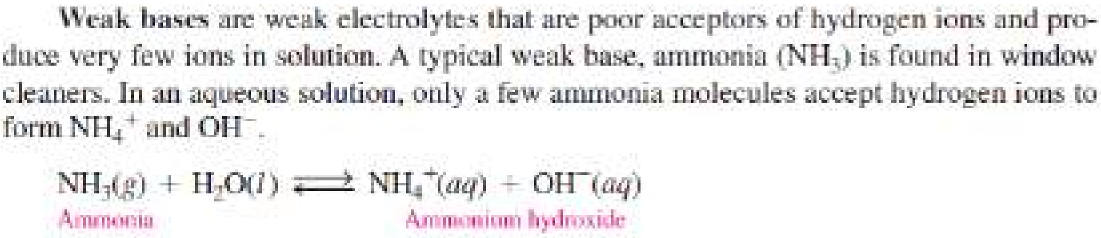
Cesium hydroxide (CsOH)

Calcium hydroxide ($Ca(OH)_2$)*

Strontium hydroxide ($Sr(OH)_2$)*

Barium hydroxide ($Ba(OH)_2$)*

*Low solubility



Weak bases are weak electrolytes that are poor acceptors of hydrogen ions and produce very few ions in solution. A typical weak base, ammonia (NH_3) is found in window cleaners. In an aqueous solution, only a few ammonia molecules accept hydrogen ions to form NH_4^+ and OH^-.

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

4.8 NEUTRALIZATION OF ACID AND BASE

A neutralization reaction is when an acid and a base react to form water and a salt and involves the combination of H+ ions and OH- ions to generate water. The neutralization of a strong acid and strong base has a pH equal to 7. The neutralization of a strong acid and weak base will have a pH of less than 7, and conversely, the resulting pH when a strong base neutralizes a weak acid will be greater than 7.

Acid-base neutralization is a process in which acid reacts with base to produce water and salt. The driving force of this reaction is formation of a low-energy and stable covalent bond in water, together with the second product, mostly ionized salt. The “neutralization” term does not mean neutral pH, but the state in which the same mole numbers of both acid and base have been mixed. To detect the moment of neutralization, we use an indicator, which for example, can change its color when neutralization is reached.

Acid-base titration When strong acid and strong base react each other or any of the strong partner reacts with the weak one (acid or base), an essentially irreversible quantitative reaction takes place. The titration is a measurement of the reactant solution concentration. The titration process is stepwise addition from a burette (drop by drop) a standardized solution (solution with known concentration) of base (or acid) to Erlenmayer conical flask containing known volume of acid (or base) solution, in the presence of proper indicator.

To calculate the concentration of the examined solution we use the formula:

$C1 \times V1 = C2 \times V2$

C1 - unknown concentration of acid (or base) in the Erlenmayer flask

C2 - known concentration of standardized base (or acid) solution in the burette

V1- volume of the acid (or base) solution in the Erlenmayer flask

V2- volume of the standardized base (or acid) solution added from the burette to the Erlemnayer flask

4.9 INDICATORS

Indicators are conjugated acid-base pairs added to a titration mixture in small molar amounts, in order to monitor the pH. The acidic and basic forms of indicators have different colors. The pH range, at which an indicator color begins to change, depends on its pK (pH at which molecule of indicator is dissociated in 50 %). Generally, we must select proper indicator for kind of titration: the indicator should change its color at or near the point of equivalence.

4.10 SAL AND TYPES OF SALTS

Salt is a solid chemical compound that occurs naturally in nature in its pure form. They are formed due to a neutralisation reaction between acids and bases. Salt is classified into different types acidic, basic, normal, and double. Acidic salt is formed when a strong acid reacts with a weak base.

Here are some types of salts:

- **Acidic salts**: Formed when a strong acid reacts with a weak base, such as NH_4Cl and $CuSO_4$
- **Basic salts**: Formed when a strong base reacts with a weak acid, such as Na_2S and CH_3COONa
- **Neutral salts**: Formed when a strong acid and base react, such as NaCl and KNO_3
- **Simple salts**: Such as NaCl, KCl, and Na_2SO_4
- **Acid salts**: Such as $NaHCO_3$ and NaH2PO4
- **Double salts**: Such as KAl $(SO_4)_2$

Some common salts include:

- **Sodium chloride (NaCl)**: Also known as table salt, this is a white solid with a cubic shape. It's used in cooking and is often found in salt shakers.
- **Calcium chloride ($CaCl_2$)**: Used to melt ice on roads in the winter
- **Copper sulfate ($CuSO_4$)**: Used in fertilizers and processed food
- **Sodium bisulfate ($NaHSO_4$)**: Used to lower the pH of solutions

Salts have high melting points due to their strong ionic bonds. For example, table salt has a melting point of 801°C.

4.11 EXERCISE:

1. a) What is the Arrhenius definition of an acid? Give an example of an acid according to this theory. b) What is the Arrhenius definition of a base? Give an example of a base according to this theory.
2. a) Give the definitions of an acid and a base on the Bronsted-Lowry theory. b) Use the Bronsted-Lowry theory to explain the reactions which happen when (i) hydrogen chloride gas dissolves in water; (ii) hydrogen chloride gas and ammonia gas react; (iii) ammonia gas reacts with a solution containing hydroxonium ions; (iv) copper(II) oxide reacts with dilute sulphuric acid to give copper(II) sulphate and water.
3. What is meant by the phrase “A strong acid has a weak conjugate base”?
4. Use the following equations to help you to explain what is meant by the statement that “water is amphoteric”.

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$$

5. a) Define the terms Lewis acid and Lewis base. b) Draw a dots-and-crosses diagram of a molecule of aluminium chloride, $AlCl_3$, showing outer electrons only. Would you expect this to behave as a Lewis acid, a Lewis base, or neither, or both? Explain your answer.
6. Which of the following might act as a Lewis base: NH_3, CH_4, F^-, OH^- ? Explain your answer