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.

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

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 = $\dfrac{1}{12}$ 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 = $\dfrac{w}{m}$ = $\dfrac{N}{N_A}$ = $\dfrac{V}{22.4}$

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.
$$= (9.11 \times 10^{-31} \text{ kg}) \times (6.02 \times 10^{23})$$
$$= 5.48 \times 10^{-7} \text{ kg}$$

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.

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

$$d_{H_2} = 0.000089 \text{ mg / ml}$$

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

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

$$n = \frac{\text{volume at STP (inlit)}}{22.4 \text{ litre}} \text{ or } \frac{\text{Volume at STP (inml)}}{22400 \text{ml}}$$

n = M × V(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).
  - $c = v\lambda$
  - $\vec{v} = \dfrac{1}{\lambda} = \dfrac{v}{c}$ $\boxed{1\ cm^{-1} = 100\ m^{-1}}$
  - $T = \dfrac{1}{v} = \dfrac{\lambda}{c}$

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 $E = hv = \dfrac{hc}{\lambda} = hc\bar{v}$

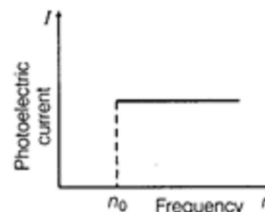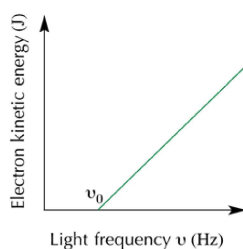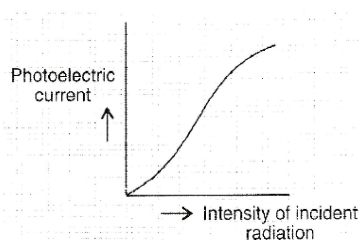- Total energy transfered = N × Energy of one photon.

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

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

Photoelectric effect

ATOMIC STRUCTURE

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

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. $\quad mvr = n \times \dfrac{h}{2\pi}$

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/z Å

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 $\quad v = 2.18 \times 10^6 \dfrac{Z}{n}$ m/s

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

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

3

ATOMIC STRUCTURE

n = number of corresponding energy of orbit

z = atomic number

Energy of electron in Bohr orbit

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

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

z = atomic number

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

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

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

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

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

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

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

                                    = TE = −KE

                                    = PE = −2KE
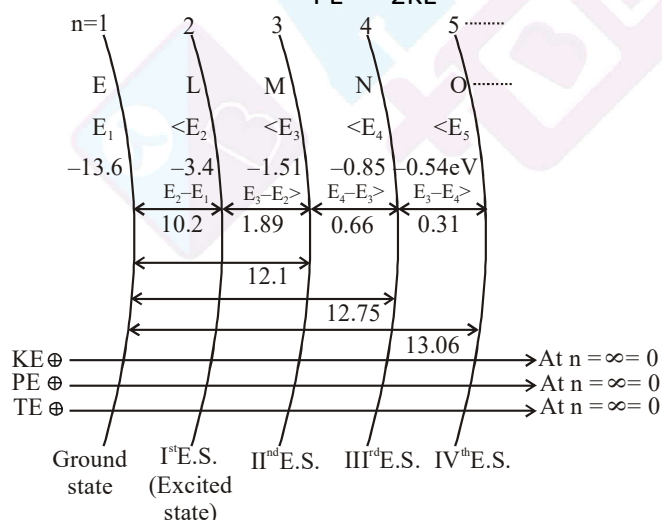
Important Shortcuts

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

ATOMIC STRUCTURE

$E = h\nu$

Where, h = planck constant,

n = the freqeuncy of the wave is related to its wavelength.

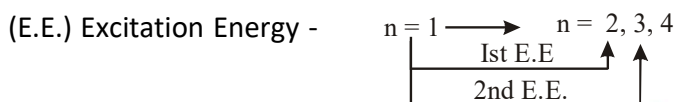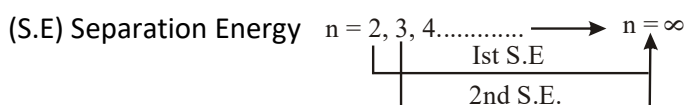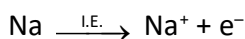T.E. of any H-like species = TE or Hydrogen × Z^2 (For same orbit)

ΔE for H like species = ΔE (For hydrogen) × Z^2 (For same transition)

Energy in n^{th} orbital for H like species = $\dfrac{E_1}{n_1}$ [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 $\xrightarrow{\text{I.E.}}$ Na$^+$ + e$^-$

(S.E) Separation Energy   n = 2, 3, 4............. $\longrightarrow$ n = ∞

	Ist S.E
	2nd S.E.

(E.E.) Excitation Energy -   n = 1 $\longrightarrow$ n = 2, 3, 4

	Ist E.E
	2nd E.E.

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)**
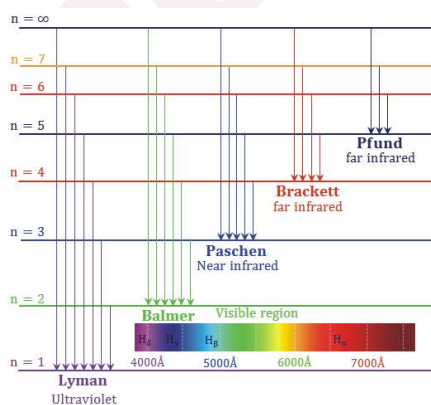
Lyman $\longrightarrow$ Any higher orbit $\longrightarrow$ 1 [Found in U.V. region]

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]

ATOMIC STRUCTURE

Rydberg Equation :

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

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

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

Where R_H = Rydberg constant = 109678 cm⁻¹ $\boxed{\dfrac{1}{R_H} = 912\text{Å}}$

= 10967800 m⁻¹

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 = $\dfrac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$

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

Maximum and minimum wavelength :

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

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

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

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

ATOMIC STRUCTURE

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 $\lambda = \sqrt{\frac{150}{V}}\text{Å}$

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.

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

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.

$\Delta E.\Delta t = h$

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

where Δx = Uncertainity in position

Δv = Uncertainity in velocity

ΔP = Uncertainity in momentum

m = Mass of particles

$\dfrac{h}{4\pi}$ = 5.27 × 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 × $\dfrac{h}{2\pi}$

Total number of e⁻s in an orbit = 2n²

Total number of orbitals in an orbit = n²

Total number of subshell in an orbit = n

2.   Azimuthal / Secondary/Subsidiary/Angular Momentum

$\Rightarrow$ Given by = Sommerfeld

$\Rightarrow$ Indicates = Subshells/sub orbit/sub level

$\Rightarrow$ Value $\Rightarrow$ 0,1..........(n–1)

$\Rightarrow$ 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(2ℓ +1)

Total number of orbitals in a sub - orbit = (2ℓ + 1)

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

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
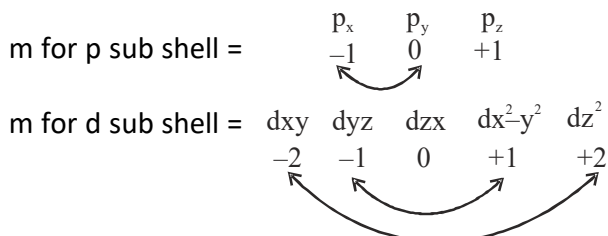
3. Magnetic Quantum number (m)

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 =
$$\begin{array}{ccc} p_x & p_y & p_z \\ -1 & 0 & +1 \end{array}$$

m for d sub shell =
$$\begin{array}{ccccc} dxy & dyz & dzx & dx^2\text{-}y^2 & dz^2 \\ -2 & -1 & 0 & +1 & +2 \end{array}$$

4. Spin Quantum no. (m_x or s)

Given by Uhlenbeck & Goldsmit

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

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

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

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}
		$d_{x^2} - d_{y^2}$
		d_{z^2}

Nodes are the spaces where the probability of finding the electron is 0.

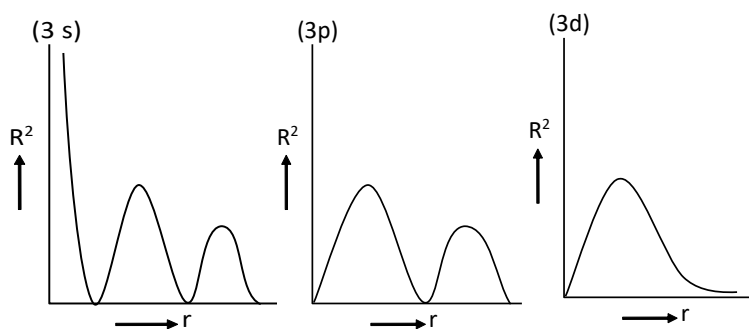To find the number of nodes in an orbital is given as follows :

Number of angular nodes = ℓ

Number of radial nodes = $n - 1 - \ell$

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

ATOMIC STRUCTURE
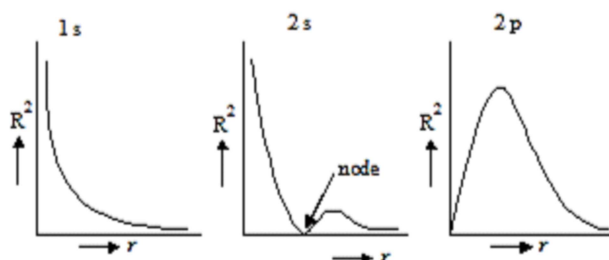
Schrodinger wave equation

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

| 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 = $\dfrac{n_A(n_A - 1)}{2} + \dfrac{n_B(n_B - 1)}{2}$

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.
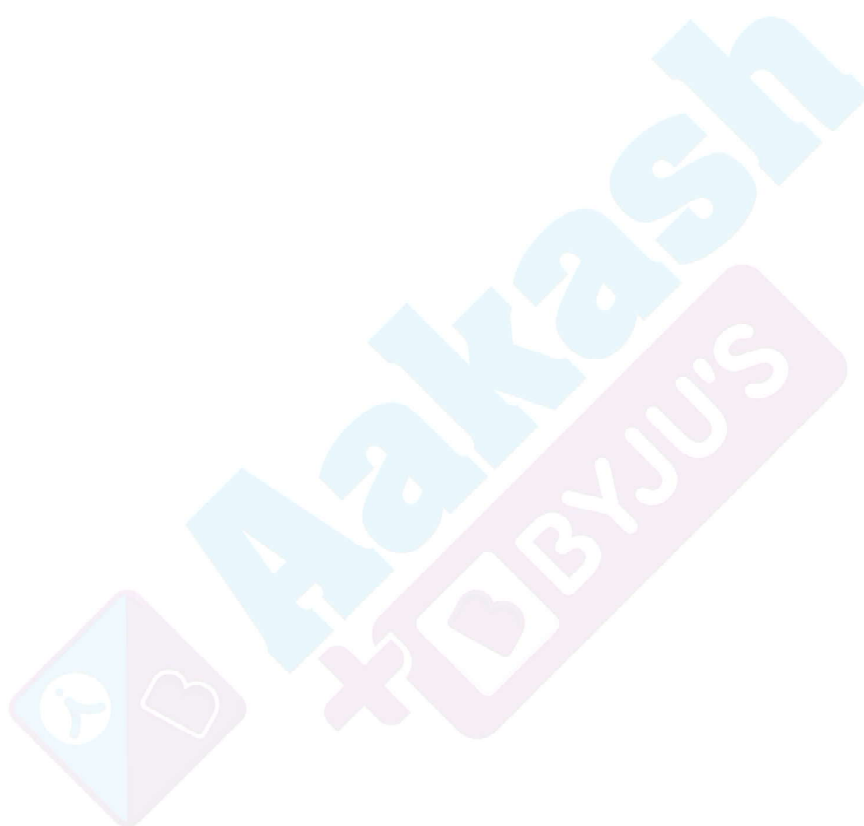
CHEMICAL BONDING

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.

```
                                    │
        ┌───────────────────────────┴───────────────────────────┐
        │                                                        │
        ▼                                                        ▼
   Strong bond                                              Weak bond
  (B.E. ≃ 200kJ/mol)                                    (B.E. ≃ 2-40kJ/mol)
        │                                                        │
   ┌────┼────┬──────┬──────┐                          ┌──────────┴──────────┐
   ▼    ▼    ▼      ▼                                  ▼                     ▼
Ionic > Covalent ≃ Co-ordinate > Metallic        H-bonding    >        Vanderwaal
                                                                             │
                                                             ┌───────────────┼───────────────┐
                                                             ▼               ▼               ▼
                                                          Keesom    >     Debye    >   Dispersion force
```

CHEMICAL BONDING
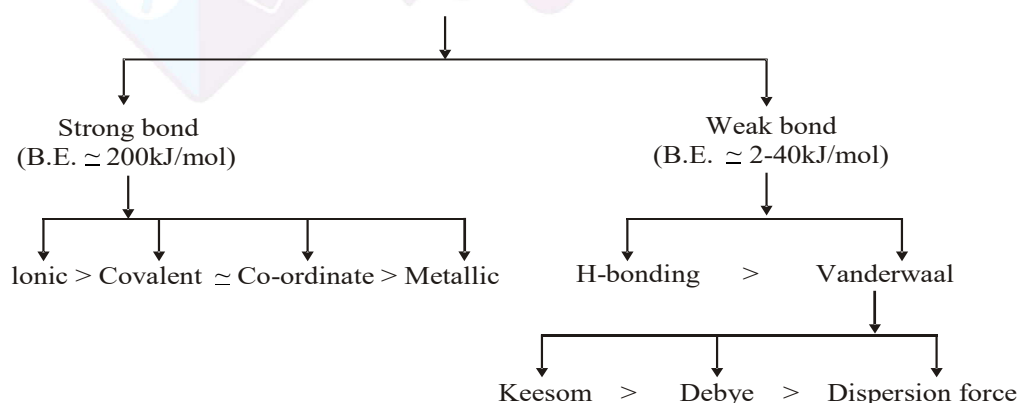
Ionic bond :

(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 $\Delta H = -$ 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.

Imp. Order Covalent solid > Ionic solid > Molecular solid

| More bond energy | > | Less bond energy |

| H-bond | > | Van der waal |

| Inter molecular H-bonding | > | Intra molecular H-bonding |

| More mass | > | Less mass |
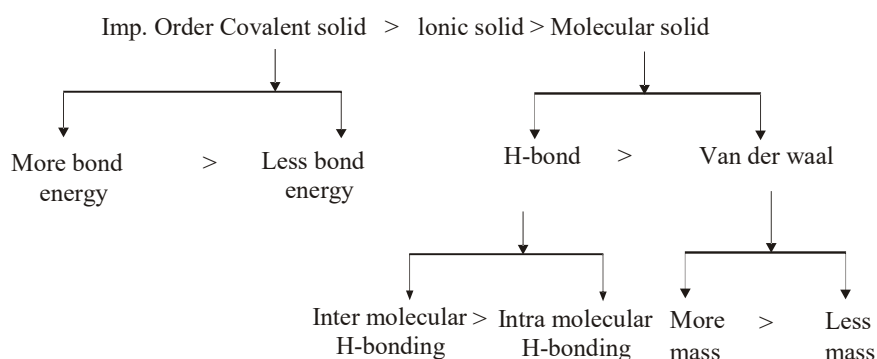
CHEMICAL BONDING

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

$Li_2O > Na_2O > K_2O > Rb_2O > Cs_2O$
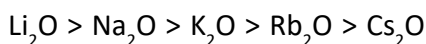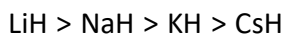
Among metal halide, fluoride has maximum m.p.

LiF > LiCl > LiBr > LiI

NaF > NaCl > NaI
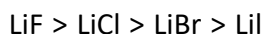
Solubility : Ionic compounds are souble in polar solvent like water.

Factor affecting solubility:

(i) Dielectric constant α solubility

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

(iii) Hydration energy α solubility

For any compound to be soluble in water

$\boxed{\text{Hydration energy > Lattice energy}}$
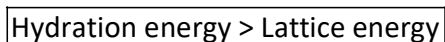
Imp. order:

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.

$\boxed{\text{Covalent character} \propto \text{Polarization} \propto \text{Zeff of cation}}$
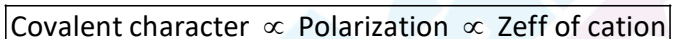
Polarization power (Ionic potential) : capacity of cation to polarize anion represented by (ϕ)

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

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 $\propto \dfrac{1}{\text{Polarization}} \propto \dfrac{1}{\text{Covalent Character}}$

(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 > Nal
$NaCl > MgCl_2 > AlCl_3$
$BaCl_2 > SrCl_2 \; CaCl_2 \; MgCl_2 > BeCl_2$

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, $\sigma-$bond is formed.
π-bond is formed after $\sigma-$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 $\sigma-$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.

CHEMICAL BONDING

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, folded square distorted tetrahedral	SbF_4^-, XeO_2F_2 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.

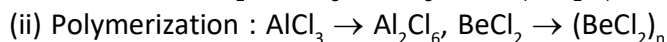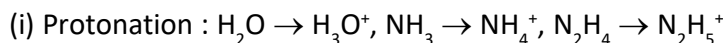Shown by '→' & direction is from donor to acceptor.

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)
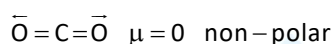
Measure the polarity in molecule (μ) = q × d

Unit debye = esu - cm

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

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

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

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

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

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 > Hl

(d) $H_2O > H_2S$,

(e) $CH_3Cl > CH_3F > CH_3Br > CH_3l$

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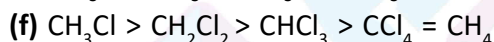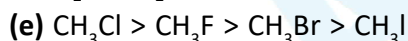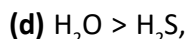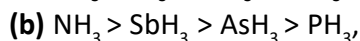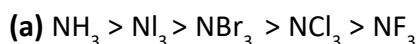
Application :

(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.
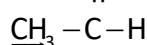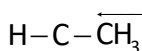
(ii) Distinguish between cis & trans form

$\mu_{cis} > \mu_{trans}$
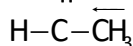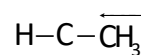
$H-C-\overleftarrow{CH_3}$ $\parallel \quad \overleftarrow{}$ $H-C-\overleftarrow{CH_3}$	$H-C-\overleftarrow{CH_3}$ $\parallel$ $\underline{CH_3}-C-H$
Additive	Substractive
$\mu \neq 0$	$\mu = 0$

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

$$\mu \propto \frac{1}{\text{bond angle}}$$
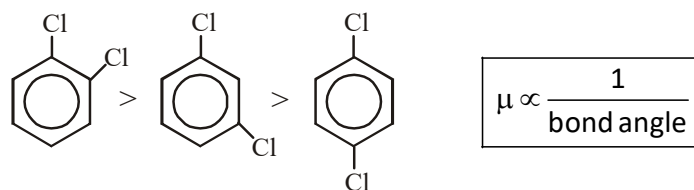
H-bonding

Given by Latimer & Rodebush.

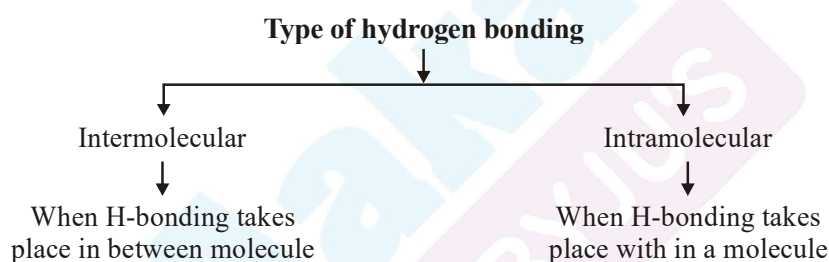Electrostatic force of attraction between H & highly electronegative atom.

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,

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

Type of hydrogen bonding

Intermolecular	Intramolecular
When H-bonding takes place in between molecule	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.
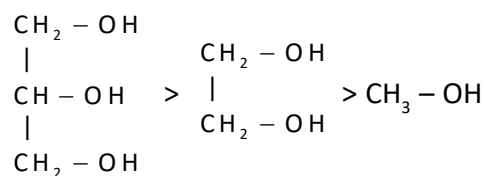
Application :

(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. $\uparrow$ volatility $\downarrow$
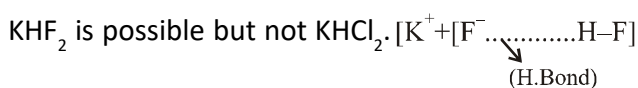
(iv) Viscosity & Surface tension :

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

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

CHEMICAL BONDING

Extent of solubility $\propto$ H-bonding

(vi) Association of molecule :

KHF_2 is possible but not $KHCl_2$. $[K^+ + [F^- \ldots\ldots\ldots H-F]$

(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

$= \dfrac{1}{2}$ number of B.M.O. $+ \dfrac{1}{2}$ 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) = $\sigma_{1s}, \sigma_{1s}^*, \sigma_{2s}, \sigma_{2s}^* \ (\pi_{2px} = \pi_{2py}), \ \sigma_{2pz} \ (\pi_{2px}^* = \pi_{2py}^*), \ \sigma_{2pz}^*$

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

(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) = $\sigma_{1s}, \sigma_{1s}^*, \sigma_{2s}, \sigma_{2s}^*, \sigma_{2pz} \ (\pi_{2px} = \pi_{2py}) \left(\pi_{2px}^* = \pi_{2py}^*\right), \sigma_{2pz}^*$

Significance of M.O.T. :

(a) Concept of bond order :

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

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.

   Factor affecting bond length

   (i)   **ΔEN value**

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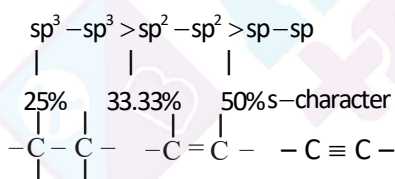
   $\Delta EN\uparrow$ B.L. $\downarrow$

   H–F < H–Cl < H–Br < H–I
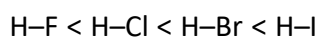
   (ii)   **Atomic size**

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

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

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

   (iv) **Hybridisation :** B.L.

   $$sp^3 - sp^3 > sp^2 - sp^2 > sp - sp$$

   25%   33.33%   50% s–character

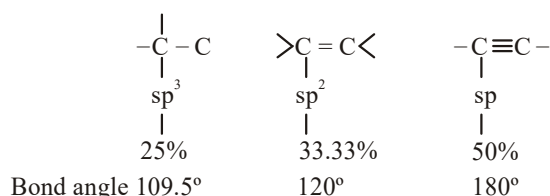 $-\overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} - \quad -\overset{|}{C} = \overset{|}{C} - \quad - C \equiv C -$
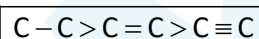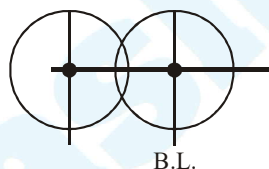
2. **Bond angle :** The angle between any two adjacent bond is known as bond angle.

   Factor affecting bond angle

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

   $-\overset{|}{\underset{|}{C}} - C \qquad\qquad >C = C< \qquad\qquad -C \equiv C-$

       sp^3 sp^2 sp

       25%   33.33%   50%

   Bond angle 109.5º   120º   180º

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

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

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.
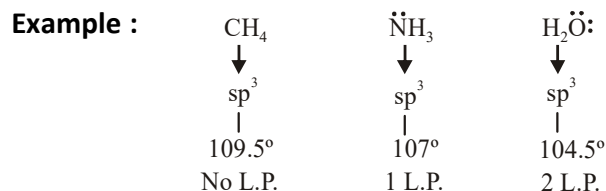
Case-II When hybridization is same, number of lone pair is same central atom is different & side atom are same then
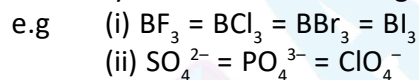
$$\boxed{\text{Bond angle} \propto \text{EN of central atom}}$$

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

Examle : Bond angle 107°   93°   91°

EN of central atom decrease →
Bond angle decrease

$$H_2\ddot{O}: > H_2\ddot{S}: > H_2\ddot{S}e: > H_2\ddot{T}e :$$
Bond angle decreases →
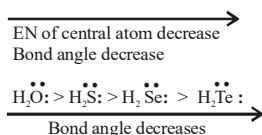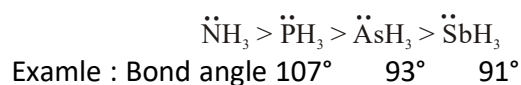
Case - III When hybridization is same , number of lone pair are same and central atom are same, but side atoms are different.

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

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

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.

$$R\!-\!\ddot{\underset{\cdot\cdot}{O}}\!-\!R$$
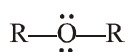
BEHAVIOUR OF GASES

1. Gas law

(i) Boyle's law : $V \propto \dfrac{1}{P}(n, T = const.)$ $\boxed{P_1V_1 = P_2V_2}$

(ii) Charle's law $V \propto T(n, P = const.)$ $\dfrac{V_2}{V_1} = \dfrac{T_2}{T_1}$

(iii) Gay lussac's law : $P \propto T(n, V = const.)$ $\dfrac{P_2}{P_1} = \dfrac{T_2}{T_1}$

(iv) Avogadro's law :

$V \propto$ moles $\propto$ number of molecules (P,T = const.)

Ideal gas equations PV = nRT

R = 0.082 lit atm mol^{-1} K^{-1}

R = 8.314 JK^{-1} mol^{-1} or 8.314 N × m K^{-1} mol^{-1}

R = 2 cal K^{-1} mol^{-1}

R = 8.314 × 10^7 erg K^{-1} mol^{-1}

2. Graham's Diffusion law :

It is applicable for non reacting gases

$r \propto \dfrac{1}{\sqrt{d}}$

$r \propto \dfrac{1}{\sqrt{VD}}$

$r \propto \dfrac{1}{\sqrt{Mw}}$ $\quad$ (P, T = const.)

$$VD = \dfrac{d_{gas}}{dH_2} = \dfrac{Mw}{2}$$

rate of diffusion $\quad r = \dfrac{\ell_{diffused\,gas}}{t_{time\,take}}$

(Where, ℓ = distance travelled by diffused gas)

$$r = \dfrac{V_{diffused\,gas}}{t_{time\,taken}}$$

$$r = \dfrac{n_{diffused\,gas}}{t_{time\,taken}}$$

3. Dalton's law of Partial Pressure

$P_{mixture} = \underbrace{P_1 + P_2 + P_3}_{Partial\,pressure} ....(T \& V const)$

$P_1 = P_{moist\,gas} = P_{dry\,gas} + P_{water\,vapours}$

It is applicable for non reacting gases.

Methods of determination of partial pressure (P_A & P_B are partial pressure)

(i) From ideal gas equation

$$P_A V = n_A RT \text{ and } P_B V = n_B RT$$

(ii) In the form of mole fraction.

$$P_A = X_A P_T = \frac{n_A}{n_t} P_T \qquad \qquad X_A + X_B = 1$$

$$P_B = X_B P_T = \frac{n_B}{n_t} P_T$$

P_T = sum of partial pressure of all gases

(iii) In the form of volume fraction

$$P_A = \frac{V_A}{V} P_T \text{ and } P_B = \frac{V_B}{V} P_T$$

(iv) If individual pressure and individual volume are given

$$P_A = \frac{V_A}{V} P_1 \text{ and } P_B = \frac{V_B}{V} P_2$$

P_1, P_2 = pressure of gases before mixing

P_A, P_B = pressure of gases after mixing

4. Kinetic gas Equation

$$PV = \frac{1}{3} m N V_{rms}^2$$

5. Average KE (KEav)

$$KEav = \frac{3}{2} nRT \qquad \text{(n moles)}$$

$$KEav = \frac{3}{2} RT \qquad \text{(1 mol or NA molecular)}$$

$$KEav = \frac{3}{2} kT \qquad \text{(1 molecule)}$$

$k = 1.38 \times 10^{-23}$ JK^{-1}

6.

$$V_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + \dots v_n^2}{N}} \qquad V_{avs} = \frac{v_1 + v_2 + v_3 \dots v_n}{N}$$

$$V_{rms} = \sqrt{\frac{3RT}{Mw}} \qquad V_{avs} = \sqrt{\frac{8RT}{\pi Mw}} \qquad V_{mps} = \sqrt{\frac{2RT}{Mw}}$$

$$V_{rms} = \sqrt{\frac{3PV}{Mw}} \qquad V_{avs} = \sqrt{\frac{8PV}{\pi Mw}} \qquad V_{mps} = \sqrt{\frac{2PV}{Mw}}$$

$$V_{rms} = \sqrt{\frac{3P}{d}} \qquad V_{avs} = \sqrt{\frac{8P}{\pi d}} \qquad V_{mps} = \sqrt{\frac{2P}{d}}$$

Vrms	:	Vavs	:	Vmps
$\sqrt{3}$	:	$\sqrt{\frac{8}{\pi}}$	:	$\sqrt{2}$
1.732	:	1.596	:	1.414
1.224	:	1.128	:	1

7. Maxwell's distributions of molecular speeds :

fraction of molecule having particular speed

Curve will start becoming flatter with increase in temperature

$T_2 > T_1$
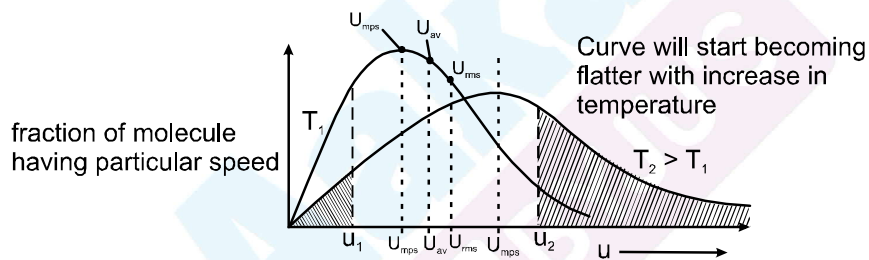
8. Variation of compressibility factor (Z) :
Variation of Z with pressure at constant temperature :

BEHAVIOUR OF GASES
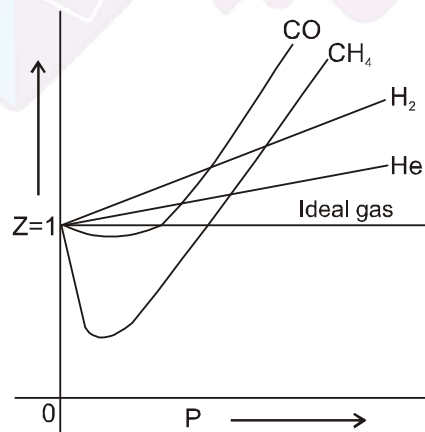
Variation of Z with pressure at different temperature (for same gas) :

$T_1 > T_2 > T_3 > T_4$
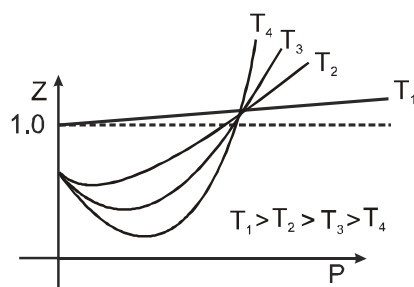
Conclusions :

Z = 1 for ideal gas ; $\qquad$ Z > 1 at all pressures for He/H$_2$

Z < 1 at low pressure (for all other gases) ; Z > 1 at high pressure (for all other gases)

Compressibility factor (z) = $\dfrac{P(V_m)obs}{RT}$

If z = 1. the gas show ideal gas behaviour

If z > 1, the gas show positive deviation

If z < 1, the gas show negative deviation

9. Vanderwaal's Equation

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$P_1 = P_R + \dfrac{an^2}{V^2} \qquad \Rightarrow \quad P_1 > P_R$

a↑ force of attraction ↑ liquification ↑

b↑ effective size of molecule ↑

incompressible vol ↑, compressible vol ↓

(i) At high pressure, Vanderwaal's equation is $\boxed{PV_m - Pb = RT}$

(ii) At low pressure, Vander waal's equation is $\boxed{PV_m + \dfrac{a}{V_m} = RT}$

Virial Equation of state :

Z is expressed in power series expansion of P or $\left(\dfrac{1}{V_m}\right)$

Z = 1 + $\dfrac{B}{V_m}$ + $\dfrac{C}{V_m^2}$ + $\dfrac{D}{V_m^3}$ + ...

Van der waal's equation in virial form :

Z = 1 + $\dfrac{1}{V_m}\left(b - \dfrac{a}{RT}\right)$

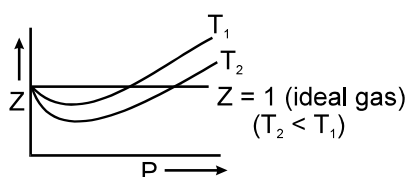If $\left(b - \dfrac{a}{RT}\right) = 0 \quad \Rightarrow$ at T = $\dfrac{a}{Rb}$; Z = 1

so at $T = \dfrac{a}{Rb}$, gas will behave as an ideal gas (or follows Boyles law)

But at constant temperature, ideal gas equation is obeying Boyles law as $T = \dfrac{a}{Rb}$, so the temperature is called Boyles' temperature.
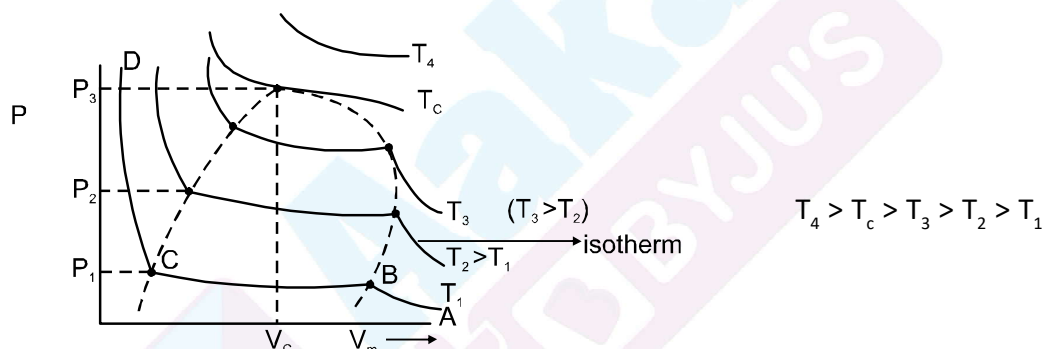
$T_B = \dfrac{a}{Rb}$
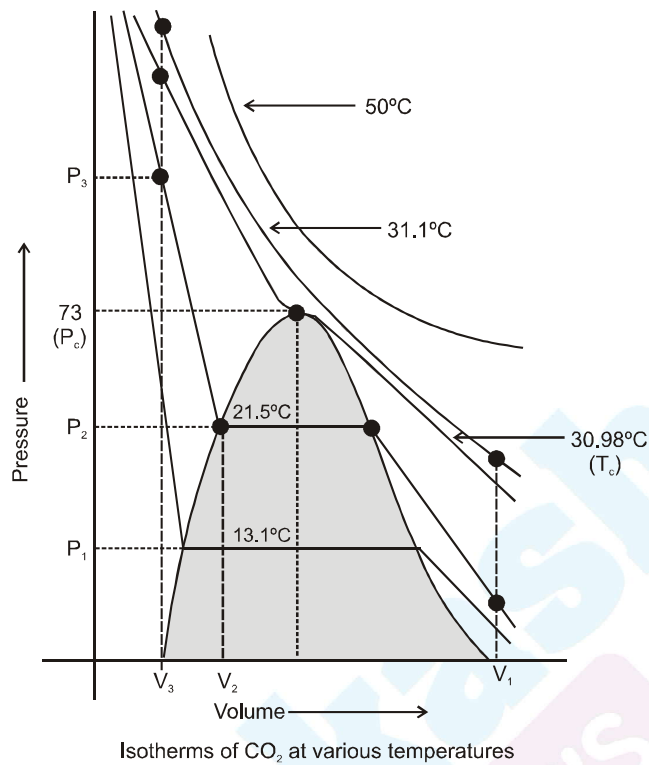
$Z = 1 - \dfrac{a}{V_m RT}$

For a single gas, if we have two graphs as above, we must conclude $T_2 < T_1$.
At Boyles' temperature 'a / RT' factor is compensated by 'b' factor, so Z = 1.

10. Critical constant of a gas (Andrews isotherm)
When pressure increases at constant temperature volume of gas decreases

$T_4 > T_c > T_3 > T_2 > T_1$

Isotherms of CO_2 at various temperatures

11. Critical point

Critical point : At this point, all the physical properties of liquid phase will be equal to physical properties in vapour such that density of liquid = density of vapour

Inversion temperature : The inversion temperature is the critical temperature below which a known ideal gas (all gases in reality) that is expanding at constant enthalpy will experience a termperature decreases, and above which will experience a temperature increases.

T_C **or critical temp :** Temperature above which a gas can not be liquified

Higher is the critical temperature, higher will be ease of liquification.

P_C **or critical pressure :** Minimum pressure which must be applied at critical temperature to convert the gas into liquid.

V_C **or critical volume :** Volume occupied by one mole of gas at T_C & P_C.

$$T_i = \frac{2a}{Rb}$$

$$T_C = \frac{8a}{27Rb}$$

$$V_C = 3b$$

$$P_C = \frac{a}{27b^2}$$

CHEMICAL EQUILIBRIUM

1. Equilibrium is a Dynamic Process :

Equilibrium is established in a system when reactants combine to form products at the same rate at which products combine to form reactants.

$$\left(\frac{dx}{dt}\right)_f = \left(\frac{dx}{dt}\right)_b \; or \, R_f = R_b$$

Chemical equilibrium can be approached from either side. A catalyst can fasten the approach of equilibrium but does not alter the state of equilibrium. System can xbe homogeneous or heterogeneous.

For a reaction in equilibrium

$$aA + bB \rightleftharpoons cC + dD$$
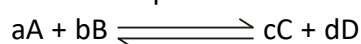
$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad \text{in terms of active mass}$$

$$K_P = \frac{[P_C]^c[P_D]^d}{[P_A]^a[P_B]^b} \quad \text{in terms of partial pressure}$$

$$K_X = \frac{[X_C]^c[X_D]^d}{[X_A]^a[X_B]^b} \qquad \text{in terms of mole fraction}$$

Partial pressure of solid is taken as unity and in calculation of partial pressure of solids their number of moles are not considered.

$K_P = K_C (RT)^{\Delta ng}$
(i) When $\Delta n_g = 0$ then $K_P = K_C$
(ii) When $\Delta n_g > 0$ then $K_P > K_C$
(iii) When $\Delta n_g < 0$ then $K_P < K_C$
$\Delta n_g = (c + d) - (a + b)$
Note : While determining Δn_g, take only gaseous species.
Properties of equilibrium constant :
For $\qquad A + B \rightleftharpoons C + D; K_C = K$

then (i) $\quad C + D \rightleftharpoons A + B; K_C = \dfrac{1}{K}$

(ii) $\quad 2A + 2B \rightleftharpoons 2C + 2D; K_C = K^2$

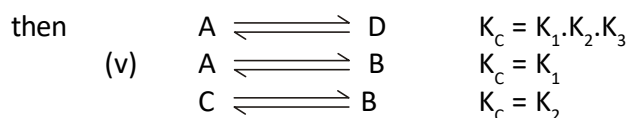(iii) $\quad \dfrac{A}{2} + \dfrac{B}{2} \rightleftharpoons \dfrac{C}{2} + \dfrac{D}{2}; K_C = \sqrt{K}$

(iv) $\quad A \rightleftharpoons B; K_C = K_1$
$\qquad B \rightleftharpoons C; K_C = K_2$
$\qquad C \rightleftharpoons D; K_C = K_3$

then $\qquad$ A $\rightleftharpoons$ D $\qquad$ $K_C = K_1 \cdot K_2 \cdot K_3$

(v) $\qquad$ A $\rightleftharpoons$ B $\qquad$ $K_C = K_1$

$\qquad$ C $\rightleftharpoons$ B $\qquad$ $K_C = K_2$

then $\qquad$ A $\rightleftharpoons$ C $\qquad$ $K_C = \dfrac{K_1}{K_2}$

Reaction quotient Q for the reversible reaction

$$A + B \rightleftharpoons C + D$$

$$Q = \frac{[C]\,[D]}{[A]\,[B]}$$

Q is taken at any condition of system.

$\Rightarrow$ If $Q = K_{eq.}$ then system is in equilibrium

$\Rightarrow$ If $Q > K_{eq.}$ system proceeds in backward side to attain equilibrium

$\Rightarrow$ If $Q < K_{eq.}$ system proceeds in forward side to attain equilibrium

For the equilibrium A $\rightleftharpoons$ nB

Degree of dissociation $\alpha = \dfrac{D - d}{D(n - 1)}$

where n is the number of moles of products from one mole of reactant, D is the theoretical vapour density (if no dissociation takes place) and d is the observed vapour density (due to dissociation or association) vapour density × 2 = molecular weight.

Vapour density × 2 = molecular weight.

Degree of dissocaition $(\alpha) = \dfrac{\text{Number of dissociated moles (x)}}{\text{Initial number of moles (a)}}$

Equilibrium constant (K) depends upon temperature and way of writting the reaction.

Le-Chatelier's principle : If the system at equilibrium is subjected to change of any one of the factors such as concentration, temperature or pressure, the system adjusts itself in such a way as to nullify the effect of that change.

The following conclusion have been derived from this principle.

(i) Increases in concentration of any substance favours the reaction in which it is used up.

(ii) High pressure is favourable for the reaction in which there is decreases in volume or number of moles.

(iii) A rise in temperature favours the endothermic reaction.

(iv) At constant volume : There is no effect of adding inert gas on the state of equilibrium at constant volume.

(v) At constant pressure : On adding of inert gas at constant pressure, the reaction proceeds in that direction where the sum of stoichiometric coefficient of gaseous components is greater.

Application of Le-Chatelier's principle :

(i) Ice water system (melting of ice) :

Ice + Heat $\rightleftharpoons$ Water
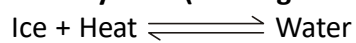
It is an endothermic process and there is decrease in volume. Thus, the favourable conditions for melting of ice are ; (a) High temperature and (b) High pressure.

(ii) Solubility of gases in liquids :

When a gas dissolves in a liquid, there is decreases in volume. Thus, increase in pressure will favour the dissolution of gas in liquid.

IONIC EQUILIBRIUM

Acid and Base

• **Arrhenius Concept :** Acid ionises in water to give H_3O^+ ion while base ionises to give OH^- ion. Ex HCl, NaOH

• **Bronsted-Lowry's Protonic Concept :** Acid is H^+ ion donor and base is H^+ ion acceptor. HCl and Cl^- is a conjugate acid - base pair. If acid is weak, its conjugate base is strong and vice-versa. A substance that can accept H^+ ion as well as can donate H^+ ion is called amphiprotic or amphoteric.

$$H_3O^+ \xleftarrow{H^+} \underset{\text{amphoteric}}{H_2O} \longrightarrow H^+ + OH^-$$
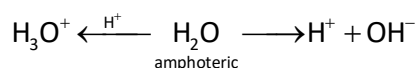
A Bronsted Lowry acid - base reaction is always favoured in the direction from the stronger to the weaker acid/base combinations.

• **Lewis concept :**

Lewis acid is an electron - pair acceptor.

Example : Electron deficient molecules : BF_3, $AlCl_3$, H_3BO_3, $BeCl_2$

Cations : H^+, Fe^{3+}, Na^+

Molecules with vacant orbitals : $SiCl_4$, SO_2

Lewis base is an electron pair donor.

Example : Molecules with donatable lone pairs : NH_3, H_2O, CH_3OH

Ion : X^-, CN^-, OH^-

Note :

$$(OH)_3B \; + \; \ddot{O}\!\!\underset{H}{\overset{H}{<}} \longrightarrow B(OH)_4^- + H^+$$
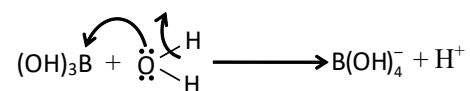
Here, Boric acid [i.e. $B(OH)_3$] acepts a lone pair. So, it is a lewis acid.

All lewis bases are bronsted Lowry bases but all the lewis acid are not bronsted acids.

IONIC EQUILIBRIUM

Dissociation of weak acid and weak base :

Weak acid	Weak base
$HA(aq.) \rightleftharpoons H^+(aq.) + A^-(aq.)$	$BOH(aq.) \rightleftharpoons B^+(aq.) + {}^-OH(aq.)$
$K_a = \dfrac{[H^+][A^-]}{[HA]}$	$Kb = \dfrac{[B^+][OH^-]}{[BOH]}$
$[H^+] = \sqrt{K_a.C}$	$[OH^-] = \sqrt{K_b.C}$
$[{}^-OH] = \dfrac{K_w}{\sqrt{K_a.C}}$	$[H^+] = \dfrac{Kw}{\sqrt{K_b \times C}}$
$pH = \dfrac{1}{2}(pK_a - \log C)$ $pH = -\log\sqrt{K_a.C}$	$pH = \dfrac{1}{2}(\log K_b - \log C)$
$pOH = 14 - \dfrac{1}{2}(pK_a + \log C)$	$pOH = 14 - \dfrac{1}{2}(\log K_b - \log C)$

Ostwald dilution law :

According to ostwald dilution low $\alpha \propto \sqrt{\text{dilution}}$

At infinite dilution , $\propto$ = 100%

For a weak acid by Ostwald dilution law

$$K_a = \frac{C\alpha^2}{(1-\alpha)} = C\alpha^2 \qquad [H^+] = C\alpha$$

$$\left[H^+\right] = \sqrt{K_aC}, pH = \frac{1}{2}\left[pK_a - \log C\right]$$

and for weak base

$$K_b = \frac{C\alpha^2}{(1-\alpha)} = C\alpha^2 \qquad [OH^-] = C\alpha$$

$$\left[OH^-\right] = \sqrt{K_bC} \qquad pOH = \frac{1}{2}\left[pK_b - \log C\right]$$

Ostwald dilution law is only applicable for weak electrolytes.

For conjugate acid-base pairs

$K_a K_b = K_w = 1 \times 10^{-14}$ at 25°C

$K_a K_b = K_w = 10^{-12}$ at 90°C

$K_w = [H_3O^+][OH^-] = 1 \times 10^{-14}$ at 298 K

K_w is called ionic product of water or autoionisation or autoprotolysis constant.

IONIC EQUILIBRIUM

In a mixture of strong acid or bases.

$$[H^+] = [H_3O^+] = \frac{\sum NV}{\sum V}, [OH^-] = \frac{\sum NV}{\sum V}$$

In a mixture of acid and base, resultant is
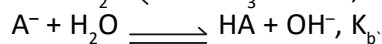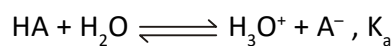(a) acidic mixture if N_1V_1 (acid) > N_2V_2 (base)

$$[H_3O^+] = \frac{N_1V_1 - N_2V_2}{V_1 + V_2}$$

(b) basic mixture if N_2V_2 (base) > N_1V_1 (acid)

$$[OH^-] = \frac{N_2V_2 - N_1V_1}{V_1 + V_2}$$

(c) neutral mixture if N_1V_1 (acid) = N_2V_2 (base)

Where K_a is the ionisation constant of acid and K_b is the ionisation constant of its conjugate base.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-, K_a$$
$$A^- + H_2O \rightleftharpoons HA + OH^-, K_{b.}$$
$$pK_a + pK_b = 14 = pKw$$
$$pH = -\log[H_3O^+]$$
$$pOH = -\log[OH^-]$$
$$pX = -\log X$$
$$pH + pOH = pK_w = 14$$

$$0 \le pH < 7 \quad 7 \quad 7 < pH \le 14$$

$$\longleftarrow \text{acidic} \longrightarrow | \longleftarrow \text{basic} \longrightarrow$$

neutral
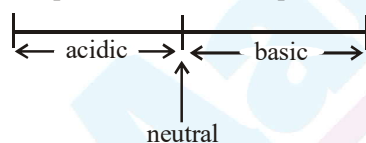
Buffers :

Buffer solutions are which have resistive nature for pH change
(i) On dilution pH of buffer solution remains unchanged.
(ii) When small amount of SA or SB is mixed in buffer solution then pH of buffer solution remains almost unchanged.
Types of buffer solution :
(i) Simple buffer solution (Aq. solution of WAWB salts)
(ii) Mixed buffer solution :
(a) Acidic buffer solution (WA + WA-SB salts)
(b) Basic buffer solution (WB + WB-SA salt)
Henderson - Hasselbalch equation for buffer

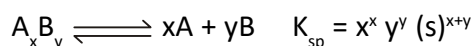**Acidic :** $pH = pK_a + \log \dfrac{[\text{conjugate base}] \text{ or } [\text{salt}]}{[\text{weak acid}]}$

IONIC EQUILIBRIUM

Basic : $pOH = pK_b + \log \dfrac{[\text{conjugate acid] or [salt}]}{[\text{weak base}]}$

Solubility product

Ionisation of weak electrolyte is decreased in the presence of common ion is called common ion effect. Solubility product of the sparingly soluble salt A_xB_y with solution (s) mol/litre in saturated solution.
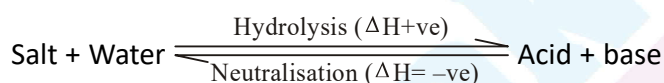
$$A_xB_y \rightleftharpoons xA + yB \qquad K_{sp} = x^x\, y^y\, (s)^{x+y}$$

Salt analysis of inorganic mixture depends on common ion effect and values of solubility products. In the presence of common ion solubility of electrolyte always decreases.

Solute AB is precipitate if $[A^+][B^-] > K_{sp}$

Group Precipitation

(i) $K_{sp} > [\ ][\ ] >$ Ionic product $\Rightarrow$ unsaturated

(ii) $K_{sp} = [\ ][\ ] =$ Ionic product $\Rightarrow$ saturated

(iii) $K_{sp} < [\ ][\ ] <$ Ionic product $\Rightarrow$ super saturated

                                           $\Rightarrow$ precipitation occurs

Salt and Salt Hydrolysis :

$$\text{Salt + Water} \underset{\text{Neutralisation } (\Delta H = -ve)}{\overset{\text{Hydrolysis } (\Delta H + ve)}{\rightleftharpoons}} \text{Acid + base}$$

Types of Salt :

(i) General (ii) acidic (iii) basic (iv) Mixed (v) Double (vi) Complex.

Types of General Salts :

(a) SA-SB   (b) SA-WB   (c) WA-SB   (d) WA-WB

Types of salt	Name of hydrolysis	Nature of aqueous solution and pH
SA - SB	—	Neutral, pH = 7
SA - WB	Cationic	Acidic, pH < 7
WA - SB	Anionic	Basic, pH > 7

	$K_a > K_b$	$K_b > K_a$	$K_a = K_b$
Hydrolysis	Cationic - anionic	Anionic - Cationic	Neutral hydrolysis
Nature	Acidic	Basic	Neutral
pH	pH < 7	pH > 7	pH = 7

IONIC EQUILIBRIUM

Summary :

Type of salt	$K_b = \dfrac{K_w}{\text{Ionisation constant of weak acid}}$	$h = \sqrt{\dfrac{K_b}{C}}$	$[H^+]$	pH
SASB	–	–	–	7
WASB	$K_h = \dfrac{K_w}{K_a}$	$h = \sqrt{\dfrac{K_w}{K_a \times C}}$	$\sqrt{\dfrac{K_w \times K_a}{C}}$	$7 + \dfrac{1}{2}pK_a + \dfrac{1}{2}\log C$
SAWB	$K_h = \dfrac{K_w}{K_b}$	$h = \sqrt{\dfrac{K_w}{K_b \times C}}$	$\sqrt{\dfrac{K_w \times C}{K_b}}$	$7 - \dfrac{1}{2}pK_a - \dfrac{1}{2}\log C$
WAWB	$K_h = \dfrac{K_w}{K_a \times K_b}$	$h = \sqrt{\dfrac{K_w}{K_a \times K_b}}$	$\sqrt{\dfrac{K_w \times K_a}{K_b}}$	$7 + \dfrac{1}{2}pK_a - \dfrac{1}{2}pK_b$

= For precipitation of common salt (NaCl), HCl gas is passed & for soap ($C_{17}H_{35}$ COONa), NaCl is mixed. For amphiprotic anion (as HCO_3^-)

$$pH = \frac{pK_1 + pK_2}{2}$$

For acidic indicator (HIn),   For basic indicator (InOH)
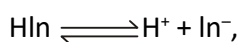
$HIn \rightleftharpoons H^+ + In^-$, $InOH \rightleftharpoons In^+ + OH^-$
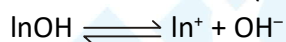
$pH = pK_{In} + \log \dfrac{[In^-]}{[HIn]}$, $pOH = pK_{In} + \log \dfrac{[In^+]}{[InOH]}$

Colour change of the indicator is explained by:
(i) Ostwald's Theory

Name of indicator	Colour in acidic medium	Colour in basic medium	Working pH range of indicators
Methyl orange (MeOH)	Orange red	Yellow	3.1 to 4.5
Methyl red	Red	Yellow	4.2 to 6.2
Phenol red	Yellow red	Red	6.2 to 8.2
Phenolphthalein (HPh)	Colourless	Pink	8.2 to 10.2

Acid-Base Titration

Type of Titration	pH range of Titration	Suitable indicators
SA/SB.	3 - 11	All indicators (MeOH, HPh etc.)
SA/WB	3 - 7	Methy orange (MeOH) and methyl red
WA/SB	7 - 11	Phenolphthalein (Hph)
WA/WB	6.5 – 7.5	Phenol red

THERMODYNAMICS

Work

Mechanical work = force × displacement = F × d

Electrical work = pot. diff. × quantity of current = E × Q

Gravitational work = gravitational force × height = mg × h

Mechanical Work = pressure × change in volume = -P ×ΔV

For expansion W = –ve ($\because V_2 > V_1$)

For compression W = +ve ($\because V_2 < V_1$)

Units of work 1 cal = 4.184×10^7 erg = 4.184 J

Enthalpy :

Enthalpy (H) is defined as the total heat contant of the system at constant pressure,

$H = E + PV$

$\Delta H = \Delta E + \Delta(PV)$

or $\quad \Delta H = \Delta E + (P_2 V_2 - P_1 V_1)$

$\Delta H = \Delta E + P\Delta V + V\Delta P$

at constant pressure $\Delta H = \Delta E + P\Delta V$

so $\quad \Delta H = \Delta E + \Delta n_g RT$ (For chemical reaction at constant temperature)

First Law of Thermodynamics

Mathematically

$q = \Delta E - w$

or $\Delta E = q + w$

q = heat absorbed or evolved (+ve if absorbed and –ve if evolved)

For Isothermal Process

$dT = 0 \therefore \Delta E = 0$ q = –W (This is true for ideal gas only)

i.e., heat absorbed is used in work done by the system.

For Adiabatic Process

$\because q = 0 \qquad \therefore \Delta E = W$

i.e., Internal energy is used up in work done by the system. If work is done on the system. Its internal energy will increase and if work is done by the system its internal energy decreases. In adiabatic process work behave as state function.

THERMODYNAMICS

For isobaric Process

$\because$ $dP = 0$ $q_P = \Delta H$

Work done

(1) For irreversible process $W = -P_{ext} \times \Delta V$

(2) For reversible process - $W = -\int_{v_1}^{v_2} PdV$

(3) For reversible isothermal process -

$$W = -2.303 \, nRT \log_{10} \frac{V_2}{V_1} = -2.303 nRT \log_{10} \frac{P_1}{P_2}$$

(4) In adiabatic process $W = \Delta E$

For an ideal gas $W = nC_v(T_2 - T_1)$

or $W = \dfrac{nR}{(\gamma - 1)}(T_2 - T_1)$

(5) When an ideal gas is freely expand in vacuum then the obtained work done is zero because $P_{ext.} = 0$

(6) Reversible expansion process are more efficient than the irrvesible expansion process.

Entropy

Entropy of a system is a measure of the degree of randomness or disorderness of the system and is denoted by S.

(1) ΔS for reversible isothermal process -

$$\Delta S = \frac{q_{rev.}}{T} = \frac{-W_{rev.}}{T} = \frac{2.303 nRT \log \dfrac{V_2}{V_1}}{T}$$

$$\Delta S = 2.303 \, nR \log \frac{V_2}{V_1} = 2.303 \, nR \log \frac{P_1}{P_2}$$

(q_{rev} = heat supplied to a system at temp. TK in a reversible manner)

(2) $\Delta S = S_{products} - S_{reactants}$

(3) $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$

$$\Delta S_{total} = \frac{+q}{T_{system}} + \frac{-q}{T_{surroudings}}$$

If $T_{system} < T_{surroundings}$ heat flows from hot region to cold one ΔS_{total} is +ve and heat flow is spontaneous.

If ΔS_{total} is –ve the process is non spontaneous.

(4) ΔS for reversible adiabatic process $\Delta S = \dfrac{q_{rev.}}{T} = O$

(5) ΔS for reversible isobaric process $= 2.303 n C_P \log \dfrac{T_2}{T_1}$

(6) ΔS for reversible isochoric process $= 2.303 n C_V \log \dfrac{T_2}{T_1}$

(7) ΔS for phase transition $q_{rev} = \Delta H_{rev} \Rightarrow \Delta S = \dfrac{\Delta H_{rev}}{T}$

- Entropy change of fusion , $\Delta S_f = \dfrac{\Delta H_f}{T}$

  (T = freezing point or melting point)

- Entropy change of vapourization, $\Delta S_v = \dfrac{\Delta H_v}{T}$ (T = boiling point)

(8) Standard entropy ($S°$) = entropy of one mole of substance at 1 atm and 25°C

Free Energy

Free energy (G) is a measure of maximum useful work done.

G = H − TS,

At constant T & P

$\Delta G = \Delta H - T\Delta S$ (Gibbs - Helmholtz equation)

$\Delta G = G_{products} - G_{reactants}$

(i) $\Delta G° = \Delta G°_{f\,products} - \Delta G°_{f\,reactants}$

(ii) $\Delta G°$ for the element = 0

(iii) $\Delta G° = - 2.303\,RT \log K$ (K = equilibrium constant)

If $\Delta G°$ is −ve, K > 1

$\Delta G° = 0$, K = 0

$\Delta G°$ is +ve , K < 1

Condition for spontaneity of a chemical reaction is ΔG = −ve

ΔH	ΔS	$\Delta H - T\Delta S$	Behaviour
−ve	+ve	$\therefore \Delta G = -ve$	Spontaneous at all temperatures
+ve	−ve	$\therefore \Delta G = +ve$	Non-spontaneous at all temperatures
+ve	+ve	$\Delta G = -ve (if \Delta H < T\Delta S)$ $\Delta G = +ve (if \Delta H > T\Delta S)$	Spontaneous Non-spontaneous
−ve	−ve	$\Delta G = -ve (if \Delta H > T\Delta S)$ $\Delta G = +ve (if \Delta H < T\Delta S)$	Spontaneous Non-spontaneous

REDOX REACTIONS

1. **Stock notations** Expressing the oxidation state of a metal by Roman numbers like. I ,II, III etc. within parenthesis is called stock notation e.g., $FeSO_4$ = Iron (II) sulphate; Na_2CrO_4 = Sodium chromate (VI) etc.

2. **Valency** of an element is only a number and as such there is no postive or negative sign attached to it. It can neither be zero nor fractional. Oxidation number, on the other hand, refers to charge and hence has either postive or negative sign. It can also be zero or fractional. For example oxidation state of C in CH_2Cl_2 is zero while that of Fe in Fe_3O_4 is $\frac{8}{3}$ and of S in $Na_2S_2O_3$ is 2.0.

3. **Calculation of oxidation state :**

   Rules I :

   The oxidation state of any atom in its elemental state is zero.

   Rules II:

   The maximum oxidation state of any atom will be equal to (+group number) and minimum oxidation state will be equal to (group number –8), where group numbers are in roman numerals. For example, Sulphur (S) is member of group VI A and hence its maximum oxidation state is +6 and minimum is = (6–8) = –2

   Exception : Cu(IB) : +1, +2

   Au (IB) : 1, +3

   Xe (0) : +2, +4, +6, +8. etc

   Rule III:

   The sum of oxidation state of all the atoms in a molecule is zero and for ions, it is equal to the ionic charge.

   Rule IV:

   The oxidation states of some elements are fixed in all their compounds.

   +1: Alkali metals (Li, Na, K, Rb, Cs, Fr) and Ag

   +2: Alkaline earth metals (Be. Mg, Ca, Sr, Ba, Ra) and Zn

   +3: Al

   –1 :F

Rule V:

Oxidation state of hydrogen is +1 in all of its compounds, except the metal hydrides, where it is −1.

Rule VI:

Oxidation state of oxygen is −2 in all of compounds except

(i) Peroxide like Na_2O_2, H_2O_2, BaO_2, etc, where it is −1.

(ii) Superoxides like KO_2, RbO_2, etc, where it is −1/2.

(iii) Some other binary compounds of alkali metals and oxygen like KO_3 (O.S. of O = −1/3), Rb_2O_3 (O.S. of O = −2/3), etc.

(iv) Oxides of fluorine, where it is positive states. For example: O.S. of O in OF_2, O_2F_2, O_3F_2 etc. are +2, +1, +2/3, respectively.

Rule VII:

The charges on different ions commonly used, should be known.

CO_3^{2-}	Carbonate ion	HCO_3^-	Hydrogen carbonate ion
SiO_4^{4-}	Silicate ion	PO_4^{3-}	Phosphate ion
HPO_4^{2-}	Hydrogen phosphate ion	$H_2PO_4^-$	Dihydrogen phosphate ion
HPO_3^{2-}	Phosphite ion	NO_3^-	Nitrate ion
NO_2^-	Nitrite ion	SO_4^{2-}	Sulphate ion
SO_3^{2-}	Sulphite ion	S^{2-}	Sulphide ion
S_2^{2-}	Pyrite ion	$S_2O_7^{2-}$	Disulphate ion
$S_2O_3^{2-}$	Thiosulphate ion	$S_2O_8^{2-}$	Peroxodisulphate ion
ClO^-	Hypochlorite ion	ClO_3^-	Chlorate ion
ClO_2^-	Chlorite ion	ClO_4^-	Perchlorate ion

Rule VIII :

In the complex compound, the overall charge on ligand should be considered in place of considering the charges on individual atoms.

4. **Peroxy linkage calculation :**

The linkage of the two oxygen atoms i.e. there are the oxygen-oxygen linkages.

(i) $(O.S)_{Cal.} > (O.S)_{max.}$; Peroxy linkage is present

(ii) $(O.S)_{Cal.} = (O.S)_{max.}$: Oxy linkage is present

(ii) $(O.S)_{Cal.} < (O.S)_{max.}$: M–M bond is persent

Calculation of no. of peroxy linkage :

$$n = \frac{\text{(Calculated oxidation state)} - \text{(Maximum oxidation state)}}{1 \, or \, 2}$$

$\Rightarrow$ If two central atom present than divide it by 1

$\Rightarrow$ If one central atom present then divide it by 2

$\Rightarrow$ When 'n' comes out to be fractional then use below formula

n = [O.S]$_{cal.}$ – [O.S]$_{max.}$ + 1

Example : H$_2$SO$_5$

$$\begin{array}{c} O \\ \parallel \\ H{-}O{-}S{-}O{-}O{-}H \\ \parallel \\ O \end{array} \quad \longrightarrow \text{Central atom}$$
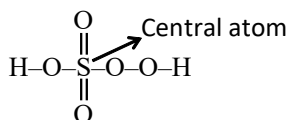
no. of peroxy linkage = $\dfrac{8-6}{2}$ = 1

Calculated O.S. of S $\rightarrow$ (+8)

Maximum O.S. of S $\rightarrow$ (+6)

i.e. (O.S.)$_{Cal.}$ > (O.S.)$_{max.}$ $\Rightarrow$ Peroxy linkage is present

Example : H$_2$S$_2$O$_7$

$$\begin{array}{cc} O & O \\ \parallel & \parallel \\ HO{-}S{-}O{-}S{-}OH \\ \parallel & \parallel \\ O & O \end{array}$$
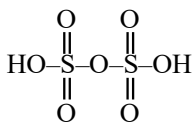
For sulphur (O.S)$_{max.}$ = +6

(O.S)$_{cal.}$ = +6

+2 + 2x – 14 = 0

2x = 12

 x= +6

Therefore, no peroxy linkage is present.

Example : H$_4$P$_2$O$_6$

For phosphorus (O.S)$_{max.}$ = +5

4(+1) + 2x – 12 = 0

2x – 8 = 0

x = +4

Therefore, no peroxy linkage is present

As (O.S)$_{max.}$ > (O.S)$_{cal.}$ $\rightarrow$ M – M bond

5. **Redox reaction :**

Redox reaction are also called electron - transfer reactions since electron are transferred from the reductant to the oxidant.

Type of redox reaction :

These are the reactions involving oxidation as well as reduction.

Examples:

$$\overset{0}{Zn} + 2\overset{+1}{H}Cl \longrightarrow \overset{+2}{Zn}Cl_2 + \overset{0}{H_2}$$
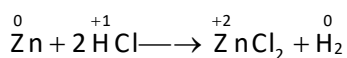
(Oxidation = Zn, Reduction = HCl)

1. Disproportionation Reaction:

The redox reaction in which the atoms of same element belonging from the same molecule or ion are oxidised as well as reduced are called disproportionation reaction. Such reaction are also called autoredox or self-redox reaction.

Examples:

$$3\overset{0}{Cl_2} + 6NaOH \longrightarrow 5Na\overset{-1}{Cl} + Na\overset{+5}{Cl}O_3 + 3H_2O$$
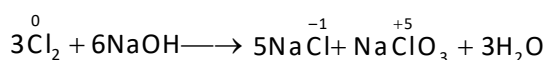
Cl–atoms are oxiidised and reduced, both

2. Comproportionation Reaction

These are just the reverse of disproportionation. Atoms of the same element, belonging to the same molecule or ion, oxidise and reduce to give the element in the commom oxidation state.

Example:

$$2H_2\overset{-2}{S} + \overset{+4}{S}O_2 \longrightarrow \overset{0}{S} + 2H_2O$$
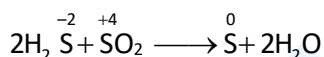
6. **Methods of Balancing Chemical reactions**
   1. Oxidation number method
   Step I: Select the species undergoing oxidation and reduction and write both the processes, separately
   StepII: Balance the atoms of responsible elements (elements responsible for change in oxidation state) by simple counting.
   StepIII: Determine the changes in oxidation state of both the process, due to the total number of atoms of responsible elements.
   StepIV: Make the changes is oxidation state of both processes, equal by multiplying with suitable numbers. Add both the processes after multiplication.
   StepV : If some reaction components are left, write them in proper side and balance them by simple counting.
   StepVI: If the reaction is not balanced at step IV or V, add some molecule or ion in the proper side, The species added should be according to the reaction and it should not create a new change in oxidation state.
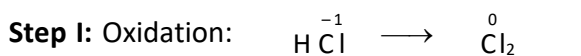   **Example :**
   $$KMnO_4 + H_2SO_4 + HCl \longrightarrow K_2SO_4 + MnSO_4 + H_2O + Cl_2$$

Solution:

Step I: Oxidation: $H\overset{-1}{C}l \longrightarrow \overset{0}{Cl_2}$

Reduction: $K\overset{+7}{M}nO_4 \longrightarrow \overset{+2}{M}nSO_4$

Step II: Oxidation: $2HCl \longrightarrow Cl_2$

Reduction: $KMnO_4 \longrightarrow MnSO_4$

Change is O.S.

Step III: Oxidation: $2H\overset{-1}{C}l \longrightarrow \overset{0}{Cl_2}$ 2

Rediuction: $K\overset{+7}{M}nO_4 \longrightarrow \overset{+2}{M}nSO_4$ 5

Change is O.S.

Steep IV: Oxidation: $2HCl \longrightarrow Cl_2$ 2]×5

Reduction: $KMnO_4 \longrightarrow MnSO_4$ 5]×2

_____

$2KMnO_4 + 10\ HCl \longrightarrow 2MnSO_4 + 5Cl_2$

Step V: $2KMnO_4 + 10HCl + 3H_2SO_4 \longrightarrow 2MnSO_4 +$

$5Cl_2 + K_2SO_4 + 8H_2O$ is the balanced reaction.
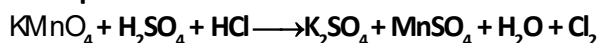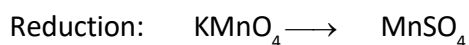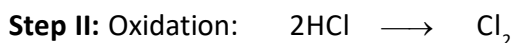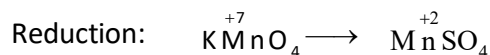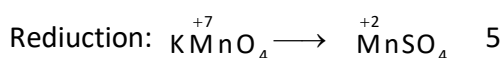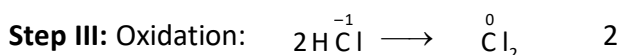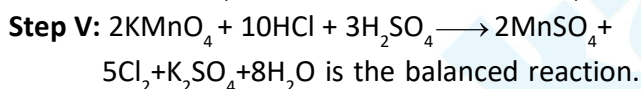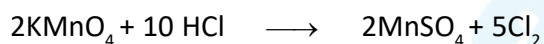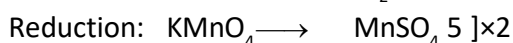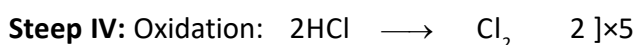
2. Ion electron method :

Step I : If the reaction is given in molecular form, convert it in the ionic form. For it, write strong acids, strong bases and all water soluble salts in ionic form and then cancel out the spectator ions (ions common in both sides).

Step II: Select the species undergoing oxidation and reduction and write them separately.

Step III: Balance the atoms of responsible element by simple counting.

Step IV: Balance the atoms of all other elements by adding some molecule or ion in the proper side. The species added should be according to the reaction and it should not create not create any new change in the oxidation state. In most of the reaction, the other elements are hydrogen or oxygen. They are balanced according to medium of the reaction.

In acidic medium:

→ Add one water molecule in the opposite side for each excess of oxygen atom.

→ Add one H^+ ion in the opposite side for each excess of hydrogen atom.

In basic medium:

→ Add one water molecule in the same side and two OH^- ions in opposite side for each excess of oxygen atom.

→ Add one OH^- ion in the same side and one water molecule in the opposite side for each excess of hydrogen atom.

REDOX REACTIONS

→ Hydrogen and oxygen atoms may also be balanced by balancing them first in acid medium and then replacing the H⁺ ions suitably by OH⁻ ions. For it, add OH⁻ ions equal in number to the H⁺ ions in both the sides and then write the combination of one OH⁻ ion and one H⁺ ion ions as an H_2O molecule. It must be noted that the combination of one H⁺ and one OH⁻ ions, in ionic form of a reaction.

Step V : Balance the charges in both process by adding proper number of electron in the proper side. The number of electrons added and the side, in which they are added, can be checked.

→ In oxidation, electrons will be added in the right side and in the reduction, left side.

→ The number of electrons lost or gained will always be equal to the change in oxidation state.

→ The number of elecrons lost or gained in a particular process in independent to the medium of reaction.

Step VI: Make the total number of electrons lost and gained equal by multiplying with suitable numbers. Add both the processes. It should be balanced reaction in ionic form.
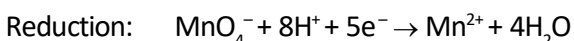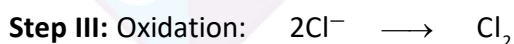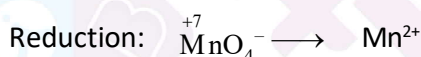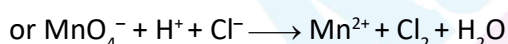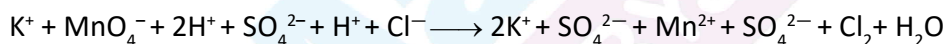
Step VII: If the original reaction was in molecular form, convert the ionic form into molecular form.

Example :

$KMnO_4 + H_2SO_4 + HCl \rightarrow K_2SO_4 + MnSO_4 + Cl_2 + H_2O$
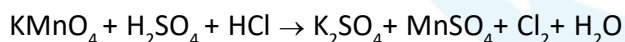
Solution:

Step I: Ionic form of the given reaction is

$K^+ + MnO_4^- + 2H^+ + SO_4^{2-} + H^+ + Cl^- \longrightarrow 2K^+ + SO_4^{2-} + Mn^{2+} + SO_4^{2-} + Cl_2 + H_2O$

or $MnO_4^- + H^+ + Cl^- \longrightarrow Mn^{2+} + Cl_2 + H_2O$

Step II: Oxidation: $Cl^- \longrightarrow \overset{0}{Cl_2}$

Reduction: $\overset{+7}{Mn}O_4^- \longrightarrow Mn^{2+}$

Step III: Oxidation: $2Cl^- \longrightarrow Cl_2$
Reduction: $MnO_4^- \longrightarrow Mn^{2+}$

Step IV: Oxidation: $2Cl^- \longrightarrow Cl_2$
Reduction: $MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$

Step V: Oxidation: $2Cl^- \longrightarrow Cl_2 + 2e^-$
Reduction: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Step VI: Oxidation: $2Cl^- \longrightarrow Cl_2 + 2e^-] \times 5$
Reduction: $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$
_____
$2MnO_4^- + 16H^+ + 10Cl^- \longrightarrow 2Mn^{2+} + 8H_2O + 5Cl_2$
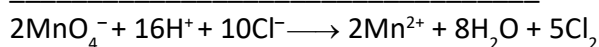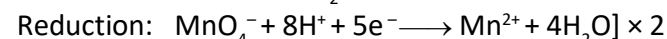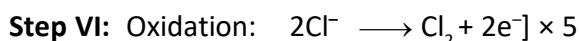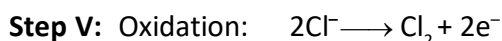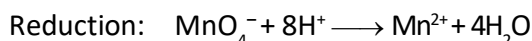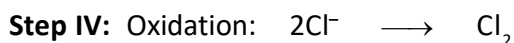
It is balanced reaction in ionic form.

Step VII: $2KMnO_4 + 10\ HCl + 3H_2SO_4 \longrightarrow 2MnSO_4 + 8\ H_2O + 5Cl_2 + K_2SO_4$ is the balanced reaction.

7. **Equivalence weight (E) :**

In general, Eq. wt. (E) = $\dfrac{\text{Atomic weight or Molecular weight}}{\text{valency factor(v.f)}} = \dfrac{\text{Mol. wt.}}{n-\text{factor}} = \dfrac{M}{x}$

Number of Equivalents = $\dfrac{\text{mass of species}}{\text{eq. wt. of that species}}$

For a solution, Number of equivalents = N_1V_1, where N is the normality and V is the volume in litres

● Equivalent mass is a pure number which, when expressed in gram, is called gram equivalent mass.
●The equivalent mass of a substance may have different values under different conditions.
● There is no hard and fast rule that equivalent weight will be always less than the molecular mass.
(a) The equivalent weight of an element is that weight of the element that will combine with or replace directly or indirectly 1.0 gm of H, 35.5 gm of Cl or 8.0 gm. of O or 108 gm of Ag.
(b) In the reaction $Mg + Cl_2 \rightarrow MgCl_2$
1 atom of Mg loses 2 electrons to become Mg^{2+} ion. If we start with 1 mole or 24 gm of Mg, we have N_A (6.023×10^{23}) number of Mg atoms which would lose $2N_A$ number of electrons and form N_A number of Mg^{2+} ions. Therefore, we get $2N_A$ number of electrons from 24 gm of Mg.

So, N_A number of electrons can be obtained from $\dfrac{24}{2}$ = 12 gm of Mg. Thus the equivalent

weight of Mg = 12.
Thus equivalent weight of an element is that weight of the element which loses or gained Avogadro number (N_A) of electrons.
Valency factor/n-factor calculation :
For Elements : Valency factor = valency of the element.
For Acids : Valency factor = number of replaceable H^+ ions per acid molecule.
v. f. for acid is the number of OH^- replaced from the base by each molecule of acid.
Example :
n factor of HCl = 1
n factor of CH_3COOH = 1
n factor of H_2SO_4 = 2

For Bases :

Valency factor = number of replacable OH⁻ ions per base molecule.

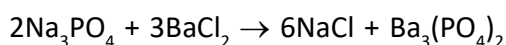Example :

n factor of NaOH = 1

n factor of $Ca(OH)_2$ = 2

n factor of $Al(OH)_3$ = 3

n factor of $B(OH)_3$ = 1 (because it is a mono basic acid)

Salts :

(i) When no atom undergoes change in oxidation state

The n-factor for such salts isdefined as the totalmoles of cationic/anionic charge present in 1 mole of the salt. For the reaction

$2Na_3PO_4 + 3BaCl_2 \rightarrow 6NaCl + Ba_3(PO_4)_2$

n-factor of Na_3PO_4 in this reaction is 3

n-factor of $BaCl_2$ in this reaction is 2

n-factor of NaCl in this reaction is 1

n-factor of $Ba_3(PO_4)_2$ in this reaction is 6

(ii) When only one atom undergoes change in oxidation state and goes in only one product

The n-factor of such salts is defined as the number of moles of electrons exchanged (lost or gained) by one mole of the salt.
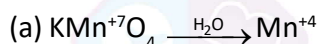
For example, let us calculate the n-factor $KMnO_4$ for the given chemical change.

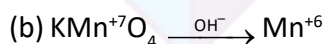$KMn^{+7}O_4 \xrightarrow{\;H^+\;} Mn^{+2}$
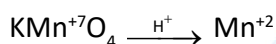
In this reaction, oxidation state of Mn changes from +7 to +2. Thus, $KMnO_4$ is acting as oxidising agent, since it is reduced

∴ n-factor of $KMnO_4 = |1 \times (+7) - 1 \times (+2)| = 5$

Similarly

(a) $KMn^{+7}O_4 \xrightarrow{\;H_2O\;} Mn^{+4}$

n-factor of $KMnO_4 = |1 \times (+7) - 1 \times (+4)| = 3$

(b) $KMn^{+7}O_4 \xrightarrow{\;OH^-\;} Mn^{+6}$

n–factor of $KMnO_4 = |1 \times (+7) - 1 \times (+6)| = 1$

It can be seen that in all above chemical changes, $KMnO_4$ is acting as oxidising agent, yet its n-factor is not same in all reactions. Thus, the n-factor of a compound is not fixed, it depends on the type and the extent of reaction it undergoes.

(iii) When only one atom undergoes change in oxidation state but goes in two products with the same oxidation state

In such case, the n-factor is calculated in the same manner as in case (ii).

For example, let us calculate the n-factor of $K_2Cr_2O_7$ for the given chemical change.

$Cr_2O_7^{2-} \rightarrow Cr^{3+} + Cr^{3+}$
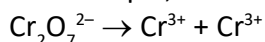
In this reaction, state of Cr changes from +6 to +3 in both products.
∴ n-factor of $K_2Cr_2O_7$ = $|2 \times (+6) - 2 \times (+3)|$ = 6

(iv) When only one atom undergoes change in oxidation state but goes in two products with different oxidation state

Consider a chemical change, $2Mn^{7+} \rightarrow Mn^{4+} + Mn^2$

Out of the two moles of Mn^{7+}, one mole Mn^{7+} changes to Mn^{+4} bygaining 3 moles of electrons and the other mole of Mn^{7+} changes to Mn^{2+} by gaining 5 mole of electrons, so in all 8 mole of electrons are gained by 2 mole of Mn^{7+}. So each mole of Mn^{7+} has gained $8/2$ = 4 mole of electrons. Thus, 4 would be the n-factor of Mn^{7+} in this reaction.

If the reaction would have been
$3Mn^{7+} \rightarrow 2Mn^{2+} + Mn^{4+}$
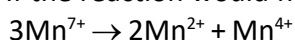
Out of 3 moles of Mn^{7+}, two moles of Mn^{7+} changes to Mn^{2+} by gaining 10 mole of electrons and one mole of Mn^{7+} changes to Mn^{4+} by gaining 3 mole of electrons. Thus each mole of Mn^{7+} have gained $13/3$ mole of electrons. Therefore, the n-factor of Mn^{7+} in this reaction would be $13/3$.

Note that n-factor can be a fraction because it is not the number of electrons exchanged but it is the number of moles of electrons exchanged which can be a fraction.

Now, if the reaction would have been $3Mn^{7+} \rightarrow Mn^{2+} + 2Mn^{4+}$. Thus, each mole of Mn^{7+} have gained $11/3$ mole of electron. Therefore, n-factor of Mn^{7+} in this reaction would be $11/3$. Salts which react in a fashion that only one atom undergoes change in oxidation state but goes in two products with different state (in one product with same oxidation state and in other with different state than in the reactant).

For such reactions also, the n-factor calculation is not possible without the knowledge of balanced chemical reaction because n-factor of reactant would depend on the fact that how much of reactant under went change to different oxidation state +y and how much of reactant remained in the same oxidation state +x.

(v) Salts or compounds which undergoes disproportionation reaction
Disproportionation reactions can be divided into two types.

(a) Disproportionation reactions in which moles of compound getting oxidised and reduced are same i.e. moles of oxidising agent and reducing agent are same. The n-factor for such compounds is calculated by either the number of mole of electrons lost or gained by one mole of the compound because in such a case, n-factor of the compound acting as oxidizing agent or as reducing agent would be same.

For example, $2H_2O_2 \rightarrow 2H_2O + O_2$

Out of 2 mole of H_2O_2 used in reaction, one mole of H_2O_2 gets oxidised to O_2 (oxidation state of O changes from –1 to –2). When 1 mole of H_2O_2 gets oxidised to O_2, the half - reaction would be $O_2^{2-} \rightarrow O_2^0 + 2e^-$ and when 1 mole of H_2O_2 gets reduced to H_2O,

the half-reaction would be $O_2^{2-} + 2e^- \rightarrow 2O^{2-}$

Thus, it is evident that one mole of H_2O_2 (which is either getting oxidised or reduced) will lose or gain 2 mole of electrons. Therefore, n-factor of H_2O_2 as oxidizing as well as reducing agent in this reaction is 2. Thus
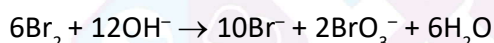

Or when the reaction iswritten as

$2H_2O_2 \rightarrow 2H_2O + O_2$
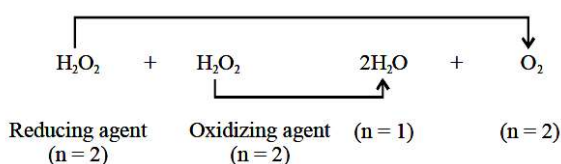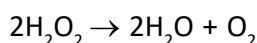
Where, H_2O_2 is not distinguished as howmuch of it functions as oxidizing agent and howmuch as reducing agent, then n-factor calculation can be done in the followingmanner. Find the number of electrons exchanged (lost or gained) using the balanced equation and divide it by the number ofmoles H_2O_2 involved in the reaction.Thus, then-factor of H_2O_2 when the reactioniswrittenwithout segregating

Oxidising and reducing agent is $\dfrac{2}{2}$

$$\underset{(n=1)}{2H_2O_2} \rightarrow \underset{(n=1)}{2H_2O} + \underset{(n=2)}{O_2}$$
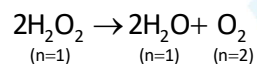
(b) Disproportionation reactions inwhichmoles of compound getting oxidised and reduced are not same.

$6Br_2 + 12OH^- \rightarrow 10Br^- + 2BrO_3^- + 6H_2O$

In this reaction, themole of electrons lost by the oxidation of some of themoles of Br_2 are same as the number ofmole of electrons gained by the reduction of rest of the moles of Br_2 of the 6 moles of Br_2 used, onemole is getting oxidized, loosing 10 electrons (as reducing agent) and 5 moles of Br_2 are getting reduced and accepts 10moles of electron (as oxidizing agent)
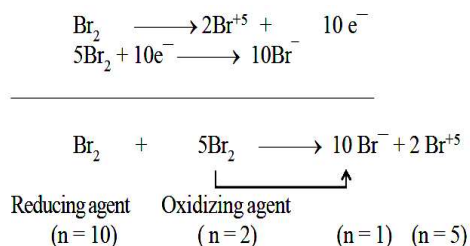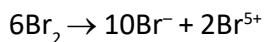
Thus, n-factor of Br_2 acting as oxidizing agent is 2 and that Br_2 acting as reducing agent has n-factor 10.

Or when the reaction is written as

$6Br_2 \rightarrow 10Br^- + 2Br^{5+}$

where, Br_2 is not distinguished as how much of it function as oxidizing agent and how much as reducing agent, then for calculating n-factor of compound in such reactions, first find the total number of electrons exchanged (lost or gained) using the balanced equation and divide it with the number of mole of Br2 involved in the reaction to get the number of mole electrons exchanged by one mole of Br_2. In the overall reaction, the number of mole of electrons exchanged (lost or gained) is 10 and the moles of Br_2 used in the reaction are 6.

Thus, each mole of Br_2 has exchanged 10/6 or 5/3 mole of electrons. Therefore , the n-factor of Br_2 when the reaction is written without segregation oxidising and reducing agent is 5/3.

$6Br_2 \rightarrow 10Br^- + 2Br^{5+}$
(N = 5/3)   (N = 1)   (N = 5)