SOME BASIC CONCEPT OF CHEMISTRY

1. Some useful Conversion Factors :

1 Å = 10^{-10} m, 1 nm = 10^{-9} m, 1 pm = 10^{-12} m, 1 litre = $10^{-3}m^3$ = 1 dm^3, 1 atm = 760 mm Hg or torr = 101325 Pa or Nm^{-2}, 1 bar = 10^5 Nm^{-2} = 10^5 Pa, 1 calorie = 4.184 J, 1 electron volt (eV) = 1.6022 × 10^{-19} J , (1 J = 10^7 ergs) 1 cal > 1 J > 1 erg > 1 eV)

2. Dalton's atomic theory :

- All matter is made up of tiny, indivisible aprticles called atoms.
- Atoms can be rearranged, combined or separated in chemical reactions.
- Atoms can neither be created nor destroyed. Further more, atoms cannot be divided into smaller particles.
- Atoms of different elements can combined with each other in fixed whole-number ratios in order to form compounds.
- All atoms of a specific element are identical in mass, size and other properties.

3. Laws of chemical combination :

- **Law of conservation of mass :**

This law states that matter can neither be created nor destroyed in other words, the total mass, that is, the sum of the mass of reacting mixture and the products formed remains constant.

- **Law of definite proportions :**

This law states that the proportion of elements by weight in a given compund will always remain exactly the same.

- **Law of Multiple Proportions :**

This law states that if two elements combine to form more than one comopund, the masses of these elements in the reaction are in the ratio of small whole numbers.

- **Gay Lussac's Law of Gaseous Volumes :**

This law states that when gases are produced or combine in a chemical reaction, they do so in a simple ratio by volume given that all the gases are at the same temperature and pressure.
This law can be considered as the law of definite proportions.

- **Avogadro's Law of chemical combination**

It stated that under the same conditons of temperature and pressure, an equal volume of all the gases contains an equal number of molecules.

4. Gram molar volume (G.M.V.) :

22.4 L of any gas at STP weigh equal to molecular mass expressed in gram . This mass is called Gram Molecular Mass and this volume is called Gram Molecular volume (G.M.V.)

Note : STP conditions are 1 atm pressure and 0° C Temperature. However if the condition taken are 1 bar and 0° C , instead of 22.4 L, we have 22.7 L (1 atm = 1.01 bar).

5. Atomic mass :

It is the average relative mass of an atom as compared with an atom of carbon – 12 isotope taken as 12.

- The mass of 1 atom = atomic mass (in amu)
- The mass of 1 mole atoms = atomic mass (in g)

eg. mass of one O atom = 16 amu
mass of 1 mole O atom = 16 g

6. Calculation of average atomic mass. If an element exist in two isotopes having atomic masses 'm_1' and 'm_2' in the percentage abundance x and y present respectively.

$$\text{average atomic mass} = \frac{m_1 \times x\% + m_2 \times y\%}{100}$$

7. Molecular mass :

Molecular mass of a substance is the average relative mass of its molecules as compared with an atom of C-12 isotope taken as 12.

- The mass of 1 molecule = molecular mass (in amu)
- The mass of 1 mole molecules = molecular mas (in g)

eg.Mass of 1 O_2 molcules = 32 amu
Mass of 1 mole O_2 molecules = 32 gm

8. For atom $\rightarrow$ 1 g atom = 1 mole
For molecule $\rightarrow$ 1 g molecule = 1 mole

9. 1 amu or 1 u = $\frac{1}{12}$ th of the mass of an atom of C-12 = 1.66×10^{-27} kg.

10. 1 mol of $H_2O \neq$ 22400 cc of H_2O (because it is liquid). Instead , 1 mol of H_2O = 18 cc of H_2O (because density of H_2O = 1g / cc)

Calculating number of moles : $n = \frac{w}{m} = \frac{N}{N_A} = \frac{V}{22.4}$

11. Fermi's is a unit of length used for expressing nuclear diameter (1 fermi = 10^{-13} cm = 10^{-15}m) (1 fermi = 1 femto).

12. The number of molecules in one ml of a gas at STP is known as Loschmidt number. Its value = $(6.02 \times 10^{23}) / 22400 = 2.687 \times 10^{19}\ ml^{-1}$.

13. Mass of one mole of electrons = Mass of one e^- × Avogadro's No.

$= (9.11 \times 10^{-31}\ kg) \times (6.02 \times 10^{23})$

$= 5.48 \times 10^{-7}\ kg$

14. Molecular weight (M.W.) = $\dfrac{\text{Mass of one molecule of a substance}}{\text{Mass of one atom of hydrogen}}$

Vapour density (V.D.) = $\dfrac{\text{Mass of a certain volume of gas or vapour}}{\text{Mass of same volume of hydrogen}}$

Molecular weight = 2 × vapour density

M.W. = 2 V.D.

$$\text{V.D.} = \frac{\text{density of gas}}{d_{H_2}}$$

$d_{H_2} = 0.000089$ mg / ml

$$\text{number of mole (n)} = \frac{\text{wt.}}{\text{MW / At wt}}$$

$$(n) = \frac{\text{number of particles}}{N_A}$$

$$n = \frac{\text{volume at STP (in lit)}}{22.4\,\text{litre}} \text{ or } \frac{\text{Volume at STP (in ml)}}{22400\,\text{ml}}$$

$n = M \times V(\text{lit})$

Where, n = number of moles

V = volume in litres

M = molarity

15. Molarity (M) = $\dfrac{\text{No. of moles}}{\text{Litres of solution}} = \dfrac{n}{V}$

Molality (m) = $\dfrac{\text{Moles of solute}}{\text{kg of solvent}} = \dfrac{x}{w}$

Mole fraction = $\dfrac{\text{No. of moles of the component}}{\text{Total no. of moles of all the component}} = \dfrac{n_A}{n_A + n_B}$

% composition = $\dfrac{\text{grams of element}}{\text{grams of total elements in the component}} \times 100$

16. Principle of atom conversion (POAC) :

This states that the total number of atoms of reactants must equal the number of atoms of products.

Mass of atom of element in reactant = Mass of atoms of element in product

Number of atoms of element in reactant = number of atoms of element in product

Moles of atoms of element in reactant = moles of atoms of element in product

Limiting reagent :

If any chemical reaction, the limiting reactant (or reagent) is a substance which is fully absorbed when the chemical reaction is complete. This reagent limits the amount of the product generated and the reaction cannot continue without it.

$$\% \text{ composition} = \frac{\text{grams of element}}{\text{total weight of the compound}} \times 100$$

Percentage yield : Reactants often yield quantities of produts that are less than those calculated based on the formulated chemical reaction.

ATOMIC STRUCTURE

- The word “atom” was given by Ostawald.

Discovery & Their Discoveres

Name of Particles	Scienteist	Mass	Charge
Electron	J.J. Thomson	9.1×10^{-31} kg	-1.6×10^{-19} cb
Proton	Goldstein	1.673×10^{-27} kg	$+1.6 \times 10^{-19}$ cb
Neutron	Chadwick	1.675×10^{-27} kg	Zero
Positron	C.D. Anderson	(same as electron)	same as proton
Anti Proton	Sugrie	(same as proton)	Electron
Neutrino	Pauli	Negligible	Zero
Meson	Yukawa	(200 times the electron)	(+, –, zero)
Isotopes	Soddy		
Isobar	Aston		
Cathode Ray	William Crooke’s		
Anode Ray	GoldStein		
Neucleus	Rutherford		
Atomic No.	Moseley		
Nomenclature of e^-	Stoney		
Charge of e^-	Millikan		
Specific charge on e^- (e/m)	J.J. Thomson		

- ## Important Definations :

(i) Atomic number (Z) = no. of protons

(ii) Mass no. (A) = number of (n + p)

(iii) Isotopes = Same Z + Different A

(Iv) Isobar = Same A + Different Z

(v) Isotones / Isoneutronic / Isotonic = same no. of neutrons

(vi) Isodiaphers = Same (number of neutrons – number of protons)

Where n = neutron and p = proton

(vii) Isosters = Molecules with same no. of atoms and electrons.

(viii) Isoelectronic = Same no. of e^-s.

Electromagnetic Radiations

- The electric & magnetic components of wave have same wavelength, frequency speed and amplitude but they vibrate in two mutually perpendicular planes.
- EM waves do not need any medium for propagation and all EM waves travel with same velocity (3×10^8 ms^{-1}).
- Relation between frequency (v), wavelength (l), wave number $(\bar{v})$ and time period (T).
  - $c = v\lambda$
  - $\vec{v} = \frac{1}{\lambda} = \frac{v}{c}$ $\quad$ $1\ cm^{-1} = 100\ m^{-1}$
  - $T = \frac{1}{v} = \frac{\lambda}{c}$

Electromagnetic Spectrum

The arrangment of various types of electromagnetic radiations in the order of their increasing or decreasing wavelength or frequency is known as electromagnetic spectrum.

Radition	Wavelength (Å)	Frequency (Hz)
Gamma rays	0.01 to 0.1	3×10^{19} to 3×10^{20}
X-rays	0.1 to 150	2×10^{16} to 3×10^{19}
UV radiations	150 to 3800	7.9×10^{14} to 2×10^{16}
Visible rays	3800 to 7600	3.95×10^{14} to 7.9×10^{14}
Microwaves	6×10^6 to 3×10^9	1×10^5 to 1×10^9

Plancks Quantum theory (Importatant Formulae)

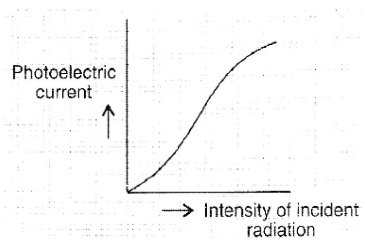
- $E = hv$ (E = Energy of one photon)

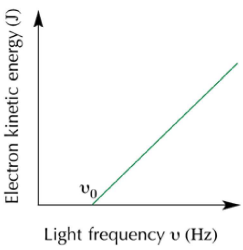
  or $\quad E = hv = \frac{hc}{\lambda} = hc\bar{v}$
- Total energy transfered = N × Energy of one photon.

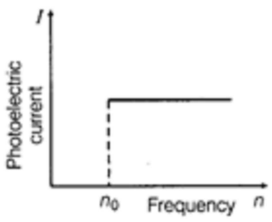
  $E_r = N \times hv = N \times \frac{hc}{\lambda} = N \times hc\bar{v}$

  Where h = planck constant $= 6.626 \times 10^{-34}$ Js
  $= 6.626 \times 10^{-27}$ erg s

Photoelectric effect







E_{photon} = Thereshold Energy (work function) + KE
$E_{photon} = h\nu_0 + KE$
Where,
h = planck's constant
ν_0 = threshold frequency
KE = kinetic energy

$$h\nu = h\nu_0 + KE$$

$$h\nu = h\nu_o + \frac{1}{2} m_e v^2$$

or $$KE = h(\nu - \nu_0)$$

Bohr's Model

Applicable for single e^- species only like H, He^+, Li^{+2} , Be^{+3} , Na^{+10} etc.
Related with particle nature of electron.
Based on Plancks Quantum theory.

Important Formula :

Angular momentum in an orbit is quantized. $mvr = n \times \frac{h}{2\pi}$

Where,

n = number of corresponding energy of orbit 1, 2, 3, ...

m = mass of the electron

v = velocity of electron

r = readius of orbit

h = planck's constant

Radius of bohr orbit = $r = 0.529\ n^2/zÅ$

n = number of corresponding energy of orbit
z = atomic number
where 0.529 Å = a_0 is called atomic unit of length (Bohr) .
Velcoity of electron in Bohr orbit.

$$v = \frac{2\pi KZe^2}{nh}$$

On solving $$v = 2.18 \times 10^6 \frac{Z}{n} m/s$$

n = number of corresponding energy of orbit
z = atomic number

$$v = 2.18 \times 10^8 \frac{Z}{\nu} cm/s$$

n = number of corresponding energy of orbit
z = atomic number
Energy of electron in Bohr orbit

Potential energy (PE) = $-\frac{KZe^2}{r}$ i.e., At r = ∞, PE = 0

k = constant = $\frac{1}{4\pi\varepsilon_0}$

z = atomic number

Kinetic energy (KE) = $\frac{1}{2}\frac{KZe^2}{r}$ i.e., At r = ∞, KE = 0

Total energy (TE) = $-\frac{2\pi^2 mK^2z^2e^4}{n^2h^2}$

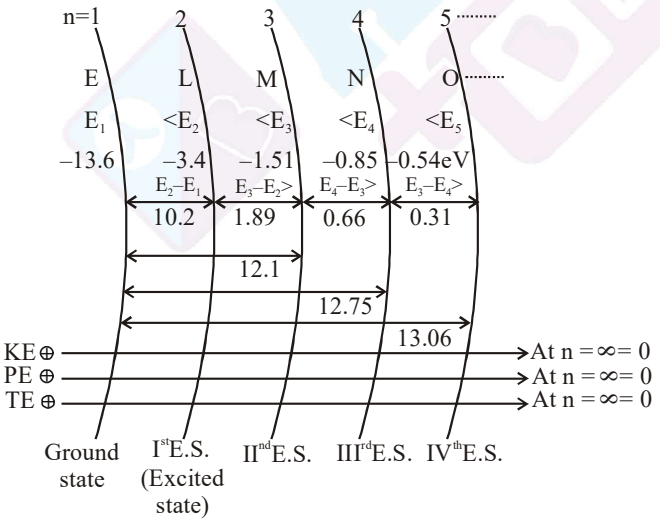
On solving TE $= -2.18 \times 10^{-18}\frac{z^2}{n^2}$ J/atom

$= -13.6 \times \frac{z^2}{n^2}$ eV/atom

$= -313.6 \times \frac{z^2}{n^2}$ Kcal/mol

$= -1313{,}6 \times \frac{z^2}{n^2}$ KJ/mol

Relation between TE, PE and KE = PE = 2 × TE
= TE = –KE
= PE = –2KE



Important Shortcuts

Transition energy ⇒ The energy change associated with a transition is related to the frequency of the electromagnetic wave.

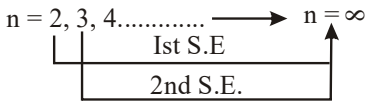
$E = h\nu$
Where, h = planck constant,
n = the freqeuncy of the wave is related to its wavelength.
T.E. of any H-like species = TE or Hydrogen × Z^2 (For same orbit)
ΔE for H like species = ΔE (For hydrogen) × Z^2 (For same transition)

Energy in n^{th} orbital for H like species = $\frac{E_1}{n_1}$ [For same atom]

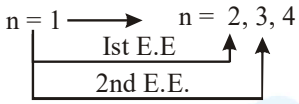
(I.E.) Ionisation Energy $\Rightarrow$ n = 1 $\rightarrow$ n = ∞
Ionisation energy $\Rightarrow$
The amount of energy required to remove an electron from an isolated gases atom.

$Na \xrightarrow{I.E.} Na^+ + e^-$

(S.E) Separation Energy



(E.E.) Excitation Energy -

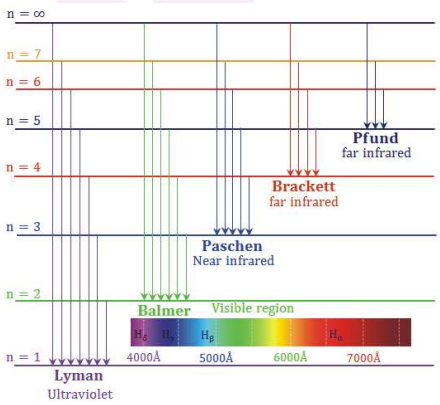


Spectrum (Important points)

Continous emission spectrum is given by incandescent sources.
Emission line spectrum is given by atoms.
Emission band spectrum is given by molecules.
More lines are observed in emission spectrum than absorption specturm.

Hydrogen Spectrum (n_2) (n_1)

Lyman $\longrightarrow$ Any higher orbit $\longrightarrow$ 1 [Found in U.V. region]
Balmer $\longrightarrow$ Any higher orbit $\longrightarrow$ 2 [Found in Visible region]
Paschen $\longrightarrow$ Any higher orbit $\longrightarrow$ 3 [Found in I.R. region]
Bracket $\longrightarrow$ Any higher orbit $\longrightarrow$ 4 [Found in I.R. region]
P fund $\longrightarrow$ Any higher orbit $\longrightarrow$ 5 [Found in I.R. region]



Rydberg Equation :

$$\bar{v} = \frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \left[\text{Where C = velocity of electromagnetic waves}\right]$$

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

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

Where R_H = Rydberg constant = 109678 cm^{-1}
= 10967800 m^{-1} $\boxed{\frac{1}{R_H} = 912Å}$

$R_H Ch$ = Energy of Ist orbit of hydrogen

$R_H Ch\ Z^2$ = Energy of Ist orbit of any hydrogen like species.

Important Point :

α line / First line/starting line/Initial line (First line of any series)

Last line/limitting line/ marginal line (Last line of any series)

Total number line in a sample of atoms (For $n_2 \rightarrow n_1$)

(T.E.L.) Total Emission lines = $\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$

But for ($n \rightarrow 1$), T.E.L. = $\frac{n(n-1)}{2}$

Maximum and minimum wavelength :

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

		For $\lambda_{max.}$	For $\lambda_{min.}$	$\lambda_{max.}$	$\lambda_{min.}$
Series	n_1	n_2	n_2		
Lyman	1	2	∞	$\lambda = \frac{4}{R}$	$\frac{1}{R}$
Balmer	2	3	∞	$\frac{36}{5R}$	$\frac{4}{R}$
Paschen	3	4	∞	$\frac{144}{7R}$	$\frac{9}{R}$
Brakett	4	5	∞	$\frac{400}{9R}$	$\frac{16}{R}$
Pfund	5	6	∞	$\frac{900}{11R}$	$\frac{25}{R}$
Humphery	6	7	∞	$\frac{1764}{13R}$	$\frac{36}{R}$

Maximum number of spectral lines = N = $\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$

Maximum number of spectrfal lines for lyman series, lines for any particular series = $n_2 - n_1$.

De-Broglie Equation (Important Formulae)

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

Where h = Planck's constant $\boxed{\because P = mv}$

P = momentum

m = mass

$\lambda = \frac{h}{\sqrt{2mKE}}$

v = velocity

KE = Kinetic Energy

$\lambda = \frac{h}{\sqrt{2mqv}}$ (for e^- if solved) than $\lambda = \sqrt{\frac{150}{V}}$ Å

m = mass

q = charge particle having charge

v = charge particle is accelerate by a potential

Important Points :

When an e^- revolves in orbit then no. of waves made by e^- = orbit number (n).

Frequency of matter waves.

$v = \frac{v}{\lambda} = \frac{vP}{h} = \frac{mv^2}{h} = \frac{2KE}{h}$ [v = frequency]

Electron microscope is on the basis of the wave nature of electron. de-Broglie on the basis of Milikan's oil drop experiment (which showed partical nature) and diffraction study (which showed wave nature) suggested the dual nature of electron.

Heisenberg Uncertainity Principle.

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

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

$v = \frac{\Delta x}{\Delta t}$

$\Delta x = v.\Delta t$

Change in kinetic energy of particle is

$\Delta E = \Delta p.V$

$\Delta p = \frac{\Delta E}{v}$

$\Delta x.\Delta p = v.\Delta t \times \frac{\Delta E}{v}$

$\Delta x.\Delta p = \Delta E.\Delta t$

Then from uncertainty principle.

$\Delta E.\Delta t = h$

$E = \frac{h}{2}$

where Δx = Uncertainity in position
Δv = Uncertainity in velocity
ΔP = Uncertainity in momentum
m = Mass of particles

$\frac{h}{4\pi} = 5.27 \times 10^{-35}$ Js (In SI unit)

Quantum Number

In an atom each shell, subshell, orbital and electron are designated by a set of four quantum numbers respectively.

1. Principal Quantum Number (By Bohr)

Indicates Size and energy of the orbit, distance of e^- from nucleus
Values in = 1,2,3,4,5.....

Angular momentum = $n \times \frac{h}{2\pi}$

Total number of e^-s in an orbit = $2n^2$

Total number of orbitals in an orbit = n^2

Total number of subshell in an orbit = n

2. Azimuthal / Secondary/Subsidiary/Angular Momentum

⇒ Given by = Sommerfeld

⇒ Indicates = Subshells/sub orbit/sub level

⇒ Value ⇒ 0,1.....(n–1)

⇒ Indicates shape of orbital/Subshell

Values of n	Values of l [Shape]	Initial from word
e.g. If n = 4	1 = 0 (s) [Spherical]	Sharp
	1 [p [Dumb bell]	Principal
	2 [d] [Double dumb bell]	Diffused
	3 [f] [Complex]	Fundamental

Total number of e^-s in a sub-orbit = $2(2\ell + 1)$

Total number of orbitals in a sub - orbit = $(2\ell + 1)$

Orbital angular momentum = $\sqrt{\ell(\ell+1)}\frac{h}{2\pi} = \hbar\sqrt{\ell(\ell+1)}h$

h = Plank's cosntant

For H & H-like species all the subshell of a shell have same energy

i.e., 2s = 2p

3s = 3p = 3d

3. Magnetic Quantum number (m)

Given by linde

Indicates orientation of orbitals ie., direction of e^- density

value of m = $-\ell$.....0.....$+\ell$

Maximum no of e's in an orbital = 2 (with opposite spin)

m for p sub shell =

p_x	p_y	p_z
-1	0	$+1$

m for d sub shell =

dxy	dyz	dzx	dx^2-y^2	dz^2
-2	-1	0	$+1$	$+2$

4. Spin Quantum no. (m_x or s)

Given by Uhlenbeck & Goldsmit

Value of s = $\pm\frac{1}{2}$

Total values of spin in an atom = $\pm\frac{1}{2}$ × number of unpaired e^-

Since Angular momentum = $\sqrt{s(s+1)}\frac{h}{2\pi}$

Rules for filling of Orbits :

1. Aufbau principle : The electron are filled up in increasing order of the energy in subshells.

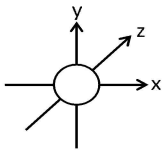
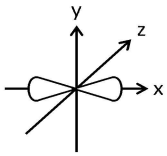
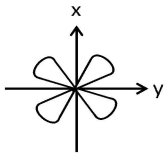
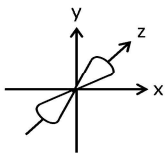
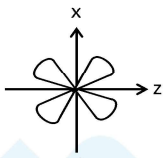
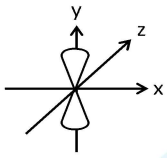
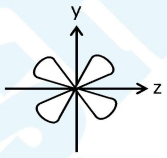
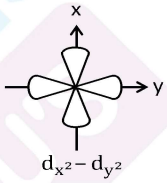
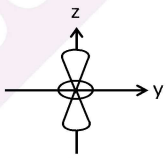
$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14} 6d^{10}$

2. (n + ℓ) rule : The subshell with lowest (n + ℓ) values is filled up first, but when two or more subshell have same (n + ℓ) value then the subshell with lowest values of n is filled up first.

3. Pauli exclusion principle : Pauli stated that no two electrons in an atom can have same values of all four quantum numbers.

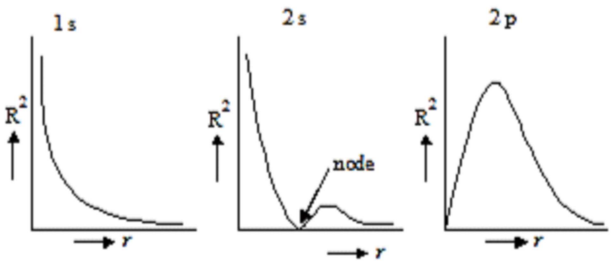
4. Hund's rule of maximum multiplicity : Electrons are distributed among the orbitals of subshell in such a way as to give maximum number of unpaired electrons with parallel spin.

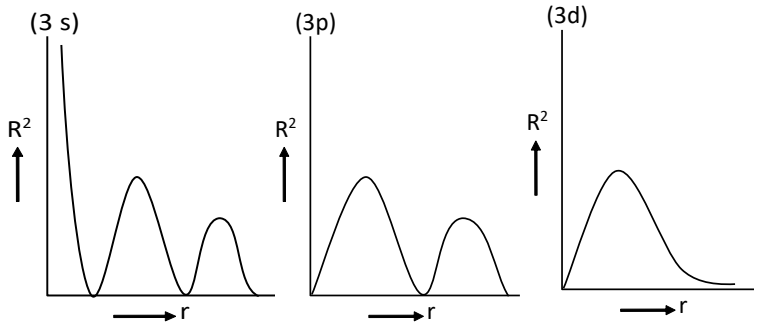
5. Shapes of orbitals :

s	p	d
Spherical	dumbbell shaped (Two lobes symmetrical)	Clover leaf shape or double dumbbell
 1s atomic orbital	 p_x	 d_{xy}
	 p_z	 d_{zx}
	 p_y	 d_{yz}
		 $d_{x^2-y^2}$
		 d_{z^2}

Nodes are the spaces where the probability of finding the electron is 0.
To find the number of nodes in an orbital is given as follows :
Number of angular nodes = ℓ
Number of radial nodes = n – 1 – ℓ
Total number of nodes = n – 1

6. Probability distribution : Probability distribution is the function that gives the probabilities of occurence of different possible outcomes for an experiment





Schrodinger wave equation

$$\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\,\Psi = 0$$

K.E. P.E. Total energy

A particle differential shows how a function depends on one variable when several are changing.

Exchange energy :

Exchange energy is the energy released when two or more electron with the same spin-exchange their position in the degenerate orbitals of a subshell.

Number of electron exchange possible = $\frac{n_A(n_A - 1)}{2} + \frac{n_B(n_B - 1)}{2}$

7. Exceptional electronic configuration :

Element	Symbol	Atomic number	Electronic configuration
Copper	Cu	29	[Ar] $4s^1 3d^{10}$
Chromium	Cr	24	[Ar] $4s^1 3d^5$
Niobium	Nb	41	[Kr] $5s^1 4d^4$
Molybdenum	Mo	42	[Kr] $5s^1 4d^5$
Ruthenium	Ru	44	[Kr] $5s^1 4d^7$
Rhodium	Rh	45	[Kr] $5s^1 4d^8$
Palladium	Pd	46	[Kr] $4d^{10}$
Silver	Ag	47	[Kr] $5s^1 4d^{10}$
Platinum	Pt	78	[Xe] $6s^1 4f^{14} 5d^9$
Gold	Au	79	[Xe] $6s^1 4f^{14} 5d^{10}$
Lanthanum	La	57	[Xe] $6s^2 5d^1$
Cerium	Ce	58	[Xe] $6s^2 4f^1 5d^1$
Gadolinium	Gd	64	[Xe] $6s^2 4f^7 5d^1$
Actinium	Ac	89	[Rn] $7s^2 6d^1$
Thorium	Th	90	[Rn] $7s^2 6d^2$
Protactinium	Pa	91	[Rn] $7s^2 5f^2 6d^1$
Uranium	U	92	[Rn] $7s^2 5f^3 6d^1$
Neptunium	Np	93	[Rn] $7s^2 5f^4 6d^1$
Curium	Cm	96	[Rn] $7s^2 5f^7 6d^1$
Lawrencium	Lr	103	[Rn] $7s^2 5f^{14} 7p^1$

The exactly half-filled & fully filled orbiatls have greater stability than other configuration. The reason for their stability are symmetry & exchange energy. The electron present in the different orbital of the same sub-shell can exchange their positions.

CHEMICAL BONDING

Introduction :

Force of attraction exist between various atoms to hold them in a molecule.

Reason for chemical bonding : To attain the maximum stability (inert gas configuration)

Condition for Chemical bonding :

(a) Force attraction > force of repulsion

(b) Potential energy should be minimum

Lewis octet rule : Every atom try to attain $8e^-$ in their outermost oribt next to the nearest inert gas configuration by donating, gaining or sharing the electron.

Exception of Lewis law :

1. Electron deficient molecule : Compound in which central atom has less then $8e^-$ in its valence shall.

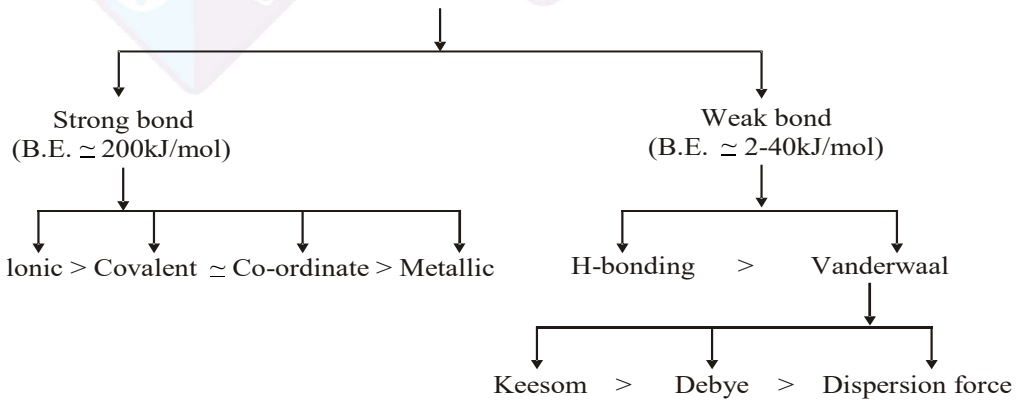
For example BeF_2, $BeCl_2$, BeI_2, BH_3, BF_3, BCl_3, BBr_3, $AlCl_3$ etc.

2. Electron rich molecule : Compound in which central atom has more then $8e^-$ in the outermost shall.

For example IF_7, SF_6, PCl_5, XeF_6 etc.

3. Odd electron molecule: The compound in which central atom has odd number of electron in their valence shall. e.g. NO, ClO_2, NO_2.

4. H, He, Li, never obeyed octet rule.



Ionic bond :

(a) Bond between cation & anion.
(b) Bond between metal & non-metal.
Except : LiCl, $MgCl_2$, $AlCl_3$, BeO etc.
(c) $\Delta EN > 1.7$

Condition for Ionic Bond formation :

(a) Size of metal should be large
I.P. should be low.
(b) Size of non-metal should be small.
E.A. should be more.
(c) Lattice energy should be high.

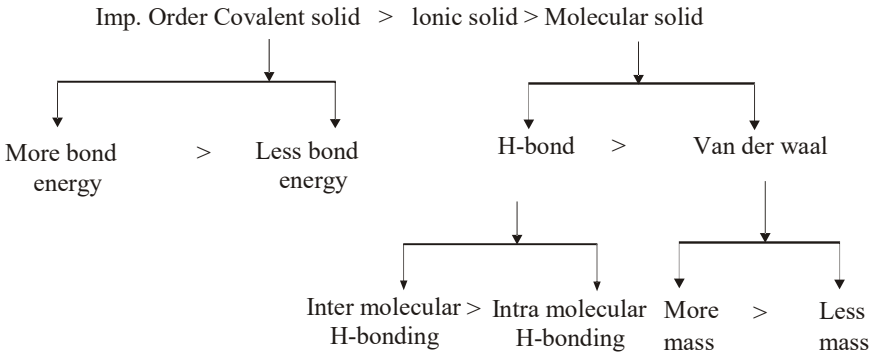
Energy involved in ionic bond formation (Born haber cycle)

ΔH = (S.E.+I.E. + D/2) – (EA +U)
= (Total energy absorbed) – (Total energy released)
For bond formation ΔH =– ive (exothermic process)

Properties of ionic Compound:

1. **Physical state**: Due to strong electrostatic force of attraction between cation & anion these compounds are hard, crystalline & brittle.
2. **Isomorphism:** Two compounds are said to isomorphs if they have similar number of electron i.e. similar configuration aof cation & anion.
e.g. [NaF, MgO] [$CaCl_2$, K_2S]

Melting point & boiling point: High M.P. & B.P. due to presence of strong electrostatic force between ions.
Covalent solid like SiO_2, B_4C, have more m.p. due to 3-D giant network.
Ionic solid like NaCl, Al_2O_3, have more m. p. due to high lattice energy.
Molecular solid like CO_2 have least melting point due to presence of weak van der waal force.
M.P. & B. P.



If molecular mass of two covalent compound are same then ΔEN will be consider.

Imp. order LiH > NaH > KH > CsH

MgO > CaO > BaO

LiCl < NaCl > KCl > RbCl > CsCl

LiF > NaF > KF > RbF > CsF

$Li_2O > Na_2O > K_2O > Rb_2O > Cs_2O$

Among metal halide, fluoride has maximum m.p.

LiF > LiCl > LiBr > LiI

NaF > NaCl > NaI

Solubility : Ionic compounds are souble in polar solvent like water.

Factor affecting solubility:

(i) Dielectric constant α solubility

(ii) Lattice energy $\alpha \frac{1}{\text{solubility}}$

(iii) Hydration energy α solubility

For any compound to be soluble in water

$\boxed{\text{Hydration energy} > \text{Lattice energy}}$

Imp. order:

No compound is 100% ionic. Every compound contain some covalent charactor due to polarization

Due to strong electrostatic force of attraction between cation & anion electron density of anion becomes more in between two ions & covalent character is developed.

$\boxed{\text{Covalent character} \propto \text{Polarization} \propto \text{Zeff of cation}}$

Polarization power (Ionic potential) : capacity of cation to polarize anion represented by (ϕ)

$$\boxed{\phi \propto \frac{\text{Charge on cation}}{\text{Size of cation}}}$$

Polarisability : Tendency of an anion to get polarized by cation.

Factor affecting polarization (fajan's rule)

(i) Charge on cation/anion $\propto$ polarization α covalent character

(ii) Size of cation $\propto \frac{1}{\text{Polarization}} \propto \frac{1}{\text{Covalent Character}}$

(iii) Size of anion $\propto$ polarization α covalent character

(iv) Pseudo inert gas configuration : Cation having pseudo inert gas configuration (i.e. 18 electron in outermost shall have more polarization power due to high Zeff.

CuCl > NaCl (Covalent Character)

[due to poor shielding effect of d e^- in Cu^{+1}]

Some important facts :

(i) Sulphides are less soluble in water than oxides of metal.

(ii) Li salts are soluble in organic solvents.

Polarization increases Covalent character
M.P. decreases $\rightarrow$
NaF > NaCl > NaBr > NaI
NaCl > $MgCl_2$ > $AlCl_3$
$BaCl_2$ > $SrCl_2$ $CaCl_2$ $MgCl_2$ > $BeCl_2$

Covalent bond :
Bond between two highly electronegative element
Mutual sharing of electron takes place.

Orbital Concept of Covalent Bond :

An orbital can accomodate at the most 2 electrons with opposite spin.
Only those orbitals will participate in bond formation which have unpaired electron.
Empty orbital accepts two electrons to complete the orbital.
Due to presence of vacant d-orbital elements can expand their octet in the presence of highly eletronegative element like F, Cl, O, N etc.
PCl_5, SF_6, IF_7, is possible but NCl_5, OF_6, are not possible.
PF_5, PCl_5, are possible but PH_5, is not.
An element which has even valency will always show even valency in excited state.
PCl_4, SF_3, SF_5 are not possible but PCl_3, PCl_5, SF_2, SF_4 & SF_6 are possible.
$\Rightarrow$ Short coming : Could not provide in formation regarding shape of molecule & strength of bonds.

Wave Mechanical Model

Two Model :
(i) Valence bond theory (VBT)
(ii) Molecular orbital theory (MOT)

(1) Valence bond theory:
Given by Heitler & London Extended by pauling & Slater.
Strength of bond α Extent of overlapping.
Extent of overlapping depends on two factors.

(i) Nature of orbital:
(a) directional orbital : p, d & f (more extent of overlapping)
(b) non- directional orbital : s (less extent of overlapping)
order of overlapping $\boxed{p - p > s - p > s - s}$
Exception $\boxed{1s - 1s > 2p - 2p}$
Nature of overlapping :
(a) Co-axial overlapping (Along the internuclear axis)
(b) Perpendicular to internuclear axis
Extent of overlapping is maximum, σ–bond is formed.
π-bond is formed after σ–bond.

For maximum bond strength :-
(i) Lower value of principal quantum number.
(ii) σ is stronger than π (when value of n is same)
(iii) Directional nature (when type of overlapping is same)

Limitation :
(i) Does not define the shape of the molecule.

Hybridisation (Pauling & Slater)
Imaginary concept
Mixing of different shape and approximate equal energy atomic orbital to give new orbital of same shape.
Hybrid orbitals always forms σ–bond. (Except - Benzyne)
In hybridization all type of orbitals can precipitate.
(Vacant, Half-filled or Fully filled)
Number of hybrid orbital formed will be equal to the number of atomic orbitals taking part in hybridization.

Valence shell electron pair repulsion theory (VSEPRT):

Given by Gillespie & Nyholm
Defines the shape of molecule

Case-I Molecules in which central atom do not have any lone pair are called symmetric structure & their shape will be according to their hybridization.

Case-II Molecules in which central atom has lone pair are known as asymmetric structure, In this case lone pair should be kept at that position where lone pair exerts minimum repulsive force.
Order of requlsion : L.P. – L.P . > L.P. – B.P. > BP. – B.P.

TYPES OF HYBRIDIZATION & POSSIBLE STRUCTURE

Type of Hybridization	No. of B.P.	No. of L.P.	Shape	Examples
1. sp-hybridization	2	-	Linear	BeF_2, CO_2 CS_2, $BeCl_2$
2. (a) sp^2-hybridization	3	-	Trigonal planar	BF_3, $AlCl_3$, BeF_3^-
(b) sp^2-hybridization	2	1	V-shape Angular	NO_2^-, SO_2, O_3
3. (a) sp^3-hybridization	4	0	Tetrahedral	CH_3, CCl_4, PCl_4^+, ClO_4^-, NH_4^+, BF_4^{-2} SO_4^{-2}, $AlCl_4^-$
(b) sp^3-hybridization	3	1	Pyramidal	NH_3, PF_3, ClO_3^-, H_3^+O, PCl_3, XeO_3, $N(CH_3)_3$, CH_3^-
(c) sp^3-hybridization	2	2	V-shape, Angular	H_2O, H_2S, NH_2^-, OF_2, Cl_2O, SF_2, I_3^+
4. (a) sp^3d-hybridization	5	-	Trigonal bipyramidal	PCl_5, SOF_4, AsF_4^-,
(b) sp^3d-hybridization	4	1	See Saw,	SbF_4^-, XeO_2F_2
			folded square distorted tetrahedral	SbF_4^- , XeO_2F_2
(c) sp^3d-hybridization	3	2	almost T-shape	ClF_3, ICl_3
(c) sp^3d-hybridization	2	3	Linear	I_3^-, Br_3^-, ICl_2^-, ClF_2^- , XeF_2
5. (a) sp^3d^2-hybridization	6	-	Square bipyramidal/ octahedral	PCl_6^- , SF_6
(b) sp^3d^2-hybridization	5	1	Square pyramidal/ distorted octahedral	$XeOF_4$, ClF_5, SF_5^- XeF_5^+
(c) sp^3d^2-hybridization	4	2	Square planar	XeF_4
6. (a) sp^3d^3-hybridization	7	-	Pentagonal bipyramidal	IF_7
(b) sp^3d^3-hybridization	6	1	Pentagonal pyramidal/ distorted octahedral	XeF_6
(c) sp^3d^3-hybridization	5	2	Pentagonal planar	XeF_5

Co-ordinate bond

This type of bond is formed by one side sharing of pair of electron between atoms. Electron pair of one atom is shared between two atom.

Atom which provide lone pair for sharing is called donor.

Atom which accepts electron pair is called acceptor.

Shown by '→' & direction is from donor to acceptor.

Necessary condition :

Acceptor should have vacant orbital.

Donor should have complete octet.

Example :

(i) Protonation : $H_2O \rightarrow H_3O^+$, $NH_3 \rightarrow NH_4^+$, $N_2H_4 \rightarrow N_2H_5^+$

(ii) Polymerization : $AlCl_3 \rightarrow Al_2Cl_6$, $BeCl_2 \rightarrow (BeCl_2)_n$

During the formation of coordinate bond, structure & shape of the molecule gets changed.

Dipole moment (μ)

Measure the polarity in molecule (μ) = q $\times$ d

Unit debye = esu - cm

1 Debye = 10^{-10} esu-cm.

Homonuclear diatomic H_2, N_2, O_2, F_2, ($\mu = 0$) $\rightarrow$ non- polar

Heteronuclear diatomic ($\mu \ \alpha \ \Delta$ EN) HF > HCl > HBr > HI

Polyatomic molecule resultant dipole moment is a vector addition of dipole moment of various bond.

$$\overleftarrow{O}=C=\overrightarrow{O} \quad \mu = 0 \quad \text{non-polar}$$

Imp. order

(a) $NH_3 > NI_3 > NBr_3 > NCl_3 > NF_3$

(b) $NH_3 > SbH_3 > AsH_3 > PH_3$,

(c) HF > HCl > HBr > HI

(d) $H_2O > H_2S$,

(e) $CH_3Cl > CH_3F > CH_3Br > CH_3I$

(f) $CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4 = CH_4$

Application :

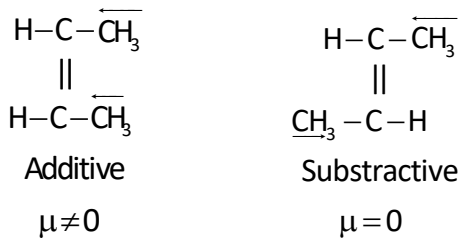
(i) Predict shape & polarity of molecule

If central atom contain lone pair than $\mu \neq 0$, moelcule will be polar & unsymmetrical shape.

If central atom surrounded with all identical atom then $\mu \neq 0$, molecule non-polar.

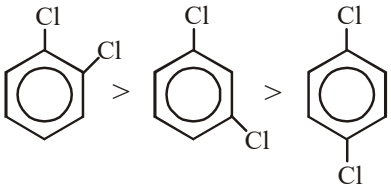
(ii) Distinguish between cis & trans form

$\mu_{cis} > \mu_{trans}$



Additive $\mu \neq 0$ | Substractive $\mu = 0$

(iii) To find out dipole moment of a substituent of benzene ring.



$$\mu \propto \frac{1}{\text{bond angle}}$$

H-bonding

Given by Latimer & Rodebush.

Electrostatic force of attraction between H & highly electronegative atom.

This is intermolecular force. i.e. why exist only in covalent molecule.

Also known as dipole-dipole attraction.

Necessary conditions :

(i) Hydrogen should be covalently bonded with highly electronegative element.

(ii) Highly electronegative element should have EN $\geq$ 3.

(iii)Hydrogen bonding is possible only in those moelcule in which H is directly attached with F, O, N,

$$\text{Strength of H} - \text{bond} \propto \text{EN of highly electronegative element}$$

Type of hydrogen bonding

↓

Intermolecular → When H-bonding takes place in between molecule

Intramolecular → When H-bonding takes place with in a molecule

Strength of intermolecular H-bond > Intramolecular H-bond.

Imp. Intramolecular H-bonding taking place only in ortho-derivative of aromatic compound.

Application :

(i) Physical state : H_2O is liquid H_2S gas.

HF is liquid HCl gas.

(ii) M.P. & B.P. : Due to presence of H-bonding M.P. & B.P. increases M.P. of alcohol > M.P. of thiol

(iii) Volatility : M.P. & B.P. ↑ volatility ↓

(iv) Viscosity & Surface tension :

$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} > \begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array} > CH_3-OH$$

(v) Solubility in H_2O : Any organic compound which get dissolved in H_2O is due to H-bonding.

Extent of solubility $\propto$ H-bonding

(vi) Association of molecule :

KHF_2 is possible but not $KHCl_2$. $[K^+ + [F^- .....H-F]$ (H.Bond)

MOLECULAR ORBITAL THEORY

Imaginary concept

Given to explain

(i) Paramagnetic nature of O_2 molecule.

(ii) Existence of species like $H_2^+ . H_2^-$ & species having fractional bond order.

Main point of M.O.T.

(a) Atomic orbital represented by ψ (wave function) participate to form molecular orbital.

(b) Z-axis is considered as main axis so p_z combination form σ moelcular orbital.

(c) The number of orbital participating in combination must have almost same energy & same symmetry. Will produce same number of orbital.

(d) Two type of molecular orbital formed.

(i) Bonding molecular (ii) Anti-bonding molecular

(e)Number of atomic orbital participating

$= \frac{1}{2}$ number of B.M.O. + $\frac{1}{2}$ number of ABMO.

(f) BMO is formed by addition of two wave function ($\psi_A + \psi_B$) when they are in same phase, represented by σ, π

(g) ABMO is formed by subtraction of two wave function ($\psi_A - \psi_B$) when they are in opposite phase, represented by σ^*, π^*.

Energy of ABMO > Energy of A.O. > energy of BMO

Imp. sequence order

for B_2, C_2, N_2 (Number of e^-'s ≤ 14) = $\sigma_{1s}, \sigma^*_{1s}, \sigma_{2s}, \sigma^*_{2s}$ $(\pi_{2px} = \pi_{2py})$, σ_{2pz} $(\pi^*_{2px} = \pi^*_{2py})$, σ^*_{2pz}

B.O. of C_2 = $\frac{8-4}{2} = 2$

(It contains two π bonds with out d bond

$\because$ last four e^- enters in π B.M.O.)

for O_2, F_2, Ne_2 (Number of e^-'s > 14) = $\sigma_{1s}, \sigma^*_{1s}, \sigma_{2s}, \sigma^*_{2s}, \sigma_{2pz}$ $(\pi_{2px} = \pi_{2py})$ $(\pi^*_{2px} = \pi^*_{2py})$, σ^*_{2pz}

Significance of M.O.T. :

(a) Concept of bond order :

Bond order = $\frac{1}{2}$ $[N_b - N_a]$

N_a = number of antibonding e^-'s

N_b = number of bonding e^-'s

If $N_b > N_a$ B.O. = +ve molecule exist

$N_b < N_a$ B.O. = –ve moelcule does not exist

$N_b = N_a$ Does not exist

(b) Stability $\propto$ B.O. α bond dissociation energy

(c) B.O. $\propto \dfrac{1}{\text{Bond length}}$

Iso electronic species have same bond order & have same magnetic property.

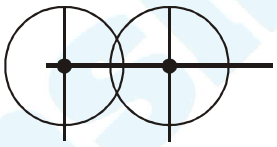
If species have fractional bond order it will always be paramagnetic.

If in two species bond order is same the stability, will be decided by counting number of antibonding e^-'s. If number of antibonding e^- more, than number of bonding e^-'s then molecule will be unstable.

Bonding parameters

Imp. points :

1. **Bond length :** Internuclear distance between two atom when they are bonded together.



B.L.

Factor affecting bond length

(i) ΔEN value

$d_{A-B} = r_A + r_B - 0.09\,(\Delta EN)$

$\Delta EN \uparrow$ B.L. $\downarrow$

H–F < H–Cl < H–Br < H–I

(ii) Atomic size

$\boxed{\text{B.L.} \propto \text{Atomic size}}$

(iii) Bond order : B.O. $\propto \dfrac{1}{\text{B.L.}}$

$\boxed{C-C > C=C > C\equiv C}$

(iv) Hybridisation : B.L.

$$\begin{array}{ccccc} sp^3-sp^3 & > & sp^2-sp^2 & > & sp-sp \\ | & & | & & | \\ 25\% & & 33.33\% & & 50\%\ s-\text{character} \\ -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- & & -\overset{|}{C}=\overset{|}{C}- & & -C\equiv C- \end{array}$$

2. **Bond angle :** The angle between any two adjacent bond is known as bond angle.

Factor affecting bond angle

(a) Hybridization : wOn increasing % s-character bond angle also increases.

$$\begin{array}{ccc} -\overset{|}{\underset{|}{C}}-C & >C=C< & -C\equiv C- \\ sp^3 & sp^2 & sp \\ 25\% & 33.33\% & 50\% \\ \text{Bond angle } 109.5^\circ & 120^\circ & 180^\circ \end{array}$$

Case-I When hybridization is same, bonded atom are same but central atom & lone pair are different.

$$B.A. \propto \frac{1}{\text{Number of L.P.}}$$

Example :

CH_4	$\ddot{N}H_3$	$H_2\ddot{O}:$
↓	↓	↓
sp^3	sp^3	sp^3
109.5°	107°	104.5°
No L.P.	1 L.P.	2 L.P.

Case-II When hybridization is same, number of lone pair is same central atom is different & side atom are same then

$$\boxed{\text{Bond angle} \propto \text{EN of central atom}}$$

$$\ddot{N}H_3 > \ddot{P}H_3 > \ddot{A}sH_3 > \ddot{S}bH_3$$

Examle : Bond angle 107° 93° 91°

$\xrightarrow{\text{EN of central atom decrease}}$
Bond angle decrease

$$H_2\ddot{O}: > H_2\ddot{S}: > H_2\ddot{S}e: > H_2\ddot{T}e:$$

$\xrightarrow{\text{Bond angle decreases}}$

Case - III When hybridization is same , number of lone pair are same and central atom are same, but side atoms are different.

$$\boxed{B.A \propto \frac{1}{\text{EN of side atom}}}$$

$OF_2 < OCl_2 < OBr_2 < OI_2$ $NF_3 < NCl_3 < NBr_3 < NI_3$

Note : Symmetrical mol. having no. l.p. and same hyb. B.A. are same.

e.g (i) $BF_3 = BCl_3 = BBr_3 = BI_3$

(ii) $SO_4^{2-} = PO_4^{3-} = ClO_4^-$

Imp. point :

In ethers oxygen has sp^3 hybridization having two L.P. but still bond angle is 110° because of large size of alkyl group.

$$R—\ddot{\underset{..}{O}}—R$$