People's Democratic Republic of Algeria

Ministry of Higher Education and Scientific Research

Ziane Achour University of Djelfa

Faculty of Sciences and Technology

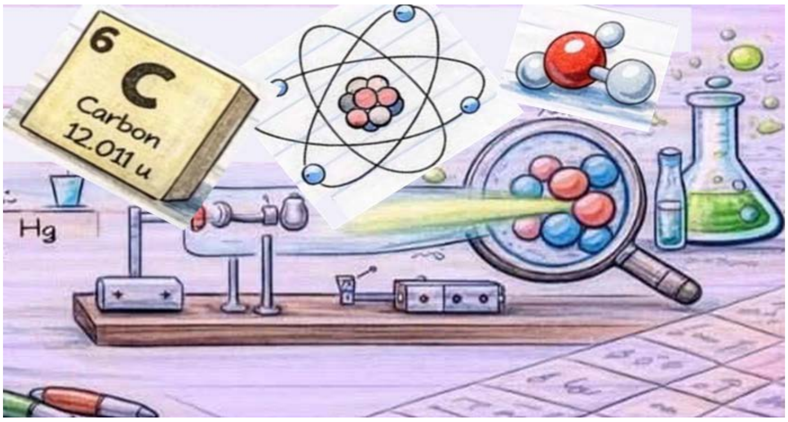
Department of Common Core in sciences and technology

Course Handout

Structure of matter

Prepared by: Dr. BENHARKAT Zohra

Senior Lecturer Class B



Level: 1st Year License Common Core ST

SUMMARY

Foreword

Chapter 1. Fundamental concepts

Chapter 2. Principal components of matter

Chapter 3. Radioactivity

Chapter 4. Electronic structure of an atom

Chapter 5. Periodic classification of the elements

Chapter 6. Chemical bonding

FOREWORD

FOREWORD

The Structure of Matter is a foundational science course exploring the physical universe build. The present document for the Structure of Matter module has been designed to meet the needs of first year License students, particularly those pursuing a first degree in Science and Technology (L1). Its primary focus is on providing comprehensive instruction in fundamental concepts of matter structure, a captivating of general chemistry. The curriculum for Common Core in Science and Technology students delineates this course into six distinct chapters and then focuses on the view of fundamental concepts, principal components of matter, radioactivity, electronic structure of an atom, periodic classification of the elements and chemical bonding.

Chapter 1.

Fundamental concepts

Chapter 1. Fundamental concepts

1.1 Introduction

Matter is anything that has mass and occupies space. Matter is neither created nor destroyed. It is composed of tiny particles which are called atoms. Atoms combine to form molecules which exist freely independently. The new word atom is developed by Democritus Greek in the 5th century. According to him atom cannot be divided. Obviously, understanding the structure of atoms is critical to understand the properties of matter.

1.2 Classification of Matter

1.2.1 Physical Classification

There are three states or forms of matter:

Solids: Rigid, fixed shape and volume.

Liquids: Fluids, no fixed shape, fixed volume.

Gases: Highly compressible, fill entire volume.

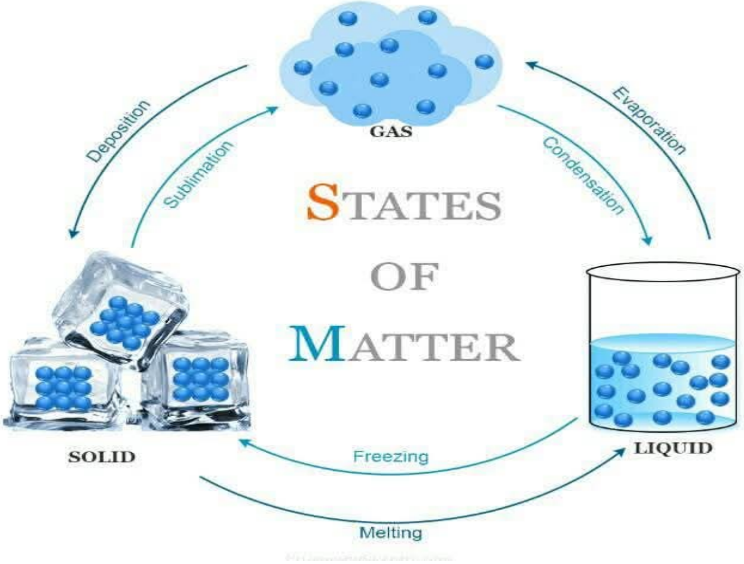


Figure 1.1 states of matter.

1.2.2 Chemical Classification

Elements: Pure substances consisting of only one type of atom.

Compounds: Pure substances formed by two or more elements in a fixed ratio.

1.3 Atoms and Molecules

1.3.1 Atomic Mass Unit (u)

The mass of atoms and subatomic particles is expressed in atomic mass unit (u).

$1\ \mathrm{u} = \frac{1}{12}$ the mass of one carbon-12 atom

$1\ \mathrm{u} = 1{,}6605\ .\ 10^{24}\ \mathrm{g}$

1.3.2 Molecule

The smallest particle of an element or compound capable of independent existence. It is a group of two or more atoms chemically bonded together.

- ✓ Molecules of elements: H_2 , O_2 , N_2 , Cl_2, P_4 , S_8 ...
- ✓ Molecules of compounds: H_2O, CO_2 , NH_3, CH_4 , NO_2 ...

1.3.3 Valency

The combining capacity of an element, which gives its ability to combine with other elements.

1.4 Mole concept

1.4.1 Mole definition

Mole is defined as the amount of a substance that contains as many particles as there are atoms in exactly 12 g of carbon-12.

Mole calculations involve conversion between:

- ➢ $\text{Mass (g)} \Leftrightarrow \text{Mole} \rightarrow \text{Mass} = \text{Moles x Molar Mass}$
- ➢ $\text{No. of Particles} \Leftrightarrow \text{No. of Particles} = \text{Moles x Avogadro's Number (Na)}$, (Exactly 12 g of C-12)
- ➢ $\text{Volume of Gas (at STP)} \Leftrightarrow \text{Moles x 22.4 L}$

1.4.2 Avogadro's Number

The number of particles (atoms / molecules/ ions) in one mole of any substance is called.

$$\boldsymbol{Na = 6.022\ x\ 10^{23}} \textbf{ particles.}$$

1.5 Chemical Calculations

1.5.1 Molar Mass

Mass of one mole of a substance's particles (atoms/ molecules/ ions).

- Molar Mass (g /mol) = Gram Molecular Mass= Mass no. in g 1mole of the substance.
- No. of Moles = Given Mass / Molar Mass.
- No. of Moles = No. of Particles / Avogadro's number (Na).
- Molar Mass = No. of given atoms x Atomic mass.

1.5.2 Percentage Composition

The percentage of each element present in a compound.

$$\text{Percentage of Element} = \frac{\text{Mass of that element}}{\text{Molar Mass of the compound}} \times 100$$

1.6 Stoichiometry and limiting Reagent

1.6.1 Stoichiometry

The branch of chemistry that deals with the quantitative relationships between the reactants and products in a balanced chemical equation.

1.6.2 Balancing Chemical Equations

Balancing chemical equations is based on the law of conservation of mass. It means matter is nether neither created nor destroyed in a chemical reaction.

- ✓ Write the unbalanced equation
- ✓ Balance the atoms of each element
- ✓ Use coefficients to balance the equation
- ✓ Ensure the total mass of reactants = the total mass of products

1.7 Laws of Chemical Combination

1.7.1 Law of Conservation of Mass

Mass can neither be created nor destroyed in a chemical reaction.

Total mass of the reactants = Total mass of the products

1.7.2 Law of Definite Proportions

A given compound always contains exactly the same elements chemically combined in a fixed ratio by mass.

1.7.3 Law of Multiple Proportions

When two elements combine to form two or more compounds, the masses of one element combined with the fixed mass of other element are in a simple whole number ratio.

E. g. $\mathrm{H_2O}$ (O:H = 8:1) and $\mathrm{H_2O_2}$ (O:H = 16:1)

1.7.4 Avogadro's Law

Equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules.

Equal volumes = Equal molecules

1 mole of any gas = $Na = 6.022\ x\ 10^{23}$ *molecules*

Chapter 2.

Principal components of matter

Chapter 2. Principal components of matter

2.1 Introduction

The word atom and atomic theory was introduced by John Dalton in 1808 in terms of an atomic model. Dalton's atomic theory was able to explain the laws of chemical combination successfully. However, it failed to explain some properties of matter. For example, it could not explain why substances like glass or ebonite when rubbed with silk or fur, generate electricity. Discovery of subatomic particles in late nineteenth and early twentieth century set a blow to Dalton's atomic model of hard sphere. In modern view of atomic theory, according to J. J. Thomson, an atom divisable into subatomic particles. Atoms can also combine in non-whole number ratio in non-stoichiometric compounds. Atoms of same element also differ in properties related to mass even in case of isotopes also.

2.2 Subatomic Particles or Constituents of Atoms

Three important subatomic particles, namely, proton, electron and neutron which are of concern to chemistry were discovered. Proton and neutron are present in the atomic nucleus and together are called nucleons. Electrons are present in the extra nuclear region in atom outside the nucleus.

2.2.1 Electron (e^-)

In the year 1897, electron was discovered by J. J. Thomson during the study of cathode rays and found that the cathode rays are a stream of very small, negatively charged particles which are 1837 times lighter than a hydrogen atom and are present in all atoms. Later these particles were named as '***electrons***'.

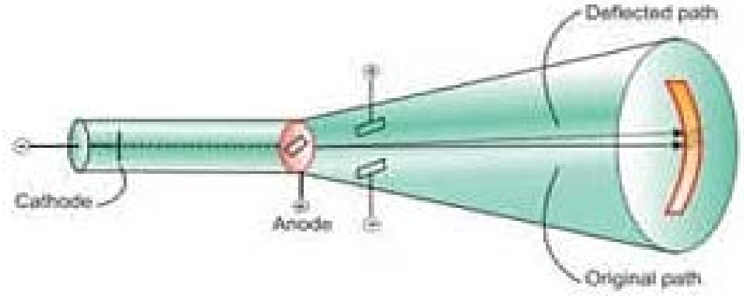


Figure 2.1 Cathode ray tube experiment.

2.2.2 Proton (p^+)

Proton was discovered by Ernest Rutherford in1919 during the study of anode rays or canal rays which original in the region between cathode and anode in discharge tube. He found in the experiment of scattering of α-particles by thin gold foil that a few α-particles bounce back. From this, he inferred the presence of massive and positively charged nucleus inside the atom. Following the discovery of nucleus in an atom, Rutherford found that fast moving α-particles transmuted nitrogen into oxygen with simultaneous liberation of hydrogen.

$$ {}^{14}_{7}\mathrm{N} + {}^{4}_{2}\alpha \longrightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H} $$

He further showed that other elements could also be transmuted, but hydrogen was always emitted. On this basis Rutherford proposed that the hydrogen nucleus must be contained inside nuclei of all the elements. Hence, the hydrogen nucleus was renamed as '***proton***'.

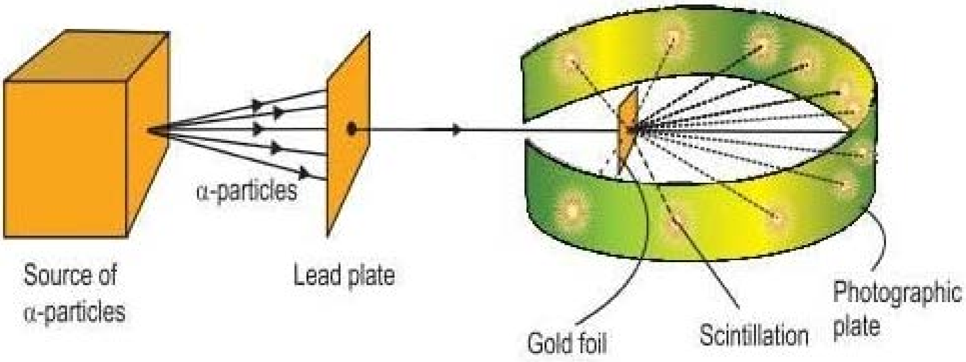


Figure 2.2 Rutherford's scattering experiment.

2.2.3 Neutron (n^0)

Existence of an electrically neutral and massive particle in the nucleus was predicted by Ernest Rutherford in1920 to account for the disparity in atomic number and atomic mass of an element. In the year 1932, James Chedwick measured velocity of protons knocked out from paraffin by an unidentified radiation from beryllium.

$$ {}^{9}_{4}\mathrm{Be} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n} $$

From that he determined the mass of the particles of the unidentified neutral radiation which came to be almost the same as that of a proton. He named this particle as '**neutron**' which was predicted by Rutherford earlier.

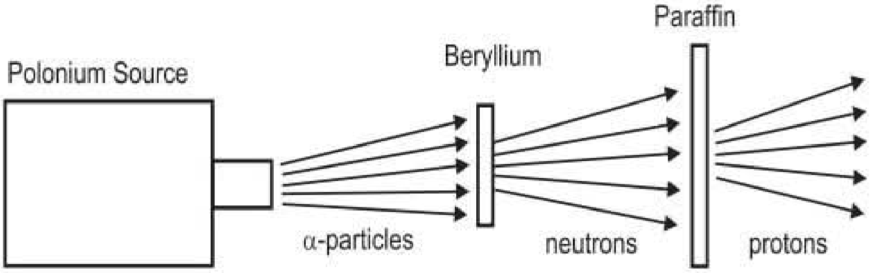
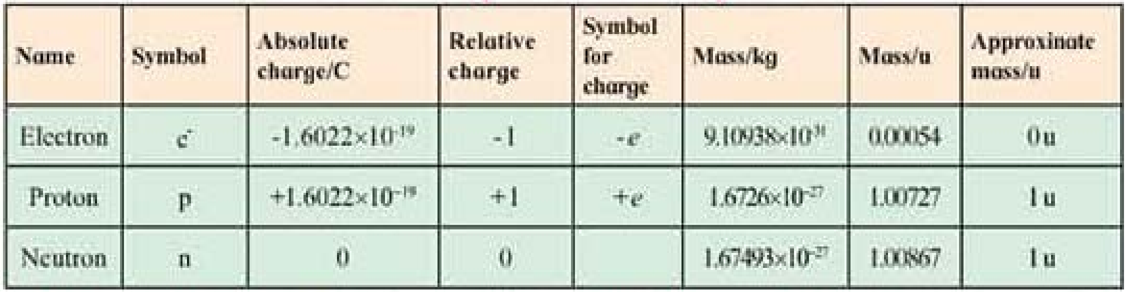


Figure 2.3 Discovery of neutron.

The properties of electron, proton and neutron are summarised in the following Table:



Name	Symbol	Absolute charge/C	Relative charge	Symbol for charge	Mass/kg	Mass/u	Approximate mass/u
Electron	e^-	-1.6022×10^{-19}	-1	$-e$	9.10938×10^{-31}	0.00054	0 u
Proton	p	$+1.6022\times10^{-19}$	+1	$+e$	1.6726×10^{-27}	1.00727	1 u
Neutron	n	0	0		1.67493×10^{-27}	1.00867	1 u

2.3 Rutherford's atomic model

During α-particle or helium nuclei bombardment experiment on 10^{-4} mm thick gold foil, Rutherford observed that:

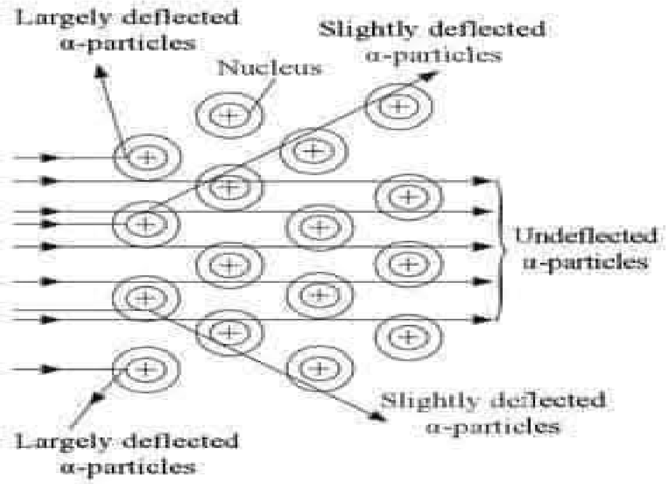
- Most part of the atom is empty as most of the α-particle passed straight through the foil without any deflection
- Electrons occupy position in this empty space (extra nuclear region).
- Centrally located solid compact small part having all positive charge and nearly the whole mass called nucleus (as few one out of 20000 α-particles get defected superior up to 90° and maximum 180°.
- The size or radius of nucleus can be calculated by this relation and Radius of atom is 10^{-10} m.
- Centrifugal force develops between electrons and nucleus so electron revolves around the sun (that is planetary or solar model).

Merits:

- Explains discovery of nucleus.
- Explains circulatory relation of electron around the nucleus.

Demerits:

- It cannot explain stability of atom.
- It cannot explain the number and velocity of electrons.
- According to him, atomic spectrum is continuous and non-linear but infact it may be linear and discontinuous.



2.4 Presentation and characteristics of an atom

2.4.1 Atomic number (Z)

Moseley postulated the frequency of the X-rays was related to the charge present on the nucleus of the atom of the element used as anticathode. The number of unit positive charges carried by the nucleus of an atom is the number of protons, which is chemical identity of an element. This number is called atomic number (Z) of the element. So, the positive charge on the nucleus is due to the protons present in it (+Ze). Atom being electrically neutral, it contains the same number of extranuclear electrons in it as its atomic number. Therefore, the total electronic charge on an atom is (−Ze). Thus in any atom,

$$\text{Atomic number (Z)} = \text{number of protons} = \text{number of electrons}$$

and for ions,

$$\text{Atomic number (Z)} = \text{number of protons}$$

Facts about Atomic Number:

- It is always a whole number, and a permanent value for each element.
- It is serial number of elements in periodic table that is, determines their exact position.
- Periodic properties are related to the atomic number of elements.

2.4.2 Mass number (A)

As can be seen from Table 1, mass of an electron is negligibly small compared to that of the nucleons. As a result the mass of an atom (atomic weight) can be considered to be concentrated in its nucleus. The approximate mass of one proton or one neutron is **1 a.m.u**. Therefore, approximate atomic mass in Daltons is numerically equal to the number of the nucleons in the atom. The number of the nucleons in the nucleus is designated by the symbol(N); and the total number of protons and neutrons, that is nucleons, in an atom is called its atomic mass number (A).

$$\text{Mass number (A)} = \text{Proton number (Z)} + \text{Neutron number (N)}$$

Therefore

$$\mathrm{A} = \mathrm{Z} + \mathrm{N}, \qquad \mathrm{N} = \mathrm{A} - \mathrm{Z}$$

2.4.3 Atom symbol

The composition of any atom is represented by element symbol (X) with the atomic mass number (A) as superscript on left and atomic number (Z) as subscript on left:

$${}^{\mathrm{A}}_{\mathrm{Z}}\mathrm{X}$$

The atom or nucleus having a unique composition as specified by ${}^{\mathrm{A}}_{\mathrm{Z}}\mathrm{X}$ is called a **nuclide**.

2.5 Isotopes and relative abundance

Some elements exist as single natural nuclide. For example ${}^{19}_{9}\mathrm{F}$. However, many elements exist naturally as mixture of two or more types of atoms or nuclides. These individual nuclides are called isotopes of that element.

All the isotopes of an element have the same number of protons but different number of neutrons in their nuclei. As the proton number is the atomic number, all the isotopes of an element have the same position in the modern periodic table and exhibit similar chemical properties.

Example: isotopes of ${}_{1}\mathrm{H}$: ${}^{1}_{1}\mathrm{H}, {}^{2}_{1}\mathrm{H}, {}^{3}_{1}\mathrm{H}$; isotopes of ${}_{6}\mathrm{C}$: ${}^{12}_{6}\mathrm{C}, {}^{13}_{6}\mathrm{C}, {}^{14}_{6}\mathrm{C}$; isotopes of ${}_{8}\mathrm{O}$: ${}^{16}_{8}\mathrm{O}, {}^{17}_{8}\mathrm{O}, {}^{18}_{8}\mathrm{O}$.

Two kinds of isotopes of some elements exist:

- ✓ Stable isotopes which have the number of neutrons nearly equal to the number of protons in their nuclei.
- ✓ Unstable or radioactive isotopes which undergo radioactive decay and are of great medical and industrial use. They have more neutrons than protons in their nuclei.

Symbol	Atomic number Z	Atomic mass number A	Neutron number $N = A - Z$	% Abundance	Stability
$^{12}_{6}C$ or C-12	6	12	6	98.9 %	Stable
$^{13}_{6}C$ or C-13	6	13	7	1.1 %	Stable
$^{14}_{6}C$ or C-14	6	14	8	< 0.00017 %	Radioactive

All the natural isotopes of an element coexist and have a definite natural isotopic abundance or relative abundance ($\boldsymbol{x_i}$), that is the mass percentage of isotope "$\boldsymbol{i}$" in the natural element, defined as follows:

$$\sum x_i = 1$$

and

$$\mathrm{M} = \sum x_i \ \mathrm{M}_i$$

Here M is atomic molar mass of an element, and its unit is g/mol.

M_i is relative isotopic mass, its unit is g/mol or u.m.a in the case of a single atom, and which is always close to the mass number A, $\mathrm{A} \approx \mathrm{M}_i$.

2.6 Isotopes separation and determination of the atomic mass

2.6.1 Bainbridge Spectrometer

Mass spectrometry allows the identification of different isotopes of an element by determining their masses and isotopic abundances. There are several types of spectrometers, among them: the Bainbridge spectrometer.

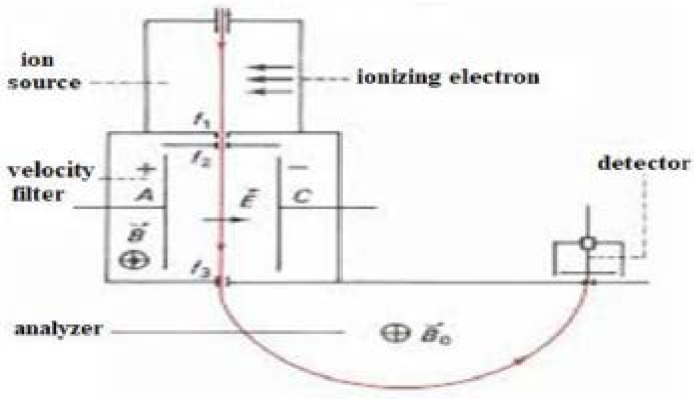


Figure 2.4 Bainbridge Spectrometer.

a. Ionization Chamber:

Electrons ionize the gas atoms; the formed ions move at different speeds as they enter the velocity filter.

b. Velocity Filter:

Ions are subjected to the simultaneous action of electric field E and magnetic field B; the forces applied to an ion with charge (q) and velocity (v) are:

- The electric force: $\mathrm{F_e = q.E}$
- The magnetic force: $\mathrm{F_m = q.v.B}$

B and E are orthogonal; $\mathrm{F_e}$ and $\mathrm{F_m}$ have parallel directions and opposite senses.

$$\mathrm{F_e = F_m \rightarrow q.E = q.v.B \rightarrow v = E/B}$$

c. Analyzer:

The ion of mass m is subjected to a constant magnetic field $\mathrm{B_0}$, and it deviates in a circular path of radius "*r*" :

$\mathrm{F_m = F_c \rightarrow q.v.B_0 = m\,.v^2/r \rightarrow m/r = q.B_0/v}$, and $\mathrm{v = E/B}$;

So, $\mathrm{m/r = q.B.B_0\,/E = constante}$

d. Detector:

The ions are collected separately according to their masses and their abundances.

2.6.2 Binding energy

The binding energy is the energy needed to separate the nucleus of an atom into its nucleons (protons and neutrons). According to Einstein equation, the binding energy is

$$\mathrm{\Delta E = \Delta m.C^2}$$

Here c is speed of light in the vaccum, $\mathrm{c = 3.10^8\ m/s.}$

$\mathrm{\Delta m}$ is mass defect and its is the difference between the total mass of the individual protons and neutrons before they combine to form a nucleus and the mass of the nucleus itself.

$$\mathrm{\Delta m = \left[Z.m_p + (A - Z).m_n\right] - m_{nucleus}}$$

2.6.3 Nuclear stability

The stability of an atomic nucleus is measured by the binding energy per nucleon, which is the ratio of the nucleus's binding energy to its mass number, defined as follows:

$$\mathrm{\frac{\Delta E}{A} = \frac{\Delta m.931{,}5}{A}\left(\frac{MeV}{nucleon}\right)}$$

Nuclei with higher binding energies by nucleon are generally more stable, while those with lower binding energies per nucleon are less stable.

Chapter 3.

Radioactivity

Chapter 3. Radioactivity

3.1 Introduction

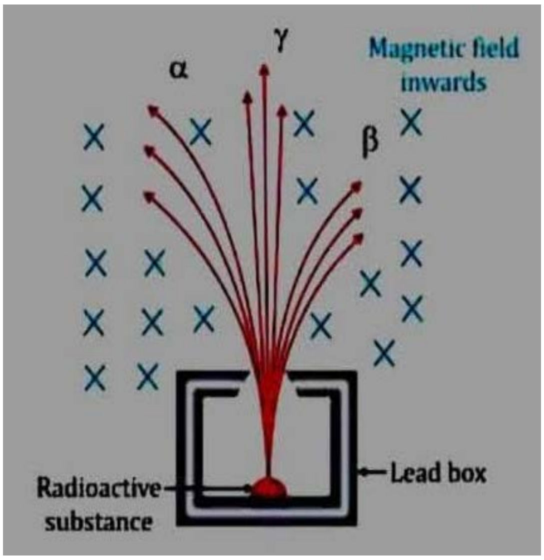
Some nuclei are naturally unstable. To attain stability these nuclei emits some subatomic particles or radiation. This phenomenon is called radioactivity. Radioactivity occurs without any externat cause. It cannot be speeded up or slowed down by any physical or chemical means. Radioactivity is a process without any defined pattern, rule or method.

3.2 Natural radioactivity

The substances which disintegrate (or decay) by the spontaneous emission of radiations are called radioactive substances like Uranium, radium, polonium, thorium, actinium etc. The isotopes of nearly all the elements of atomic number higher than 82 (i.e. lead) are radioactive. These are called natural radioactive substances. The phenomenon of radioactivity cannot be due to the orbital electrons which could easily be affected by such changes. it should therefore be the property of the nucleus. Thus. radioactlvity is a nuclear phenomenon.lt is the process of spontaneous emission of α, β and γ radiations from the nuclei of atoms during their decay.

3.2.1 Radioactivity as Emission of α, β and γ Radiations

Rutherford experimentally found that on subjecting the radiations given out by a radioactive substance to a magnetic field in a direction perpendicular to their path. They separate out into three distinct constituants.

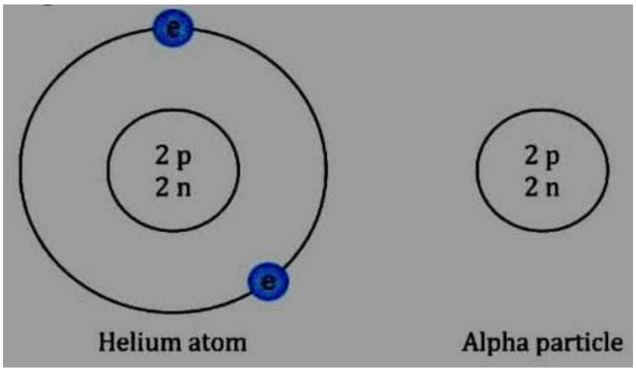


- Those which turn to the left (as given by Fleming's left-hand rule) must be positively charged and are called alpha (α) particles.
- Those which turn to the right must be negatively charged and are called beta (β) particles. The β particles are devlated more than the α-particles.

- Those which pass undeviated must be uncharged (or neutral) and are called gamma (γ) radiations. γ-radiations are electromagnetic waves similar to light and are therefore not affected by the magnetic field.
- Similarly, if the radiations given out by a radioactive substance are subjected to an electric field in a direction perpendicular to their path, they again separate out into three constituents.

3.2.1.1 Properties of α-Particles

- ✓ An α-particle consists of two protons and two neutrons. it is the same as a doubly ionised helium atom. it is represented as : $^{4}_{2}\mathrm{He}$ or He^{++}.
- ✓ The mass of an α particle is roughly four times the mass of a proton, and its charge is twice the charge of a proton.
- ✓ Their speed is of the order of $10^{7}\ \mathrm{m\ s^{-1}}$
- ✓ An α-particle strongly ionises the gas through which it passes. The ionising power of α-particles is roughly 100 times that of β-particles and roughly 10^{4} times that of γ-radiation.
- ✓ An α-partlcle rapidly loses its energy as it moves through a medium and therefore its penetrating power is quite small. its penetrating power is roughly 1/100 times that of a β-particle and 10^{-4} times that of γ-radiation.
- ✓ They are positively charged, so they are deflected by electric and magnetic fields.
- ✓ They affect a photographic plate.
- ✓ They cause fluorescence on striking a fluorescent material.
- ✓ They destroy the living cells and cause biological damage.



3.2.1.2 Properties of β-Particles

- ✓ β-particles are fast-moving electrons emitted from the nucleus of an atom and represented as $_{-1}^{0}\beta$ or $^{-1}_{0}\mathrm{e}$.
- ✓ Although β-particles and cathode rays are both fast-moving electrons, they differ in their origin. β-particles are given out from the nucleus, while the cathode rays are given out from the orbital electrons.
- ✓ The speed of β particles is of the order of $10^{8}\ \mathrm{m\ s^{-1}}$, but less than $3 \times 10^{8}\ \mathrm{m\ s^{-1}}$.

- ✓ β-particles ionise the gas through which they pass. Their ionising power is roughly 1/100 times that of α-particles but nearly 100 times that of γ-radiation.
- ✓ Their penetrating power is more than that of α-particles.
- ✓ β-particles are negatively charged, so they get deflected by electric and magnetic fields. The deflection of a β-particle is more than that of an α-particle because a β-particle is lighter than an α-particle.
- ✓ They affect a photographie plate.
- ✓ They cause fluorescence on striking a fluorescent material.
- ✓ They produce X-rays when they are stopped by metals of high atomic number and high melting point such as tungsten.

3.2.1.3 Properties of γ-Particles

- ✓ They are electromagnetic waves such as X-rays and light, but they differ from X- rays and light in wavelength.
- ✓ The speed of γ-radiations is the same as the speed of light.
- ✓ The ionising power of γ-radiations is low. it is 10^{-4} times that of α-particles and 10^{-2} times that of β-particles.
- ✓ Their penetrating power is high. it is about 10^{4} times that of α-particles and 10^{2} times that of β-particles.
- ✓ Like X-rays and light, γ-radations are not deflected by electric and magnetic fields because they are not charged particles.
- ✓ They affect a photographie plate.
- ✓ They cause fluorescence when they strike a fluorescent material.
- ✓ Like X-rays, γ-radiations are also diffracted by crystals.

3.2.2 Radioactive Emissions

3.2.2.1 α-Emission

If an unstable nucleus contains more neutrons than the number of protons, than it may emit two protons and two neutrons lightly bound together in a single particle, known as an α-particle. A stream of α-particles is called α-rays.

$$^{A}_{Z}\mathrm{X} \longrightarrow \ ^{A-4}_{Z-2}\mathrm{Y} + \ ^{4}_{2}\mathrm{He}$$

$^{A}_{Z}\mathrm{X}$ is parent nucleus.

$^{A-4}_{Z-2}\mathrm{Y}$ is daughter nucleus.

$^{4}_{2}\mathrm{He}$ is alpha (α) particle.

3.2.2.2 β-Emission

In emitting a β-particle, the number of nucleons in the nucleus remains the same, but the number of neutrons is decreased by one and the number of protons is increased by one. In other words, by the emission of a β-particle, the mass number A does not change, but the atomic number Z is increased by one.

$$\mathbf{{}^{A}_{Z}X \longrightarrow {}^{A}_{Z+1}Y + \beta^{-1}}$$

3.2.2.3 γ-Emission

The γ-rays take no mass and no electric charge from the nucleus, i.e. no neutrons or protons are lost, and hence, the nucleus does not decay into a different nucleus. i.e. there is no change in the mass number A and atomic number Z of the nucleus in γ emission.

$$\left[{}^{A}_{Z}X\right]^{*} \longrightarrow {}^{A}_{Z}X + \gamma$$

The star (*) indicates the excited state of the nucleus.

3.3 Artificial radioactivity and nuclear reactions

The total sum of masses of product nuclei is always less than the total sum of the masses of reactant nuclei in a nuclear change due to radioactive phenomena. This implies that there is a loss in mass. In 1905, Einstein suggested that mass and energy are interchangeable. The energy E released due to the loss in the mass $\Delta\mathrm{m}$ is $\mathrm{E} = \Delta\mathrm{m.c}^2$, where c is the speed of light. 1 kg mass is equivalent to 9×10^{16} J or 2.5×10^{10} kWh of energy. 1 a.m.u. of mass is equivalent to $931\ \mathrm{MeV}$ of energy.

3.3.1 Nuclear Fission

Nuclear fission is the process in which a heavy nucleus is splits into two light nuclei nearly of the same size by bombarding it with slow neutrons. In each fission reaction, a tremendous amount of energy of approximately $190\ \mathrm{MeV}$ is released.

It was first observed by German Scientist Otto Hahn and Fritz Strassmann in 1983 in nuclear fission heavy nucleus splits into two smaller nuclei with liberation of energy.

When Uranium with Z = 92 is bombarded with neutron, it splits into two fragments namely barium (Z =56) and krypton (Z = 36) and a large amount of energy is released which appears due to decrease in the mass.

General equation for fission reaction is,

$${}^{A}_{Z}X + {}^{1}_{0}n \longrightarrow \left[{}^{A+1}_{Z}X\right]^{*} \longrightarrow \mathrm{Y} + \mathrm{Z} + \mathrm{neutrons} + \mathrm{Energy}$$

$$\mathbf{{}^{235}_{92}U + {}^{1}_{0}n \rightarrow \left({}^{236}_{92}U\right) \rightarrow {}^{144}_{56}Ba + {}^{89}_{36}Kr + 3\,{}^{1}_{0}n + Energy}$$

3.3.2 Nuclear Fusion

Nuclear fusion is the process in which two light nuclei combine to form a heavy nucleus and release a huge amount of energy. This is because the mass of the product nucleus is less than the sum of masses of the two combining nuclei.

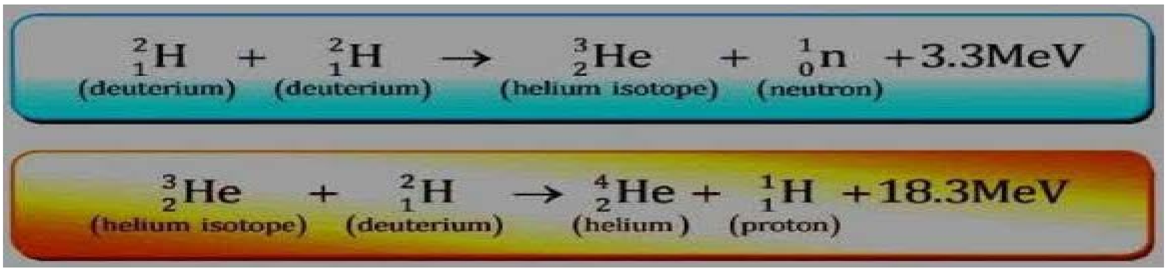
According to the mass-energy equivalence relation this loss in mass is released in form of energy $E = \Delta m.c^2$.

Thus in all, three deuterium nuclei fuse to form a helium nucleus with a release of 21,6 MeV energy. A part of this energy is obtained in form of the kinetic energy of neutron and proton.

When two nuclei approach each other, due to their positive charge, the electrostatic force of repulsion between them becomes too strong that they do not fuse. Thus, nuclear fusion is not possible at ordinary temperature and ordinary pressure.

Example:

When two deuterium nuclei (^2_1H) fuse, nucleus of helium isotope ^3_2He is formed and 3,3 MeV energy is released. This helium isotope again gets fused with one deuterium nucleus to form a helium nucleus ^4_2He and 18,3 MeV of energy is released in this process.



$$^2_1H + {}^2_1H \rightarrow {}^3_2He + {}^1_0n + 3.3MeV$$

(deuterium) (deuterium) (helium isotope) (neutron)

$$^3_2He + {}^2_1H \rightarrow {}^4_2He + {}^1_1H + 18.3MeV$$

(helium isotope) (deuterium) (helium) (proton)

3.4 Kinetics of the radioactive decay

3.4.1 Activity

The time rate of decay of a radioactive element is called activity. Thus, the number of nuclei decayed per second of a radioactive element is called radioactive.

3.4.2 SI-Unit of activity

SI-unit of activity is Becquerel 'Bq'. One Becquerel $(1Bq)$ is the activity of a radioactive element when 1 unstable nucleus decays each second.

$$1Bq = 1 \text{ decay /second}$$

Activity is also measured in another unit called Curie 'Ci'. One Curie $(1Ci)$ is the activity of a radioactive element when 3.7×10^{10} unstable nuclei decay each second.

$$1Ci = 3.7 \times 10^{10} \text{ decay /second}$$

3.4.3 Half-Life $(T_{1/2})$

Half-life is the time interval in which half of a radioactive sample decays.

$$N(t) = N_0 \,.\left(\frac{1}{2}\right)^{t/T_{1/2}}$$

Where N_0 is the initial number of nuclei, and $N(t)$ is nuclei remaining after time t.

3.5 Uses of radioactivity

Some uses of radioisotopes are given below

3.5.1 Medical use

- Diseases such as leukaemia and cancer are cured by radiation therapy. Radiations from cobalt-60 (Co) are used to treat cancer by killing the cells in the malignant tumour of the patient.
- The salts of weak radioactive isotopes such as radio-sodium chloride, radio-iron and radio-iodine are used for diagnosis. Such radioisotopes are called tracers.
- γ-rays emitted by radio isotopes are used to sterilise bandages, dressings, syringes and other equipment to make them free of germs. This method is quicker, more reliable and cheaper than sterilisation by heat.

3.5.2 Scientific use

- α particles emitted from radio isotopes are used as projectiles for nuclear reactions. The scattering of α particles from the nucleus helps in estimating the size of the nucleus and in understanding the nature of nuclear forces.
- The radioactive tracers are used in agricultural science to study the growth of plants with respect to the chemical manure used.
- The age of rocks and hence buried plants is estimated by the study of the rate of decay of ${}^{14}_{6}\mathrm{C}$ in the remains of dead plants. The process is called carbon dating.

3.5.3 Industrial use

- Radio isotopes are used as fuel for atomic energy reactors.
- Radio isotopes are used by engineers in factories to avoid the accumulation of charge on moving parts due to friction.
- The ionising effect of radiations front radio isotopes is used in making certain luminescent signs.
- The thickness of paper, plastic and metal sheets is controlled during manufacture when the penetrating power of β-radiations emitted from radio isotopes is known.

Chapter 4.

Electronic structure of an atom

Chapter 4. Electronic structure of an atom

4.1 Introduction

At the time when different models of atomic structure were being put forth, some results obtained from the studies of interactions of radiation with matter required to be correlated to atomic structure. Niels Bohr utilized these results to get over the drawbacks of Rutherford atomic model. These results were: (1) wave particle duality of electromagnetic radiation and (2) line emission spectra of hydrogen.

4.2 Wave particle duality of electromagnetic radiation

A dilemma was posed by electromagnetic radiation in the world of science. Phenomena such as diffraction and interference of light could be explained by treating light as electromagnetic wave. On the other hand, the black-body radiation or photoelectric effect could not be explained by wave nature of light, and could be accounted for by considering particle nature of light. The only way to resolve the dilemma was to accept that light has dual behaviour. When light interacts with matter it behaves as a stream of particles called photons, when light propagates, it behaves as an "**electromagnetic wave"**.

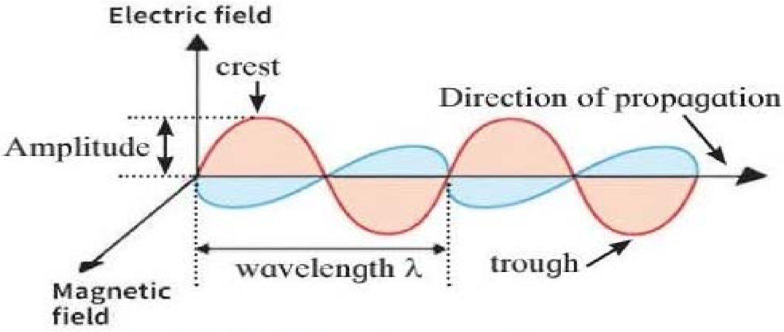


Figure 4.1 Electromagnetic wave.

The characteristics of the electromagnetic radiation are:

Wavelength (λ):

It is the distance between two successive crests or troughs. it is measured in meter (m), Angstrom $(\mathrm{A}°)$ or nanometers (nm) etc.

Frequency (ν):

It is the number of waves per second passing at a given point. its unit is Hertz (Hz).

$$\nu = \frac{C}{\lambda}$$

c is the speed of light, $\mathrm{c} = 3.10^{8}\,\mathrm{m/s}$.

Wave number $\bar{\nu}$:

It is the number of waves speed in one cm.

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

4.3 Corpuscular theory of light

It was first introduced by Newton. According to this theory, light is propagated in the form of small invisible particles.

4.3.1 Planck's quantum theory

It was introduced by Max Planck and then extended by Einstein. Quantum theory states that hot vibrating body does not emit or absorb energy continuously but emits or absorbs discontinuously in the form of small energy packets or bundles known as quanta and photon in case of light energy.

The energy of radiation (E) is directly proportional to frequency of radiation(ν).

$$\mathrm{E} \propto \nu$$

$$\mathrm{E} = \mathrm{h}.\nu = \frac{\mathrm{h.c}}{\lambda} = \mathrm{h.c.}\bar{\nu}$$

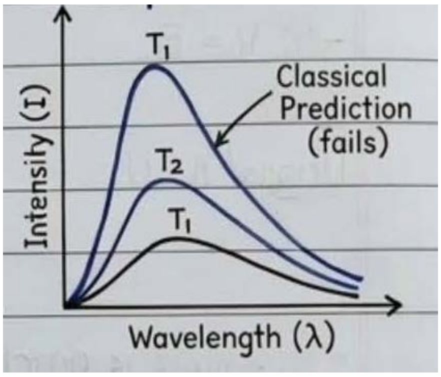
Here h is Planck's constant and its values is 6.6253×10^{-34} $\mathrm{J.s}$ or $\mathrm{kg.m^2.s^{-1}}$, λ is wavelength and $\bar{\nu}$ is wave number.

Absorption or emission in the form of multiples of quantum is known as quantization of energy that is,

$$\mathrm{E} = \mathrm{n.h.}\nu$$

At a given temperature, the intensity of radiation increases with wavelength, approaching towards maximum and then starts decreasing.

As Planck's quantum theory can explain only the black body radiations so Einstein extended quantum theory to all types of electromagnetic radiations.



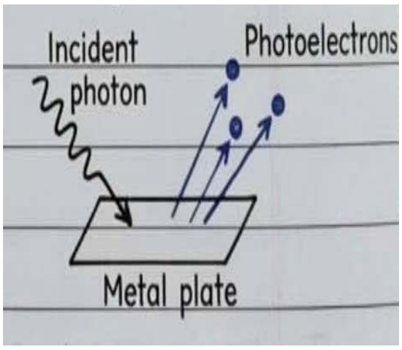
4.3.2 Photoelectric effect

It was introduced by P. Lenard and explained by Einstein based on Planck's theory. it is the emission of electrons from a metal surface on exposing it to radiation of suitable frequency or wavelength. it is readily shown by alkali metal having very low ionization energy.

When a photon strikes the metal, its energy is absorbed by the electrons and emission of electrons takes place. The electrons which are emitted are known as photoelectrons.

A part of the energy of photon is used to escape the electron from the attrative forces and the remaining energy is used in increasing the kinetic energy of electron.

Maximum kinetic energy of phoroelectrons = Absorbed energy - Work function



Work function (W_0 or φ) is the minimum energy ($h\nu_0$) required by an electron to escape from the metal surface.

$$K.E = h\nu - W_0 \quad \text{with} \quad K.E = \frac{1}{2} m.v^2$$

$$\frac{1}{2} m.v^2 = h\nu - h\nu_0 = hc\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)$$

where E is energy of radiation, ν_0 and λ_0 are threshold frequency and wavelength respectively.

Here threshold frequency is the minimum frequency of light radiation needed for electron emission.

- If $\nu > \nu_0 \Longrightarrow K.E > 0$: electron is emitted.
- If $\nu = \nu_0 \Longrightarrow K.E = 0$: electron is not emitted (remains on surface).
- If $\nu > \nu_0 \Longrightarrow K.E > 0$: no emission of electrons.

The minimum potential at which the photoelectric current reaches zero, is called the stopping potential, V_0

$$eV_0 = h(\nu - \nu_0)$$

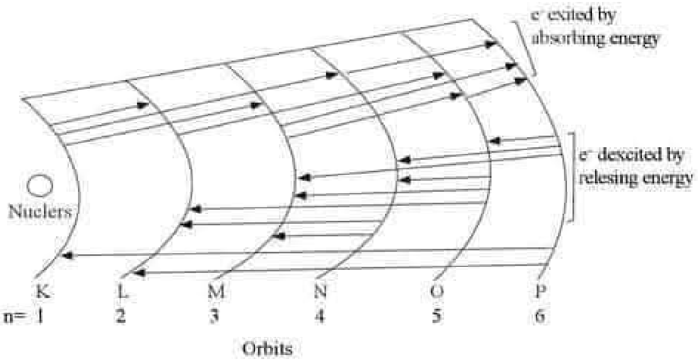
So photoelectric effect is proportional to frequency of light radiation. i.e. the rate of emission of photoelectrons from a metallic surface is directly proportional to the intensiry of light falling on it.

Kinetic energy of photoelectrons is directly proportional to the frequency of incident radiation, but independent of intensity of light.

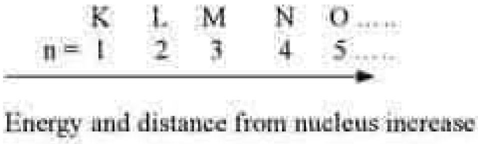
4.4 Bohr's atomic model

4.4.1 Bohr's theory postulates

Bohr introduced circular orbit concept based on linear hybrid combination of classical and early quantum physics and Planck's quantum theory and its main postulates are as follows:



1- Around the nucleus there are circular regions or spherical surfaces which are called "**orbits**" or "**shells**". Each orbit has a fix amount of energy so it is called energy level.



2- Angular momentum (mvr) of an electron moving in any orbit is quantized and given as

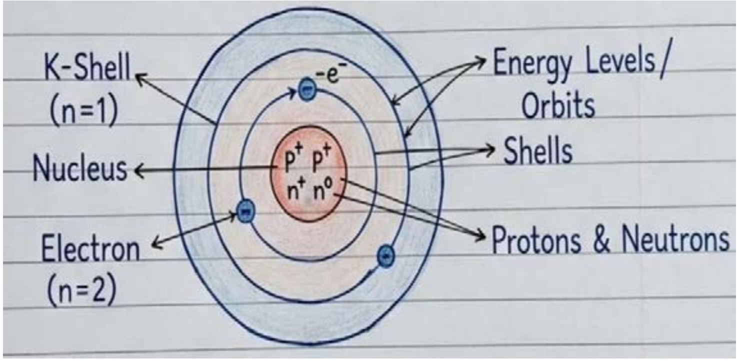
$$\mathrm{mvr} = \mathrm{n}\frac{\mathrm{h}}{2\pi} = \mathrm{nh}$$

Here h is Planck's constant and n is an integer.

3- An electron revolves round the nucleus in a particular orbit having definite energy that is why these orbits are called stationary states or levels. When electron changes its orbit energy change occurs in quanta which is given as

$$\Delta \mathrm{E} = \mathrm{E}_2 - \mathrm{E}_1 = \mathrm{h}.\nu = \frac{\mathrm{h}.\mathrm{c}}{\lambda}$$

4- in excited state electron jumps from lower orbit to higher orbit or energy level by absorbing energy in quanta. While in de-excited, electron jumps from higher to lower orbit energy level by releasing energy in quanta.



4.4.2 Bohr's theory for hydrogen atom

Bohr's theory is used to derive the energies of orbits, that is, the stationary states, in hydrogen atom. The results of Bohr's theory for hydrogen atom are summarized here.

a. The stationary state for electron are numbered n= 1, 2, 3,...... . These integers are known as principal quantum numbers.

b. The radii of the stationary states are

$$\mathrm{r}_\mathrm{n} = \mathrm{a}_0.\mathrm{n}^2$$

where $\mathrm{a}_0 = 0.53\ \mathrm{A}°$. Thus, the radius of the first stationary state, called the Bohr radius.

c. The most important property associated with the electron is the energy of its stationary state. It is given by the expression

$$E_n = \frac{\overline{R}_H}{n^2} \quad \text{, where n= 1, 2, 3,......}$$

$\overline{R}_H$ is the Rydberg constant for hydrogen and its value is $\overline{R}_H = -2.18 \times 10^{-18}\ J = -13.6\ (eV)$

Therefore, the energy of electron in the n^{th} shell, called quantized energy levels equation, is

$$E_n = \frac{-13.6}{n^2}\ (eV)$$

The lowest energy state is called the "**ground state**".

- For hydrogen $(Z = 1)$: $E_1 = -13.6\ eV$ **(Ground state)**

$E_\infty = 0\ eV$ **(Ionized state)**

d. Bohr theory can be applied to hydrogen-like species (hydrogenic species) which contain only one electron such as $He^+,\ Li^{2+},\ Be^{3+},\ B^{4+}$, etc.

Energies of the stationary states associated with these species are given by :

$$E_n = \frac{-13.6\ Z^2}{n^2}\ (eV)$$

and radii by the expression

$$r_n = \frac{a_0 . n^2}{Z}$$

where Z is the atomic number.

d. Velocities of electrons can also be calculated from the Bohr theory. Qualitatively it is found that the magnitude of velocity of an electron increases with increase of Z and decreases with increase in the principal quantum number n.

Velocity of electron in the n^{th} shell

$$v_n = 2.18 \times 10^{-6} \frac{Z}{n}\ (m/s)$$

4.4.3 Spectrum of hydrogen atom

The atoms of hydrogen in gas discharge tube emit radiations whose spectrum shows line characteristics (line spectra) and lies in the infrared, visible and ultraviolet region of the electromagnetic spectrum.

The line emission spectrum obtained from atomic hydrogen can be explained quantitatively using Bohr's theory. According to postulates of Bohr's theory, radiation is emitted when electron moves from an outer orbit of higher principal quantum number (n_i) to an inner orbit of lower principal quantum number(n_f). The energy difference (ΔE) between the initial and final orbit of the electronic transition corresponds to the energy of the emitted radiation. From the results derived from Bohr's theory ΔE can be expressed as

$$\Delta E = E_f - E_i$$

and the energy E of an orbit is related to its principal quantum number n by the equation

$$E_n = \frac{\overline{R}_H}{n^2}$$

Combining these two equations, we get:

$$\Delta E = \overline{R}_H \left(\frac{1}{n_f{}^2} - \frac{1}{n_i{}^2}\right)$$

This expression can be rewritten in terms of wave number of the emitted radiation in the following steps.

$$\Delta E = \frac{h.c}{\lambda} = \overline{R}_H \left(\frac{1}{n_f{}^2} - \frac{1}{n_i{}^2}\right)$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\overline{R}_H}{h.c}\left(\frac{1}{n_f{}^2} - \frac{1}{n_i{}^2}\right)$$

Bohr's theory successfully accounts for the empirical Rydberg equation for the line emission spectrum of hydrogen. In the Rydberg equation n_i and n_f are integers. Bohr's theory assigns physical meaning to them as principal quantum numbers corresponding to the concentric orbits. The integers in Rydberg equation, stand for the final orbit, n_f of electronic transition and n_i for the initial orbit.

The final Rydberg equation is given by:

$$\bar{\nu} = \frac{1}{\lambda} = R_H \left(\frac{1}{n_f{}^2} - \frac{1}{n_i{}^2}\right) \quad \text{where } n_i > n_f$$

R_H is the Rydberg constant for hydrogen, $R_H = 1{,}09678 \,.\, 10^7 \text{ m}$ or $R_H = 1{,}1 \,.\, 10^7 \text{ m}$

For hydrogen-like species, Rydberg equation is

$$\bar{\nu} = \frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_f{}^2} - \frac{1}{n_i{}^2}\right) \quad \text{where } n_i > n_f$$

The emission lines comprising five series thus, are result of electronic transitions from the excited hydrogen atoms as follow

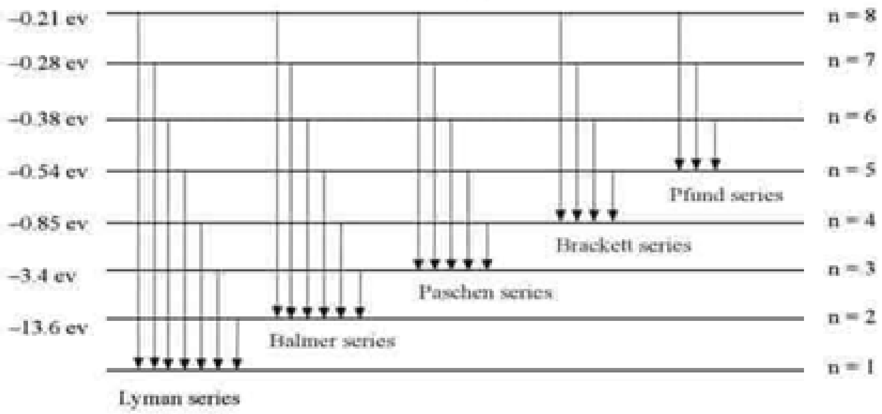


Figure 4.2 Energy level diagram of hydrogen spectrum.

4.4.4 Limitations of Bohr model

1. Bohr's atomic model failed to account for finer details of the hydrogen atom spectrum observed in sophisticated spectroscop experiments.
2. Bohr model was unable to explain the spectrum of atoms other than hydrogen.
3. Bohr theory could not explain the splitting of spectral lines in the presence of a magnetic field or electric field.
4. Bohr theory failed to explain the ability of atoms to form molecules by chemical bonds.

It was, therefore, thought that a better theory was needed to explain salient features of atomic structure.

4.5 Dual nature theory

With the limitations of Bohr model for hydrogen atom becoming transparent, attempts were made to develop a better and general model for atom. This was possible because two important developments took place after the Bohr model was postulated. These developments were:

1. de Broglie's proposal of dual behaviour of matter, and
2. Heisenberg uncertainty principle.

4.5.1 de Broglie Equation

In Bohr model an electron is regarded as a charged particle moving in well defined circular orbits about the nucleus. In contrast to this de Broglie proposed in 1924 that matter should exhibit a dual behaviour, that is, both particle and wave like properties. This means that electron should have momentum, p, a property of particle as well as wavelength, λ, a property of wave. He gave the following relation between λ and p of a material particle.

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

De Broglie's prediction was confirmed by diffraction experiments (a wave property).

4.5.2 Heisenberg uncertainty principle

In the year 1927 Werner Heisenberg stated the uncertainty principle: "it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron". In other words the position and momentum of an electron cannot be determined with the same certainty. If the certainty of determination of one property of the two is high, it means that the uncertainty of its determination is low. In that case the uncertainty of determination of the other property is very high.

Mathematically Heisenberg uncertainty principle is expressed as:

$$\Delta x \,.\, \Delta p \geq \frac{h}{4\pi} \qquad \text{or} \qquad \Delta x \,.\, \Delta v \geq \frac{h}{4\pi m}$$

Here Δx is the uncertainty in position and Δp (or Δv) is the uncertainty in momentum (or velocity).

A further implication of the uncertainty principle is that for an electron having certain energy one can only determine its probability at a particular point x around the nucleus. Bohr’s model describes concentric orbits as well defined paths of the electron rotating about the nucleus and calculate energy of electron occupying these orbits. Bohr model assumes that both position and momentum, of the electron in hydrogen atom are known exactly at the same time, which is ruled out by the Heisenberg uncertainty principle. Hence, no attempt was made to extend the Bohr model to other atoms. A different approach to atomic model which would account for particle duality of matter and would be consistent with Heisenberg uncertainty principle was required. This became possible with the development of quantum mechanics.

4.6 Quantum mechanical model of atom :

A new branch of science, called quantum machanics, was developed in 1926 by Werner Heisenberg and Erwin Schrodinger based on uncertainty principle and wave motion, respectively. Quantum mechanics based on the ideas of wave motion. Schrodinger developed the fundamental equation of quantum mechanics which incorporates wave particle duality of matter.

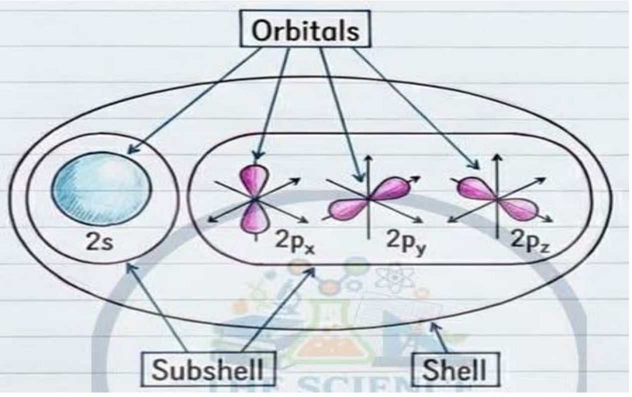
4.6.1 Schordinger wave equation

The Schordinger equation or wave equation is written as

$$\widehat{\mathrm{H}}\Psi = \mathrm{E}.\Psi$$

Here $\widehat{\mathrm{H}}$ is mathematical operator called Hamiltonian, Ψ is the wave function, E is the total energy of the system.

When Schordinger equation is solved for hydrogen atom, the possible value of energy E that the electron may have along with the corresponding wave function Ψ are obtained. As a natural consequence of solving this equation, a set of three quantum numbers characteristic of the quantized energy levels and the corresponding wave functions are obtained. These are principal quantum number (n), azimuthal quantum number (l) and magnetic quantum number (m).

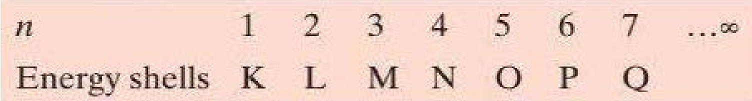


4.6.2 Quantum numbers

These are the parameters required to characterize an orbital or an electron. The orbital is defined as the space occupied by the electrons around the nucleus of an atom where the probability of finding an electron is the maximum. The characteristic features of the four quantum numbers are described as follows:

4.6.2.1 Principal quantum number (n)

It describes the size and energy of the shell. n=1, 2, 3, 4.... represents K, L, M, N shells and so on.

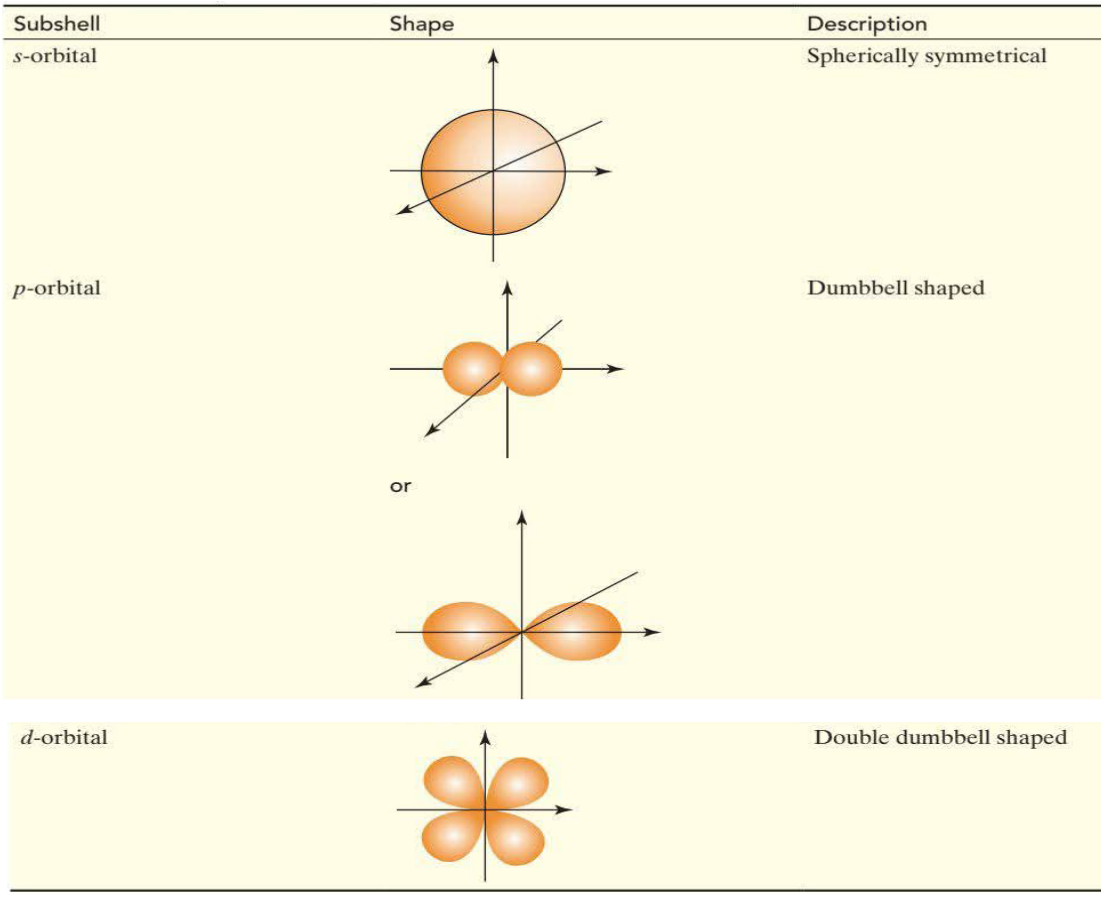


n	1	2	3	4	5	6	7	…∞
Energy shells	K	L	M	N	O	P	Q	

4.6.2.2 Azimuthal quantum number (l)

It describes the shape of the orbital (not of electron) and number of subshells in a shell. For a given value of n, l can have values 0 to $(\mathrm{n}-1)$.

l	0	1	2	3	4
Subshell or sub-energy level	*s*	*p*	*d*	*f*	*g*

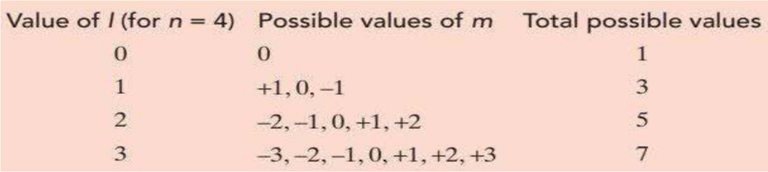


Subshell	Shape	Description
s-orbital		Spherically symmetrical
p-orbital	or	Dumbbell shaped
d-orbital		Double dumbbell shaped

Figure 4.3 The shapes of subshells.

4.6.2.3 Magnetic quantum number (m)

It describes indicates the possible orientations of an orbital in space. Its values vary from -1 to $+1$.



Value of l (for $n = 4$)	Possible values of m	Total possible values
0	0	1
1	+1, 0, –1	3
2	–2, –1, 0, +1, +2	5
3	–3, –2, –1, 0, +1, +2, +3	7

The different values of m for a particular value of l gives the possible orientations of the corresponding orbital in space. Each possible orientation is considered as a particular orbital.

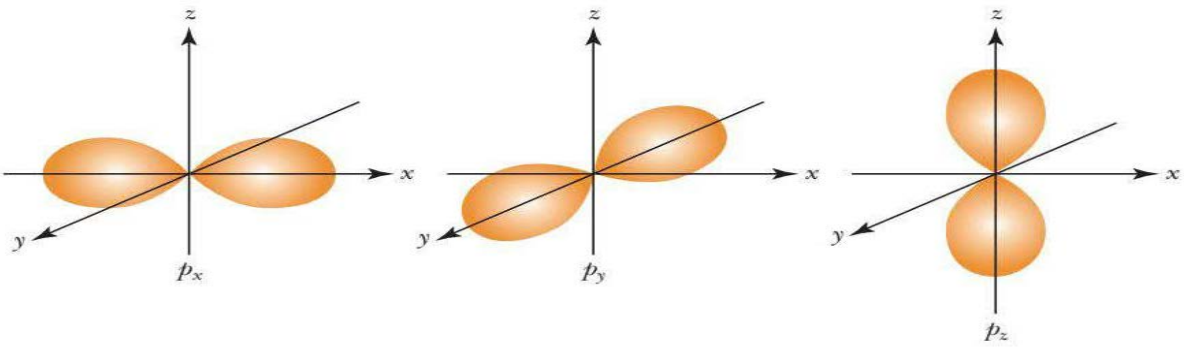


Figure 4.4 The orientation of three *p*-orbitals.

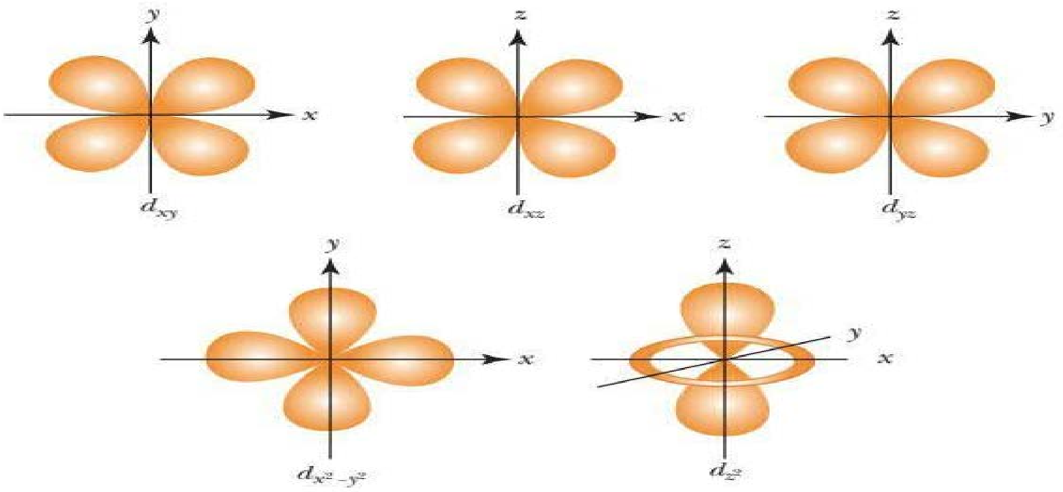
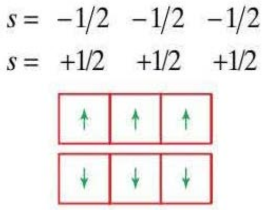


Figure 4.5 The orientation of five *d*-orbitals.

4.6.2.4 Spin quantum number (S)

It describes an electron only (not the orbital) and it characterizes the spin of an electron. An electron is not only moving around the nucleus but also spinning about its own axis. It has value $+1/2$ or $-1/2$.



4.6.3 Rules for filling of orbitals in atom

4.6.3.1 Aufbau principle

The electrons are filled up in the empty orbitals of an atom from the lowest energy orbital to the higher energy orbital. The energy sequence of empty orbitals is given in Figure, in which the energy of the subshells increases along the directions of arrow. This is known as the element's electronic configuration.

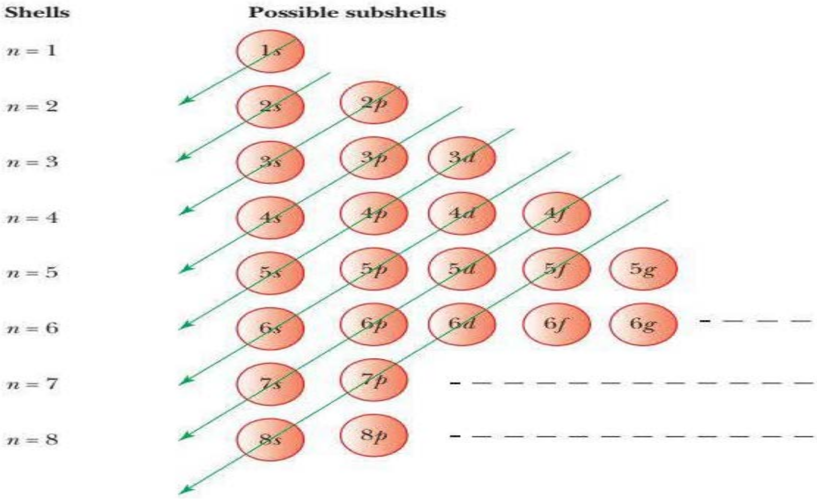


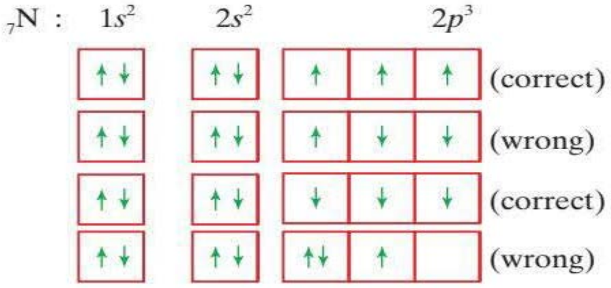
Figure 4.6 Sequence of filling of energy levels.

4.6.3.2 Pauli's exclusion principle

The Pauli's exclusion principle states that no two electrons in one atom can have the same values of all four quantum numbers or an orbital in a subshell can accommodate a maximum of two electrons of opposite spin.

4.6.3.3 Hund's rule

It states that pairing of electrons in orbitals of *p*, *d* and *f* subshells does not take place till each orbital belonging to that subshell has got one electron each.



Chapter 5.

Periodic classification of the elements

Chapter 5. Periodic classification of the elements

5.1 Introduction

Historically, elements with similar or related properties were grouped together into family of elements. For example, lithium, sodium and potassium formed the family of active metals whereas copper, silver and gold formed the family of noble metals. Based on the systematic relationships among the elements, a chart known as periodic table evolved that reflected systematic trends in physical and chemical properties of elements. Periodic table is the arrangement of elements in a tabular form on the basis of their properties that facilitates the systematic study of properties of elements.

The early attempts at classification of elements were based on the experimental observation on the limited number of elements that were known at that time.

5.2 Mendeleev's periodic table

The earliest version of the current form of periodic table was presented simultaneously by Dmitri Mendeleev of Russia and Lothar Meyer of Germany. Both the scientists arranged the elements in order of increasing atomic weights and observed that elements with similar properties (in families) appeared at regular intervals.

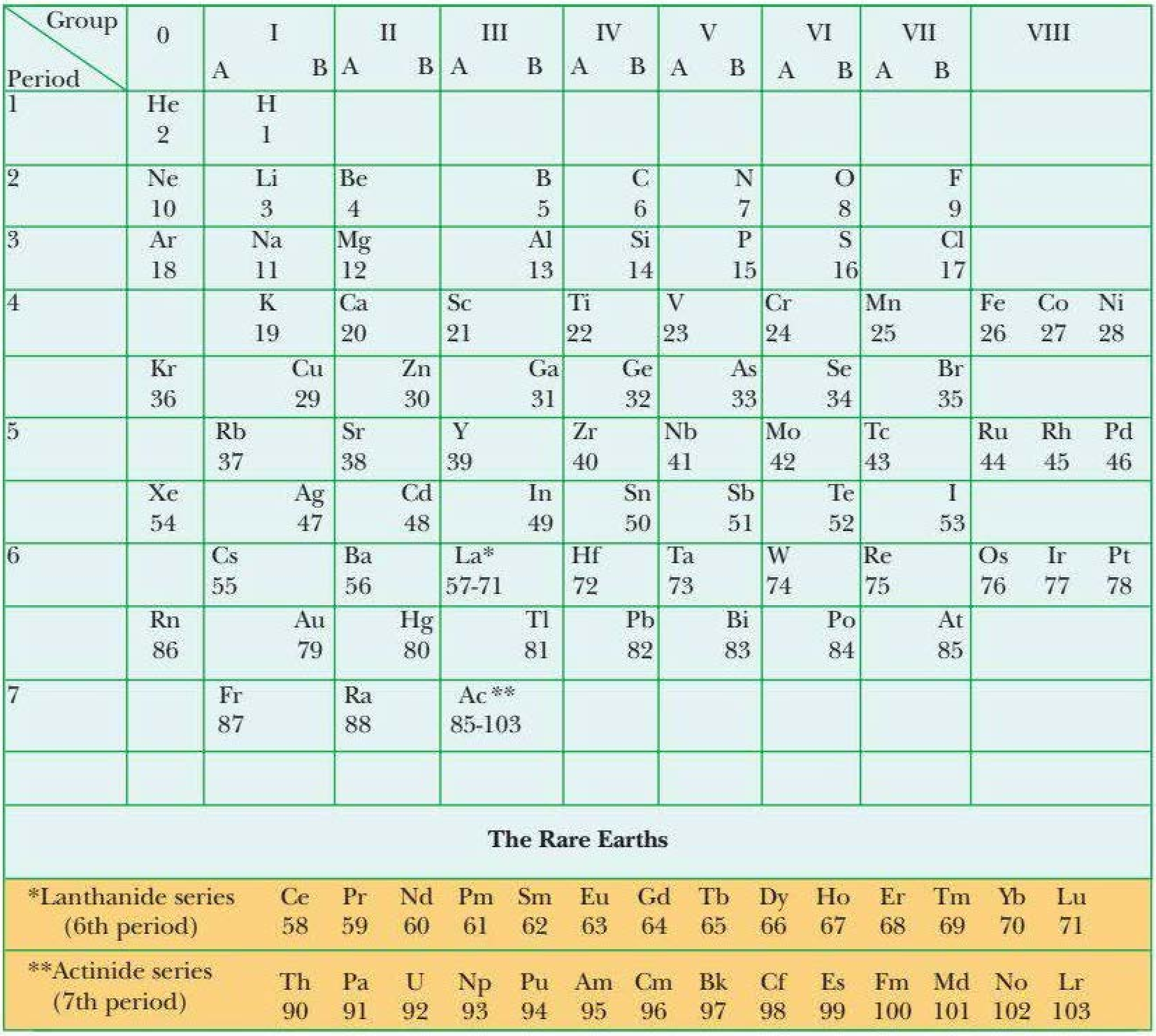
Mendeleev's periodic law stated that the physical and chemical properties of elements are the periodic function of their atomic weights. In1871, Mendeleev published a short periodic table which :

1. Consisted of only 63 elements. Inert gases were not included as these were not discovered at that time.
2. These elements were arranged in seven horizontal rows called as periods and eight vertical columns called as groups.
3. Some vacant sites were specified for undiscovered elements and their properties predicted. These were found true and verified when these elements were discovered later.

In the periodic table, so constructed, the elements in the same families (e.g., lithium ,sodium, potassium) were arranged in vertical columns designated as Groups I, II, III, IV, V, VI,VII,VIII. The horizontal rows were referred to as series.

Mendeleev's periodic table was later modified after the discovery of inert gases and several other elements. The inert gases were placed in new Group 0. Each long period was divided into two series, named as "odd" and "even" depending on the serial number. The first seven elements formed the even series and the last seven elements formed the odd series (not including the inert gases). The vertical Groups I to VII were further divided into two subgroups A and B to accommodate elements with difference in properties. The elements of even series in the long periods were placed in subgroup A while the elements of odd series were placed in the B subgroup. The Group 0 was not split further and in Group VIII three sets containing three elements each were placed.

The designation of the subgroups A and B given here is quite arbitrary and the new designation is given in the long form Periodic table as per the latest Convention.



Group / Period	0	I A	I B	II A	II B	III A	III B	IV A	IV B	V A	V B	VI A	VI B	VII A	VII B	VIII
1	He 2	H 1														
2	Ne 10	Li 3		Be 4			B 5		C 6		N 7		O 8		F 9	
3	Ar 18	Na 11		Mg 12			Al 13		Si 14		P 15		S 16		Cl 17	
4		K 19		Ca 20		Sc 21		Ti 22		V 23		Cr 24		Mn 25		Fe Co Ni 26 27 28
	Kr 36		Cu 29		Zn 30		Ga 31		Ge 32		As 33		Se 34		Br 35	
5		Rb 37		Sr 38		Y 39		Zr 40		Nb 41		Mo 42		Tc 43		Ru Rh Pd 44 45 46
	Xe 54		Ag 47		Cd 48		In 49		Sn 50		Sb 51		Te 52		I 53	
6		Cs 55		Ba 56		La* 57-71		Hf 72		Ta 73		W 74		Re 75		Os Ir Pt 76 77 78
	Rn 86		Au 79		Hg 80		Tl 81		Pb 82		Bi 83		Po 84		At 85	
7		Fr 87		Ra 88		Ac** 85-103										

The Rare Earths

*Lanthanide series (6th period)	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
**Actinide series (7th period)	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103

Figure 5.1 Modern version of Mendeleev's short periodic table.

Important characteristics of modern version of Mendeleev's short periodic table are listed as follows:

I. Horizontal rows or Periods:

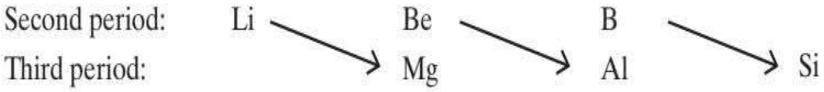
1. First period consists of 2 elements and is known as very short period.
2. Second period consists of 8 elements and is known as first short period.
3. Third period consists of 8 elements and is known as second short period.
4. Fourth period consists of 18 elements and is known as first long period.
5. Fifth period consists of 18 elements and is known as second long period.
6. Sixth period consists of 12 elements and is known as very long period.
7. Seventh period is an incomplete period.

II. Vertical columns or Groups

1. Group I A elements are called as alkali metals (expect H).
2. Group II A elements are called as alkaline earth metals.
3. Group V B elements are called as pnicogens.
4. Group VI B elements are called as chalcogens.
5. Group VII B elements are called as halogens.
6. Group 0 elements are called as inert gases.

III. Other features

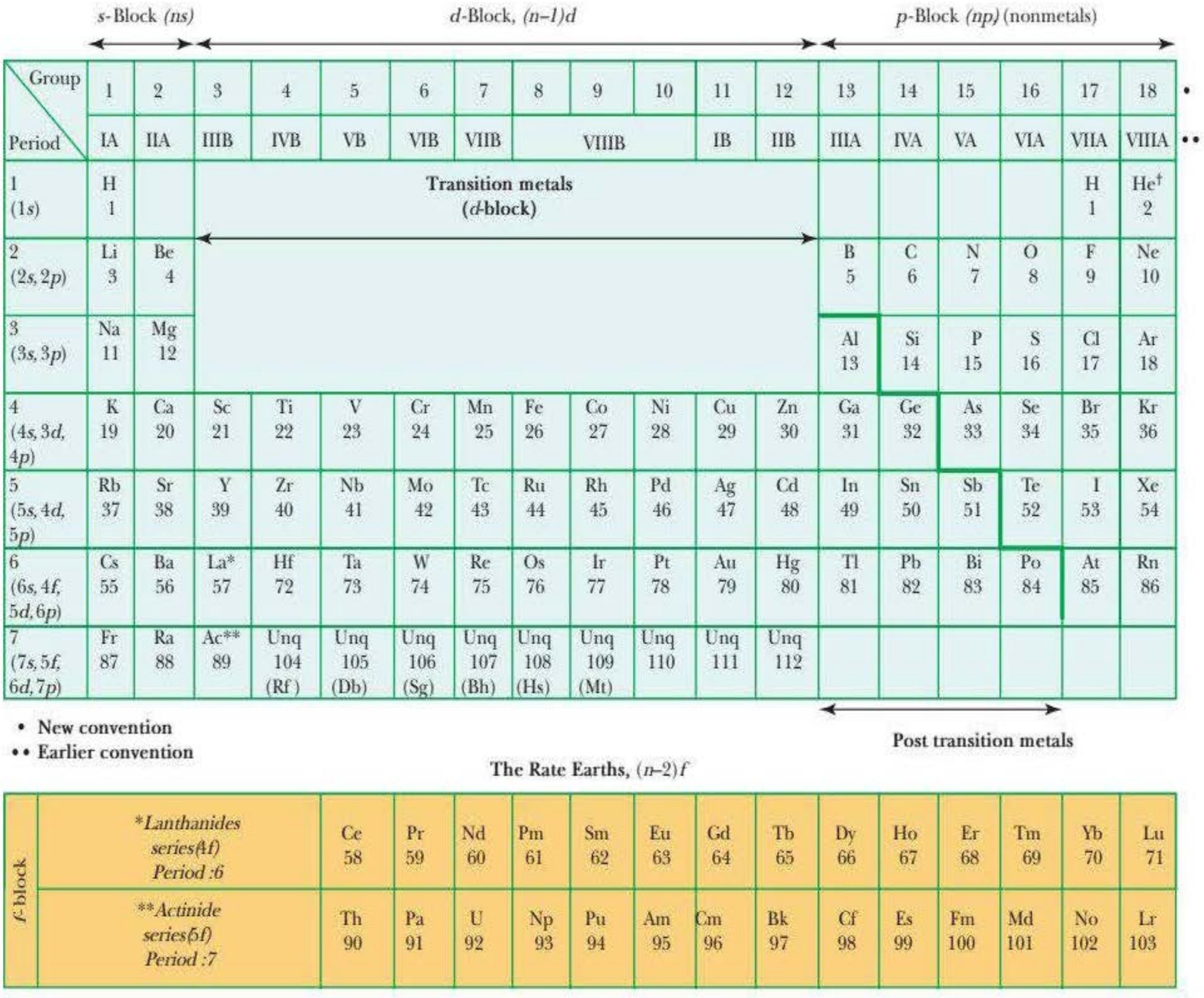
1. Lanthanides or Lanthanoids or Rare earths: These include elements from Ce (58) to Lu (71). The word earths refer to the oxides and in fact elements are found in nature first in the form of their oxides. Hence they are called as rare earths. The name sometimes confuses to suggest thal their availability may be rare which is not correct. Rather, they occur widely in nature and usually together.
2. Actinides or Actinoids: These include elements from Th (90) to Lr (103).
3. Coiuage metals: These include Cu,Ag and Au. These metals were once used as currency.
4. Noble metals: These include Ag, Au, Pt and Hg. They are so called because of their very low reactivity.
5. Transuranium metals: Elements beyond U (92) are known as transuranium metals.
6. The elements of third period are called as bridging elements because the concept of subgroups A and B starts after this period. Also, these elements maintain some similarities in properties with both subgroups A and B elements.
7. Diagonal relationship: There are three set of elements, that is, (Li, Mg). (Be, Al) and (B, Si), which, though, placed in different groups, show some similarities in their properties. This kind of similarity in properties is known as diagonal relationship and is attributed to their similar sizes.



5.3 Modern periodic table

According to the modern periodic law, the physical and chemical properties of the elements are the periodic functions of their atomic number. The long form of periodic table based upon the modem periodic law is depicted in following Figure. Note that the arrangement of A and B subgroups is different from that in the modified form of Mendeleev's periodic table. The left and right corners of the table are assigned as subgroups A and the middle of the periodic table is assigned as subgroups B.

We have learnt that the assignment of all the electrons in an atom into specific shells or orbitals (*s*, *p*, *d*, *f*) is known as the element's electronic configuration. The elements can be arranged in the long form of the periodic table based on the electronic configuration and classified as s, p, d and f-block elements.



Group Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18 •
	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA ••
1 (1s)	H 1		Transition metals (d-block)														H 1	He† 2
2 (2s, 2p)	Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
3 (3s, 3p)	Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
4 (4s, 3d, 4p)	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
5 (5s, 4d, 5p)	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
6 (6s, 4f, 5d, 6p)	Cs 55	Ba 56	La* 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
7 (7s, 5f, 6d, 7p)	Fr 87	Ra 88	Ac** 89	Unq 104 (Rf)	Unq 105 (Db)	Unq 106 (Sg)	Unq 107 (Bh)	Unq 108 (Hs)	Unq 109 (Mt)	Unq 110	Unq 111	Unq 112						

- • New convention
- •• Earlier convention

f-block															
	*Lanthanides series(4f) Period :6	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
	**Actinide series(5f) Period :7	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103

Figure 5.2 The long form of Modern Mendeleev's.

1. *s*-block elements: If the last electron enters into s-orbital, the elements are called as s-block elements. The general valence (outermost) shell electronic configuration is given by ns^{1-2}.

Alkali metals: [IG] ns^1

Alkaline earth metals: [IG] ns^2

where IG represents the inert gas core.

2. *p*-block elements: If the last electron enters into the p-orbital, the elements are called as p-block elements. The general valence shell electronic configuration is $\mathrm{ns}^2\ \mathrm{np}^{1-6}$. The p-block elements are placed in Group number III A to VIII A (13 to 18).

- **a.** Valence shell electrons for s-block elements is equal to the number of electrons in the s orbital having the highest principal quantum number.
- **b.** Valence shell electrons for p-block elements are equal to the number of electrons in the s and p orbitals having highest principal quantum number.
- **c.** The total number of valence shell electrons is equal to its group number according to A and B convention.

d. He (ns^2) is excluded from *p*-block in terms of electronic configuration and it is better to consider it as s-block element. But according to its chemical behavior it is justified to place it in the Group 0, that is, Group 18.

3. *d*-block elements: If the last electron enters into d orbital, the elements are called as d-block elements (except Thorium). The general valence shell electronic configuration is:

$$\mathrm{ns}^{0-2}\ (\mathrm{n}-1)\mathrm{d}^{1-10}$$

or $\mathrm{ns}^{1-2}\ (\mathrm{n}-1)\mathrm{d}^{1-10}$ (except for palladium)

Total valence shell electrons of d-block elements = Total number of electrons in the outermost shell (ns orbital) and penultimate shell [$(n-1)$ *d* orbitals].

4. f-block elements: If the last electron of the elements enters into f-orbital, they are considered as f-block elements. The general valence shell electronic configuration is:

$$\mathrm{ns}^2\ (\mathrm{n}-1)\mathrm{d}^{0-1}(\mathrm{n}-2)\mathrm{f}^{1-14}$$

Total valence shell electrons = Electrons present in ns, $(n-1)\ d$ *and* $(n-2)f$ *orbitals or subshells.*

5.4 Periodic trends in properties

The trends that occur in the characteristic properties of the elements in the periodic table allow us to accurately predict the properties and reactions of these elements.

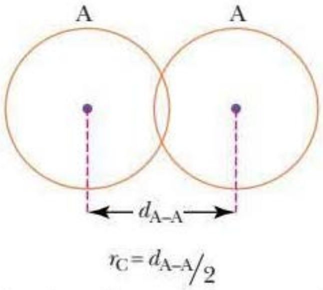
5.4.1 Atomic radius

The radius of the atom is the distance from the nucleus to the outermost electron or up to point at which the probability of finding of electron is the maximum. Since the atoms are not available in the atomic state in most of the cases, three kinds of atomic radii are measured for any atom and these are covalent radius, van der Waals radius and metallic radius. The three types of radii are discussed as follows:

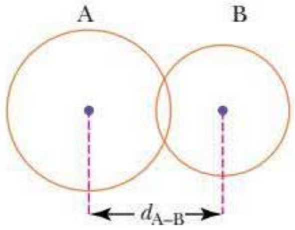
5.4.1.1 Covalent radius

The covalent radius of an element represents the contribution of that element to the length of a bond that is predominantly covalent. For example, the covalent radius of any element A is taken to be one half of the internuclear distance in the homonuclear diatomic molecule A_2.

When two different atoms are covalently bonded then the equation given by Schomaker and Stevenson is used to obtain the covalent radius.



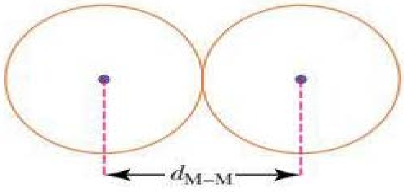
Covalent radius of homonuclear diatomic molecule.



Covalent radius of heteronuclear diatomic molecule.

5.4.1.2 Metallic radius

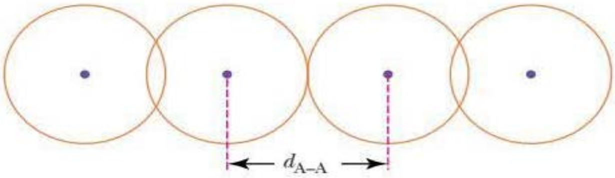
For metals the metallic radius is defined as half of the internuclear distance separating two adjacent metal atoms in a metallic lattice.



Metallic radius

5.4.1.3 Van der Waals radius

The sum of the van der Waals radii of two atoms is the shortest distance between two immediately adjacent atoms (either of same or different elements) in the structure of the solid compound in which they are not bonded to each other.

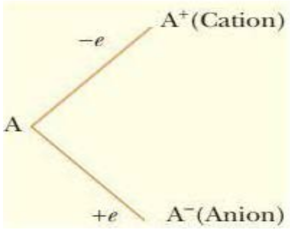


van der Waals radius

5.4.2 Ionic radius

When a positive ion is formed, the number of positive charges on the nucleus exceeds the number of electrons and effective nuclear charge is increased, resulting in the remaining electrons being attracted more strongly by the nucleus. Thus a positive ion is always smaller than the corresponding atom and more the electrons removed smaller is the ion.

When a negative ion is formed, one or more electrons are added to an atom and the effective nuclear charge is reduced. The electron cloud expands and the size of negative ion is more than that of the atom.



Thus the order of radius is

$$A^- > A > A^+$$

5.4.3 Ionization energy

Ionization energy (IE) is the energy required to remove an electron from an isolated gaseous atom in it ground state. It is measured in $\mathrm{eV.atom^{-1}}$ or $\mathrm{kJ.mol^{-1}}$.

$$A(g) \xrightarrow{IE} A^+(g) \quad \Delta H_1 = +ve$$

Ionization energy depends upon the following factors:

- It decreases when shell number or the radius increases.
- It increases when Z_{eff} increases.
- It decreases when σ (shielding constant) increases.
- It is more for half-filled and rully-filled electronic configurations.
- It also depends upon the orbitals from which the electron is removed. If the principal qantum number is the same, then the energy required for removal of electrons from different orbital shows the following order: *s >p>d>f*.

5.4.4 Electron affinity

Electron affinity is the energy released when one mole of electron is added to one mole of an element in its isolated gaseous state (ground state).

$$\mathrm{A(g)} \xrightarrow{+e} \mathrm{A}^- \quad \Delta H = -x \text{ kJ mol}^{-1}$$

It is represented as EA and its unit is $\mathrm{eV.atom^{-1}}$ or $\mathrm{kJ.mol^{-1}}$ or $\mathrm{kcal.mol^{-1}}$. It is also known as electron gain enthalpy and represented as by $\Delta\mathrm{H_{eg}}$.

According to the old convention, for an element A

$$\mathrm{A} + e \rightarrow \mathrm{A}^- \quad \Delta H_{\mathrm{eg}} = (-)x \text{ kJ mol}^{-1}$$

The negative sign indicates that energy is released. For those cases in which energy is absorbed the EA value considered as zero.

According to the new convention. $\Delta\mathrm{H_{eg}}$ may be negative or positive depending upon the circumstance and

$$\mathrm{EA} = \Delta\mathrm{H_{eg}} \qquad \text{(at absolate zero temperature)}$$

at any other temperature

$$\Delta\mathrm{H_{eg}} = -\mathrm{EA} - \frac{5}{2}\mathrm{RT}$$

Electron affinity depends upon a number of factors, that include:

- It decreases when radius increases.
- It increases when Z_{eff} increases.
- It decreases when σ (shielding constant) increases.

EA of half-filled and full-filled electronic configuration is less.

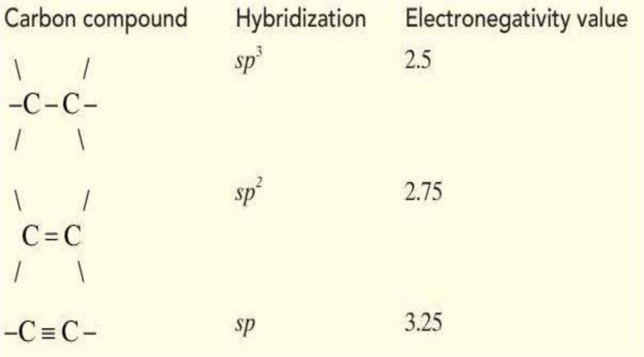
EA order for addition of electron in different orbitals having the same principal quantum number is s>p>d>f.

5.4.5 Electronegativity

In 1931, Pauling defined electronegativity of an atom as the tendency of the atom to attract electrons (bond pair) towards itself when comhined in a compound. It is a unitless and dimensionless quantity.

Electronegativity depends upon the following factors :

- It decreases when radius increases.
- It increases when Z_{eff} increases.
- It decreases when σ increases.
- It increases when the oxidation state of an element increases.
- It increases as much the percentage of s character in hybrid orbital increases. For example,



Carbon compound	Hybridization	Electronegativity value
\ / –C–C– / \	sp^3	2.5
\ / C=C / \	sp^2	2.75
–C≡C–	sp	3.25

If two atoms have similar electronegativities, that is similar tendencies to attract electrons, the bond between them is largely covalent. But when the difference between the electronegativities is large, the bond bas high degree of polar character.

According to the approache of Mulliken scale, which is based on the ionization energy and electron affinity of the element, the electronegativity is given by the relation

$$\chi = \frac{\mathrm{IE} + \mathrm{EA}}{2}$$

The periodic variations of electronegativity are:

- In a period, the electronegativity increases from left to right as Z_{eff} increases
- In a group, the electronegativity decreases in general.

Chapter 6.

Chemical bonding

Chapter 6. Chemical bonding

6.1 Introduction

Atoms are usually not capable of free existence but groups of atoms of the same or different elements exist as one species, e.g., H_2, O_2, P_4, S_8, H_2O. A group of atoms existing together as one species and having characteristic properties is called a molecule. Obviously, there must be some force which holds these atoms together within the molecules. This force which holds the atoms together within a molecule is called a chemical bond.

6.2 Chemical bond

Chemical bond is an attractive force which holds various constituents (atoms, molecules or ions) together in different species. Chemical bonds devided into two types:

1. Bonds which constitute molecules or formula units. These are ionic bonds, covalent bonds and co-ordinate or dative bonds.
2. Bonds which hold various particles in solid or liquid state of the substances. These, are also called intermolecular forces. These are metallic bonds, dipole-dipole forces, Van der Waals forces and hydrogen bonds.

Cause of chemical combination: Chemical bonding takes place due

- To acquire a state minimum energy and maximum stability.
- To convert atoms into molecule to acquire stable noble gas configuration.

6.3 Lewis theory

6.3.1 Lewis-Kossel Approach to Chemical Bonding

Lewis theory gave the first explanation of a covalent bond in terms of electrons that was generally accepted. If two electrons are shared between two atoms, this constitutes a bond and binds the atom together. For many light atoms, a stable arrangement is attained when the atom is surrounded by eight electrons.

Thus the atom of different elements combine with each other in order to complete their respective octets (i.e., 8 elcetrons in their outermost shell) or duplet (i.e., outermost shell having 2 electrons) in case of H, Li and Be to attain stable nearest noble gas configuration.

This can occur in two ways:

1. By complete transference of one or more electrons from one atom to another. This process is referred to as elcetrovalency and the chemical bond formed is termed as electrovalent bond or ionic bond.
2. By sharing of electrons. This can occur in two ways as follows:

a. When the shared electrons are contributed by the two combining atoms equally, the bond formed is called covalent bond.
b. When these electrons are contributed entirely by one of the atoms but shared by both, the bond formed is known as a coordinate bond, also called dative bond.

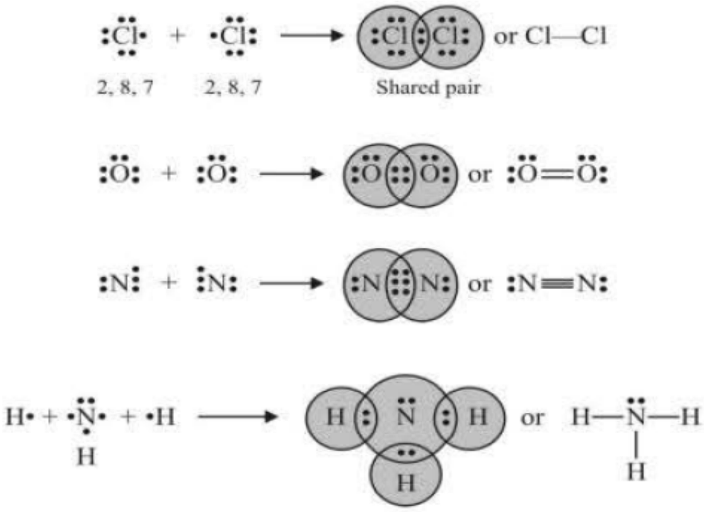
6.3.2 Lewis symbols

In the formation of a molecule, only the outer shell electrons are involved and they are known as valence electrons. The inner shell elcctrons are well protected and are generally not involved in the combination process. It is, therefore, quite reasonable to consider the outer shell electrons, i.e., valence shell electrons while discussing chemical bonds.

GN. Lewis introduced simple symbols to denote the valence shell electrons in an atom. The outer shell electrons are shown as dots surrounding the symbol of the atom. These symbols are known as Lewis symbols or electron dot symbols. These symbols ignore the inner shell electrons. A few examples are given below

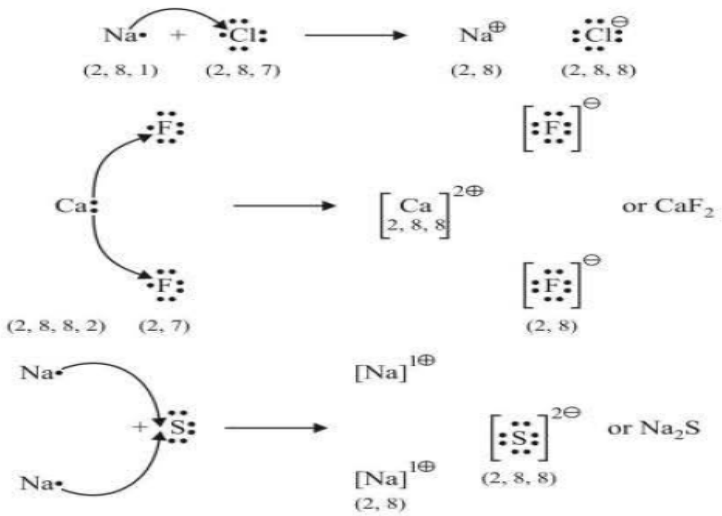
6.3.3 Covalent bond

The bond formed between the two atoms by mutual sharing of electrons between them so as to complete their octets or duplets in case of elements having only one shell is called covalent bond or covalent linkage and the number of electrons contributed by each atom is known as covalency.



6.3.4 Ionic bond

When a bond is formed by complete transference of electrons from one atom to another so as to complete their outermost orbits by acquiring 8 electrons (i.e., octet) or 2 electrons (i.e., duplet) in case of hydrogen, lithium etc. and hence acquire the stable nearest noble gas configuration, the bond formed is called ionic bond or electrovalent bond.



6.3.5 Limitations of Lewis concept of covalent bond

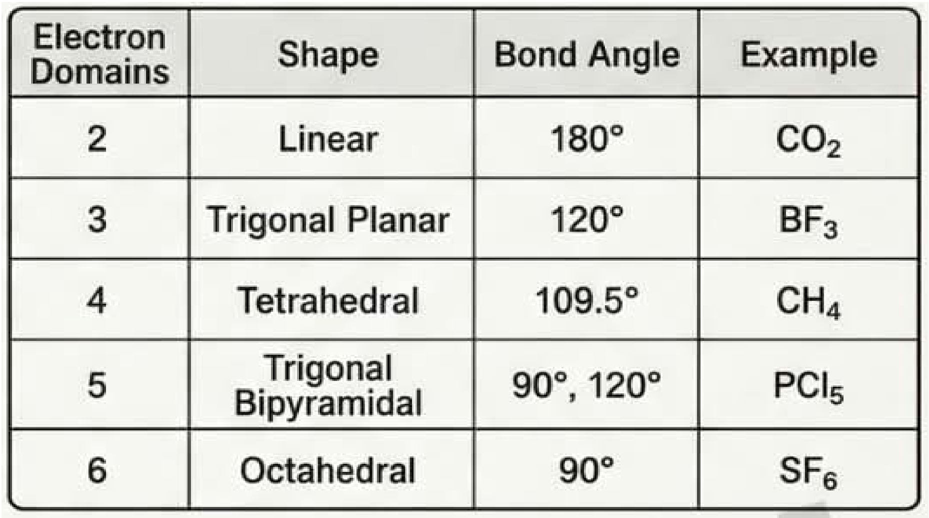
Lewis-Langmuir concept of covalent bond has the following limitations:

1. It could not explain how the atoms are held together in the molecules like H_2, Cl_2 etc. in which there are no ions and hence there are no electrostatic forces of attraction, i.e., it Could not explain the formation of a covalent bond.
2. It could not explain the shapes of molecules containing covalent bonds.
3. It could not explain the release of energy during the formation of a covalent bond.

6.4 Valence shell electron pair repulsion (VSEPR) theory

The first simple theory that was put forward to explain the shapes of molecules is known as Valence Shell Electron Pair Repulsion (VSEPR) theory.This theory was given by Sidgwick and Powell in 1940 and was further improved by Nyholm and Gillespie in 1957.

The electron pairs surrounding the central atom repel one another and move so far apart from one another that there are no further repulsions between them. As result, the molecule has minimum energy and maximum stability.



Electron Domains	Shape	Bond Angle	Example
2	Linear	180°	CO_2
3	Trigonal Planar	120°	BF_3
4	Tetrahedral	109.5°	CH_4
5	Trigonal Bipyramidal	90°, 120°	PCl_5
6	Octahedral	90°	SF_6

Calculation of total number or electron pairs, bond pairs and lone pairs and predicting the shapes of the molecules and ions:

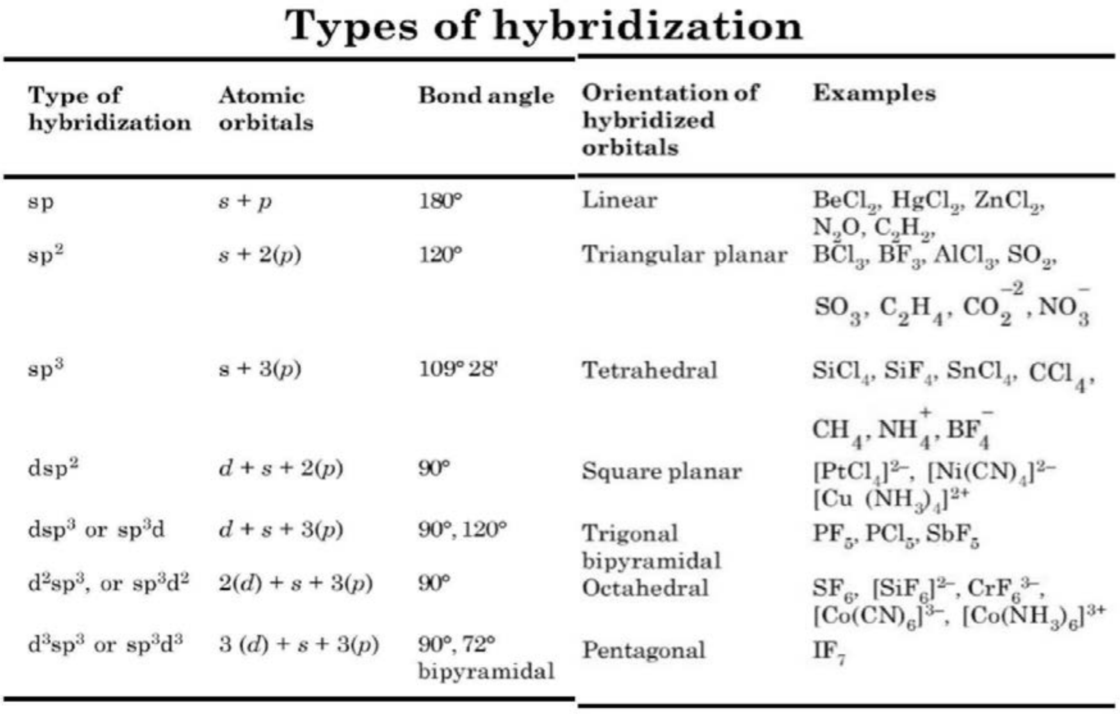
1. Total no. of electron pairs around the cenral atom = $\frac{1}{2}$ (no. of valence electrons around the cenral atom + no. of atoms linked to cenral atom by single bonds)
2. For negative ions, add number of electrons equal to the units of negative charge on the ion to the valence electrons of the central atom
3. For positive ions, subtract number of electrons equal to the units of positive charge on the ion from the valence electrons of the central atom.
4. No. of bond pairs (shared pairs) = No. of atoms linked to central atom by single bonds
5. No. of lone pairs = Total no. of electron pairs - No. of shared pairs.

6.5 Hybridization

It is used to explain the shape of molecules. It is a process of inter mixing of orbitals of slightly different energies and redistribute their energies to give rise to niew set of orbitals of same energy, size and shape.

The new orbital formed are called hybrid or hybridized orbitals. The number of hybridized orbital formed is equal to the number of combining pure orbitals.

6.5.1 Type of hybridization

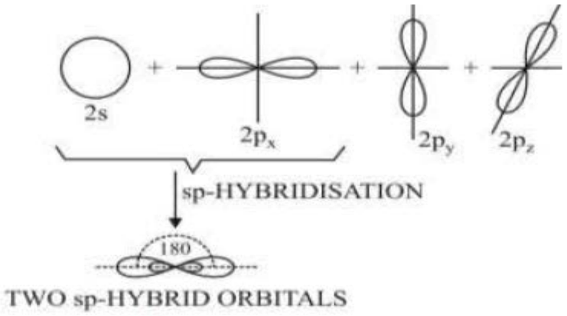


Types of hybridization

Type of hybridization	Atomic orbitals	Bond angle	Orientation of hybridized orbitals	Examples
sp	$s + p$	180°	Linear	$BeCl_2$, $HgCl_2$, $ZnCl_2$, N_2O, C_2H_2,
sp^2	$s + 2(p)$	120°	Triangular planar	BCl_3, BF_3, $AlCl_3$, SO_2, SO_3, C_2H_4, CO_2^{-2}, NO_3^-
sp^3	$s + 3(p)$	109° 28'	Tetrahedral	$SiCl_4$, SiF_4, $SnCl_4$, CCl_4, CH_4, NH_4^+, BF_4^-
dsp^2	$d + s + 2(p)$	90°	Square planar	$[PtCl_4]^{2-}$, $[Ni(CN)_4]^{2-}$ $[Cu\ (NH_3)_4]^{2+}$
dsp^3 or sp^3d	$d + s + 3(p)$	90°, 120°	Trigonal bipyramidal	PF_5, PCl_5, SbF_5
d^2sp^3, or sp^3d^2	$2(d) + s + 3(p)$	90°	Octahedral	SF_6, $[SiF_6]^{2-}$, CrF_6^{3-}, $[Co(CN)_6]^{3-}$, $[Co(NH_3)_6]^{3+}$
d^3sp^3 or sp^3d^3	$3\ (d) + s + 3(p)$	90°, 72° bipyramidal	Pentagonal	IF_7

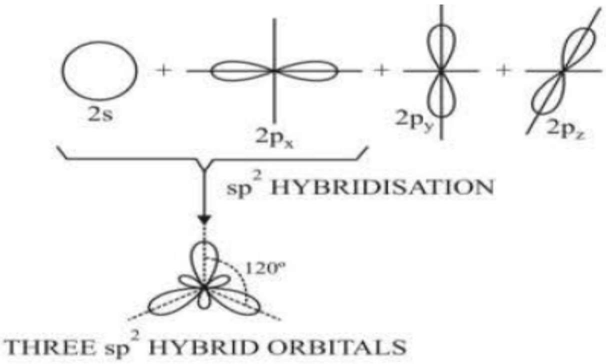
6.5.1.1 Diagonal or *sp* hybridization

When one s and one p orbital belonging to the same main shell of an atom mix together 10 form two new equivalent orbitals, the type of hybridization is called sp hybridization or diagonal hybridization. The new orbitals formed are called sp hybrid orbitals.



6.5.1.2 Trigonal or sp^2 hybridization

When one sand two p orbitals of the same shell of an atom mix to fom three new equivalent orbitals, the type of hybridization as called sp^2 hybridization or trigonal hybridization. The new orbitals formed are called sp^2 hybrid orbitals.



6.5.2 Predicting hybridization

Calculate the number of hybrid orbitals (h) to be formed by the central atom as follows:

$$h = \frac{1}{2}[VE + MA - c + a]$$

VE is the no. of valence electrons of the central atom.

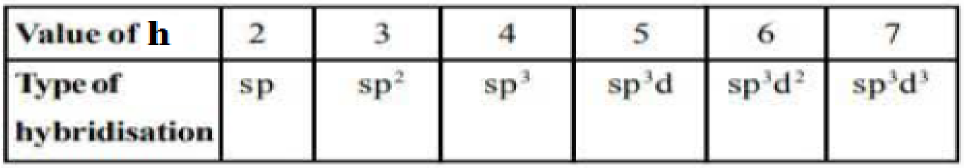
MA is the no. of monovalent atoms or groups surrounding the central atom.

c is the charge on the cation if the given species is a polyatomic cation.

a is the charge on the anion if the given species is a polyatomic anion.

Note that only monovalent atoms (MA) or groups are to be considered. For divalent ions, $MA = 0$.

If $h = 2$, it means that two hybrid orbitals are to be formed. Hence, hybridization is sp. If $h = 3$, it means three hybrid orbitals are to be formed. Hence, hybridization is sp^2 and so on, as given below



Value of h	2	3	4	5	6	7
Type of hybridisation	sp	sp^2	sp^3	sp^3d	sp^3d^2	sp^3d^3

Bibliographical

Bibliographical

[1] A. Sevin, "CHIMIE GENERALE". Dunod, 2016.

[2] B. Fosset, J. B. Baudin, F. Lahitète, "Chimie tout-en-un". Dunod, Paris, 2013.

[3] É. Bardez, "CHIMIE GÉNÉRALE". Dunod, Paris, 2009.

[4] P. Frajman, A. Demolliens, C. Gauthier, "Chimie". Nathan, 2008.

[5] R. Chang, K. A. Goldsby, "Chimie générale". 4e edition, CHENELIERE EDUCATION.