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Facultyof Technologie

1st year LMD- ST

Course

Structure of Matter

Presented by:

Prof.Dr. Merzak Doulache

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Preamble

This course handout is intended for students in the common core material sciences (SM), technical sciences (ST), preparatory classes (CP)…etc. The basic concepts in the field of the structure of matter were more detailed in this course.

Chapter I relates to the qualitative and quantitative aspects of matter as well as the main constituents of the atom. The second chapter relates to the fundamentals of nuclear radioactivity (nuclear reactions and law of radioactive decay).Chapter III deals with the quantification of energy in the semi-atomic model (wave-particle duality of light, optical spectrum of hydrogen, classical models of the atom) and the quantum model of the atom where a theory necessary for the rigorous description of the properties of the atom is introduced. Chapter IV is dedicated to the periodic classification of the elements where several points will be treated (classification of elements and periodic variations in element properties). The last chapter is reserved for the chemical bond (Lewis structure, the covalent bond, the ionic bond, the VSEPR method, the covalent bond in the quantum model, the polarized bond, hybridization of atomic orbitals, intermolecular bonds).

This handout represents a summary of the courses that I have taught over the past ten years in the technical sciences (ST) departments at the University of Laghouat. It is strictly personal work which comes from my own experience.

Chapter I: Basic concepts of chemistry

I.1. Introduction:

Chemistry is the science of molecules and their transformations. It deals with the composition, structure and properties of matter. These aspects can be best described and understood in terms of basic constituents of matter atoms and molecules.

Chemistry plays an important role in meetinghuman needs for food, health care products and other materials aimed at improving the quality of life.

I.2. Nature of matter:

Anything which has mass and occupies space is called matter. Everything around us, for example, book, pen, pencil, water, air, all living beings etc. are composed of matter. You know that they have mass and they occupy space.

You are also aware that matter can exist in three physical states *viz.* solid, liquid and gas (Fig.I.1).

Fig. I.1: Arrangement of particles in solid, liquid and gaseous state

I.2.1. Solids:the particles are held very close to each other in an orderly fashion and there is not much freedom of movement. So, the solids have definite volume and definite shape.

I.2.2. Liquids: the particles are close to each other but they can move around.Thus, the liquids have definite volume but not thedefinite shape. They take the shape of the container in which they are placed.

I.2.3. Gases: the particles are far apart as compared to those present in solid or liquid states and their movement is easy and fast. The Gases have neither definite volume nordefinite shape. They completely occupy the container in which they are placed.

These three states of matter areinter-convertible by changing the conditions of temperature and pressure (Fig. I.2).

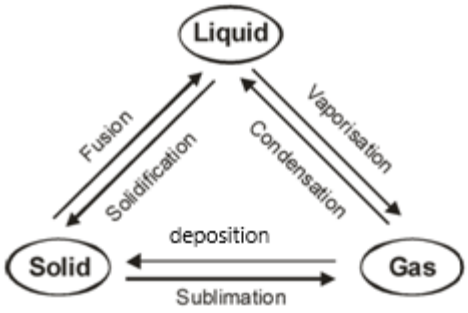


Fig. I.2: Inter-conversion of the three states of matter.

On heating a solid usually changes to aliquid and the liquid on further heating changes to the gaseous (or vapour) state. In the reverse process, a gas on cooling liquefies to the liquid and the liquid on further cooling freezes to the solid.

I.3. Classification of matter:

At the macroscopic or bulk level, mattercan be classified as mixtures or pure substances. These can be further sub-divided as shown in Fig. I.3.

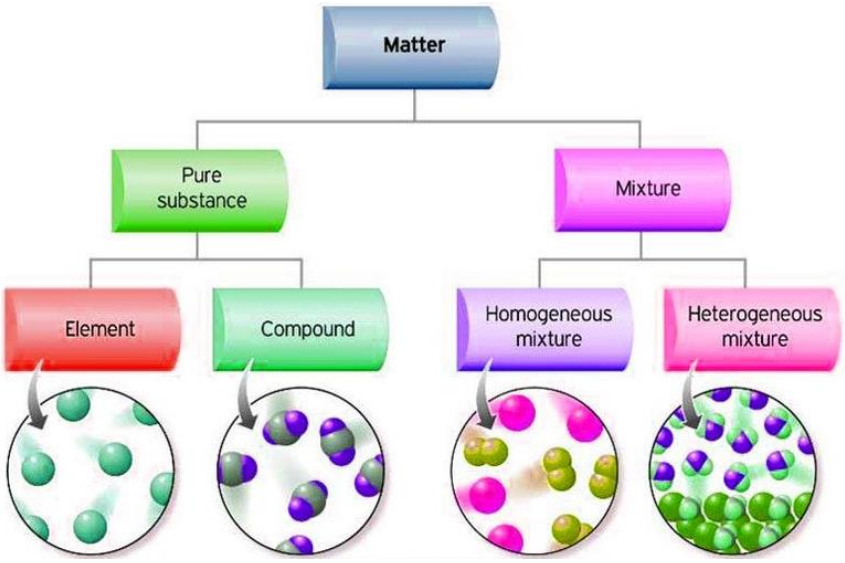


Fig.I.3: Classification of matter

Many of the substances present aroundyou are mixtures. For example, sugar solution in water, air, tea etc., are all mixtures.

I.3.1. TheMixture:contains two or more substances present in it (in any ratio) which are called its components. A mixture may be homogeneous orheterogeneous.

a) Homogeneous mixture:the components completely mix with each otherand its composition is uniform throughout.For example,Sugar solution, and air etc.

b) Heterogeneous mixtures: the composition is not uniform throughout and sometimes the different components can be observed. For example, the mixtures of salt and sugar, grains and pulses along with some dirt (often stone) pieces.

Note: It is worthwhile to mention here that thecomponents of a mixture can be separated by using physical methods such as simple hand picking, filtration, crystallisation, distillation etc.

I.3.2. Pure substances:

a pure substance is an element or compound made up of one type of particle. Pure substances have a fixed composition with definite properties.For example, copper, silver, gold,water, glucose …etc.

Pure substances can be further classifiedinto elements and compounds.

a) Elements:consists of only one type of particles. These particles may be atoms (Cu, Fe, Ag and Na) or molecules (O_2, O_3, N_2 and H_2 gases).

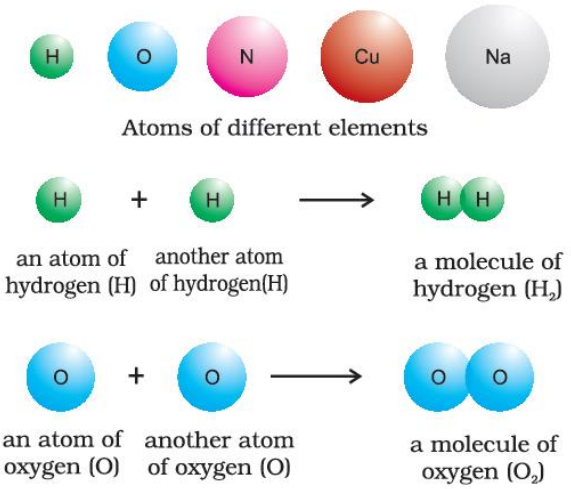


Fig. I.4: A representation of atoms and molecule.

b) Compounds: two or more atoms of different elements combine to give the molecule.The examples of some compounds are water, ammonia, carbon dioxide, sugar etc. The molecules of water andcarbon dioxide are represented in Fig I.5.

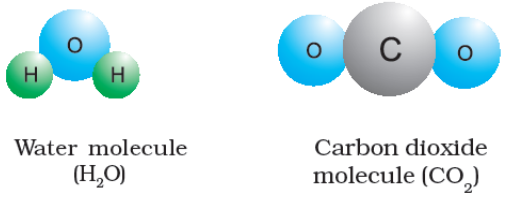


Fig. I.5: A depiction of molecules of water and carbon dioxide

I.4. Atoms and Molecules:

I.4.1. Atom:

The word "atom" comes from the Greek "atomos", meaning something which cannot be split. Thus, it is the smallest unit of an element made up of nucleus and electrons that has all of the properties of an element.

I.4.2. Molecule:

Molecule is the smallest particle of the substance which can exist independently. It can be subdivided as.

a) Homoatomicmolecules made up of same kind of atoms (same elements).

For example: He, Cu, O_2, H_2, O_3 etc.

b) Heteroatomicmolecules made up of different kind of atoms (different elements). For example: H_2O, H_2SO_4, NO etc.

I.5. Mole concept and molar masses:

I.5.1. Mole:A moleis defined as the quantity of a pure substance that contains 6.0221367 x 10^{23}particles (atoms, ions, molecules) of that substance. This numberis called Avogadro's number and is represented by N_A. Avogadro's number of gas molecules occupy a volume of 22.4 L at N.T.P.

I.5.2. Atomic mass:atomic mass is equal to the mass of one mole of atom divided by Avogadro's number. For example: $m^{12}_6C = \frac{12}{\mathcal{N}_A}$ ($grams$)= 1.992642 x10^{-23} g

Note: a special unit has been defined, of which the atomic masses can be expressed simply: it is the atomic mass unit (amu). This unitis defined as a mass exactly equal to one-twelfth of the mass of one carbon – 12 atom.

$$1 \text{ amu} = \frac{\text{mass of } {}^{12}_{6}\text{C atom}}{12}$$

What is the relationship between the amu and the gram?

one mole of carbon has a mass of 12 g which contains N_A atoms of carbon

$$1 \text{ amu} = \frac{12}{\mathcal{N}_\text{A}} \times \frac{1}{12}$$

$$1 \text{ amu} = \frac{1}{\mathcal{N}_\text{A}} = 1.66056 \times 10^{-24}\text{g} = 1.66056 \times 10^{-27}\text{kg}$$

Today, amu has been replaced by « u » which is known as unified mass

Note: one mole of an element whose mass in grams is numerically equal to its atomic mass.

For example: the atomic mass of oxygen is 16 u, therefore gram atomic mass (1 mole) of oxygen= 16 g

I.5.2. Molecular mass: It is algebraic the sum of the atomic mass of the elementspresent in the molecule.

For example: Molecular mass of CH_4 = (1 × 12) + (4 × 1) = 16 u

Problem 1.1:

Calculate the molecular mass of glucose ($C_6H_{12}O_6$) molecule.

Solution:

Molecular mass of glucose ($C_6H_{12}O_6$)

= 6(12.011 u) + 12(1.008 u) + 6(16.00 u)

= (72.066 u) + (12.096 u) + (96.00 u)

= 180.162 u

I.6. Components of a solution:

I.6.1. Solute: is the substance present in smaller amount.

I.6.2. Solvent: is the substance present in larger amount.

I.6.3. Solution: is the homogenous mixture of two or more substance.

Fig.I.6: Components of a solution

I.7. The concentrations:

The concentration of a solution or the amount of substance present in its given volume can be expressed in any of the following ways.

I.7.1. Molarity: It is the number of moles of solute present in one litre of solution. It is denoted by M.

$$\text{Molarity (M)} = \frac{\text{No. of moles solute}}{\text{Volume of solution in litre}} \; ; \left(\frac{\text{mol}}{\text{L}}\right)$$

Problem I.2:

Calculate the molarity of NaOH in the solution prepared by dissolving its 4 g in enough water to form 250 mL of the solution.

Solution

Sincemolarity (M)

$$\mathrm{M} = \frac{\text{n. of moles solute}}{\text{Volume of solution in litre}} = \frac{\text{mass of NaOH / molar mass of NaOH}}{0.250\ \mathrm{L}}$$

$$= \frac{\frac{4\mathrm{g}}{40\ \mathrm{g.mol^{-1}}}}{0.250\ \mathrm{L}} = \frac{0.1\ \mathrm{mol}}{0.250\ \mathrm{L}} = 0.4\ mol/L$$

I.7.2. Molality: It is defined as the number of moles of solutepresent in 1 kg of solvent. It is denoted by m.

$$\text{Molality (m)} = \frac{\text{No. of moles of solute}}{\text{mass of solvent (in kg)}}\ ;\left(\frac{\mathrm{mol}}{\mathrm{kg}}\right)$$

Problem I.3:

The density of 3 M solution of NaCl is 1.25 g mL–1. Calculate the molality of the solution.

Solution

M = 3 mol L–1

Mass of NaClin 1 L solution = 3 × 58.5 = 175.5 g

Mass of 1L solution = 1000 × 1.25 = 1250 g

(since density = 1.25 g mL–1)

Mass of water in solution = 1250 –75.5 = 1074.5 g

$$\text{Molality} = \frac{\text{No. of moles of solute}}{\text{mass of solvent in kg}} = \frac{3\ \mathrm{mol}}{1.0745} = 2.79\ \mathrm{m}$$

I.7.3. Normality (N): It is the number of gram equivalents (n_{eq}) of solute in one litre of solution and is denoted by N .

$$Normality\ (N) = \frac{\text{n. of gram equivalents of solute}}{\text{Volume of solution in litre}};\ \frac{g.eq}{L}$$

with

$$\mathrm{n_{eq}} = \frac{\text{massof solute}}{\text{equivalent weight}\ (w)}$$

Equivalent weight is given by the following equation;

$$w = \frac{\text{molar mass of solute}}{\alpha}$$

Where α is the number of equivalents and is determined according to the chemical nature of the compound (salts, acids or bases).

- **For salt:** it is net positive or negative valency

Example: $CaCl_2$the ionic form is (Ca^{2+}, $2Cl^-$) ↔α =2

NaCl the ionic form (Na^+, Cl^-) ↔ α =1

- **For acid:**it isthe number of H^+ ions that can be displaced from one molecule of a substance.

Example: HCl ↔ α = number of H^+ ions in acid =1

H_2SO_4 ↔ α =number of H^+ ions in acid =2

- For base:It is the number of OH^- ions that can be displaced from one molecule of a substance.

Example: NaOH ↔ α = number of OH^- ions in the base =1

$Al(OH)_3$ ↔ α =number of OH^- ions in base =3.

Note:the relationship between M and N is given by the following equation:

$$\text{Normality} = \alpha \times \text{Molarity}$$

I.7.4. Mole fraction: It is the ratio of moles of a constituent to the total number of molesin a solution. Let A be solute and B is solvent then mole fraction of solute (x_A)

$$x_A = \frac{n_A}{n_A + n_B}$$

Generalizing for a mixture containing "*i*" constituents:

$$x_i = \frac{n_i}{\sum_{i=1}^{n} n_i}$$

Problem I.4:

A solution is prepared by dissolving 30.0 g of methanol, CH_3OH in 70.0 g of water, H_2O. Calculate the mole fraction of methanol in the solution.

Solution:

Molar mass of CH_3OH = 32.0 g mol^{-1}

$$n_{CH_3OH} = \frac{30.0\ g}{32.0\ g/mol} = 0.9375\ mol$$

Molar mass of H_2O = 18.0 g mol^{-1}

$$n_{H_2O} = \frac{70.0\ g}{18.0\ g/mol} = 3.889\ mol$$

$$x_{CH_3OH} = \frac{n_{CH_3OH}}{n_{CH_3OH} + n_{H_2O}} = \frac{0.9375}{0.9375 + 3.889} = 0.19$$

I.7.6. Mass percent: is the mass of the solute in grams per 100 grams of the solution

$$\%\text{w/w} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100$$

Problem I. 5:

A solution is prepared by adding 2 g of a substance A to 18 g of water. Calculate the mass per cent of the solute.

Solution:

$$\%\text{w/w} = \frac{\text{mass of A}}{\text{mass of solution}} \times 100$$

$$\%\text{w/w} = \frac{2\text{ g}}{2\text{g of A} + 18\text{g of water}} \times 100 = \frac{2\text{ g}}{20\text{g}} \times 100 = 10\%$$

I.7.7. Volume percent (%V/V): The percentage of volume of solute per volume of solution.

$$\%\text{V/V} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100$$

Problem I.7:

Calculate the volume of antifreeze required to make 5 dm^3 of a solution of antifreeze, which is 20% by volume.

Solution:

$$\%\text{V/V} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100$$

$$20\% = \frac{\text{volume of solute}}{5\text{ dm3}} \times 100$$

V_{solute}= 1 dm^3

I.7.8. Density:density is the ratio between mass and volume or mass per unit volume

$$\rho_{\text{solution}} = \frac{\text{m}_{\text{solution}}}{\text{V}}$$

The SI unit of density is kilogram per cubic meter (kg/m^3). It is also frequently represented in the cgs unit of grams per cubic centimeter (g/cm^3).

I.8. International System of Units (SI):

The SI system has seven *base units* and they are listed in Table 1.1. These units pertain to the seven fundamental scientific quantities. The other physical quantities, such as speed, volume, density, etc., can be derived from these quantities.

Table I.1 : Base PhysicalQuantities and theirUnits

Base Physical Quantity	Symbol for Quantity	Name of SI Unit	Symbol for SI Unit
Length	l	metre	m
Mass	m	kilogram	kg
Time	t	second	s
Electric current	I	ampere	A
Thermodynamic temperature	T	kelvin	K
Amount of substance	n	mole	mol
Luminous intensity	I_v	candela	cd

The SI system allows the use of prefixes toindicate the multiples or submultiples of a unit. These prefixes are listed in Table I.2.

Table I.2: Prefixes used in the SI System

Multiple	Prefix	Symbol
10^{-24}	yocto	y
10^{-21}	zepto	z
10^{-18}	atto	a
10^{-15}	femto	f
10^{-12}	pico	p
10^{-9}	nano	n
10^{-6}	micro	μ
10^{-3}	milli	m
10^{-2}	centi	c
10^{-1}	deci	d
10	deca	da
10^{2}	hecto	h
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G
10^{12}	tera	T
10^{15}	peta	P
10^{18}	exa	E
10^{21}	zeta	Z
10^{24}	yotta	Y

I.9.Constituents of the atom:

An atom is an electrically neutral, spherical entity composed of a positively charged central nucleus surrounded by negatively charged electrons.

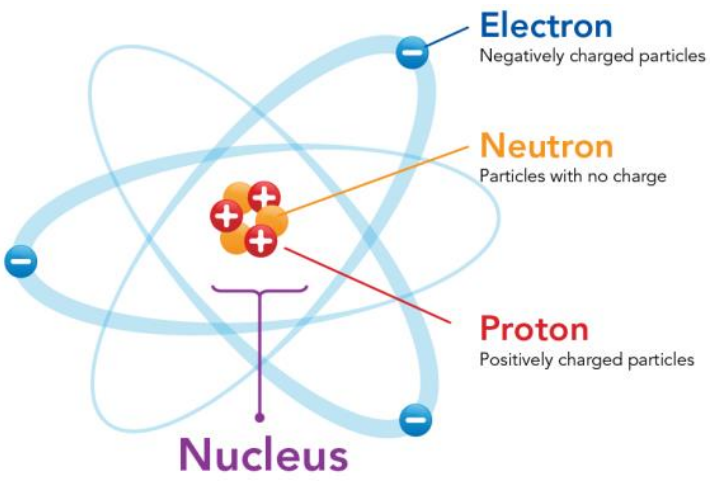


Fig.I.7: Constituents of the atom.

I.9.1. Nucleus: The nucleus contains the **protons (p)**, which have positive charges, and **neutrons (n)**, which are neutral (uncharged). A proton has a mass of 1.0073 amu and a charge of 1+

Neutrons are very slightly heavier than protons; protons are 1836 times heavier than electrons.

I.9.2.Electrons (e):have negative charges, surround the nucleus, and account for most of the atomic volume.

Note: The number of electrons equals the number of protons in the nucleus of a neutral atom.

The properties of these fundamental particles are summarized in Table I.3.

Table I.3. Properties of Subatomic Particles

Name	Location	Charge (C)	Unit Charge	Mass (amu)	Mass (g)
electron	outside nucleus	-1.602×10^{-19}	1−	0.00055	0.00091×10^{-24}
proton	nucleus	1.602×10^{-19}	1+	1.00727	1.67262×10^{-24}
neutron	nucleus	0	0	1.00866	1.67493×10^{-24}

I.10. Atomic number and mass number:

I.10.1. Atomic number (Z):

The atomic number of an atom is the number of protons in the nucleus and is given the symbol Z.

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

Since the atom is neutral, the atomic number also equals the number of electrons.

I.10.2. Mass number (A):

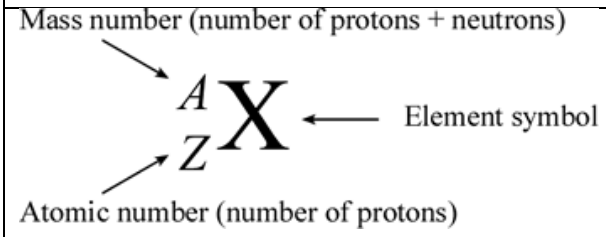
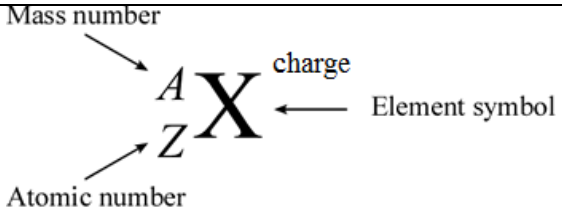
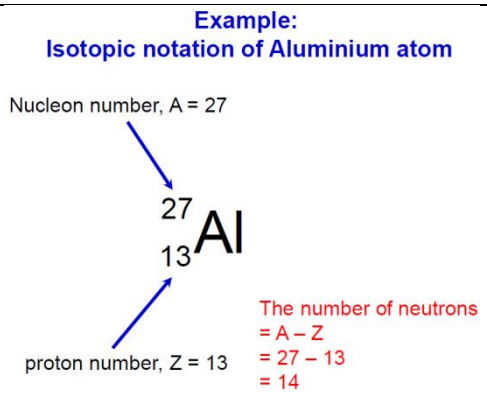
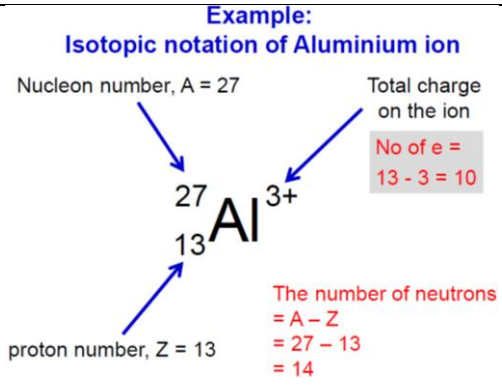
The mass number of an atom is the number of protons and neutrons in the nucleus and is given the symbol A.

$$\text{mass number (A)} = \text{number of protons (Z)} + \text{number of neutrons (N)}$$

$$A = Z + N$$

I.11. Atomic Symbols (isotopic notation):

The atomic symbol specifies information about the nuclear mass, atomic number, and charge on a particular element. Every element has a one- or two-letter symbol based on its English or Latin name.

Isotopic notation of Neutral atom	Isotopic notation of ion
	
	

I.12. Isotopes:

Isotopes isdefinesastwoormoreatomsofthesameelementthathavethesamenumberofprotonsintheirnucleus butdifferentnumberofneutrons.Hydrogen can be used as an example.

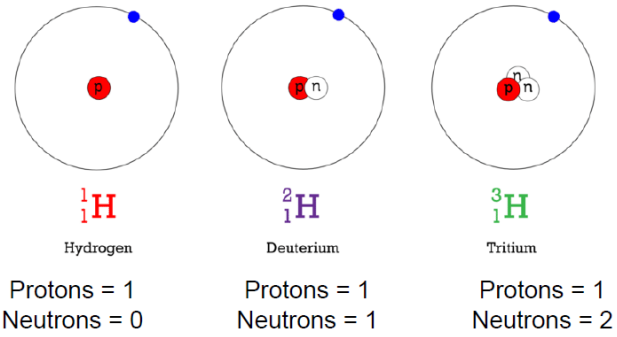


Fig.I.8: Isotopes of hydrogen element.

I.13. Average atomic mass:

The mass of an element shown in a periodic table is a weighted, average mass of all the isotopes present in a naturally occurring sample of that element. This is equal to the sum of each individual isotope's mass multiplied by its fractional abundance(percentage abundance).

$$\text{average atomic mass} = \frac{\sum_i Q_i m_i}{100}$$

Q: therelative / fractional / ratio / percentage abundanceof isotopes of the element in the mixture

M: theisotopic mass of the element

Example:

The element boron is composed of two isotopes: About 19.9% of all boron atoms are ^{10}B with a mass of10.0129 amu, and the remaining 80.1% are ^{11}B with a mass of 11.0093 amu. The average atomic mass for boron is calculated to be:

boron average mass = (0.199 × 10.0129 amu) + (0.801 × 11.0093 amu)

= 1.99 amu + 8.82 amu

= 10.81 amu

Problem I.8:

Naturally occurring chlorine consists of ^{35}Cl (mass 34.96885 amu) and ^{37}Cl (mass 36.96590 amu), with an average mass of 35.453 amu. What is the percent composition of Cl in terms of these two isotopes?

Solution:

The average mass of chlorine is the fraction that is ^{35}Cl times the mass of ^{35}Cl plus the fraction that is ^{37}Cl times the mass of ^{37}Cl.

average mass = [Q(^{35}Cl) × mass of ^{35}Cl) + (Q(^{37}Cl) × mass of ^{37}Cl)

and Q(^{35}Cl) + (Q(^{37}Cl)=1

If we let x represent the fraction that is ^{35}Cl, then the fraction that is ^{37}Cl is represented by 1.00-x.

Substituting this into the average mass equation, we have:

35.453 amu = (x × 34.96885 amu) + [(1.00 − x) × 36.96590 amu]

35.453 = 34.96885x + 36.96590 − 36.96590x

1.99705x = 1.513

$$x = \frac{1.513}{1.99705} = 0.7576$$

So solving yields: x = 0.7576, which means that 1.00 − 0.7576 = 0.2424. Therefore, chlorine consists of75.76% 35Cl and 24.24% 37Cl.

I.14. Mass spectrometer:

The mass spectrometer is an instrument that helps to investigate the presence and abundances of the isotopes of an element and the masses of molecules.The essential parts of a mass spectrometer are: an ionization chamber, an acceleration chamber, a deflection chamber and a detection system (Fig. I.9).

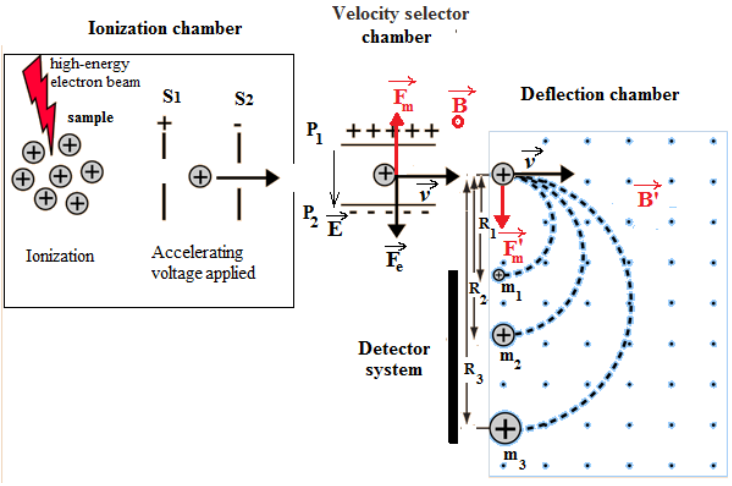


Fig.I.9: Schematic representation of a mass spectrometer.

The principle involved is that different ions are separated according to their masses (mass / charge ratio) when moving in a magnetic field.The mass spectrometer was used;

(a) To identify the presence of different isotopes in a sample.

(b) To show the relative abundance of the isotopes of an element.

(c) To calculate relative atomic and molecular masses.

(d) It helps in identifying compounds if they come from an unknown source.

I.14.1. Ionization chamber:

Atoms are first ionized (by electron bombardment) in the ionization chamber resulting in the formation of entities that have lost one or more electrons. Positive ions are admitted as a fine beam through slits S_1 and S_2.

I.14.2.Velocity selector chamber:

This fine beam then enters into a velocity selector. Only the ions of a particular velocity are allowed to come out from the velocity selector. The velocity selector consists of two plane parallel plates P_1 andP_2, which produces a uniform electric field, it also has an electromagnet which produces a uniform magnetic field. These electric and magnetic fields are at right angles to each other and to the direction of the beam. The electric field and magnetic field are so adjusted in such a way that the deflection produced by one field is nullified by the other so that the ions do not suffer any deflection within the velocity selector.
Let E be the electric field intensity, B be the magnetic induction respectively and q be the charge on the positive ion.
The force exerted by the electric field is:

$$F_e=qE$$

The force exerted by the magnetic field is:

$$F_m=qvB$$

Where v is the velocity of positive ions.
We have,

$$Fe=F_m$$

$$qE=qvB\Rightarrow v=E/B$$

The ions having this velocity are allowed to pass through the velocity selector.

I.14.3. Deflection chamber: the ions enter in deflection chamber. The positive ions having the same velocity are again influenced by another strong uniform magnetic field of induction at right angles to the plane of the paper acting inwards. These ions then move in a circular path of radius R and strike the photographic plate. The centripetal force is provided by this magnetic field. Therefore,

$$\mathrm{F_m} = \mathrm{q}.v.B' = \mathrm{m}\frac{v^2}{\mathrm{R}}$$

$$\frac{q}{m} = \frac{v}{B'.\mathrm{R}}$$

Usingv=E/B,

we get

$$m = \frac{qBB'\mathrm{R}}{E}$$

I.14.4. Detector system:

Ions having different masses trace different semi-circular paths and produce dark lines on the plate. The distance between the opening of the chamber and the position of the dark line is equal to the diameter 2R from which radius R can be calculated.

By knowing B,B′,E and R, the mass of the positive ions and isotopic masses can be calculated.

Note: There are different types of spectrographs: J.J Thomson, Dempster, Bainbridge, Aston…etc. All these devices separate the different isotopes of the same element by the action of electric and magnetic fields.

Problem I.9:

A researcher uses a mass spectrometer in a carbon dating experiment (Figure 4). The incoming ions are a mixture of $^{12}C^{+}$ and $^{14}C^{+}$, and they have speed v = 1.0×10^{5} m/s. The strength of the magnetic field is 0.10 T. The mass of the electron is 9.11×10^{-31} kg. The mass of the proton and the mass of the neutron are both 1.67×10^{-27} kg. The researcher first positions the ion detector to determine the value of r for $^{12}C+$ and then moves it to determine the value of r for $^{14}C^{+}$. How far must the detector move between detecting $^{12}C^{+}$ and $^{14}C^{+}$?

Solution:

Determine the mass of each isotope.

$m_{C12} = 6m_p + 6m_n + 5m_e = 12\times1.67\times10^{-27}$ kg + $5\times 9.11\times10^{-31}$kg

$mC_{12} = 2.004 \times 10^{-26}$ kg (two extra digits carried)

$m_{C14} = 6m_p + 8m_n + 5m_e = 14\times1.67\times10^{-27}$ kg + $5\times9.11\times10^{-31}$ kg

$m_{C14} = 2.338 \times 10^{-26}$ kg (two extra digits carried)

Calculate the radius of curvature of each particle.

$$r_{C12} = \frac{m_{C12}v}{qB}$$

$$r_{C12} = \frac{(2.004 \times 10^{-26})kg \times 1.0 \times 10^{5}\frac{m}{s}}{1.6 \times 10^{-19}C \times 0.1\ \frac{kg}{C.s}}$$

r_{C12}=0.1252 m

$$r_{C14} = \frac{m_{C14} v}{qB}$$

$$r_{C14} = \frac{(2.338 \times 10^{-26}) kg \times 1.0 \times 10^{5} \frac{m}{s}}{1.6 \times 10^{-19} C \times 0.1 \frac{kg}{C.s}}$$

r_{C12}=0.1461 m

Calculate how far the detector must move.

$\Delta d=(r_{C14}- r_{C12})$

$=(0.1461- 0.1252)$

$\Delta d= 0.04$ m

Statement: The ion detector must move a distance equal to thedifference in thediameters of the circular trajectories, so it must move a distance of 0.04 m.

I.15. Mass - Energy Equivalence Equation (Einstein's formula):

I.15.1. Mass Defect(missing mass): Mass defect refers to the difference in mass between of a nucleus and the sum of the masses of the protons, neutrons that is its constituent particles. In simple terms what you will found is that the actual mass of the nucleus is always going to be different than the sum of the indivisual mass of the total number of neutrons and protons. To put in a mathematical way

$$\Delta m=Zm_p+(A-Z)m_n-m_{nuc}$$

I.15.2. Binding Energy: Nuclear binding energy is the minimum energy that would be required to disassemble the nucleus into its component parts (neutrons and protons), and is therefore given by:

$$\Delta E = \Delta m.c^2$$

E: energy (measured in joules, J)

m: mass (measured in kilograms, kg)

c : the speed of light (measured in metres per second, ms^{-1})

Note: For convenience, nuclear binding energies are sometimes expressed in mega electron volts (MeV), where 1 MeV = 10^6eV = 1.60 x 10^{-13} J).

Let's now find how much 1 amu does in MeV correspond to. This oftens comes in your exam with 2 marks. Here is how we do it. Well obviously using Einstein's formula $E = mc^2$

$$E = 1.6605 \times 10^{-27}\,\text{kg} \times (2.9979 \times 10^{8})^2 \times (\frac{\text{m}}{\text{sec}})^2 = 15.0639 \times 10^{-11}\text{J} = \frac{15.0639\times10^{-11}\,J}{1.0622\times10^{-13}\frac{J}{MeV}} = 931.5\ \text{MeV}$$

So, 1 amucorresponds to 931.5 MeV of energy.

Problem I.10:

Calculate the binding energy of α-particle($_2{}^4$He nucleus) which has a mass of m=4.001506 amu.

Solution:

This nucleus contains 2 protons and 2 neutrons. Now sum of the masses of the indivisual constituents can be calculated as follows:

$m' = 2 \times 1.007276$ amu $+ 2 \times 1.008665$ amu $= 4.031882$ amu

so, the mass defect of the nucleus is:

$\Delta m = 4.031882$ amu $- 4.001506$ amu $= 0.030376$ amu.

Hence the binding energy will be

$\Delta E = \Delta m \times 931.5$ MeV/amu $= 0.030376$ amu $\times 931.5$ MeV/amu $= 28.29$ MeV.

Well this is the amount of energy gets released from one single ^{4}He nucleus.

Now if I take 4 g of ^{4}He it will contain Avogadro's number of nuclei. Then the release of energy will be 28.29 MeV $\times$ 6.023×10^{23} Mol^{-1} which is almost, after doing a little bit of algebra, 2.56×10^6 mega joules of energy.

Chapter II: Radioactivity and Nuclear reaction

II.1.Introduction:

Radioactivity is a phenomenon in which some elements emit small particles called radiation, to form another element. This is in contrast to the accepted Dalton postulate of indestructibility of an atom. However, only elements with unstable nuclei known as radioactive are capable of undergoing natural radioactivity while stable nuclei do not. All elements having atomic number greater than 83 are radioactive and they undergo nuclear

II.2.Types of Radioactivity:

Some nuclei are unstable; hence they emit sub-atomic particles or electromagnetic radiation in a phenomenon known as radioactivity. Radioactivity can be of two types namely, natural and artificial radioactivity.

II.2.1. Natural Radioactivity:

This is a type of radioactivity that occurs spontaneously, emitting electromagnetic radiation and particles which include beta, positron and alpha particles. The occurrence of this type of decay or emission occurs, depends on the position of nuclei whether above, below or sides of the stability/belt region. Most naturally radioactive nuclei lie outside this belt.

II.2.2. Artificial radioactivity:

It is a non-spontaneous form of radioactivity which requires effect of bombardment of the nuclei with sub-atomic particles. It is otherwise known as anthropogenic or induced radioactivity. Juliot and his wife, Irene Curie discovered artificial radioactivity in 1934 in which aluminum nuclei is bombarded with He nuclei to form new element with emission of electromagnetic ray or particles:

$$^{4}_{2}\mathrm{He} + {}^{27}_{13}\mathrm{Al} \rightarrow {}^{30}_{14}\mathrm{P} + {}^{1}_{1}\mathrm{n}$$

II.3. Type of radiation:

Recall that isotopes are atoms of the same element that have different numbers of neutrons. Isotopes of atoms with unstable nuclei are called radioisotopes. These unstable nuclei emit radiation to attain more stable atomic configurations in a process called radioactive decay. During radioactive decay, unstable atoms lose energy by emitting radiation. The three most common types of radiation are alpha (α), beta (β), and gamma (γ). Table II.1 summarizes some of their important properties.

Table.II.1: The Three Main Forms of Radioactive Emissions

Property	**Alpha Radiation**	**Beta Radiation**	**Gamma Radiation**
Symbol	**α**	**β**	**γ**
Composition	Alpha particles	beta particles	high-energy electromagnetic radiation
Description of radiation	heliumnuclei	electrons	photons
Charge	**2+**	**1-**	**0**
Mass	$6.64 \times 1\,0^{-27}$ kg	$9.11 \times 1\,0^{-31}$ kg	**0**
ApproximateEnergy	5 MeV	0.05 to 1 MeV	1 MeV
Relative penetrating power	blocked by paper	blocked by metal foil	not completely blocked by lead or concrete

II.3.1. Alpha radiation (α):

Alpha radiationis a stream of particles moving at about one-tenth of speed light. Each particle is the nucleus of a helium atom ($^4_2$He). They are large and heavy, so they cannot travel very far, they cannot penetrate the skin. If a substance that emits α-particles gets inside the body by being inhaled or swallowed, the α can damage internal organs.We can represent the emission of an alpha particle with a chemical equation as follows:

$$^{A}_{Z}X^{*} \rightarrow {}^{A-4}_{Z-2}Y + {}^{4}_{2}He(\boldsymbol{\alpha})$$

Example:

$$^{226}_{88}Ra^{*} \rightarrow {}^{222}_{86}Rn + {}^{4}_{2}He(\boldsymbol{\alpha})$$

II.3.2. Beta particle (β):

A beta particle is a very fast-moving electron that is emitted when a neutron in an unstable nucleus converts into a proton. Beta particles are represented by the symbol βor $_{-1}^{0}$e. They have a 1- charge. Their mass is so small compared with the mass of nuclei involved in nuclear reactions that it can be approximated to zero. Beta radiation consists of a stream of fast-moving electrons. An example of the beta decay process is the decay of iodine-131 into xenon-131 by beta-particle emission, as shown in following equation:

$$^{131}_{35}I^{*} \rightarrow {}^{131}_{54}Xe + {}_{-1}^{0}e(\boldsymbol{\beta})$$

Note that the mass number of the product nucleus is the same as that of the original nucleus (they are both 131), but its atomic number has increased by 1 (54 instead of 53). This change in atomic number occurs because a neutron is converted into a proton, as shown by the following equation.

$$^{1}_{0}n \rightarrow {}^{1}_{1}\mathrm{p} + {}^{0}_{-1}\mathrm{e}$$

II.3.3. Gamma rays(γ):

Gamma rays are photons, which are high-energy (short wavelength) electromagnetic radiation. They are denoted by the symbol γ. Because photons have no mass and no charge, the emission of gamma rays does not change the atomic number or mass number of a nucleus. Gamma rays almost always accompany alpha and beta radiation, as they account for most of the energy loss that occurs as a nucleus decays. For example, gamma rays accompany the alpha-decay reaction of uranium-238.

$$^{238}_{92}U \rightarrow {}^{236}_{92}U \rightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}He + 2\gamma$$

The 2 in front of the γ symbol indicates that two gamma rays of different frequencies are emitted. Because gamma rays have no effect on mass number or atomic number, it is customary to omit them from nuclear equations.

II.4. Laws of radioactive disintegration:

• There is an equal probability for all nuclei of a radioactive element to decay.

• The rate of spontaneous disintegration of a radioactive element is proportional to the number of nuclei present at that time.

$$\frac{\mathrm{dN}}{\mathrm{dt}} \propto \mathrm{N} \quad (\mathrm{II}.1)$$

N: number of atoms present at time t.

Removing proportionality sign, we get

$$\frac{dN}{dt} = -\lambda . N \quad (\mathrm{II}.2)$$

λ: decay constant of the element.

Negative sign indicates that as t increases N decreases. Rewriting Eq. (II.2) as

$$\frac{dN}{dt} = -\lambda . N \leftrightarrow \frac{dN}{N} = -\lambda . dt \ (\mathrm{II}.3)$$

$$N_t = N_0 e^{-\lambda . t} (\mathrm{II}.4)$$

Integrating both sides, we have

$$\int \frac{dN}{N} = -\lambda \int dt \ (\mathrm{II}.5)$$

$$\ln N=-\lambda t+C \quad \text{(II.6)}$$

where C is constant of integration and is evaluated by the fact that at t=0, number of atoms of radioactive element is N_0. Using this condition, we get

$$C=\ln(N_0) \quad \text{(II.7)}$$

Substituting this value of C in Eq (II.6), we get

$$\ln(N)= -\lambda t+\ln(N_0) \quad \text{(II.8)}$$

or

$$ln\frac{N}{N_0} = -\lambda t \text{(II. 9)}$$

Thus**,**

$$\boldsymbol{N_t = N_0 e^{-\lambda.t}} \text{(II. 10)}$$

It's the law of radioactivity

II.4.1. Activity (A):

The number of radioactive nuclei cannot be measured directly. One can only determine the rate of transformation called the activity by measuring the particles emitted. It is proportional to the number of atoms:

$$A = - dN/dt = -\lambda N \quad \text{(II.11)}$$

The activity represents the number of disintegrations per second and it is measured in Becquerel Bq. [Bq] = dps. The old unit of activity was Curie Ci and represented the activity of 1g of Radium-226. $1Ci = 3.7 \cdot 10^{10}$ Bq, so 1 mCi = 37 MBq; and 1 µCi = 37 kBq.

The exponential nature of this equation shows that it takes an infinite time for the whole of the radioactive material to disintegrate.

$$A = -\frac{dN}{dt} = \lambda . N \quad \text{(II. 13)}$$

Substituting for N from Eq. (II.10)

$$N = N_0 e^{-\lambda.t}$$

$$A = \lambda\, N_0 e^{-\lambda.t} \text{(II. 14)}$$

Substituting $A_0 = \lambda\, N_0$

$$\boldsymbol{A = A_0 e^{-\lambda.t}} \text{(II. 15)} \text{ Activity Law}$$

A_0 is the activity at t = 0. The exponential factor shows that the activity is decreasing in the same fashion as N.

II.4.2. Half-life:

The half-life is defined as the time elapsed when the intensity of the radiation is reduced to one half of its original value.

The half-life can be mathematically expressed as the point in time when N(t) is one half of N_0 (Fig. II.1). Replacing this expression in the law of radioactivity, where t1/2 is the half-life, gives:

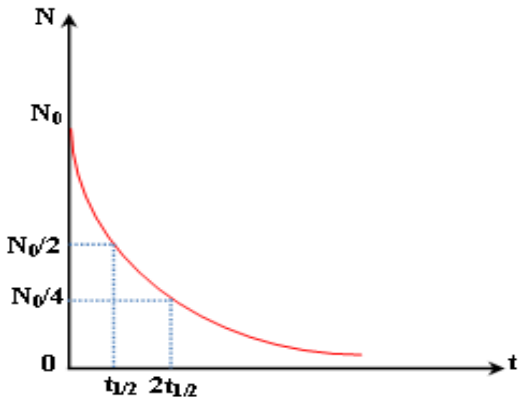


Fig.II.1: The figure demonstrates the meaning of the half-life

$$N_t = N_0 e^{-\lambda t_{1/2}} \Rightarrow \frac{N_0}{2} = N_0 e^{-\lambda t_{1/2}} \Rightarrow \frac{1}{2} = e^{-\lambda t_{1/2}}$$

Taking the logarithm of both sides of the above equation and solving for the half-life $t_{1/2}$ gives:

$$\frac{1}{2} = \ln 2 = \lambda\, t_{1/2} \Rightarrow t_{1/2} = ln\frac{2}{\lambda}$$

Each radioisotope has its own characteristic half-life. Half-lives for several radioisotopes are given in Table II.2. Notice the large range of values for half-lives, from millionths of a second to billions of years!

Table II.2: Half-Lives of Several Radioisotopes

Radioisotope	Symbol	Half-life
Polonium-214	^{214}Pb	163.7 µs
Cobalt-60	^{60}Co	5.272 y
Radon-222	^{222}Ra	3.8 d
Phosphorus-32	^{32}P	14.28 d
Carbon-14	^{14}C	5730 y

Exercise 01:

How long does it take for 60.0 percent of a sample of radon to decay? ($T_{1/2}$ = 3.8d)

Solution 01:

$$\frac{N}{N_0} = e^{-\lambda t} \Rightarrow ln\frac{N}{N_0} = -\lambda t \Rightarrow ln\frac{N_0}{N} = \lambda t$$

$$t = \frac{1}{\lambda} ln\frac{N_0}{N}$$

$$\text{Here } \lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{3.8\text{d}}$$

And $N=(1-0.600)N_0=0.400N_0$

So that,

$$t = \frac{3.8\text{d}}{0.693} \ln\frac{1}{0.400} = 5.05 \text{ d}$$

Exercise 02:

Q. Find the activity of 1.00 mg of radon, ^{222}Rn, whose atomic mass is 222 u and $T_{1/2}$ = 3.8d.

Solution 02:

The decay constant of radon is

$$\text{Here } \lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{3.8\text{d}(86.400 \text{ s/d})} = 2.11 \times 10^{-6} s^{-1}$$

The number N of atoms in 1.00 mg of ^{222}Rn is

$$N = \frac{1.00 \times 10^{-6}\ kg}{222u \times 1.66 \times 10^{-27}} = 2.71 \times 10^{18}\ atoms$$

So,

$$A = (2.11 \times 10^{-6})(2.71 \times 10^{18}) = 5.72 \times 10^{18} \text{ decay/s}$$

Exercise 03:

Plutonium^{239}Pu, has a half life of 24,360 years.

1. What is the decay constant?

2. How much of 1kg ^{239}Pu is left after t=100, 1,000, 10,000, 24,360, 100,000years?

Solution 03:

$$\lambda = \ln\frac{2}{t_{1/2}} = \ln\frac{2}{24360 \text{ y}} = 2.85 \times 10^{-5} \text{y}^{-1}$$

$$N_{Pu}(t) = N_0 e^{-\lambda.t} \Rightarrow N_{Pu}(100y) = 1kg\ e^{-2.85\times10^{-5}\text{y}^{-1}.100\ y}$$

$N_{Pu}(100y) = 0.9972\ kg$

$N_{Pu}(1000y) = 0.9719\ kg$

$N_{Pu}(10000y) = 0.7520\ kg$

$N_{Pu}(24360y) = 0.5\ kg$

$N_{Pu}(100000y) = 0.0578\ kg$

II.5. Types of Nuclear Reactions:

Although the number of possible nuclear reactions is enormous, nuclear reactions can be sorted by type. Most nuclear reactions are accompanied by gamma emissions. Some examples are:

II.5.1. Nuclear Fission:

Isotopes of unstable nuclei with atomic number greater than 80 are capable of undergoing a nuclear reaction called nuclear fission, in which they split into nuclei of intermediate masses and emit one or more neutrons. The energy generated is called atomic energy. Some fission reactions are spontaneous while some are not spontaneous; hence, the non-spontaneous require activation energy from bombardment. A given nucleus is split in many ways liberating enormous energy a typical example is shown below.

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{236}_{92}U \rightarrow ^{140}_{54}Xe + ^{94}_{38}Sr + 2^{1}_{0}n$$

II.5.2.Nuclear Fusion:

This is coming together of small nuclei to form heavy nucleus. However, the fusion reaction require a temperature of about 1,000,000,000 °C to overcome the repulsion of Hydrogen nucleus, after which they are forced to undergo fusion. Nuclear fusion reactions, which are responsible for the production of the heaviest elements, are capable of releasing very large amounts of energy. You already have some everyday knowledge of this fact—the Sun is powered by a series of fusion reactions as hydrogen atoms fuse to form helium atoms.

$$4\ ^{1}_{1}H \rightarrow ^{4}_{2}\mathrm{He} + 2\beta + energy$$

Scientists have spent several decades researching nuclear fusion. It is a promising source of energy and has several advantages compared to nuclear fission.

II.5.3. Nuclear Transmutations:

Nuclear transmutationsare nuclear reactions resulting from the collisions between nuclei or between a nucleus and a neutron.

For example, nuclear transmutations can occur using high-velocity α-particles:

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

II.6. Energy of a nuclear reaction:

During nuclear changes, either some mass is converted into energy or some energy is converted into mass. Which occurs is dependent upon the specifics of the individual reaction. From this change in mass we can calculate its energy equivalent using Einstein's equation, $\Delta E = mc^2$.

- Determining the Energy Change of a Nuclear Reaction

To find the energy change for a nuclear reaction you must know the masses of each species in the equation for the reaction. To calculate the energy change for a nuclear reaction:

- Calculate the sum of the masses of all of the products, and the sum of the masses of all the reactants,
- Calculate the change in mass by subtracting the combined mass of the reactants from the combined mass of the products,
- Convert the change in mass into its equivalent change in energy using Einstein's equation.
- Convert the energy change from J/atom to kJ/mol of atoms.

Example: Calculate the energy change for the following nuclear reaction. The masses of each species are given below.

1 neutron + $^{235}U \rightarrow ^{89}Rb + ^{144}Ce$ + 3 electrons + 3 neutrons

Masses:

neutron = 1.00867 amu

electron = 0.00055 amu

uranium-235 = 234.9934 amu

rubidium-89 = 88.8913 amu

cerium-144 = 143.8817 amu

- Calculate the combined masses of the products and of the reactants.

Mass of Products = 88.8913 amu + 143.8817 amu + 3 (0.00055 amu) + 3 (1.00867 amu) = 235.8007 amu

Mass of Reactants = 1.00867 amu + 234.9934 amu = 236.0021 amu

- Calculate the change in mass for the reaction (mass of products - mass of reactants).

Δmass = 235.8007 amu - 236.0021 amu = - 0.2014 amu

- Convert the change in mass into energy using Einstein's equation. Remember to change the mass into kilograms.

$\Delta E = (- 0.2014 \text{ amu})(1.6606 \times 10^{-27} \text{ kg/amu})(2.9979 \times 10^{8} \text{ m/s})^2 = - 3.006 \times 10^{-11}$ J

- Convert the energy change per atom of uranium-235 into kJ/mol of uranium-235.

(- 3.006 x 10^{-11} J/atom)(1 kJ/1000 J)(6.023 x 10^{23} atoms/mol) = - 1.811 x 10^{10} kJ/mol of U-235

Note: The negative sign indicates that this nuclear reaction is exothermic.

II.7. Radioactivity Applications:

The modern world has come to witness application of radiation activityof sub-atomic particles and electromagnetic rays in various spheres of human life. This has contributed immensely to the improvement of quality of life. Radionuclei have found application in archeological research, agricultural practices, diagnosis, treatment of various diseases condition and nuclear power reactor etc.

II.7.1 Use of Radionuclide in Archeology/EnvironmentalStudies

Radiological dating is a technique by environmentalist, archeologist, geologist and history to determine the age of artifact is it plants or animals, such as wood, fibres, natural pigment bone and cotton. This is done by measuring the amount of carbon-14, a natural occurring radioactive form of carbon.

II.7.2 Uses of Radioactivity in Agricultural Activities:

The use of radiation of sub atomic particles to improve agricultural practices is a major landmark in human endeavour. Absorption of gamma rays helps in eliminating dangerous strain of *Ecoherichia coli*bacteria particularly in red meat. The use of pesticide DDT has been confirmed toxic, to human and animal that is repeatedly exposed to it.

This has been effectively replaced by a radiological technique. This is used indirectly to sterilise the males' larva producing no offspring. The food item treated does not carry radioactive rays.

II.7.3 Industrial Uses:

There are many application of radioactivity in industry and engineering. It helps in industries when precision is of importance and required. The flow of liquid or gas through a pipeline can be monitored by injection of a sample containing a radioactive substance. Leaks in pipes can also be detected easily, thereby preserving life.

II.7.4 Medical Uses:

The use of nuclides as radioactive tracers in medicine has been globally acknowledged. A radiation detector can be used to follow the path of the element throughout the body system. Cobalt radiation treatment for cancerous tumor is well known. Solution of Na is injected into bloodstream to follow the flow of blood and locate obstruction to circulatory system.

Thallium – 201 to technetium -99 have been used to survey damage from heart disease. Iodine – 123 concentrate in the thyroid gland, liver and certain part of the brain. This radioactive type is used to monitorgoiter and often thyroid problems.

II.7.5 Scientific Research:

The pathway of clinical drug can be investigated using radioactive tracers.

Using labelled radioactive compound like $^{14}CO_2$helps identify intermediate molecules. Example is photosynthetic process. Labelled$^{14}CO_2$ helps tracing intermediate molecule.

Uranium - 235 is used in binding nuclear power plant includes nuclear research as well as generating energy to drive industries.

Chapter III: Electronic structure of atom

III.1. Introduction:

Historically, results observed from the studies of interactions of radiations with matter have provided immense information regarding the structure of atoms and molecules. Neils Bohr utilised these results to improve upon the model proposed by Rutherford. Two developments played a major role in the formulation of Bohr's model of atom. These were:

- Dual character of the electromagnetic radiation which means that radiations possess both wave like and particle like properties, and
- Experimental results regarding atomic spectra which can be explained only by assuming quantized electronic energy levels in atoms.

III.2. Wave Nature of Electromagnetic Radiation:

III.2.1. Waves:

A wave is an oscillation or periodic movement that can transport energy from one point in space to another. Some waves require a material medium to propagate (water surface, sound waves); others even propagate in a vacuum (electromagnetic waves).

These radiations are characterised by the properties, namely, frequency (υ), wavelength (λ) and amplitude.

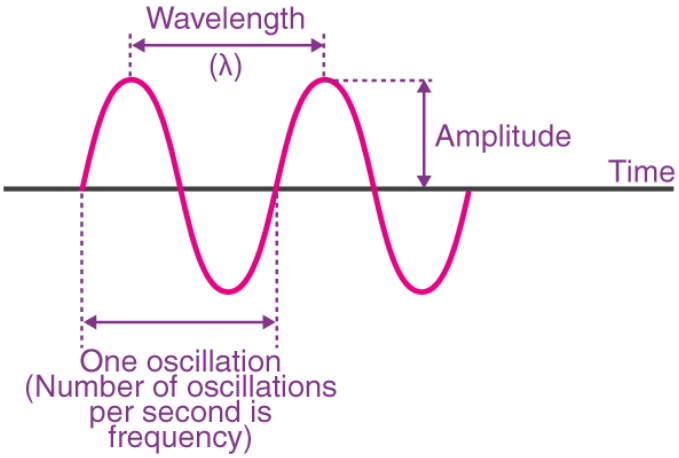


Fig. III.1: Properties of waves

a) Frequency: It is defined as the number of waves that pass a given point in one second. The SI unit for frequency (υ) is hertz (Hz, s^{-1})

$$\upsilon = \frac{1}{\mathrm{T}}$$

b) Wavelength: it is the distance between identical points on successive waves. The SI unit for wavelength (λ) is meter (m).

c) Amplitude: is the vertical distance from the midline of the wave to the peak (or trough).

Note: The other commonly used quantity specially in spectroscopy, is the wavenumber ($\bar{\upsilon}$). It is defined as the number of wavelengths per unit length. Its units are reciprocal of wavelength unit, i.e., m^{-1}.

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

However commonly used unit is cm^{-1} (not SI unit).

III.2.2. Electromagnetic waves (Electromagnetic radiations):

As James Clerk Maxwell showed (1873), electromagnetic waves consist of an electric field oscillating in step with a perpendicular magnetic field, both of which are perpendicular to the direction of travel. These waves can travel through a vacuum at a constant speed of 2.998×10^8 m/s, the speed of light (denoted by c). Simplified picture of electromagnetic wave is shown in Fig. III.2.

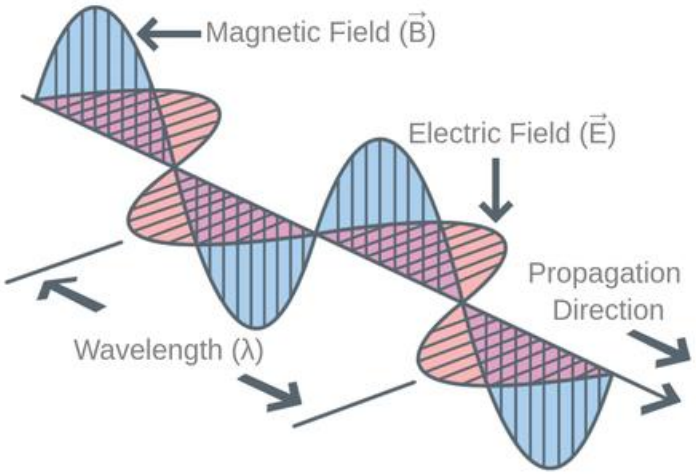


Fig. III.2: Electromagnetic waves

The product of a wave's wavelength (λ) and its frequency (ν), λν, is the speed of the wave. Thus, for electromagnetic radiation in a vacuum:

$$c = 2.998 \times 10^8 ms^{-1} = \lambda\nu$$

Wavelength and frequency are inversely proportional: As the wavelength increases, the frequency decreases

III.2.3. Electromagnetic spectrum:

The figure III.3 shows the electromagnetic spectrum, the range of all types of electromagnetic radiation. Each of the various colors of visible light has specific frequencies and wavelengths associated with them, and you can see that visible light makes up only a small portion of the electromagnetic spectrum.

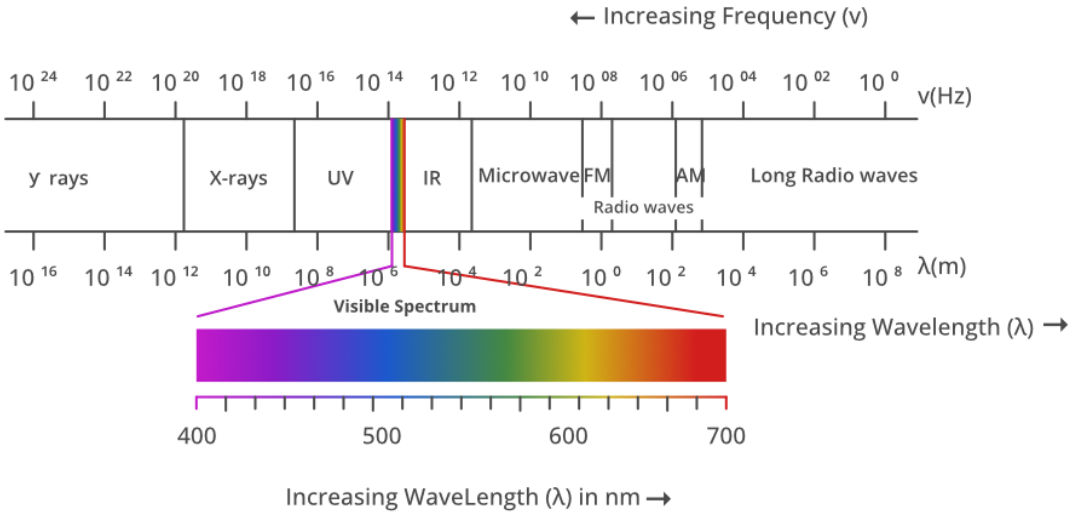


Fig. III.3: Electromagnetic spectrum

Problem II.1:

The wavelength range of the visible spectrum extends from violet (400 nm) to red (750 nm). Express these wavelengths in frequencies (Hz).(1nm = 10^{-9} m)

Solution II.1:

Using equation 2.5, frequency of violet Light equation 2.5, frequency of violet light

$$\upsilon = \frac{C}{\lambda} = \frac{3 \times 10^8}{400 \times 10^{-9}} = 7.50 \times 10^{14}\text{Hz}$$

Frequency of red light

$$\upsilon = \frac{3 \times 10^8}{750 \times 10^{-9}} = 4.0 \times 10^{14}\text{Hz}$$

The range of visible spectrum is from 4.0 × 10^{14} to 7.5 × 10^{14} Hz in terms of frequency units.

Problem II.2:

Calculate (a) wavenumber and (b) frequency of yellow radiation having wavelength 5800 Å.

Solution II.2:

(a) Calculation of wavenumber ($\bar{\upsilon}$)

λ =5800Å =5800 × 10^{-8} cm= 5800 ×10^{-10} m

$$\bar{\upsilon} = \frac{1}{\lambda} = \frac{1}{5800 \times 10^{-10}} = 1.724 \times 10^6 m^{-1}$$

(b) Calculation of the frequency

$$\upsilon = \frac{C}{\lambda} = \frac{3 \times 10^{8}}{5800 \times 10^{-10}} = 5.172 \times 10^{14}\text{Hz}$$

III.3. Spectrum:

Different source of light/radiation produces two types of spectrum:

•Continous spectrum

•Line spectrum

III.3.1. Continous spectrum

This spectrum consists of all wavelengths of visible light-called continuous spectrum if the white light is passed through a slit and then passed through a glass prism, series of colours is seen. Each colour represents different wavelength.

The continuous spectrum has no discrete line that separate the colours. Each colour merges into next without a break.

Example: sun light and the light from incandescent light bulbs

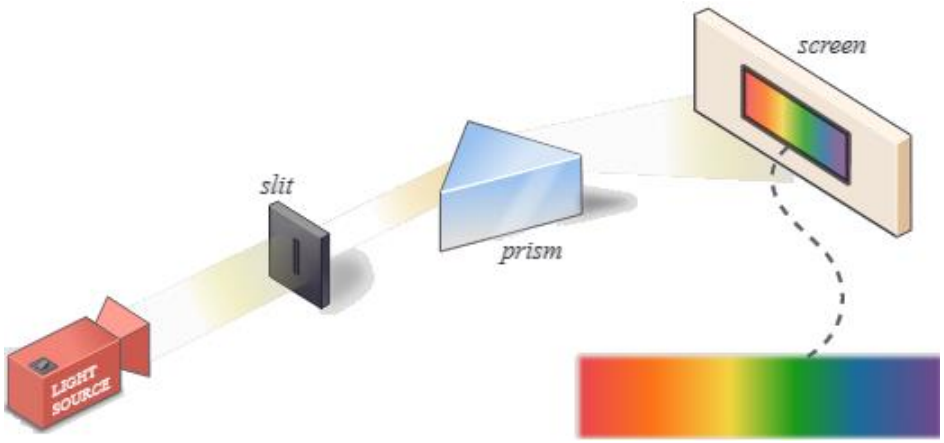


Fig. III.4: Continous spectrum

III.3.2. Line spectrum (discontinuous spectrum):

When a light from a discharge tube containing a particular element passed through a slit and then passed through a glass prism, a series of line produced.

A line spectrum is a series of discrete lines with certain wave lengths. Each line corresponds to light of a particular wavelength. The series of wavelengths produced this way is called atomic emission spectrum.

Source: light of discharge tube of element such as hydrogen, sodium etc.

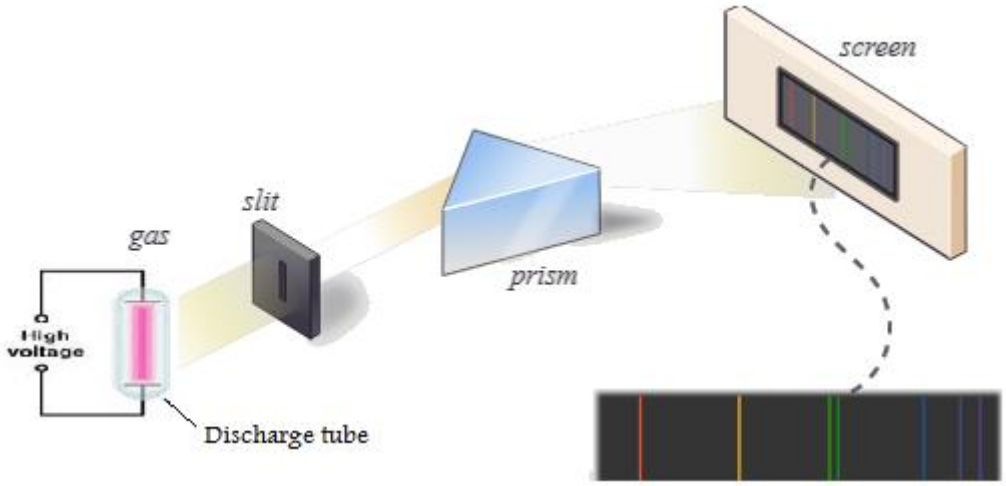


Fig. III.5: Line spectrum

III.4. Particle Nature of Electromagnetic Radiation: Planck's Quantum Theory

III.4.1. Photoelectric Effect:

In 1887, H. Hertz performed a very interesting experiment in which electrons (or electric current) were ejected when certain metals (for example potassium, rubidium, calcium etc.) were exposed to a beam of light as shown in Fig.III.6.

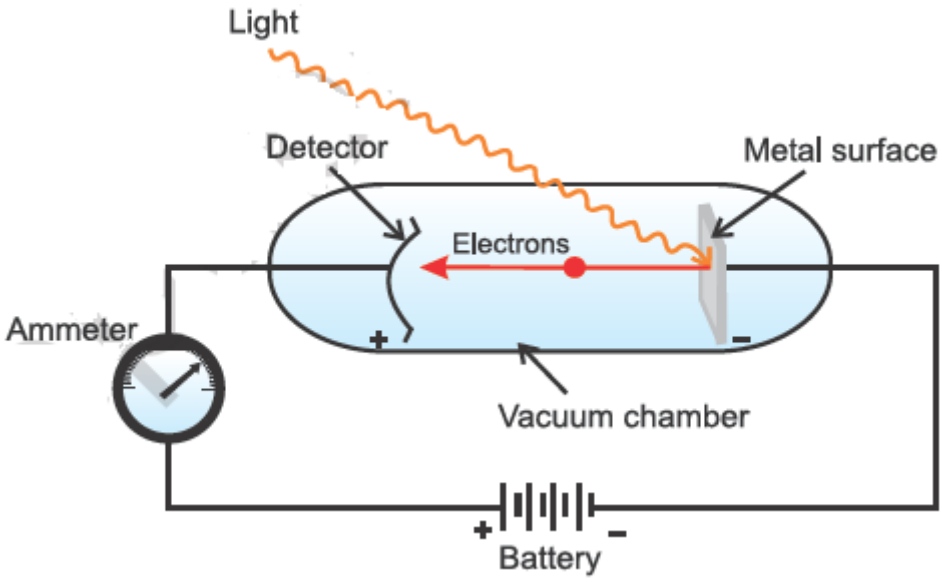


Fig.III.6: Equipment for studying the photoelectric effect.

The phenomenon is called **Photoelectric effect**. The results observed in this experiment were:

(i) The electrons are ejected from the metal surface as soon as the beam of light strikes the surface.

(ii) The number of electrons ejected is proportional to the intensity or brightness of light.

(iii) For each metal, there is a characteristic minimum frequency, υ_0 (also known as threshold frequency) below which photoelectric effect is not observed. At a frequency $\upsilon > \upsilon_0$, the ejected electrons come out with certain kinetic energy. The kinetic energies of these electrons increase with the increase of frequency of the light used.

III.4.2. Quantification of energy (the quantum, Max Planck 1900):

Planck suggested that atoms and molecules could emit (or absorb) energy only in discrete quantities and not in a continuous manner, a belief popular at that time. Planck gave the name **quantum** to the smallest quantity of energy that can be emitted or absorbed in the form of electromagnetic radiation. The energy (E) of a quantum of radiation is proportional to its frequency (υ) and is expressed by following equation

$$E = h\upsilon$$

The proportionality constant, 'h' is known as Planck's constant and has the value 6.626×10^{-34} J s.

III.4.3. The photon (Einstein 1905):

In 1905, Einstein introduced the **photon** (particle has mass and zero charge propagating at the speed of light c) which has a quantum of energy: $\mathbf{E = m\,c^2}$.

Conclusion:

The particle nature of light posed a dilemma for scientists. On the one hand, it could explain the black body radiation and photoelectric effect satisfactorily but on the other hand, it was not consistent with the known wave behaviour of light which could account for the phenomena of interference and diffraction. The only way to resolve the dilemma was to accept the idea that light possesses both particle and wave-like properties, i.e., light has dual behaviour.

III.5. Line Spectrum of Hydrogen:

When an electric discharge is passed through gaseous hydrogen, the H_2 molecules dissociate and the energetically excited hydrogen atoms produced emit electromagnetic radiation of discrete frequencies (or wavelength).

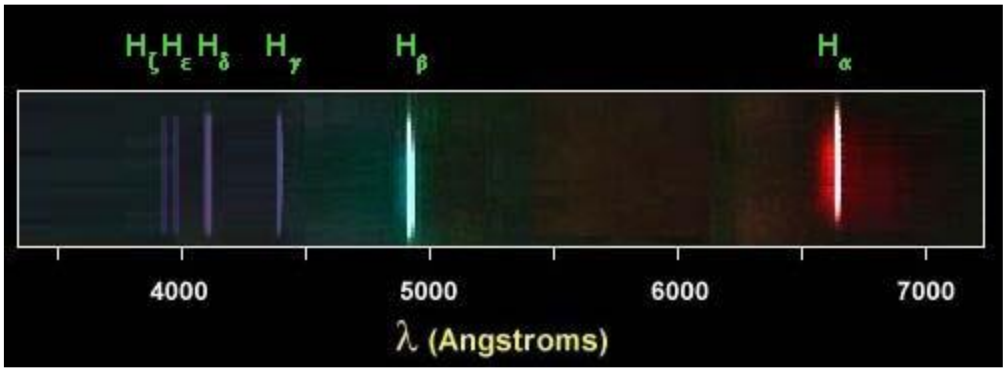


Fig.III.7: Line Spectrum of hydrogen atom .

The Swedish spectroscopist, Johannes Rydberg, noted that all series of lines in the hydrogen spectrum could be described by the following expression:

$$\overline{\upsilon} = \frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where n_1 and n_2 are integers and $n_1 < n_2$, R_H is the Rydberg constant (1.097×10^7 m^{-1}) and Z is the atomic number (Z=1)

Formation of line spectrum

•When an electron of a hydrogen atom at its (n=1) absorbs sufficient amount of energy (photons), it will excite to a higher energy level.

•At higher energy level, electron is unstable. It will fall back to a lower energy level.

•During the transition (falls from higher to lower energy level), energy will be released in a form of light (photon) at definite wavelength and frequency.

•Since the energy is quantized (fix in value), the wavelength produced can be seen as line in the spectrum.

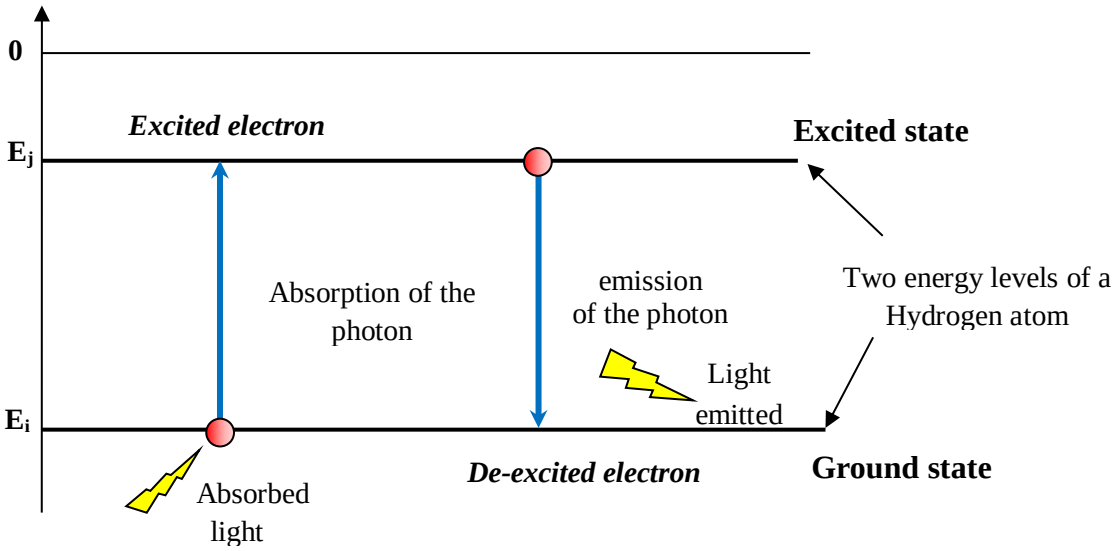


Fig. III.8: Absorption and emission of energy.

The energy released when electron drops from higher to lower energy level is given by following equation: between the two levels is related to the frequency (and wavelength) of the emitted photon:

$$\Delta E = E_j - E_i = \frac{hc}{\lambda}$$

III.6. Bohr's atomic model:

Neils Bohr (1913) was the first to explain quantitatively the general features of hydrogen atom structure and its spectrum. Though the theory is not the modern quantum mechanics, it can still be used to rationalize many points in the atomic structure and spectra. Bohr's model for hydrogen atom is based on the following postulates:

- The electron in the hydrogen atom can move around the nucleus in a circular path (orbits) of fixed radius and energy.
- Energy is only emitted or absorbed by an electron as it moves from one allowed energy state to another
- The angular momentum of an electron in a given stationary state can be expressed as in equation below

$$m_e v\, r = n\frac{h}{2\pi};\quad n = 1, 2, 3, \ldots\ldots$$

Thus an electron can move only in those orbits for which its angular momentum is integral multiple of $h/2\pi$ that is why only certain fixed orbits are allowed.

III.6.1. Orbital radius:

Bohr assumed that the centripetal force (=mv^2/r) required for rotation is provided by inward electrostatic force of attraction (F) between the positively charged nucleus and the negatively charged electrons

$$F = \frac{Z\,e^2}{4\pi\varepsilon_0 r^2}\text{; where } \varepsilon_0 \text{ is the permittivity of free space } (8.85 \times 10^{-12}\ \text{F/m})$$

In accordance with Newton's third law of motion

$$\sum \vec{F}_{ext} = m_e\,\vec{a}\,;\ and\ \vec{a} = \overrightarrow{a_N} + \overrightarrow{a_T}$$

As the electron has a uniform circular path, the tangential acceleration (a_T) is zero and the acceleration is equal to the normal acceleration (a_N=v^2/r)

$$F = \frac{Z\,e^2}{4\pi\varepsilon_0 r^2} = \frac{m_e v^2}{r} \qquad \text{classic macanic low (III. 1)}$$

From Bohr's quantum condition

$$m_e v\,r = n\frac{h}{2\pi} \qquad \text{modern relationship (III. 2)}$$

Where n = 1, 2, 3, . . ., ∞ is an integer, each value of n is associated with a different orbit (Fig. III.9).

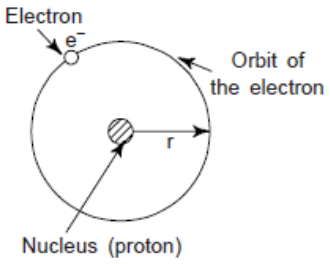


Fig. III. 9: Bohr's atomic model for hydrogen atom with circular orbit

From Eq. (1),

$$v^2 = \frac{Z\,e^2}{4\pi\varepsilon_0 m_e r} \text{ (III. 3)}$$

From Eq. (2), we have

$$v = \frac{n\,h}{2\pi\,r\,m_e} \Rightarrow v^2 = \frac{n^2h^2}{4\pi^2 r^2 m_e^2} \text{ (III. 4)}$$

Eliminating v from Eqs. (III.3) and (III.4), one obtains

$$\frac{Z\,e^2}{4\pi\varepsilon_0 m_e r} = \frac{n^2h^2}{4\pi^2 r^2 m_e^2} \text{ (III. 5)}$$

which yield

$$r_n = \frac{\varepsilon_0 n^2 h^2}{\pi m_e Z e^2} \quad \text{(III. 6)}$$

Substituting the values of constants, i.e., h = 6,62 x 10^{-34} Js ; ε_0 = 8.85 x 10^{-12} Fm^{-1} ; e = 1.6 x10^{-19} C; m_e = 9.1 x10^{-31} kg, Z=1

$$\boldsymbol{r_n = 5.3x10^{-11}\, n^2\ (m) = 0.53\, n^2\ (Å)}$$

We can see that the radii of the stationary orbits are proportional to the square of the principal quantum number n, i.e., they are in the ratio of 1: 4: 9: 16: . . . The orbit with n = 1 has the smallest radius.

For hydrogen (Z = 1), this radius is known as Bohr radius (a_0) and is equal:

$$a_0 = 0.53 \text{ Å}$$

The radius r_n of the orbits of the hydrogen atom is quantized and can only take discrete values such as for example:

• n = 1 → r_1 = 0.53 Å

• n = 2 → r_2 = 2.12 Å.

Velocity of the revolving electron, i.e., orbital velocity

Substituting the value of radius, r from relation (6) in Eq. (III.4), one obtains

$$v = \frac{Z\, e^2}{2\varepsilon_0 nh} \quad \text{(III. 7)}$$

We see that the electron velocity also depend on the quantum numbers *n*, i.e., velocity of the electron is inversely proportional *n* and is the highest in the smallest orbit having *n* = 1. The velocities become progressively less in the orbits of increasing radii. For hydrogen, the velocity of the electron in the Bohr orbit is

$$v = 2.18 \text{ x } 10^6 \text{ m.s}^{-1}$$

This velocity is about 1/137 times the velocity of light *c* (= 3 x 10^8 m/s).

III.6.2. Total Energy (E_k)

The energy of an electron revolving around the nucleus in a orbit is of two parts:

a) Kinetic Energy (E_k): The K.E. is

$$E_k = \frac{1}{2} m_e v^2 = \frac{Z\, e^2}{8\pi\varepsilon_0 r} \quad \text{(III. 8)}$$

Substituting the value of *r* from Eq. (III.6) in Eq. (III.8), one obtains

$$E_k = \frac{Z\,e^2}{8\pi\varepsilon_0 r} \quad (III.9)$$

b) Potential energy (E_p):

The potential energy is due to the position of nuclear electron in the orbit, i.e. the electron lies in the electric field of the positive nucleus, i.e. E*p* = the product of electrical potential (U) and nuclear charge (e).

$$E_p = -e \times U = -\frac{Z\,e^2}{4\pi\varepsilon_0 r} \quad (III.10)$$

$$U = \frac{Z\,e}{4\pi\varepsilon_0 r} \quad (III.11)$$

Total energy :

Total orbital energy *E* is the sum of,

$$E = E_k + E_p = \frac{Z\,e^2}{8\pi\varepsilon_0 r} - \frac{Z\,e^2}{4\pi\varepsilon_0 r} = -\frac{Z\,e^2}{8\pi\varepsilon_0 r} \quad (III.12)$$

Substituting the value of *r* from Eq. (III.6), one obtains,

$$E_n = -\frac{Z^2 m_e e^4}{8\varepsilon_0{}^2 h^2 n^2} \quad (III.13)$$

Substituting the values of constants, i.e., h = 6,62 x 10^{-34} Js ; ε_0 = 8.85 x 10^{-12} Fm^{-1} ; e = 1.6 x10^{-19} C; m_e = 9.1 x10^{-31} kg, Z=1 in eq. III.13 we obtain,

$$E_n = -\frac{2.17 \times 10^{-18} Z^2}{n^2}(\text{Joule}) \quad (III.14)$$

$$\boldsymbol{E_n = -13.6\frac{Z^2}{n^2}\ (eV)} \quad \boldsymbol{(III.15)}$$

Thus the total energy of an electron in the first orbit

$$E_1 = -13.6\frac{Z^2}{1^2} = -13.6\,Z^2 \text{ eV}$$

Similarly, the total energy of an electron in the second orbit (n=2)

$$E_2 = -13.6\frac{Z^2}{2^2} = -3.4\,Z^2 \text{ eV}$$

and in the third orbit

$$E_3 = -13.6\frac{Z^2}{3^2} = -1.51\,Z^2 \text{ eV}$$

Similarly $E_n = 0$ as $n \to \infty$

The energy of the electron given by Eq. (III.15) is negative. So as n increases, i.e., as the electron goes to orbits of larger radii, En increases and converges to the limiting value En = 0

as n →∞. En is the lowest for the smallest orbit for which n= 1. Further the negative sign of the total energy of an electron shows that the electron is bound to the nucleus by the attractive forces. To separate it from the bound of the nucleus, some work is required to be done. The total energy of an electron is known as binding energy or Work function and it is considered to be a positive quantity.

If we plot the different energies on a diagram, we obtain the energy diagram of the hydrogen atom:

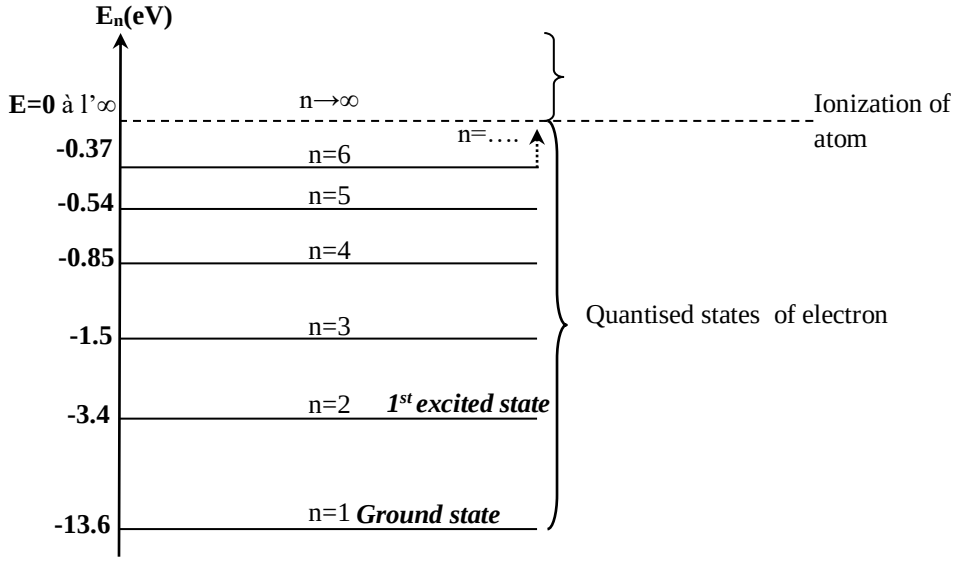


Fig. III.10: Energy level diagram for hydrogen atom.

III.6.3. Orbital frequency:

If the electron, initially in an orbit of quantum number n_i, makes a transition to a final orbit of quantum number n_f, then its energy changes from E_i to E_f where we have from Eq. (13)

$$E_i = -\frac{Z^2 m_e e^4}{8\varepsilon_0{}^2 h^2 n_i{}^2} \quad (16)$$

and

$$E_f = -\frac{Z^2 m_e e^4}{8\varepsilon_0{}^2 h^2 n_f{}^2} \quad (17)$$

If $n_i > n_f$, then $E_i > E_f$. According to Bohr's postulate, we have in this case

$$\Delta E = |E_f - E_i| = h\upsilon = \frac{hc}{\lambda} \Rightarrow \frac{1}{\lambda} = \frac{|E_f - E_i|}{hc}; as\ E = -\frac{Z^2\, m_e e^4}{8\pi\varepsilon_0{}^2 h^2 n^2} \quad \text{eq. (III. 13)}$$

So that the frequency of the emitted radiation is

$$\frac{1}{\lambda} = \frac{Z^2 m_e e^4}{8\varepsilon_0{}^2 h^2 n^2}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \quad (III. 18)$$

This theoretical relationship is identified with Rydberg's experimental relationship

$$\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \quad \textbf{(III. 19)}$$

$$R_H = \frac{m_e e^4}{8\pi\varepsilon_0{}^2 h^3 c} \quad \text{(III. 20)}$$

Theoretical value of R_H: 1.0974 x 10^7 m^{-1}.

Experimental value of RH: 1.0968 x 10^7 m^{-1}.

This good agreement made it possible to validate the Bohr model.

III.6.4. Hydrogen spectral series:

Experimentally, we observe in the emission spectrum of the hydrogen atom several numbers of distinct lines, grouped by series, three of which are shown in the figure below.

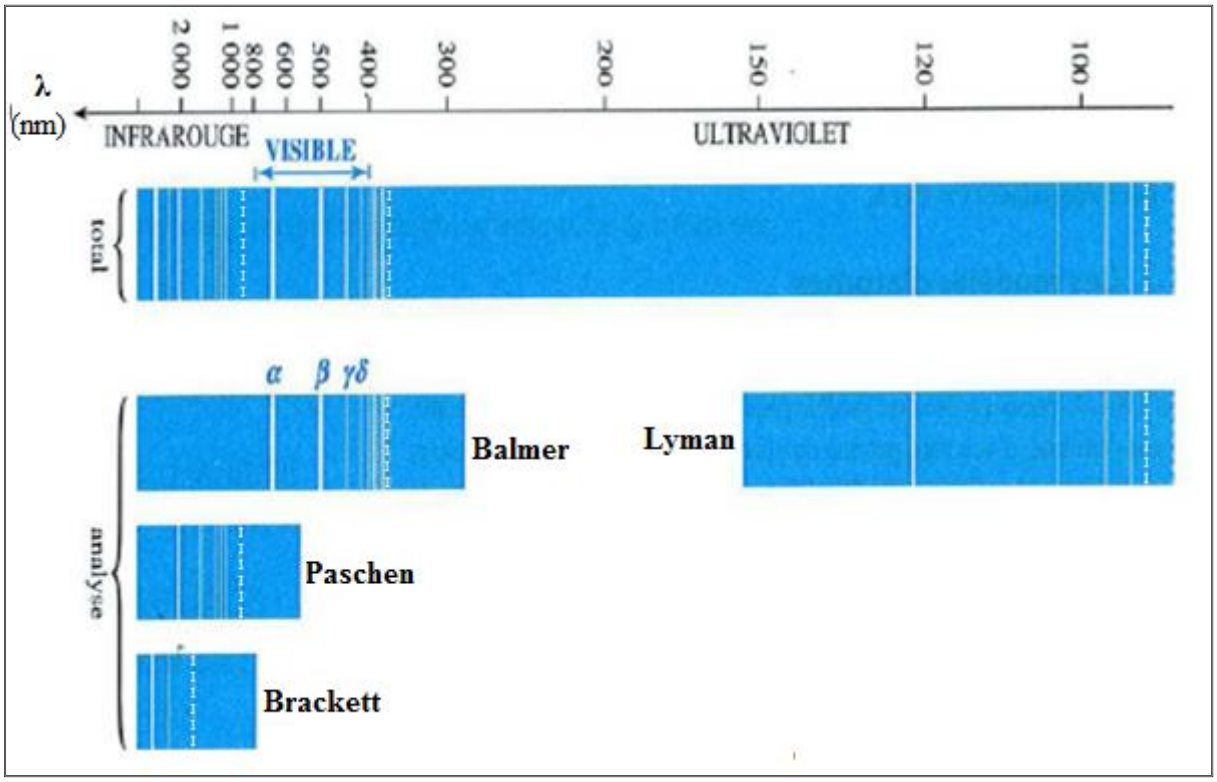


Fig.III.11: Hydrogen spectral series, For each series, the limit line is shown in dotted lines.

The five series correspond to the transitions are summarized in the diagram below.

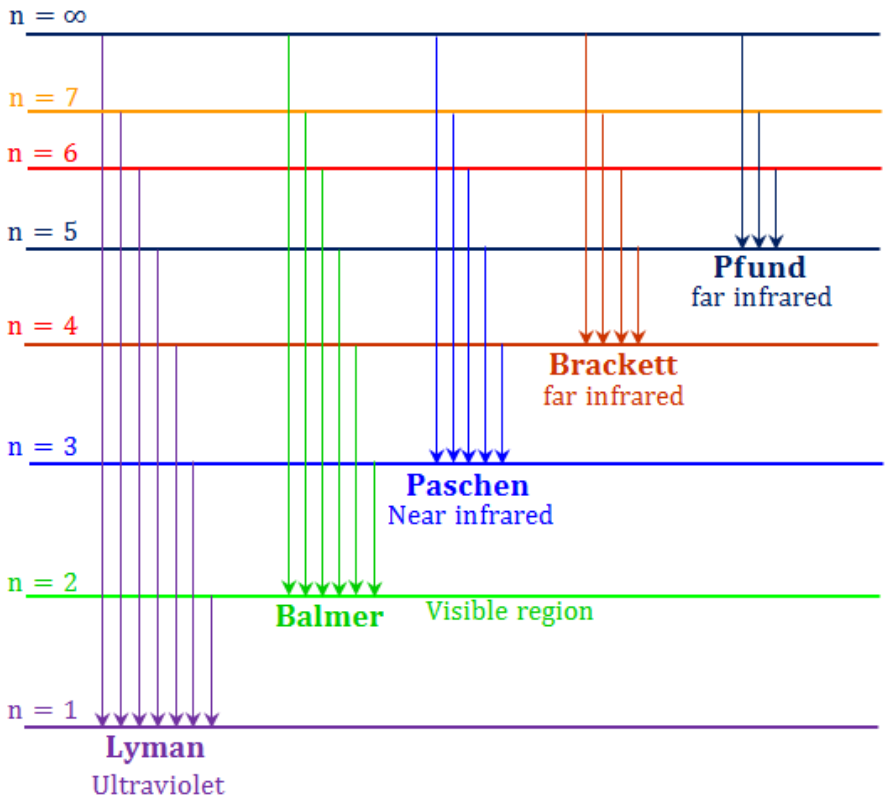


Fig. III.12: The electron energy level diagram for the hydrogen atom.

- Lyman series: correspond to the transitions towards the level n = 1 from the levels going from n = 2 to ∞.

- Balmer series: correspond to the transitions towards the level n = 2 from the levels going from n = 3 to ∞.

- Paschen series: correspond to the transitions towards the level n = 3 from the levels going from n = 4 to ∞.

- Brackett series: correspond to the transitions towards the level n = 4 from the levels going from n = 5 to ∞.

- Pfund series: correspond to the transitions towards the level n = 5 from the levels going from n = 6 to ∞.

- Humphreys: correspond to the transitions towards the level n = 6 from the levels going from n = 7 to ∞.

Note:

Bohr's theory can also be applied to the ions containing only one electron, similar to that present in hydrogen atom. For example, He^{+} Li^{2+}, Be^{3+} and so on. The energies of the stationary states associated with these kinds of ions (also known as hydrogen like species) are given by the expression.

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

and radii by the expression

$$r_n = \frac{0.529\ n^2}{Z}\ (Å)$$

For the frequency the equation is

$$\frac{1}{\lambda} = Z^2 R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where *Z* is the atomic number.

III.6.5. Limitations of Bohr's Model:

Although the Bohr's model of hydrogen atom is rather successful and the idea of quantization of atomic energy is correct, the model is unsatisfactory in the following respects:

- The assumptions made that only circular orbits are allowed whereas elliptical orbits are also possible.

Obviously, these assumptions are inexplicable and arbitrary.

- This model of the atom cannot be generalized to deal with complex atoms, i.e., systems with two or more planetary electrons.
- The model gives no information regarding the arrangement of distribution of electrons in the atom.
- Model does not provide any explanation for chemical bonding.
- The model was also unable to explain the splitting of spectral lines in the presence of magnetic field (Zeeman effect) or an electric field (Stark effect).

These inadequacies led to the development of a more "advanced" model: the quantum mechanical model of the atom.

Problem III.3:

What are the frequency and wavelength of a photon emitted during a transition from $n = 5$ state to the $n = 2$ state in the hydrogen atom?

Solution III.3:

Since $n_i = 5$ and $n_f = 2$, this transition gives rise to a spectral line in the visible region of the Balmer series. From equation (III.19)

$$\Delta E\ = 2.18 \times 10^{-18} J \left(\frac{1}{5^2} - \frac{1}{2^2}\right) = -4.58 \times 10^{-19} J$$

It is an emission energy.

The frequency of the photon (taking energy in terms of magnitude) is given by

$$\upsilon = \frac{\Delta E}{h} = \frac{4.58 \times 10^{-19} J}{6.626 \times 10^{-34} J.s} = 6.91 \times 10^{14}\ Hz$$

$$\lambda = \frac{c}{\upsilon} = \frac{3 \times 10^{8}\ ms^{-1}}{6.91 \times 10^{14}\ s^{-1}} = 434\ nm$$

Problem III.4:

Calculate the energy associated with the first orbit of He^{+}. What is the radius of this orbit?

Solution III.4:

$$\mathbf{E_n} = -\mathbf{2.18} \times 10^{-18} \left(\frac{Z^2}{n^2}\right)\ \text{J}$$

For He^{+}, n = 1, Z = 2

$$\mathbf{E_n} = -\mathbf{2.18} \times 10^{-18} \left(\frac{2^2}{1^2}\right) = -\mathbf{8.172} \times 10^{-18}\ \text{J}$$

The radius of the orbit is given by equation :

$$r_n = \frac{0.529\ n^2}{Z}\ (\text{Å})$$

Since n = 1, and Z = 2

$$r_n = \frac{0.529\ 1^2}{2} = 0.2645\ \text{Å}$$

III.7. Towards quantum mechanical model of atom:

In view of the shortcoming of the Bohr's model, attempts were made to develop a more suitable and general model for atoms. Two important developments which contributed significantly in the formulation of such a model were:

1. Dual behaviour of matter,
2. Heisenberg uncertainty principle.

III.7.1. Dual behaviour of matter (de Broglie's relation 1924):

de Broglie deduced a fundamental relation between the wave length of moving particle and its momentum by making use of Einstein's mass energy relationship and Planck's quantum theory. The material particle as a wave satisfies the Planck's relation for a photon, i.e.

$E = h\upsilon$ …….. (1)

where h is Planck's constant and υ is the frequency of the wave. The frequency for light wave is υ .

At the same time, Einstein's mass energy relationship is applicable to it, i.e.

$E = mc^2$ (for a photon) …….. (2)

or $h\nu = mc.\ c = p.c$ (p = momentum, p = m.c, mass x velocity)

Or,

$$\frac{hc}{\lambda} = p.c$$

Or,

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

Here, λ corresponds to the wave character of matter and p its particle character. This is known as de Broglie's relation. From this relationship, it is concluded that "the momentum of a moving particle is inversely proportional to the wavelength of the wave associated with it".

It is important to note here from above discussion that de Broglie's relation is applicable to material particles of all sizes and dimensions but the wave character is significant only for micro objects like electrons and is negligible for macro objects hence cannot be measured properly. This infers that de Broglie's relation is more useful for smaller particles.

Problem III.5:

What will be the wavelength of a ball of mass 0.1 kg moving with a velocity of 10 m s^{-1} ?

Solution III.5:

According to de Brogile equation

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{0.1 \times 10} = 6.626 \times 10^{-34} m$$

Problem III.6:

The mass of an electron is 9.1×10^{-31} kg.

If its K.E. is 3.0×10^{-25} J, calculate its wavelength.

Solution III.6:

Since

$$KE = \frac{1}{2} m_e v^2$$

$$v = \sqrt{\frac{2KE}{m_e}} = \sqrt{\frac{2 \times 3.0 \times 10^{-25}}{9.1 \times 10^{-31}}} = 812\ ms^{-1}$$

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{9.1 \times 10^{-31} \times 812} = 8967 \times 10^{-10} m = 896.7\ nm$$

Problem III.7:

Calculate the mass of a photon with wavelength 3.6 Å.

Solution III.7:

λ= 3.6 Å = 3.6×10^{-10}m

Velocity of photon = velocity of light

$$m = \frac{\mathrm{h}}{\lambda v} = \frac{6.626 \times 10^{-34}}{3.6 \times 10^{-10} \times 3 \times 10^{8}} = 6.135 \times 10^{-29} kg$$

III.7.2. Heisenberg's Uncertainty Principle:

According to classical mechanics, a moving electron behaves as a particle whose position and momentum could be determined with accuracy. But according to de Broglie, a moving electron has wave as well as particle character whose precise position cannot be located because a wave is not located at a particular point rather, it extends in space. To describe the character of a subatomic particle that behaves like a wave, Werner Heisenberg in 1927 formulated a principle known as Heisenberg's Uncertainty Principle. According to the principle "**It is impossible to determine simultaneously both the position as well as the momentum (or velocity) of a moving particle at the same time with certainty (or accurately)"**

He also proposed a mathematical relationship for the uncertainty principle by relating the uncertainty in position with the uncertainty in momentum which is given below:

$$.\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

$$or\ \Delta x \times \Delta(mv) \geq \frac{h}{4\pi}$$

$$or\ \ \Delta x \times \Delta v \geq \frac{h}{4\pi m}$$

where Δx is the uncertainty or error in the position of the particle, Δ p and Δ x are the uncertainties in its momentum and velocity and h is Planck's constant.

This equation states that the product of Δx and Δp can either be greater than or equal to (≥) but never smaller than h / 4π.

Problem II.7:

A microscope using suitable photons is employed to locate an electron in an atom within a distance of 0.1 Å. What is the uncertainty involved in the measurement of its velocity?

Solution III.7:

$$\Delta x \times \Delta v = \frac{h}{4\pi m}$$

$$\Delta v = \frac{h}{4\pi m \Delta x}$$

$$= \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 0.1 \times 10^{-10} \times 9.11 \times 10^{-31}} = 0.579 \times 10^{7} ms^{-1}$$

Problem II.8:

A golf ball has a mass of 40g, and a speed of 45 m/s. If the speed can be measured within accuracy of 2%, calculate the uncertainty in the position.

Solution II.8

The uncertainty in the speed is 2%, i.e.,

$$\Delta v = 45 \times \frac{2}{100} = 0.9\ ms^{-1}$$

Using the following equation

$$\Delta x = \frac{h}{4\pi m \Delta v}$$

$$= \frac{6.626 \times 10^{-34}}{4 \times 3.4 \times 40 \times 10^{-3} \times 0.9} = 1.46 \times 10^{-33} m$$

This is nearly ~ 10^{18} times smaller than the diameter of a typical atomic nucleus.

As mentioned earlier for large particles, the uncertainty principle sets no meaningful limit to the precision of measurements.

III.7.3. Quantum Mechanics:

In 1926, Erwin Schrödinger derived a complex mathematical formula to incorporate wave and particle characteristics. The branch of science that takes into account this dual behavior of matter is called quantum mechanics.

For a system (such as an atom or a molecule whose energy does not change with time) the Schrödinger equation is written as

$$H\psi = E\psi$$

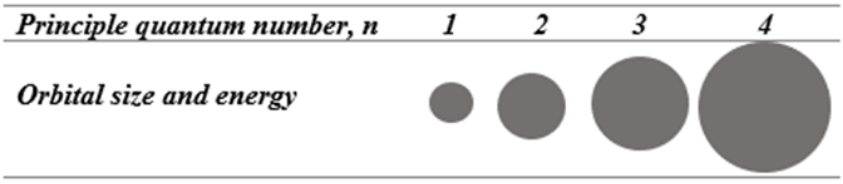
where *H* is a mathematical operator called Hamiltonian. Schrödinger gave a recipe of constructing this operator from the expression for the total energy of the system. The total energy of the system takes into account the kinetic energies of all the sub-atomic particles (electrons, nuclei), attractive potential between the electrons and nuclei and repulsive potential among the electrons and nuclei individually. Solution of this equation gives *E* and ψ.

III.7.4. Orbitals and Quantum Numbers:

The complete solution to Schrodinger's equation for the hydrogen atom yields a set of wave equations ψ and corresponding energies E. These wave functions are called orbitals. An atomic orbital is a mathematical function that describes the wave-like behavior of an electron in an atom. Each atomic orbital in an atom is characterized by a unique set of three quantum numbers (principal quantum number *n*, Angular momentum quantum number *l* and magnetic quantum number m_l) arise as a natural consequence in the solution of the Schrödinger equation.

a) The principal quantum number (*n*):

The principal quantum number determines the size and to large extent the energy of the orbital. It is a positive integer with value of n = 1, 2, 3..... .



The principal quantum number also identifies the shell. With the increase in the value of (*n*),

the number of allowed orbital increases and are given by (n^2). All the orbitals of a given value of *n* constitute a single shell of atom and are represented by the following letters.

n	1	2	3	4	5	6	7
Notation	**K**	**L**	**M**	**N**	**O**	**P**	**Q**

b) Angular momentum quantum number (*l*): It defines the three dimensional shape of the orbital. For a given value of *n*, *l* can have *n* values ranging from 0 to *n* – 1, that is, for a given value of *n*, the possible value of *l* are : *l* = 0, 1, 2, ...(*n*–1)

For example, when *n* = 1, value of *l* is only 0. For *n* = 2, the possible value of *l* can be 0 and 1. For *n* = 3, the possible *l* values are 0, 1 and 2.

Each shell consists of one or more subshells or sub-levels. The number of subshells in a principal shell is equal to the value of *n*. For example in the first shell (*n* = 1), there is only one sub-shell which corresponds to *l* = 0. There are two sub-shells (*l* = 0, 1) in the second shell (*n* = 2), three (*l* = 0, 1, 2) in third shell (*n* = 3) and so on. Each sub-shell is assigned an azimuthal quantum number (*l*). Sub-shells corresponding to different values of *l* are represented by the following symbols.

l	**0**	**1**	**2**	**3**	**4**
Notation	***s***	***p***	***d***	***f***	***g***

c) Magnetic orbital quantum number (m_l):

gives information about the spatial orientation of the orbital with respect to standard set of co-ordinate axis. For any sub-shell (defined by '*l*' value) $2l+1$ values of m_l are possible and these values are given by :

$$m_l = -l, -(l-1), -(l-2) \ldots 0, 1 \ldots (l-2), (l-1), l$$

Thus for $l = 0$, the only permitted value of $m_l = 0$, [2(0)+1 = 1, one *s* orbital]. For $l = 1$, m_l can be –1, 0 and +1 [2(1)+1 = 3, three *p* orbitals]. For $l = 2$, $m_l = -2, -1, 0, +1$ and +2, [2(2)+1 = 5, five *d* orbitals]. It should be noted that the values of m_l are derived from *l* and that the value of *l* are derived from n.

d) Spin Quantum Number (*s or* m_s):

A new (4^{th}) quantum number called the Electron Spin Quantum Number ($\mathbf{m_s}$) is introduced. The electrons spin on its own axis like a top, in clockwise and anti-clockwise directions. The two directions of spinning is denoted by spin quantum number as:

$$s = +\frac{1}{2} \; and \; s = -\frac{1}{2}$$

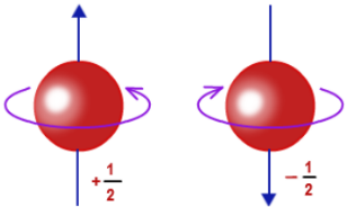


Fig. III.13: The direction of spinning motion of electron

The spin quantum numbers are also denoted by **up-half arrow** (↑) and **down-half arrow** (↓).

Allowed values of the quantum numbers of electrons in atoms are briefly summarized in Table III.1.

Table III.1: Allowed values of the quantum numbers

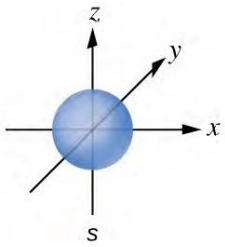
n ***(shell)***	***l*** ***(subshell)***	**Orbital notation**	m_l	m_s	**No. of orbitals ($2l+1$)**	**No. of e- ($2n^2$)**
1	0	1s	0	+½ ,-½	1	2
2	0	2s	0	+½, -½	1	8
	1	2p	+1,0,-1	+½, -½	3	

3	0	3s	0	+½, -½	1	18
	1	3p	+1,0,-1	+½, -½	3	
	2	3d	+2,+1,0,-1,-2	+½, -½	5	
4	0	4s	0	+½, -½	1	32
	1	4p	+1,0,-1	+½, -½	3	
	2	4d	+2,+1,0,-1,-2	+½, -½	5	
	3	4f	+3,+2,+1,0,-1,-2,+3	+½, -½	7	

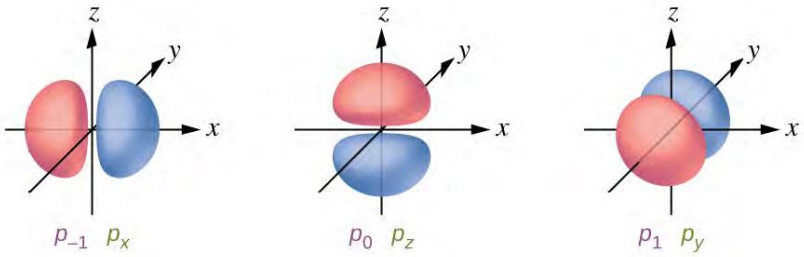
The *s* subshell electron density distribution is spherical and the *p* subshell has a dumbbell shape. The *d* and *f* orbitals are more complex. These shapes represent the three-dimensional regions within which the electron is likely to be found (Fig. III.14).

III.7.5. Representations of orbitals:

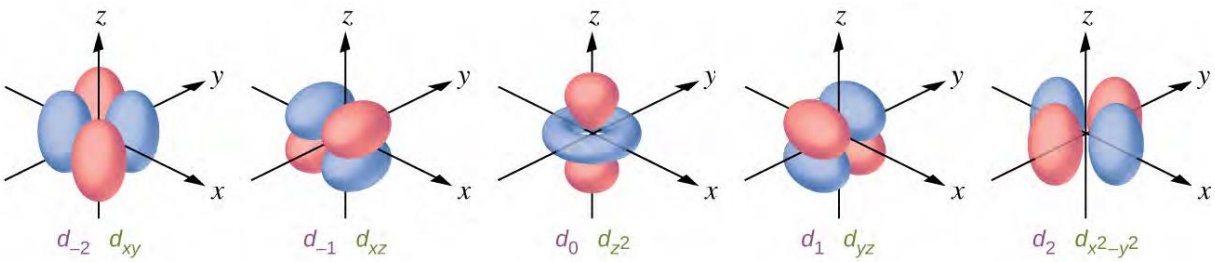
The *s* subshell: 1 orbital



The p subshell: 3 orbitals



The *d subshell:* *5* orbitals



The f subshell: 7 orbitals

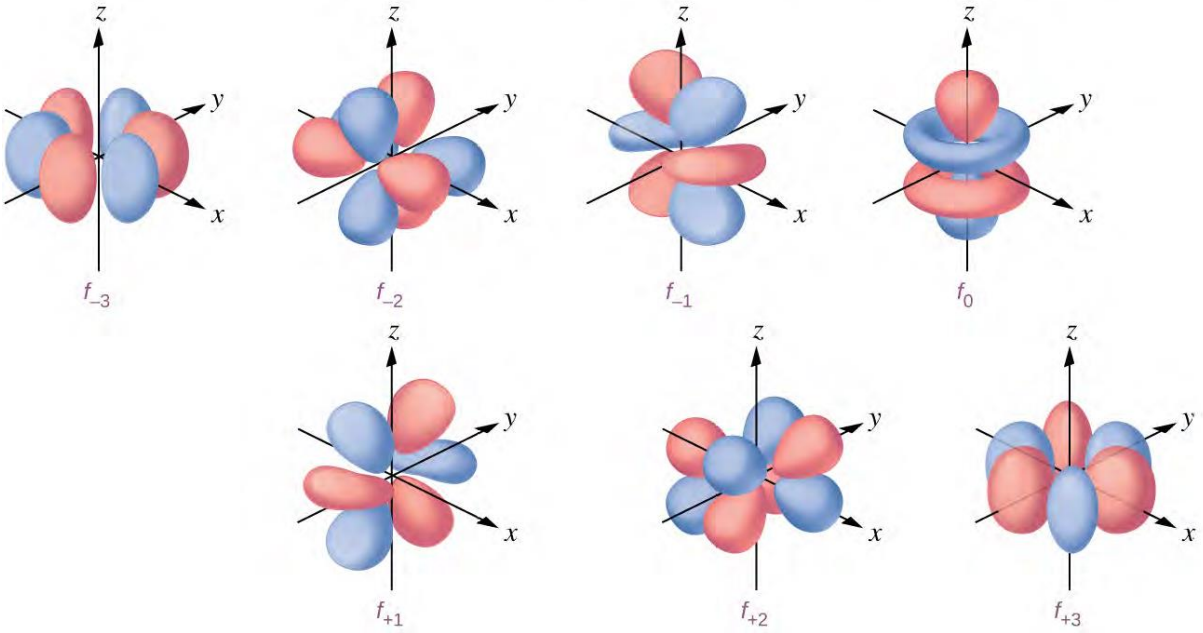


Fig. III.14: Shapes of *s*, *p*, *d*, and *f* orbitals.

III.8. Electronic configurations:

Electron configurations tell us how the electrons are distributed among the various orbitals of an atom. To obtain the distribution of electrons in the different orbitals for the ground state of the atom (lowest energy state), it will be necessary to proceed according to the following filling rules:

III.8.1. Rules for filling, stability and saturation:

a) Aufbau Principle:

The word "*aufbau*" in German means "building up". The building up of orbitals means the filling up of orbitals with electrons. The principle states: In the ground state of the atoms, the orbitals are filled in order of their increasing energies. For this, the filling of the orbitals by the electrons will be carried out by increasing values of: $n + \ell$. When $n + \ell$ is the same for two orbitals, the one with the smaller value of n is filled first. The order may be remembered by using the method given in Fig. III.15.

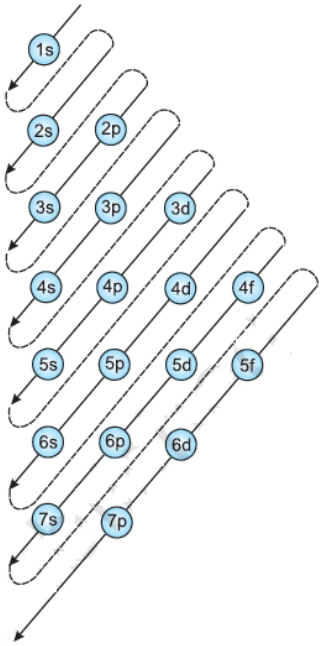


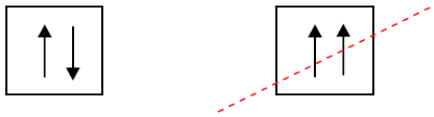
Fig. III.15: order of filling of orbitals.

This rule reflects the fact that the orbitals fill in the following order:

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

b) Pauli's Exclusion Principle:

No two electrons in an atom can have the same four quantum numbers. Electrons in a given orbital must have the same values of *n*, *l* and *m* but they must have different values of *s*. Only two values of *s* are possible, + ½ and – ½.

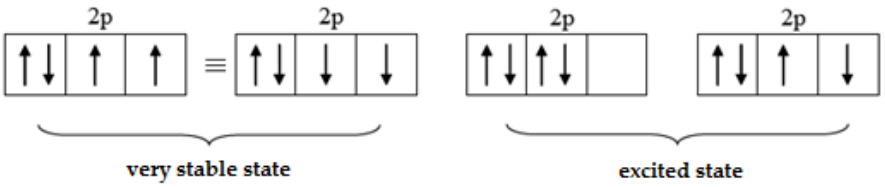


possible impossible

c) Hund's Rule:

This rule deals with the filling of electrons into the orbitals belonging to the same subshell (that is, orbitals of equal energy, called degenerate orbitals). It states: pairing of electrons in the orbitals belonging to the same subshell (*p*, *d* or *f*) does not take place until each orbital belonging to that subshell has got one electron each i.e., it is singly occupied.

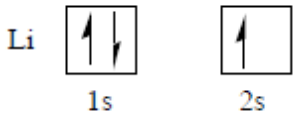
***Example*:** let us take the case of 4 electrons described by the 2p subshell.



Note: The electronic configuration of different atoms can be represented in two ways. For example:

(i) *spdf* ..... notation:

(ii) Orbital diagram : each orbital is represented by a box and each electron is represented by a half arrow (or arrow). This representation is called Orbital diagram



Example:

***spdf* notation**	**Orbital diagram**
$^{9}F: \ 1s^2 2s^2 2p^5$	$^{9}F:$ $1s^2$ $2s^2$ $2p^5$
$^{10}Ne: 1s^2 2s^2 2p^6$	$^{10}Ne:$ $1s^2$ $2s^2$ $2p^6$

III.8.2. The valence electrons and the core electrons:

Electrons in subshells not occupied in the nearest noble-gas element of lower atomic number are referred to as outer-shell electrons, or valence electrons. The electrons in the inner shells are the core electrons.

Note: To simplify the writing of electronic configurations, we replace all or part of the core electrons with the chemical symbol of the noble gas which has this number of electrons.

Example:

$^{11}Na \ \underbrace{[Ne]}_{1s^2 2s^2 2p^6} \ 3s^1$; $^{12}Mg \ [Ne]3s^2$; $^{13}Al \ [Ne]3s^2 3p^1$; $^{14}Si \ [Ne]3s^2 3p^2$

$^{16}S \ [Ne]3s^2 3p^4$; $^{22}Ti \ [Ar]4s^2 3d^2$; $^{23}V \ [Ar]4s^2 \underbrace{\uparrow \ \uparrow \ \uparrow \ \ \ }_{3d^3}$

$^{18}Ar \ [Ne]3s^2 3p^6$; $^{19}K \ [Ar]4s^1$; $^{20}Ca \ [Ar]4s^2$; $^{21}Sc \ [Ar]4s^2 3d^1$

III.8.3. Stability of Completely Filled and Half Filled Subshells:

In certain elements such as Cu, or Cr, where the two subshells (4*s* and 3*d*) differ slightly in their energies, an electron shifts from a subshell of lower energy (4*s*) to a subshell of higher energy (3*d*), provided such a shift results in all orbitals of the subshell of higher energy getting either completely filled or half filled. The valence electronic configurations of Cr and Cu, therefore, are $3d^5\ 4s^1$ and $3d^{10}\ 4s^1$ respectively and not $3d^4\ 4s^2$ and $3d^9\ 4s^2$. It has been found that there is extra stability associated with these electronic configurations.

Example:

Element	Configuration according to Aufbau	Actual configuration
$_{24}Cr$	$_{18}[Ar]\ 4s^2\ 3d^4$	$_{18}[Ar]\ 3d^5\ 4s^1$
$_{29}Cu$	$_{18}[Ar]\ 4s^2\ 3d^9$	$_{18}[Ar]\ 3d^{10}\ 4s^1$
$_{42}Mo$	$_{36}[Kr]\ 5s^2 4d^4$	$_{36}[Kr]\ 4d^5 5s^1$

III.9. Electron Shielding and Effective Nuclear Charge:

If an electron is far from the nucleus, then at any given moment, many of the other electrons (inner) will be between that electron and the nucleus (Figure below). Hence the inner electrons will screen of shield a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between nucleus and the electron farther away. As a result, the electron farther away experiences an effective nuclear charge (Z_{eff} / Z*) that is less than the actual nuclear charge Z. The reducing effect on nuclear charge by the inner electrons for an outer electron is termed as screening or shielding. This effect is called electron shielding.

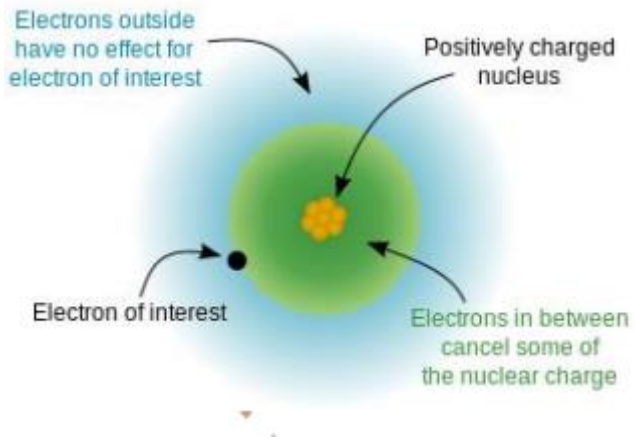


Fig. III.16: Shielding by the inner electrons

Shielding therefore 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 by the inner

electrons. Z_{eff} can be calculated by subtracting the magnitude of shielding (S / σ) from the actual nuclear charge (Z) and the effective nuclear charge Z_{eff} of an atom is given by the equation:

$$\mathbf{Z_{eff} = Z - S}$$

Where S is called screening or shielding constant can be calculated by Slater's rule.

III.9.1. Slater's Rule:

Slater had proposed some empirical set rules to calculate the screening constant (S/σ) of various electrons present in different orbitals of an atom or ion.

According to this rule,

1. The electrons of the atom or ions are grouped as follows: (1s) (2s,2p) (3s,3p) (3d) (4s,4p) (4d) (4f) (5s,5p) etc.
2. Electrons to the right (in higher subshells and shells) of an electron do not shield it. i.e., contribute Zero.
3. For ns or np valence electrons:

a) each other electron in the same group contributes 0.35 (0.30 for 1s).

b) each electron in an (n-1) group contributes 0.85.

c) each electron in an (n-2) and lower group contributes 1.00.

4. For nd or nf valence electrons:

a) each other electron in the same group contributes 0.35

b) each electron in a lower group (to the left) contributes 1.00

Example:

Calculate the effective nuclear charge on one of the 2p electrons in the oxygen atom ($_8O$)

Electron configuration: $1s^2\ 2s^2\ 2p^4$

Electrons are grouped as: $(1s^2)\ (2s^2\ 2p^4)$ or $(1s^2)\ (2s\ 2p)^6$

Obviously, $2p^1$ electron is excluded from the calculation.

5 other electrons in valence shell contribute 5 x 0.35=1.75

2 electrons belonging to (1s) i.e., in the (n-1) group contribute 0.85 each, 2 x 0.85 = 1.70

Total (σ) = (1.75) + (1.70) = 3.45

$$Z^* = Z - \sigma \Rightarrow Z^* = 8 - 3.45 = 4.55$$

III.9.2. Energy and orbital radius poly-electronic atoms:

Slater's rule allows a simple estimate of the energy of the orbitals. By analogy with the expression for the energy of the orbitals of the hydrogen atom, we can write according to Slater:

$$E_i = -13.6 \times \frac{Z^*}{n_i^2} \text{ (eV)}$$

Note: we can use this estimation to calculate the orbital radius of atom:

$$\mathrm{r_n} = \frac{0.529\, n^2}{Z^*} \text{ (Å)}$$

Chapter IV: Classification of elements and periodicity of properties

IV.1. Introduction:

The periodic table arranges atoms based on increasing atomic number so that elements with the same chemical properties recur periodically. When their electron configurations are added to the table (Fig.III.1), we also see a periodic recurrence of similar electron configurations in the outer shells of these elements. Because they are in the outer shells of an atom, valence electrons play the most important role in chemical reactions the outer electrons have the highest energy of the electrons in an atom and are most easily lost or shared than the core electrons. Valence electrons are also the determining factor in some physical properties of the elements.

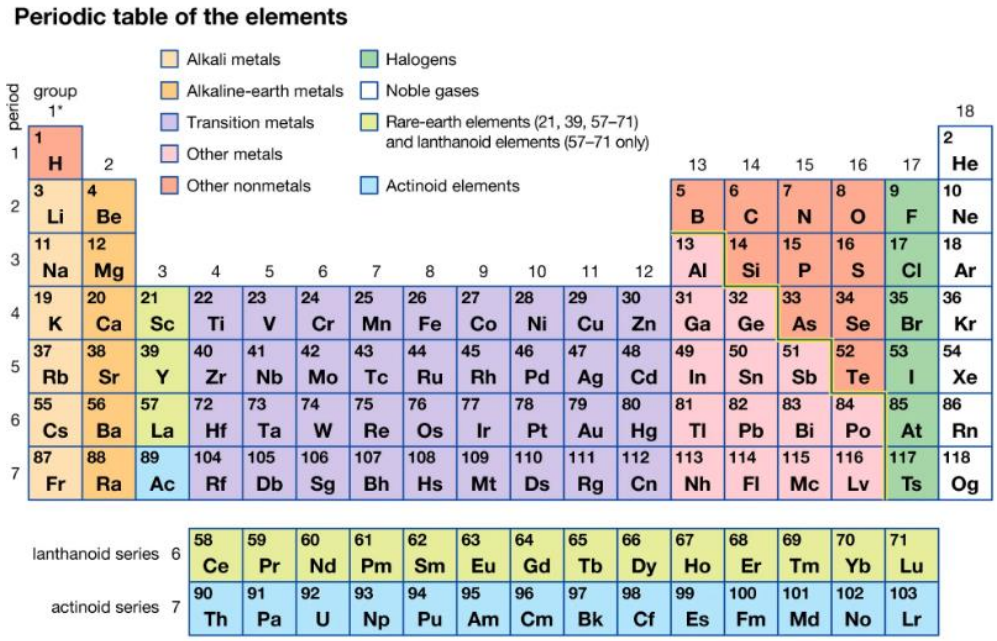


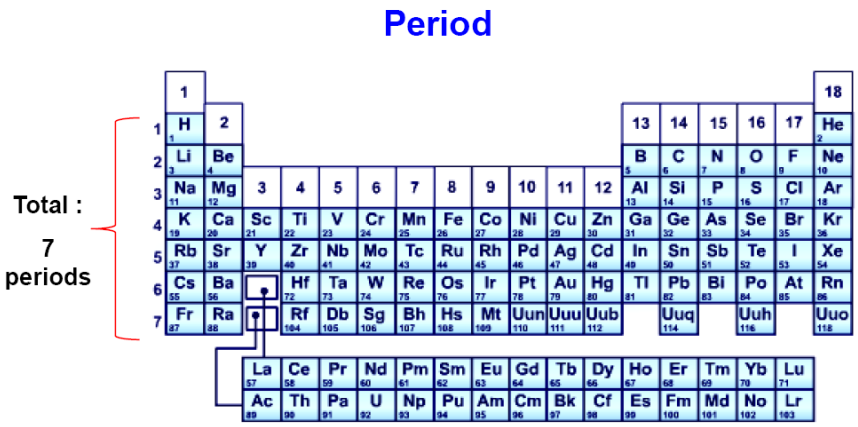
Table IV.1: The periodic table of elements

IV.2. Classification of elements:

- Elements are arranged in order of increasing proton number in periodic table
- Vertical column known as group
- Horizontal row known as period
- Block of elements is classified based on its electronic configuration.

IV.2.1. Period:

Each horizontal row of the table is called a period. The period containing a set of elements arranged in the order of increasing proton number. Each row represents the number of energy levels present in an atom of the element



The elements in each period posses an identical number of quantum levels (*n*) or having the same number of shell.

Example:

Na: $1s^2\ 2s^2\ 2p^6\ \mathbf{3}s1$

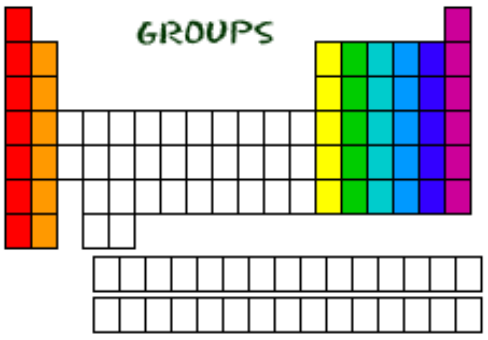
Cl : $1s^2\ 2s^2\ 2p^6\ \mathbf{3}s^2\mathbf{3}p^5$

} *n*=3⇒ period 3

Note: Period = HIGHEST value of principle quantum number *(n)*, in the electronic configuration

IV.2.2. Groups:

The columns in the periodic table are called Groups. There are18 groups, each elements in the same group have the same number of valence electrons and similar chemical properties.



Example: Sodium (Na) and potassium, (K) are both found in group1; they both have one valence electron.

Note: To determine group of the elements :

Block *s*: same as number of valence electrons

Block *d*: same as number of valence electrons

Block *p*: number of valence electrons + 10

IV.2.3. Block:

Based on the electronic configuration, the type of orbital occupied by electron of the highest energy determines the block of the element. Therefore, there are 4 blocks exists in the periodic table namely *s*, *p*, *d* and *f* (Fig. IV.2).

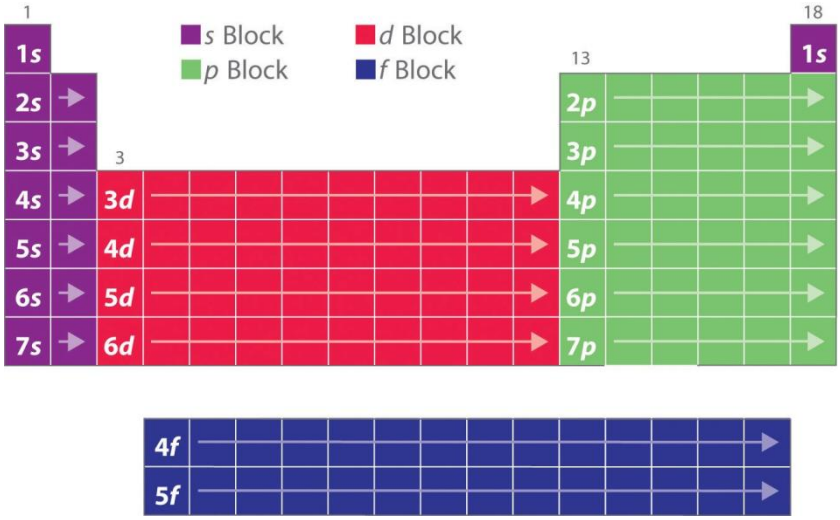


Fig. IV.2: The type of elements in the Periodic Table based on the orbitals that are being filled.

a) The *s*-Block Elements:

The elements of Group 1 (alkali metals) and Group 2 (alkaline earth metals) which have ns^1 and ns^2 outermost electronic configuration belong to the *s*-Block Elements.

Example:

$_{11}$Na: $1s^2 2s^2 2p^6 3s^1$

$_{20}$Ca: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

b) The *p*-Block Elements:

Elements in groups 13 to 18 in periodic table. The outermost electronic configuration varies from ns^2np^1 to ns^2np^6 in each period.

Example:

$_{13}$Al: $1s^2 2s^2 2p^6 3s^2 3p^1$

$_{52}$Te: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10} 5s^2 5p^4$

c) The *d*-Block Elements:

Also known as transition elements. These are the elements of Group 3 to 12 in the center of the periodic table. These elements have the general outer electronic configuration $(n\text{-}1)d^1ns^2$ to $(n\text{-}1)d^{10}ns^2$ and are classified as the transition metals.

Example:

$_{23}$V: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$

d) The *f*-Block Elements:

The elements, whose valence electrons lie in the *f* subshell are known as *f*-block elements. These are shown at the bottom of the periodic table. They are characterised by the outer electronic configuration $(n\text{-}2)f^{1\text{-}14}\ (n\text{-}1)d^{0-1}ns^2$. There are two inner transition series:

a- The lanthanide series: lanthanide (La) through lutetium (Lu)

b. The actinide series: actinide (Ac) through lawrencium (Lr)

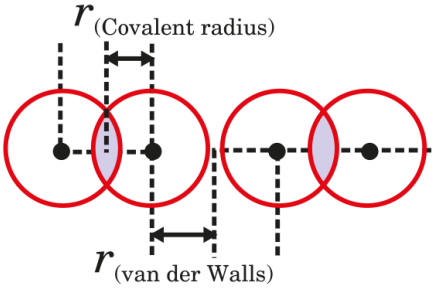
Example:

$_{71}$Lu:$_{54}$[Xe] $6s^2\ 4f^{14}\ 3d^1$

IV.3. Periodic variations in element properties:

IV.3.1. Atomic Radius: There are two common ways in which we can define atomic radius.

a) The covalent radius (r_{cov}): is defined as the half-distance between the nuclei of two atoms of the same element joined in a single covalent bond.



b) van der Waal's Radius (r_{vdw})

Van's radius is defined as one-half the distance between the centres of nuclei of two nearest like atoms belonging to two adjacent molecules of the element in the solid state.

Example: The values of the atomic radii of some elements are given in Table IV.1.

Table IV.1: Some atomic radii (in nm)

Li 0.163	**Be** 0.109	…	**B** 0.082	**C** 0.065	**N** 0.055	**O** 0.047	**F** 0.041	**Ne** 0.036
Na 0.217	**Mg** 0.168	…	**Al** 0.137	**Si** 0.115	**P** 0.100	**S** 0.088	**Cl** 0.078	**Ar** 0.071
K 0.332	**Ca** 0.256	...	**Ga** 0.146	**Ge** 0.129	**As** 0.116	**Se** 0.105	**Br** 0.096	**Kr** 0.088

We observe that;

In a period left to right, electrons are pulled close to the nucleus by the increased Z, So atomic radius decreases with increase in atomic number (Z).

In a group top to bottom, atomic radius increases due to successive addition of shell (n increase).

b) Ionic radius:

Ions are not the same size as the atoms from which they are derived, anions being larger and cations smaller, but they follow the same periodic trends.

Table IV.2: Examples of atomic radii and those of the corresponding ions.

Elément	Ion	Z	Atomic radius (A°)	Ionic radius (A°)
Al	Al^{3+}	13	1.43	0.50
Zn	Zn^{2+}	30	1.38	0.74
N	N^{3-}	7	0.92	1.71

We observe that;

Cation radius < Atomic radius – due to more no. of protons than number of electron coloumbic force increases, size decreases.

Anion radius > Atomic radius – Due to more number of electron than number of protons (Electron-Electron repulsion increase, coloumbic force of attraction decreases).

IV.3.2. Ionization Energy (IE):

Is the energy required to remove an electron from a gaseous atom in its ground state. The losing of an electron is an Endothermic process (require energy).

$$X_{(g)} \rightarrow X^{+}_{(g)} + e^{-}$$

The quantity of energy is usually expressed in terms of a mole of atoms (kJ/mole)

First ionization energy (I_1) to remove the 1st electron $X_{(g)} + \rightarrow X^{+}_{(g)} + e^{-}$

Second ionization energy (I_2) to remove a 2nd electron $X^+_{(g)} \rightarrow X^{2+}_{(g)} + e^-$

The energy required to remove the third electron is the third ionization energy, and so on.

The second ionization energy will be higher than the first ionization energy because it is more difficult to remove an electron from a positively charged ion than from a neutral atom. In the same way the third ionization enthalpy will be higher than the second and so on.

Table IV.3: Energies of 1st and 2sd ionization of alkali metals.

Ionization energie (eV)		
	I_1	I_2
Li	5.39	75.6
Na	5.14	47.3
K	4.34	31.8
Rb	4.18	27.4
Cs	3.89	23.4

Fig. IV.3 shows the relationship between the first ionization energy and the atomic number of several elements.

Within a period, As Z increases and electrons are added in the same principal quantum shell (n), the attraction between nucleus and electrons increased. So more energy has to be cost to remove electron. Therefore, in the same period, alkali metal is with the lowest IE and noble gas is with the highest IE

Within a group, As the increasing Z down a group, new electron is added in a new principal shell (n) which increase atomic radius, that is the distance between outer electron and nucleus increased, so attractive force between outer electron and nucleus decreased, hence to remove electron less energy will require.

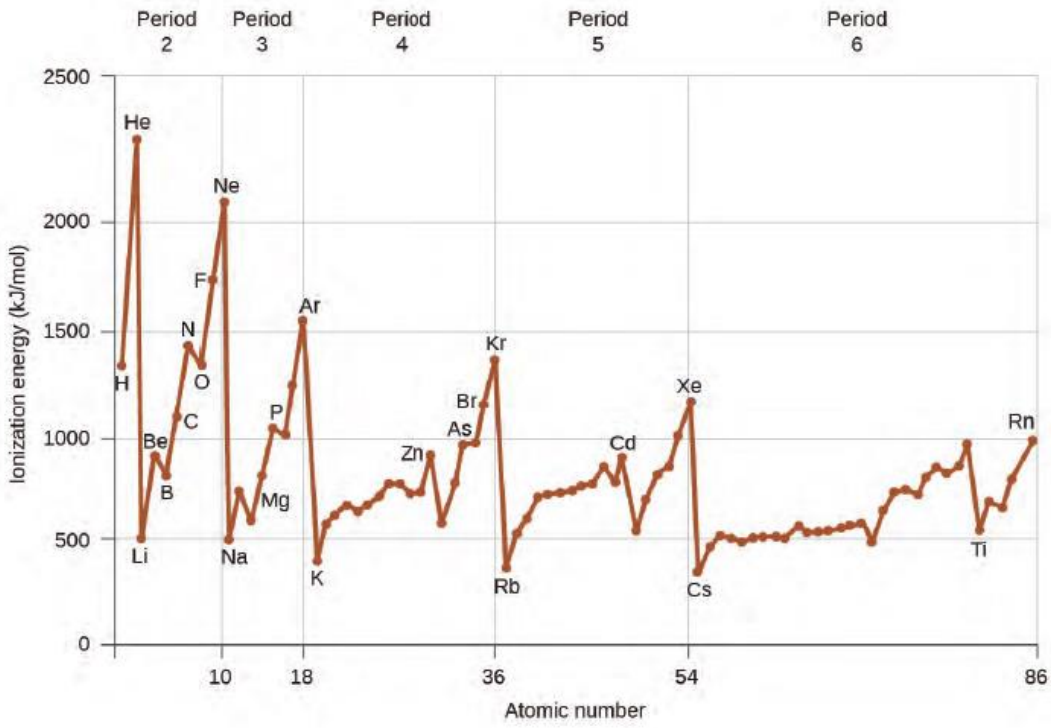


Fig.IV.3: The first ionization energy of the elements in the first five periods are plotted against their atomic number.

Note:

There are some systematic deviations from this trend, however. Note that the ionization energy of $_5$B is less than that of $_4$Be. This means that an *s* electron is harder to remove from an atom than a *p* electron in the same shell. The electron removed during the ionization of Be ([He]$2s^2$) is an *s* electron, whereas the electron removed during the ionization of B ([He]$2s^2 2p^1$) is a *p* electron; this results in a lower first ionization energy for boron. Thus, we see a small deviation from the predicted trend occurring each time a new subshell begins.

Another deviation occurs as orbitals become more than one-half filled. The first ionization energy for $_8$O ([He]$2s^2 2p^4$) is slightly less than that for $_7$N ([He]$2s^2 2p^3$). Looking at the orbital diagram of oxygen, we can see that removing one electron will eliminate the electron–electron repulsion caused by pairing the electrons in the 2*p* orbital and will result in a half-filled orbital (which is energetically favorable).

IV.3.3. Electron Affinity (EA):

The amount of energy released when an electron is added to a neutral gaseous atom to form a negative gaseous ion

$X_{(g)} + e^- \rightarrow X^-(g)$

Electron affinity is expressed in Kj/mole. First electron affinity (EA_1) is to add the 1st e to a neutral gaseous atom to form a uni negative ion.

$X_{(g)} + e^- \rightarrow X^-_{(g)}$

Second electron affinity (EA_2) is to addition of an electron to a anion to form a di-negative ion in gaseous state. $X^-_{(g)} + e^- \rightarrow X^{2-}_{(g)}$

Depending on the element, the process of adding an electron to the atom can be either endothermic (positive) or exothermic (negative). The figure III.4 shows the electron affinities of elements.

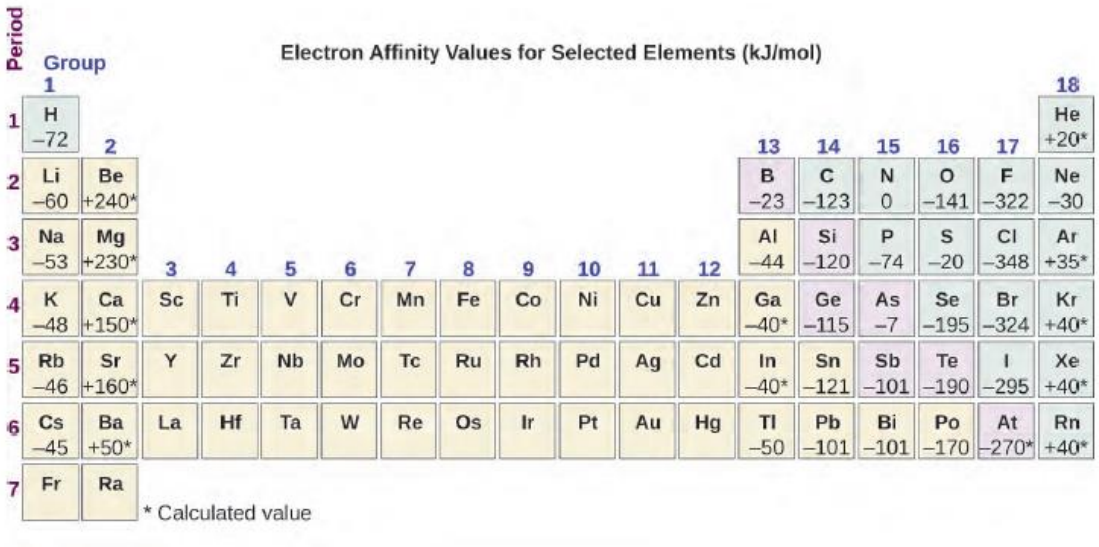


Fig.IV.4: This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.

On moving across a period, the atomic size decreases and hence the force of attraction exerted by the nucleus on the electrons increases. Consequently, the atom has a greater tendency to attract additional electron i.e., its electron affinity increases.

On moving down a group, the atomic size increases and therefore, the effective nuclear attraction decreases and thus electron affinity decreases.

- EA values of metals are low while those of non-metals are high.
- Halogens have high electron affinities. This is due to their strong tendency to gain an additional electron to change into the stable ns2np6 configuration.

IV.3.4. Electronegativity (χ):

Electronegativity is the relative tendency of an atom to attract electrons to itself when chemically bonded with another atom.

$$\overset{+\delta}{A} \longrightarrow \overset{-\delta}{B}$$

A more electronegative element attracts a share pair of electron more than the other. For the measurement of electronegativity, different scale are used, these are discussed below:

a. Mulliken's Electronegativity:

In 1934, Mulliken proposed that the electronegativity of an element is proporsonal to the average of Ionisation energy and electron affinity, both expressed in eV.

$$\chi = \frac{I_1 + EA}{2}$$

b. Pouling's scale of electronegativity:

It is based on the difference in electronegativity between two atoms A (χ_A) and B (χ_B), calculated from the dissociation energy of the diatomic molecules A–A (E_{A-A}), B–B (E_{B-B}) and A–B (E_{A-B}) by the relation:

$$\Delta_{AB} = E_{A-B} - \frac{1}{2}[E_{A-A} + E_{B-B}]$$

Pauling proposed the following relationship:

$$|\chi_A - \chi_B| = \sqrt{\frac{\Delta_{AB}}{96.39}}$$

with Δ_{AB} is the additional binding energy calculated in kJ.mol^{-1}.

As the (unitless) value of χ is relative, Pauling gave the most electronegative element, fluorine, the highest value ($\chi_F \approx 4$), which serves as a reference for determining the electronegativity of the others elements. Following table groups the values of χ for the elements of block *s*, *p* and *d* (Fig.III.5).

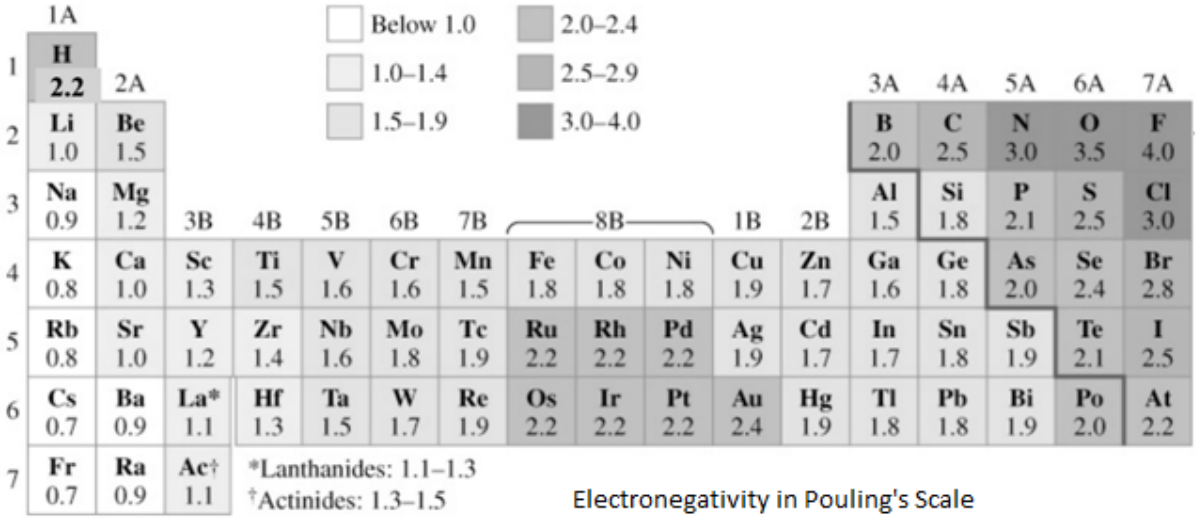


Fig.IV.5: Electronegativity in pouling's scale

Electronegativity increases across period. As Z increases and electrons are added in the same principal quantum shell (n), the attraction between nucleus and electrons increased, hence Z*

increases. Therefore, in the same period from left to right electronegativity increased. Thus, alkali metal is with the lowest electronegativity and halogen has the highest electronegativity. electronegativity decreases moving down a group. As the increasing atomic number down a group, new electron is added in a new principal shell (n) which increase atomic radius, while Z* remain constant per electron at the periphery. So, electronegativity decreases on descending a group. For transitional metals the electronegativity falls slightly on moving down from 3d to 4d series but again get increased for 5d series due to lanthanide contraction. For the post transitional elements the enhanced electronegativity is arises for the 4th period elements due to d contraction.

Chapter V: Chemical bonding

V.1. Introduction:

A chemical bond consists of an attraction between atoms that allows the formation of chemical substances which contain two or more atoms. The bond is caused by the electrostatic force of attraction between opposite charges, either between electrons and nuclei, or as the result of a dipole attraction.

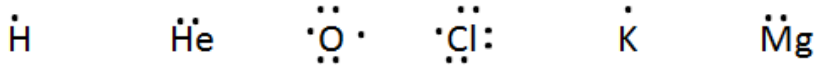
There are many approaches to understand the bonding in molecules as explained in the following topics.

V.2 Lewis approach to chemical Bonding:

Lewis postulated that atoms achieve the stable octet when they are linked by chemical bonds. In the case of sodium and chlorine, this can happen by the transfer of an electron from sodium to chlorine thereby giving the Na^+ and Cl^- ions. In the 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. In the process each atom attains a stable outer octet of electrons.

V.2.1. Lewis Symbols:

Lewis introduced simple notations to represent valence electrons in an atom. These notations are called **Lewis symbols**. For example, the Lewis symbols for the elements of second period are as under:



The number of dots around the symbol represents the number of valence electrons.

V.2.2. Octet Rule

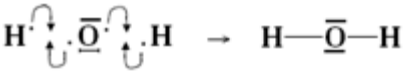
Lewis in 1916 developed an important theory of chemical combination between atoms known as **electronic theory** of **chemical bonding**. According to this, atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have an octet in their valence shells. This is known as **octet rule**.

V.2.3.Lewis structure: A chemical formula (diagram) which shows the arrangement of the atoms and valence electrons in the species.

Example: Water (H_2O). The oxygen nucleus has two H nuclei attached.

$_8O$: $1s^2$, $2s^2$, $2p^4$ and $_1H$: $1s^1$. For the H_2O molecule we have a total of 6 + 2 x 1 = 8 e- of valence. Lewis structure of H_2O:

$_8O$: .... / $2s^2\ 2p^4 \Rightarrow$ 6 valence electrons



V.3.Types of chemical Bond:

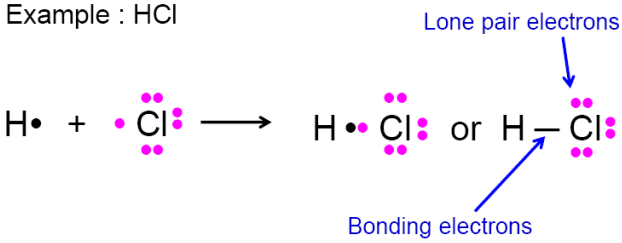
V.3.1. The covalent bond:

The covalent bond formed by sharing one or more pairs of valence electrons between the bonded atoms.

The shared pair is represented as a pair of dots or a line:

A:B or A–B

Example : HCl



V.3.1.1.Type of covalent bond:

a) Single bond: One pair of shared bonding electrons; represented by a line

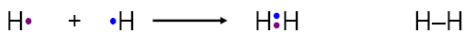
Example: Formation of hydrogen (H_2) molecule.

i. Electronic configuration of H atom is $1s^1$.

ii. Each hydrogen atom share one electron pair between them to attain the helium gas configuration ($1s^2$).

iii. The two hydrogen atoms are thus joined by a single covalent bond.

Lewis structure



b) Double bond: Two pairs of shared bonding electrons; represented by a double line

Example: Formation of oxygen (O_2) molecule.

i. Electronic configuration each oxygen atom is $1s^2\mathbf{2s^2 2p^4}$.

ii. The number of valence electrons in each oxygen atom is 6. (Total valence electrons of both oxygen atoms - 6+6=12).

iii. Each atom **shares two electron pairs** between them to attain the octet number of electrons.

iv. The two oxygen atoms are thus joined by two covalent bonds (double bond).

Lewis structure

c) Triple bond: Three pairs of shared bonding electrons; represented by a triple line

Example: Formation nitrogen (N_2) molecule.

i. Electronic configuration of each nitrogen atom is $1s^2\mathbf{2s^2 2p^3}$.

ii. The number of valence electrons in each nitrogen atom is 5. (Total valence electrons of both nitrogen atoms - 5+5=10).

Lewis structure

iii. Each atom **shares three electron pairs** between them to attain the octet number of electrons.

iv. The two nitrogen atoms are thus joined by three covalent bonds (triple bond).

Note:

-The shared electrons are called a **shared pair** or **bonding pair electrons**

-The outer-level electron pair that is not involved in bonding is called a **lone pair**, or **unshared pair electrons**.

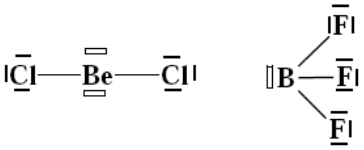
V.3.1.2. Limitations of the Octet Rule

The octet rule, though useful, is not universal. It is quite useful for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table. There are two types of exceptions to the octet rule.

a) The incomplete octet of the central atom:

In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons.

Examples are $BeCl_2$ and BF_3.



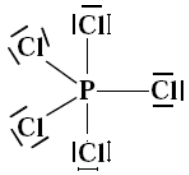
Be and B have 2 and 3 valence electrons only. Some other such compounds are $AlCl_3$ and BCl_3.

b) The expanded octet (Hypervalent Compound):

Elements in and beyond the third period of the periodic table have, apart from 3*s* and 3*p* orbitals, 3*d* orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Obviously the octet rule does not apply in such cases.

Some of the examples of such compounds are: PF_5, SF_6 and PCl_5.

Exemple : PCl_5



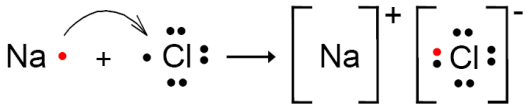
V.3.2. Ionic Bond (Electrovalent Bond):

It is formed by complete transfer of e^-s from one to another atom, so as to complete their octet by acquiring 8 electrons or duplet in case of H_2. and hence acquire the nearest stable noble gas configuration.

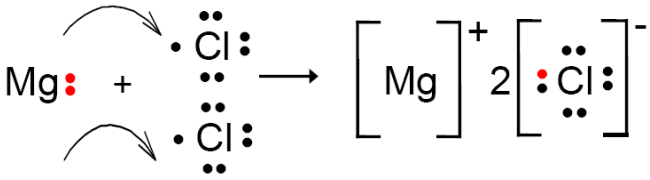
Example: NaCl molecule

The sodium atom loses electron so that its number of electrons become smaller than its number of protons it becomes a positively charged ion. The second atom (Cl) now has more electrons than it has protons and becomes a negatively charged ion.

Example 1: NaCl molecule

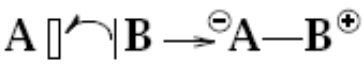


Example 2: $MgCl_2$ molecule



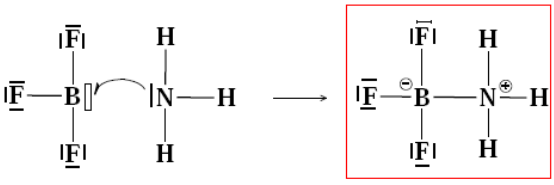
V.3.3. Coordinate bond:

It is formed when shared pair of electrons comes only from one atom. There is no mutual sharing of electrons.



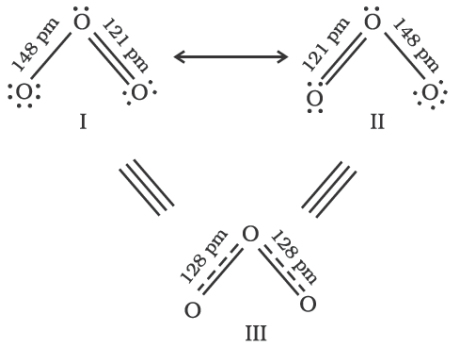
The one that donates electron is called donor atom and other is called acceptor. The bond is also called dative bond.

Example: boron trifluoride BF_3 and ammonia NH_3 form an addition compound.



V.4. Resonance: When a molecule is represented by two or more hybrid structures and that structure are different in the position of electrons not in atoms is known as Resonance.

For example, the ozone, O_3 molecule can be equally represented by the structures I and II shown below:



The two structures shown above constitute the canonical structures or resonance structures and their hybrid i.e., the III structure represents the structure of O_3 more accurately. This is also called **resonance hybrid**. Resonance is represented by a double headed arrow.

V.5. Bond parameters:

V.5.1. Bond Length

Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule. Each atom of the bonded pair contributes to the bond length (figure). In the case of a covalent bond, the contribution from each atom is called the covalent radius of that atom.

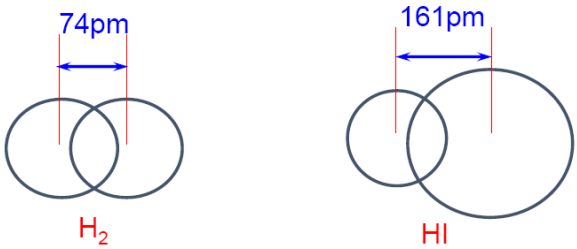


Figure: Bond length in $H_2$and HI

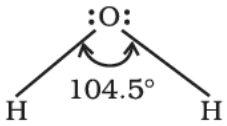
Bond length decreases in the order

single > double > triple

Table V.I: Comparison of the bond length

Bond Type	Bond length (pm)	Bond Type	Bond length (pm)	Bond Type	Bond length (pm)
C – H	107	O – H	96		
C – O	143	C = O	122	C ≡ O	113
C – C	154	C = C	133	C ≡ C	120
C – N	143	C = N	138	C ≡ N	116
N – O	136	N = O	122	N ≡ O	108

V.5.2. Bond Angle: It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion. Bond angle is expressed in degree which can be experimentally determined by spectroscopic methods. It gives some idea regarding the distribution of orbitals around the central atom in a molecule/complex ion and hence it helps us in determining its shape. For example H–O–H bond angle in water can be represented as under:



V.5.3. Bond Energy:

It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state. The unit of bond enthalpy is kJ mol-1. For example, the H-H bond enthalpy in hydrogen molecule is 435.8 kJ mol^{-1}.

$H_{2(g)} \rightarrow H_{(g)} + H_{(g)}$; E = 435.8 kJ mol^{-1}

Similarly the bond enthalpy for molecules containing multiple bonds, for example O_2 and N_2 will be as under:

O_2 $(O=O)_{(g)} \rightarrow 2O_{(g)}$; E= 498 kJ mol^{-1}

$N_2(N \equiv N)_{(g)} \rightarrow N_{(g)} + N_{(g)}$; E= 946.0 kJ mol^{-1}

It is important to note, that larger the bond dissociation enthalpy, stronger will be the bond in the molecule. For a hetero-nuclear diatomic molecules like HCl, we have

$HCl_{(g)} \rightarrow H_{(g)} + Cl_{(g)}$; E = 431.0 kJ mol^{-1}

In case of polyatomic molecules, the measurement of bond strength is more complicated. For example, in case of H_2O molecule, the enthalpy needed to break the two O–H bonds is not the same.

V.6. Valence-Shell Electron-Pair Repulsion Theory (VSEPR):

The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them.

V.6.1. Electron-group Arrangement and Molecular Shape:

The **electron-group arrangement** is defined by both bonding and nonbonding electron groups. The **molecular shape** is the three-dimensional arrangement of nuclei joined by the bonding groups. This is defined only by the relative positions of the nuclei.

Molecular shape is classified using the designation

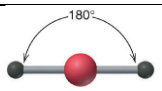
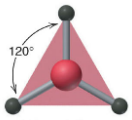
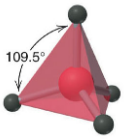
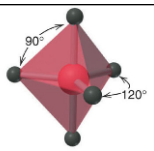
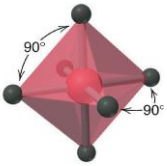
AX_mE_n

A = central atom

X = surrounding atom

E = nonbonding valence-electron group

m and *n* are integers

m+n	Basic geometry	Shape
2	linear	
3	trigonal planar	
4	tetrahedral	
5	Trigonal bipyramidal	
6	octahedral	

V.6.2. Electron-pair Geometry versus Molecular Structure:

We differentiate between these two situations by naming the geometry that includes *all* electron pairs the **electron pair geometry**. The structure that includes only the placement of the atoms in the molecule is called the **molecular structure**. The electron-pair geometries will be the same as the molecular structures when there are no lone electron pairs around the central atom, but they will be different when there are lone pairs present on the central atom.

The following procedure uses VSEPR theory to determine the electron pair geometries and the molecular structures:

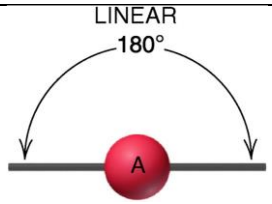
1. Write the Lewis structure of the molecule or polyatomic ion.

2. Count the number of regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one region of electron density.

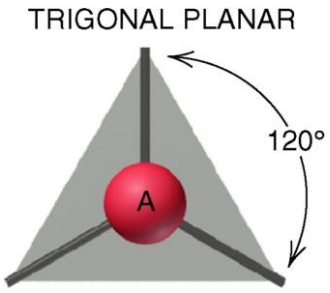
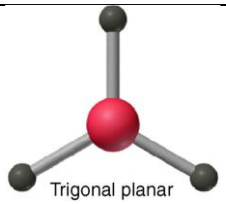
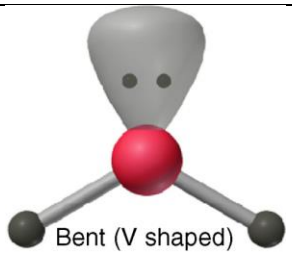
3. Identify the electron-pair geometry based on the number of regions of electron density: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral

4. Use the number of lone pairs to determine the molecular structure. If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds.

a) Linear electron pair geometry (AX_2):

electron pair geometry	**molecular formula**	**molecular structure**	**Exemple**
	**AX_2**		CS_2, HCN, BeF_2

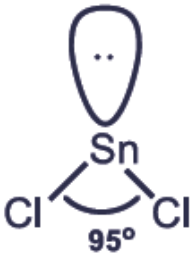
b) Trigonal planar electron pair geometry (AX_3, AX_2E):

electron pair geometry	**molecular formula**	**molecular structure**	**Exemple**
	**AX_3**		SO_3, BF_3, NO_3^-, CO_3^{2-}
	AX_2E		SO_2, O_3, $PbCl_2$, $SnBr_2$

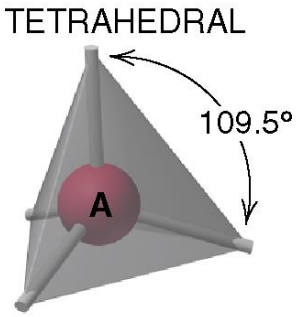
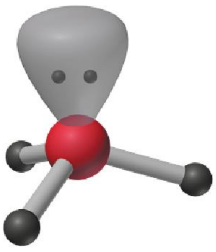
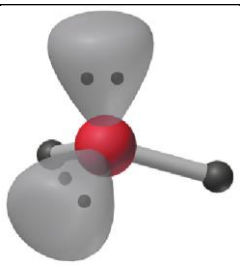
Note:

A lone pair repels bonding pairs more strongly than bonding pairs repel each other. This decreases the angle between the bonding pairs.

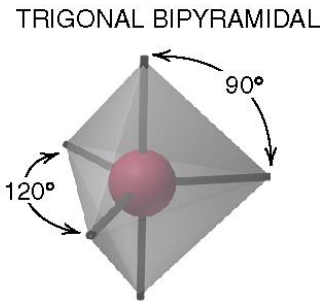
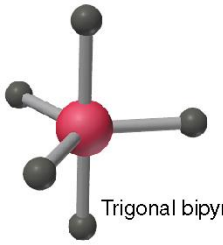
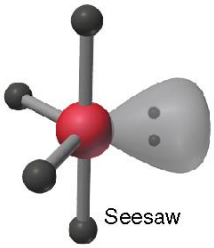
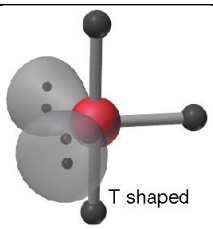
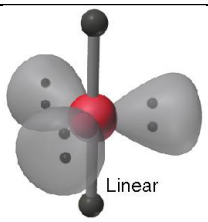
Example: $SnCl_2$



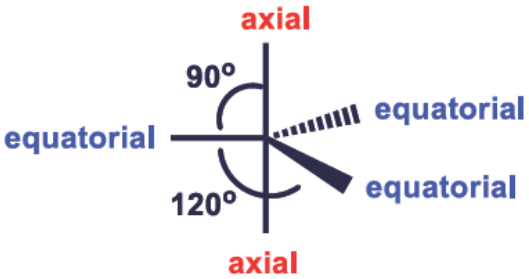
c) Tetrahedral electron pair geometry (AX_4, AX_3E, AX_2E_2):

electron pair geometry	molecular formula	molecular structure	Exemple
	**AX_4**	 Tetrahedral	CH_4, $SiCl_4$, SO_4^{2-}, ClO_4^-
	AX_3E	 Trigonal pyramidal	NH_3, PF_3 ClO_3^-, H_3O^+
	AX_2E_2	 Bent (V shaped)	H_2O, OF_2, SCl_2

d) Trigonal bipyramidal electron pair geometry (AX_5, AX_4E, AX_3E_2, AX_2E_3):

electron pair geometry	molecular formula	molecular structure	Example
	**AX_5**		PF_5, AsF_5, SOF_4
	AX_4E		SF_4, XeO_2F_2 IF_4^+, $IO_2F_2^-$
	AX_3E_2		ClF_3, BrF_3
	AX_2E_3		XeF_2, I_3^-, IF_2^-

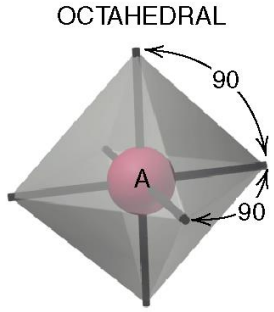
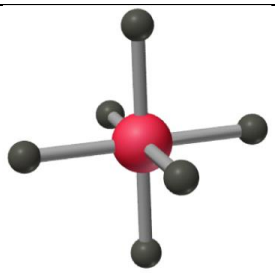
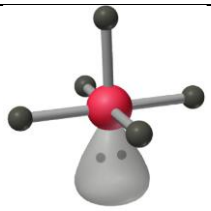
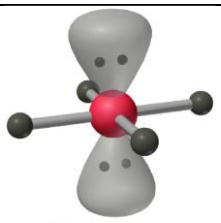
Note: A five electron-group system has two different positions for electron groups, and two ideal bond angles.



Equatorial-equatorial repulsions are weaker than axial-equatorial repulsions.

Where possible, lone pairs in a five electron-group system occupy ***equatorial*** positions.

e) Octahedral electron pair geometry (AX_6, AX_5E, AX_4E_2):

electron pair geometry	molecular formula	molecular structure	Example
	**AX_6**		SF_6, IOF_5
	AX_5E		BrF_5, TeF_5^-, $XeOF_4$
	AX_4E_2		XeF_4, ICl_4^-

V.7. Dipole Moment:

V.7.1. Definition:

An electric dipole is a positive charge, q, and a negative charge, q, of equal magnitude that are separated by a distance (d). A dipole is characterized by its electric dipole moment (μ).

$$\mu = q.d$$

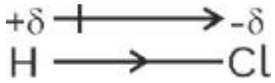
μ can be represented as a **vector**, a quantity having both direction and magnitude. Dipole vectors are shown as arrows pointing along the bond from the less electronegative atom toward the more electronegative atom.

The crossed end of the arrow is the positive end and the arrow head is the negative end.

μ is expressed in Coulomb meters (C.m). This greatness is also often expressed in Debye:

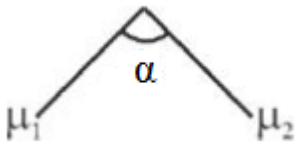
1 Debye = 0.33×10^{-29} C.m

Example:



V.7.2. Molecular Dipole:

The dipole moment for a molecule is the resultant dipole moment obtained from the vector sum of the individual bond dipole moments. Molecules that have a dipole moment are said to be polar. Molecules with μ= 0 are said to be nonpolar.



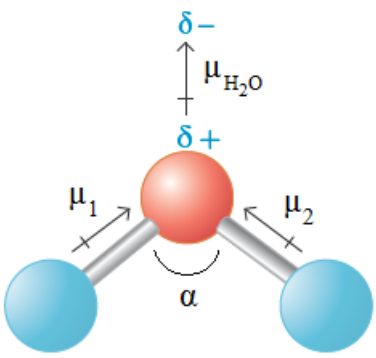
$$\mu = \sqrt{\mu_1^2+\mu_2^2 + 2\,\mu_1\mu_2 cos\alpha}$$

For example, in water molecule (H_2O) there are two identical O-H bonds each of bond moment of 1.5 debye. The net moment of water molecule is 1.84 debye. Hence

$$1.84 = \sqrt{(1.5)^2 + (1.5)^2 + 2 \times 1.5 \times 1.5\ cos\alpha}$$

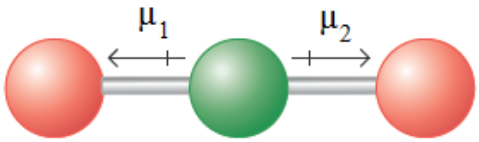
α=104.5°

Hence two O-H bonds are directed at an angle of 104.5° with respect to each other.



In molecule of carbon dioxide, the bond polarities extend equally and symmetrically in different directions, canceling each other's effect and causing each molecule as a whole to be nonpolar.

The dipole moment in case of CO_2 is zero. This is because the two equal bond dipoles point in opposite directions and cancel the effect of each other.



V.7.3.The ionic character of chemical bond (δ):

The ionic character of chemical bond is the ratio between the experimental dipole moment (μ_{exp}) of this bond and the theoretical dipole moment (μ_{theo}) of the corresponding purely ionic bond.

$$\delta = \frac{\mu_{exp}}{\mu_{theo}}$$

μ_{theo}= q.d

Example:

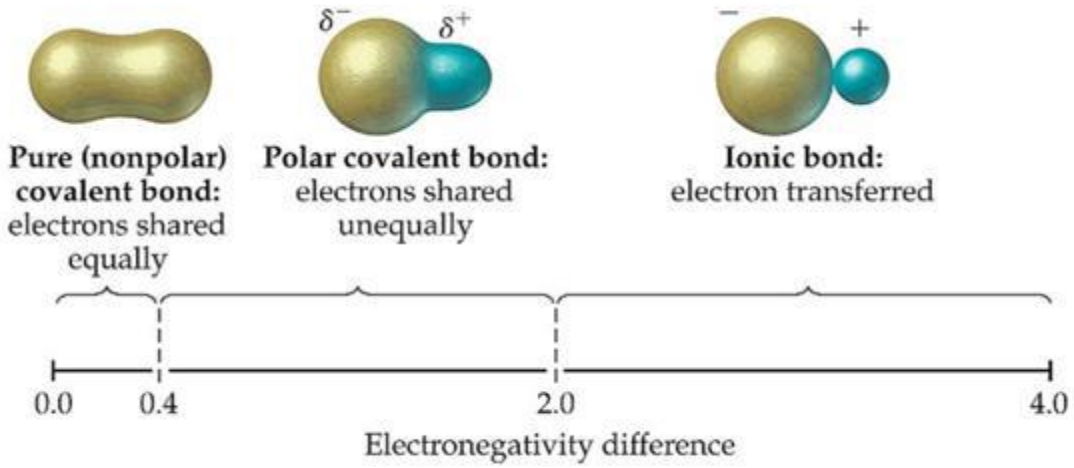
for H — Cl molecule, μ_{exp} = 1.08 Debye. The length of the H — Cl bond is equal to 0.128 nm.

We will therefore have:

$$\delta = \frac{1.08 \times 0.33\ 10^{-29}}{1.6\ 10^{-19} \times 0.128\ 10^{-9}}$$

$\delta = 0.17 \Rightarrow {}^{+0.17}H — Cl^{-0.17}$

Note: Bond polarity is based on difference in electronegativity between atoms in a bond. Bond polarity is a measure of how equally or unequally the electrons in any covalent bond are shared.



V.8. Molecular Orbital Theory (MOT) :

The molecular orbital theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features are:

(a) Just as electrons of any atom are present in various atomic orbitals, electrons of the molecule are present in various molecular orbitals.

(b) Molecular orbitals are formed by the combination of atomic orbitals of comparable energies and proper symmetry.

(c) An electron in an atomic orbital is influenced by one nucleus, while in a molecular orbital it is influenced by two or more nuclei depending upon the number of the atoms in the molecule. Thus an atomic orbital is monocentric, while a molecular orbital is polycentric.

(d) The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals called bonding molecular orbital and anti-bonding molecular orbitals are formed.

(e) The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.

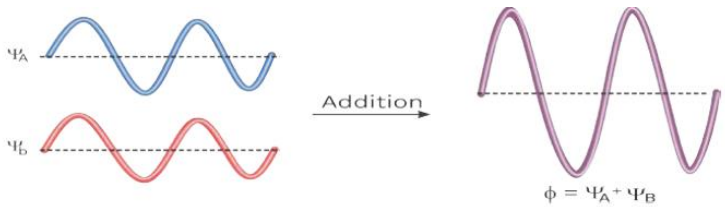
(g) The molecular orbitals like the atomic orbitals are filled in accordance with the Aufbau principle obeying the Pauli Exclusion Principle and the Hund's Rule of Maximum Multiplicity.

V.8.2. Formation of Molecular Orbitals: Linear Combination of Atomic Orbitals (LCAO)

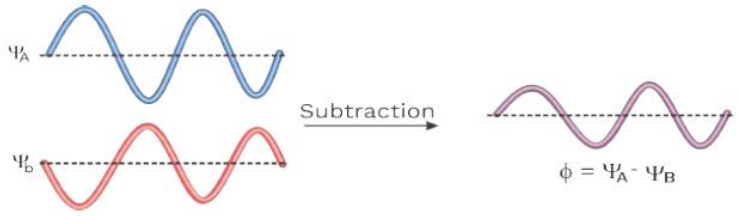
The combination of orbitals to form bonds is viewed as the combination of wave functions.

Atomic wave functions (AOs) combine to form molecular wave functions (MOs).

Addition of AOs forms a bonding MO, which has a region of high electron density between the nuclei.



Subtraction of AOs forms an antibonding MO, which has a node, or region of zero electron density, between the nuclei.



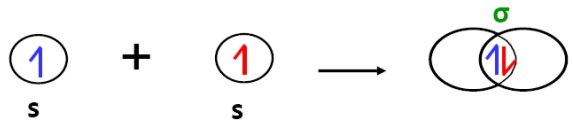
V.8.3. Types of Overlapping and Nature of Covalent Bonds:

The covalent bond may be classified into two types depending upon the types of overlapping:

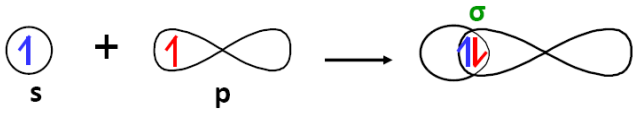
V.8.3.1 Sigma bond (σ):

This is called as head on overlap or axial overlap. This can be formed by any one of the following types of combinations of atomic orbitals.

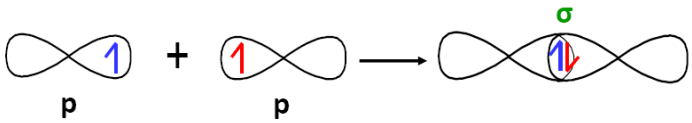
***a) s-s* overlapping** : In this case, there is overlap of two half filled *s*-orbitals along the internuclear axis as shown below :



***b) s-p* overlapping:** This type of overlap occurs between half filled *s*-orbitals of one atom and half filled *p*-orbitals of another atom.

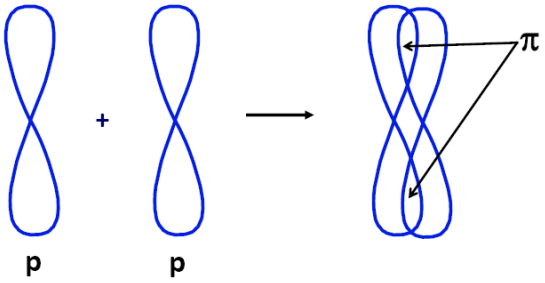


***c) p-p* overlapping** : This type of overlap takes place between half filled *p*-orbitals of the two approaching atoms.



V.8.3.2. Pi(*π*) bond :

A π Bond is a covalent bond formed from the side to side overlap of two p orbitals.



V.8.4. Molecular Orbital Diagrams

An ***MO diagram***, just like an atomic orbital diagram, shows the relative energy and number of electrons in each MO.

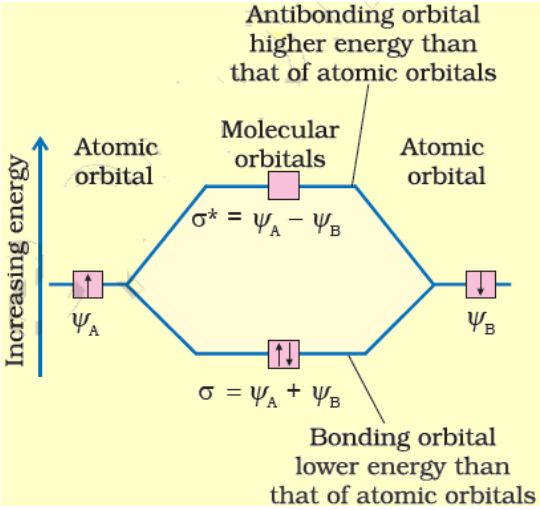
The MO diagram also shows the AOs from which each MO is formed.

• MOs are filled in order of increasing energy.

• An MO can hold a maximum of 2 e- with opposite spins.

• Orbitals of equal energy are half-filled, with spins parallel, before pairing spins.

Electrons are placed in MOs just as they are in AOs. A molecular electron configuration shows the type of MO and the number of e- each contains.



V.8.5. Bond order: Bond order (b.o.) is defined as one half the difference between the number of electrons present in the bonding and the antibonding orbitals i.e.,

$$\text{Bond order (b.o.)} = \tfrac{1}{2}(N_b - N_a).$$

A positive bond order (i.e. Nb> Na) means a stable molecule while a negative (i.e. $N_b < N_a$) or zero (i.e., $N_b = N_a$) bond order means an unstable molecule.

V.8.6. Magnetic nature:

If all the molecular orbitals in a molecule are doubly occupied, the substance is diamagnetic (repelled by magnetic field). However if one or more molecular orbitals are singly occupied it is paramagnetic (attracted by magnetic field), e.g., O_2 molecule.

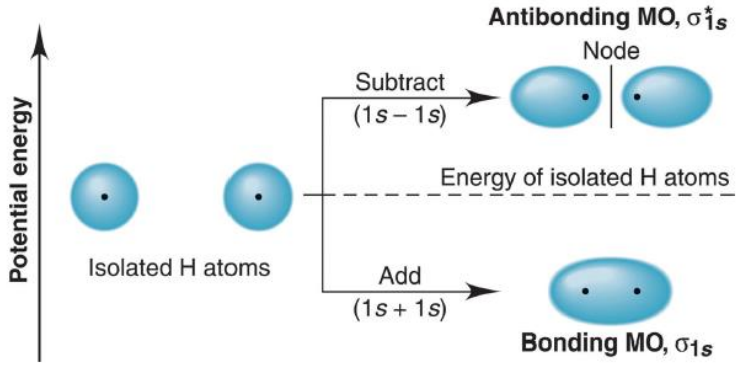
V.8.7. Condition for the combination of atomic orbitals:

The linear combination of atomic orbitals to form molecular orbital takes place only if the following conditions are satisfied.

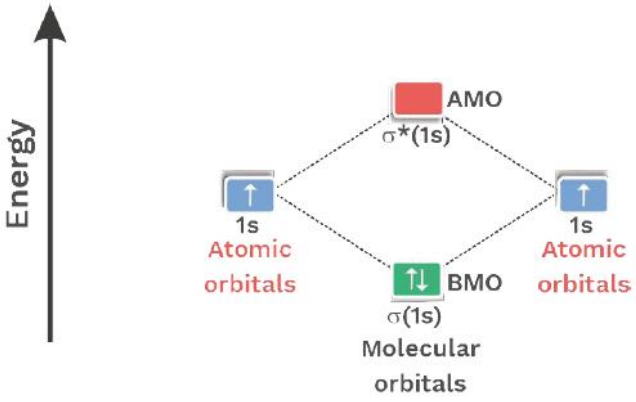
1. The combining atomic orbitals must have the same or nearly the same energy ($\Delta E<12$ eV).
2. The combining atomic orbitals must have the same symmetry about the molecular axis. By convention z-axis is taken as the molecular axis. It is important to note that atomic orbitals having the same or nearly the same energy will not combine if they do not have the same symmetry. For example, 2pz orbitals of one atom can combine with 2pz orbital of the other atom but not with the 2px or 2py orbitals because of their different symmetries.
3. The combining atomic orbitals must overlap to the maximum extent. Greater the extent of overlap, the greater will be the electron-density between the nuclei of a molecular orbital.

V.8.7.1 Combination of s orbitals:

The s orbital has spherical symmetry because its value at a point depends only on the distance of this point from the nucleus.



Example: Hydrogen molecule (H_2)

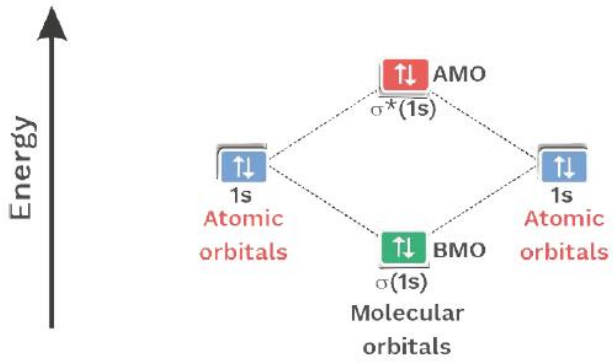


H_2 bond order = 1/2(2 – 0) = 1

H_2 configuration: $(\sigma_{1s})^2$.

This means that the two hydrogen atoms are bonded together by a single covalent bond. Since no unpaired electron is present in hydrogen molecule, therefore, it is diamagnetic.

Example 2: Energy Level Diagram for He_2



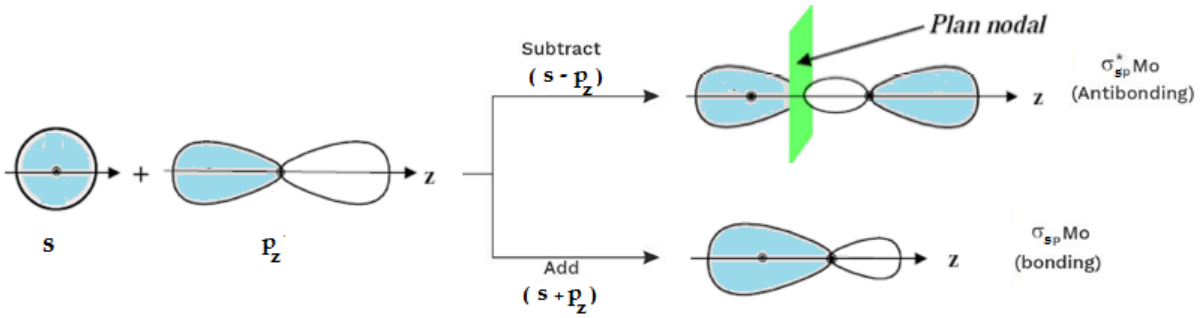
Bond order=1/2(2-2)=0

He_2 configuration: $(\sigma_{1s})^2 (\sigma^*_{1s})^2$

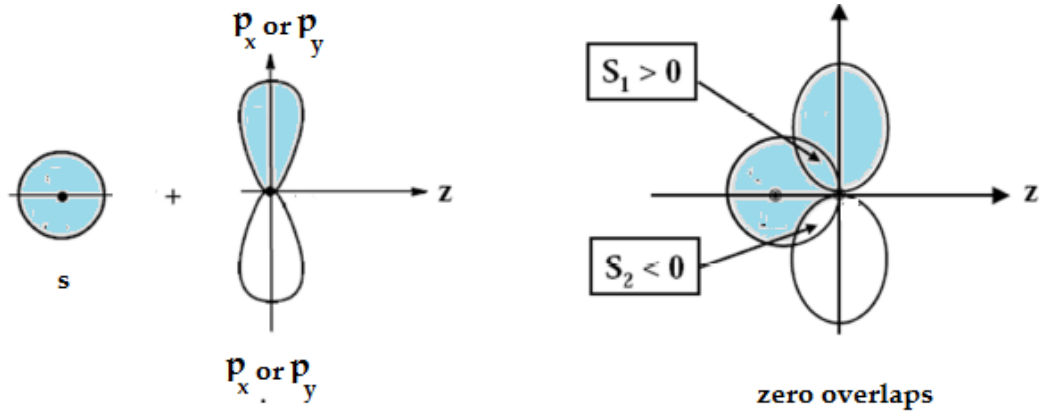
The molecular orbital description of He_2 predicts two electrons in a bonding orbital and two electrons in an antibonding orbital, with a bond order of zero, in other words, no bond. This is what is observed experimentally. The noble gas He has not a significant tendency to form of free atoms.

V.8.7.2. Combination of s and p orbitals.

a) Axial overlap of s orbital and p_z orbital

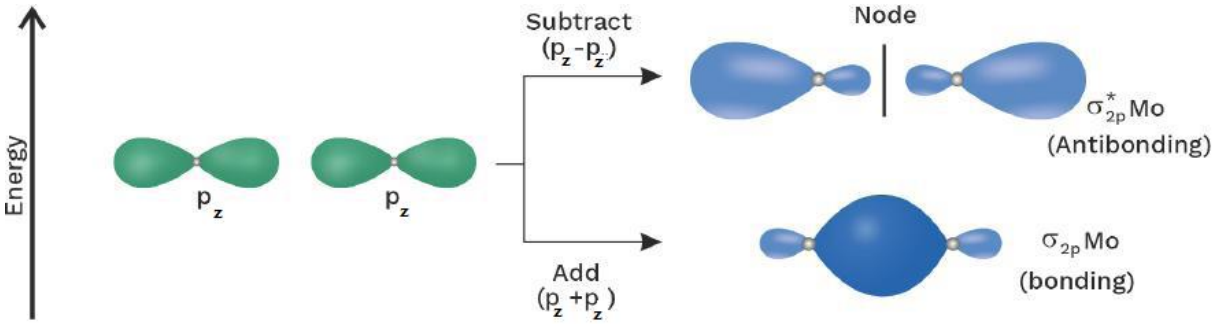


b) Overlap between s orbital and a p_x or p_y orbital.

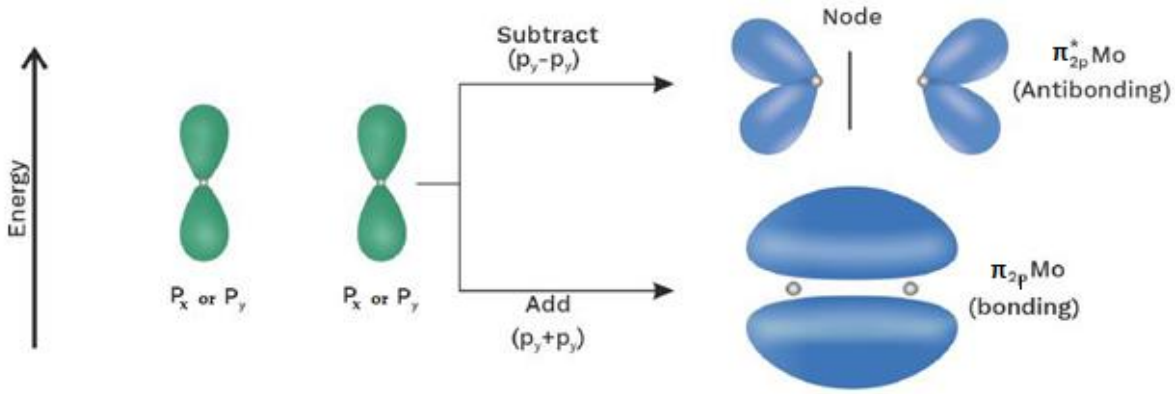


V.8.7.3. Combination of p orbitals:

a) Axial overlap of P_z orbitals :



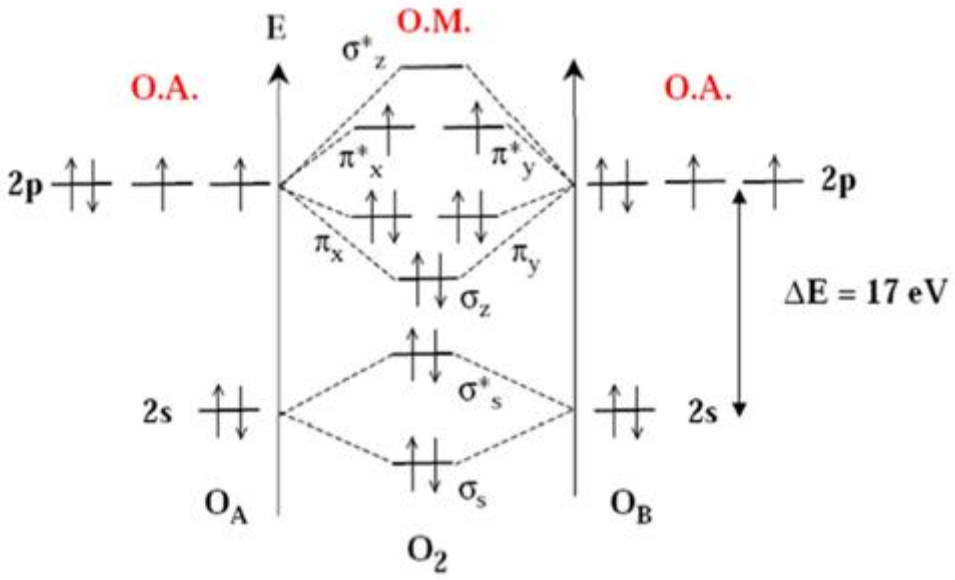
b) Lateral overlap between p_x or p_y orbitals.



Example: Energy Level Diagram for O_2

data : $E_{2s}(O) = -34$ eV ; $E_{2p}(O) = -17$ eV

No combination between 2s and $2p_z$, because $\Delta E > 12$ eV



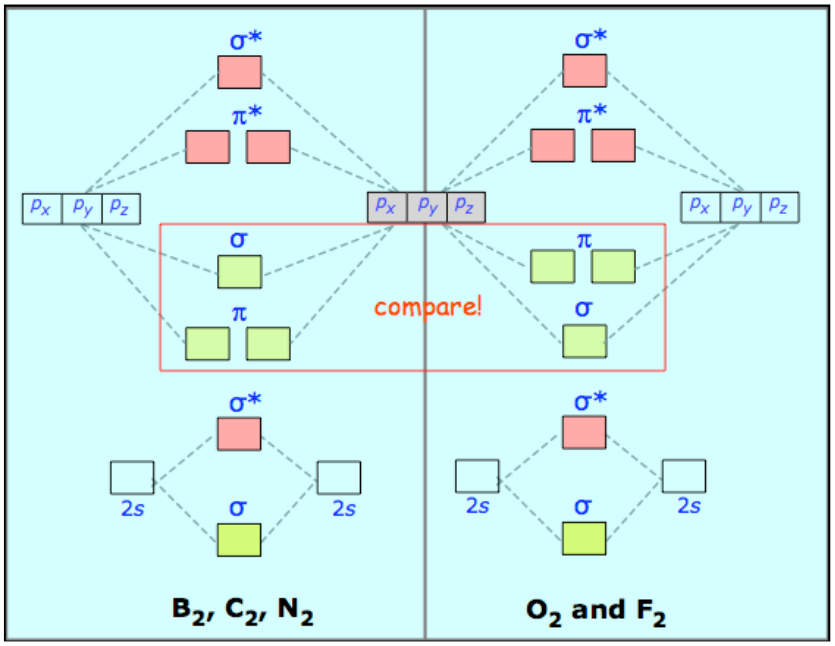
Bond order = ½(10-6)= 2

Magnetic character – paramagnetic (due to unpaired electron)

Electronic configuration

$\sigma_s^2, \sigma_s^{*2}, \sigma_z^2, (\pi_x^2, \pi_y^2), (\pi_x^{*1}, \pi_y^{*1}), \sigma_z^{*0}$

Note: The sp interactions only occur if the difference Δsp between the s and p levels is sufficiently small (ΔE<12 eV). In practice we will admit that such sp interactions exist for B_2, C_2 and N_2 while they do not exist for O_2, F_2 and Ne_2.



V.9. Hybridization:

Valence bond theory (overlapping concept) explains the formation of various molecules but it fails to account for geometry and shapes of various molecules. In order to explain the cases of linear, planar and other such structures, the VBT has been supplemented by the concept of hybridization. This is a hypothetical concept and was introduced by Pauling and Slater.

According to them, the atomic orbitals combine to form a new set of equivalent orbitals known as hybrid orbitals. Unlike pure orbitals, the hybrid orbitals are used in bond formation. The phenomenon is known as hybridisation, which can be defined as the process of intermixing of the orbitals of slightly different energies in the formation of a new set of orbitals of equivalent energies and shape.

V.9.1. Features of Hybrid Orbitals

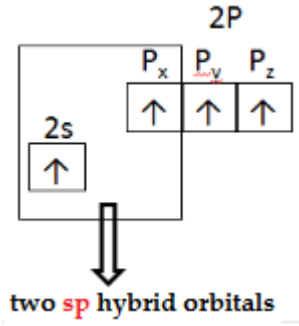
-The ***number*** of hybrid orbitals formed ***equals*** the number of atomic orbitals mixed.

-The ***type*** of hybrid orbitals formed ***varies*** with the types of atomic orbitals mixed.

-The ***shape*** and ***orientation*** of a hybrid orbital ***maximizes*** overlap with the other atom in the bond.

V.9.2. Types of Hybridization

(a) sp hybridization: Mixing of one s+one p=Two sp hybrid orbitals. Each sp hybrid orbital has 50% s-character and 50% p-character.

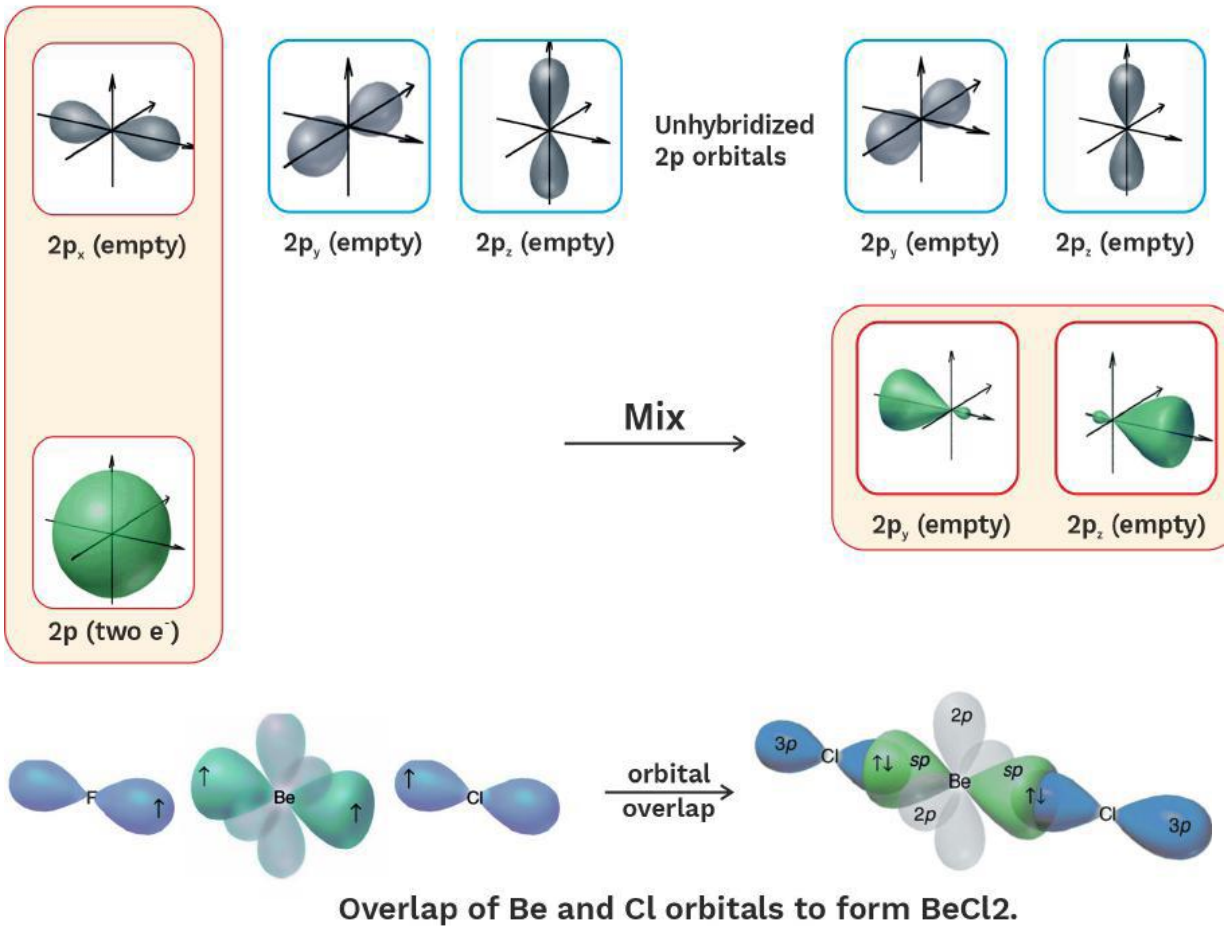


Such a molecule in which the central atom is sp hybridised and linked directly to two other central atoms possesses linear geometry. This type of hybridisation is also known as diagonal hybridisation. The two sp hybrids point in the opposite direction along the Z-axis with projecting bigger positive lobes and very small negative lobes, which provides more effective overlapping resulting in the formation of stronger bonds.

Example $BeCl_2$:

The ground state electronic configuration of Be is $1s^2\ 2s^2$. In the excited state one of the 2s-electrons is promoted to vacant 2p orbital to account for its divalency. Once 2s and 2p-orbitals

get hybridised to form two sp hybridised orbitals. These two sp hybrid orbitals are oriented in opposite direction forming an angle of 180º. Each of the sp hybridised orbital overlaps with the 2p-orbital of chlorine axially and forms two Be-Cl sigma bonds.



Overlap of Be and Cl orbitals to form BeCl2.

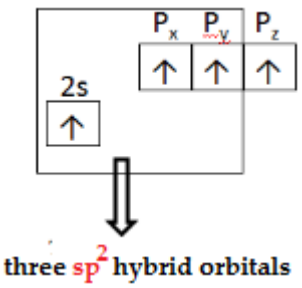
More examples of sp hybridisation:

(a) C ≡ N, H – C ≡ C – H

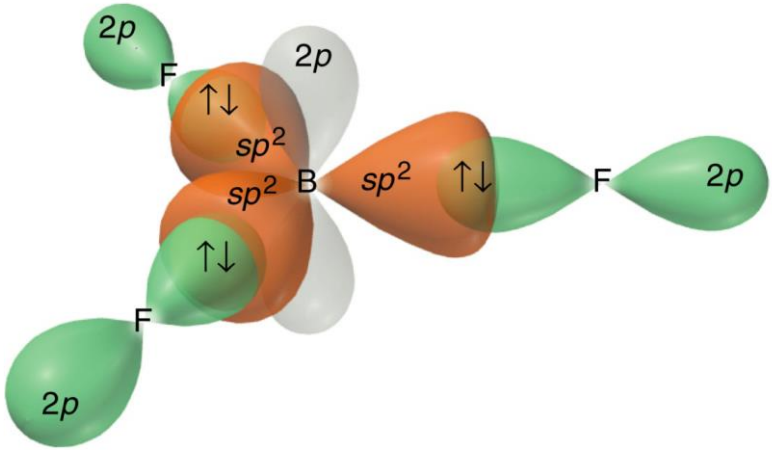
(b) $H_2C = C = CH_2$

(c) N^{3-} (azide ion), BeF_2, $HgCl_2$, NO_2^- (nitronium ion), N_2O

(b) sp^2 hybridization : Mixing of one s+two p=Three sp^2 hybrid orbitals.

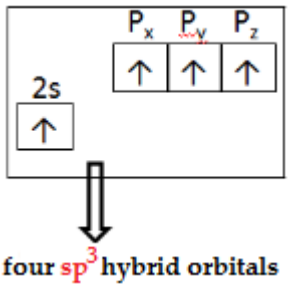


For example, in BF_3 molecule, the ground state electronic configuration of central B(boron) atom is $1s^2\ 2s^2\ 2p^1$. In the excited state, one of the 2s electrons is promoted to vacant 2p orbital. As a result, boron has three unpaired electrons. These three orbitals (one 2s and two 2p) hybridise to form three sp^2 hybrid orbitals. The three hybrid orbitals so formed are oriented in a trigonal planar arrangement and overlap with 2p orbitals of F to form three B–F bonds. Therefore, in BF_3, the geometry is trigonal planar with bond angle of 120º.

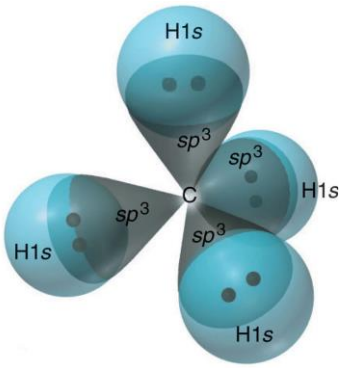


Other examples: SO_2 , $SnCl_2$, $NOCl_2$, O_3 , NO_3 NO^-_2

c) sp^3 hybridization: This type of hybridization can be explained by taking the example of CH_4 molecule in which there is mixing of one s-orbital and three p-orbitals of the valence shell to form four sp^3 hybrid orbitals of equivalent energies and shape. There is 25% s-character and 75% p-character in each sp3 hybrid orbital.

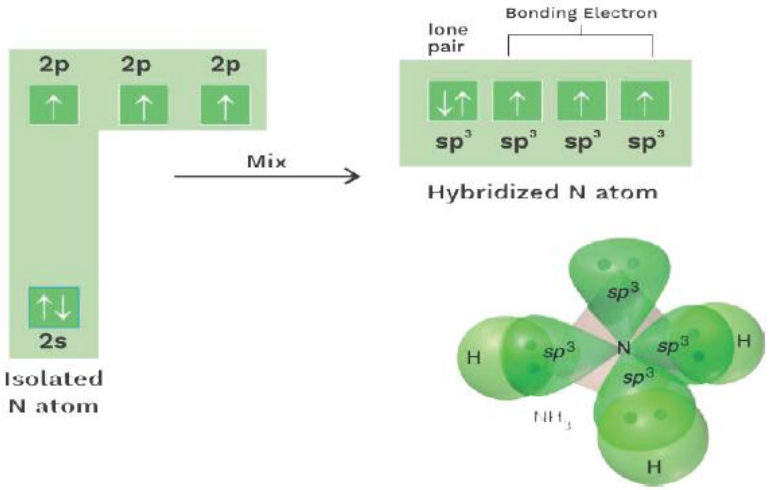


The four sp^3 hybrid orbitals so formed are directed towards the four corners of the tetrahedron. The angle between sp^3 hybrid orbital is 109.5º as shown in figure.

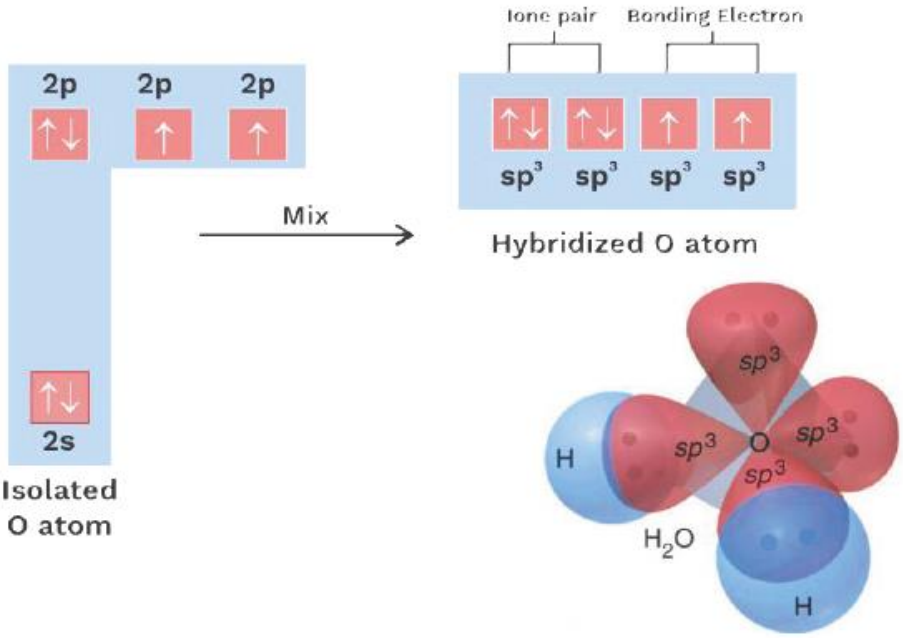


The structure of NH_3 and H_2O molecules can also be explained with the help of sp^3 hybridisation.

NH_3



H_2O



V.9.3. Other types of hybridizations:

To obtain the other types of molecular geometry AX_5 and AX_6 we will use hybrid orbitals involving d-type atomic orbitals: sp^3d for AX_5 and sp^3d^2 or d^2sp^3 for AX_6.

The most frequent cases of hybridization of atomic orbitals correspond to the geometric shapes already described in the VSEPR method (Table below):

Table: Main types of hybridization.

Theoretical form Molecular type Hybridization Main examples			
linear	AX_2	sp	$HC{\equiv}CH$; $BeCl_2$
trigonale planar	AX_3	sp^2	$H_2C{=}CH_2$; BF_3
Tetrahedral	AX_4	sp^3	CH_4 ; NF_3
Bipyramidal trigonale	AX_5	sp^3d ($ds + sp^2$)	PCl_5 ; SF_4
Octahedral	AX_6	sp^3d^2	SF_6 ; IF_5

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