

SOME BASIC CONCEPTS OF CHEMISTRY

Chapter - 1

- Significant Figures:** The number of meaningful digits present in a number are called significant figures. All the meaningful digits are certain except last digit which is uncertain. Rules for determining significant figures are :

 - All non zero digits present in a number are significant.
 - The leading zeros are not significant but zeros between two nonzero digits are significant.
 - Zeros in the end of the number and after the decimal are significant. But, if otherwise, the zeros are not significant.
 - Exact numbers have an infinite number of significant figures.
 - During addition and subtraction the result should contain same number of decimal places as are in the term with the least number of decimal places.
 - During multiplication and division the result must contain same number of significant figures as are in the least precise term used in calculation.
 - To round off the number, the digit to be retained is increased by one if it is followed by a digit greater than 5 and it is retained as such if it is followed by a digit smaller than 5. If it is followed by 5 only then it is retained as such if it is an even digit and increased by one if it is an odd digit
- Laws of Chemical Combination**

 - Law of conservation of mass :** In all the physical and chemical changes the total mass of the reactants is equal to that of the products.
 - Law of definite proportion:** Since mass is conserved, a sample of a pure compound whatever its source may be, always consists of the same elements combined in the same proportion by mass.
 - Law of multiple proportion:** When two elements combine to form two or more compounds then the masses of one of the elements which combine with a fixed mass of the other, bear a simple ratio to one another.
 - Law of reciprocal proportions :** The ratio by mass in which two elements combine with the fixed mass of third element is either the same or simple multiple of the ratio in which they combine with each other.
 - Gay lussac's law of gaseous volumes :** Gases combine or produced in a chemical reaction in the simple ratio by volume provided all gases are at same temperature and pressure.
 - Avogadro's law :** Equal volumes of all the gases contain equal number of molecules under similar conditions of temperature and pressure.
- Dalton's Atomic Theory :**

 - Matter consists of indivisible particles called atoms.
 - Atoms of same element are identical in size, shape and mass but atoms of different elements are not identical in these respects.
 - Atoms of same or different elements combine together to form compound atoms (now called molecules)
 - Atoms of different elements combine in a fixed ratio to form compounds.
 - Chemical reactions involve reorganization of atoms. These are neither created nor destroyed in a chemical reaction.
- One Atomic Mass Unit (amu) :** It is a mass unit equal to exactly one twelfth the mass of a carbon -12 atom.
The new symbol used is 'u' (unified mass) in place of amu.
- Atomic mass :** It is the average relative mass of an atom as compared to that of carbon atom (C - 12) taken as 12u .
 - Molecular mass :** It is the average relative mass of a molecule of a substance as compared to that of carbon atom (C - 12) taken as 12u . It is equal to the sum of atomic masses of all the elements present in the molecule.
 - Equivalent weight :** Equivalent weight of an element is defined as the number of parts by weight of the element which combine with or displace from a compound 1.00 part by wt. of hydrogen, 8 parts by wt. of oxygen or 35.5 parts by wt. of chlorine. Broadly, a simple formula can be used,

$$E = \frac{M(\text{Mol. mass})}{n_f (\text{n factor})}$$

Where n_f = Valency in case of atom
 = Total positive or negative oxid. number of atom in molecule
 = Basicity or Acidity
 = Change in oxid. number in case of a redox reaction.

No. of gram equivalent = $\frac{\text{wt in gm}}{\text{Eq. wt}}$

 - Dulong and Petit's law :**
$$\text{At. wt (approx.)} = \frac{6.4}{\text{sp.heat (in cal.)}}$$
- Mole**

 - A mole is the amount of a substance that contains as many entities (atoms, molecules, ions or other particles) as there are atoms in exactly 0.012 kg (or 12 gm) of the carbon-12 isotope. This number was found equal to 6.022×10^{23} .
 - This number is also known as Avogadro's constant.

- (c) The mass of 1 mol of any substance is defined as its molar mass.
- (d) The molar volume (V_m) of a substance is the volume of one mole of that substance (gas). This volume is same for all the gases at STP (Temp. 0°C , Press 1 Atm) i.e., equal to 22.4L.
- (e) No. of moles of a substance, $(n) = \frac{w(\text{in gm})}{\text{molar mass}}$, $(n) = \frac{\text{volume in Lt. at NTP/STP}}{22.4 \text{ L}}$,

7. Percentage Composition :

$$\text{Mass \% of an element} = \frac{\text{mass of that element in the compound}}{\text{molar mass of the compound}} \times 100$$

8. **Empirical and Molecular Formula :** Empirical formula represents the simplest whole number ratio of various atoms present in a compound while molecular formula shows the exact number of different types of atoms present in a molecule of a compound.

$$\text{Emp. F.} = \frac{\text{Mol. F.}}{n} \quad \text{where} \quad n = \frac{\text{molar mass}}{\text{emp. formula mass}}$$

Determination of emp. formula involves following steps:

- (a) Relative no. of atoms = $\frac{\text{mass \% of element}}{\text{atomic mass}}$
- (b) Divide these rel. no. of atoms of various elements with the smallest one to get the simplest atomic ratio.
- (c) Multiply these atomic ratios if needed, with suitable integer to get the simplest whole number ratio, which determines emp. formula.

$$\text{Molar mass} = 2 \times \text{vapour density}$$

9. **Stoichiometry:** Stoichiometry represents the relationships of different properties of various reactants and products present in a chemical change. The chemical equation must be balanced from which we can know following relations.

- (a) mol-mol relationship (b) mass-mass relationship (c) mass-volume relationship.

using these relationships we can also predict the limiting reagent which is defined as : It is the reactant which is entirely consumed during the reaction leaving some of the other reactant unconsumed.

10. Concentration of a Solution :

(a) **Mass percent :** $\frac{\text{mass of solute}}{\text{mass of solution}} \times 100$

(b) **Mole fraction (x) :** $\frac{\text{number of moles of a component present in a solution}}{\text{total number of moles of the solution}}$

$$x_A = \frac{n_A}{n_A + n_B} \quad x_B = \frac{n_B}{n_A + n_B}, \quad x_A + x_B = 1$$

- (c) **Molarity (M) :** It is the number of moles of the solute dissolved per litre of the solution.

$$\text{Molarity (M)} = \frac{\text{no. of moles of the solute}}{\text{vol. of solution in litres}} = \frac{\text{mass of solute in gram}}{\text{molar mass} \times \text{vol. of solution in litres}}$$

- (d) **Molality (m) :** It is the number of moles of the solute present per kg. of the solvent

$$\text{Molality (m)} = \frac{\text{no. of moles of the solute}}{\text{mass of solvent in kg}} = \frac{\text{mass of solute in gram}}{\text{molar mass} \times \text{mass of solvent in kg}}$$

- (e) **Normality (N) :** It is the number of gram equivalent of a solute dissolved per litre of the solution.

$$\text{Normality (N)} = \frac{\text{no. of gram equivalents of solute}}{\text{vol. of solution in litres}} = \frac{\text{mass of solute in gram}}{\text{equivalent weight in gram} \times \text{vol. of solution in litres}}$$

- (f) **Parts per million (ppm) :** Parts per million of a component is its mass in gram present in one million gram of the solution

$$\text{ppm of A} = \frac{\text{mass of A in gram}}{\text{total mass of solution in gram}} \times 10^6$$

- (g) **Normality equation :** $N_1 V_1 = N_2 V_2$

- (h) **Molarity equation :** $n_1 M_1 V_1 = n_2 M_2 V_2$ n_1 & n_2 are n-factors

1. Discovery of Electrons :

When high voltage electric discharge is passed through a gas at very low pressure then rays travel from cathode to anode called cathode rays. These rays travel in straight line. These contain negatively charged particles called electrons.

Charge & mass of electron : Thomson determined the charge (e) to mass (m_e) ratio of electron and found equal to

$1.758820 \times 10^{11} \text{ C kg}^{-1} \approx 1.76 \times 10^{11} \text{ C kg}^{-1}$. RA Millikan determined the charge present on electrons by oil drop experiment which was $-1.6 \times 10^{-19} \text{ C}$. Electrons are basic constituent of all atoms.

Then mass of electron can be calculated as : $m_e = \frac{e}{e/m_e} = \frac{1.6 \times 10^{-19} \text{ C}}{1.7588 \times 10^{11} \text{ C/kg}} \approx 9.11 \times 10^{-31} \text{ kg}$

2. Discovery of Protons :

Goldstein (1886) performed discharge tube experiment using perforated cathode by taking a gas at low pressure and found some rays travel in the direction opposite to cathode rays. These pass through the holes in the cathode and are called anode rays or canal rays. These rays are produced by knocking out of electrons from the gaseous atoms. These rays have following properties.

- (a) They also travel in straight lines and contain positively charged particles.
- (b) The charge to mass ratio is found different for different gases taken in a discharge tube.
- (c) The mass of these particles is found different for different gases.
- (d) The smallest and lightest positive ion was formed by hydrogen and was called proton.

3. Discovery of Neutrons :

In 1932, Chadwick discovered these particles by bombarding a thin sheet of beryllium by α - particles. These are neutral particles with slightly greater mass than proton.

mass of electron = $9.11 \times 10^{-31} \text{ kg}$ mass of proton = $1.673 \times 10^{-27} \text{ kg}$ mass of neutron = $1.675 \times 10^{-27} \text{ kg}$

4. Thomson Model :

According to this model, atom is a sphere with uniform positive charge in which electrons are embedded symmetrically into it. It is known as **plum pudding, raisin pudding or water melon** model.

5. Rutherford Model :

Rutherford performed α - particle scattering experiment by bombarding these particles on a thin gold foil and concluded that :

- (i) Most of space in atom is empty because most of α - particles passed through the foil.
- (ii) The positive charge has to be concentrated in a very small volume that repelled and deflected few positively charged α - particles. This very small portion of the atom was called nucleus.
- (iii) The volume of nucleus is very small as compared to total volume of atom. The radius of nucleus (10^{-13} cm) is about $\frac{1}{100,000}$ of that of atom (10^{-8} cm).

Based upon these observations Rutherford gave a nuclear model of atom as :

- (i) An atom consists of tiny positively charged part called nucleus. The whole mass of an atom is present in it.
- (ii) The electrons are outside the nucleus and revolve around nucleus at high speed in circular paths called orbits in the same manner as planets revolve around sun. Hence electrons are also called planetary electrons.
- (iii) Electrons and nucleus are held together by electrostatic force of attraction.

Atomic number (Z)	= number of protons in the nucleus of an atom. = number of electrons in a neutral atom
mass number (A)	= number of protons + number of neutrons
Isotopes	= same atomic number but different mass numbers e.g., ${}^1_1\text{H}$, ${}^2_1\text{D}$, ${}^3_1\text{T}$
Isobars	= same mass number but different atomic numbers e.g., ${}^{14}_6\text{C}$, ${}^{14}_7\text{N}$
Isotones	= different atomic numbers but same number of neutrons e.g. ${}^{14}_6\text{C}$, ${}^{16}_8\text{O}$

6. Electromagnetic Theory of Waves :

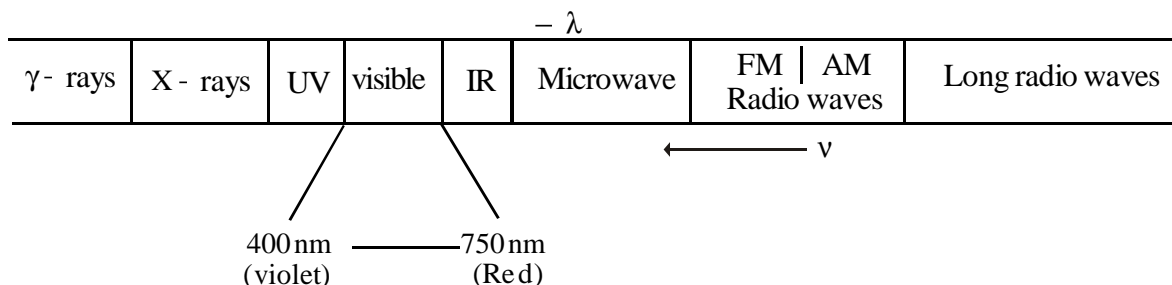
Maxwell gave this theory whose main postulates are :

- (a) The energy is emitted from any source continuously in the form of radiations (waves).
- (b) The radiations are associated with electric and magnetic fields oscillating perpendicular to each other and perpendicular to the direction of propagation of the radiation

- (c) These radiations possess wave character and travel with velocity of light (c). Their frequency (ν) and wavelength (λ) are related with velocity (c) as: $c = \nu \times \lambda$. Wave number ($\bar{\nu}$) = $1/\lambda$
- (d) These waves require no medium for their propagation.

7. Electromagnetic Spectrum :

When these electromagnetic radiations are arranged in the increasing order of wavelengths or decreasing order of frequencies a spectrum is obtained called electromagnetic spectrum as given below:



8. Black Body Radiations :

When a perfectly black body is heated it emits radiations called black body radiations. These radiations first become red, then yellow and finally become white and then blue on heating.

9. Photoelectric Effect :

When radiations with certain suitable frequency strike the metal surface the electrons are ejected from the surface of metal. It is called photoelectric effect and electrons emitted are called photo electrons. Main postulates of this effect are :

- Electrons are ejected from metal surface by the radiations with a certain minimum frequency (ν_0) called threshold frequency. And minimum energy ($E_0 = h\nu_0$) required to eject the electrons is called work function (W_0).
- The kinetic energy and velocity of the electron ejected depends upon the frequency of the incident radiation and is independent of its intensity.
- The number of photo electrons ejected is proportional to the intensity of incident radiation and not upon its frequency.

10. Limitations of Electromagnetic Theory of Waves :

This theory was able to explain the phenomenon of interference, diffraction etc. but it could not explain the following :

- The phenomenon of black body radiations
- The photoelectric effect
- The line spectra of atoms.

11. Particle Nature of Electromagnetic Radiations :

Planck's quantum theory : To explain the phenomenon of 'Black body radiations' and 'Photo electric effect' Max Planck (1900) put forward a theory called Planck's quantum theory whose postulates are :

- The energy is radiated or absorbed by a body not continuously but discontinuously in the form of small energy packets.
- Each packet is called quantum. In case of light, the quantum is called 'photon'.
- The energy of a quantum is directly proportional to the frequency (ν) of the radiation.

$$E \propto \nu \quad E = h\nu \quad E = \frac{hc}{\lambda} \quad \because \left(\nu = \frac{c}{\lambda} \right) \text{ where 'c' is velocity of light and '}\lambda\text{' is wavelength.}$$

where 'h' is Planck's constant. Its value is 6.626×10^{-34} Js.

According to Planck's theory, energy is always emitted in integral multiple of $h\nu$, e.g., $h\nu$, $2h\nu$, $3h\nu$, etc.

12. Explanation of Black Body Radiations and Photoelectric Effect :

(a) **Black body radiations :** On heating a black body its energy increases and photons of different energy or different wavelength are emitted and thus it changes its colour.

(b) **Photoelectric effect :**

- Light of a particular frequency on striking the metal surface take out the electron if energy of photon of incident light is sufficient to overcome the force of attraction of electron by the nucleus. Hence to eject out an electron from the metal surface incident light must have a certain minimum frequency (ν_0).

(ii) If the frequency of incident light (ν) is more than threshold frequency (ν_0) then excess of energy ($h\nu - h\nu_0$) is equal to the

$$\text{kinetic energy of ejected electron. } \frac{1}{2} mu^2 = h\nu - h\nu_0 \quad \text{or } h\nu = h\nu_0 + \frac{1}{2} mu^2 \quad \text{or } h\nu = W_0 + \frac{1}{2} mu^2$$

(iii) One electron is ejected out by one photon. Hence more the number of photons present in the light more number of electrons will be ejected out of metal surface. So number of electrons ejected out depend upon the intensity of light and not its frequency.

13. Dual Behaviour of Electromagnetic Radiations.

Photoelectric effect and black body radiations show particle nature of light. Diffraction and interference explains wave nature of light. It shows that light possesses both particle as well as wave like properties, i.e., light has dual behaviour.

14. Types of Spectra

(a) **Continuous spectrum:** A continuous band of light of different frequencies is called continuous spectrum, e.g., visible spectrum. A similar spectrum is produced when a rainbow forms in the sky.

(b) **Emission spectrum:** The spectrum of radiations emitted by a substance that has absorbed energy by heating it or by irradiating it. It involves bright lines separated by dark bands. It is also called atomic spectrum. It is characteristic of an element. Each element has a characteristic pattern of lines. Such spectrum is also called line spectrum because the emitted radiations are identified by the appearance of bright lines in the spectrum.

(c) **Absorption spectrum:** It is like photographic negative of emission spectra. A continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths. The missing wavelengths which correspond to the radiation absorbed by the matter leave dark spaces in bright continuous spectrum. It is called absorption spectrum.

15. **Hydrogen Spectrum:** If a discharge is passed through hydrogen gas at a low pressure, some hydrogen atoms are formed, which emit light in the visible region. This can be studied by using Spectroscope or Spectrometer, and is found to comprise of series of lines of different wavelengths. It forms following five series of line spectrum of hydrogen :-

Lyman series in U.V. region, Balmer series in visible region, Paschen series, Brackett series and Pfund series in I.R. region.

Balmer formula and Rydberg formula: Balmer gave a formula to determine the wave number $\left(\bar{\nu} = \frac{1}{\lambda}\right)$ of the lines of Balmer series

$$\text{as. } \bar{\nu} = R \left[\frac{1}{2^2} - \frac{1}{n^2} \right], R = 1.097 \times 10^7 \text{ m}^{-1}.$$

Rydberg formula (given below) can determine the wave number ($\bar{\nu}$) of all the five series of H-spectrum.

$$\bar{\nu} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right].$$

In it $R_H = 1.097 \times 10^7 \text{ m}^{-1}$ and for different series values of n_1 and n_2 are as :

Lyman series $n_1 = 1, n_2 \geq 2$ Brackett series $n_1 = 4, n_2 \geq 5$

Balmer series $n_1 = 2, n_2 \geq 3$ Pfund series $n_1 = 5, n_2 \geq 6$

Paschen series $n_1 = 3, n_2 \geq 4$

16. Drawbacks of Rutherford's Model of Atom

(i) According to Maxwell's electromagnetic theory, charged particles when accelerated must emit electromagnetic radiations. Therefore, an electron in an orbit will emit radiations, the energy carried by radiations comes from electronic motion. Its path will become closer to nucleus and ultimately, should spiral into nucleus within 10^{-8} s. But actually this does not happen.

Thus, Rutherford's model cannot explain the stability of atom if the motion of electron is described on the basis of classical mechanics and electromagnetic theory.

(ii) Second drawback of Rutherford's model is that it does not give any idea about distribution of electrons around the nucleus and about their energies.

(iii) It fails to explain the line spectrum of hydrogen.

17. Postulates of Bohr's Theory:

(a) The electrons revolve around the nucleus in a circular path of fixed radius and energy. These paths are called orbits, stationary states or allowed energy levels.

(b) So long as an electron revolves in an orbit it neither loses nor gains energy continuously. This state of atom is called **ground state**

(c) The permitted orbits for revolution of an electron are those only in which the angular momentum of the electron is an integral multiple of

$$h/2\pi \text{ i.e., } mvr = \frac{nh}{2\pi}$$

(d) Electron may jump from its normal energy level to some higher energy level by absorbing definite amount of energy. This state of atom is called **excited state**. Due to short life in excited state the electron immediately jumps back to the ground state and emits energy in the form of light of suitable frequency or wavelength

$$\Delta E = h\nu = E_2 - E_1, E_2 \text{ and } E_1 \text{ are energies of electron in excited and ground states respectively.}$$

18. Achievements of Bohr's Theory

- (i) It could successfully explain the stability of atom.
- (ii) It could explain spectrum of hydrogen and unit-electron species.
- (iii) It could help to calculate energy and velocity of electrons in various energy levels.
- (iv) It helped to calculate radius of various energy levels in hydrogen and hydrogen like species.

For H-atom and other single electron systems

For H-atom $z = 1$

For He⁺ ion $z = 2$

For Li²⁺ ion $z = 3$

$$E_n = \frac{-2\pi^2 m z^2 e^4}{n^2 h^2} = \frac{-1312 z^2}{n^2} \text{ kJ mol}^{-1} = \frac{-2.18 \times 10^{-18} z^2}{n^2} \text{ J atom}^{-1}$$

$$r_n = \frac{n^2 h^2}{4\pi^2 m e^2 z} = \frac{0.0529 n^2}{z} \text{ nm} \quad \text{velocity, } v_n = \frac{2\pi e^2 z}{nh} = \frac{2.188 \times 10^6 \times z}{n} \text{ ms}^{-1}$$

19. Zeeman and Stark effects

- (a) **Zeeman Effect:** The splitting of spectral lines in strong magnetic field is called Zeeman effect. It is associated with magnetic quantum number.
- (a) **Stark effect:** The splitting of spectral lines in electric field is called Stark effect.

20. Drawbacks of Bohr's Theory:

- (i) According to Bohr's theory atom is circular planar but actually it is three dimensional in nature.
- (ii) It could not explain spectrum of multi-electron atoms.
- (iii) It could not explain Zeeman and Stark effect.
- (iv) it could not explain shape of molecules.
- (v) It was not in accordance with Heisenberg's uncertainty principle.

21. Quantum mechanical model: It is a mathematical theory that developed from quantum theory and is used to explain the behaviour of atoms, molecules, and elementary particles. It is developed on the basis of Heisenberg's uncertainty principle and dual behaviour of matter.

- (a) **Dual behaviour of matter:** Light radiations are associated with dual behaviour, matter should also be associated with dual behaviour. It means matter is associated with both wave as well as particle. The wave nature of beam of electron has been confirmed by Davisson and Germer experiment. The diffraction pattern obtained when beam of electron is made to fall on nickel crystal is similar to that of X-rays which is associated with wave like behaviour. Particle nature of electron is proved with the help of photoelectric effect, i.e., each photoelectron causes one scintillation (flash) on ZnS screen showing particle nature of electron.
- (b) **de Broglie equation:** Every particle can be considered to be associated with a wavelength and wave properties. The wavelength of moving particles or objects can be calculated with the help of de Broglie equation. de Broglie relation states that the wavelength associated with a moving object or an electron is inversely proportional to the momentum

of the particle. $\lambda = \frac{h}{mv} = \frac{h}{p}$, where p is momentum of particle = mv

' λ ' is wavelength, ' m ' is mass, and ' v ' is velocity of particle or of a moving object.

' h ' is Planck's constant. This relationship has been verified by an experiment.

- (c) **Heisenberg's uncertainty principle:** It is not possible to determine the exact position and velocity simultaneously for a sub-atomic particle like electron at any given instant to an arbitrary degree of precision. Consequently, it is not possible to talk of path of the electron

in which it moves. If ' Δx ' is uncertainty in position and ' Δv ' is uncertainty in velocity, then

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

where ' h ' is Planck's constant ' m ' is mass and $\pi = 3.142$ or $\frac{22}{7}$

22. Main Features of Quantum Mechanical Model of Atom :

- (a) Quantum mechanics deals with the study of motions of the microscopic objects that have both wave like and particle like properties.
- (b) The fundamental equation of quantum mechanics was developed by Schrodinger, which can be written in following forms :

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

where Ψ is the amplitude of the wave, coordinates of electron are (x, y, z) , E is total energy of electron, V is its potential energy, m is the mass of electron, h is Planck's constant.

In short, eq. (i) can be written as : $\bar{H}\Psi = E\Psi \dots\dots\dots (ii)$

Here H is Hamiltonian operator, equal to $-\frac{h^2}{8\pi^2 m} \nabla^2 + V$ and $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

This equation incorporates wave-particle duality and it is quite complex and higher mathematics is needed to solve it. Solution of this equation gives E and ψ , which involves three numbers n, ℓ, m_ℓ , called quantum numbers

23. Quantum Numbers : Three quantum numbers are derived from Schrodinger's wave equation and the fourth one is derived from the spectrum of sodium vapour.

a) **Principal quantum number (n) :** It specifies the location and energy of an electron. Values of n are 1,2,3 etc. represent different shells K, L, M etc. respectively.

- Main energy level whose angular momentum is $nh / 2\pi$.
- Max. no. of electrons in n th shell = $2n^2$ and maximum number of orbitals in n th shell = n^2

b) **Azimuthal or angular quantum number (l) :**

- For a particular value of n, l can have values from 0 to $n - 1$. Each value of l represents a subshell.
- This gives shape of a subshell or an orbital
- The orbital angular momentum of an electron is $(h / 2\pi) \sqrt{l(l+1)}$

c) **Magnetic quantum number (m_l) :**

- This gives the orientation of a particular subshell
- There are $2l + 1$ possible values of m_l from $-l$ to $+l$ including zero. Each value of m_l represents an orbital.
- p-orbital, has 3 possible values i.e. $-1, 0, +1$ represented by p_x, p_y, p_z

d) **Spin quantum number (m_s) :**

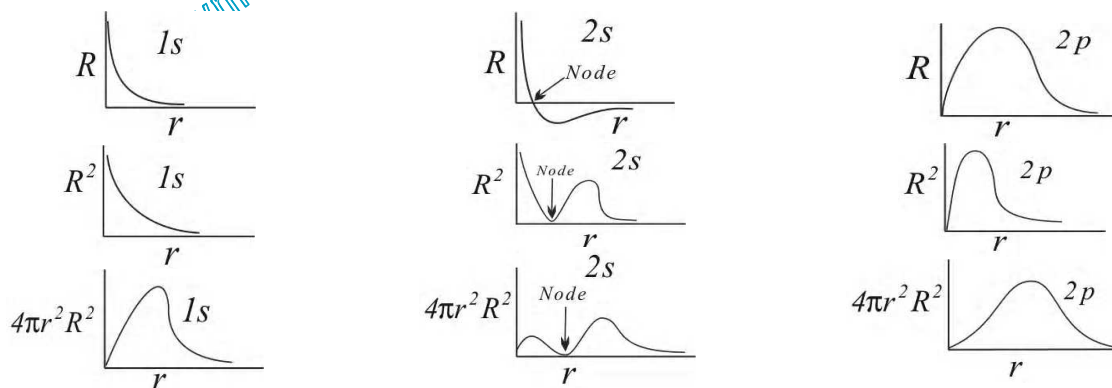
- This arises due to the spin of electron about its own axis. It has two possible values i.e. $+(1/2)$ or $-(1/2)$.
- The value of spin angular momentum is given by $(h / 2\pi) \sqrt{s(s+1)}$

24. Radial Wave Function and Radial Probability

The wave function $\psi(x, y, z)$ is represented as $\psi(r, \theta, \phi)$ in polar coordinates where

$x = r \sin \theta \cos \phi, y = r \sin \theta \sin \phi, z = r \cos \theta$. The total wave function $\psi(r, \theta, \phi) = R_{nl}(r)\theta_{l,m}(\theta)\phi_m(\phi)$

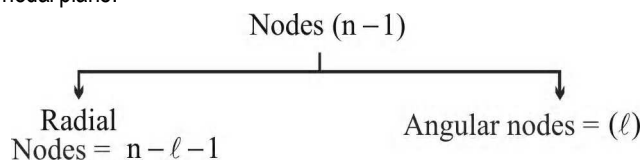
- The plots of radial wave function R , radial probability density R^2 and radial probability function $4\pi r^2 R^2$ for 1s, 2s and 2p orbitals as a function of the distance r from the nucleus are shown below :



25. Shapes of Orbital : Orbitals are purely mathematical concept and in fact doesn't exist in an atom. It is a three dimensional space where probability of finding an electron is maximum.

Type of orbital	Azimuthal Quan. no.	Shape
s	0	Spherical
p	1	Dumb – bell
d	2	Double dumb – bell
f	3	

26. **Nodes and Nodal Plane** : The region where probability of finding an electron is zero is known as node or nodal surface and the plane containing node is called nodal plane.



27. **Pauli's Exclusion Principle**: "NO two electrons in an atom can have the same set of four quantum numbers". It can also be stated as: An orbital can have maximum two electrons and they must be of opposite spin quantum numbers.

28. **Energy of orbitals** :

(a) For H- atom : It depends upon value of n only, e. g.

$$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f .$$

(b) For multielectron systems : It depends upon value of both n and l, e. g.

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s .$$

29. **Filling of Electrons in Orbitals of an Atom** :

(a) **Aufbau's principle** :

- Electrons are filled up in orbitals in order of increasing energies i. e in the order :

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p.$$

- (n + ℓ) rule**: The orbitals are filled up with electrons in the increasing order of (n + ℓ) values i. e., the orbitals with lower value of (n + ℓ) is filled up first. If two or more orbitals have same value of (n + ℓ) the one with lower value of n is filled up first.

(b) **Pauli's exclusion principle** : An orbital can have maximum two electrons and with opposite spin

(c) **Hund's rule of maximum multiplicity** : The pairing of electrons in an orbital of same subshell (p, d or f) will not take place unless the available orbitals of a given subshell contain one electron each with same spin.

(d) **Extra stability of completely filled and half filled orbitals**: Filling up of some orbitals do not follow the Aufbau principle. it is due to extra stability of half filled and completely filled orbitals. Their stability is due to (i) symmetry of half filled and full filled orbitals (ii) more exchange energy in these cases, e. g. in Cr and Cu .

1. History of Classification of Elements :

- (a) **Doebereiner law of triads** : He arranged the elements in group of three, such that atomic weight of middle element is average of first and third element. These elements resembled in their properties.

Element	Atomic weight	Element	Atomic weight	Element	Atomic weight
Li	7	Ca	40	Cl	35.5
Na	23	Sr	88	Br	80
K	39	Ba	137	I	127

Limitation. He could not classify all the elements discovered at that time into triads.

- (b) **Newlands law of octaves.** He arranged the elements in increasing order of their atomic weights and found that any given element has similar properties to the eighth element that followed it. The relationship was same as that existing between musical note and its octave.

Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
K	Ca					

- (c) Lothar Meyer reported similarity in the properties like atomic volume, m. p and b.p after regular intervals in the graph against atomic mass.

2. Mendeleev's Periodic Law : Properties of elements are periodic function of their atomic masses.

3. Mendeleev's Periodic Table : Nine groups (I to VIII & Zero). I to VII are divided in A & B subgroups. VIIIth group contains three columns.

4. Modern Periodic Law : The physical and chemical properties of the elements are periodic functions of their atomic numbers.

5. Long Form of Periodic Table :

The periodic table based upon atomic number is called long form of periodic table. In it the horizontal rows are called periods (equal to the principal quantum number of outermost electron). Elements having similar outer electronic configurations in their atoms are grouped in vertical column known as groups or families. There are 18 groups and seven periods in this periodic table. First period contains two elements and is the shortest period. The 2nd and 3rd periods are short periods (8 elements). The 4th and 5th periods are long periods (18 elements). 6th period is the longest (32 elements), 7th period is incomplete

6. s-Block Elements :

- These are the elements in which last electron enters the s - orbital of the outermost shell.
- These are elements of group-1 (alkali metals) and group-2 (alkaline earth metal).
- Outermost electronic configuration is ns^1 and ns^2 respectively.
- They are very reactive, have low ionization enthalpy, greater metallic character, and hence are electro positive metals and form mostly ionic compounds (except Li, Be).
- They are good reducing agents.
- Their metallic character and reactivity increases down the group.

7. p-Block Elements :

- These are the elements in which last electron enters p - orbital of the outermost shell.
- These belong to groups 13 to 18.
- Outermost electronic configuration is $ns^2 np^{1-6}$.
- Each period ends with a noble gas.
- Most of these are non metals and the non-metallic character increases along a period and decreases down the group. Some of the elements in this block are metalloids and metals.
- Group 17 elements are known as halogens.
- Group 16 elements are known as chalcogens , meaning ore forming.

8. d-Block Elements (Transition Elements) :

- These are the elements in which last electron enters the d- orbital of penultimate shell (2nd last shell)
- These are elements of group 3 to 12.
- Have inner d-orbital partly filled either in atomic state or in any of its oxidation state.
- Outer most electronic configuration is $(n - 1)d^{1-10} ns^{1-2}$
- Mostly form coloured ions and exhibit variable valency.
- However Zn, Cd and Hg do not show most of the properties of transition elements.
- All are metals, less reactive than s-block elements but more reactive than group 13, 14 metals.

9. **f-Block Elements :**

- These are the elements in which last electron enters the f - orbital of ante penultimate shell.
- These are two rows of elements at the bottom of Periodic Table called the Lanthanoids $_{58}\text{Ce} - _{71}\text{Lu}$ and Actinoids $_{90}\text{Th} - _{103}\text{Lr}$
- Outermost electronic configuration is $(n - 2)f^{1-14}(n - 1)d^{0-1}ns^2$.
- They are called inner transition elements as these are transition elements within transition series.
- All are metals, show variable oxidation state.
- All actinoid elements are radio active. Only one lanthanoid (promethium, Pm) is radioactive.

10. **Atomic Radii :** This is the distance from the centre of the nucleus to the outer most shell of atom. There are various types of radii.

(a) **Covalent radii :** This is equal to the half of the internuclear distance between two identical atoms bonded through a covalent bond.

Inter nuclear distance $A - B$ between two dissimilar atoms of AB molecule will be

$$A - B = r_A + r_B - 0.09 (x_A - x_B)$$

Where r_A & r_B are the covalent radii of atoms A and B and x_A & x_B are their electronegativity.

(b) **van-der Walls radii :** This is equal to half of the distance between the centre of nuclei of two non bonded atoms of two adjacent molecules in solid state. Generally covalent radius is smaller than this.

(c) **Metallic radii :** This is one half of distance between the adjacent atoms of a metal in its solid lattice. It is higher than single covalent radii, smaller than van-der Walls radii.

11. **Ionic Radii :** It is the distance from the nucleus of an ion up to the point it has its influence in the ionic compound. The size of cation is smaller whereas size of anion is greater. It increases with increase in coordination number. More covalent character less ionic radii of cation.

12. **Variation of Atomic and Ionic Radii :** Atomic radii of the element decrease when we move left to right across a period whereas it increases down the group, ionic radii also increase in a group from top to bottom.

13. **Isoelectronic Ions :** Ions with same number of electrons but different atomic numbers. Size decreases with increase in atomic number.

For example $\text{N}^{3-} > \text{O}^{2-} > \text{F}^- > \text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$

14. **Valence :** Valence of an element is $n - 8$ where n is equal to the number of valence electrons. On moving from left to right in each short period (2nd and 3rd), the valence with respect to oxygen increases from 1 to 7 (Na_2O to Cl_2O_7) while that with respect to hydrogen rises from 1 to 4 (NaH to SiH_4) and then falls to 1 (PH_3 to HCl).

15. **Ionization Enthalpy :** (Δ_{IE})

- This is the energy required to remove outer most electron from an isolated gaseous atom.
- I.E decreases with increase in size of atom or ion.
- Higher the nuclear charge, higher is the I.E.
- More the screening effect, less is the I.E.
- I.E decreases down the group and increases along the period.
- I.E is higher in half filled and full filled electronic configurations. For example : I.E of N (half filled) is more than O (Partially filled). Ionization enthalpy also depends upon the type of orbital from which electron is removed. More penetrated s- electrons cannot be removed easily (penetration effect). Hence I.E of Be ($2s^2$) is more than B ($2p^1$).

16. **Electron Gain Enthalpy** $\Delta_{\text{eg}}\text{H} :$

- It is the amount of energy released when an extra electron is added to an isolated gaseous atom.
- First Ege is exothermic whereas the second Ege is endothermic.
- Smaller the size of atom and more the nuclear charge, more negative is the value of Ege.
- Atoms having stable electronic configuration have positive Ege.
- Ege becomes more negative along a period and becomes less negative down the group. Halogens have maximum negative value of Ege in their respective periods. Chlorine has the highest negative Ege value. F and O have less negative value of Ege than Cl and S respectively due to more compact sizes of 2p orbitals of F and O than 3p orbitals of Cl and S and hence more interelectronic repulsion in 2p orbitals of F and O -atoms.

17. Electronegativity :

- It is the tendency to attract a shared pair of electron in a covalent bond.
- Smaller the size of atom, higher is the value of E.N.
- EN increases along a period and decreases down the group.
- F is most electronegative element.
- Electronegativity difference causes polarity in a bond.

• **Mullikan scale** -
$$E.N = \frac{I.E + E.A}{2}$$
 or
$$E.N = \frac{1}{2} (\Delta_1 H - \Delta_{eg} H)$$

• **Pauling scale** - Based on bond energies
$$\Delta E.N = x_B - x_A = k \sqrt{\Delta'}$$

where Δ' (ionic resonance energy) = $D_{A-B} - \sqrt{D_{A-A} \cdot D_{B-B}}$ D – Bond dissociation energy.

- $k = 0.208$ (where B.E in kcal/mol)

$= 0.108$ (where B.E in kJ/mol) or
$$x_B - x_A = 0.102 \sqrt{\Delta} \text{ (in kJ mol}^{-1}\text{)}$$

$$\Delta = D_{A-B} - \frac{1}{2} (D_{A-A} + D_{B-B})$$

- Electronegativity helps in predicting % Ionic character

If $x_A - x_B = 0$, bond is purely covalent
 $= 1.7$, bond is 50 % ionic and 50 % covalent
 < 1.7 , bond is polar covalent
 > 1.7 , bond is more ionic and less covalent

18. Nature of Oxides : The acidic nature of oxides increases in a period from left to right but basic nature increases in a group from top to bottom.

e. g. acidic nature in a period : $Na_2O < MgO < Al_2O_3 < SiO_2 < P_4O_{10} < SO_3 < Cl_2O_7$

Basic nature in a group : $Li_2O < Na_2O < K_2O < Rb_2O < Cs_2O$.

19. Anomalous Behaviour of Second Period Elements : The first element of groups 1,2 and 13 to 17 differ in many properties from the other elements of their respective groups. It is due to following reasons :

(a) Smaller size (b) large charge / radius ratio (c) high electronegativity (d) absence of d-orbitals, in these elements.

20. Diagonal Relationship : The elements of 2nd period have many properties similar to the elements of third period of next group, it is called diagonal relationship. For example Li and Mg, Be and Al, B and Si, etc. have diagonal relationship. it is due to their (a) almost similar sizes (b) nearly equal electronegativities.

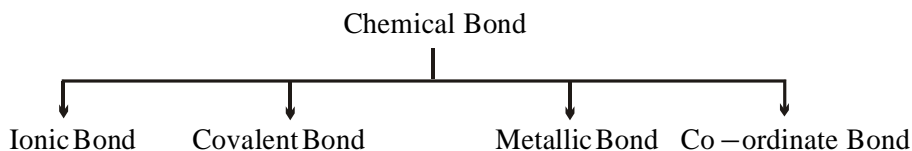
21. Reducing / Oxidising nature : Reducing nature of elements decreases and oxidising nature increases from left to right in a period. But in a group reducing nature increases from top to bottom in general.

22. Nomenclature of Elements with Atomic Number Above 103.

Atomic number	Name	Symbol	IUPAC Official name	IUPAC Symbol
104	Unnilquadium	Unq	Rutherfordium	Rf
105	Unnilpentium	Unp	Dubnium	Db
106	Unilhexium	Unh	Seaborgium	Sg
107	Unilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassium	Hs
109	Unnilennium	Une	Meitnerium	Mt
110	Ununillium	Uun	Darmstadtium	Ds
111	Unununnium	Uuu	Röntgenium	Rg
112	Ununbium	Uub		
113	Ununtrium	Uut		
114	Ununquadium	uuq		
115	Ununpentium	Uup		
116	Ununhexium	Uuh		
117	Ununseptium	Uus		
118	Ununoctium	Uuo		

1. **Chemical Bond** : It is the force which holds the atoms together in a molecule. The causes of formation of bond are (i) Tendency of atoms to complete their octets or duplets by rearrangement of their valence electrons (octet theory). (ii) The system acquires minimum energy when atoms are at some equilibrium distance where attractive forces dominate over repulsive forces.

2. **Types** :



3. **Ionic Bond** : It is the electrostatic force of attraction between oppositely charged ions which are formed by complete transference of electrons from one atom to another to get complete octet or duplet.

a) **Favourable conditions to form ionic bond** :

- Formed between electro positive element (group 1, 2, 13) and electro negative element group (15, 16, 17)
- $\Delta E.N \geq 2$ • Lower I.E of one atom and more negative Ege of second atom • Higher lattice energy.
- Larger cations, smaller anions.

b) **Properties** :

Crystalline, stronger force of attraction, thermally stable, low volatility, high density, high m.p and b.p, highly soluble in polar solvent, good conductor of electricity in molten or solution state, nondirectional bond .

4. **Covalent Bond** :

Covalent bond is formed by sharing of electrons by two atoms to complete their octet or duplet. (octet theory)

a) **Favourable conditions to form covalent bond** :

- Formed between two electronegative elements (group 14, 15, 16, 17)
- $\Delta E.N < 1.9$ • Small cation, larger anions (Fajan's rule) • High charges on cation and anion (Fajan's rule)

b) **Properties of covalent compounds**

- Compounds containing covalent bonds under normal condition of P, T, exists as a gas or liquid of low b. p. due to weak vander Waal's force.
- Relatively low m.p and b. p. , generally non-conductor, soluble in nonpolar solvent.
- As the bond is rigid and directional, compounds with covalent bond show isomerism.
- Covalency of an atom is equal to the number of covalent bonds formed by the atom.

c) **Lewis structure of simple molecules or ions** To write Lewis structure of molecules and ions, following steps are used :

- (i) Calculate the total number of valence electrons (V) after subtracting for the cation or adding for the anion.
- (ii) Calculate the number of electrons (N) for complete octets of all the atoms.
- (iii) Calculate the number of electrons (S) present as shared pairs by subtracting V from N, i.e., $S = N - V$
- (iv) Draw the skeletal structure representing the shared pairs.
- (v) Complete the structure by showing the unshared electrons ($U = V - S$)

d) **Formal charge** The charge present at each atom of a covalent compound (neutral, or ion) is called its formal charge, which is

$$\text{Formal charge at an atom} = \left[\begin{array}{c} \text{Total number of its} \\ \text{valence electrons} \end{array} \right] - \left[\begin{array}{c} \text{Total number of non} \\ \text{bonding electrons around it} \end{array} \right] - \frac{1}{2} \left[\begin{array}{c} \text{Total number of} \\ \text{bonding electrons} \end{array} \right]$$

e) **Drawbacks of octet theory**

- Octet theory cannot explain
 - (i) Nature of force between atoms in the molecules like H_2, Cl_2 etc.
 - (ii) Formation of $BCl_3, BeCl_2, AlCl_3$ etc. (electron deficient compounds)
 - (iii) Formation of PCl_5, SF_6, IF_7 etc.
 - (iv) Formation of odd electron molecules like NO, NO_2 etc.
 - (v) Shapes of molecules

5. **Bond Length:** It is the average distance between the nuclei of two bonded atoms. It depends upon
- **Size of the atom:** Bond Length increases with increase in the size of atom ($\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$)
 - **Multiplicity of bond :** Bond length decreases with the multiplicity of bond ($\text{C} - \text{C} > \text{C} = \text{C} > \text{C} \equiv \text{C}$)
 - **Type of hybridisation :** More s-character, shorter is the bond length, greater is the acidity with comparable compound.
6. **Bond Energy:** It is the energy required to break one mole of bonds of particular type of a substance in gaseous state.
7. **Bond Angle :** It is the internal angle between the orbitals containing electron pairs in the valence shell of central atom in a molecule
- More lone pairs on central atom, smaller is the bond angle due to lp - bp repulsion.
 - More electronegative central atom, more is the bond angle.
 - More electronegative surrounding atom, less is the bond angle.
8. **Resonance :** In some molecules all the properties cannot be explained by single structure and the molecule is supposed to have many structures, but none of these can explain all the properties of the molecule. These different possible structures are called resonating structures and the actual structure is inbetween of all these structures, called resonance hybrid. This phenomenon is called resonance. Main features of resonance are :
- (a) Different structures have same positions of atoms, almost equal energies, same number of shared and unshared electrons.
 - (b) The difference in the energy of the most stable resonating structure and resonance hybrid is called resonance energy.
 - (c) Resonating structures are imaginary.
 - (d) Greater the resonance energy, greater will be the stability of the molecule.
 - (e) More the number of canonical forms of nearly same energy, greater is the stability of molecule.
9. **Valence Bond Theory (VBT)**
Proposed by Heitler and London and extended by Pauling and Slater. The postulates are
- Overlapping of atomic orbitals of valence shell of two atoms leads to formation of a covalent bond.
 - Half filled orbital and opposite spin electrons are used.
 - σ - bond is formed by head on overlapping, π - bond is formed by lateral overlapping. σ - bond is formed by s - s, s - p or p - p overlapping but in π - bond formation no s - orbital can take part.
 - Greater the overlapping, stronger is the bond.
 - σ - bond is stronger than π - bond and σ - bond is directional while π - bond is non-directional.
 - The direction of bond is same as the direction of overlapping of orbitals.
 - The strength of σ - bond follows the order s - s > s - p > p - p .
 - Paired electrons are shifted to higher energy levels while forming a bond.
 - VBT cannot explain paramagnetic behaviour of O_2 .
10. **Shapes of Molecules :** Shapes of molecules can be determined by following two concepts :
- a) **Valence shell electron pair repulsion (VSEPR) theory :** Main postulates of this theory are
- (i) The electron pair surrounding the central atom repel one another to the extent that there are no further repulsions between them. Thus the molecule will have minimum energy and maximum stability.
 - (ii) If a central atom is bonded to similar atoms and contains no lone pair of electrons, the shape of molecule is symmetrical or regular. e. g. CH_4 , BF_3 etc.
 - (iii) If central atom is bonded with different atoms or is surrounded by lone pairs of electrons also along with bond pairs, then the shape of molecule is unsymmetrical or it has irregular geometry.
 - (iv) The order of repulsion between electron pairs is as.
Lonepair-lonepair>lonepair-bondpair>bond pair - bond pair.
- The regular geometry is :
- | | 2 | 3 | 4 | 5 | 6 | 7 |
|------------|--------|-------------------|--------------|----------------------|------------|------------------------|
| Bond pairs | 2 | 3 | 4 | 5 | 6 | 7 |
| Geometry | Linear | Triangular planar | Tetra hedral | Trigonal bipyramidal | Octahedral | Pentagonal bipyramidal |
- b) **Hybridization :** "It is the phenomenon of intermixing of a number of orbitals of an atom with slightly different energies and then redistribution of their energies to form new orbitals of identical shape and equal energy."
- No. of hybrid orbitals = no. of atomic orbitals intermixed
 - Hybrid orbitals form σ -bond on overlapping.
 - It does not take place in isolated atom. It occurs only during bond formation
 - Hybrid orbitals tend to remain far apart, therefore, repulsion order is lp - lp > lp - bp > bp - bp .
- Total number of hybrid orbitals of central atom
= Number of its σ - bond pairs + Number of lone pair of electrons around central atom
- Different types of hybridization are sp , sp^2 , sp^3 , sp^3d , sp^3d^2 , sp^3d^3
 - Hybrid orbitals are directional in nature

11. Dipole Moment (μ):

It is equal to the product of magnitude of the charge and the distance between the centres of +ve and -ve charges of a dipole. i.e

$$\mu = e \times d$$

- Common in covalent compound when formed between two dissimilar atoms.
- Used to predict the extent of polarity in a molecule.
- A vector quantity so follows vector addition or subtraction rule in predicting net dipole moment of a molecule.

$$\mu_r = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta}$$

Increases with increase in $\Delta E.N$. i.e $HI < HBr < HCl < HF$

$$\% \text{ Ionic character} = \frac{\mu_{\text{expt}}}{\mu_{\text{Theoretical}}} \times 100$$

- Can predict the shape of molecule, H_2O – bent, BeF_2 – linear.
- Can distinguish between cis and trans isomers.
- Can distinguish between o-, m-, p- isomers.

12. Molecular Orbital Theory (MOT)

The theory was developed by Hund & Mulliken. Basic postulates are

- The atomic orbitals of comparable energies and proper symmetry of two atoms are mixed up to form molecular orbitals.
- The MO is the electron cloud surrounding more than one nucleus.
- Total number of MO = Total number of A.O
- Two A.O. combine to form two M.Os. One is anti bonding M.O and the other is bonding M.O. The energy of bonding MO is less than antibonding MO.
- The filling up of electrons in M.Os must follow Aufbau's principle, Pauli exclusion principle and Hund's rule.

$$\bullet \text{ Bond order} = \frac{N_b - N_a}{2} \quad \bullet \text{ Bond order} \propto \text{Bond energy} \propto \frac{1}{\text{Bond length}}$$

$N_b \rightarrow$ Number of electrons in bonding M. O.

$N_a \rightarrow$ Number of electrons in antibonding M. O.

- Bonding M.O = σ, π, δ Anti bonding M.O = $\sigma^*, \pi^*, \delta^*$
- The energy order of molecular orbitals :

i) Upto N_2 molecule: $\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \pi_{2px} = \pi_{2py} < \sigma_{2pz} < \pi_{2px}^* = \pi_{2py}^* < \sigma_{2pz}^*$

ii) For O_2, F_2 etc : $\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \sigma_{2pz} < \pi_{2px} = \pi_{2py} < \pi_{2px}^* = \pi_{2py}^* < \sigma_{2pz}^*$

13. Co-ordinate Bond :

- One of the group or atom must have lone pair of electron whereas the other must have the incomplete octet or duplet. Represented by “ — ”
- Also known as dative bond. Shown by $H_3O^+, NH_4^+, O_3, SO_2, SO_3, H_2SO_4$.

14. Other Bonds:

- a) **H-bonding** : It is weak electrostatic force of attraction between an electronegative atom and already covalently bonded H-atom with some other electronegative atom. It is formed by the compounds in which H is attached to N, O, F.
- It's strength is about 1/10th of covalent bond
 - The atom with small size and high electronegativity form strong H-bonding.
 - Of two types (i) Intermolecular (between two molecules of same or different compounds) e.g in HF, H_2O, NH_3 etc.
 - (ii) Intramolecular (within a molecule) e.g in o - Nitrophenol, salicylaldehyde etc.
 - Used to predict high b.p & density of water, solubility of alcohols and carboxylic acids in water, acidic character of o, p- nitro phenols etc.
- b) **Dipole-dipole interactions** :
- These exist between molecules having permanent dipoles e.g. $H - Cl, I - F$ etc.
- c) **Ion - dipole interactions**:
- Between an ion and a polar molecule e-g hydration of ions like Na^+, Mg^{2+} etc
 - Smaller the ion, more the dipole moment, stronger will be these interactions
- d) **Ion-induced dipole interactions** : Between an ion and a dipole induced by the ion in a nonpolar molecule
- e) **Dipole-induced dipole interactions** : Between a dipole and an induced dipole in a non polar molecule.
- f) **Dispersion forces** : Between two nonpolar substances. The forces are between an instantaneous dipole and an induced dipole e.g in O_2, N_2, He, Ne, Ar etc.

Note : Dipole-dipole, dipole-induced dipole and dispersion forces are called van der waal's forces.

A. GASEOUS STATE

1. Independent Variables of Gas

To describe the state of any gas, we need four independent variables i.e. amount (no. of moles), volume, pressure and temperature.

(a) **No. of Moles,** $n = \frac{\text{mass in gram}}{\text{molar mass}} = \frac{w}{M}$

(b) **Volume,** $1\text{L} = 10^{-3}\text{m}^3 = 1\text{dm}^3 = 10^3\text{cm}^3$ S.I unit is m^3 .

(c) **Pressure** $1\text{atm} = 76\text{cm of Hg} = 760\text{mm of Hg} = 1.01325\text{bar} = 1.01325 \times 10^5\text{Pa}$

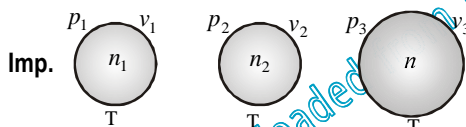
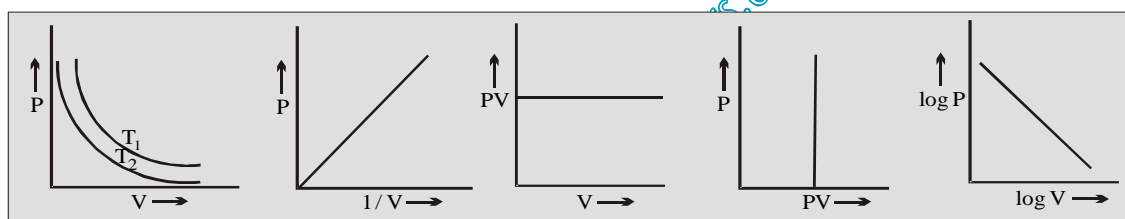
$1\text{Pa} = 1\text{Nm}^{-2} = 1\text{kgm}^{-1}\text{s}^{-2}$ $1\text{bar} = 100\text{kPa} = 10^5\text{Pa} = 0.987\text{atm}$

S.I unit of pressure is pascal (P_a). Pressure of a gas is measured by manometer and atmospheric pressure is measured by barometer.

Temperature $T^\circ\text{K} = t^\circ\text{C} + 273.15$

2. Boyle's Law : The pressure of a fixed amount of gas is inversely proportional to its volume at constant temperature. $P \propto \frac{1}{V}$ or $P = \frac{K}{V}$

$\therefore \boxed{PV = K}$ or $\boxed{P_1V_1 = P_2V_2 = K}$ (when n, T constant)

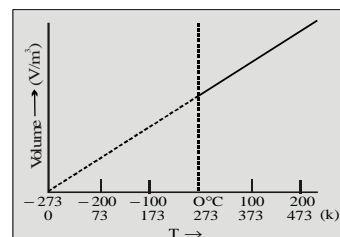


If $n = n_1 + n_2$, then $\boxed{P_1V_1 + P_2V_2 = P_3V_3}$

3. Charles's Law : At constant pressure, the volume of a given mass of a gas increases or decreases by $\frac{1}{273.15}$ of its volume at 0°C for every one degree rise or fall in temperature. OR When P is constant, the volume of a given mass of a gas is directly proportional to the absolute temperature.

$V \propto T$ (n, P constant, T in K)

$V = KT$ or $\frac{V}{T}$ is constant. $\therefore \boxed{\frac{V_1}{T_1} = \frac{V_2}{T_2}}$



4. Gay-Lussac's Law : At constant volume, pressure of a given mass of a gas is directly proportional to the temperature in kelvin.

$P \propto T$ at constant volume or $P = KT$ or $\frac{P}{T} = \text{constant}$ or $\boxed{\frac{P_1}{T_1} = \frac{P_2}{T_2}}$ (n, V) constant

5. Avogadro's Hypothesis : Under similar conditions of pressure and temperature, equal volumes of all gases contain equal number of moles or molecules. $V \propto n$ (P,T constant).

- One mole of any gas contains 6.023×10^{23} molecules which is known as Avogadro's no.
- At NTP or STP (0°C and 1atm), one mole of gas has the volume of 22.4L . Now a days STP has 273.15K temp. and 1bar pressure. Under these conditions molar volume of an ideal gas is taken equal to 22.7Lmol^{-1}

6. **Equation of State** : Combining Boyle's, Charle's and Avogadro's law

$$V \propto \frac{1}{P} \text{ at constant } T \text{ (Boyle's law)}$$

$$V \propto T \text{ at constant } P \text{ (Charle's law)}$$

$$V \propto n \text{ at constant } P \text{ \& } T \text{ (Avogadro's law)}$$

Hence $V \propto \frac{nT}{P}$ or $V = \frac{nRT}{P}$ or $PV = nRT$ Where R is universal gas constant.

$$\text{or } \frac{PV}{T} = nR \text{ (Constant)}$$

$$\text{or } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$P = \frac{n}{V} RT = \frac{w}{M} \frac{RT}{V} = \frac{w}{V} \frac{RT}{M} = \rho \frac{RT}{M}$$

$$R = 0.0821 \text{ L atm/K/mol} = 8.314 \text{ J/K/mol} = 2 \text{ cal/K/mol} = 0.083 \text{ Lbar K}^{-1} \text{ mol}^{-1}$$

7. **Dalton's Law of Partial Pressure** : At constant temperature, total pressure of a mixture of gases (non reacting) is equal to the sum of the partial pressures of the constituent gases.

$$P = P_1 + P_2 + P_3 + \dots$$

$$\text{Partial Pressure} = \frac{\text{mole of that gas}}{\text{total moles in mixture}} \times \text{total pressure} = \text{mol fraction of gas} \times \text{total pressure}$$

8. **Graham's Law of Diffusion or Effusion** :

- At constant T and P, the rate of diffusion or effusion of different gases are inversely proportional to the square roots of their densities.

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} \quad \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \quad \frac{v_1/t_1}{v_2/t_2} = \sqrt{\frac{M_2}{M_1}}, \text{ if } t_1 = t_2, \frac{v_1}{v_2} = \sqrt{\frac{M_2}{M_1}}, \text{ if } v_1 = v_2, \frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$$

- When no. of moles of diffusing gases are different.

$$\frac{r_1}{r_2} = \frac{n_1}{n_2} \sqrt{\frac{d_2}{d_1}} = \frac{n_1}{n_2} \sqrt{\frac{M_2}{M_1}}$$

- When pressure is different

$$\frac{r_1}{r_2} = \frac{P_1}{P_2} \sqrt{\frac{M_2}{M_1}}$$

- Molecular wt. of a mixture of gas = $\sum M_i n_i$, where M_i is mol. mass of i^{th} gas and n_i is its mol fraction.

9. **Kinetic Theory of Gases** : Important assumptions

- Gas consists of large no. of minute discrete particles having negligible volume in comparison to the volume of the container.
- No intermolecular force of attraction exists.
- Particles move randomly and collide with each other and with the walls of the container
- The pressure of gas is due to the collisions of the gas molecules on the walls of the container.
- Collisions of gas molecules are perfectly elastic
- The average kinetic energy of the gas molecules is directly proportional to the absolute temperature

$$PV = \frac{1}{3} m n u^2 \quad m - \text{mass of one molecule, } n - \text{no. of molecules, } u - \text{rms speed}$$

$$u = \sqrt{\frac{3RT}{M}}$$

$$\alpha = \sqrt{\frac{2RT}{M}}$$

$$v = \sqrt{\frac{8RT}{\pi M}}$$

$$u = \sqrt{\frac{3P}{D}}$$

$$\alpha = \sqrt{\frac{2P}{D}}$$

$$v = \sqrt{\frac{8P}{\pi D}}$$

$$\therefore u : v : \alpha = 1 : 0.92 : 0.82$$

$$PV = \frac{3}{2} kT \quad [k - \text{ Boltzmann constant, } k = \frac{R}{N_A}]$$

$$\alpha : v : u = 1 : 1.128 : 1.224$$

$$K.E = \frac{3}{2} RT \text{ or } K.E \propto T$$

10. Real Gases : All the ideal gases obey the gas laws and the relation $PV = nRT$ at all pressures and temperatures. But real gases are those which do not obey these laws perfectly under all conditions particularly at high pressure and low temperature. It is due to following two assumptions of kinetic theory of gases which are not applicable to real gases :

- There is no force of attraction between the gas molecules
- Volume of the molecules of a gas is negligible as compared to the total volume possessed by the gas. The real gases can be liquified at low temperature and high pressure and the volume of gas molecules cannot be neglected, particularly at high pressure.

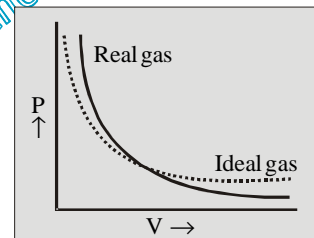
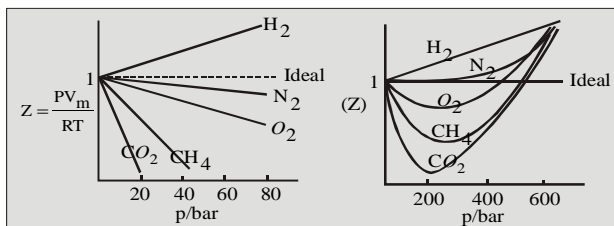
11. Compressibility Factor

For real gas, the equation is,

$$PV = ZnRT$$

$$\therefore Z = \frac{PV}{nRT} = \frac{PV_m}{RT}$$

Z – Compressibility factor $V_m \rightarrow$ molar volume



If $Z > 1$, repulsive force $\therefore V_m > 22.4 \text{ L}$

$Z < 1$, attractive force $\therefore V_m < 22.4 \text{ L}$

$Z = 1$, ideal gas $\therefore V_m = 22.4 \text{ L}$

12. van der Waal's Equation of State :

To get the gas equation for real gases two corrections are made in ideal gas equation i.e. pressure correction ($\frac{an^2}{V^2}$) to account for attractive forces between gas molecules and volume correction (nb) to account for the volume of gas molecules. This equation given is called **van der Waal's** equation.

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT, \text{ where } a \text{ and } b \text{ are van der Waal's constant.}$$

- For one mole of a gas, excluded volume = $b = V_E = 4N_o V_m$.
- Gases which have large values of a and small values of b can be liquified easily.
- Unit of a is $\text{atm. L}^2 \text{mol}^{-2}$ or $\text{Pa.m}^6 \text{mol}^{-2}$ (S.I. unit) and that of b is L mol^{-1} or $\text{m}^3 \text{mol}^{-1}$ (S.I. unit).
- Boyle's temperature** : It is a temperature at which all gases behave ideally. So it is different for different gases.

13. Liquifaction of Gases : Gases can be liquified by applying high pressure and low temperature but more important factor is temperature. A gas can never be liquified if its temperature is greater than a particular temperature howsoever high the pressure may be. This temperature above which gas cannot be liquified is called critical temperature (T_c). The minimum pressure required to liquify the gas at critical temperature is called critical pressure (P_c) and volume of one mole of the gas at T_c and P_c is called critical volume (V_c). For CO_2 gas. $T_c = 304.1\text{K}$, $P_c = 73.9 \text{ bar}$, $V_c = 0.0956 \text{ litre}$.

(B) LIQUID STATE

The liquid state is intermediate between gaseous and solid state. The molecular interactions are quite strong in liquid state and that is why they have definite volume. On the other hand the molecules of liquid have so much freedom that they can flow readily and take up the shape of container due to continuously making and breaking of weak vander Waal's bonds between molecules.

1. **Vapour Pressure** : When there is an equilibrium between the liquid and its vapours, the pressure exerted by vapours on the walls of the container is called vapour pressure. Vapour pressure is directly proportional to temperature and depends upon the nature of the liquid. It is independent of the amount of liquid.
2. **Evaporation** : The process of changing liquid into vapours is called evaporation. There are some molecules in liquid which have relatively high kinetic energy and when are at liquid surface, they overcome force of attraction and change into vapour state causing evaporation. When high energy molecules leave the surface, the average kinetic energy decreases leading to a fall in temperature of the liquid, that is, why evaporation causes cooling.
3. **Boiling Point** : The temperature at which the vapour pressure of a liquid is equal to external pressure is called boiling point of liquid . If external pressure is one atm. then b.p. is called normal b.p., if it is one bar then b.p. is called standard b.p. Higher the vapour pressure of liquid, lower will be boiling point. Lower the vapour pressure of liquid, higher will be boiling point.
4. **Surface Tension** : It is defined as energy required to increase the surface area of the liquid by one unit (m^2) . It is represented by γ (gamma). The liquid surface, tends to attain minimum surface area due to surface tension, i.e., acquires spherical shape. **Surface tension** is also defined as force acting per unit length perpendicular to the line drawn on the surface. Its unit is Nm^{-1} in S.I unit and has dimensions $kg\ s^{-2}$. It can also be expressed in terms of surface energy per unit area, as Jm^{-2} . It depends upon the temperature and nature of the liquid.
5. **Viscosity** : The ease with which a fluid can flow is determined by the property called viscosity. It is defined as resistance offered to the flow of liquid due to internal friction between layers of fluids as they pass over each other. The force acting between two liquid layers (F) is related with coefficient of viscosity (τ) as :

$$F = \eta A \frac{dv}{dx} \dots\dots(i) \quad A - \text{area, } \frac{dv}{dx} \rightarrow \text{velocity gradient.} \quad \text{Here if } A = 1 \text{ and } \frac{dv}{dx} = 1 \text{ then } \tau = F.$$

So coefficient of viscosity is defined as : the force of friction required to maintain unit velocity difference between two parallel layers separated by unit distance each with unit-area. S.I unit of τ is $Nm^{-2}.s$ or Pa.s. Common unit is poise, $1 \text{ poise} = 1g\ cm^{-1}s^{-1}$, viscosity also depends upon nature of the liquid and temperature.