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SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT-I – BONDS TO BANDS – SCYA1101

1. Introduction

In this chapter, we shall give an overview of the properties of solids and how quantum mechanics helps us to understand these properties. In

the solid state, a material at a given temperature and pressure has a well definite shape. The forces of interaction between the atoms in the solid must be strong and the bonds between them are stable under existing conditions. In subsections, we used quantum mechanics to understand how these bonds are formed. We have considered the crystalline solids, in which the bonds allow the formation of regular arrays of atoms within the solid. In other subsections, we give an introductory treatment of energy bands and the band theory of solids to explain the electrical conductivity and why some solids are conductors, whereas others are semiconductors or insulators. Most important among these is the idea of a bond, and the use of frontier-orbital arguments. Interpretative constructs, such as the density of states, the decomposition of these densities and crystal orbital overlap population, allow a recovery of bonds, a finding of the frontier orbitals that control structure and reactivity in extended systems as well as discrete molecules.

Electromagnetic Wave

Electromagnetic wave or radiation is a wave that consists of oscillating electric and magnetic fields which is characterized by wavelength λ and frequency ν (number of oscillations per second). The wavelength and frequency of the wave is related to velocity c (3×10^8 ms^{-1}) of the wave by $c = \lambda \nu$

Black Body Radiation

An ideal black body is an object that absorbs all the radiations falling on it. A hollow enclosure or chamber having a small hole is an appropriate black body because it absorbs all the radiation entering it due repeated reflections inside the enclosure. The radiation emitted from such a black body is called black body radiation. A perfect absorber is also a perfect emitter of radiation. The intensity of the total radiation emitted per unit surface area from a black body depends on temperature (T) and is independent of the nature of the solid.

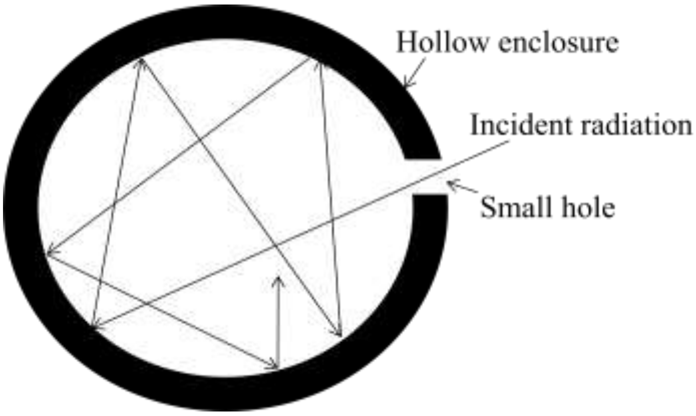


Fig 1: Black body radiation

Laws of Radiation

The radiation emitted by a heated body is explained by the laws of radiation.

1. Wien's law

The wavelength λ_m corresponding to the maximum energy density $\rho(v)dv$ is inversely proportional to the temperature T.

$$\lambda_m \propto \frac{1}{T}$$

$$\lambda_m = \frac{b}{T}$$

$$\lambda_m T = b$$

where b is called Wien's constant and value of b is 2897 microkelvin.

2. Rayleigh-Jean's law

Rayleigh derived an equation for the distribution of energy density called the Rayleigh-Jean's law

$$\rho(v)dv = \frac{8\pi v^2}{c^3} K_B T dv$$

where $\rho(v)dv$ is the radiation density and K_B is the Boltzmann constant (1.38×10^{-23} JK^{-1}).

3. Planck's law of radiation

Max Planck derived an expression for energy density of a black body radiation called as Planck's radiation law and is given by

$$\rho(v)dv = \frac{8\pi h v^3}{c^3} \frac{1}{(e^{(hv/K_B T)} - 1)} dv$$

Planck introduced a constant h known as Planck's constant (value of h = 6.626×10^{-34} Js). He proposed a Planck's quantum theory based on energy quantization to explain the black body radiation.

The black body emits radiation in a wide spectrum of wavelengths. The distribution of energy of emitted radiation over different frequencies is called as energy density and is given by $\rho(\nu)d\nu$. At any temperature T, the energy density $\rho(\nu)d\nu$ increases with increase in ν, reaches a maximum and then drops to zero. With increase in T, the maximum of curve shifts to higher frequency (i.e) shorter wavelength side.

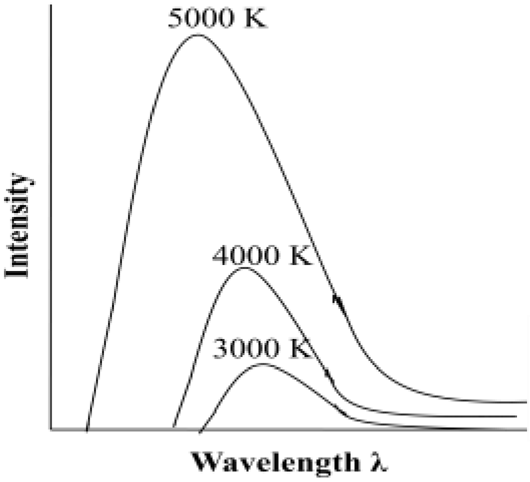


Fig 2: Planck's law of Black body radiation

Planck's quantum theory of radiation

According to this theory

1. Energy is absorbed or emitted in the form of discrete sets of small bundles of energy known as quanta.
2. Each quantum is associated with certain amount of energy E = hν, where h is Planck constant and ν is the frequency of radiation.
3. A body can emit or absorb energy only in integral multiples of quantum (i.e) 1hν, 2hν, 3hν………nhν.

Photoelectric effect

In 1905, based on the Planck's idea of energy quantization, Albert Einstein discovered law of the photoelectric effect. According to photoelectric effect, when a light photon of a certain frequency ν strikes the surface of metal, electrons are emitted from the metal. The photon transfers its energy hν to the electrons and this is used to overcome the binding energy (ω) and to increase kinetic energy $\left(\frac{1}{2}mv^2\right)$ of the emitted electrons.

$$h\nu = \omega + \frac{1}{2}mv^2$$

since $\omega = h\nu_0$, where ν_0 is the threshold frequency

$$h\nu = h\nu_0 + \frac{1}{2}mv^2$$

$$\frac{1}{2}mv^2 = h\nu - h\nu_0$$

$$\frac{1}{2}mv^2 = h(\nu - \nu_0)$$

This equation is called the Einstein photoelectric equation.

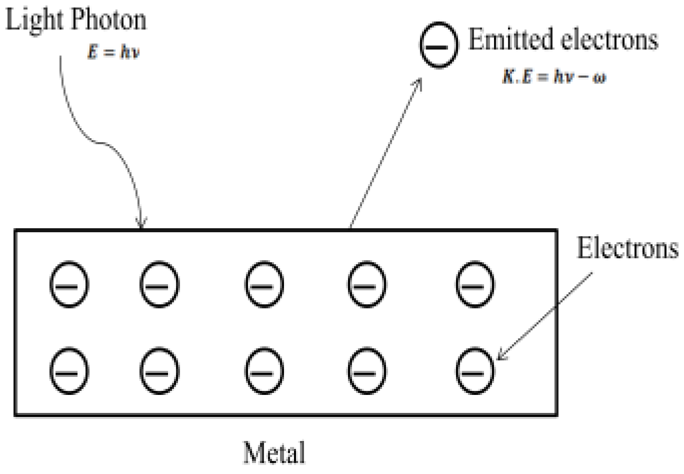


Fig 3: Photoelectric effect

Observations

1. Light with minimum frequency called the threshold frequency ν_0 is necessary to cause emission of electron by photoelectric effect. (If $\nu < \nu_0$ there is no photoelectric effect)
2. Kinetic energy of emitted electrons is directly proportional to frequency and independent of intensity of incident radiation.

Wave – Particle duality of electrons – de Broglie's hypothesis

Louis de Broglie in 1924 proposed that the quantization of energy of an atom can be explained only when electrons exhibit wave-particle dual behaviour. This hypothesis was verified through electron diffraction experiment by Davisson and Germer. The electrons produce diffraction patterns similar to light waves when passed through a nickel crystal which confirms the wave nature of electrons. de Broglie hypothesis can be derived by using Einstein's energy mass relationship

$$E = mc^2 \quad \ldots..1$$

where c is velocity of photon and m is mass of photon.

According to Planck's, the energy of photon is quantized which inherently possess the duality nature of particle, since energy of photon E is a particle property and frequency ν is a wave property.

$$E = h\nu \quad \ldots..2$$

Thus from equations 1 and 2

$$h\nu = mc^2 \ \Rightarrow \nu = \frac{mc^2}{h}$$

In wave theory of light, the frequency ν and wavelength λ is related to each other by the equation $\nu\lambda = c$

Therefore,

$$\lambda = \frac{c}{\nu} = \frac{ch}{mc^2} = \frac{h}{mc} = \frac{h}{p}$$

where p is the momentum of the photon $p = mc$

de Broglie proposed that the wavelength or frequency of electron similar to the photon is related to the momentum of the electron

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

where λ = wavelength of electron, m = mass of electron, p = momentum of electron, h = Planck's constant.

de Broglie hypothesis of wave-particle duality is applicable to all subatomic particles such as neutrons, protons etc.

Heisenberg's Uncertainty Principle

Heisenberg stated that "it is not possible, even in principle to measure both position and momentum of an electron simultaneously". This is known as Heisenberg Uncertainty principle. Mathematically it is expressed as

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

where Δx is the uncertainty in position of the electron, Δp is the uncertainty in momentum of the electron and h is the Planck's constant. If the position of an electron is determined with high accuracy then its momentum becomes uncertain. Similarly, if the momentum of the electron is measured precisely then its position will be uncertain. This principle holds good only for microscopic particles however, it does not apply to larger bodies (i.e) both momentum and position can be determined accurately at the same time.

2. Theory of Wave Motion

The de Broglie, Heisenberg uncertainty principle and electron diffraction experiments established the dual nature of electrons as particle as well as wave. A particle is localized it cannot be present in more than one place at same time whereas wave cannot be localized at a point and varies from a point to point in space. In order to insight the behaviour of electrons it is necessary to understand the characteristics of wave motion.

Classical Waves and Wave Equation

Consider the wave motion in vibration of a string, the vertical displacement of string from its mean position is called the amplitude of wave or vibration. This amplitude is a function of position (x) and time (t) and denoted as Ψ(x,t).

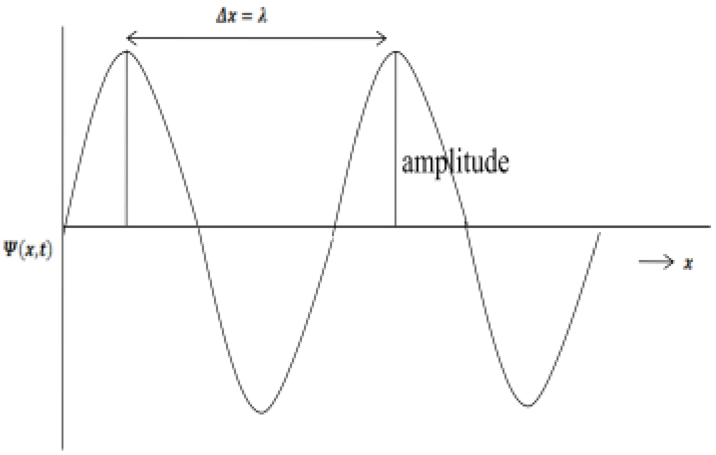


Fig 4: Classical wave

Here the wave makes same amplitude at regular intervals of Δx which is λ the wavelength of the wave. The velocity of wave c is given by λ/t, the frequency ν (number of waves per unit time) will be c = λ/t⇒ 1/t = c/λ (ν=c/λ) and the wave number (number of waves per unit distance) will be ῡ = 1/λ. The periodic nature of Ψ(x,t) propose the sine or cosine function of x and t where x is position coordinate and t is time coordinate. The expression for wave function is obtained by solving the equation of the wave motion which is not in the scope of this book

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 \Psi}{\partial t^2} \qquad \ldots..1$$

where Ψ=Ψ(x,t). By applying separation of variables method, function Ψ(x,t) is separated into a product of two functions

$$\Psi(x,t) = \Psi(x).\Phi(t) \quad \dots..2$$

where Ψ(x) is a function of x only and Φ(t) is a function of t only. Substituting equation 2 in 1 and diving by Ψ(x). Φ(t) on both sides gives

$$\frac{c^2}{\Psi}.\frac{\partial^2\Psi}{\partial x^2} = \frac{1}{\Phi}.\frac{\partial^2\Phi}{\partial t^2} \quad \dots..3$$

The left hand side of equation 3 depends only on x and right hand side depends only on t however both sides are equal and are equated to a constant $-k^2$

$$\frac{c^2}{\Psi}.\frac{\partial^2\Psi}{\partial x^2} = \frac{1}{\Phi}.\frac{\partial^2\Phi}{\partial t^2} = -k^2 \quad \dots..4$$

Thus two equations are obtained from equation 4

$$\frac{\partial^2\Psi}{\partial x^2} = -\frac{k^2}{c^2}\,\Psi \quad \dots..5$$

$$\frac{\partial^2\Phi}{\partial t^2} = -k^2\Phi \quad \dots..6$$

Here equation 5 is the time-independent wave equation called as amplitude equation. The general solutions for equations 5 and 6 are

$$\Psi(x) = A\,sin\left(\frac{kx}{c}\right) + Bcos\left(\frac{kx}{c}\right) \quad \dots..7$$

$$\Phi(t) = C\sin(kt) + D\cos(kt) \quad \dots..8$$

where A,B,C and D are arbitrary constants.

The other solutions of equation 5 are

$$\Psi(x) = A\exp\left(\pm\frac{2\pi ix}{\lambda}\right) \quad \dots..9$$

These exponential functions are expressed in trigonometric functions as

$$\exp(\pm ikx) = coskx \pm i\,sinkx \quad \dots..10$$

Stationary Waves

Waves expressed by the equation 5 are called running waves in which Ψ is a function of time. However, electron waves in atoms and molecules are stationary waves in which Ψ does not change with time. A classical example of such wave is the wave in a vibrating string clamped at two ends.

Thus equation 5 may be expressed as

$$\frac{\partial^2\Psi}{\partial x^2} = -\frac{4\pi^2}{\lambda^2}\,\Psi \quad \dots..11$$

$$\because\ \frac{k}{c} = \frac{2\pi}{\lambda c}$$

here Ψ(x) is expressed as Ψ. The wave does not vibrate at the ends x = 0 and x = L and this is called as boundary conditions.

The first boundary condition x = 0, Ψ becomes 0 from equation 7 and B becomes zero

$$0 = A\, sin\left(\frac{2\pi}{\lambda}\,.0\right) + Bcos\left(\frac{2\pi}{\lambda}\,.0\right) = B \quad \ldots..12$$

The second boundary condition x = L and B = 0, Ψ becomes 0

$$0 = A\, sin\left(\frac{2\pi}{\lambda}\,.L\right) \quad \ldots..13$$

Equation 13 is satisfied when

1. A = 0, but Ψ becomes zero everywhere and for all values of x which is not acceptable.
2. $\frac{2\pi}{\lambda}\,.L = n\pi$, where n = 0, ±1, ±2, ±3 …

or $\lambda = \frac{2L}{n}$ and is acceptable.

The solution of the wave equation is $\Psi = A\sin\frac{n\pi x}{L}$ where A is maximum amplitude of the wave. The equation becomes zero at boundary conditions and integral number of half wavelength between the clamped ends of the string. The points where Ψ becomes zero is called node.

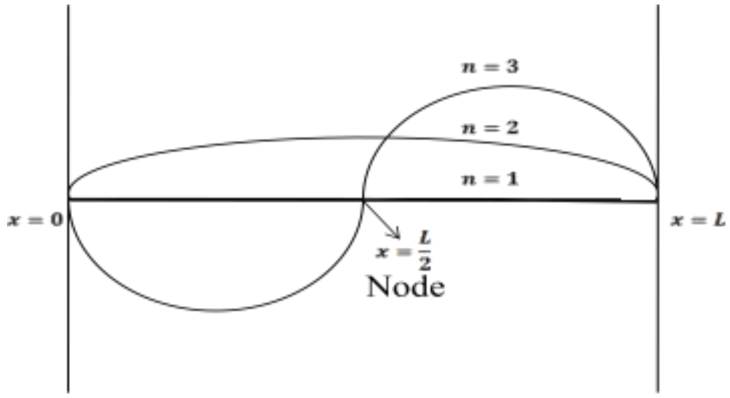


Fig 5: Stationary wave - Vibration in clamped string

For example when n = 0, Ψ = 0 everywhere, when n = 1, Ψ = 0 only at x = 0 and x = L, and there is no node, when n = 2, Ψ becomes zero at x = L/2 which is a node, for n = 3, Ψ becomes zero at x = L/3 and 2L/3 thus two nodes are present and so on.

Schrodinger Equation for Particle Waves

Erwin Schrodinger proposed that if electrons have both particle and wave behaviour the equation of wave motion can be applied to them. He used the time-independent wave equation to explain the particle wave. For an electron of wavelength λ moving along x-coordinate,

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{4\pi^2}{\lambda^2}\,\Psi \quad \dots..14$$

From de Broglie relationship, $\lambda = \frac{h}{mv}$ and substituting in equation gives

$$-\frac{4\pi^2 m^2 v^2}{h^2}\Psi = -\frac{8\pi^2 m T\Psi}{h^2} = -\frac{8\pi^2 m(E-V)}{h^2}\Psi \quad \dots..15$$

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{8\pi^2 m(E-V)}{h^2}\,\Psi \quad \dots..16$$

where Ψ = Ψ(x), T is kinetic energy, V is potential energy and E is total energy of the electron (E=T+V). This is known as Schrodinger equation for particle (electron) of mass m moving in one dimensional motion. For three dimensional motion, the equation will be a partial differential equation with three coordinates x,y and z.

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} = -\frac{8\pi^2 m(E-V)}{h^2}\Psi \quad \dots..17$$

Conditions for Acceptable Wave Function

The conditions for an acceptable wave function Ψ are

1. It must be finite.
2. It must be single-valued at all points.
3. It must be continuous.

If these three conditions are obeyed then the function Ψ is called a well-behaved wave function.

Motion of Quantum Mechanical Particle

The quantum mechanical particle such as electrons in atoms and molecules can execute translational, rotational and vibrational motion. However, the common type of motion is translational or linear when they move freely.

For linear motion of free particle which is not affected by any force or potential barrier and free to move in limitless space, the equation 16 becomes Schrodinger equation for free particle is given by

$$\frac{\partial^2\Psi}{\partial x^2}+\frac{8\pi^2mE}{h^2}\Psi=0 \;\; \ldots..18$$

Here potential energy V is a constant and assumed to be zero since the free particle is not subjected to any potential barrier.

3. Particle in one dimensional box

Consider a particle is moving in a limited space like bounded electrons in atoms and molecules serves as particle in a box model. If the limited space is a one dimensional box of length L with infinite high walls at the two ends, the particle is not subjected to any force inside the box where potential energy V = 0 and outside the box it is infinity thus V = ∞.

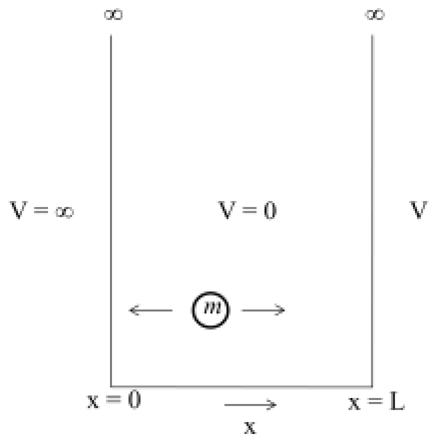


Fig 6: Particle in one dimensional box of length L

Hence the potential energy is discontinuous (high at x = 0 and x = L and inside the box is zero), thus the Schrodinger equation should be considered inside and outside the box separately.

The Schrodinger equation outside the box (where V = ∞) will be

$$\frac{\partial^2\Psi}{\partial x^2}+\frac{8\pi^2m(E-\infty)}{h^2}\Psi=0 \;\; \ldots..19$$

$$-\frac{h^2}{8\pi^2m}\frac{\partial^2\Psi}{\partial x^2}+\infty\Psi=E\Psi \;\; \ldots..20$$

The Schrodinger equation inside the box 0 ≤ x ≥ L (where V = 0)

$$\frac{\partial^2\Psi}{\partial x^2}+\frac{8\pi^2m\,(E-0)}{h^2}\Psi=0 \;\; \ldots..21$$

$$-\frac{h^2}{8\pi^2 mE}\frac{\partial^2\Psi}{\partial x^2} = E\Psi \quad .....22$$

The probability of finding a particle outside the box, (i.e) $\Psi^2 = 0$ due the large potential energy ($V = \infty$) present in these regions $x < 0$ and $x > L$ and thus $\Psi = 0$. Since Ψ must be continuous (i.e) it cannot rise and fall suddenly thus Ψ must be zero at $x = 0$ and $x = L$. This is the boundary condition for this system.

The Schrodinger equation inside the box is written as

$$\frac{\partial^2\Psi}{\partial x^2} + k^2\Psi = 0 \quad .....23$$

$$k^2 = \frac{8\pi^2 mE}{h^2} \quad .....24$$

Equation 23 is satisfied by well behaved functions such as sin kx, cos kx, e^{ikx} and e^{-ikx}.

Wave function and Energy of the particle

The wave function is described either in terms of real form such as sin kx and cos kx and complex forms such as e^{ikx} and e^{-ikx}.

The general solution of real form of wave function is given as

$$\Psi = A\, sin\, kx + B \cos\, kx \quad .....25$$

where A and B are arbitrary constants. The values of A, B and k are determined by applying boundary conditions to equation 25

i. At x = 0, Ψ becomes 0

$$0 = A\, sin\,(k.0) + B\cos\,(k.0)$$

Thus B = 0 and hence $\Psi = A\, sin\, kx$ for all values of x

ii. At x = L, Ψ becomes 0

$$0 = A\, sin\,(k.L) + 0\cos\,(k.L)$$

Thus $0 = A \sin kL$

This expression is satisfied if either A = 0 or kL = $n\pi$.

Case 1: If A = 0, B = 0, then Ψ becomes 0 everywhere which not acceptable.

Case 2: Thus kL = $n\pi$ or k = $n\pi$/L where n is an integer (1,2,3…) but not zero (if $n = 0$, Ψ becomes 0)

The wave function and energy of the particle in one dimensional box is given as

$$\Psi = A\, sin\frac{n\pi x}{L} \quad .....26$$

$$E = \frac{n^2h^2}{8mL^2} \quad .....27$$

Quantization

In the energy equation 27, the terms h, m and L are constants and energy E depends only on integer n. Thus energy is quantized (i.e) have discrete set of values and the integer *n* is a quantum number. Hence a particle confined to move in a limited space and its energy is quantized.

Energy levels

The figure 1.7 shows the quantization of energy of a particle in one dimensional box. The allowed energy levels are drawn as horizontal lines which shows that for a value of n, energy E does not change with position x of the particle.

The lowest energy level E_1 is not zero but $\frac{h^2}{8mL^2}$ (n = 1) and is also called the "zero point energy". The energy E depends on n^2 which shows that increase in *n*, increases the spacing between energy levels

$$\Delta E = E_{n+1} - E_n = [(n+1)^2 - n^2]E_1 = (2n+1)E_1$$

Since E is proportional to $\frac{1}{L^2}$

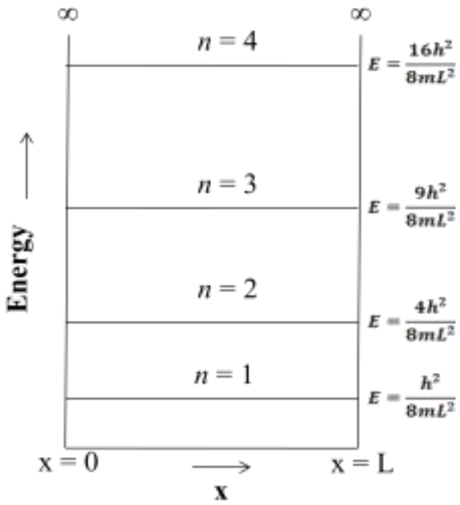


Fig 7: Energy levels for particle in one dimensional box

Case 1: when the box is small the energy spacing (ΔE) is greater (i.e) the quantization is pronounced.

Case 2: when the box is wider, ΔE decreases and in limiting case of L⟶∞ (free particle) the quantization vanishes.

Similarly ΔE is also proportional to $\frac{1}{m}$ thus for macroscopic system (large m) the energy levels are closely spaced and there is no quantization.

Value of A

The value A is determined by the normalization of wave function which is given by

$$\int_0^L \Psi^2 d\tau = \int_0^L A^2 sin^2 \frac{n\pi x}{L} dx = 1$$

$$we\ know\ that\ sin^2 x = \frac{(1 - cos\ 2x)}{2}$$

$$\int_0^L A^2 sin^2 \frac{n\pi x}{L} dx = \frac{A^2}{2} \int_0^L \left(1 - cos \frac{2n\pi x}{L}\right) dx = 1$$

$$\frac{A^2}{2} \left\{ [x]_0^L - \left[\frac{\sin 2n\pi x/L}{2n\pi/L}\right]_0^L \right\} = 1$$

$$\frac{A^2 L}{2} = 1$$

$$A = \sqrt{\frac{2}{L}}$$

Thus the normalized wave function is $\Psi = \sqrt{\frac{2}{L}}\ sin \frac{n\pi x}{L}$

Physical meaning of wave function Ψ- Probability density

In Schrodinger wave equation, Ψ is not a physically observable quantity and does not have any direct physical meaning. However it is used to explain all the observable physical quantities and this function is known as wave function. The physical interpretation of square of wave function Ψ^2 is a measure of the probability of finding a particle in specified small volume of space. Ψ^2 is considered if Ψ is real function and ΨΨ* is considered when Ψ is complex and Ψ* is its complex conjugate but the product ΨΨ* is always real.

The normalized wave function is used to calculate the probability density (i.e) the probability of finding the particle at different points in the one dimensional box. The probability density is given as

$$\Psi^2 = \frac{2}{L}\ sin^2 \frac{n\pi x}{L}$$

varying between 0 and $\frac{2}{L}$. The probability of particle in a box has maximum probability at certain points depending on value of *n* and is given as

$$P = \int_a^b \Psi^2 \, dx = \frac{2}{L}\int_a^b sin^2 \frac{n\pi x}{L} dx$$

i. For n = 1, the maximum probability $\left(\frac{2}{L}\right)$ occurs at x = $\frac{L}{2}$

ii. For n = 2, the maximum probability occurs at x = $\frac{L}{4}$ and x = $\frac{3L}{4}$ on both side of the middle point and is zero at x = $\frac{L}{2}$ and so on.

The probability will never be negative and these curves are always symmetric about the reflection plane at the middle of the box.

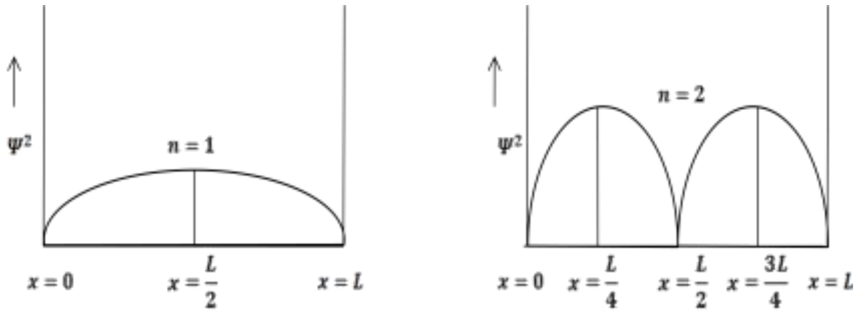


Fig 8: Probability density curves of particle in one dimensional box for n = 1 and n = 2 energy levels

4. Schrodinger equation for hydrogen atom

Hydrogen atom is a two particle system which contains one electron (of mass m and charge –e) and one proton (nucleus of mass M and charge +Ze). Consider x_1,y_1,z_1 and x_2,y_2,z_2 as the Cartesian coordinates for the proton and electron respectively which are separated by a distance r. Since the proton mass is very much greater than electron, the reduced mass calculated will be considered as the mass of the electron.

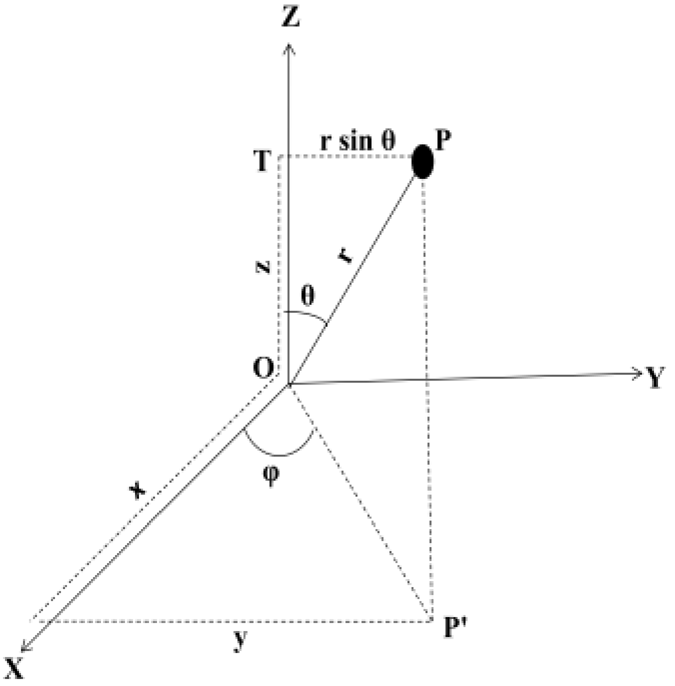


Fig 9: Relationship between Cartesian and spherical coordinates

In hydrogen atom two types of motions are involved i) translational motion of hydrogen atom as a whole and ii) the internal motion of electron and nucleus relative to each other. The Schrodinger equation involving these motions is

$$\hat{H}\Psi_T = E_T\Psi_T$$

where $\Psi_T = \Psi\ (x_1,y_1,z_1,\ x_2,y_2,z_2)$ and E_T is the total wave function and total energy(translational energy and internal energy) of the hydrogen atom. The spatial rotation of electron around the nucleus (containing proton) can be explained by two angular variables φ (azimuthal angle) and θ (zenith angle) and radial distance r from the nucleus.

The Schrodinger equation of hydrogen atom is

$$\hat{H}(r,\theta,\varphi)\Psi(r,\theta,\varphi) = E\Psi(r,\theta,\varphi)$$

The hydrogen atom Hamiltonian contains kinetic energy operator T in terms of spherical coordinates and spherically symmetrical potential energy. The potential energy is given by

$$V = \frac{Ze^2}{(4\pi\varepsilon_0)r}$$

The Cartesian coordinates are converted to spherical coordinates in terms of radius r and angle φ measured between 0 to 2π and angle θ measured between 0 to π. The relationship between x, y and z and r, θ and φ is given as

PT = OP' = r sin θ

x = OP' cos φ = r sin θ cos φ

y = OP' sin φ = r sin θ sin φ

z = OT = r cos θ

Thus the time-independent Schrodinger equation for hydrogen atom

$$\left\{\frac{h^2}{8\pi^2 m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2 sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]-\frac{ze^2}{4\pi\varepsilon_0 r}\right\}\Psi\,(r,\theta,\varphi)$$
$$=E\Psi(r,\theta,\varphi)$$

This equation can be separated into spherical harmonic function Y(θ,φ) and radial function R(r) by using product wave function.

$$\Psi(r,\theta,\varphi)=R(r)\ Y(\theta,\varphi)$$

Here the spherical harmonic functions give the information about the position of electron around the proton and the radial function R(r) tells the distance of electron form the proton. The energy term E_n and the solution for R(r) and Y(θ,φ) depends only on one quantum number *n* (principal quantum number. However, the other three quantum numbers are necessary for proper description of complete wave function.

$$E_n=\frac{me^4}{8\varepsilon_0^2 h^2 n^2}$$

5. Quantum Numbers

Four quantum numbers are necessary to define an orbital. The combination of these four quantum numbers of electrons in an atom is described by a wave function satisfied by Schrodinger equation. The quantum numbers are used to account for the electronic configuration of an electron in an atom and the probable position of electron in an atom.

The quantum numbers explain the shells, subshell, orbitals and spin of electrons. The four quantum numbers are

1. Principal quantum number (n)

The principal quantum number characterizes the principal electron shell which decides the energy of an electron and the probable position of the electron from the nucleus. Thus *n* describes the size of the orbital and energy level in which the electron is placed. The larger the value of *n*, larger is the size of orbital which show that the electron is at longer distance from the nucleus. When *n* = 1, it belongs to first principal shell (ground state) and lowest energy level. When electron absorb energy it is excited to the higher principal shells (n = 2, 3, 4,…). Thus *n* takes integral values 1, 2, 3… ∞ except zero since when *n* = 0, the energy of atom becomes zero and the atom doesn't exists. The value of *n* describes the shells K, L, M, N…. in the atom.

2. *Azimuthal quantum number (l)*

The azimuthal quantum number or orbital quantum number characterize the shape of the orbital and the subshell to which electron belong to. Each *l* value indicates subshell which is designated as *s, p, d, f.* Each subshell corresponds to unique shape. It also determines the number of angular nodes of the orbital which will be equal to the number of *l* values. The value of *l* is subshell to which electrons belong to and it depends on *n* values and can have integral values from 0 to *n*-1. Thus

$l = 0, 1, 2…. (n-1)$.

3. *Magnetic quantum number (m_l)*

The magnetic quantum number represents the number of orbitals and orientation of orbitals in a subshell. The value of m_l is based on the value of *l* and can have a total of (*2l*+1) values. Thus magnetic quantum number has values as $m_l = -l, \dots, 0, \dots, +l$

Table 1: *l* and m_l value for *s, p, d, f* subshells

Subshell	***l* value**	**m_l value**
S	0	0
P	1	-1, 0, +1
D	2	-2, -1, 0, +1, +2
F	3	-3, -2, -1, 0, +1, +2, +3

Table 2: Total number of orbitals in subshells

Principal quantum number (*n*)	**Subshell corresponding to azimuthal quantum number (*l*)**	**Magnetic quantum number (m_l)**	**Name of the subshell orbital**	**Total number of orbital in subshells**
n = 1, 2, 3, …	*s* (l =0)	$m_l = 0$	s	1
	p (l = 1)	$m_l = 0$	p_z	3
		$m_l = \pm1$	p_x	
			p_y	
	d (l = 2)	$m_l = 0$	d_{z^2}	5
		$m_l = \pm1$	d_{xz}	
			d_{yz}	
		$m_l = \pm2$	d_{xy}	
			$d_{x^2-y^2}$	
	f (l = 3)	$m_l = 0$	f_{z^3}	7
		$m_l = \pm1$	f_{xz^2}	
			f_{yz^2}	
		$m_l = \pm2$	f_{xyz}	
			$f_{z(x^2-y^2)}$	
		$m_l = \pm3$	$f_{x(x^2-3y^2)}$	
			$f_{y(3x^2-y^2)}$	

4. Spin quantum number (m_s)

The spin quantum number refers the direction of spin of an electron in an orbital. The direction of spin can be clockwise (m_s = + ½) or anticlockwise (m_s = - ½).

Assigning Electrons to Orbitals

Three set of rules govern the filling of electrons in the orbital. They are

1. Aufbau principle

Aufbau principle states that the electrons in an atom occupy the orbital of lowest energy before filling the higher energies. Thus electrons are filled in increasing order of energy

1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 6*s*, 4*f*, 5*d*, 6*p*, 7*s*,…..

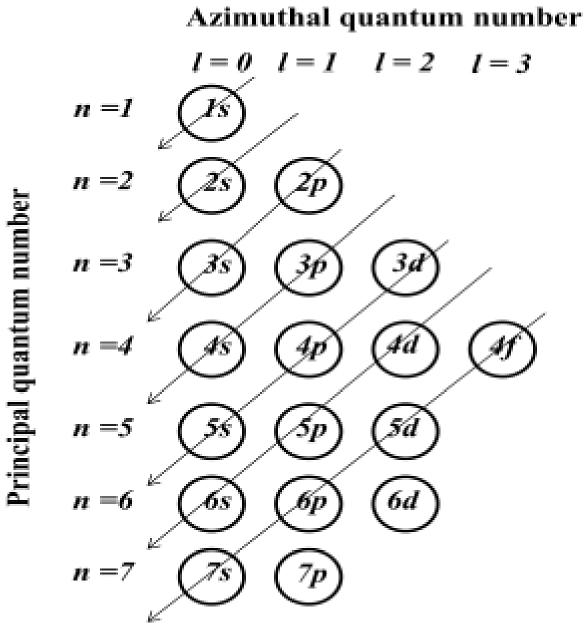
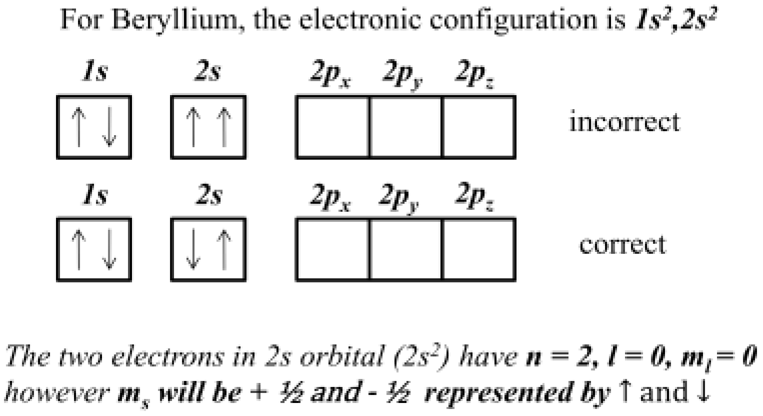


Fig 10: Aufbau principle

2. Pauli-Exclusion principle

It states that no two electrons in the same atom can have all the four quantum number the same. The electrons in each orbital have three quantum numbers *n*, *l* and m_l same but the fourth quantum number m_s will be different. Thus a single orbital can accommodate a maximum of two electrons with opposite spin. The *s*-orbital can accommodate 2 electrons, *p*-orbital can hold till 6 electrons (each 3 orbitals hold 2 electrons), the five *d*-orbitals can accommodate 10 electrons and seven *f*-orbitals can hold 14 electrons.



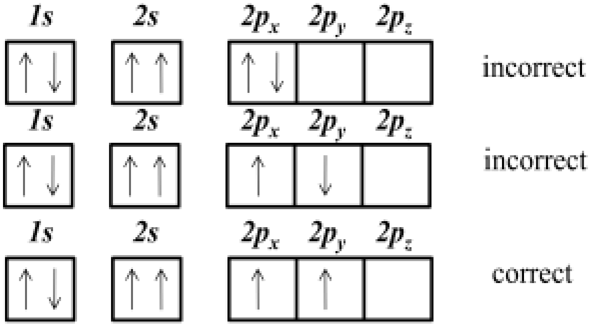
For Beryllium, the electronic configuration is $1s^2,2s^2$

The two electrons in 2s orbital ($2s^2$) have $n = 2, l = 0, m_l = 0$ *however* m_s ***will be + ½ and - ½ represented by*** ↑ and ↓

3. Hund's rule

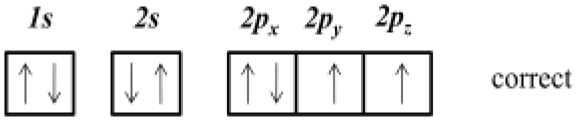
According to Hunds rule, every orbital in a subshell should be filled with atleast one electron before pairing of electrons takes place. Further the electrons in singly filled orbitals of subshell have the same spin.

For Carbon, the electronic configuration is $1s^2, 2s^2, 2p^2$



Electrons in orbitals of same subshell have same spin

For Oxygen, the electronic configuration is $1s^2, 2s^2, 2p^4$



Thus pairing of electrons occurs only after all orbitals in subshell is atleast filled with one electron

6. Angular and Radial Wave Functions

Thus the complete wave fuction of hydrogen-like atoms is given as

$$\Psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)\ Y_{lm}(\theta,\varphi)$$

Each wave function has two parts the radial wave function $R_{nl}(r)$ and angular wave function (spherical harmonics) $Y_{lm}(\theta,\varphi)$. The radial wave function depends on the quantum numbers *n* and *l* whereas the angular wave function depends on only *l* and *m*. The radial wave function describes the size of the atomic orbital (i.e) the distance between the electron and nucleus. The angular wave function describes the shape of the atomic orbital. The real forms of radial and angular wave functions and complete wave function for s and p orbitals of hydrogen atom ($Z = 1$ and $a_0 = 1$) is given below

Table 3: Radial, Angular wave function and complete wave function of *s* and *p* orbitals

Quantum numbers ***n,l,m***	**Radial wave function** **(R*nl*)**	**Angular wave function** **(Y*lm*)**	**Complete wave function** **(Ψ*nlm*)**
n =1, l =0, m=0	$R_{10} = 2e^{-r}$	$Y_{00} = \frac{1}{\sqrt{4\pi}}$	$\Psi_{1s} = \Psi_{100} = \frac{1}{\sqrt{\pi}}\ e^{-r}$
n =2, l =0, m=0	$R_{20} = \frac{1}{2\sqrt{2}}\ (2-r)e^{-r/2}$	$Y_{00} = \frac{1}{\sqrt{4\pi}}$	$\Psi_{2s} = \Psi_{200} = \frac{1}{4\sqrt{2\pi}}\ (2-r)e^{-r/2}$
n =2, l =1, m= +1	$R_{21} = \frac{1}{2\sqrt{6}}\ r\ e^{-r/2}$	$Y_{1\ +1} = \sqrt{\frac{3}{4\pi}}\,sin\theta\ cos\varphi$	$\Psi_{2px} = \Psi_{21+1}$ $= \frac{1}{4\sqrt{2\pi}} re^{-r/2}\ sin\theta\ cos\varphi$
n =2, l =1, m= -1	$R_{21} = \frac{1}{2\sqrt{6}}\ r\ e^{-r/2}$	$Y_{1\ -1} = \sqrt{\frac{3}{4\pi}}\,sin\theta\ sin\varphi$	$\Psi_{2py} = \Psi_{21-1}$ $= \frac{1}{4\sqrt{2\pi}}\ re^{-r/2}\ sin\theta\ sin\varphi$
n =2, l =1, m= 0	$R_{21} = \frac{1}{2\sqrt{6}}\ r\ e^{-r/2}$	$Y_{10} = \sqrt{\frac{3}{4\pi}}\ cos\ \theta$	$\Psi_{2pz} = \Psi_{210} = \frac{1}{4\sqrt{2\pi}}\ r\ e^{-r/2}\ cos\ \theta$

7. Wave Function and Orbital Shapes

The wave function Ψ(r,θ,φ) of hydrogen atom is known as atomic orbitals. Atomic orbital is a wave function that explains the behavior of an electron in atom or region of space. Orbital of different systems varies only with nuclear charge Z. The probability of finding an electron in atom is described by Ψ^2 (square of wave function of atomic orbital).

Orbital Shapes

Each orbital is represented by a number and a letter where the number (1, 2, 3, …) indicates the energy level of the electron in the atom and letter (*s, p, d, f*) denotes the shape of the orbital. From the solution of Schrodinger wave equation, diagrammatic representation of shapes of atomic orbitals is drawn using the boundary surface diagrams. A boundary surface diagram is a boundary surface for an orbital represented in a space where the value of probability density Ψ^2 is a constant.

1. s-orbital

Boundary surface diagram of *s*-orbital is spherical with nucleus at the center. All the *s*-orbitals 1*s*, 2*s*, 3*s*,… are spherically symmetrical but their size and energy increases with increase in principal quantum number (n) values (1*s* < 2*s* < 3*s*…..).

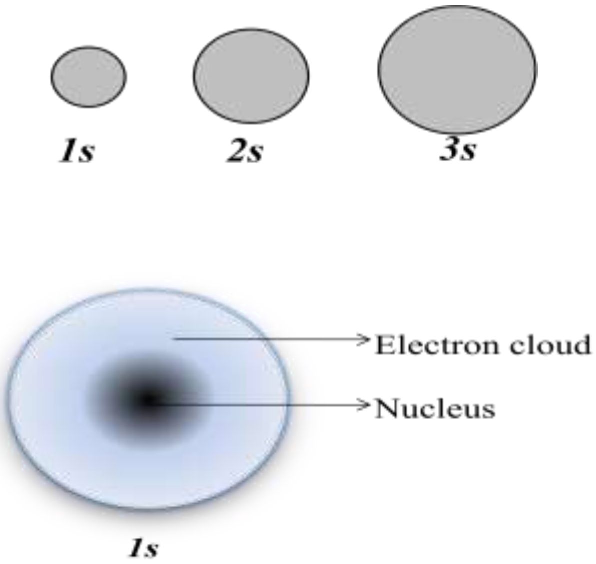
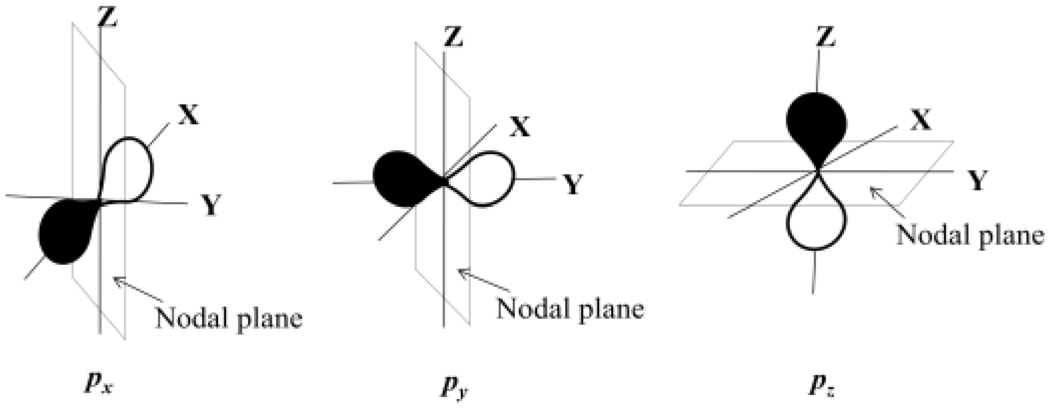


Fig 11: Boundary surface diagram of *s*-orbital

2. p-orbital

Boundary surface diagram of *p*-orbital show two lobes on either side of plane passing through the center of the nucleus called nodal plane that bisects the two lobes. Unlike *s*-orbital, the *p*-orbital has three orientations that are designated as p_x, p_y and p_z which lie on x, y, z axes which are mutually perpendicular to each other. These three *p*-orbitals have same energy, size and shape. The size and energy of the *p*-orbital increase with increase in n values ($2p < 3p < 4p$…).



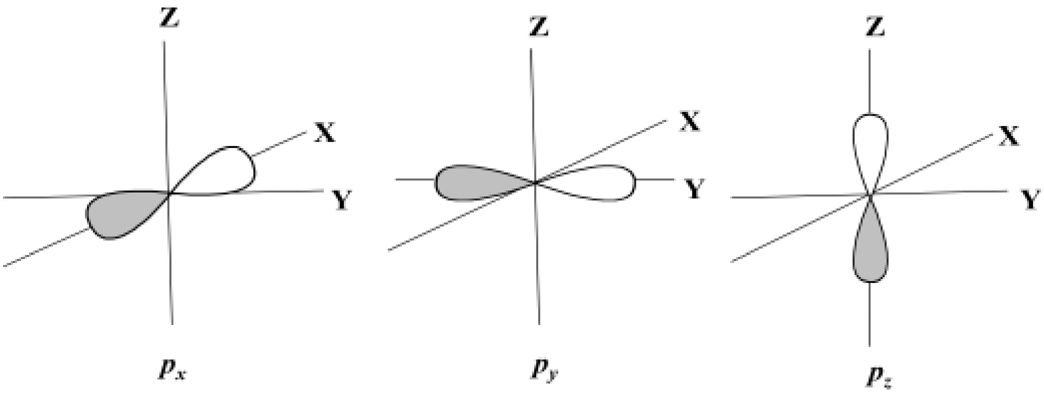
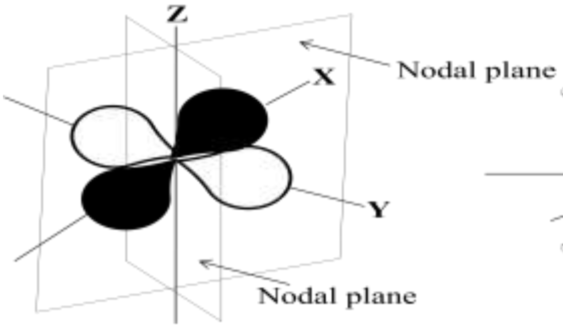


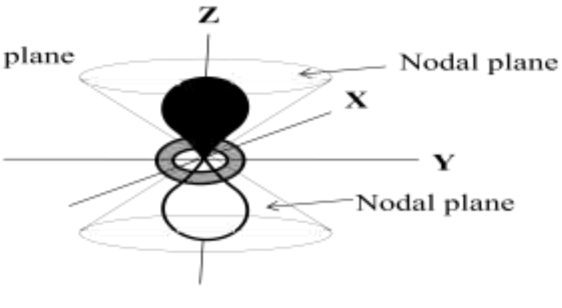
Fig 12: Nodal planes and Boundary surface diagram of p- orbitals

3. d-orbital

Boundary surface diagram of four of the five *d*-orbitals (d_{xz}, d_{yz}, d_{xy}, $d_{x^2-y^2}$) consists of four lobes arranged in a plane which is intersected by two perpendicular nodal planes. The fifth *d*-orbital d_{z^2} show two lobes in z-axis and a doughtnut of electron density in the xy plane. However the energy of all five *d*-orbitals is same. The size and energy of *d*-orbital increases with increase in n values (3*d* < 4*d* < 5*d*…).



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



d_{z^2}

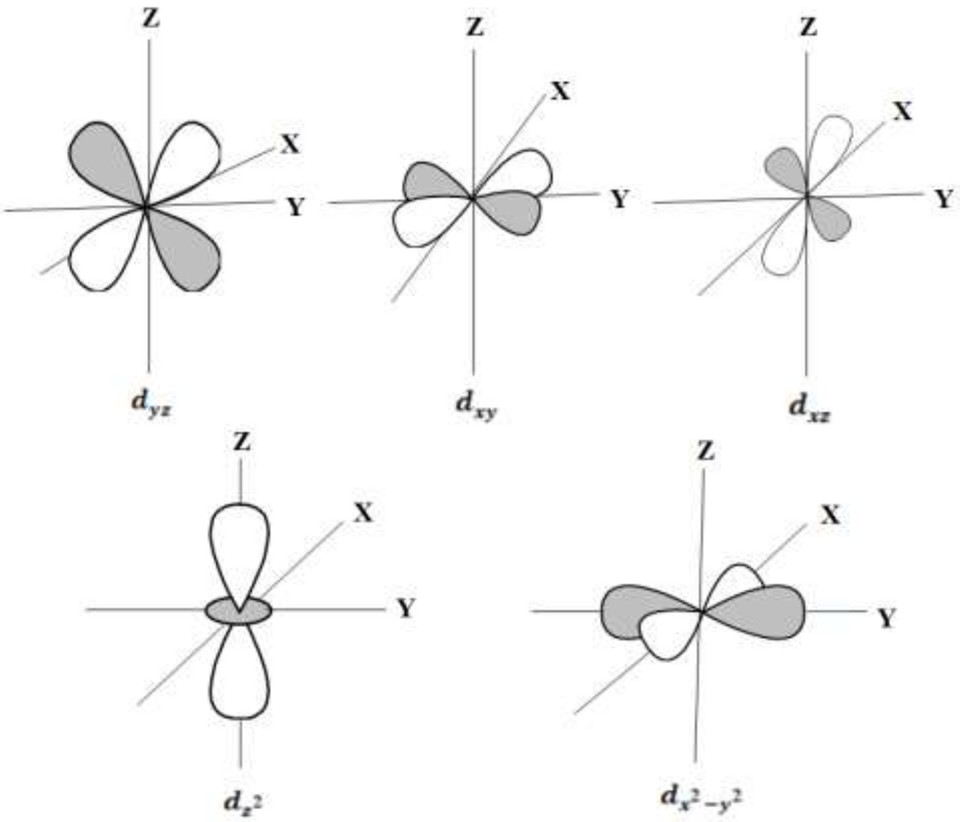


Fig 13: Nodal planes and Boundary surface diagram of *d*-orbitals

4. f-orbital

When $n = 4$ and $l = 3$, the subshell consists of seven f-orbitals. The boundary surface diagrams show that each f-orbital has three nodal surfaces and thus their shapes are complex and difficult to represent by simple diagram.

8. Theory of Bond Formation

Two theories which explain the bond formation are

1. Valence bond theory
2. Molecular orbital theory

1. Valence Bond Theory (VB Theory)

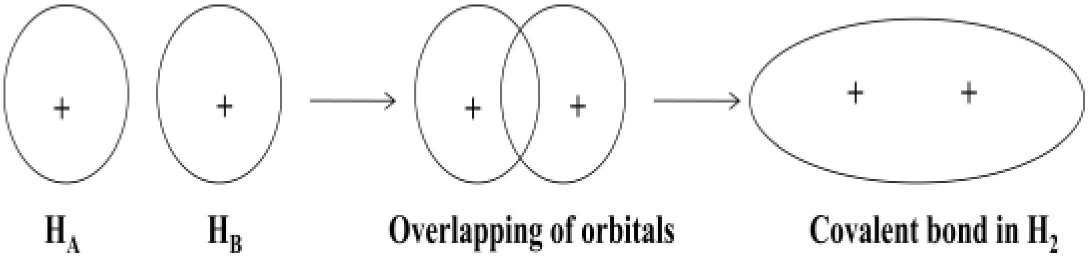
Valence bond theory explains the formation of covalent bonds in molecules based on the number of valence electrons and does not consider the other electrons in the atom. The VB theory is based on the concept of atomic orbital overlap. Atomic orbital overlap is the interaction of two atomic orbitals of two atoms followed by sharing of electrons of atoms.

Salient features of Valence bond theory

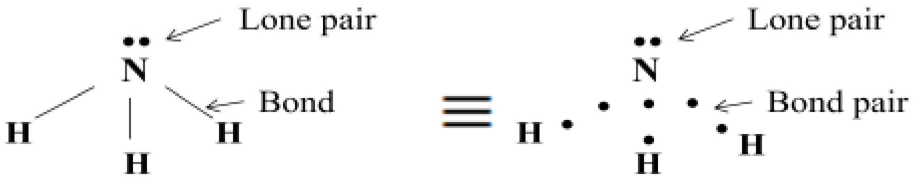
1. According to this theory covalent bonds are formed between atoms that are sufficiently closer and can overlap their atomic orbitals.
2. Covalent bond is formed by a pair of electrons shared by two atoms.
3. Lone pair of electrons does not involve in bond formation.

Formation of covalent bond in H_2 molecule

Consider two hydrogen atoms H_A and H_B which are far away from each other. Each hydrogen atom contains one electron in 1s atomic orbital. When the two hydrogen atoms come closer there is overlap of these two 1s atomic orbitals resulting in the covalent bonding. Now the electron in H_A can revolve around nuclei of H_B and vice versa. Thus after bond formation the two electrons lose their identity and cannot distinguish which electron belong to H_A and H_B. The two electrons can move into orbitals of two atoms. These electrons are equally shared between the orbitals and form a covalent bond.



- Pairing of electrons results in decrease of energy of the system
- This leads to the formation of bond between the atoms which produce a molecule
- It increases the stability of the system, thus a molecule of hydrogen is more stable than two hydrogen atoms
- The atoms involved in the bond formation attain stable electronic configuration (Noble gas configuration)
- A pair of electrons shared by two atoms creates a covalent bond
- ***Bond pair and Lone pair***
- A pair of electrons between two bonded atoms constituting the bond is known as bond pair and pair of electrons which does not involve in bonding is known as lone pair.

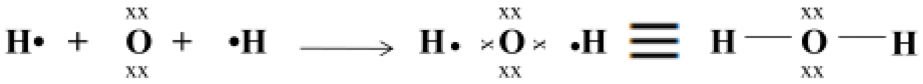


- Atom may contain non-bonding electron pair (i.e) a pair of valence electrons present on a bonded atom which does not involve in bonding. For example, NH3 contains three bond pair and one non-bonding electron pair (lone pair) and water has two bond pair and two lone pairs.

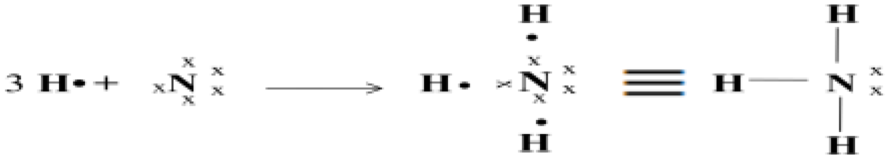
VB theory to some molecules

1. HF: In HF molecule, singly filled 1s orbital of H atom overlap with singly filled 2p orbital of F to form H – F covalent bond. The three lone pair of electrons remains as non-bonding electron pair on F atom.

2. H_2O: In H_2O molecule, O atom contains two singly filled 2p orbitals which overlap with singly filled 1s orbital of each H atom to form two O – H bonds. Two lone pair of electrons is present as non-bonding electron pair on O atom.



3. NH_3: In NH_3 molecule, N atom contains three singly filled 2p orbitals which overlap with singly filled 1s orbital of each H atom to form three N – H bonds. One lone pair of electrons is present as non-bonding electron pair on N atom.



Types of orbital overlap

Depending on the types of atomic orbital involve in bonding, different types of bonds are possible.

1. σ bond: A covalent bond formed by end-to-end or head-to-head overlap of atomic orbitals of two atoms such as overlap of s – s, s – p_x p_x – p_x atomic orbitals is called a σ bond.

2. π bond: when p orbitals of two atoms approach along and have a lateral overlap such as overlap of p_z – p_z or p_y – p_y atomic orbitals is called a π bond.

Success of VB theory

1. It successfully explains the covalent bond formation in molecules by using concept of atomic orbital overlap.
2. According to this theory electron pairing results in decrease of energy of the system which contributes to stability of the system.
3. It also explains the geometries of many covalent molecules.
4. It clearly depicts the strength of σ bond and π bond.
5. Application of VB theory has lead to development of stereochemistry of carbon compounds.

Limitations of VB theory

1. This theory ignores the electrons other than the valence electrons.
2. It does not explain the partial ionic character of bonds.
3. It does not explain the bond formation in complex multi-atom molecules.
4. It cannot account for coordinate bond in which one atom donates both the electrons required for bond formation.
5. It does not explain the bond formation in molecules like H_2^+ and He_2^+ which involves sharing of single electron.

2. Linear Combination of Atomic Orbitals–Molecular Orbitals (LCAO-MO)

In the VB theory even after the formation of the molecule, the atomic orbitals remain as such and retain their identity with respect to their atoms.

In the MO theory, after the formation of the molecule, the valence electrons lose their identity and they no longer belong to individual atoms but belong to molecule as a whole.

Salient features of Molecular Orbital theory

1. According to MO theory the atomic orbitals (AO) of the atoms combine to form new orbitals known as molecular orbitals (MO).
2. Molecular orbitals are described by wave functions based on quantum chemistry.
3. Overlapping of two AO results in formation of two MO (i.e) one bonding MO and one antibonding MO.

Wave function

1. Every atom can possess full set of s,p,d,f orbitals but not all of them will have electrons
2. The space where there is more probability of finding electrons is called atomic orbital.
3. The representation of AO is called electron probability density diagram which show the most probable distribution of electron cloud around the nuclei.
4. Each AO is described by a wave function.
5. For example wave function of 1s and 2p orbital is shown below where r is the distance between electron and nucleus.

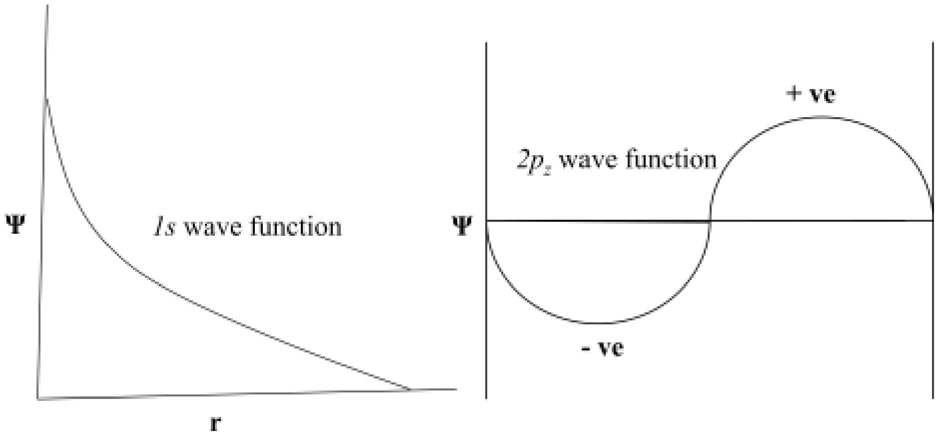


Fig 14: wave function of *1s* orbital and *2p* orbital

- The wave function of the 1s orbital is always positive sign (above the reference axis)
- The wave function of 2p orbital is sometimes positive sign (above the axis) and sometimes negative (below the axis). Thus changes sign from positive to negative.
- The above fact is represented as electron probability density diagram (AO) with + or – sign. These two sign indicates the relative probabilities and – sign does not show that the probability is negative.

- The probability density diagram describes the shape of the atomic orbital. Shapes of 1s orbital and 2pz orbital are shown below.

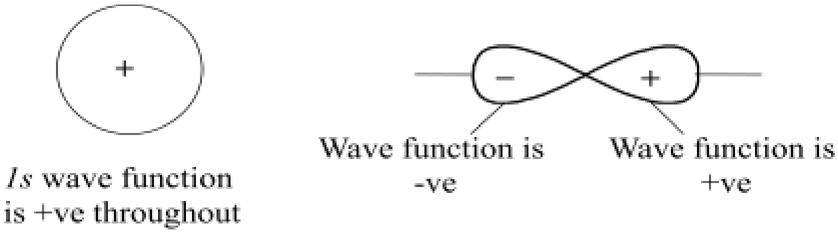
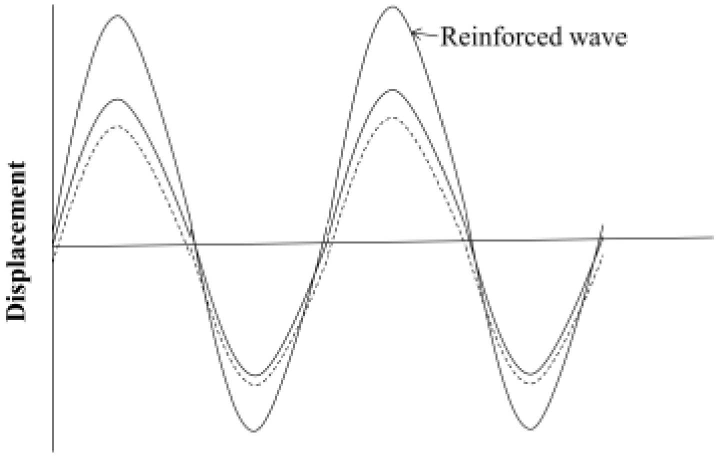


Fig 15: Probability density diagram of 1s orbital and 2p orbital

Combination of wave function: Bonding and Antibonding molecular orbitals

Two waves can overlap in two different ways to form bonding molecular orbital or antibonding molecular orbital. The overlap of the positive part of one AO with positive part of another AO and negative part of one AO with negative part of another AO reinforces and produce a larger wave known as bonding molecular orbital. Similarly the overlap of the positive of one AO with the negative part of another AO results in destruction of wave and produces an antibonding molecular orbital.



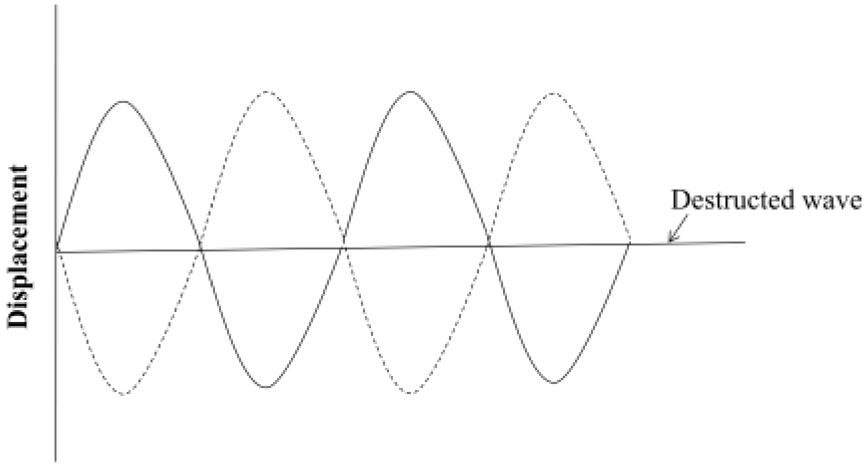


Fig 16: Formation of bonding and antibonding molecular orbital by reinforcement and destruction of two AO waves

9. LCAO – MO of H_2

Molecular orbital is described by wave function similar to atomic orbital. The wave function of MO is obtained by Linear combination of atomic orbitals method. This concept can be explained by considering hydrogen molecule H_2. Hydrogen molecule has two hydrogen atoms H_A and H_B whose atomic orbitals are described by wave function φ_A and φ_B. These two atomic orbitals overlap (i.e) $\varphi_A \pm \varphi_B$ and produce a new wave function known as molecular orbital. Such algebraic sum of functions is called as linear combination. The two normalized LCAO wave functions are

$$\Psi_b = N_b\,(\varphi_A + \varphi_B) \qquad \ldots\ldots 1$$

$$\Psi_a = N_a\,(\varphi_A - \varphi_B) \qquad \ldots\ldots 2$$

where Ψ_b and Ψ_a are wave function, N_b and N_a are Normalization constant of bonding and antibonding molecular orbitals respectively. The numerical value of N_b and N_a was calculated to be 0.71 ($\sim\sqrt{1/2}$). The energy of LCAO-MO's Ψ_b and Ψ_a is represented as E_b and E_a and is given as

$$E_b = \frac{\int \Psi_b\,\hat{H}\,\Psi_b\,d\tau}{\int \Psi_b\,\Psi_b\,d\tau} = \frac{N_b^2 \int (\varphi_A + \varphi_B)\,\hat{H}\,(\varphi_A + \varphi_B)d\tau}{1} \qquad \ldots\ldots 3$$

$$E_b = N_b^2 \int \varphi_A\,\hat{H}\,\varphi_A\,d\tau + \int \varphi_A\,\hat{H}\,\varphi_B\,d\tau + \int \varphi_B\,\hat{H}\,\varphi_A\,d\tau + \int \varphi_B\,\hat{H}\,\varphi_B\,d\tau \ldots.4$$

where Ĥ is the Hamiltonian operator (total energy operator). Substituting the integrals with symbols

$$Q_A = \int \varphi_A \, \hat{H} \, \varphi_A \, d\tau \qquad \text{.....5}$$

$$Q_B = \int \varphi_B \, \hat{H} \, \varphi_B \, d\tau \qquad \text{.....6}$$

$$\beta = \int \varphi_A \, \hat{H} \, \varphi_B \, d\tau = \int \varphi_B \, \hat{H} \, \varphi_A \, d\tau \qquad \text{.....7}$$

Since both the atoms A and B are H atom, $Q_A = Q_B = Q$ and the energy equation 4 becomes

$$E_b = 2N_b^2(Q + \beta) \qquad \text{.....8}$$

Similarly

$$E_a = 2N_a^2(Q - \beta) \qquad \text{.....9}$$

Here integral Q represents the energy of an electron in the orbital φ_A or φ_B that is equal to the ground state energy of hydrogen atom. The integral β represents the energy of interaction between the orbitals φ_A and φ_B. It is called exchange integral and is inherently negative. Thus an electron occupying bonding MO, Ψ_b is more stable and an electron in Ψ_a is less stable than electron in in a pure atomic orbital, φ_A or φ_B. The actual energy of stabilization and destabilization is obtained by substituting Normalization constant N_a and N_b ($N_a = N_b = \sqrt{½}$) in equation 8 and 9.

$$E_b = (Q + \beta) \qquad \text{.....10}$$

$$E_a = (Q - \beta) \qquad \text{.....11}$$

This is depicted in the energy level diagram as

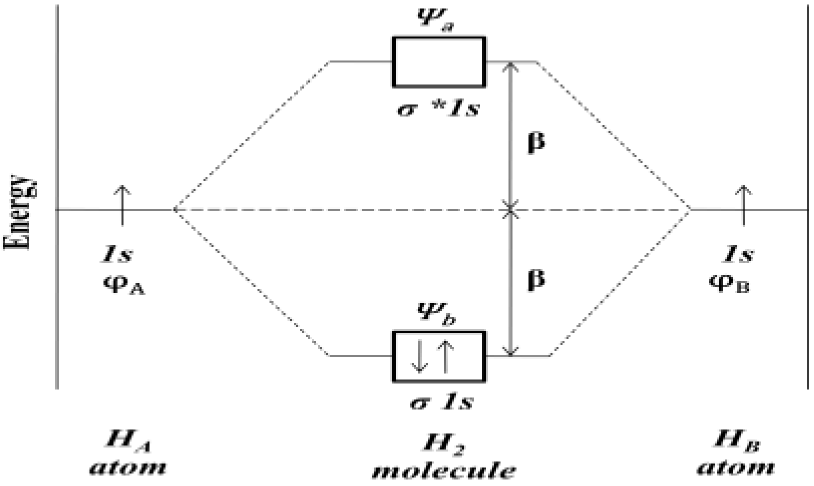


Fig 17: Energy level diagram for formation of bonding and antibonding MO of H_2 molecule

As the bonding and antibonding orbitals are formed when the AO overlap, energy changes occur. The formation of the bonding MO (Ψ_b) decreases the energy and that of antibonding MO (Ψ_a) increases the energy.

- The energy of the bonding MO is lower than that of antibonding MO.
- The energy difference between AO and bonding MO is called stabilization energy and it is denoted as β.
- The energy difference between AO and bonding MO is denoted as β.
- Each MO can accommodate two electrons with opposite spins similar to AO.
- The energy of each electron is decreased by β and hence the total reduction in energy of the system is 2β. This denotes the bond energy.
- This reduction in energy is the driving force for bond formation.
- When two AO of H atoms combine, it forms lower energy bonding MO which is designated as *σ 1s* and higher energy antibonding MO which is designated as *σ* 1s.*
- The two electrons each from AO of H atom occupy the lower energy bonding MO with opposite spins.
- In homonuclear diatomic molecule such as H_2 molecule, each H atom has an electron and they occupy the lower energy MO σ1s. Hence the MO configuration for H_2 is $\sigma 1s^2$.

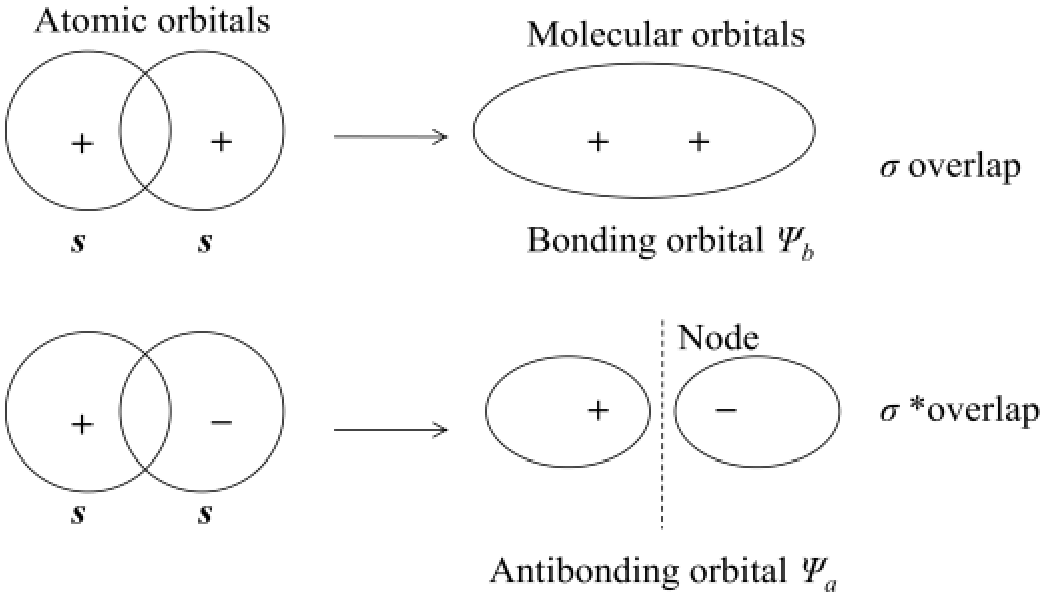


Fig 18: Combination of *s – s* atomic orbitals to form bonding and antibonding molecular orbitals

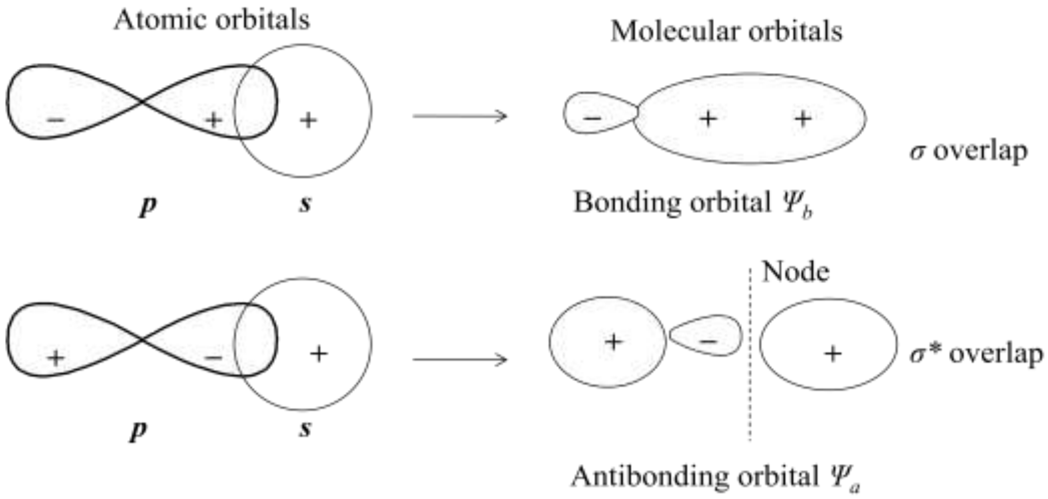


Fig 19: Combination of *s* – *p* atomic orbitals to form bonding and antibonding molecular orbitals

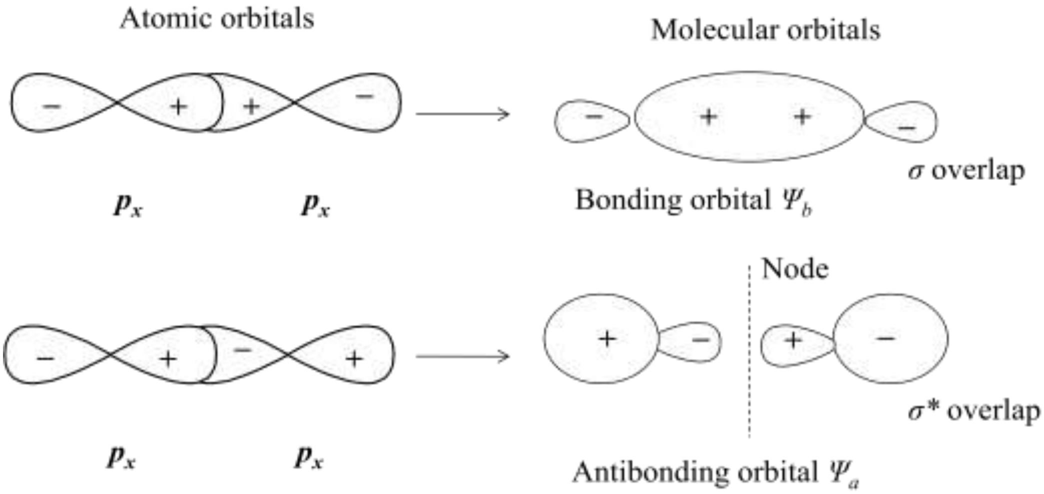


Fig 20: Combination of p_x – p_x atomic orbitals to form bonding and antibonding molecular orbitals

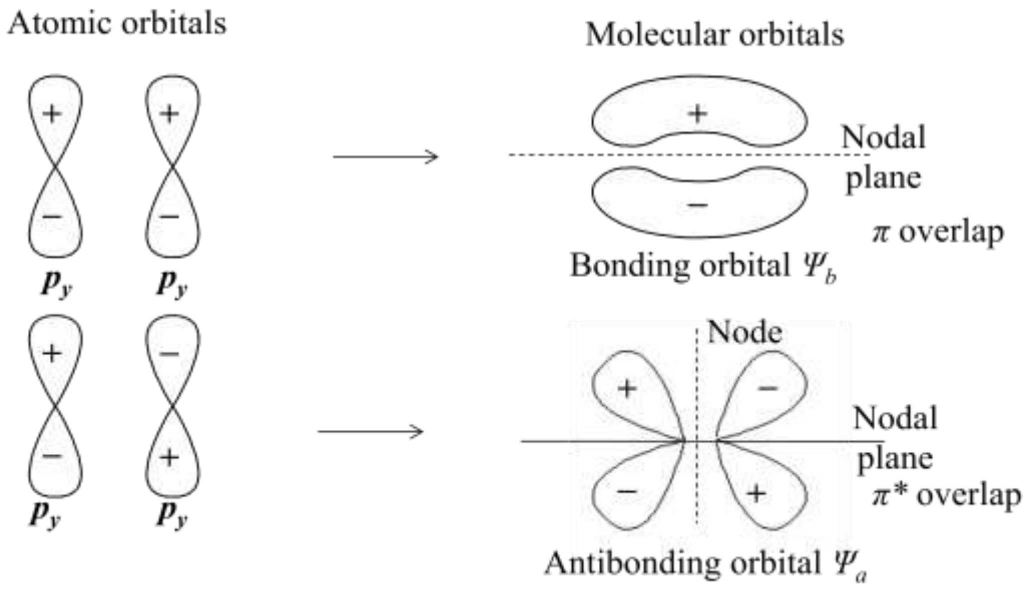


Fig 21: Combination of p_y– p_y atomic orbitals to form bonding and antibonding molecular orbitals

10. Band Theory

Band theory is a quantum model which gives an insight about the possible energies of electrons in the solids in order to understand the electrical and optical properties of solids. It is the molecular orbital theory of covalent bands extended to solids. A single atom has discrete energy states or energy levels of electrons, however in the case of assembly of atoms, situation is somewhat different. Like when two atoms come closer, their atomic orbitals get overlapped to form new orbits called molecular orbitals (bonding and antibonding).When large number of atoms are in close association as in case of solids, the discrete nature of energy levels of atoms vanishes and there are formation of large number of energy levels having close energy differences, which in the other sense can be called a band of energy levels or energy bands.

In order to understand band theory of solids, let us imagine the construction of lithium metal by adding Li-atoms one at a time, forming Li^2 then Li^3, Li^4, Li^5 and so on, until we have Li^N, where N is a very large number of the order of 10^{20}.

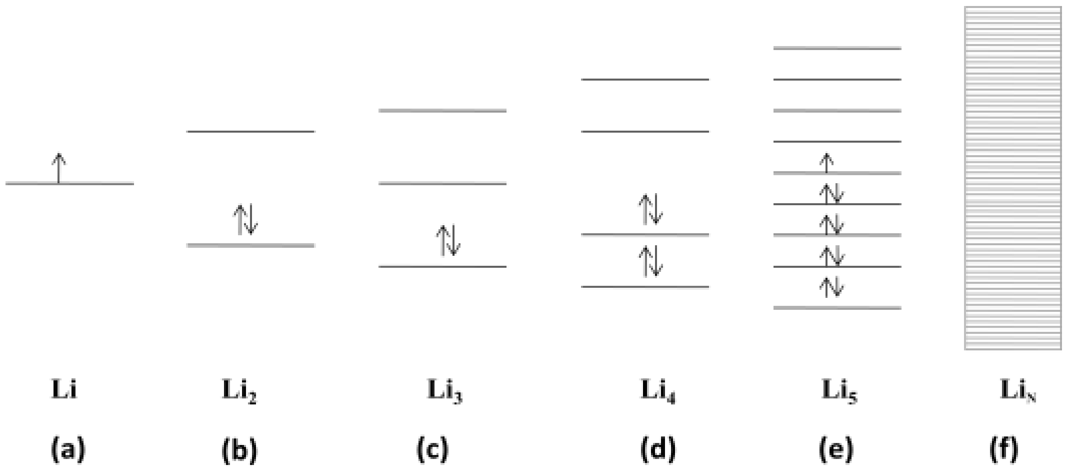


Illustration of band theory: (a) single Li-atom with one 2s-valence electron, (b) Li_2 with two M.O., one filled and one vacant, (c) Li_3 with three M.O., (d) Li_4 with four M.O., (e) Li_9 with nine M.O., half-filled, (f) LiN with a band of N M.O.

Electrons in the solids having allowed energies belong to the allowed energy bands. The allowed energy bands can be separated by forbidden band to which the electron energy in the solid does not belong. The allowed energy bands are of two types called valence band and conduction band. In a solid valence band and conduction band can be separated by a forbidden band as incase of semiconductors and insulators. Hence the solids have three types of energy bands which are valence band, forbidden band and conduction band.

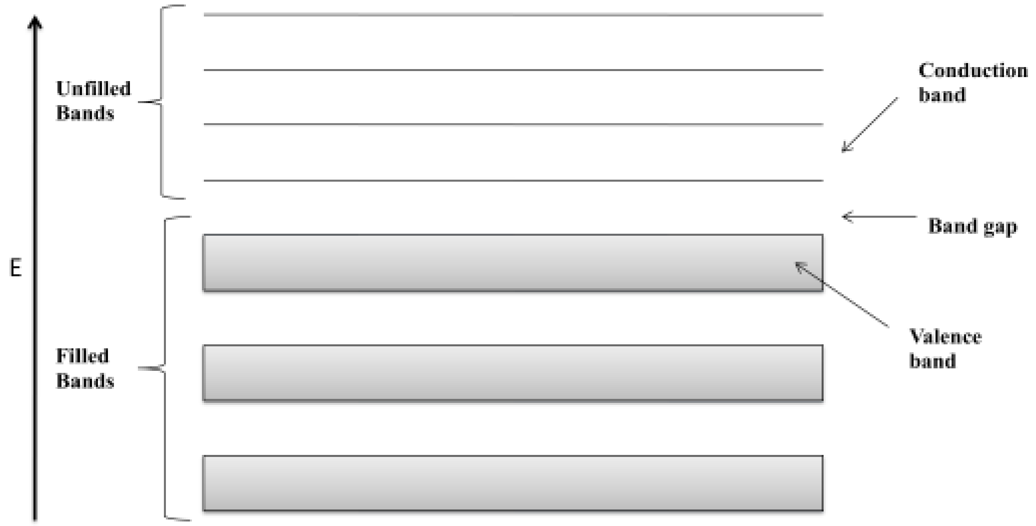


Fig 22: Energy bands in solids

Salient features of band theory:

Solids are made up of giant molecules, in which a very large number of spherical atoms are arranged in a regular close-packed pattern in the form of crystals.

When the atoms are brought together in solids, the atomic orbitals of the valence shells ‘interact’ forming molecular orbitals. During interaction between these atoms, they influence each other and constitue one single system of electrons while the inner shells remain intact and are not affected.

The individual energies within an energy band are so-close together and considered to be continuous. Consequently, an electron in a solid crystal can occupy any of these large number of energy level, within the band. Thus, a **band** is a *group of infinitesimally energy levels in a solid/crystal*.

Depending upon the composition of a solid/crystal, the bands are of three types.

1. Valence band:

Valence band is the band of energy levels occupied by the valence electrons. It is lowest in energy among three types of bands. Valence band is generally fully filled in insulators, however incase of conductors valence band is partially filled by electrons. This band is below the forbidden band and valence electrons are present in this band. In conductors valence electrons are free to move in this band and are easily transferred into the conduction band without giving any external energy.

2. Conduction band:

The next permitted band, above the valence band, is called the conduction band and the electrons occupying this band are called conduction electrons. It is the band of orbitals in which electrons are present which have been jumped from the valence band. It is higher in energy than the valence band and forbidden band. Electrons in this band have enough energy to move freely and if some external force is applied in the form potential difference across the ends of solid, electrons flow in a particular direction which we called the flow of charge or electric current. This band is responsible for the conduction of electricity.

3. Forbidden band:

Electrons are not present in this band. Conductors do not have this band. Insulators have stronger forbidden band and is wider. The solid acts as a conductor when the valence electrons are transferred into conduction band. This band restricts the electrons to move into

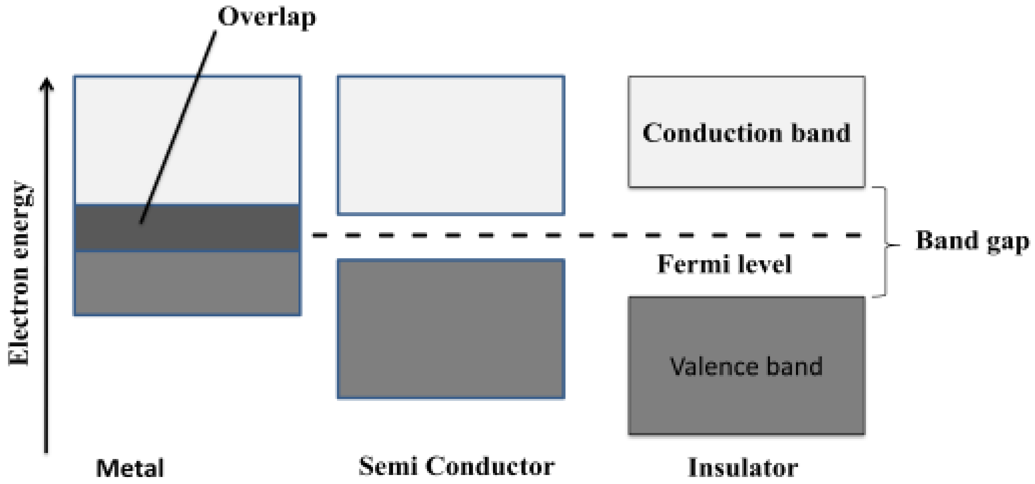


Fig 23: Valence, conduction and forbidden (band gap) in solids

conduction band. Being stronger and wider in solids, electrons cannot be transferred into conduction band, so they are bad conductors of electricity.

On the basis of presence of forbidden band gap energy and band gap size, solids can be distinguished into three types namely conductors, insulators and semi-conductors.

A. Conductors:

In conductors there is zero band gap energy. Valence band and conduction band are overlapped. So the electrons in the valence band can easily move into conduction band. Presence of large number of free electrons in the conduction band results in the flow of electric current. Metals have zero band gap energy. So the electrons in the valence band are free to move into the conduction band without gaining any additional energy and hence they are good conductors of electricity.

B. Insulators:

Insulators have large band gap energy and band gap size .It is difficult for an electron from a valence band to gain energy and move into conduction band. Absence of free electrons in the conduction band of insulators restricts the flow of electric current in insulators. So the insulators are poor conductors of electricity. The conductivity of semiconductors is 24 orders of magnitude less than conductors.

C. Semiconductors:

Semiconductors have small band gap energy and band gap width. The band gap in semiconductors is approximately 1 eV and it is possible for an electron in the conduction band to gain this small amount of energy and enter into conduction band to have some conductivity. Conductivity of semiconductors is between that of insulators and conductors which is about 4-16 orders of magnitude less than conductors. It is further possible for the semiconductors to decrease or tailor this band gap energy, which find its useful applications in electronics and photoelectronics. Semiconductors are being used in the electronic devices such as radios, computers, mobile phones, televisions, automobiles, amplifiers. Semiconductors are being used in the formation of integrated circuits, transistors, diodes, photovoltaic cells etc.

Examples of semiconductors include silicon, germanium, antimony, boron, tellurium, selenium etc.

Type of semiconductors

Semiconductors are classified into two types as:

***i. Intrinsic semiconductors*.**

Intrinsic semiconductors are extremely pure (above 99.9999% pure) elements like silicon, germanium and selenium, having four valence electrons in their atoms and their forbidden gap energy is about 1 eV. These metals have crystalline structures, in which each atom forms four covalent bonds by sharing with four neighbouring atoms. In such semiconductors, the energy gap is so small (about 1 eV) that even at ordinary temperature, there are many valence electrons, which possess sufficient energy to jump across the forbidden gap to conduction band. Intrinsic semiconductors are also called undoped semiconductors.

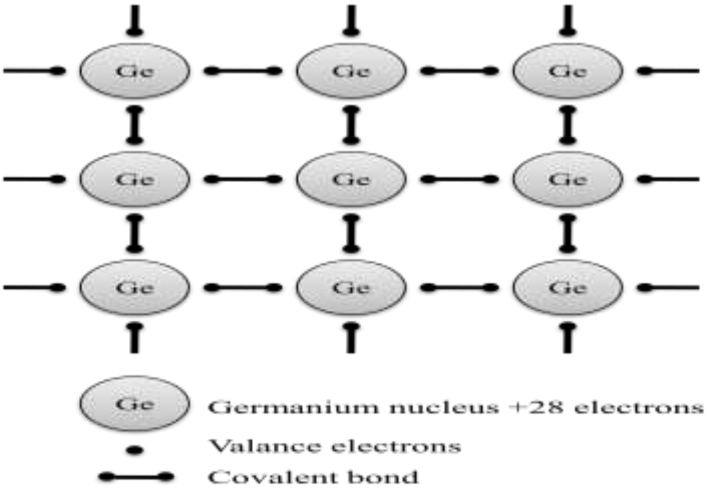


Fig 24: Intrinsic semiconductor

ii. Extrinsic semiconductors.

Extrinsic semiconductor are basically intrinsic semiconductors, whose conducting properties have been improved by adding extremely small amounts of specific substitutional impurities called doping agent or dopants. The addition of doping agent reduces the energy gap (Eg), thereby allowing more electrons to flow from valence band to the empty conduction band. Usually, 1 part of doping agent is added to 106 parts of parent element (Si, Ge, etc.). By appropriate doping, the conductivity of an intrinsic semiconductor may be increased by 10,000 times. Dopants added to the extrinsic semiconductor gives desired electrical and optical properties to the semiconductor.

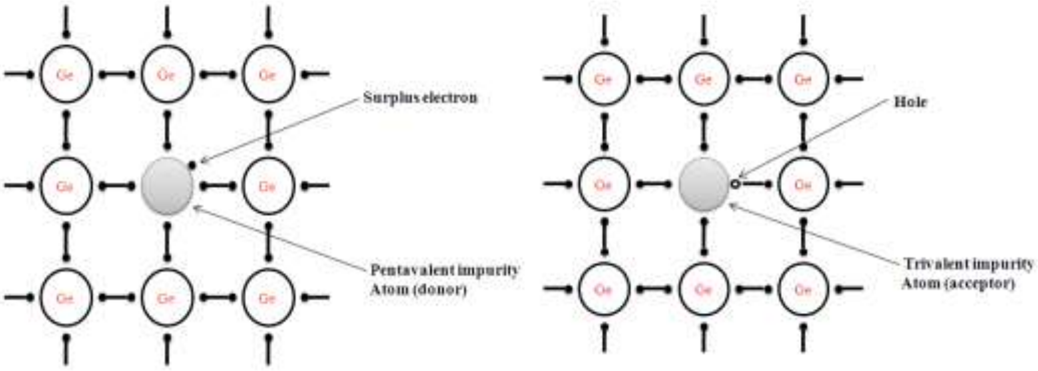


Fig 25: Extrinsic semiconductor

Based on the nature of the doping agent added, the extrinsic semiconductors are of following two classes:

Doping

Doping is a process of adding an impurity to the semiconductor in order to modulate the properties and obtain the desired electrical, optical and structural properties of the semiconductor. The impurity added to the semiconductor is called dopant. Dopants are of two types which include n-type and p-type dopants. Generally doping is done to increase the conductivity of semiconductors. Doping increases the charge carriers that results in the increased electrical conductivity of semiconductor. Higher the increase in the number of charge carriers in the semiconductor higher is its electrical conductivity. Doping atoms occupy the lattice positions of the semiconductor. They increase the number of charge carriers of the semiconductor in the form of electrons and holes. Electrons are negatively charged but the holes attain the positive charge. Generally group III and group V elements of periodic table are extensively used as dopants.

Types of Extrinsic semiconductor:

1. n-type semiconductor :

It is an excess negatively charged electrons containing semiconductor and obtained by adding extremely small quantitye of a pentavalent element impurity like phosphorus, arsenic or antimony to pure intrinsic semiconductor crystal lattice like silicon, germanium, tellurium etc.

Conduction Process: The doping atom forms four covalent bonds with the surrounding four Si atoms of intrinsic semiconductor with the help of four of its five valence electrons, while the fifth excess electron remains loosely bound to the donor atom. This loosely bound excess electron is easily excited from the valence band to the conduction band, when an electric field is applied. Thus, conduction is due to movement of excess electrons present in an n-type semiconductor. In other words, the electrical conductivity of an n-type semiconductor is dependent only on the number of free or excess electrons present in the conduction band. This results in the increase of negatively charged electrons and hence n-type semiconductor is formed. Here n stands for negative charge or sign. Increase of charge carriers in the form of negatively charged electrons increases the electrical conductivity of semiconductor.

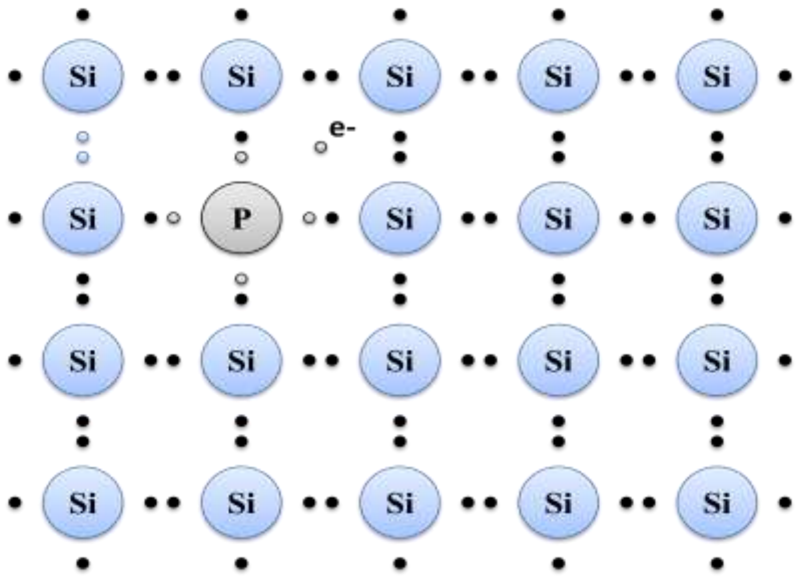


Fig 26: n-type semiconductor

2. p-type semiconductor :

It is an excess positively charged holes-containing semiconductor and is obtained by adding an extremely small quantity of trivalent element like boron, aluminum to the pure intrinsic semiconductor crystal lattice like silicon, germanium, etc.

Conduction process: All the three valence electrons present in the trivalent doping agent (an acceptor atom) form three covalent bonds with the surrounding three of the four atoms, thereby one bond in one of the four surrounding Ge atoms is left incomplete. This gives rise to a positive hole. The positive holes so formed in the crystal lattice conduct current, when electric field is applied. During this type of conduction process, a hole travels to an adjacent atom by acquiring an electron and re-establishing a new covalent bond, by breaking an existing covalent bond in the adjacent atom and creating a new hole of it. In this way, holes are filled by electrons from one atom to another and creating new holes in sequence in the crystal lattice. The movement of holes through the crystal of a p-type extrinsic semiconductor is nothing but movement of a positive electric charge. Holes carry the current by accepting electrons and move in the opposite direction to that of electrons during the flow of electric current. Thus, in such a semiconductor, the positively charged holes are in excess and the only charge-carriers during conduction.

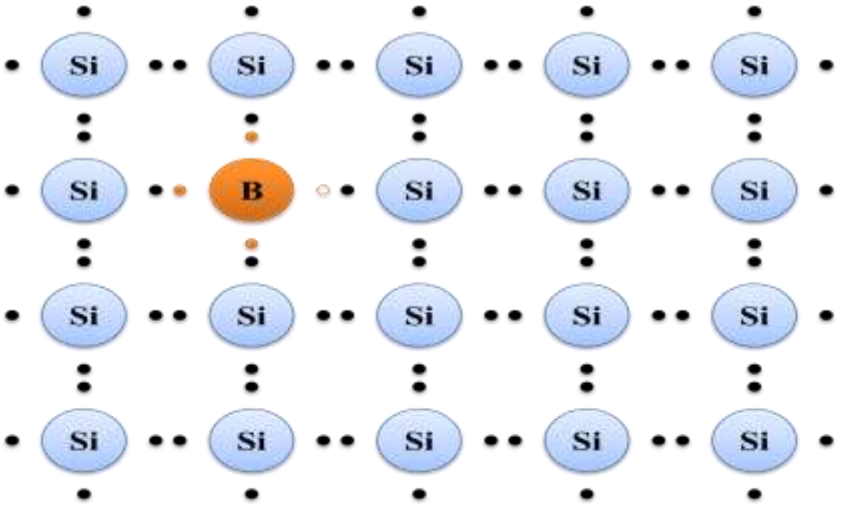


Fig 27: p-type semiconductor

Role of Arsenic doping on Silicon:

Arsenic is a V group element or pentavalent.It is doped with silicon semiconductor to form n-type semiconductor. Arsenic atom enters into lattice position of silicon atom and bonds covalently with four silicon atoms. The fifth electron of arsenic is free to move in the semiconductor which results in the increase of charge carriers and hence conductivity of semiconductor. Not only with silicon, arsenic can also be doped with other semiconductors.

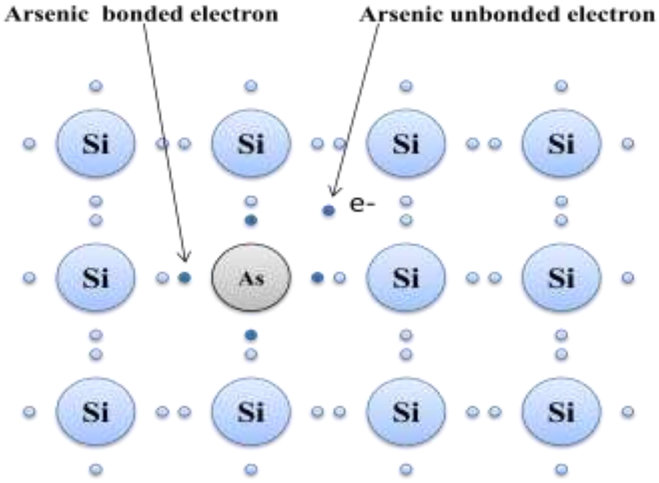


Fig 28: Doping of arsenic with silicon

Role of Gallium doping on Silicon:

Gallium belongs to third group of periodic table. It is trivalent element. It can be doped with silicon to form p-type semiconductor. It has only three valence electrons in its outer most shell. In the lattice structure, it is surrounded by four silicon atoms and hence creating electron deficient sites called holes. These holes are ready to accept the electrons and increase the electrical conductivity of semiconductor. Germanium can also be doped with gallium to form p-type semiconductor.

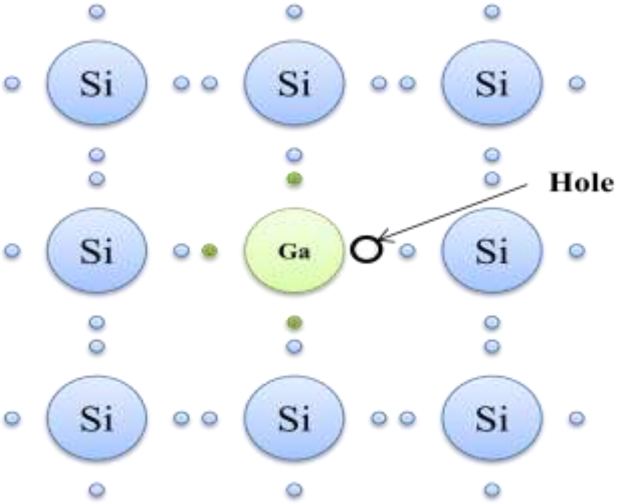


Fig 29: Doping of gallium with silicon

11. Superconductors

Ordinary metals conduct electricity and their specific conductivity is around 106 ohm-1cm-1. It has been found that for a number of metals and alloys, the electrical resistance disappears abruptly and completely at temperatures, a few degrees above absolute zero. Low temperature research has led to the discovery of an amazing phenomenon of superconductivity.

Superconductors are materials ***which conduct electricity without any electrical resistance***. The maximum temperature in which a superconducting material exhibits superconductivity, is called its critical temperature (T_c). Materials in superconducting state become diamagnetic and are repelled by magnets. The phenomenon of superconductivity was first observed by Heiki Kammerlingh Onnes, a Dutch physicist in 1913 and found that mercury became superconducting at 4K (at boiling point of liquid helium). This astonishing work earned him the 1973 Nobel Prize in physics. Thereafter in 1986 scientists Karl Muller and Johannes Bednorz developed superconductors by cooling oxide of copper, lanthanum and barium to 40 degrees Kelvin, greater than zero degree Kelvin as was thought to be required for the material to be a superconductor. Decades after, superconductors have been developed at 164 degrees Kelvin under high pressure.

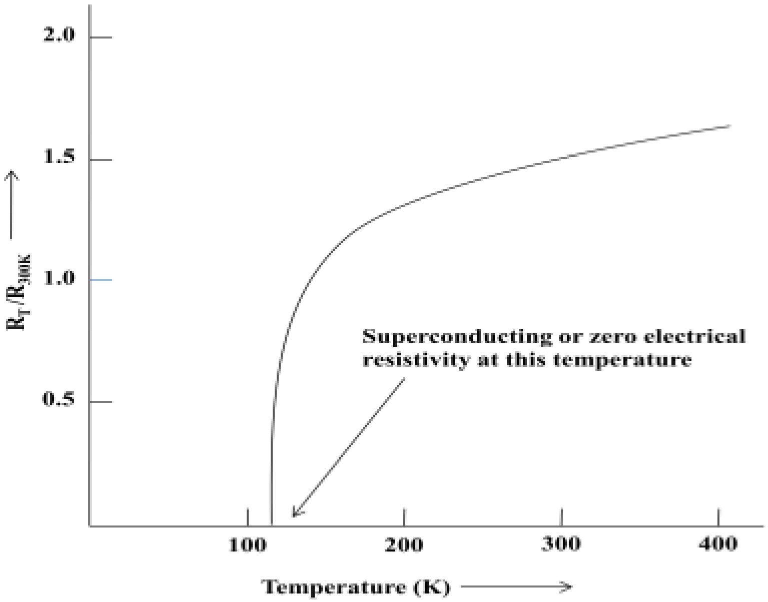


Fig 30: Electrical resistivity on going to zero absolute in a superconducting material.

Properties of superconductors:

1. They posses greater resistivity than other elements at room temperature.
2. The transition temperature for different isotopes of a superconductive element decreases with the atomic mass of the isotope.
3. On adding impurity to a superconducting element, the critical temperature is lowered.
4. During transition, neither thermal expansion nor elastic properties change.
5. In superconducting state, all electromagnetic effects disappear.
6. When a low magnetic field is applied to a superconductor and this if cooled to low temperature below its transition temperature, then the superconductor expels all magnetic flux. This is known as **Meissner** effect.

High temperature superconductors:

In 1986, George Bednorz and Alexmuller found that an oxide of La, Ba and Cu lost its reisitance around 35k. In 1987, Paul Chu and Wu Jr reported that a ceramic compound, $YBa_2Cu_3O_{7-y}$ ($y \leq 0.5$) is superconducting upto 100K. This compound is also known as 1:2:3 compound, due to its Y:Ba:Cu stoichiometry.

Preparation of 1: 2: 3 compound:

0.750g of yttrium oxide (Y2O3), 2.622g of barium carbonate (BaCO3) and 1.1581g of cupric oxide (CuO) is taken in a mortar and grind the mixture to fine powder with the help of pestle. Then, transfe the powder to a porcelain crucible and place it in a furnace maintained at 920-930^0 C for about 10-12 hours. Allow the mixture to cool gradually in the furnace itself, when the mixture absorbs the requisite amount of oxygen from the atmosphere. When the temperature of the furnace becomes about 1000C, the crucible is taken out and cooled in air. The resulting compound is 1: 2: 3 having composition $YBa_2Cu_3O_{7-y}$ and exhibits superconductivity well above 77K. The structure of 1: 2: 3 compound is similarly like mineral perovskite ($CaTiO_3$) structure.

Applications of superconductivity:

The phenomenon of superconductivity has many applications such as:

1. Superconducting magnets capable of generating high fields with low power consumptions are being employed in scientific tests and research equipments.

2. They are also used for magnetic resonance imagind (MRI) in the medical field as a diagnostic tool.
3. It is used as a magnet for high-energy particle accelerators.
4. It is used as a memory or storage elements in computers.
5. It is used in high-speed magnetically levigated trains.
6. It is used in high-speed switching and signal transmission for computers.

Solved Problems

1. When a radiation of wavelength 500 nm strikes a metal surface, electrons are emitted from the surface of a metal. The kinetic energy for one electron emitted from the metal is 1 x 10^{-19}J. Calculate the minimum energy required to remove an electron from a metal (binding energy).

Solution:

Wavelength λ =500 nm

Incident radiation energy

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{500 \times 10^{-9}} = 3.975 \times 10^{-19} J$$

$$h\nu = \omega + \frac{1}{2} m v^2$$

The minimum energy required to remove an electron from a metal is

$$\omega = h\nu - \frac{1}{2} m v^2 = (3.975 \times 10^{-19}) - (1 \times 10^{-19}) = \ 2.975 \times 10^{-19} J$$

2. Calculate the wavelength of an electron having velocity 6 x 10^{6} ms^{-1}and mass 9.1 x 10^{-31} Kg.

Solution: The wavelength of an electron

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{6.626 \ \times 10^{-34} Js}{(9.1 \times 10^{-31}\, Kg) \times (6 \times 10^{6} ms^{-1})}$$

$$= 1.2 \times 10^{-9}\, m \; or \; 1.2\, nm$$

3. Calculate the uncertainty in position for a ball of mass 0.2 Kg moving with a speed of 10 ms^{-1}is measured at an accuracy of 1%.

Solution: The momentum of the ball is given by

$$p = mv = 0.2\,Kg \times 10ms^{-1} = 2\,Kg.ms^{-1}$$

Thus uncertainty in momentum is calculated from momentum and % of accuracy

$$\Delta p = 2 \times 0.01 = 0.02\,Kg.ms^{-1}$$

$$\Delta x = \frac{h}{\Delta p} = \frac{6.626 \times 10^{-34}Js}{0.02\,Kg.ms^{-1}} = 3.31 \times 10^{-32}m \quad \because 1\,J = 1\,Kg.m^2$$

4. Calculate the zero point energy of an electron of mass 9.1 x 10^{-31}Kg in one dimensional box of length 1Å.

Solution: The energy of electron in one dimensional box is

$$E = \frac{n^2h^2}{8mL^2} = \frac{n^2\ \times (6.626\ \times 10^{-34}Js)^2}{8 \times (9.1 \times 10^{-31}\,Kg) \times (1 \times 10^{-10}m)^2}$$

$$= n^2 \times 4.16 \times 10^{-20}Js^2$$

The zero point energy is the lowest energy level or first energy level

$$E_1 = 1^2 \times 4.18 \times 10^{-20}Js^2$$

5. Calculate the energy difference between E$_4$ and E$_3$ for an electron in a one dimensional box of length 12Å.

Solution: The energy of electron in one dimensional box is

$$E = \frac{n^2h^2}{8mL^2} = \frac{n^2\ \times (6.626\ \times 10^{-34}Js)^2}{8 \times (9.1 \times 10^{-31}\,Kg) \times (12 \times 10^{-10}m)^2} = n^2 \times 4.16 \times 10^{-20}Js^2$$

The electron in lowest energy level or first energy level

$$E_1 = 1^2 \times 4.18 \times 10^{-20}Js^2$$

$$\Delta E = E_4 - E_3 = (2n+1)E_1 = (6+1) \times 4.16 \times 10^{-20}$$

$$= 2.912 \times 10^{-20}Js^2 or\ Watt\ second$$

6. Determine the value of A in wave function of particle in one dimensional box of length L and find out the normalized wave function of it by normalization method.

Solution: The value A is determined by the normalization of wave function which is given by

$$\int_0^L \Psi^2 d\tau = \int_0^L A^2 sin^2 \frac{n\pi x}{L} dx = 1$$

$$we\ know\ that\ sin^2 x = \frac{(1 - cos\ 2x)}{2}$$

$$\int_0^L A^2 sin^2 \frac{n\pi x}{L} dx = \frac{A^2}{2} \int_0^L \left(1 - cos \frac{2n\pi x}{L}\right) dx = 1$$

$$\frac{A^2}{2} \left\{ [x]_0^L - \left[\frac{\sin 2n\pi x/L}{2n\pi/L} \right]_0^L \right\} = 1$$

$$\frac{A^2 L}{2} = 1$$

$$A = \sqrt{\frac{2}{L}}$$

Thus the normalized wave function is $\Psi = \sqrt{\frac{2}{L}}\ sin \frac{n\pi x}{L}$

QUESTIONS:

PART-A

1. What is a black body radiation?
2. Recall Rayleigh-Jean’s Law.
3. What is Planck’s law of radiation?
4. Summarize the photoelectric effect.
5. How is kinetic energy of emitted electrons related to frequency and intensity of incident light?
6. Tell de Broglie’s hypothesis.
7. Define Heisenberg’s Uncertainty principle.
8. What are the conditions for acceptable wave functions?
9. Define zero point energy for 1D box.
10. What happens to spacing of energy levels when length of one dimensional box increases?
11. Outline the wave function and energy for a particle in 1D box.
12. What is probability density?
13. List out the types of quantum numbers.
14. Define Aufbau principle.
15. Explain Pauli’s exclusion principle.

16. Define Hund’s rule.
17. Draw the structure of p-orbitals.
18. Determine the number of orbitals in d subshell.
19. Compare the bonding and antibonding molecular orbitals.
20. Explain conductors, semiconductors and insulators with a neat diagram.
21. What are super conductors? Give example.
22. Differentiate between n-type and p-type semiconductor.
23. List out the properties of superconductors.
24. List out the applications of superconductors.
25. Define Meissner effect.

PART-B

1. Elaborate the LCAO-MO method in the formation of hydrogen molecule.
2. Formulate the Schrodinger wave equation for a particle in one dimensional box and determine the wave function and energy of the particle.
3. Determine the value of A in the wave function of particle in 1D box by Normalization method.
4. Outline the time-independent Schrodinger equation of hydrogen atom using φ and θ.
5. Explain the various shapes of atomic orbitals with neat sketch.
6. Summarize the significance of four quantum numbers.
7. Explain band theory of solids with neat diagram.
8. Discuss the various types of semiconductors with suitable examples.
9. Explain the role of doping of arsenic and gallium on silicon with neat diagram.
10. Write a note on superconductor with suitable example.

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SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT-II – MOLECULAR SPECTROSCOPY – SCYA1101

1. Introduction

Spectroscopy is the branch of science dealing with the study of interaction of electromagnetic radiation with matter like atoms and molecules. The interaction of EMR with matter gives rise to two types of spectra namely atomic spectra and molecular spectra. Atomic spectrum arises from the transition of electrons from one energy level to another due to changes of energy in the atom. Molecular spectrum involves transition of electrons between rotational and vibrational energy levels in addition to electronic transition. Therefore molecular spectrum is much more complicated than the atomic spectrum. Moreover, molecular spectrum consists of bands composed of innumerable closely packed lines. Molecular Spectroscopy provides a clear image of how diatomic and polyatomic molecules interact by looking at the Frequency, Wavelength, Wave number, Energy, and molecular process also provides most useful information regarding the shape and size of molecules, the bond angles, bond lengths, strength of bonds and bond dissociation energies. Hence molecular spectroscopy is of great use in determining structure and constitution of compounds. Before taking up their systematic study, it is necessary that the students must learn about electromagnetic spectrum and molecular energy levels.

Electromagnetic Radiations (EMR)

Electromagnetic radiation is a form of energy that is produced by oscillating electric and magnetic fields, traveling through a vacuum or matter. They propagate through space along a linear path and with a constant velocity. The oscillations in the electric and magnetic fields are perpendicular to each other, and to the direction of the wave’s propagation. Figure 1 shows an example of plane-polarized electromagnetic radiation, consisting of a single oscillating electric field and a single oscillating magnetic field.

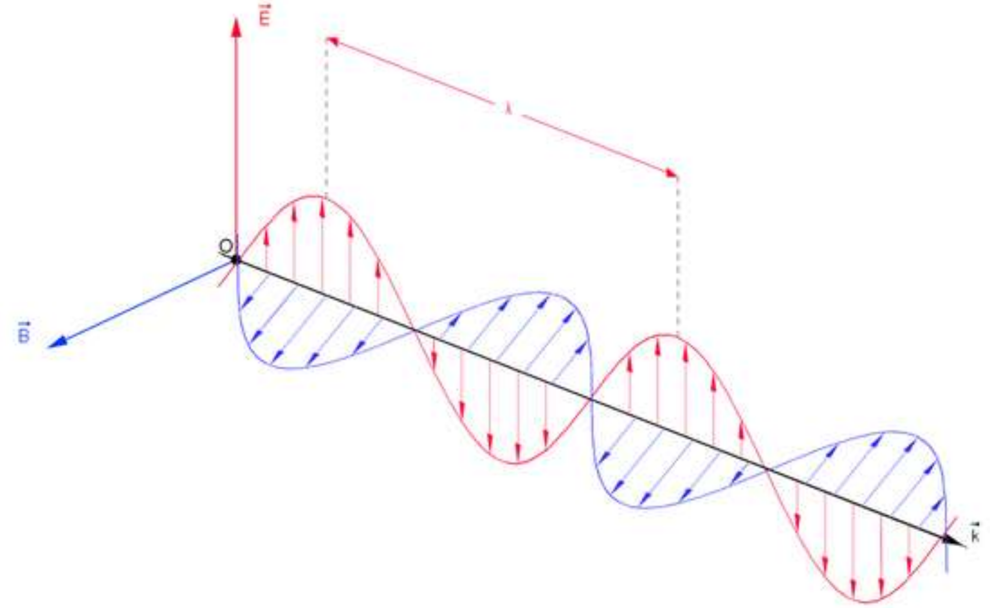


Fig 1: Electromagnetic radiation

Characterization of EMR

The electromagnetic radiations are generally characterized by wavelength (λ), frequency(ν), wave number (ῡ) and energy(E).

Wavelength (λ): The linear distance between successive crests or trough of a wave is known as wavelength. It is usually expressed in centimetre or millimetres.

Frequency (ν): The number of vibrations or oscillations per second is known as frequency. It is expressed in Hertz.

Wave number (ῡ): The reciprocal of wavelength is known as wave number. It is expressed in cm^{-1}.

Energy of EMR (E): Electromagnetic radiations consist of particles having small packets of energies called quanta or photons. Photons possess the characteristic of wave and travel with the speed of light. The amount of energy corresponding to one photon is expressed by Planck's equation as

$E = h\nu$ or $E = \frac{hc}{\lambda}$

Where h – Planck's constant ($6.62x10^{-34}$J)

ν - frequency in Hz

λ – wavelength in cm.

Unit conversion:

1 μm = 10^{-6} m

1 nm = 10^{-9} m = 10 Å

Interaction of EMR with Matter

In order to interact with the electromagnetic radiation, the molecules must have some electric or magnetic effect that could be influenced by the electric or magnetic components of the radiation.

1. In NMR spectroscopy, for example, the nuclear spins have magnetic dipoles aligned with or against a huge magnetic field. Interaction with radiofrequency of appropriate energy results in the change in these dipoles.
2. Rotations of a molecule having a net electric dipole moment, such as water will cause changes in the directions of the dipole and therefore in the electrical properties.
3. Vibrations of molecules can result in changes in electric dipoles that could interact with the electrical component of the electromagnetic radiation.
4. Electronic transitions take place from one orbital to another. Owing to the differences in the geometry, size, and the spatial organization of the different orbitals, an electronic transition causes change in the dipole moment of the molecule
5. The above examples suggest that a change in either electric or magnetic dipole moment in a molecule is required for the absorption or emission of the electromagnetic radiation.

Electromagnetic spectrum

Electromagnetic spectrum is the arrangement of various types of electromagnetic radiations in order of their increasing wavelengths or decreasing the frequencies.

Regions of the electromagnetic spectrum

NMR	**ESR**	**MICRO WAVE**	**INFRA RED**	**VISIBLE &UV**	**X-RAY**	**γ- RAY**	**Unit**
10 m	100 cm	1 cm	100 μm	1 μm	10 nm	100 pm	Wavelength (λ)
10^{-1}	10^{-2}	1	100	10^{4}	10^{6}	10^{8}	Wave number (cm^{-1})
10^{-3}	10^{-1}	10	10^{3}	10^{5}	10^{7}	10^{9}	Energy (Joules/mole)

Since, cosmic rays have the highest frequencies while radio waves have the lowest frequencies. All the types of radiations of electromagnetic radiations travel with the same speed of light but they differ in their wavelength from each other. The arrangement of different types of emr with increasing order of their wavelength are cosmic rays < γ-rays < X-rays < ultraviolet rays < visible < infrared rays <micro waves<radio waves.

Energy levels in molecules

The electronic transitions in an atom are due to absorption or emission of electromagnetic radiation. We have further stated that electronic transitions in an atom are quantized and the resulting line emission spectra correlate with the difference between the electronic energy levels. There are more possibilities for transition between various energy levels in the polyatomic molecules than those in individual atoms. The total energy of a molecule is the sum of four different types of energy, viz., translational, rotational. vibrational and electronic. Therefore, absorption or emission of energy (electromagnetic radiation) may cause changes in some or all of these types of energy, and molecular spectra provide a method of measuring these changes. Before going into further details of molecular energy changes, their measurements and interpretation, let us first define the energy types present in molecules. Energy can be stored either as potential energy or kinetic energy, in a variety of ways including:

- **Translational energy (E_{trans}):** Translational Energy (E_{trans}) is concerned with the overall movement of the molecules along the three axes. It is significant only in gases and to a lesser extent for liquids. In solids, translational energy is minimum. Here small amounts of energy stored as kinetic energy. This is unquantized (can take any value) and hence is not relevant to spectroscopy .
- **Rotational energy (E_{rot}):** involves the spinning of molecules about the axes passing through their centre of gravity. Here, kinetic energy associated with the tumbling motion of molecules. This is quantized.

- **Vibrational energy (E_{vib})**: is associated with vibrations within a molecule such as the stretching or the bending of bonds. In stretching type, the bond length varies but in bending type, bond angle varies. Here, the oscillatory motion of atoms or groups within a molecule (potential energy ↔ kinetic energy exchange). This is quantized.

- **Electronic energy (E_{elec})**: involves changes in the distribution of electrons by the promotion of electrons to higher levels on absorption of energy. This is similar to electronic energy changes in atoms. Here energy stored as potential energy in excited electronic configurations. This is quantized.

If E is the energy of a molecule, it can be expressed as the sum of translational, rotational, vibrational and electronic contributions.

$$E = E_{trans} + E_{rot} + E_{vib} + E_{elec}$$

The energies of molecules with spacing of energy levels of different types of energy as shown in fig 2. It is clear that electronic levels are much more widely spaced than vibrational levels, which in turn are more widely spaced than rotational levels.

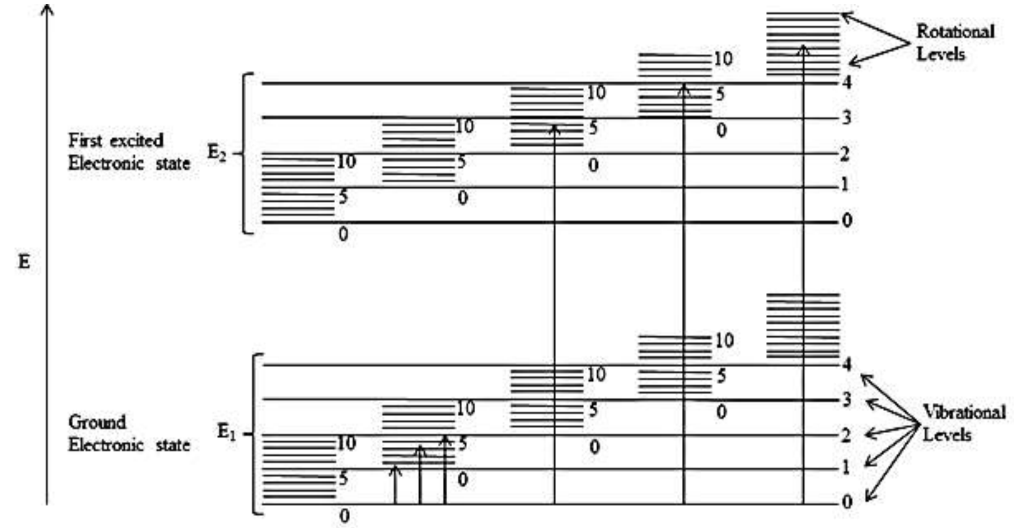


Fig 2: Representation of Electronic, Vibrational and Rotational energy levels

2. Microwave Spectroscopy

When a gas molecule is irradiated with microwave radiation, a photon can be absorbed through the interaction of the photon's electronic field with the electrons in the molecules. For the microwave region this energy absorption is in the range needed to cause transitions between rotational states of the molecule. However, only molecules with a permanent dipole that changes upon rotation can be investigated using microwave spectroscopy. This is due to the fact that their must be a charge difference across the molecule for the oscillating electric field of the photon to impart a torque upon the molecule around an axis that is perpendicular to this dipole and that passes through the molecules center of mass.

This interaction can be expressed by the transition dipole moment for the transition between two rotational states

Probability of Transition = $\int \psi_{rot\ (F)}\mu^\wedge\ \psi_{rot}(I)\ d\tau$

Where $\Psi_{rot(F)}$ is the complex conjugate of the wave function for the final rotational state, $\Psi_{rot(I)}$ is the wave function of the initial rotational state , and μ is the dipole moment operator with Cartesian coordinates of μ_x, μ_y, μ_z. For this integral to be nonzero the integrand must be an even function. This is due to the fact that any odd function integrated from negative infinity to positive infinity, or any other symmetric limits, is always zero.

Selection Rule:

In addition to the constraints imposed by the transition moment integral, transitions between rotational states are also limited by the nature of the photon itself. A photon contains one unit of angular momentum, so when it interacts with a molecule it can only impart one unit of angular momentum to the molecule. This leads to the selection rule that a transition can only occur between rotational energy levels that are only one quantum rotation level (J) away from another.

$\Delta J = \pm 1$

Where J is the rotational quantum number

Degrees of Freedom

A molecule can have three types of degrees of freedom and a total of 3N degrees of freedom, where N equals the number of atoms in the molecule. These degrees of freedom can be broken down into 3 categories.

- **Translational**: These are the simplest of the degrees of freedom. These entail the movement of the entire molecule’s center of mass. This movement can be completely described by three orthogonal vectors and thus contains 3 degrees of freedom.

- **Rotational**: These are rotations around the center of mass of the molecule and like the translational movement they can be completely described by three orthogonal vectors. This again means that this category contains only 3 degrees of freedom. However, in the case of a linear molecule only two degrees of freedom are present due to the rotation along the bonds in the molecule having a negligible inertia.
- **Vibrational**: These are any other types of movement not assigned to rotational or translational movement and thus there are 3N – 6 degrees of vibrational freedom for a nonlinear molecule and 3N – 5 for a linear molecule. These vibrations include bending, stretching, wagging and many other aptly named internal movements of a molecule. These various vibrations arise due to the numerous combinations of different stretches, contractions, and bends that can occur between the bonds of atoms in the molecule.

Each of these degrees of freedom is able to store energy. However, In the case of rotational and vibrational degrees of freedom, energy can only be stored in discrete amounts. This is due to the quantized break down of energy levels in a molecule described by quantum mechanics. In the case of rotations the energy stored is dependent on the rotational inertia of the gas along with the corresponding quantum number describing the energy level.

Classification of Molecules Based on Moment of Inertia:

Microwave rotational spectroscopy uses microwave radiation to measure the energies of rotational transitions for molecules in the gas phase only (due to intermolecular interactions hindering rotations in the liquid and solid phases of the molecule). It accomplishes this through the interaction of the electric dipole moment of the molecules with the electromagnetic field of the exciting microwave photon. In microwave spectroscopy, molecules may be classified in to 5 categories based on their shape and the inertia around their 3 orthogonal rotational axes. These 5 categories include diatomic molecules, linear molecules, spherical tops, symmetric tops and asymmetric tops.

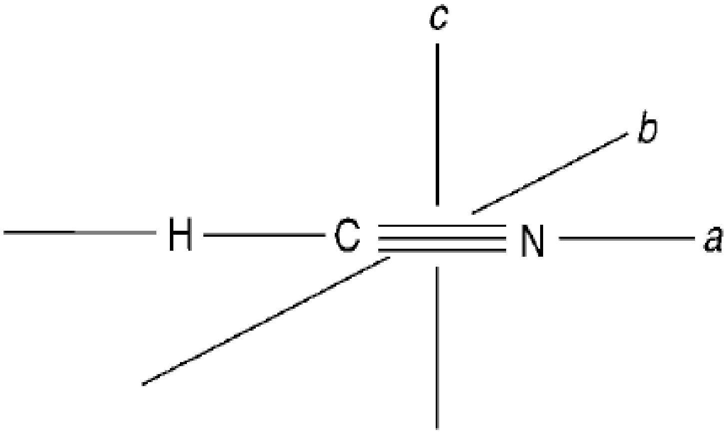
The moment of inertia I of any molecule about any axis through the centre of gravity is given by

$$I = \sum m_i r_i^2$$

Where m_i and r_i are the mass and distance of atom i from the axis. There is one of these axes, conventionally labeled the c axis, about which the moment of inertia has its maximum value and a second axis, labeled the a axis, about which the moment of inertia has its minimum value. It can be shown that the a and c axes must be mutually perpendicular. These with a third axis, the b axis, which is perpendicular to the other two, are called the principal axes of inertia and the corresponding moments of inertia I_A, I_B and I_C are the principal moments of inertia. In general, according to convention $I_C \geq I_B \geq I_A$.

1. **Linear molecules:** In these molecules, atoms are arranged in a straight line, such as HCl, HCN, Carbon oxy sulphide (O=C=S) etc., the three directions of rotations may be taken as a) about the bond axis b) end-over-end rotations in the plane of the paper, and c) end-over-end rotation at right angles to the plane. It is evident that the moments of b and c are the same (i.e. $I_B = I_C$) while that of I_A is very small, taken as approximation, $I_A = 0$, For a linear molecule the separation of lines in the rotational spectrum can be related directly to the moment of inertia of the molecule. Since the moment of inertia is quadratic in the bond lengths, the microwave spectrum yields the bond lengths directly, provided the atomic masses are known. Thus, for linear molecules we have

$\mathbf{I_B = I_C}$, $\mathbf{I_A = 0}$



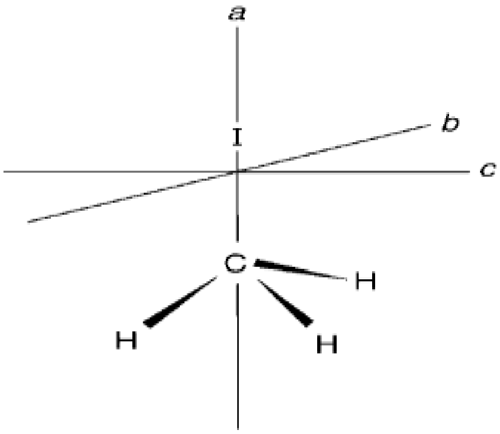
2. **Symmetric tops:** In symmetric top, two moments of inertia are the same. For example, methyl fluoride, where three hydrogen atoms are bonded tetrahedrally to the carbon as shown below.

As in the case of linear molecules, the end-over-end rotation in, and out of, the plane of the paper are still identical and so we have $I_B = I_C$. The moment of inertia about the C-F bond axis is small, so such a system of molecules spinning about this axis can be imagined as a top.

Symmetric tops: $\mathbf{I_B = I_C \neq I_A \quad I_A \neq 0.}$

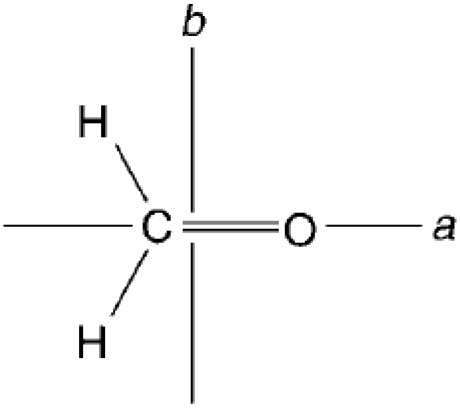
There are two subdivisions of this class,

if $I_B = I_C > I_A$, then the molecule is said to be **prolate**. For example: Methyl fluoride, Methyl iodide, since the heavy iodine nucleus makes no contribution to I_a.



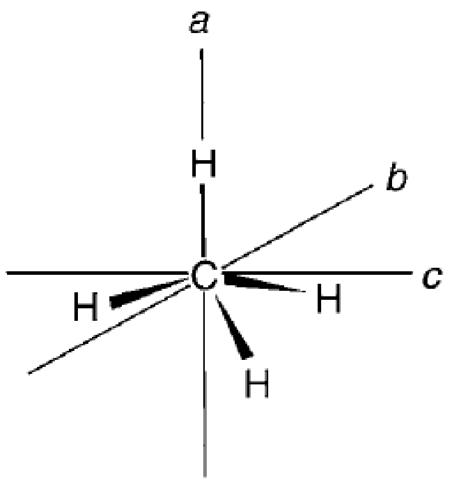
Where as if $I_B = I_C < I_A$, then it is said to be **oblate**. For example: Boron trichloride which is planar and symmetrical. In this case, $I_A = 2I_B = 2I_C$.

3. **Asymmetric tops:** These molecules have three orthogonal rotational axes that all have different moments of inertia and most molecules fall into this category. Unlike linear molecules and symmetric tops, these types of molecules do not have a simplified energy equation to determine the energy levels of the rotations. These types of molecules do not follow a specific pattern and usually have very complex microwave spectra. For example H_2O and vinyl chloride.



Asymmetric tops : $I_A \neq I_B \neq I_C$

4. **Spherical tops:** Spherical tops are molecules in which all three orthogonal rotations have equal inertia and they are highly symmetrical. This means that the molecule has no dipole and for this reason spherical tops do not give a microwave rotational spectrum. For example: Methane.



Spherical tops : $I_A = I_B = I_C$

3. Rotational Spectra of Diatomics

Consider a linear rigid diatomic shown in Fig 3.

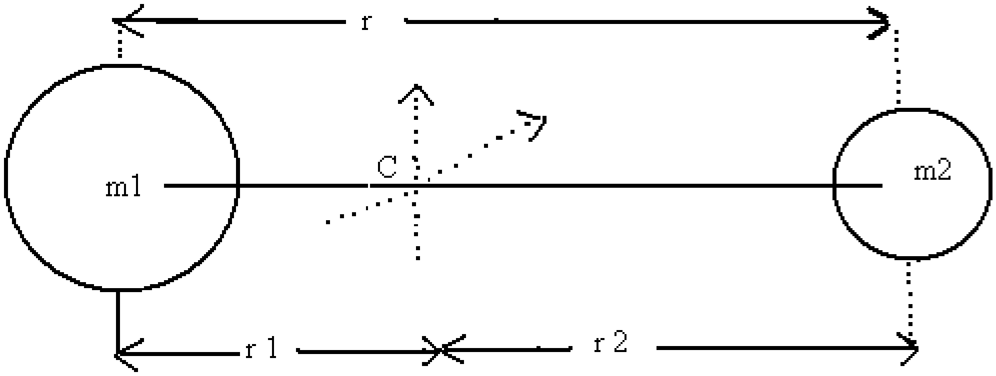


Fig 3: A rigid diatomic with masses m_1 and m_2 joined by a thin rod of length $r = r_1 + r_2$ the centre of mass is at C.

The two independent rotations of this molecule are with respect to the two axes which pass though C and are perpendicular to the “bond length” r. The rotation with respect to the bond axis is possible only for “classical” objects with large masses. For quantum objects, a “rotation” with respect to the molecular axis does not correspond to any change in the molecule as the new configuration is indistinguishable from the old one.

The center of mass is defined by equating the moments on both segments of the molecular axis.

$$m_1 r_1 = m_2 r_2 \tag{1}$$

The moment of inertia is defined by

$$\mathrm{I} = m_1 r_1^2 + m_2 r_2^2 \qquad (2)$$

$$= m_2 r_2 r_1 + m_1 r_1 r_2$$

$$= r_1 r_2 \quad (m_1 + m_2) \qquad (3)$$

Since $m_1 r_1 = m_2 r_2 = m_2 \ (r - r_1), \ (m_1 + m_2) \ r_1 = m_2 r$ Therefore,

$$r_1 = \frac{m_2 r}{m_1 + m_2} \quad \text{and} \quad r_2 = \frac{m_1 r}{m_1 + m_2} \qquad (4)$$

Substituting the above equation in (3), we get

$$I = \frac{m_1 m_2 \ r^2}{(m_1 + m_2)} = \mu r^2, \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \qquad (5)$$

Where μ, the reduced mass is given by

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \qquad (6)$$

The rotation of a diatomic is equivalent to a “rotation” of a mass μ at a distance of r from the origin C. The kinetic energy of this rotational motion is K.E. = $L^2/2I$ where L is the angular momentum, Iω where ω is the angular (rotational) velocity in radians/sec. The operator for L^2 is the same as the operator L^2 for the angular momentum of hydrogen atom and the solutions of the operator equations $L^2 \ Y_{lm} = l\,(l + 1)\ Y_{lm}$, where Y_{lm} are the spherical harmonics.

The quantized rotational energy levels for this diatomic are

$$E_J = \frac{h^2}{8\pi^2 I} \quad J\,(J + 1) \qquad (7)$$

The energy difference between two rotational levels is usually expressed in cm^{-1}. The wave number corresponding to a given ΔE is given by

$$\upsilon = \Delta E / hc, \quad \mathrm{cm}^{-1} \qquad (8)$$

The energy levels in cm^{-1} are therefore,

$$E_J = B \quad J\,(J + 1) \quad where \quad B = \frac{h}{8\pi^2 Ic} \qquad (9)$$

The rotational energy levels of a diatomic molecule are shown in Fig 4.

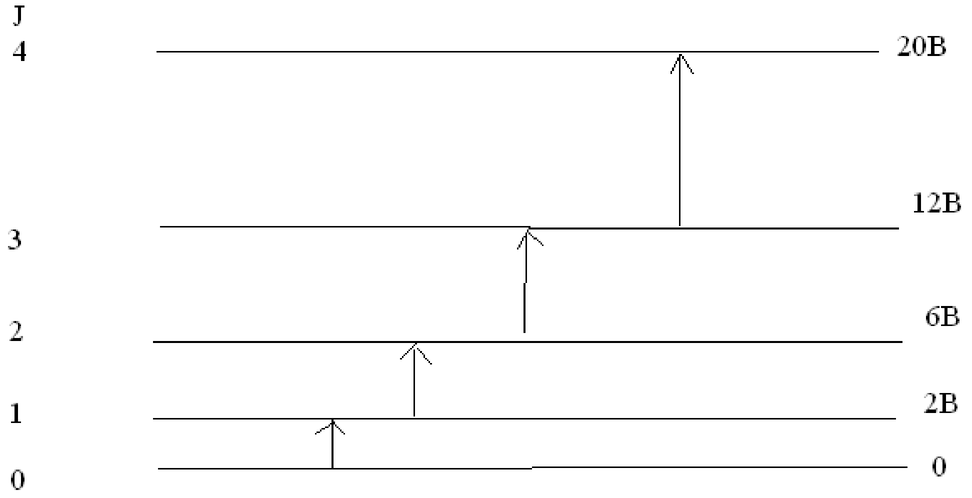


Fig 4: Rotational energy levels of a rigid diatomic molecule and the allowed transitions

The selection rule for a rotational transition is,

$$\Delta J = \pm 1 \qquad (10)$$

In addition to this requirement, the molecule has to possess a dipole moment. As a dipolar molecule rotates, the rotating dipole constitutes the transition dipole operator μ. Molecules such as HCl and CO will show rotational spectra while H_2, Cl_2 and CO_2 will not. The rotational spectrum will appear fig 5 as follows

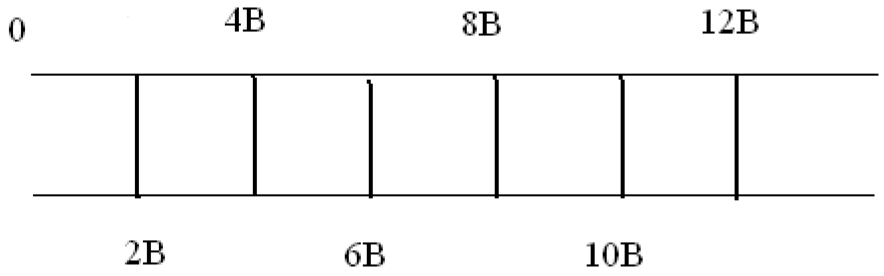


Fig 5: Rotational spectrum of a rigid diatomic. Values of B are in cm^{-1}. Typical values of B in cm^{-1} are 1.92118 (CO), 10.593 (HCl), 20.956 (HF), $^1H_2$ (60.864), $^2H_2$ (30.442), 1.9987 (N_2).

From the value of B obtained from the rotational spectra, moments of inertia of molecules I, can be calculated. From the value of I, bond length can be deduced.

Calculation of "J" for CO molecule

Example 1: Calculate J value of first three rotational transitions of CO molecule if its bond length is 112.8 pm. Given C^{12} = 12.0001 amu and O^{16} = 15.9994 amu.

(Note: to convert amu in to mass multiplied by 1.66 x 10^{-24})

Solution:

I = μr^2

$$\mu \quad = \quad \frac{m_1 \, m_2}{m_1 \; + m_2} \; = \frac{15.9994 x 12.001}{15.9994 + 12.001} \text{ x } 1.66 \text{ x } 10^{-24}$$

μ = 1.1383 x 10^{-23}g

therefore I = 1.1383 x 10^{-23}g x (112.8 x 10^{-10} $)^2$ = 1.447 x 10^{-39}

we know that

B = h/(8π^2 Ic) = 6.626 x 10 $^{-34}$/(8 x $(3.14)^2$ x 1.447 x 10^{-39}x 3 x 10^{10})

= 1.9351 cm^{-1}

Therefore the rotational transition of CO molecule for first three transition levels is as follows

$\Delta\nu$ (J = 0 to J = 1) = 2B

= 2 x 1.9351 = 3.870 cm^{-1}

$\Delta\nu$ (J = 1 to J = 2) = 4B

= 4 x 1.9351 = 7.7404 cm^{-1}

$\Delta\nu$ (J = 2 to J = 3) = 6B

= 6 x 1.9351 = 11.6106 cm^{-1}

4. Rotational Spectra of Polyatomics

Linear molecules such as OCS and HC≡CCl have spectra similar to diatomics. In diatomics as well as linear triatomics, $I_A = I_B$; $I_C = 0$. I_A, I_B and I_C are the three moments of inertia of molecules along three independent axes of rotation. Just as any translation can be decomposed into three independent components along three axes such as x, y and z, any rotation can be decomposed into rotations along three axes A, B, and C. The way to choose these axes is to have the simplest values of I_A, I_B and I_C. Since triatomics are heavier than the constituent diatomics, their moments of inertia are larger and the values of rotational constants, B, are smaller, in the range of 1 cm^{-1}. The value of I_A or I_B determined from the B value gives the total length of the triatomic. To determine the two bond lengths in the linear triatomic, we need to determine the moment of inertia $I_{A'}$ of an isotope of the triatomic. From two values of I_A and $I_A{}'$, we can determine the two bond lengths.

The rotational spectra of asymmetric molecules for whom $I_A \neq I_B \neq I_C$ can be quite complicated. For symmetric tops, two moments of inertia are equal ie.,

$$I_A = I_B \neq I_C ; \quad I_C \neq 0$$

In CH_3Cl for example, the main symmetry axis is the C – Cl axis. We need two quantum numbers to describe the rotational motion with respect to I_A and I_C respectively. Let J represent the total angular momentum of the molecule and K the angular momentum with respect to the C – Cl axis of the symmetric top. J takes on integer values and K cannot be greater than J (recall that $m_l \leq | l |$ for orbital angular momentum). The (2J + 1) "degeneracy" is expressed through the 2J + 1 values that K can take.

$$K = J, \ J-1, \ldots\ldots 0, \quad -(J-1), \ -J$$

The rotational energies of a symmetric top are given by

$$E_{J,K} \ / hc = BJ(J+1) + (A-B) \ K^2, \quad cm^{-1}$$

The moments of inertia are related to B and A as

$$B = \frac{h}{(8\pi^2 I_c \,.c)} \qquad \text{and} \qquad A = \frac{h}{(8\pi^2 I_A c)}$$

As the energy depends on K^2, energies for states with + K and – K are doubly degenerate. Thus there will be J + 1 levels and (2J + 1) states for each values of J.

The selection rules for the symmetric top are,

$\Delta J = \pm 1$ and $\Delta K = 0$

It can be easily shown hat

$$(E_{J+1,K} - E_{J,,K})/hc = 2\,BJ\,(J+1)$$

This implies that the spectrum is independent of the value of K. The physical meaning is as follows. K refers to the rotation about the symmetry axis such as the C - Cl axis. A rotation about this axis does not change the dipole moment. We mentioned in the section on the rotational spectra of diatomics that the molecular dipole moment has to change during the rotational motion (transition dipole moment operator of Eq 5) to induce the transition. Rotation along the axis A and B changes the dipole moment and thus induces the transition.

By using rotational or microwave spectroscopy, very accurate values of bond lengths can be obtained. For example, in HCN, the C-H length is 0.106317 ± 0.000005 nm and the CN bond length is 0.115535 ± 0.000006 nm. The principle of the microwave oven involves heating the molecules of water through high speed rotations induced by microwaves. The glass container containing water however remains cold since it does not contain rotating dipoles.

5. Vibrational Spectroscopy

The pure vibrational spectra and the vibrational – rotational spectra are observed in near IR region. Since the energy changes in vibrational transitions are always larger than those in pure rotational transitions, so the molecules in the gaseous state exhibit vibrational-rotational spectra. This spectrum is shown only by molecules possessing either permanent dipole moment or the dipole moment arising due to vibration of atoms in molecules. These molecules are IR active for example CO, NO, HCl, CN etc. The homo nuclear diatomic molecules like O_2, N_2 and Cl_2 have no permanent dipole moment of their own however, when they are subjected to electromagnetic radiation it induces an oscillating dipole moment and excite them to undergo vibrational – rotational transitions. Pure vibrational spectroscopy can be observed only in liquid, where interaction between the molecules inhibit rotation. The IR spectroscopy is highly useful in the determination of molecular structure and for identification of functional groups in organic compounds.

Definition: Interaction of Infrared radiation with matter

Spectral Range of IR Radiation:

Near IR: 12000 cm^{-1} to 4000 cm^{-1}
MID IR: 4000 cm^{-1} to 620 cm^{-1}
Far IR: 300 cm^{-1} to 10 cm^{-1}

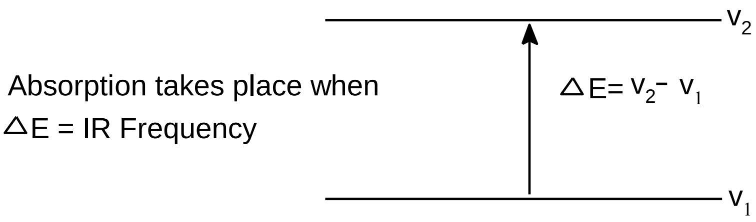
Principle: Vibrational spectroscopy principle can be explained in two different approaches.

1. Classical Approach

Oscillating polar group produces stationary alternate electric fields (SAEF). These SAEFs can be presented in the form of frequency or energy. If the SAEF energy matches with IR radiation, the oscillating group absorbs energy and shows signal at corresponding frequency in the IR spectrum.

2. Quantum Approach

Irradiation of sample with IR radiation brings about changes in vibrational levels of molecules. The transition of molecule from lower vibrational energy level to higher vibrational energy level. The transition is induced by absorption of photon of IR light of appropriate frequency, which matches with energy gap between the two levels.



IR transition in a molecule

6. Vibrations of Diatomic Molecules (Simple Harmonic Oscillator)

Taking the simple case where a diatomic molecule may be considered as a simple harmonic oscillator. Consider a diatomic molecule in which the atoms are linked by a covalent bond. The bond acts like a spring. The stiffness or elasticity of the spring (bond) is determined by a factor called force constant. The force constant is a measure of bond strength between two atoms.

An oscillator in which the resorting force(F) is directly proportional to the displacement , in accordance with Hook's we have

$$F=-kx$$

Where x is the displacement and is equal to the distance to which the atoms have been stretched (R) minus equilibrium distance between the atoms (Re) i.e. x = R – Re, k in equation is called force constant. The negative sign indicates that the force is the restoring force, and has a direction opposite to that of the displacement. Thus if x=1 cm, k= -F. Hence **force constant** may be defined as the restoring force per unit displacement (or per cm) of a harmonic oscillator. It is found to be related to the equilibrium vibration frequency ω_e according to equation

$$\omega_e = \frac{1}{2\pi}\sqrt{\frac{k}{\omega}}$$

Where μ is the reduced mass of the system.

To calculate k, equation can be rewritten as follows:

$$k = 4\pi^2 \omega_e^2 \mu$$

$$k = 4\pi^2 \omega_e^2 \frac{m_1 m_2}{m_1 + m_2}$$

Where m_1 and m_2 are the masses of the oscillating atoms.

Vibration of Polyatomic Molecules

Degrees of freedom:

The number of variables required to describe the motion of molecule or atom

Translational motion:

The atom shifts from one point to another point in 3 dimensional space. It is a permanent displacement.

Rotational motion:

Roational of an atom through fixed axis.

Vibrational motion:

The motion brings change in bond angle and bond distance between connecting atoms

Normal mode:

It is a molecular vibration where some or all atoms vibrate together with the same frequency in a defined manner.

Poly atomic molecules show more than one fundamental vibrational absorption bands. The number of these fundamental bands is related to the degrees of freedom in a molecule. The number of degrees of freedom is equal to the sum of coordinates necessary to locate all the atoms of a molecule in space. Each atom has three degrees of freedom corresponding to the three Cartesian coordinates (X, Y, Z) which necessary to describe its position on relative to other atoms in a molecule(fig 2.6.).

Therefore the total number of degrees of freedom in a molecule containing N-atoms is equal to 3N which includes rotational, vibrational and translation degrees of freedom.

Total number of degrees of freedom (3N) = Translational + Vibrational + Rotational

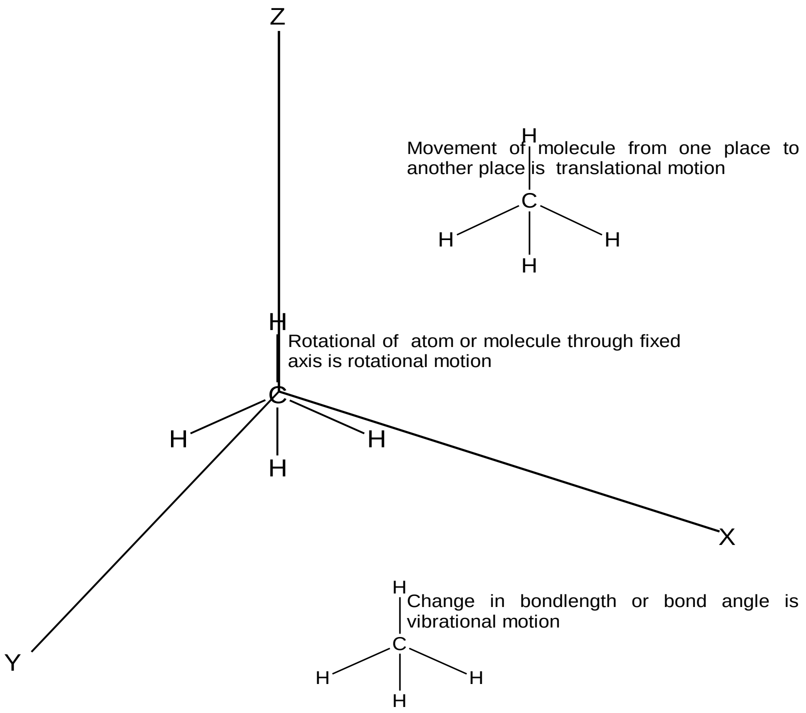


Fig 6: Representation of degrees of freedom of a methane molecule

S.No.	**degrees of freedom**	**Monoatomic**	**Poly atomic**	
			Linear molecule	**Non linear molecules**
1	Total	3	3N	3N
2	Translational	3	3	3
3	Rotational	0	2	3
4	Vibrational	0	3N-5	3N-6

We need 3-coordinates to specify the centre of gravity of a molecule in space. Hence the centre of gravity of the molecule has three independent translational degrees of freedom.

Vibrational Degrees of Freedom for Linear Molecule

If the molecule is linear then two independent modes of rotation about x and y axis are possible. Therefore the number of coordinates or degrees of freedom necessary to specify the vibrational transition is

Total degrees of freedom for polyatomic molecule = Translational + Rotational + Vibrational

3N = 3 + 2 + Vibrational

Vibrational Degrees of freedom = 3N-5

For example: CO_2, CO, HCl, Acetylene

Vibrational Degrees of freedom for CO = 3N-5 = 3 x 2 – 5 = 1

Vibrational Degrees of freedom for C_2H_2 = 3N-5 =3 x 4 – 5 = 7

Vibrational Degrees of freedom for CO_2 = 3N-5 =3 x 3 – 5 = 4

Degrees of Freedom of Vibration for Non-linear Molecule

In case of non-linear molecules, 3 rotational coordinates(x,y,z) are needed to specify the molecular orientation about the centre of gravity.

Total degrees of freedom for polyatomic molecule = Translational + Rotational + Vibrational

3N = 3 + 3 + Vibrational

Vibrational degrees of freedom = 3N – 6

Vibrational Degrees of freedom for H_2O = 3N-6 = 3 x 3 – 6 = 3

Vibrational Degrees of freedom for CH_4 = 3N-6 = 3 x 5 – 6 = 9

Vibrational Degrees of freedom for NH_3 = 3N-6 = 3 x 4 – 6 = 6

Vibrational Degrees of freedom for C_6H_6 = 3N-6 = 3 x 12 – 6 = 30

7. Types of Molecular Vibration

Vibration: Periodic displacement of atoms or nuclei from their equilibrium position is the vibration.

Classification: There are two types of molecular vibrations namely stretching and bending vibrations.

1. **Stretching Vibration:** The change in bond length between connecting atoms without altering the bond axis or bond angle is known as Stretching vibration. Stretching vibration are two types (Fig.)

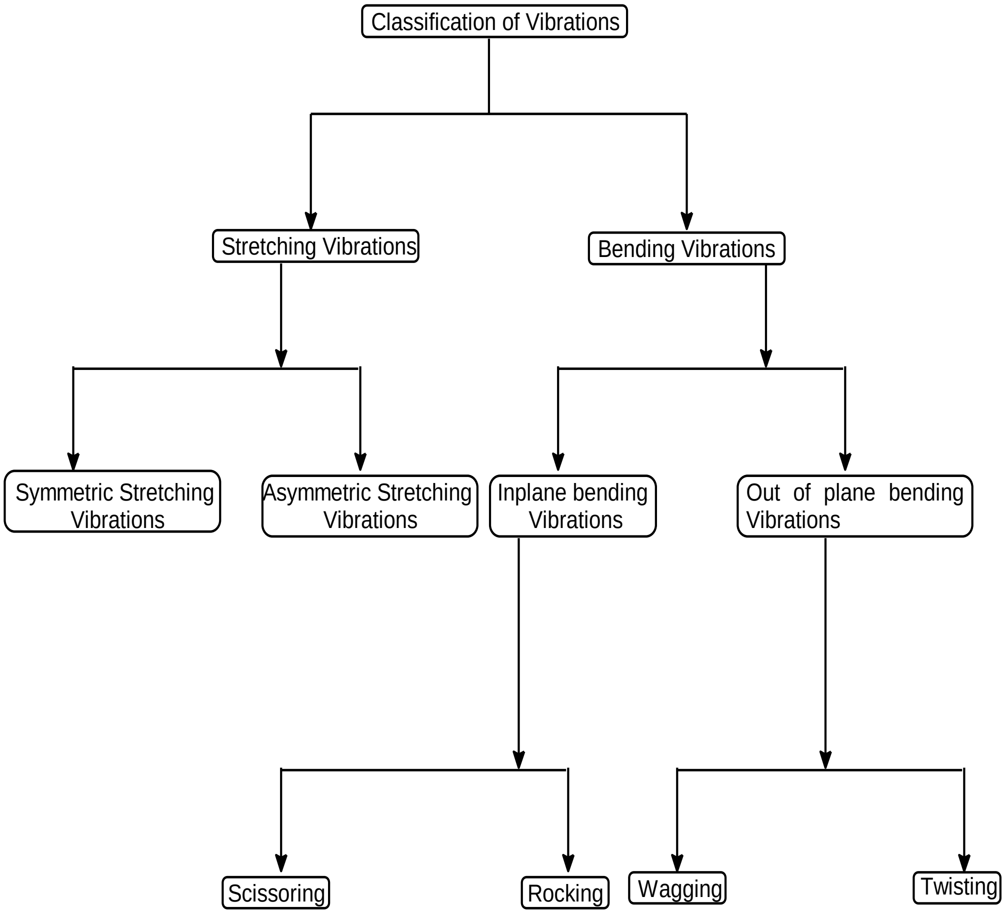
a. Symmetric stretching vibration:

At the time of vibration reference bonds subjected to either expansion or compression (i.e. Opposite direction of movement)

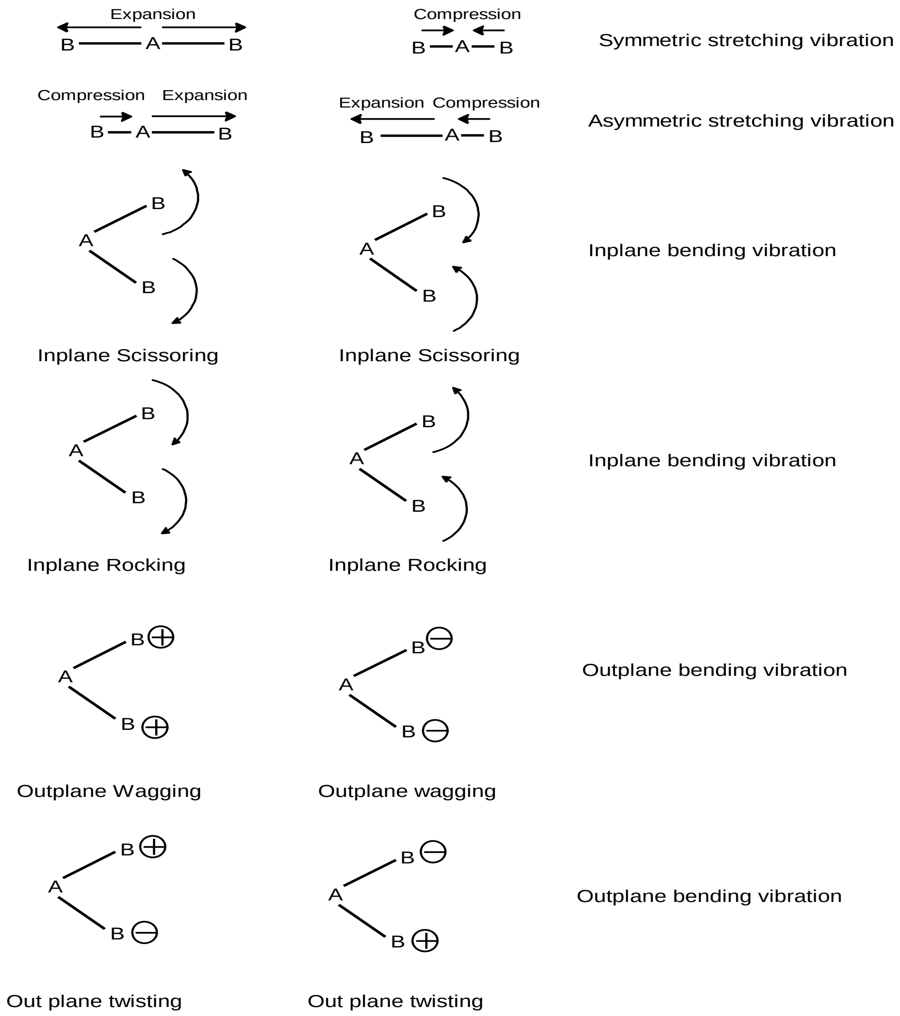
b. Asymmetric stretching vibration:

At the time of vibration reference bonds subjected to compressed and other is expanded (i.e. same direction of movement)

2. **Bending Vibrations:** The change in bond angle between connecting atom by changing the bond angle in and out of the bond axis plane is known as bending vibration. Bending vibration are four types (Figure).



Schematic Representations of types of Vibrational Modes



a. **Scissoring:** The connecting atoms joined to a central atom move towards and away from each other in the same plane and change the bond angle.

b. **Rocking:** The connecting atoms joined to a central atom move back and forth in the same direction.

c. **Twisting:** One of the atom moves up the plane while the other atom moves down the plane with respect to the central atom.

d. **Wagging:** The two atoms move up or below the plane with respect to the central atom.

In pending vibrations, rocking and scissoring vibrations occur in the same plane (in plane vibrations) whereas twisting and wagging occur out of plane. In some cases, because of symmetry factors two or more vibrational modes may be identical with same energy. Such vibrations are generally referred to as degenerate modes

Vibration Modes of CO_2 Molecule

CO_2 is a linear triatomic molecule, therefore it has 3N – 5 = 3 x 3 – 5 = 4 fundamental modes of vibration. The four modes of vibration are symmetrical stretching, antisymmetrical stretching and two bending modes (fig 2.7.). During the stretching vibration, there is no change in the dipole moment. Hence, this symmetrical stretch will not absorb radiation, and hence it is IR inactive.

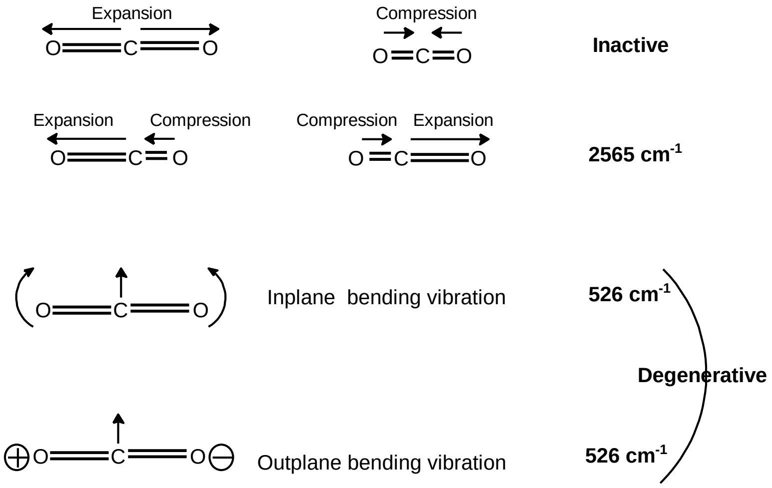
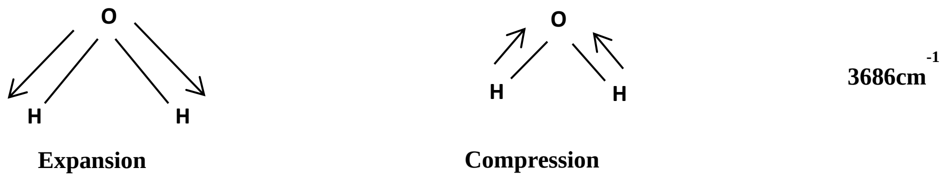


Fig 7: Representation of stretching and bending molecular vibrations of CO_2 Molecule

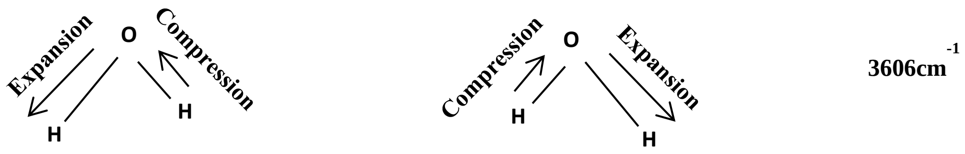
During the asymmetrical stretching, there is a change in the dipole moment and hence this mode is IR active. Two bending modes have the same energy and are said to be degenerate, i.e. only one absorption band is expected due to the two bending modes of vibrations. Therefore for linear CO_2 molecule we get total two absorption band in the spectrum.

Vibrations modes of H_2O molecule

Symmetrical stretching



Asymmetrical stretching



Inplane scissoring

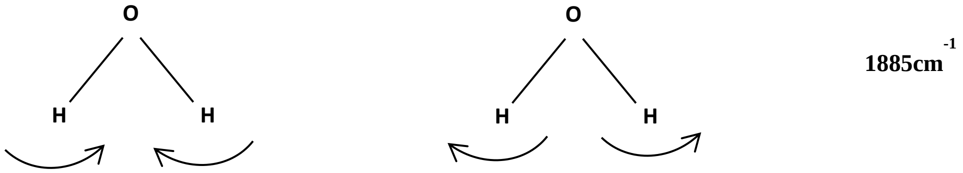


Fig 8: Representation of stretching and bending molecular vibrations of H_2O Molecule

Water is a bent, non-linear triatomic molecule. Therefore it has 3N – 6 = 3 x 3 – 6 = 3 fundamental modes of vibrations (fig 2.8.). The three modes of vibrations are a bending mode, a symmetrical stretching and an unsymmetrical stretching mode. All the three modes of vibration involve changing in dipole moment and hence they are IR active.

8. Determination of Force Constant

Calculate the force constant of CO molecule having $\bar{\upsilon}$ = 2143 cm^{-1}

For C ≡ O molecule the $\bar{\upsilon}$ = **2143 cm^{-1}**

In $^{12}C - ^{16}O$ the atomic mass of C = 12.00 amu and O = 16.00 amu

The reduced mass is calculated from $\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{192}{28} = 6.857\ amu$

1 amu = 1.66 x 10^{-27} Kg

The reduced mass

$\mu = 6.857\ amu \times (1.66 \times 10^{-27} Kg) = 1.1383 \times 10^{-26} Kg$

We know that $\nu = \frac{c}{\lambda} \Rightarrow\ \nu = c\bar{\upsilon} = (3 \times 10^{10}\ cm\ s^{-1}) \times (2143\ cm^{-1})$

Thus $\nu = 6.429 \times 10^{13} s^{-1}$

The angular frequency is given as $\omega = 2\pi\nu$

$$\omega = 2\pi\nu = 2 \times 3.14 \times 6.429 \times 10^{13} s^{-1} = 4.037 \times 10^{14} s^{-1}$$

From classical mechanics, the angular frequency ω is

$$\omega = \sqrt{\frac{k}{\mu}}$$

$$\omega^2 = \frac{k}{\mu}$$

Thus $k = \mu\omega^2 = (1.1383 \times 10^{-26} Kg) \times (4.037 \times 10^{14} s^{-1})^2 = 1855\ Kg\ s^{-2}$

$$\because 1\ Newton = 1 Kg\ m\ s^{-2}$$

The force constant $k = 1855\ Nm^{-1}$

9. Electronic Spectroscopy

The spectroscopy deals with study of electromagnetic radiation with matter. Thus it gives the information about the transition between rotational and vibrational energy levels with the addition of electronic energy levels. It is observed in the visible and ultraviolet region of spectrum. Absorption spectra are obtained when the electrons in the molecule are promoted from the lower electronic state to higher electronic excited state by the absorption of radiation. On the other hand, emission spectra are obtained from the transition of electrons from higher excited state to lower electronic state. An Electronic transition in molecules is accompanied by vibrational transition and the spectra consist of a series of bands. Each band has a number of lines due to rotational transition. Hence, the whole rotational – vibrational spectrum is superimposed on the electronic spectrum and this process produces a very complex band system.

Types of Electronic Transitions in Organic Molecules

Electrons in a molecule can be classified into three different types

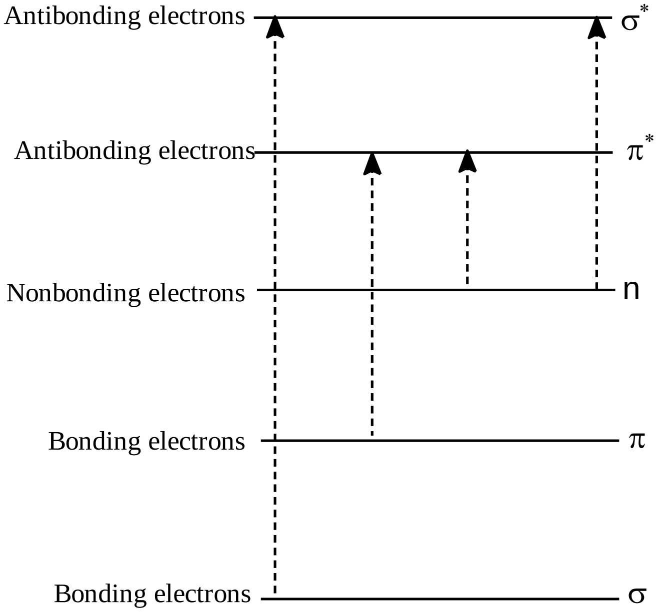
1. Bonding σ–orbital: electron in a single covalent bond is tightly bound and hence radiation of high energy is required to excite them.

2. Non-bonding n-orbital: electrons attached to atoms as loan pair. These electrons are not involved in bonds. For example: Oxygen, Nitrogen and Chlorine. The non-bonding electrons can be excited at a lower energy than tightly bound bonding electrons.

3. Bonding π-orbital: electrons in double or triple bond can be excited relatively easily. Molecules containing a series of alternating double bonds, the π-electrons are delocalized and require less energy for excitation.

According to molecular orbital theory, when a molecule is excited by the absorption of energy, its electrons are promoted from a bonding to anti bonding orbital (higher energy states). The anti bonding orbital associated with σ-bond is called σ* orbital and the electron transition is represented as σ – σ*. The anti bonding orbital associated with the π-bond is known as π* orbital and the corresponding transition is denoted as π – π*. Since non-bonding electrons are not directly involved in bonding, there is no corresponding anti-bonding orbital for them. So the major electronic transitions within the electronic transitions are σ – σ*, n – σ*, π – π* and n – π*. When the selection rules are applied, the first three transitions are usually allowed whereas n – π* transition is forbidden. The energy required for various transitions follows the order σ – σ* > n – σ*> π – π* > n – π*.

Electronic Energy levels



Characteristics of electronic transitions:

1. Electronic transitions are appeared as broad bands due to their higher energy transitions.
2. During electronic transition there should be change in dipole moment (i.e. Ground state and Excited state dipole moment should not be the same)
3. During electronic transition retention of multiplicities is allowed
4. During electronic transition change in angular momentum should be zero or +/- 1

Types of Electronic Transitions in Organic Compounds

1. σ → σ * transition: The energy required for this transition is high (i.e. very short wavelengths; 150nm), which is not coming under UV spectral range. The saturated alkanes will undergo this type of transition.
2. n → σ * transition: The saturated hydrocarbons attached to hetero atoms will undergo this type of transition. Example: Alcohols, amines, ether and water. The energy required for this transition is 180-190 nm.
3. π → π * transition: The unsaturated hydrocarbons, carbonyl compounds, cyanides and azo compounds will undergo this type of transition. Ex: Alkenes, Alkynes, Aldehyde and Ketone. The energy required for this transition is very low (i.e. very longer wavelengths).
4. n → π * transition: The carbonyl compounds will undergo this type of transition. Ex: Aldehydes, Ketone and cyanide.

The differences between π → π * and n → π *

S.No.	π → π *	n → π *
1	Allowed transition	Forbidden transition
2	High energy transition	Lower energy transition
3	Molar extinction coefficient (ε) value lies between 100 to 10000	Molar extinction coefficient (ε) value is < 100
4	More intense than n → π *	More intense than π → π *

10. Mathematical Derivation of Beer- Lambert's Law

Beer- Lambert's law:

When a beam of monochromatic radiation passes through a transparent absorbing medium, the rate of decrease of intensity of radiation with the thickness of the absorbing medium is proportional to the intensity of incident radiation and concentration of the medium.

$$-\frac{dI}{dx} \alpha \ cI$$

where $-\frac{dI}{dx}$ = decrease of intensity of radiation with the thickness of the absorbing medium

c = concentration of the absorbing medium

dI = Change in intensity of incident light (range is from I_0 to I)

dx = Change in thickness of medium (range is from 0 to b)

$$-\frac{dI}{I} = \varepsilon c dx$$

$\varepsilon = \text{Molar extintion coefficient}$

$$-\frac{dI}{I} = cdx$$

$$\int_{I_o}^{I} \frac{dI}{I} = -\int_{x=0}^{x=b} \varepsilon c dx$$

$$\log[I]_{I_o}^{I} = -\varepsilon c[x]_0^b$$

$$\log I - \log I_o = -\varepsilon bc$$

$$\log\frac{I}{I_o} = -\varepsilon bc$$

$$T = -\varepsilon bc$$

$T = \text{Transmittance}$

$$\log\frac{I_o}{I} = \varepsilon bc$$

$$A = \varepsilon bc$$

$A = \text{Absorbance or Optical density}$

Beer – Lamberts Law:

The absorbance of a solution is directly proportional to the concentration of the medium when thickness of the medium is fixed and directly proportional to the thickness of the medium when the concentration is fixed.

11. LASER

LASER is an abbreviation for Light Amplification by Stimulated Emission of Radiation.

Properities of LASER light

1. Coherence: It is a crucial property of laser, that exists due to stimulated emission. It simply denotes that the wavelength of the waves of emitted light is in phase. When we talk about the ordinary light source for example LED, then it does not show the property of coherence because it gets generated due to the process of spontaneous emission of a photon.

2. Monochromaticity: A light emitted by the laser diode is monochrome in nature that means that it has a single wavelength.

3. Brightness: Brightness of a light is basically determined by the power per unit surface area per unit solid angle.

4. Directionality: A laser light is highly directional this means that the light emitted by a laser diode does not show much divergence.

Construction of Laser

Basically, every laser system essentially has an active/gain medium, placed between a pair of optically parallel and highly reflecting mirrors with one of them partially transmitting, and an energy source to pump active medium. The gain media may be solid, liquid, or gas and have the property to amplify the amplitude of the light wave passing through it by stimulated emission, while pumping may be electrical or optical. The gain medium used to place between pair of mirrors in such a way that light oscillating between mirrors passes every time through the gain medium and after attaining considerable amplification emits through the transmitting mirror.

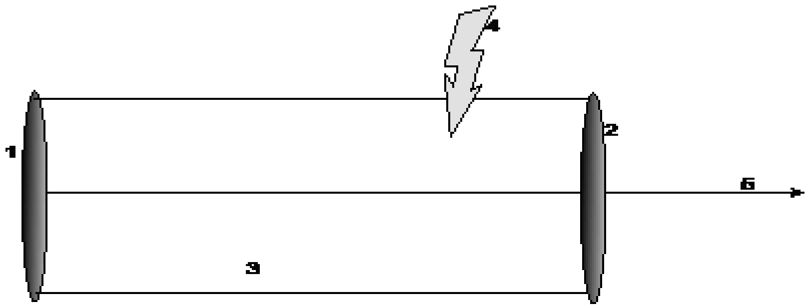
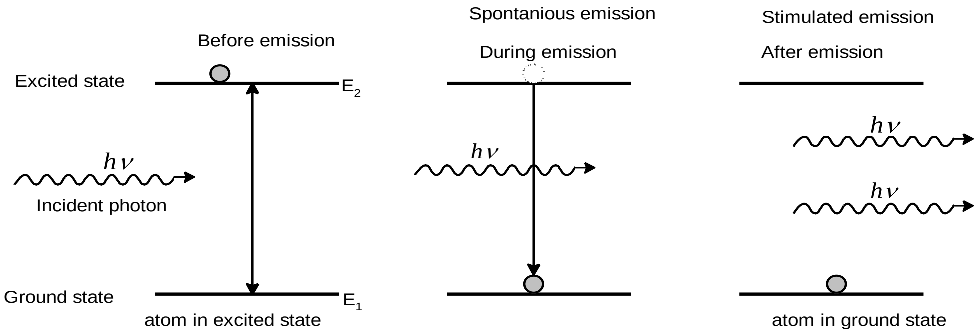


Fig 9: Basic geometry of laser cavity 1) 100% 2) 95% reflecting mirror 3) active medium 4) Pumping source and 5) Laser output

Stimulated Emission

Let us consider an active medium of atoms having only two energy levels: excited level E2 and ground level E1. If atoms in the ground state, E1, are excited to the upper state, E2, by means of any pumping mechanism (optical, electrical discharge, passing current or electron bombardment), then just after few nanoseconds of their excitation, atoms return to the ground state emitting photons of energy

$h\nu = E_2 - E_1$.



$$E_2 - E_1 = \Delta E = h\nu$$

Fig 10: Representation of Spontaneous and Stimulated emission

According to Einstein’s 1917 theory, emission process may occur in two different ways, either it may induced by photon or it may occur spontaneously.

The former case is termed as stimulated emission, while the latter is known as spontaneous emission. Photons emitted by stimulated emission have the same frequency, phase, and state of polarization as the stimulating photon; therefore they add to the wave of stimulating photon on a constructive basis, thereby increasing its amplitude to make lasing. At thermal equilibrium, the probability of stimulated emission is much lower than that of spontaneous emission (1 : 1033), therefore most of the conventional light sources are incoherent, and only lasing is possible in the conditions other than the thermal equilibrium.

Laser Diode

A semiconductor device that generates coherent light of high intensity is known as laser diode. Semiconductor lasers also known as quantum well lasers are smallest, cheapest, can be produced in mass, and are easily scalable.

Construction of Laser Diode

The active layer of undoped GaAs is placed between the P and N type of AlGaAs layers. The thickness of this active layer is of few nanometers. The aim of sandwiching this layer in between p and n-type layers is to increase the area of electron and hole combination. Resultantly increasing the emitted radiation. The laser output is taken from active region of the laser diode.

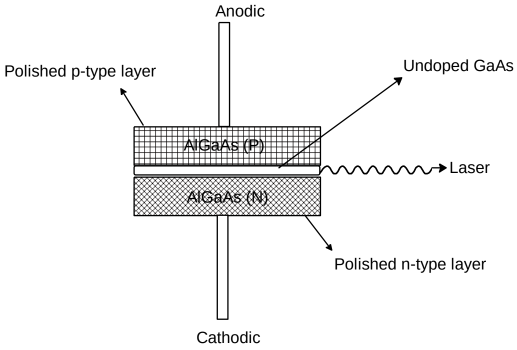


Fig 11: Laser Diode

The working of a laser diode involves 3 processes: absorption, spontaneous emission and stimulated emission.

i. Absorption: The ground state electron will absorb energy from pumping source and excites to the excited state. This is known as absorption.

ii. Spontaneous Emission: The excited electron decays without external influence and emits a photon, that is called "spontaneous emission".

iii. Stimulated Emission: The excited-state atom is perturbed by an electric field of frequency, it may emit an additional photon of the same frequency and in phase, thus augmenting the external field, leaving the atom in the lower energy state. This process is known as stimulated emission.

Advantages of laser diode

1. The operational power in case of laser diodes is less as compared to other light emitting devices.

2. It is small in size thus allows better handling.
3. Laser diodes generate light of high efficiency.

Disadvantages of laser diode

1. As it provides a light of high density, thus sometimes puts adverse effects on eyes.
2. It is expensive.

Applications of laser diode

1. Telecommunication and in defence industries.
2. Optical fiber communication also uses a laser beam for signal transmission as optical fibers requires highly focused beam.
3. It is highly used in laser printers also.

Gas Lasers

Gas lasers are widely available in almost all power and wavelengths and can be operated in pulsed and continuous modes. Based on the nature of active media, there are three types of gas lasers.

1.Atomic Gas lasers: He:Ne Laser

2.Ionic Gas lasers: Argon Ion Laser

3.Molecular Gas lasers: CO_2, N_2 Lasers, Excimer lasers

Most of the gas lasers are pumped by electrical discharge. Electrons in the discharge tube are accelerated by electric field between the electrodes. These accelerated electrons collide with atoms, ions or molecules in the active media and induce transition to higher energy levels to achieve the condition of population inversion and stimulated emission.

The argon-ion laser (Fig 12), one of a number of ‘ion lasers’, consists of argon at about 1 Torr, through which is passed an electric discharge. The discharge results in the formation of Ar^+ and Ar^{2+} ions in excited states, which undergo a laser transition to a lower state. These ions then revert to their ground states by emitting hard ultraviolet radiation (at 72 nm), and are then neutralized by a seriesof electrodes in the laser cavity. One of the design problems is to find materials that can withstand this damaging residual radiation. There are many lines in the laser transition because the excited ions may make transitions to many lower states, but two strong emissions from Ar^+ are at 488 nm (blue) and 514 nm (green); other transitions occur elsewhere in the visible region, in the infrared, and in the ultraviolet.

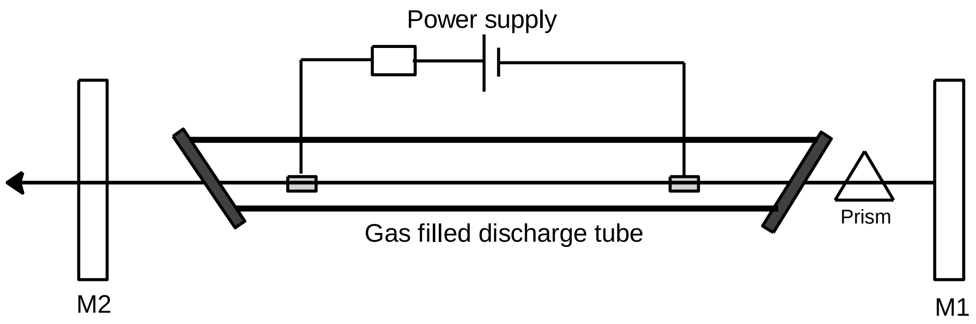


Fig 12: Construction of gas laser system (argon ion laser with prism-based wavelength tuning)

Excimer Laser

Excimers are molecules such as ArF, KrF, XeCl, and so on, that have repulsive or dissociating ground states and are stable in their first excited state. Usually, there are less number of molecules in the ground state; therefore direct pumping from ground state is not possible. Molecules directly form in the first excited electronic state by the combination of energetic halide and rare gas ions. Usually a mixture of halide such as F2 and rare gas such as Ar is filled into the discharge tube. Electrons in the discharge tube dissociate and ionize halide molecules and create negative halide ions. Positive $Ar+$ and negative $F-$ ions react to produce $ArF*$ molecules in the first excited bound state, followed by their transition to the repulsive ground state to commence lasing action. Various excimer lasers are developed in the wavelength range of 120–500 nm with 20−15% efficiency and up to 1 J peak and 200 W average powers. These lasers are widely used in materials processing and characterizations as well as for the pumping of dye lasers.

Applications:

1. Refractive surgery in ophthalmology
2. Gene manipulation in bioengineering.

QUESTIONS

PART-A

1. What is an electromagnetic spectrum?
2. Draw an electromagnetic spectrum with variable energy
3. What is rotational energy?
4. Define basic principle of microwave spectroscopy
5. Write down the selection rule for rotational spectroscopy

6. Define degrees of freedom
7. Which of the following diatomic molecules have a rotational microwave spectrum: IF, O_2, KCl, Cl_2.
8. Identify the molecules that will exhibit a pure rotational absorption microwave spectrum: N_2O, NO_2, $CClF_3$, NF_3, SF_6, CH_4, CO_2.
9. What are the various types of electronic transitions.
10. What is the necessary condition for a molecule to absorb infrared radiation?
11. Calculate vibrational degrees of freedom for CO_2.
12. Calculate fundamental bands for the linear molecules.
13. How many fundamental bands are observed in the IR spectrum of benzene?
14. Define spontaneous emission
15. Define stimulated emission
16. Differences between $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions
17. Define LASER

PART-B

1. Explain in detail about the classification of molecules based on moment of inertia.
2. Explain rotational spectra of diatomic molecules with energy level spectrum.
3. Explain rotational spectra of polyatomic molecules.
4. Calculate J (1 to 3) values of CO molecule.
5. Explain the types of vibrations and its diagrammatic representation.
6. Calculate the force constant of CO molecule having $\bar{\upsilon} = 2143\ \text{cm}^{-1}$
7. Explain the construction, working principle and advantages and disadvantages of diode laser
8. Explain the electronic transitions in organic molecules with suitable examples.
9. Define Beer Lamberts law and derive its mathematical formulae.

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SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT-III – FUNCTIONAL MATERIALS – SCYA1101

1. Introduction

Functional Materials comprises all materials including inorganic, organic, hybrid, nano materials, ceramics, soft materials with specific functions as

- Adaptive Materials: Materials which response to stimuli as sensors, actuators and as energy harvesters.
- Electronic Materials: Materials like semiconductors, dielectrics, ferroelectrics, superconductivity materials used in health care and molecular devices.
- Magnetic Materials: Materials with spintronics, superconductivity and molecular magnets finds its application in diagnosis as body scanner as well in data storage.
- Optical Materials: Materials like lenses, mirrors, polarizers, detectors, modulators used in photonics and in advanced optical technologies.

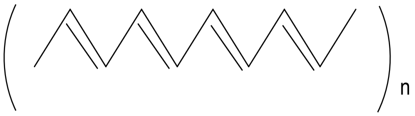
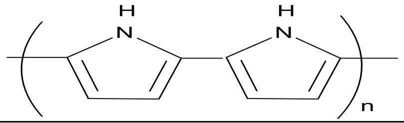
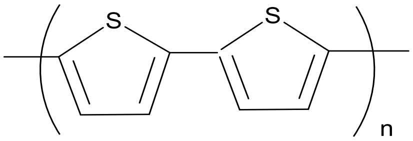
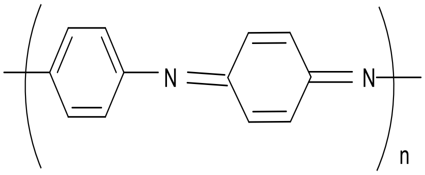
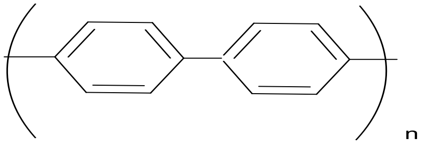
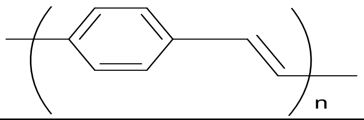
Of these functional materials, electronic materials have attained a giant leap in the last few decades through the development of conducting polymers. These polymers are considered as an alternative to semiconductor silicon based electronic technology. They can be tuned from insulating to semiconducting to metallic by chemical modification and possess unique properties like light weight, flexible, easier processability and fabrication. These materials have in-filtered into our day-to-day life with a wide range of products including consumer goods like LED television, AMOLED (Active Matrix Organic Light Emitting Diode) in cell phones display to their applications in space, aeronautics and non- linear optics. Hence, the conducting polymers with wide applicability and unique properties can be regarded as "Materials of 21st century".

2. Conducting Polymers

Conventional Polymers like polyethylene, polypropylene, polyvinyl chloride etc., are usually characterized by their light weight, ease of fabrication, insulating nature have replaced materials in several areas of application from household water bottles to rockets. Their insulating property has been in renaissance through the invention of certain class of polymers called "Conducting Polymers." Researchers have focused for more than a decade on the synthesis of these polymers as they exhibit semiconducting properties. Conducting polymers possess unique characteristics in their structure by exhibiting conjugation (those possess an extended π bond along the polymeric back bone) and are linear in nature. The increase in conductivity in these polymers can be described as, conventional polymers usually consists of σ bonds and the charge created on any given atom in the polymeric chain is not mobile while in case of conducting polymer, the charges created on the polymeric chain are mobile due to the presence extended π conjugation.

Some of the examples of conducting polymers with their properties are given in Table 1

Table 1: Characteristics of conducting polymer

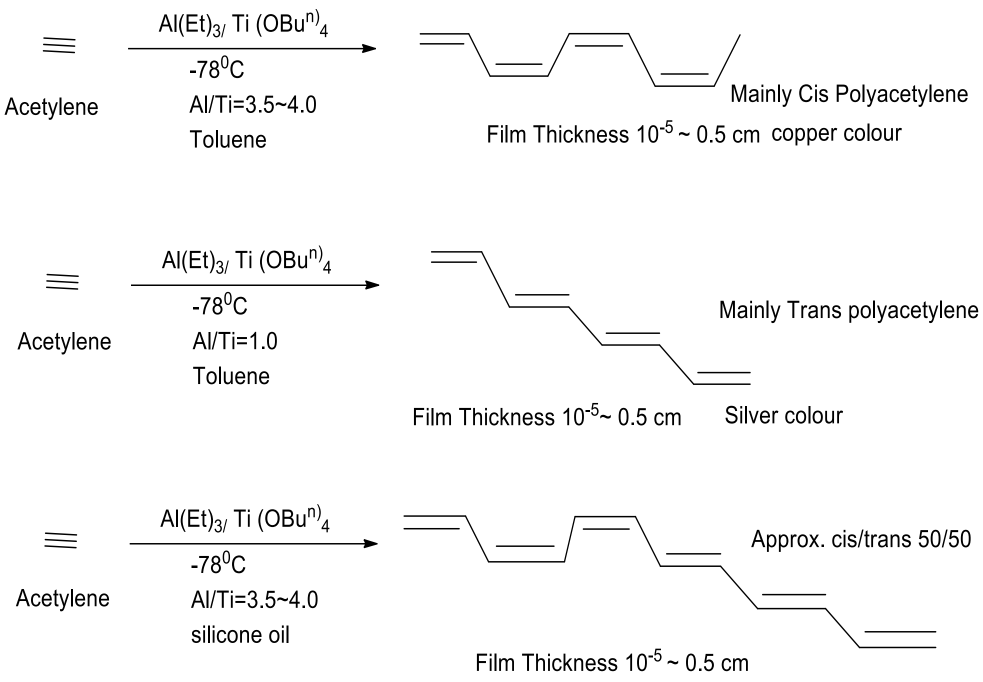
Conducting Polymer	**Structure**	**Band gap (eV)**	**Maximum Conductivity Scm^{-1}**
Trans Polyacetylene		1.5	1.5 □ 10^5
Polypyrrole		3.0	2000
Polythiophene		2.0	100
Polyaniline		3.6	10
Polyphenylene		3.4	1000
Polyphenylene-vinylene		2.32	1000

Examples of Conducting Polymers

A. Polyacetylene (PA)

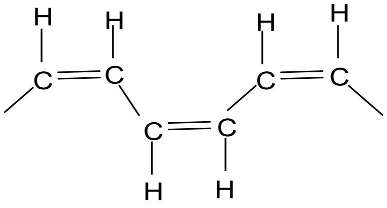
The first conducting polymer synthesized was polyacetylene which dates back to last century. Polyacetylene is the simplest molecular framework possessing conjugated polymer.

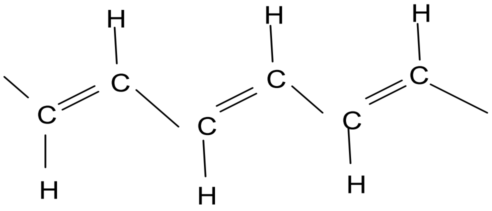
In 1977, Shirakawa and his colleagues (Japan) prepared polyacetylene as shiny metallic film by contacting acetylene gas with a soluble Ziegler-Natta catalyst and their reactions are given below.



Polyacetylene formed can exists in two isomeric forms namely

i. Cis-Polyacetylene: The hydrogen atoms are arranged on same side of C=C bond . 2)Trans Polyacetylene : The hydrogen bonds are arranged alternatively to C=C bond.


Cis Polyacetylene


Trans Polyacetylene

The PA films are insoluble, infusible and are unstable in nature which renders it as an unattractive material for technological applications.

The major resurgence in the discovery of PA has been made through collaboration with MacDiarmid (USA) where the conductivity of the PA is increased by 10 orders of magnitude by a process known as doping. The conduction mechanism in PA by doping was developed by Heeger. H.Shirakawa, AG MacDiarmid and A J Heeger were awarded Nobel prize in Chemistry in the year 2000 for the discovery and development of conductive polymers. A brief biography of the Nobel laureates is given in box 3.1.

B. Polyaniline (PAni)

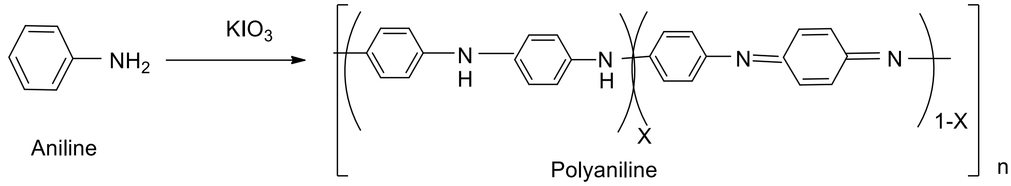
Polyaniline is a aromatic conjugated polymer, synthesized by electrochemical oxidation of aniline using ammonium peroxodisulphate or potassium iodate as oxidizing agent.

Biography of Nobel Laureates in Discovery of Polyacetylene

Alan Graham MacDiarmid was born April 14, 1927, in Masterton, New Zealand. Coming from a self-described “poor family,” he was forced to leave high school at age 16 in order take a part-time job after his father retired . His job allowed him to apply himself as a part-time student and he was able to complete his B.Sc. in 1948. MacDiarmid then received a Fulbright fellowship to attend the University of Wisconsin, earned aa Ph.D. in 1953. MacDiarmid maintained his Chair position at Penn until the end of his career, but also held positions at the University of Texas at Dallas, becoming the James Von Ehr Chair of Science and Technology and professor of chemistry and physics there in 2002.

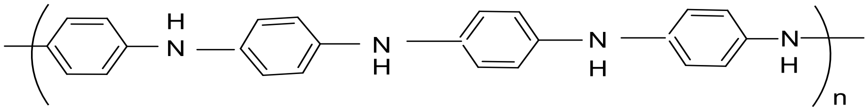
Hideki Shirakawa (1936-) was born August 20, 1936, in Tokyo. Spending his childhood in in the small city of Takayama, he entered Tokyo Institute of Technology in April of 1957 and received a Doctor of Engineering degree in March of 1966. In 1979, he moved to the University of Tsukuba, where he was appointed associate professor. He was later promoted to full professor in 1982 and formally retired from the University of Tsukuba as professor emeritus at the end of March 2000, shortly after being awarded the Nobel Prize in Chemistry with Heeger and MacDiarmid.

Alan Jay Heeger was born January 22, 1936, in Sioux City, Iowa. mathematics . After completing his B.S. in 1957, he began graduate studies in physics at Berkeley, ultimately joining the research group of Alan Portis After completing his Ph.D. in 1982, Heeger moved to the University of California, Santa Barbara (UCSB), where he still actively pursues research in conjugated materials. Learning that MacDiarmid had some experience with sulfurnitride chemistry, he approached him about working together on a study of this new polymer



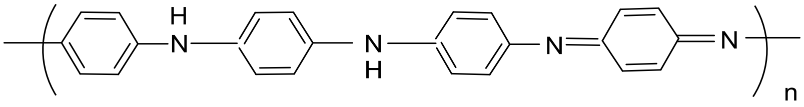
Polyaniline has a unique structure consisting of an alternating arrangement of benzene rings and nitrogen atoms. The nitrogen atoms exist either as an imine (in an sp^2 hybridized state) or as amine(in an sp^3 hybridized state). Depending on the relative concentration of nitrogen, polyaniline exists in three different oxidation state.

i. Leucoemeraldine: When X=1, a completely reduced state of PAni exists, consisting of only benzenoid amine structure.



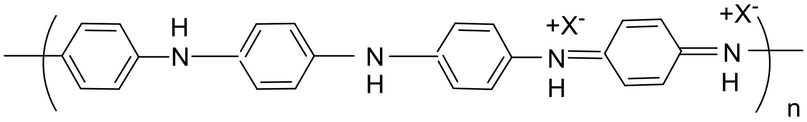
Leucoemeraldine
Pale Brown, Insulating

ii. Emeraldine: When X=0.5, PAni consists of a partially reduced benzenoid amine and partially oxidized quinoid imine.



Emeraldine
Blue, Insulating

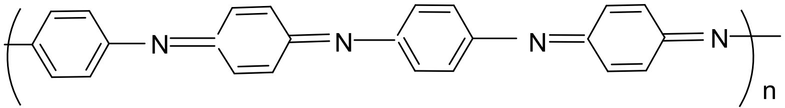
The protonated emeraldine is green in colour and is highly conductive in nature.



Protonated Emeraldine

Green, Partially oxidized
conducting form

iii. Pernigraniline: When X=0, PAni consists of a completely oxidized quinoid imine structure.



Pernigraniline
Black, Insulating

3. Electrical Conductivity in Conjugated Conducting Polymers

The electrical conducting in conducting polymers is different from inorganic semiconductors in two aspects:

1. Polymers are macromolecular in nature and lack long range of orderliness.
2. Doping in a polymer is a charge-transfer process.

Doping

Doping involves a partial redox or non-redox reaction (acid reaction) occurring at the polymeric chain. It is carried out by exposing the polymeric film or powder to dopants. Dopants are chemical species or agents which are used in doping process. a) Redox doping is of two types

i. p-Doping (oxidation Doping): It is an oxidation reaction where an electron is removed from the valence band leaving the polymer with a positive charge.

$$\text{Polymer} + X \longrightarrow [\text{Polymer}]^{n+} + X^{n-} \quad X=I_2, Br_2, AsF_5$$

ii. n-Doping (Reduction doping): It is reduction reaction where an electron is added to the conduction band leaving the polymer with a negative charge.

$$\text{Polymer} + M \longrightarrow [\text{Polymer}]^{n-} + M^{n+} \quad M=\text{Na, Li, K Naphthalide.}$$

iii. Non-Redox doping (Protonic acid): It is an acidic reaction where a proton is added to the polymeric chain leaving the polymer with a positive charge.

$$\text{Polymer} + HCl \longrightarrow [\text{Polymer-H}]^{+} + Cl^{-}$$

These doping reactions occur in conjugated polymers with π electrons, since the electrons can be easily added or removed from the polymeric chain to form polyions which exhibit high electrical conductivity.

Conduction Mechanism in Polymers

The interaction of a polymer unit cell with all its neighbours in a polymeric chain leads to the formation of electronic band. The highest occupied electronic levels or molecular orbitals constitute the valence band(VB) and the lowest unoccupied levels represent the conduction band (CB). The difference in energy between the VB and CB is known as band gap energy which determines the intrinsic electrical property of polymers. On doping, the electrical conductivity of the polymer is increased due to the formation of self-localized excitations such as solitons, polaron and bipolaron (quasi-particles). These particles arises from strong interaction between the charge on the polymeric chain (electron or hole) acquired as a result of doping and the molecular structure.

Thus, the charge carrying species in doped conjugated polymers are not free electrons or holes but quasi-particles which move relatively free through the polymeric chain.

Conduction in PA

The nature of charge carriers and the mechanism of doping in trans-polyacetylene (PA) is explained as follows;

The trans-PA exists in two alternate structures (A and B) with same ground state energies known as degenerate state. When these two degenerate states dimerizes, a structural defect (kink) occurs in the chain with a change in bond alternation. A single unpaired electron exists where the structural defect occurs and it produce an energy level at the centre of the band gap, known as neutral, positive or negative soliton. The neutral soliton carries a single electron which possess 1/2 spin and exhibit paramagnetic behaviour. It can move along the chain without any distortion. In a pure (undoped) trans PA, there are only neutral solitons which are on an average of 1 in every 3000 CH units.

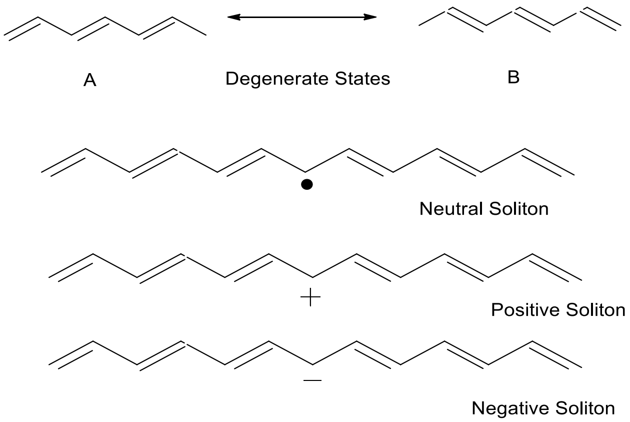


Fig 1: A) and B) Degenerate States of trans-PA C)PA chain with a defect (neutral, Positive and Negative soliton)

When trans-PA is doped a number of neutral solitons is used (at very low doping level) to form charged solitons. In some cases, a charge transfer can occur directly between a doping agent and VB or CB to produce an ion radical in the chain (i.e a defect pair). The mechanism of p and n-doping in trans-PA is as follows and the reactions are given in Fig 2.

During doping, an electron is added (or removed) to the bottom of the conduction band (or from the top of the valence band) of trans-PA, the conduction (valence) band is partially filled and a radical anion (or cation), polaron is formed. The formation of polaron causes the injection of states from the bottom of the CB and top of the VB into the band gap. The polaron carries both charge and spin exhibiting paramagnetic behaviour. The addition (or removal) of second electron on the chain with a negative (positive) polaron results in bipolaron (spinless). The bipolaron further lower their energy by dissociating into two spinless charged soliton (positive charge in p-doping and negative charge in n-doping)which occupies at one-half of the band gap energy. The number of polaron, bipolaron and soliton formed increases with the doping level. At high doping, polaron, bipolaron and soliton near to the individual dopant ions could overlap leading to new band between (or even overlapping) the VB and CB through which electrons can flow. Doping of trans-PA by I_2/CCl_4 introduces positive charges which is delocalized over 12-15 CH units to give positive soliton thereby the conductivity increases from 10^{-7} to 10^{3} S/cm (or by the order of 10^{10}).

Conduction in PAni

The emeraldine base of polyaniline consists of equal proportion of amino (-NH-) and imine (=N-) sites. On doping with acids like HCl, dl-camphor sulphonic acid as given in Fig 3, the imino nitrogen are protonated to form bication salt, bipolaron. It is highly unstable due to the presence of C=N bonds of quinoid imine which dissociates to form polaron. The positive charges on the polaron are delocalized over the entire polymeric chain which are stabilized by resonance. The resulting emeraldine salt has a conductivity of 300 S/cm, increased by the order of 10^{11} magnitude.

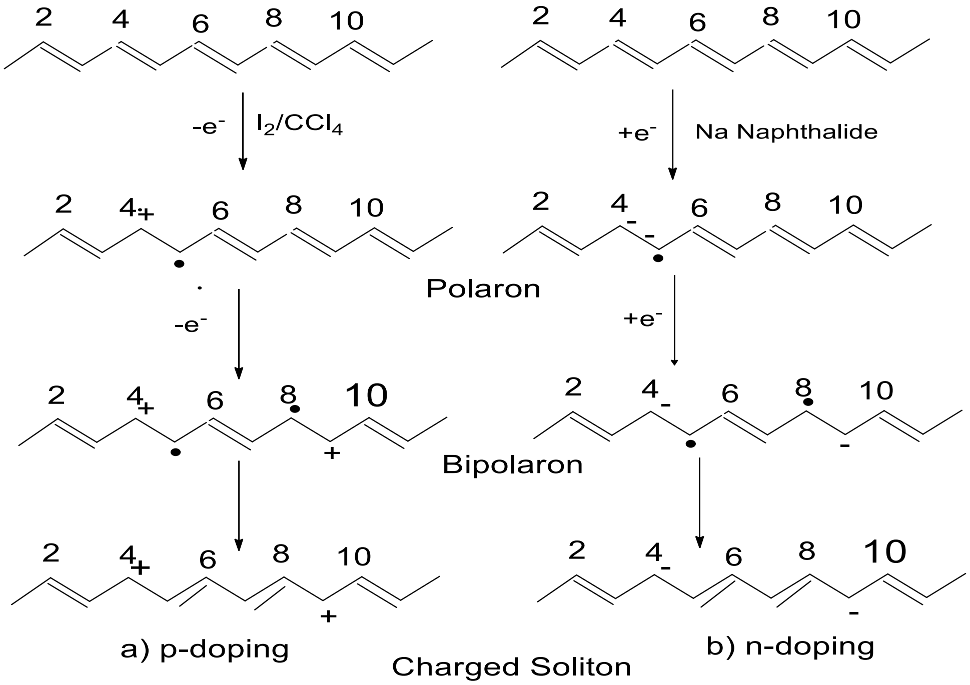


Fig 2: a) p-doping b) n-doping in trans-PA

In general, polymers forming soliton energy level can accomodate either 0, 1 or 2 electrons with unusual spin and charge property. When the electrons are removed (i.e) Zero, a positive soliton of zero spin results. When two electrons are accommodated, a negative soliton of zero spin is observed. Both these charged solitons are non-magnetic. A neutral soliton carries a single electron and exhibits paramagnetic behaviour.

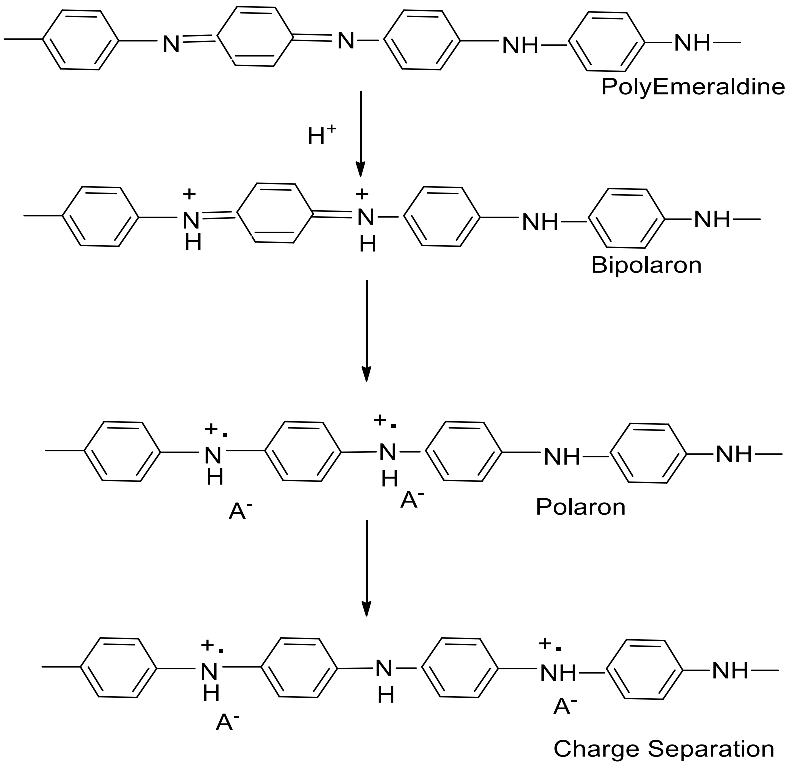
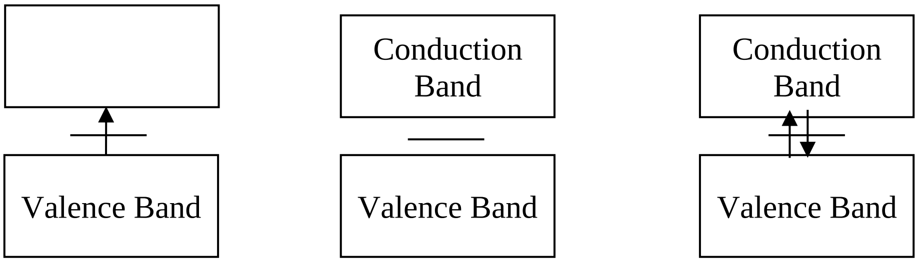


Fig 3: Protonic acid doping in Polyaniline.



a) S^0 b) S^+ c) S^-

Fig 4: Charge and spin separation in a) Neutral Soliton (S^0), b) Positive Soliton (S^+) c) Negative Soliton (S^-)

Factors influencing the electrical conductivity

The conductivity in organic polymers is influenced by the following factors:

1. Conjugation length: Conductivity of the polymer increases with the increase in the length of the polymer chain as well as the number of conjugation.
2. Doping level: Conductivity of the polymer increases with increase in doping level until the saturation point.
3. Temperature: Conductivity of the polymer increases with increase in temperature and becomes constant at a particular temperature.
4. Frequency: Conductivity increases with increase in frequency of current.

Applications of conducting polymer

- In rechargeable light weight batteries
- In optically display devices.
- In electronic devices such as diodes, transistors.
- In solar cells, drug delivery system for human body.
- In molecular wires and switches.
- In photovoltaic devices.
- In antistatic coatings for clothing.

4. Organic Solar Cell (osc)

The process by which light is converted into electricity using conducting polymers is the basis of photovoltaics. A photovoltaic cell consists of a silicon PN junction diode with a glass window at the top surface of P material with nickel plated ring act as positive terminal (anode) and a metal contact at the bottom act as cathode as shown in Fig 5.

Working of Photovoltaic cell

When solar light falls on the photovoltaic cell, the photon excites some of the electrons in the semiconductor to form electron-hole (negative-positive) pairs. since there is an internal electric field (due to p-n structure) these pairs are induced to separate. As a consequence, electrons move to the negative electrode while the holes move to the positive electrode. A conducting wire connects the negative electrode, load and positive electrode in series to form a circuit. As a result, current is generated and is applied to the external load.

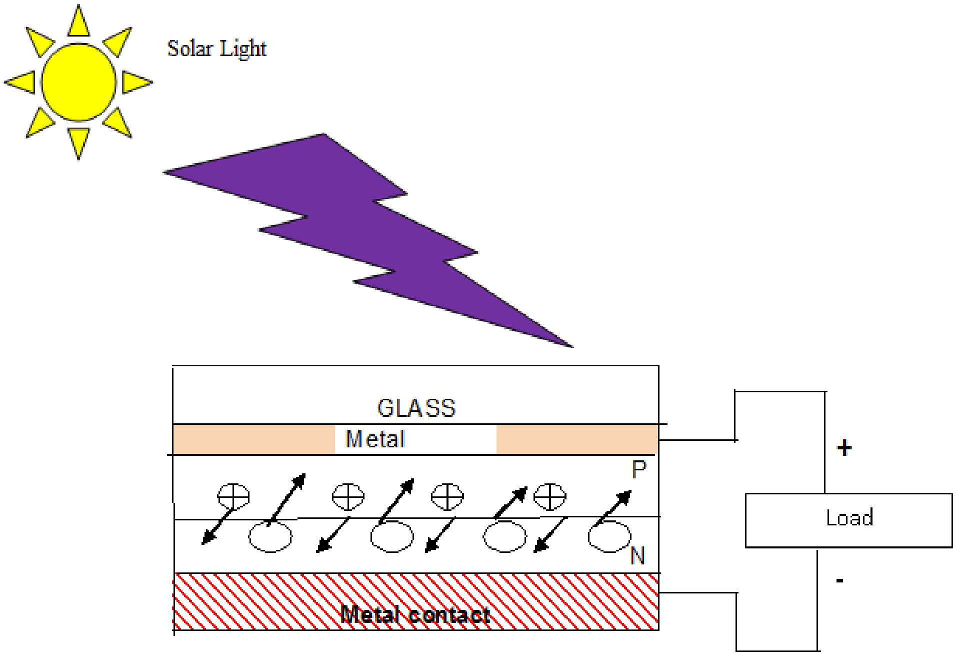


Fig 5: Structure and working of Solar photovoltaic cell

Organic solar cell (OSC) possess same architecture as photovoltaic cell except the PN junction diode is replaced by the doped conducting polymer. The advantages of organic solar cell (OSCs) are it offers low cost solution processing, flexible substrates and high speed processing. The major disadvantage of OSC is the low power conversion efficiency.

Structure of OSC

All organic solar cells have a planar layered structure where the organic active layer is sandwiched between two different electrodes, one of them is transparent conductive Indium tin oxide (ITO) and the other electrode is aluminium. The polymer solar cells have different architectures.

i. Single layer cell: An organic polymer is sandwiched between two electrodes. The photoactive region is very thin and the positive and negative photoexcited charges travel through the same material where recombination losses are high.

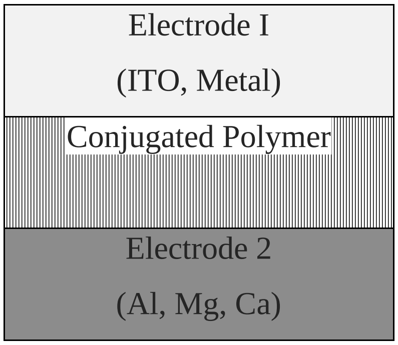


Fig 6: Single Layer organic solar cell.

ii. Bi-layer cell: The sandwiched organic polymer consists of two constituents, electron donor and electron acceptor layer at ITO and Al electrodes respectively. The donor constituents are conjugated polymers of PPV, polythiophene and their derivatives with low band gap energy. The electron acceptor materials are C60 and conjugated polymer with cyano group having strong electron affinity. The lowest occupied molecular orbital (LUMO) level of donor material should be 0.3 -0.4 eV higher than that of acceptor.

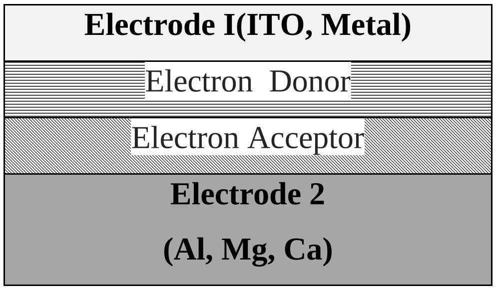


Fig 7: Bi Layer organic solar cell.

iii. Bulk heterojunction: The organic polymer consists of a nanoscale blend of donor and acceptor materials. The size of the blend is of nms allowing excitons to dissociate at the interface. It requires a percolating network that allows charge separation to occur. It has an advantage over other structures as they can be made thick enough for effective photon absorption.

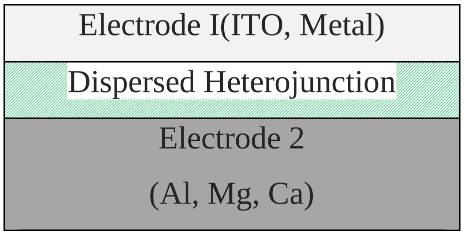


Fig 8: Dispersed heterojunction organic solar cell.

Principle and Working of OSC

The process of conversion of light into electricity by organic polymers takes place in following steps:

1. Exciton generation
2. Exciton diffusion
3. Exciton dissociation
4. Charge transport.

1. Exciton Generation: Absorption of photon from the solar spectrum by organic conducting polymers with bandgap energy 1.1eV - 2.0 eV produces electrostatically coupled electron-hole pairs called excitons.

2. Exciton diffusion: The photogenerated excitons are characterized by small life time of few picoseconds which limits the mobility of excitons to 5-10nm called exciton diffusion length. As the excitons are dissociated within this range, exciton diffusion length play a crucial role in the performance of the OSCs.

3. Exciton dissociation: It refers to splitting of electrostatically bounded electron-hole pair into free charges. The dissociation of excitons occurs at the donor-acceptor interfaces or junctions. The donor and acceptor materials are designed in such a way that there exists a difference in LUMO levels of the donor and acceptor materials. For efficient dissociation, the difference in energy level of LUMO of donor and acceptor should be higher than that of exciton binding energy.

$$\Delta(\mathrm{LUMO}_D - \mathrm{LUMO}_A) > \text{exciton binding energy.}$$

4. Charge transport: The charges produced travel through specific electrode materials which are connected to external circuit. The donor material serves to transport holes while the electrons travel within the acceptor material.

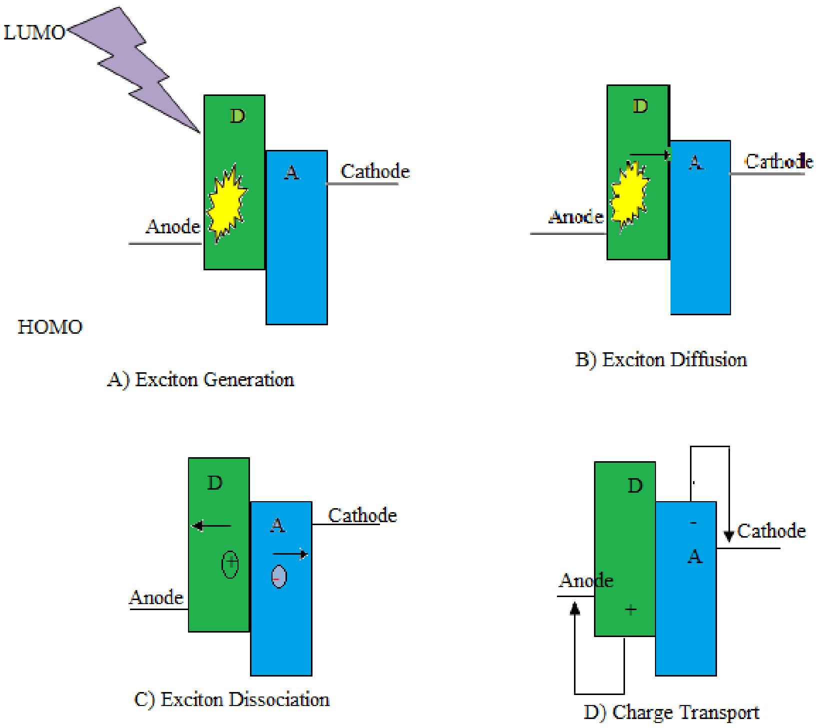


Fig 9: Principle and Working of Organic solar cell.

Advantages of OSC

- The cells are light in weight, flexible and semi-transparent in nature.
- They are 1000 times thinner than silicon solar cells.
- They are easy to integrate and offers short energy payback time.

Disadvantages of OSC

- Low efficiency compare to silicon solar cells.
- They are stable in dark but degrade in light conditions.
- Lifetime is less compare to silicon cells as they degrade rapidly in moisture and air.

3.4.3 Applications of OSC

- Portable power supply.
- Emergency power source.
- Electric Fences.
- Toys, calculator and watches.

5. Organic Light Emitting Diode(oled)

Light Emitting Diode (LED) works on the principle of electroluminescence (The process of converting electricity to light energy is known as electroluminescence.) An electroluminescent structure presented in Fig 10 consists of 4 layers, two inorganic electroluminescent material (doped semiconductor) capable of emitting electrons and holes with two electrodes.

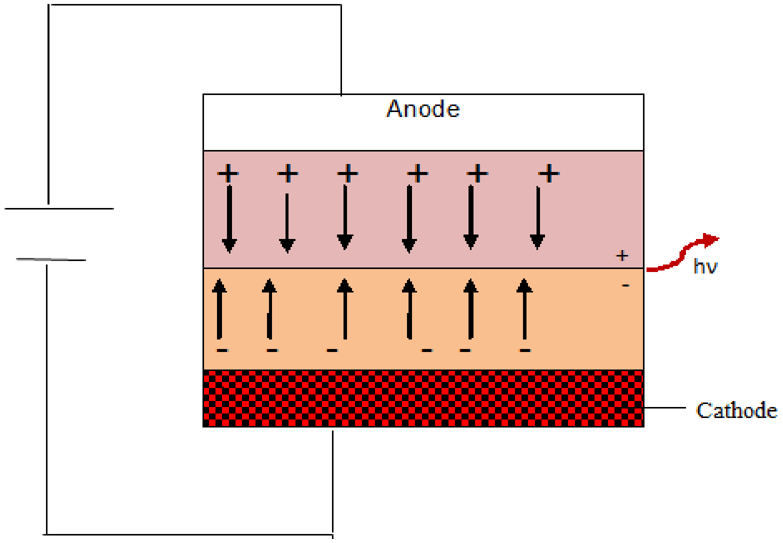


Fig 10: Structure of Electroluminescent Cell

One of the electrode, anode is Indium Tin oxide (ITO) and the other is a metallic layer act as cathode. On applying voltage, holes and electrons are created on the luminescent material connected to anode and cathode respectively. The emission of light occurs by radiative combination of electron-hole pair to form exciton. The relaxation of excess exciton energy occurs by the emission of monochromatic light. When the electroluminescent doped semiconductor is substituted by conjugated polymer with same functionality, the LED is referred as organic light emitted diode (OLED).

Structure of OLED

An OLED is a light emitting diode consists of emissive electroluminescent organic film which emits light in response to electric current. The construction of single layer OLED is represented in Fig 11. An OLED consists of a glass substrate which is coated by a transparent ITO, act as anode. A conjugated polymer (Poly phenylenevinylene (PPV) or Poly alkyl thiophene (PAT) or Poly ethylene dioxythiophene(PEDOT)) is deposited onto the substrate by spin coating technique. On the top of the polymer layer, a metallic layer of Al or Ca is deposited by vacuum evaporation

, forms the cathode. By applying bias voltage at the electrodes, emission of light is obtained through the transparent electrode.

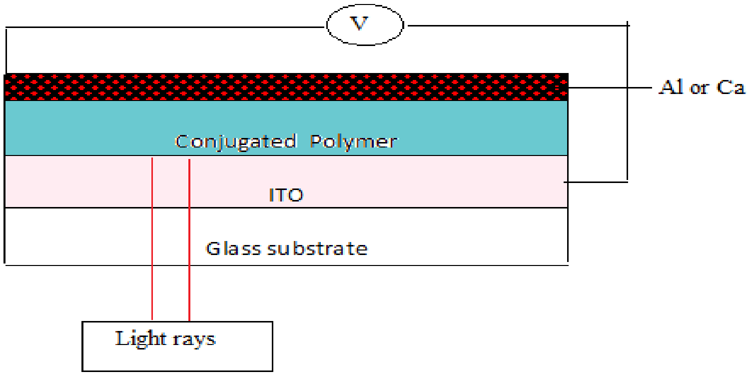


Fig 11: Structure of single layer Organic Light Emitting Diode.

Components of OLED

1. The components of OLED consists of
2. Substrate : It may be plastic, glass which holds the OLED.
3. Transparent Anode: It is a transparent material of ITO which injects holes to the polymeric material .
4. Conjugated Polymer: It is an emissive layer where light is emitted. eg: PPV, PAT, PEDOT.
5. Hole transport layer: It is placed between anode and emissive layer in order to increase the hole transport. eg: Triphenyl amine derivatives.
6. Electron Transport layer: It is placed between cathode and emissive layer and act as hole blocking layer. eg: 1,3,4-Oxadiazole derivatives.
7. Cathode: A metallic layer of Al or Ca which injects electrons to the polymeric material.

Working of OLED

According to Su, Schrieffer and Heeger theory, electron-electron interactions are neglected and the electroluminescent properties of polymeric substances are based on strong electron-phonon interactions. Based on this theory, for non-degenerate ground state polymers, injection of charges leads to the formation of either singly or doubly charged polarons. Neutral species, excitons can be generated either by the fusion of two polarons with opposite charges or by photoexcitation due to electron-hole separation. The steps involved in the operation of OLED is as follows and is illustrated in Fig 12

1. By applying bias voltage, charges of opposite sign are injected into the active polymeric material to form positive and negative polarons (P+ and P-).
2. The charges (P+ or P-)move in the polymer towards oppositively charged electrode, driven by electric field.
3. Polarons of opposite sign combine to generate excitons.
4. The excitons undergoes radiative combination by the emission of monochromatic light.

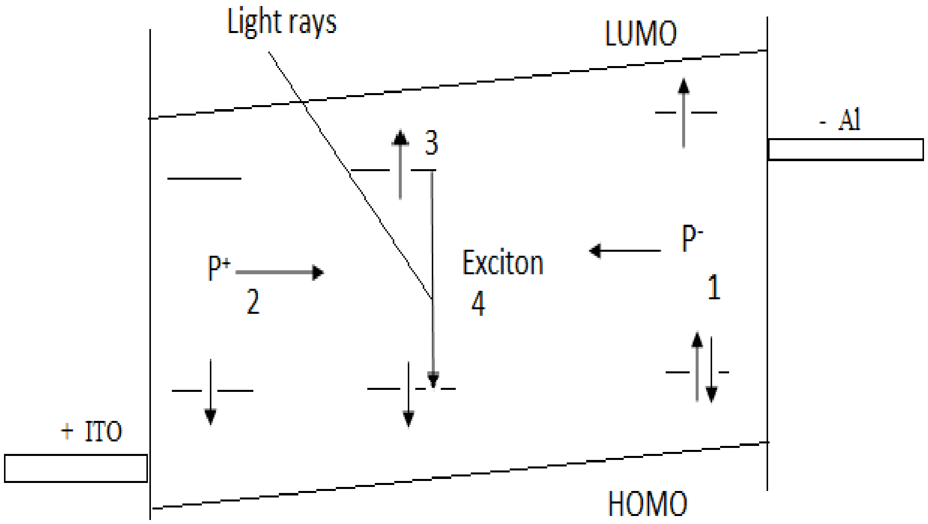


Fig 12: Working of Organic Light Emitting Diode.

The factors controlling the polymeric structures are as follows and it plays a significant role in the development of OLEDs.

1. The band gap of the conducting polymer should be in the range of 2.0- 3.0 eV, is responsible for electroluminescence.
2. The electron affinity and ionization potential of the polymer strongly affects the injection of charges into the electrode.
3. The solid state packing of the polymer influences the stability and emission efficiencies of the polymer.
4. The surface polarity of the polymer is responsible for the adhesion between the active polymer and the electrodes, an important factor in charge injection.
5. The active polymeric layer is resistant to oxidation and temperature for the lifetime of the device.

Advantages of OLED

1. Light weight, flexible and can be easily processed.
2. High Resolution and high reliability.
3. Consumes less power.
4. Highly energy efficient.
5. High levels of brightness and intensity.

Disadvantages of OLED

1. OLEDs exhibit colour imbalance on long usage due to the lifetime of the organic materials.
2. Expensive in nature.
3. Poor resistance to water and moisture.

Applications of OLED

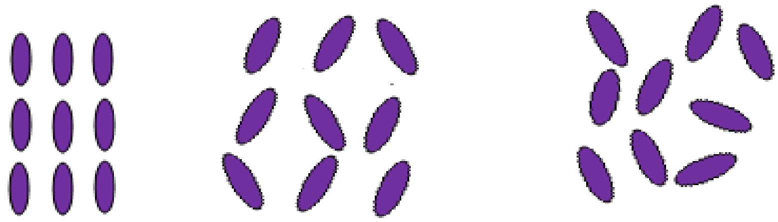
1. Used in flat panel display screen such as cell phones, laptops, digital cameras.
2. Used in remote controls, indicator lights.
3. Used in fibre data communication.

6. Liquid Crystals

Liquid crystals possess unique properties and play an important role in modern technology. In 1988, an Austrian botanist , Friedrich Reinitizer observed that a material, Cholesteryl benzoate shows two melting points. On heating the solid benzoate, it changes into a hazy liquid which on further heating becomes a clear transparent material. Liquid crystals are characterized by rod-like molecular structure with strong dipole and rigidity along the molecular axis. The tendency of the molecules (mesogens) in liquid crystal points to a common axis, called director leads to a condition called anisotropy.

Liquid crystals are highly anisotropic fluids which exists between the boundaries of a solid phase and conventional liquid phase. The structure of the liquid crystal is described by the following parameters:

1. Positional Order: The average molecules or group of molecules exhibits translational symmetry.
2. Orientational Order: The molecules align along the director axis on a long-range basis.
3. Bond orientational order: The adjacent molecules are joined by the line without regular spacing.

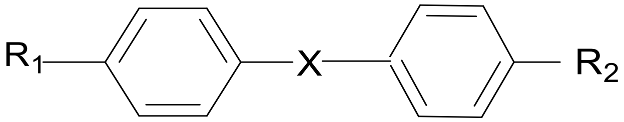


(a) Solid (b) Liquid Crystals (c) Liquids

Fig 13: Molecular orientations in different States of matter.

The chemical structure of the liquid crystal consists of

1. Long, narrow elongated molecules with molecular interaction leading to attraction between the molecules. The most common liquid crystal molecule are of the type:



A central core of benzene rings is linked by X, may be diazo, azoxy, nitrones, esters or Schiff bases. The end groups R_1 and R_2 may be alkyl, alkoxy or acyl group.

2. Presence of unsaturation in their structure increases the polarizability as well as intermolecular attractions for the formation of mesophase.

3. Presence of carboxylic groups at the end of the chain and the absence of bulky functional groups are responsible for the stability of the liquid crystal.

Thermography

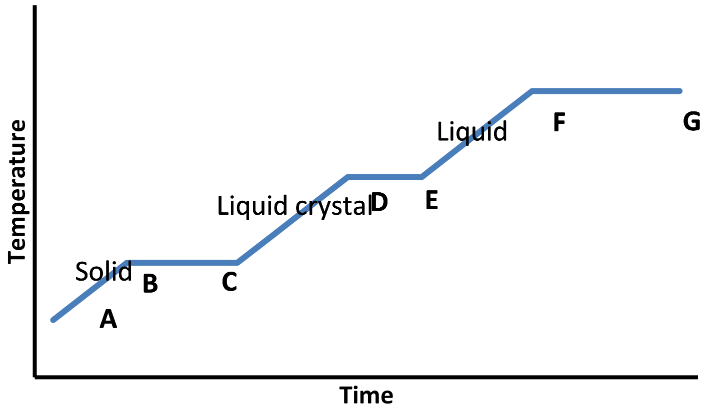


Fig 14: Thermographic behaviourof a solid showing mesomorphism

The phase change observed on heating a solid showing mesomorphic behaviour is represented in the form of temperature-time graph known as thermography. On heating a solid, its temperature starts rising until it changes to liquid crystal as shown by the curve AB in Fig 14.

The temperature now remains constant as long as both the phases (solid and Liquid crystal) are present as presented by the curve BC. When the solid completely changes to liquid crystal, the temperature again starts rising as seen in curve CD until the liquid crystal changes to liquid. The temperature remains constant as long as the two phases (liquid crystal and liquid) are present together as seen in curve DE. When the liquid crystal completely changes to liquid, the temperature again starts rising (curve EF) and continues till it reaches a vapour state. The temperature again becomes constant as long as the liquid and vapour are present together (Curve FG).

Classification of Liquid Crystal

Liquid crystals are states of matter consisting of long range molecules, exhibiting optical activity, ability to form mono crystals in the presence of electric or magnetic field and are sensitive to temperature. They are broadly classified into two types:

1. Thermotropic liquid crystals: They are formed by the variation of temperature and is of three types: a. Nematic structure b. Cholesteric structure C. Smectic

a) Nematic Structure: The molecules in nematic structure are arranged parallel or nearly parallel to each other along the long molecular axes. The structure is one dimensional and are mobile in three directions. It is the highest temperature mesophase in thermotropic liquid crystal. The molecules possess no translational order with rod-like molecules tend to align parallel to each other with uniaxial symmetry. Eg: p-methoxybenzylidene-p'-n-butyl aniline (MBRA), p-azoxyanisole (PAA), p-n-hexyl-p'-cyanobiphenyl, p-quinquephenyl.

b) Cholesteric Structure: It is composed of nematic mesogenic molecules containing a chiral centre, which produces intermolecular forces that favours alignment between molecules at a slight angle to one another. It is a stack of two-dimensional nematic -like layers forming a continuous helical pattern. A byproduct of the helical structure has the ability to selectively reflect colour light at wavelength in the visible spectrum equal to the pitch length (the distance the director takes to rotate one full turn in the helix). Eg: Cholesterylnonanoate, 2-methylbutyl-pp(p'-methoxybenzylidene-amino) cinnamate.

c) Smectic structure: The word "smectic " is derived from the Greek word for soap. The molecules show a degree of translational order and tend to align themselves in layers or planes. There are eight sematic structures observed and their properties with characteristics are given in the Table. 3.2

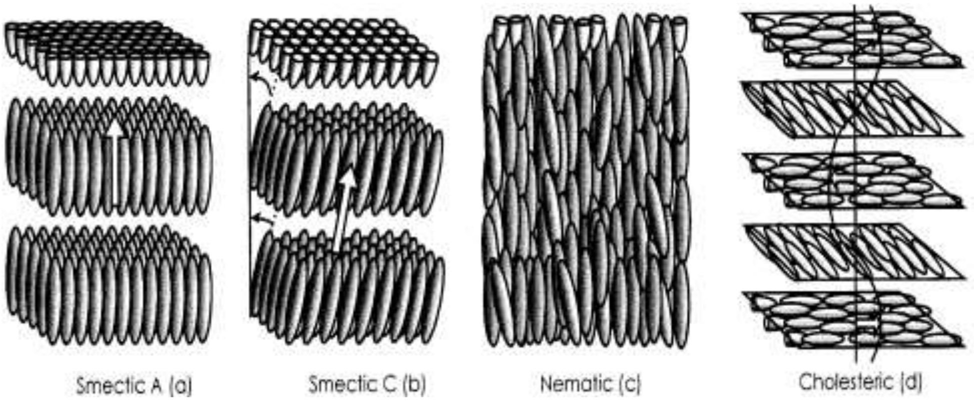


Fig 15 : Molecular Orientation in Smectic, Nematic and Cholesteric phase.

Table 3.2 Characteristic Features of Smectic A-H Liquid crystal structures.

Unstructured Smectics	**Molecular Organization**	**Optical Properties**	
		Optical figure	**Textures**
Smectic A	Layer structure, Molecular axes are orthogonal to the layers, Random arrangement of mesogens within the layers. Eg: ethyl p-(p'-phenylbenzal amino) benzoate	Uniaxial Positive	Focal conic (Fan shaped or polygon), Homogeneous, pseudoisotropic
Smectic C	Layer structure, Molecular axes are titled to the layers, Random arrangement of mesogens within the layer Eg: p-n-octyloxybenzoic acid	Biaxially positive	Broken focal conic, Homogeneous
Smectic D	Cubic Eg: p'-n-octadecyloxy-3'-nitrodiphenyl-p-carboxylic acid	Isotropic	Mosaic
Smectic F	Layer structure Eg: 2-(p-pentylphenyl)5-(p-pentyloxyphenyl) pyrimidine	Uniaxially positive	Broken focal conic with concentric axes
Structured Smectics			

Unstructured Smectics	**Molecular Organization**	**Optical Properties**	
		Optical figure	**Textures**
Smectic B	Layer structure, Molecular axes are orthogonal or titled to the layers, hexagonal arrangement of mesogens within the layers. Eg: ethyl p-ethoxybenzal-p'-aminocinnamate	Uniaxial or biaxial positive	Mosaic, pseudoisotropic and Homogeneous
Smectic E	Layer structure, Molecular axes are orthogonal to the layers, ordered arrangement of mesogens within the layers. Eg: diethylp-terphenyl-p,p''-carboxylate	Uniaxial positive	Mosaic, pseudoisotropic
Smectic G	Layered structure with ordered arrangement within the layers Eg: 2-(p-pentylphenyl)-5-(p-Pentyloxyphenyl) pyrimidine	Uniaxial positive	Mosaic
Smectic H	Layered structure with ordered arrangement within the layers Eg: 4-butyloxybenzl4-ethylaniline	Uniaxial or biaxial positive	Mosaic

2. Lyotropic Liquid crystal: Lyotropicmesophases occur in concentrated solution of rod-like molecules in an isotropic solvent , water. They are important in soaps, gels and colloids. The amphiphilic soap molecules are arranged in bilayer structure with a minimum contact between the hydrocarbon chain and the water molecules.

There are also lamellar, cubic and hexagonal arrangement of amphiphilic molecules in water solution. Eg: sodium stearate, α-Lecithin

7. Liquid Crystal Display(LCD)

Liquid crystal technology has been applied in many areas of science and device technology. They are used as displays in digital wrist-watches, calculators, television displays and panel meters. They can be used to record, store and display images.

The liquid crystal cell design shown in Fig 16 consists of a thin film of liquid crystal at room temperature which is sandwiched between two electrodes (glass coated with metal or ITO).

The thickness of the liquid crystal film is 6-25 micrometers and is controlled by a glass spacer which is chemically inert. The cell is hermetically sealed in order to eliminate oxygen and moisture both of which chemically attacked by the liquid crystal.

Principle

A thin film of liquid crystal is placed between two sheets of glass, one of which is coated with an electrically conductive material (electrode) as shown in Fig 17. When an electric current is not applied, the molecules are uniformly oriented so that the light can pass through the cell. When the current is applied, the molecular alignment changes and the cell appears opaque or dark. Hence, a number is displaced in black against a silvery background.

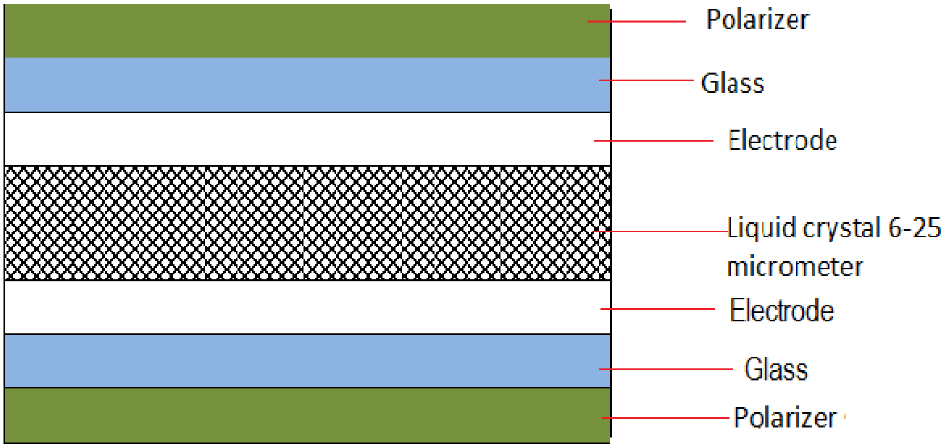


Fig 16: Design of Liquid crystal cell.

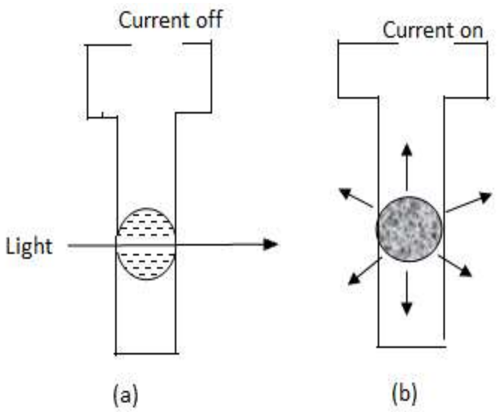
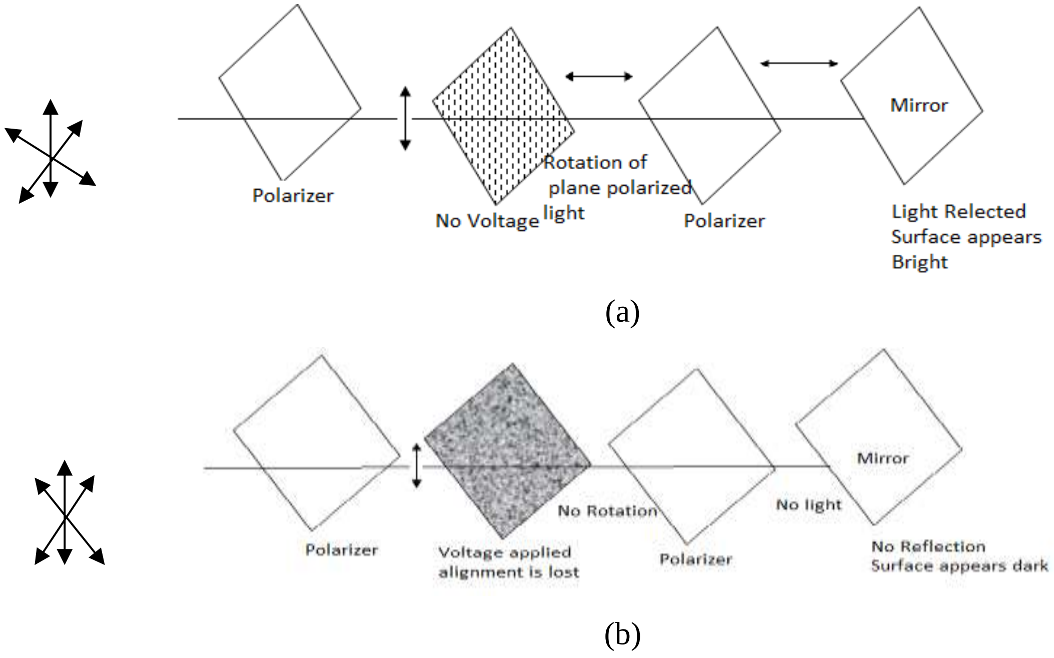


Fig 17: Principle of Liquid Crystal cell. (a) Light passes through Nematic crystal (b) Light is scattered due to disorderliness of the molecules.

Working

The cell with the nematic liquid crystal is placed between the two crossed polarizer as shown in Fig 18. Polarized light entering the cell follows the twist of the nematic liquid crystal and is rotated 90^0 allowing the passage of light through the second polarizer. When an electric field is applied, the molecular alignment in the liquid crystal changes in such as a way that polarization is not altered and no light is transmitted. Hence, if a mirror is placed behind the second polarizer it appears black or if a electrode is shaped in a numeric pattern of segment is placed , then a numeric display will appear on a black back ground on applying the current.



(a)

(b)

Fig 18: Working of Liquid crystal display . (a) in the absence of electric field (b) in the presence of electric field.

There are two modes by which liquid crystal operates namely 1) Dynamic scattering and 2) field-effect scattering.1) In dynamic scattering, when the electric field is not applied, the cell containing twisted nematic liquid crystals is transparent. On applying the electric field, the cell becomes opaque. The cell is prepared by rubbing the glass surface directionally or by chemically treating the surface by adding a chiral compound to nematic liquid crystals. Digital display are made by photoetching a seven-segment pattern onto one of the ITO coated onto glass electrodes. 2) In Field-effect display is mostly used in watch and pocket-calculator displays. A liquid crystal watch displays hours and minutes, the quartz crystal controls the oscillating circuit with a frequency of 32,768 Hz. Each of the time pulses is decoded to give outputs that are needed for seven-segment display.

Advantages of LCD

- Less power consumption
- Better clarity even in the presence of bright light.

Disadvantages of LCD:

- LCD can be viewed up to 165^0 and the picture suffers from side.
- Non-flexible .

Compare and contrast between LCD and OLED.

- OLEDs displays are light in weight, flexible and are in deeper-blacks compare to LCD.
- OLED offers a much better viewing angle at 170^0 while LCD can be viewed up to 165^0 and the picture suffers from side.
- OLEDS offers high contrast ratio, sharper picture and fast response time compare to LCD.
- OLEDs consumes less power than LCD.
- No geographical constraints with OLED while LCD screens lose contrast at high temperature and lose brightness and speed at low temperature environment.
- OLED consists organic compounds which emits light in response to electric field while LCD uses twist and untwist mechanism in response to electric field.
- Both OLED and LCD are vulnerable to water damage and degrades more rapidly in the presence of oxygen.
- Both OLED and LCD have poor readability and display in bright ambient light.
- Pixels get stuck in both OLED and LCD either through usage or during initial manufacturing process.

QUESTIONS

PART-A

1.What are conducting Polymers?

2.Define doping.

3.Give the isomeric forms of PA.

4.Draw the different oxidation states of polyaniline.

5.What are solitons?

6.Differentiate soliton and polaron.

7.Define Electroluminescence.

8.Give the merits and demerits of OLED.

9.What are excitons?

10. What is an organic photovoltaics?

11. What are the advantages and limitations of OSC?

12. What are liquid crystal?

13. Classify liquid crystals.

14. Differentiate between thermotropic and lyotropic liquid crystals.

15. Compare OLED and LCD.

PART-B

1.Describe the synthesis of polyacetylene and explain its isomeric forms.

2.Describe electronic conduction in conjugated conducting polymers.

3.Explain in detail the mechanism of p-doping in trans-PA.

4.Explain in detail the mechanism of n-doping in trans-PA.

5.Describe the mechanism of protonic acid doping in polyaniline.

6.Explain the principle, construction and working of OLED.

7.Describe the construction and working of OSC.

8.Explain in detail the classification of liquid crystals with their characteristics.

9.Give a detailed account on liquid crystal display.

10. Write short note on polyaniline.

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SCHOOL OF SCIENCE AND HUMANITIES
DEPARTMENT OF CHEMISTRY

UNIT-IV – Carbon Materials for Health, Stealth & Energy – SCYA1101

1. Introduction to Carbon and its Materials

Carbon (C) is a nonmetallic element belonging to Group 14 (IV a) of the periodic table. Though it makes only upto 0.025% of the earth's crust, it forms more compounds than all the other elements combined. The cosmic product of the "burning" of three helium nuclei of atomic number 4 is the carbon nucleus of atomic number 12. Elemental carbon is a minor component on the earth's crust. However, carbon compounds form minerals such as dolomite, magnesite, marble and limestone by combining with the carbonates of calcium and magnesium. Carbon occurs widely in the form of coal and as organic compounds in the form of petroleum, natural gas, plant and animal tissue. Carbon gets recycled through carbon cycle where the carbon dioxide present in the atmosphere is converted into carbohydrates by plants during photosynthesis and the reverse reaction of the release of the carbon dioxide back into the atmosphere during metabolism by animals. More than a million carbon compounds are known to exist and several new carbon compounds are getting added to the already existing list on a day to day basis. This diversity and complexity is due to the tendency of carbon atoms for bonding with each other in forming ring, chain and three dimensional conformations and also due to its capacity to bond with other atoms.

Allotropes of Carbon

Elemental carbon exists in several forms having different physical properties. The well known allotropes are graphite and diamond. They differ in their physical properties due to differential arrangements of carbon atoms in their structure. Diamond and graphite occur naturally on earth and are chemically inert. Diamond (composed of a three-dimensional crystalline array of carbon atoms) is the hardest naturally occurring substance and is a poor conductor of heat and electricity. Graphite (composed of stacked sheets of two-dimensional hexagonal arrays of carbon atoms), on the other hand, is soft and slippery and is a good conductor of heat and electricity. The third allotrope of carbon is fullerene, consisting of a variety of molecules made of only carbon atoms. Spheroidal, closed-cage fullerenes are called buckminsterfullerenes or buckyballs. Cylindrical fullerenes are called carbon nanotubes (CNTs). They were discovered in 1985 while simulating the chemical reactions occurring in the atmosphere of giant stars under laboratory conditions. Fourth form of carbon molecule which is crystalline and magnetic is the Q-carbon. They are also synthetic and the scientists have speculated its formation within the planetary cores containing hot environmental conditions. Other types of carbon molecules which are amorphous or are less crystalline are carbon black, charcoal, lamp black, coal and coke.

2. Fullerenes

Fullerene or Buckminsterfullerene denotes a series of hollow carbon molecules forming either a closed cage ("buckyballs") or a cylinder (carbon "nanotubes") structure. Fullerene was found to have the structure of a truncated icosahedron and was first discovered by Sir Harold W. Kroto, Richard E. Smalley and Robert F. Curl in the year 1985. During an experiment with laser to vaporize graphite rods in the atmosphere of helium, the chemists obtained a cage like molecules composed of 60 carbon atoms (C_{60}) joined by single or double bonds to form a hollow sphere comprising of 12 pentagonal faces and 20 hexagonal faces, a structure resembling a soccer ball. The C_{60} molecule was named buckminsterfullerene (or buckyball) after the American architect R. Buckminster Fuller constructed a geodesic dome on the same structural principles. The most stable form of a carbon aggregate containing several thousands of atoms is found to be the closed bucky ball. Discovery of fullerenes have led to an entirely new understanding of the behavior of sheet materials and their properties.

Fig 1: Buckminsterfullerene (C_{60})

Studies on fullerenes indicated that C_{60} and C_{70} are exceptionally stable and provided convincing evidence for the cage structure proposal. There were developments in the discovery of other metastable species, such as C_{28}, C_{36}, and C_{50} and also confirmed the presence of "endohedral" complexes, in which an atom is trapped inside the cage and the size of the entrapped atom determining the size of the smallest surrounding possible cage.

Fullerenes are the only pure, finite form of carbon which due to its high symmetry, need no atoms to satisfy their surface chemical bonding requirements as in the case of other allotropes of carbon such as the diamond and graphite.

Related to this are the carbon "onions" consisting of carbon cages one inside the other. They have millions of carbon particles in dozens of concentric shells.

Preparation

The first method of production of fullerenes was by laser vapourization of carbon in an inert atmosphere. This method resulted in the synthesis of microscopic amounts of fullerenes. In the year 1990, a new apparatus was developed by Wolfgang Krätschmer and Donald R. Huffman where an arc was used to vaporize graphite to produce fullerenes in substantial yield. Macroscopic quantities of fullerenes can be synthesized by this method. Metals like alkali, alkaline earth metals and lanthanoids can be trapped in a fullerene cage by vaporizing graphite rods impregnated with the selected metal.

Method of Synthesis

Fullerenes are produced by Kratschmer–Huffman method. It is a straightforward and low cost method for generating large quantities of fullerene containing carbon soot. It consists of a chamber which is filled with helium gas at a pressure of 100 torr. An electric arc is produced by a power supply for 10-15 seconds. This results in the vapourization of graphite to form soot inside the chamber. The chamber is then cooled for 5-10 minutes and the pressure inside is brought down to atmospheric pressure. By scraping the deposited soot, around 10% yield of C_{60} can be obtained. The fullerenes in the soot can be extracted by dissolving it in a small amount of toluene. After extraction, toluene is removed by rotary evaporator which leave behind a solid mixture of mostly C_{60} along with small amounts of larger fullerenes. Pure C_{60} can be obtained by liquid chromatography where the mixture is dissolved in toluene and by passing through a column of activated charcoal mixture of silica gel, the magenta colored C_{60} comes out first followed by the red colored C_{70}. The colored solutions are collected separately and the toluene is removed using rotary evaporator.

In the Krätschmer-Huffman (KH) experiment, carbon radicals are produced by slow evaporation of a resistively heated graphite rod where the density of the carbon vapour is far lower than that obtained with the pulsed laser vaporization. Also, the rate of cooling of the condensing carbon vapour is much slower in the KH method that greatly assists the clustering in the critical size range to form C_{60}. By adjusting the helium buffer gas pressure, the rate of migration of the carbon vapours from the hot graphite rod can be controlled for the C_{60} formation. The experimental factors that can be modified to maximize the yield of the fullerene clusters in the soot are the vaporization current density and the helium partial pressure.

Another method of synthesis involves the use of AC (alternating current) or DC (direct current) to produce C_{60} and the other fullerenes in good yield and is followed in the commercial synthesis of fullerenes.

Other techniques for the synthesis of fullerenes include hydrocarbon combustion, low-pressure helium sputtering, electron beam evaporation and inductively coupled RF evaporation for the vaporization of the graphite targets.

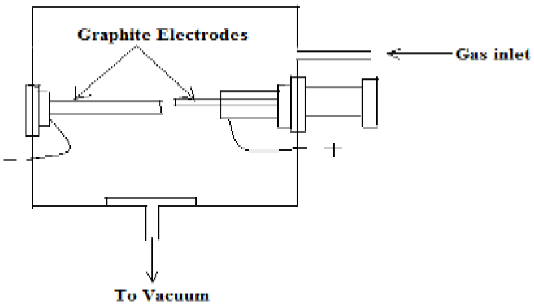

Fig 2: Synthesis of fullerenes

Properties

In fullerene, each carbon is bonded to three other carbom atoms and are sp^2 hybridised. The C_{60} molecule has two bond lengths – the 6:6 ring bonds are the double bonds and are shorter than 6:5 bonds. C_{60} molecule is not superaromatic as it tends to avoid double bonds in the pentagonal rings, resulting in poor electron delocalization. Hence it behaves as an electron deficient alkene and therefore reacts readily with electron rich species. The molecule can readily accept and donate electrons. The molecule can readily add atoms of hydrogen and halogens. The halogen groups can be replaced by other functional groups, such as phenyl, thus opening new routes to the synthesis of wide range of novel fullerene derivatives exhibiting advanced materials behaviour.

Important crystalline compounds of C_{60} with alkali and alkaline earth metals have shown to exhibit superconductivity at relatively high temperatures above 19 K. Superconductivity is observed in the range of 19-40 K, equivalent to -254 to -233^{o}C or -425 to -387^{o}F.

Metals can be physically trapped in a fullerene cage ($M@C_{60}$) and the resulting compounds have been extensively studied. Alkali, alkaline earth metals and early lanthanoides may be trapped by fullerenes cages by using graphite rods containing the metal.

Fullerenes are soluble in common solvents such as benzene, toluene and chloroform.

Applications

Fullerene applications are wide ranging from additives to polymers, photoconductors, photoresists and from bio-active agents to cosmetics. Buckminsterfullerenes have a wide range of electrical properties. It may alternately exist in insulating, conducting, semiconducting, or superconducting forms.

- Fullerenes are active molecules and are used as antioxidants as they can readily react with radicals due to its high affinity for electrons. This property is due to the presence of large number of conjugated double bonds. Fullerenes have low energy unoccupied molecular orbital and can react with a number of radicals. A single C_{60} molecule can interact with upto 34 methyl radicals and therefore is called “radical sponge”. Radical sponge is added to cosmetics for preventing skin damage and premature aging without any side effects.
- Fullerenes are used as antiviral agents. This application is due to its unique molecular structure, antioxidant effect and biological compatibility. The important and the most exciting aspect of fullerene is its ability to suppress the replication of human immunodeficiency virus (HIV) so as to delay the onset of the acquired immunodeficiency syndrome (AIDS).
- Fullerenes form conjugates with proteins and DNA which has a potential application in developing anticancer therapy. Fullerenes get excited upon light irradiation and while returning to the ground state they releases energy which splits up oxygen to generate singlet oxygen that is cytotoxic in nature.
- Fullerenes are a class of inorganic carriers showing good biocompatibility, greater selectivity, retain biological activity and can undergo easy diffusion. Fullerenes are used in the delivery of hydrophobic drugs for their slow release with safety and great efficacy at the site of action. The surface of fullerene is covered with a chemotherapeutic agent which gets transported and target the cancer cell.
- Fullerene reagent forms a protective layer on DNA and helps in extending the life of DNA of the endosomes.
- Fullerenes are excellent electron acceptors and are used in organic photovoltaic cells in complexed and polymer forms to produce bulk heterojunctions.
- Fullerenes have optical limiting properties and are used in protective eye wear and sensors for protecting the eyes or the sensor.

- A Fullerene molecule can hold upto 36 hydrogen atoms during the breaking and the formation of the C=C bonds. The color of the hydrogenated fullerenes changes from black to brown, red, orange and finally to yellow depending on the increase in the hydrogen content. These materials are highly promising in the development of a better, safer and more efficient hydrogen storage devices.
- Fullerenes can form lightweight metals with greater tensile strength without compromising on the ductility of the metal. This is due to the small size and high reactivity of the sp^2 hybridized carbon atom. This enables dispersion strengthening metal matrix by the interaction of fullerenes with the metals.
- Closed fullerene structures containing sulfides of tungsten and molybdenum are found to exihibit excellent solid-lubricant properties. They act as dry lubricants in coating application.

3. Vander Waals Solid

A. Graphene

Graphene is the thinnest compound known to man at one atom thick. It is the lightest material known (with 1 square meter weighing around 0.77 mg), the strongest compound discovered (100-300 times stronger than steel with a tensile strength of 130 GPa and Young's modulus of 1 TPa), the best conductor of heat at room temperature and also the best conductor of electricity. Graphene has uniform light absorbing ability across the visible and near-infrared parts of the spectrum.

Structure of Graphene

Graphene is a monolayer of carbon atoms, tightly bound in a honeycomb lattice. It is an allotrope of carbon in the form of a plane of sp^2 hybridized carbon atoms with a molecular bond length of 0.142 nm. Layers of graphene stacked on top of each other form graphite with an interplanar spacing of 0.335 nm. The layers of graphene are held together by van der Waals forces, which can overcome during exfoliation of graphene from graphite.

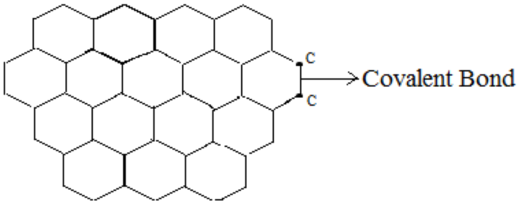

Fig 3: Structure of Graphene

Preparation

Graphene was synthesized first by chemical vapour deposition (CVD) method. CVD method is an expensive and complex process which involves the use of toxic chemicals to grow graphene as a monolayer by exposing platinum, nickel or titanium carbide to ethylene or benzene at high temperatures. This method had many drawbacks that made graphene unavailable for developmental research and commercial uses. However, studies on the graphene's interfacial adhesive energy has proved the possible separation of graphene effectively even from metallic surfaces thereby reducing the toxic waste that gets generated during the synthesis. Consistent research is being carried out to produce graphene on custom substrates with control over impurities such as ripples, doping levels, domain size and relative crystallographic orientation of the graphene layers.

B. Graphene Oxide

Graphene oxide is a material consisting of a monomolecular layer of graphite with various oxygen functionalities such as epoxide, carbonyl, carboxyl and hydroxyl groups. Graphene oxide is an exfoliated form of graphite oxide in water using sonification, ultimately producing single or few layer of graphene called graphene oxide (GO). Graphene oxide is a dispersion consisting of a few layers of flakes or monolayer flakes. The most common method of producing graphite oxide is the Hummers or the Offeman method in which graphite is treated with a mixture of sulphuric acid, sodium nitrate and potassium permanganate. Most common method of preparation of graphite oxide is by the oxidation of graphite using oxidising agents like potassium permanganate in sulfuric acid. Sodium nitrate is now replaced with a combination of phosphoric acid and sulphuric acid and has been found to be more efficient with an increase in the oxidation level upto 70%. Graphene oxide is a by-product of this oxidation where the interplanar spacing between the layers of graphite gets increased. The main difference between graphite oxide and graphene oxide is the interplanar spacing between the individual atomic layers of the compounds, caused by water intercalation which disrupts the sp^2 bonding network and thereby making it an electrical insulator. During oxidation, oxygenated functionalities are introduced in the graphite structure which not only expand the layer separation but also makes the material hydrophilic. The main difference between graphite oxide and graphene oxide is, thus, the number of layers. Chemical reduction of graphene oxide is currently viewed as the most suitable method of mass production of graphene.

Properties

The important advantage of graphene oxide is its easy dispersibility in water and other organic solvents. Its dispersibility in different matrices, due to the presence of the oxygen functionalities, is a very important property while mixing the material with ceramic or polymer matrices for the improved mechanical and electrical properties. Graphene oxide's properties can be altered by introducing functional groups which results in a chemically modified graphenes with more adaptable properties and makes it useful for various applications.

For example, substituted amines are introduced for the organic covalent functionalization in order to increase the dispersibility of the chemically modified graphenes in organic solvents for its utilization in optoelectronics.

C. Reduced Graphene Oxide

Reduced graphene oxide (rGO) is prepared by reduction of graphene oxide by thermal, chemical or electrical treatment methods. It can also be prepared by reducing the electrically insulating graphene oxide using hydrazine. Due to the toxic nature of hydrazine, alternatives to hydrazine including $NaBH_4$, ascorbic acid and HI have been used. Different reducing agents results in various carbon to oxygen ratio and chemical compositions in rGO. Electrochemical reduction of graphene oxide is a method that has been shown to form very high quality reduced graphene oxide, having identical structure similar to pristine graphene. The reduced graphene oxide resembles graphene and there is always some oxygen functional groups inside or on the surface of the reduced graphene oxide causing structural defects.

Properties

rGO can be made as a thin film from an aqueous dispersion of GO in water and has moderate conductivity. Hence it is attractive for use in electronic devices. Graphene oxide act as an electrical insulator due to the disruption of the sp^2 bonding networks. For increasing the conductivity, graphene oxide has to be reduced during which the honeycomb hexagonal lattice would be recovered. This reduced graphene oxide is difficult to disperse due to its tendency to form aggregates.

Applications

Carbon forms the basis for all known life on earth, making graphene potentially an eco-friendly, sustainable solution for an almost limitless number of applications. Applications within different scientific disciplines have exploded since discovery of graphene with huge impact being made in high-frequency electronics, bio, chemical and magnetic sensors, ultra-wide bandwidth photodetectors and energy storage and generation. Other promising areas of application are composites, energy, telecommunications, electronics, sensors and imaging and biomedical technologies.

Nanocomposites of rGO have been used for high capacity energy storage in lithium ion batteries. Electrically insulating metal oxide nanoparticles adsorbed onto rGO has been found to increase the performance of these materials in batteries. Increased energy storage capacity and cycle stability are shown to be present for Fe_3O_4 on rGO compared to pure Fe_3O_4 or Fe_2O_3. Large surface area rGO has been synthesised using microwaves for exfoliation and reduction of GO and is useful as an energy storage material in supercapacitors.

Chemically modified graphene oxides carrying porphyrin-functionalized primary amines and fullerene-functionalized secondary amines show increasing performances in nonlinear optics.

Graphene - Mechanical properties

Graphene, a new two dimensional material containing a monolayer of covalently bonded carbon atoms has unique mechanical and transport properties. Graphene has high in-plane stiffness-Young modulus and superior strength. The exceptional mechanical properties of graphene makes it a superstrong structural and functional material.

A graphene membrane which was mechanically deposited onto a substrate was found to show both non-linear elastic behaviour and brittle fracture. Graphene has Youngs modulus (E) of 1 TPa, a third order elastic stiffness (D = -2.0 TPa) and an internal strength (int) of 130 GPa. Extremely high values of E and int makes graphene an attractive material for structural and other applications. Also, graphene can be bent easily that can be exploited in practice.

The presence of defects influence the plastic deformation and fracture. Usually observed defects in graphene are vacancies, Stone-Wales defects, dislocations and grain boundaries. Dislocations and grain boundaries cause the most significant effects on its mechanical properties. Dislocations serve as carriers of plastic flow in graphene whereas, grain boundaries decreases its strength characteristics.

According to nanoindentation measurements of graphene membranes, the upper bound for the in-plane breaking stress is found to be 35 GPa and this value is much lower than the intrinsic strength (130 GPa) of pristine graphene.

Bending of graphene sheet during compression has been exploited in the design of polycrystalline graphene specimens and those with tuned folded structures are found to affect both the transport and mechanical characteristics. This feature is also found to be interesting for the design of nanodevices based on folded graphene specimens.

Due to ultrahigh strength of graphene, its inclusions are effectively used in the enhancement of both strength and fracture toughness in composite materials. Nanocomposites were fabricated using ceramic matrixes and inclusions in the form of graphene platelets (GPLs) for the improved fracture toughness of the ceramic materials. For example, silicon nitride with 1 wt% GPL nanocomposites with homogeneously dispersed GPLs have been fabricated in which each GPL consisted of several graphene layers of thickness in the range of 1-10 nm. The mechanism behind the dominant toughening are crack branching, crack deflection and crack bridging. Inclusions in the form of graphene sheets are also found to enhance the mechanical characteristics in polymer-based nanocomposites. Youngs modulus of the nanocomposite with 0.125% weight fraction of graphene inclusions is found to be 65% greater than that of the graphene free counterpart.

Role of graphene inclusions in the form of sheets and platelets as strengthening and toughening structural elements in nanocomposites is a promising breakthrough compared to nanoparticles and carbon nanotubes.

Inspite of commendable achievements, studies on the mechanical properties exhibited by graphene are in their infancy with many important problems yet to be explored and remain unsolved in the new and intriguing research area related to graphene.

Graphene - Electrical properties

Graphene is used to make supercapacitors with high capacities, high power densities, longevity and also the development of electronic components has been progressing at a high rate. Batteries and capacitors have been limiting due to size, power capacity and efficiency. Laser-scribed graphene (LSG) supercapacitors demonstrated power density comparable to that of high-power lithium-ion batteries. LSG supercapacitors are highly flexible, light, quick in charge, thin and very inexpensive to produce. Graphene is used to boost capacity, charging rate and longevity. Graphene tin oxide as an anode in lithium ion batteries has higher potential capacity and almost no reduction in storage capacity between charges which effectively makes technology such as electronically powered vehicles a much more viable mode of transport.

Graphene can be used to improve energy generation, including the improvement of perovskite solar cells (PSCs) which are highly promising next-generation solar power sources with very high efficiency. Addition of reduced graphene oxide spacer layer to a PSC, resulted in a low-cost production of PSCs with 20% efficiency.

Graphene is used in energy storage in advanced electrodes. Graphene combined with silicon nanoparticles form anode that maintain 92% of their energy capacity over 300 charging-discharing cycles, with a high maximum capacity of 1500 mAh per gram of silicon. The energy density values achieved are well above 400 Wh/kg. Thin film of graphene was produced using spray-coating deposition technique which enabled its large-scale production for the development of supercapacitors with very high power densities. Graphene-metal oxide hybrid electrodes exhibit up to 1100 mAh g^{-1} for the first 10 cycles and the specific energy density is maintained at 1000 mAh g^{-1}, even after 130 cycles. By hybridizing the metal oxide matrix with graphene, the interaction between the interstitial ions and the hybrid matrix is vastly improved for enhanced conductivity. Due to the large surface area of graphene, the metal ions can be stored via surface adsorption and induced bonding.

Graphene is an ideal candidate for radio frequency (RF) flexible electronics. The flexible nature of graphene allows for various electronic devices on flexible substrates such as the graphene-based supercapacitors, wearable touch panels, strain sensors, self-powered triboelectric sensors, flexible and robust touchscreen devices etc.

Graphene based photonic devices are becoming highly promising because of the ability of graphene to absorb light over a large bandwidth. Graphene is an excellent heat conductor which is highly useful in the reduction of heat consumption in graphene based photonic devices.

Graphene Hall sensors with carrier mobility in excess of 200,000 $cm^2V^{-1}s^{-1}$ with current-related sensitivity up to 5700 V/AT and voltage-related sensitivity up to 3 V/VT has been demonstrated in graphene encapsulated boron nitride. Flexible graphene Hall sensors has been found to have sensitivity similar to that of the rigid silicon Hall sensors.

4. Graphene based Energy Storage Devices in Space Application

Modern energy storage device for electric automobiles, small and large electronic appliances and modern aircraft is the lithium-ion battery. The lithium-ion battery has energy densities of the order of 100 Wh/kg and require long charging times. Ultracapacitors, on the other hand, can be recharged in seconds. However, their energy densities are lower than that of lithium-ion batteries. Increase in the performance of both types of devices have been made with the addition of nanostructured electrodes to lithium-ion batteries and by the use of activated carbon in ultracapacitor electrodes. Incorporation of the nanostructured electrodes have reduced the ion diffusion distances and introduction of the dopants have increased the ion transport efficiency in lithium-ion batteries. Activated carbon used in the ultracapacitors have resulted in the increase in the energy densities which is still lower than those of the lithium-ion batteries. Development of the thin film ultracapacitors with graphene electrodes have made possible to attain energy densities comparable to those of thin-film lithium ion batteries and power densities comparable to those of activated carbon ultracapacitors. The surface area of graphene is larger than that of the activated carbon, allowing for ultracapacitors with very large capacitances. An energy storage device with these characteristics could be used for robotic and Martian exploration missions and crewed habitats.

Graphene's usefulness has already been established on earth and now the recent area of research is to extend its applications in space.
One of the important possible uses of graphene in space applications is its testing in space-like applications. Graphene was tested for its ability to enhance the performance of satellites' cooling systems by employing the material's unique thermal qualities. Graphene is being used in what are called as loop-heat pipes, which are pumps that move fluid without the need for any mechanical parts. This mechanism is very important for space operations as there will be no wear and tear.

For space application, the metallic wick, the main element of the loop-heat pipe, would be coated with graphene. Graphene's thermal properties enable improved heat transfer and the porous structure of the material increases the surface area by which the liquid comes into contact and allows it flow through the wick. The results of this micro-gravity test revealed a high performance of the graphene-coated wicks compared to untreated ones and the coated wicks are tested in a low-gravity parabolic flight. With its success, researchers are working on the development of a prototype that uses graphene on a satellite or space station for testing in space. Related to this is a research initiative dedicated to developing new technologies based on graphene called the "Graphene Flagship" to test graphene for light sails which could lead to a new way of propelling satellites in space using light from lasers or the sun. "Graphene flagship" is a collaboration between the European Space Agency and academic consortium to carry out zero gravity test during a parabolic flight using graphene.

5. Carbon Nanotubes

Carbon nanotubes (CNTs) are molecules consisting of rolled-up two dimensional sheets of graphene, containing hexagons and pentagons, forming cylinder.

CNTs have carbon atoms which are sp^2 hybridized and are bonded with each other forming strong covalent bonds. This feature along with the nanotubes' tendency to rope together through van der Waals forces, provide the opportunity to develop ultra-high strength, low-weight materials with highly conducting electrical and thermal properties which makes them attractive for various applications. Carbon nanotubes are first discovered by S. Ijima in the year 1991.

Single-walled and Multiwalled Carbon Nanotubes

CNTs are of two types. They are single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Single-walled carbon nanotubes (SWCNTs) are cylinders containing only one cylinder made of single graphene sheet. Several graphene sheets when folded to form cylinders one inside the other are called multi-walled carbon nanotubes.

SWCNTs have diameter in the range of 1-2 nm and length in the range of 1-100 μm. MWCNTs have outer diameter in the range of 2-20 nm and inner diameter 1-3 nm. They have length in the range of 1-100 μm with inter tubular distance of 0.34 nm. The two types of CNTs have length reaching even millimeters starting from micrometers.

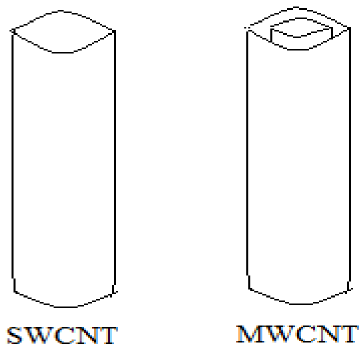

Fig 4: Types of CNTs

Synthesis of CNTs

i. Chemical Vapour Deposition (CVD) method

CVD method, also called as thermal CVD, consists of forming carbon nanotubes by decomposing an organic gas over a substrate coated with metal catalyst nanoparticles.

Thermal CVD method consists of a quartz tube enclosed in a furnace. The substrate made of silica, mica, quartz or alumina on which the CNTs has to be formed is placed inside the furnace. The substrate is coated with metal catalyst nanoparticles like Fe, Co or Ni. Carbon precursors such as acetylene (C_2H_2), ethylene (C_2H_4) or methane (CH_4) gas is passed into the furnace and the temperture inside is fixed in the range of 500-900°C. At these temperatures, the carbon precursor starts to dissolve in the metal catalyst till the point of supersaturation. The saturated carbon starts to precipitate in the form of cylinders which are called the carbon nanotubes.The diameter of the tube is determined by the size of the nanoparticles used as the catalyst. Thermal CVD can be used to produce both SWCNTs and MWCNTs.

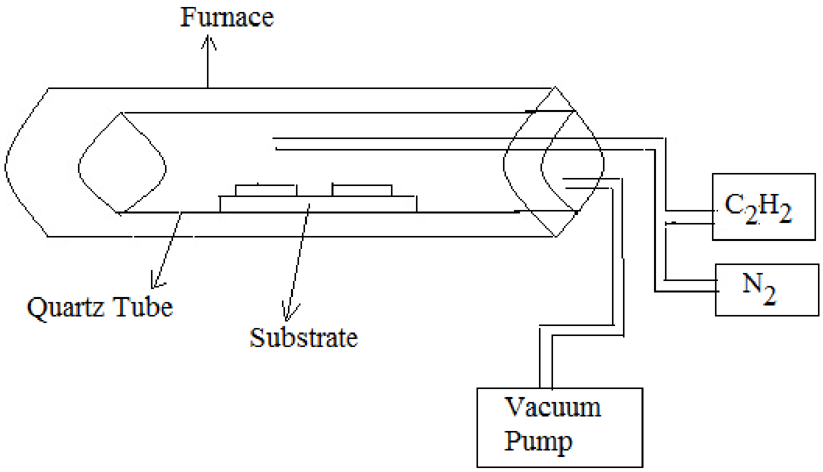

Fig 5: Thermal CVD

ii. Laser Ablation method

Laser ablation method consists of a furnace, a quartz tube with a window on one side, a graphite target doped with metal catalyst such as cobalt or nickel at the center of the tube. An argon flow system is maintained at a constant pressure and flow rate. A water-cooled copper collector is present outside the furnace.

A continuous or pulsed laser beam from Nd:YAG (Neodymium-doped-yttrium aluminium garnet) is made to fall on the graphite target through the window and the furnace temperature is maintained at 1200°C. When the laser beam falls on the graphite target, the target gets vaporised to form carbon particles containing atoms and molecules. The formed carbon atoms and molecules are sweeped by the flowing argon gas having a flow rate of 1 cm s^{-1} and a pressure of 500 torr. When the carbon particles reaches the water cooled copper collector, they undergo condensation and grow in the form of carbon nanotubes.

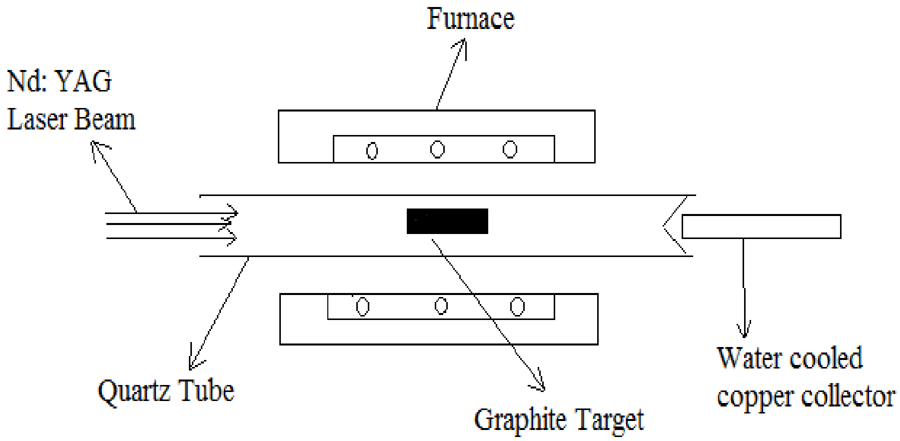

Fig 6: Laser Ablation Method

Laser ablation method has several advantages such as high quality single walled carbon nanotubes can be produced, diameter of the nanotubes can be controlled and growth dynamics can be followed.

Properties of Carbon Nanotubes

i. Electrical Properties

The electrical property of carbon nanotubes depends on the direction of rolling-up of the graphene sheets, called helicity (chirality) and the diameter of the nanotube. Helicity is the rolling of the hexagonal chains with respect to the tube axis. There are three different types of CNTs based on helicity. They are armchair, zigzag and chiral carbon nanotubes.

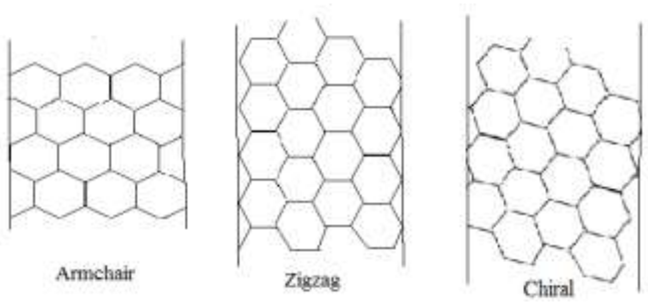

Fig 7: Types of carbon nanotubes

Turning a graphene sheet by 30 degrees will convert the configuration from armchair to zigzag or vice versa. SWCNTs' conductivity depends on the chiral vector. They behave like a metal and have high electrical conductivity or can show semiconducting property or can be non-conducting. A slight change in helicity can transform its metal conductivity to semiconducting type.

Armchair tubes (n, m) are metallic as they are highly symmetrical and the conditions for the metallic property to dominate are n - m = 0 or (n - m)/3 = integer, where n and m are the chiral vectors. Examples: (8, 2), (6, 3) and (7,7) tubes are metallic.

Zigzag and chiral tubes are either metallic or semiconducting. Semiconducting property dominates when (n – m)/3 ≠ integer. Examples: (9,1), (5,3) tubes are semiconducting.

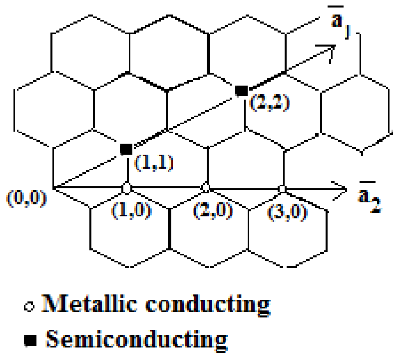

Fig 8: Vector representation of metallic and semiconducting carbon nanotubes

Metallic CNTs have high conductivity and can carry billion amperes of current per square centimeter whereas a copper wire can carry only million amperes of current per quare centimeter due to resistive heating which melts the copper wire at high currents. The high conductivity for CNTs is due to minimum defects and hence imparts low resistance to the flow of current. Due to high thermal conductivity, their is no resistive heating during the flow of high currents in CNTs.

The low conductivity in the case of chiral and zigzag forms is due to the replacement of hexagonal rings with pentagonal or heptagonal rings. This type of defect can affect the electrical conductivity severely in CNTs. For SWCNTs, the band gap is in the range of 0.4 – 1 eV and is found to decrease with the increase in the inverse diameter of the nanotube.

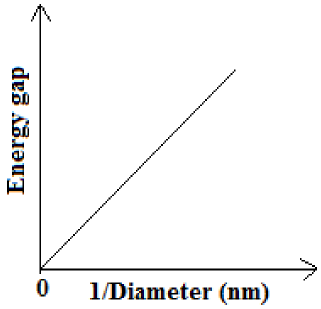

Fig 9: Plot of Energy gap versus Diameter of carbon nanotubes

ii. Mechanical Properties

CNTs also have unique thermal and mechanical properties that render them with highly beneficial properties for the development of new materials.

a. Tensile strength: It is the amount of stress required to pull a material. CNTs are very strong and have tensile strength which is 100 times more than that of steel having the same diameter. The tensile strength of CNTs is around 45 billion pascals whereas for steel it is only 2 billion pascals. This high tensile strength for CNTs is due to the following reasons:

i) Strong interlocking of the carbon atoms through covalent bond.

ii) CNTs does not have weak points like grain boundaries, dislocations etc and is considered to be a single molecule.

b. Youngs modulus: It is the measure of elasticity or flexibility of the material. The elasticity is inversely proportional to the Youngs modulus value. CNTs have high Youngs modulus value

(1.28 – 1.8 TPa) compared to that of steel (0.21 TPa) which shows that CNTs are 5 to 10 times harder than steel.

c. Thermal Conductivity:

CNTs have high thermal conductivity as they don't get heated or get cooled very well. Thermal conductivity of CNTs is 10 times that of silver, 15-20 times that of copper and 2 times that of diamond. CNTs conduct heat through the material by the vibration of the covalent bonds present between the carbon atoms. The strong covalent bonds are helpful in transmitting the heat throughout the nanotube thereby providing good thermal conductivity.

d. Density: Density of CNTs is one fourth that of steel and half that of aluminium. Hence CNTs are light weight materials having density in the range of 1.33 – 1.44 g/cm^3.

Applications of Carbon Nanotubes

Carbon Nanotubes have wide variety of applications in different fields. Carbon nanotubes are ideal candidates for use in electronic devices, chemical/electrochemical and biosensors, transistors, electron field emitters, lithium-ion batteries, white light sources, hydrogen storage cells, cathode ray tubes (CRTs), electrostatic discharge (ESD) and electrical-shielding applications.

Important applications of CNTs are:

- Carbon nanotubes (CNTs) have large surface area, high chemical stability and controlled surface chemistry. Hence they are used as catalyst support.
- CNTs are used as additives to synthetics by removing the agglomeration in order to spread evenly on the substrate. They can be chemically bonded with the substrate, like a plastic material, by functionalizing it on the surface.
- CNTs can store high weight percentage of hydrogen without any leakage. Therefore used in hydrogen-oxygen fuel cells to store hydrogen.
- CNTs are used in various biomedical applications. The physical properties of CNTs, such as mechanical strength, electrical conductivity, and optical properties, are of great value for creating advanced biomaterials with increased solubility and biocompatibility, enhanced material compatibility and cellular responsiveness. CNTs are used in targeted drug delivery due to its adaptability under different conditions.

- CNTs are used as actuators where there is conversion of electrical energy to mechanical energy for inducing movements.
- CNTs act as sensing materials in sensors for the detection of pressure, temperature, mass, light, stress, strain etc. Though studies have shown that CNTs are robust and inert structures, their electrical properties are found to be extremely sensitive to the effects of charge transfer and chemical doping by various molecules. Sensors based on CNTs are field effect transistors (FET). CNTs-FETs have been widely used to detect gases such as greenhouse gases in environmental applications. Functionalization of CNTs have made them even more selective to the target analyte. For example, flexible hydrogen sensors have been made using single-walled carbon nanotubes decorated with palladium nanoparticles.
- Semiconducting SWCNTs are now considered as strong candidates for the next generation of high-performance, ultra-scaled and thin-film transistors as well as for opto-electronic devices to replace silicon electronics. CNTs act as ideal field emitters due to high current density, low turn-on and operting voltage. Thin film CNTs are used in making thin film solar cells, organic LEDs and touch screens as they are transparent to visible light to produce electricity.
- CNTs are stiff, tough and strong having superior mechanical properties and are useful in the production of very strong, light weight materials that find applications in building, structural engineering and aerospace.
- “Nano inks” which is an ink formulation based on CNT dispersions are found to be highly useful in Printed electronics and in making transparent electrodes, thin-film transistors, light-emitting devices and solar cells.
- CNTs are used in making aircraft components due to its high fatigue strength.
- Efficient water transport through carbon nanotubes with openings of less than one nanometer have been used as high flow membranes in energy-efficient water purification. They are found to provide protection against biological agents due to their very small pore size which is less than 5 nanometers wide.

QUESTIONS

PART-A

1. What are allotropes of carbon? Name them.
2. What are fullerenes?
3. Define graphene.
4. Differentiate graphene oxide and reduced graphene oxide.
5. Why graphene called as van der Waals solid?
6. Mention any two applications of fullerenes.
7. List out any two important properties of graphene oxide.
8. Mention two appliactions of rGO.
9. What are carbon nanotubes?
10. Name the two types of CNTs.
11. How are SWCNTs classified based on chirality?
12. Differentiate SWCNT and MWCNT.
13. Give the advantages of Laser ablation method of synthesis of CNTs over thermal CVD method.

PART-B

1. Explain in detail about the various allotropes of carbon.
2. What are fullerenes? Explain the Krätschmer and Huffman method of synthesis of fullerenes with a neat diagram.
3. Comment on the important properties of fullerenes.
4. Discuss the applications of fullerenes.
5. Write short note on graphene, graphene oxide and reduced graphene oxide.
6. Explain the structure of graphene with a neat diagram.
7. Write short note on the mechanical properties of graphene.
8. Explain the electrical properties of graphene.
9. Elaborate on the use of graphene in space applications.
10. Differentiate SWCNT and MWCNT with appropriate diagrams.
11. Explain in detail the thermal method of synthesis of CNTs with a neat diagram.
12. Explain laser ablation method of synthesis of CNTs with a diagram.
13. Discuss on the mechanical properties of CNTs.
14. Elaborate the electrical properties of CNTs with respect to chirality.
15. Write in detail the various applications of CNTs.

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SCHOOL OF SCIENCE AND HUMANITIES
DEPARTMENT OF CHEMISTRY

UNIT-V – ENGINEERING MATERIALS – SCYA1101

1. Introduction: Phase Equilibria

A system is a part of the universe, which is focused for chemical study. The rest of the system is called surroundings. The system and surroundings are separated by a real or imaginary surface called boundary. When a system is uniform throughout physically and chemically, it is called as homogeneous system. When a system has two or more parts, it is a heterogeneous system. If equilibrium is present between these parts, it is called heterogeneous equilibria. Phase rule explains heterogeneous equilibria. It predicts qualitatively the effect of pressure, temperature and concentration on heterogeneous equilibria. That is, it gives information about the behaviour of heterogeneous equilibrium systems when they are subjected to changes in variables like temperature, pressure and concentration.

2. The Gibbs Phase Rule

***Phase Rule Statement**:* Phase rule was discovered by J.W. Gibbs in 1875 and is known as Gibbs Phase Rule. For a heterogeneous system in equilibrium at a definite temperature and pressure, Gibbs phase rule relates that the number of degrees of freedom equals to the difference in the number of components and the number of coexisting phases plus two provided the equilibrium is not influenced by external effects such as gravity, electrical and magnetic forces, surface tension, etc.

***Mathematical Statement**:* The phase rule is mathematically stated as: $F = C - P + 2$

Where,

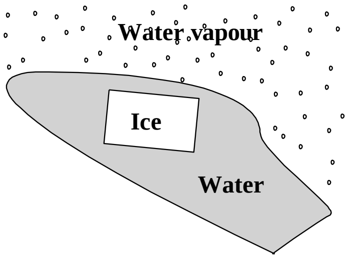
- ✓ P is the number of Phases present in equilibrium.
- ✓ C is the number of Components for the system.
- ✓ F is the number of Degrees of Freedom for the equilibrium.
- ✓ 2 indicate the variables: Temperature and Pressure.

Terms Involved in Phase Rule

i. Phase

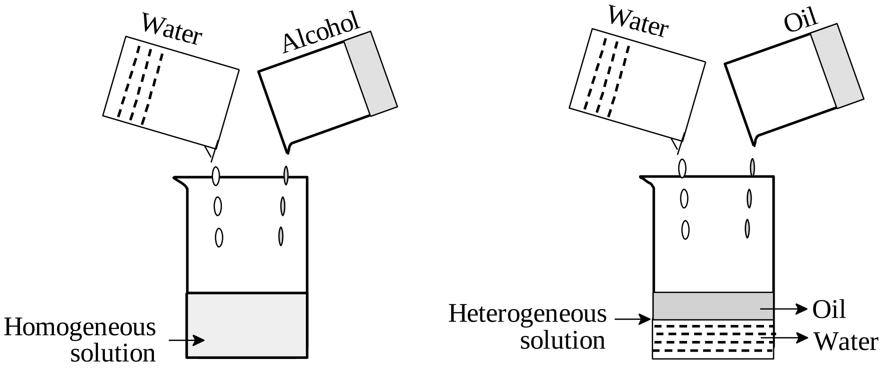
Definition: Phase is a homogeneous, physically distinct, and mechanically separable part of a system, which is separated from other parts of system by definite boundaries.

a. Freezing water system: Freezing water system consists of three phases namely liquid water, solid ice and water vapour. Each phase is physically distinct and homogeneous.



Floating of ice cube in water

b. Liquids: If two liquids are miscible (alcohol and water), they are considered as one liquid phase only. If two liquids are immiscible (Oil and water), they are considered as two separate phases.



c. Gases: A pure gas or a mixture of any number of gases is considered as a single phase. This is because gases are completely miscible in all proportions.

- ✓ Pure oxygen gas – Single phase
- ✓ Mixture of CO and N_2 – Single phase
- ✓ Mixture of CO(g) and H_2O(g) – Single phase

d. Solids: Each solid is considered as a separate phase. For example, a heterogeneous mixture of $CaCO_3$ and CaO consists of two solid phases. Each allotrope of a substance is considered as a single phase. For example, carbon exhibits allotropy graphite and diamond. They are considered as two separate phases.

e. **Solution:** A solution (solute and solvent) is considered as a single phase only (Glucose in water).

ii. Components

Definition: The number of components of a system is the minimum number of chemical constituents required to express the composition of all the phases present in the system.

While expressing the chemical composition of all the phase present in the system,

- ✓ *all the selected or chosen constituents must be included and*
- ✓ *for this purpose positive, negative or zero quantities of constituents may be used*

a. The freezing water system: This system consists of three phases namely ice, water and water vapour. All the three phases are different physical form of same chemical substance (water). Hence this is considered as one-component system.

b. **A system of saturated solution of NaCl:** This system consists of three phases namely solid NaCl, NaCl solution and water vapour. The chemical composition of all the three phases can be expressed in terms of NaCl and H_2O. Hence it is a two-component system.

c. **Thermal decomposition of $CaCO_3$**

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

This system consists of three phases namely, solid $CaCO_3$, solid CaO and gaseous CO_2. Though the system has three different constituents, it is considered as a two-component system. This is because the chemical composition of all the three phases can be expressed in terms of any two of the three chemical constituents present.

$CaCO_3$ and CaO are chosen as Two Components		**$CaCO_3$ and CO_2 are chosen as Two Components**		**CaO and CO_2 are chosen as Two Components**	
Phase	**Chemical Composition**	**Phase**	**Chemical Composition**	**Phase**	**Chemical Composition**
$CaCO_3$	$CaCO_3 + 0CaO$	$CaCO_3$	$CaCO_3 + 0CO_2$	$CaCO_3$	$CaO + CO_2$
CaO	$0CaCO_3 + CaO$	CaO	$CaCO_3 - CO_2$	CaO	$CaO + 0CO_2$
CO_2	$CaCO_3 - CaO$	CO_2	$0CaCO_3 + CO_2$	CO_2	$0CaO + CO_2$

d. Dissociation of NH_4Cl in vacuum

$$NH_4Cl\ (s) \rightleftharpoons NH_3\ (g) + HCl\ (g)$$

This system consists of two phases namely, solid NH_4Cl and gaseous mixture containing NH_3 and HCl. The composition of both the phases can be expressed in terms of only one constituent namely, NH_4Cl. Hence it is a one-component system.

Phase	Chemical Composition
Solid NH_4Cl	x NH_4Cl
Gaseous phase xNH_4Cl	x NH_3 + x HCl

If the concentration of NH_3 is not equal to that of HCl i.e., $NH_{3(g)} \neq x\ HCl_{(g)}$, then the system becomes two component system. Suppose y mole of HCl is added to x NH_4Cl, then the chemical composition of solid and gaseous phases is expressed in terms of NH_4Cl and HCl as follows.

Phase	Chemical Composition
Solid NH_4Cl	x NH_4Cl + 0 HCl
Gaseous phase x NH_4Cl + y HCl	x NH_3 + x HCl + y HCl

iii. Degree of freedom (or) Variance of a system

Definition: The number of degrees of freedom of a system is the minimum number of independent variable factors such as temperature, pressure and concentration (composition) required to describe the system completely. A system having one, two, three and zero degrees of freedom are usually called ***univariant, bivariant, trivariant and invariant system*** respectively.

a. Consider a one component system consisting of two phases

$$\text{Water} \rightleftharpoons \text{Water vapour}$$

$$P = 2 ; C = 1$$

$$F = C - P + 2$$

$$F = 1 - 2 + 2$$

$$F = 1$$

To define such a system, only one variable factor (either temperature or pressure) is needed. Hence the system is ***univariant.***

b. Consider a one component system consisting of one phase: Water vapour.

$P = 1 ; C = 1$

$F = C - P + 2$

$F = 1 - 1 + 2$

$F = 2$

To define such a system, two variable factors (temperature and pressure) are needed. Hence the system is ***bivariant.***

c. Consider a one component system:

Ice $\rightleftharpoons$ *Water* $\rightleftharpoons$ *Water vapour*

$P = 3 ; C = 2$

$F = C - P + 2$

$F = 1 - 3 + 2$

$F = 0$

To describe this equilibrium system, no need to specify any variable factors, because all the three phases can occur in equilibrium only at a particular temperature and pressure. Hence this system does not have any degree of freedom ***(invariant or zero variant).***

Uses of phase rule

- ✓ The phase rule takes no account of the nature or amount of substances.
- ✓ Phase rule is applicable to macroscopic systems. Therefore it is not necessary to have information about molecular structure.
- ✓ It gives information about the behaviour of systems when they are subjected to changes in variables such as temperature, pressure and concentration.

Limitations of phase rule

- ✓ The phase rule takes into account only the variable factors like temperature, pressure and the composition. The influences of factors such as electric, magnetic, gravitational, surface forces etc. are ignored.
- ✓ The phase rule is applicable only to heterogeneous systems in equilibrium.
- ✓ In phase rule, time is not a variable factor because this rule applies to a system in equilibrium. The equilibrium state is independent of time factor.

Phase Diagram

Definition: Phase diagram is a graph obtained by plotting one degree of freedom against another. If temperature is plotted against pressure, it is known as temperature-pressure diagram. If temperature is plotted against composition, it is known as temperature–composition diagram.

Significance: They help in studying and controlling the various processes such as phase separation, solidification of metals, and change of structure during heat treatment like annealing, quenching, tempering etc.

3. Phase Diagram of Water System (Application of Phase Rule to One Component System)

The water system is an example of one component system. It consists of three phases namely solid ice, liquid water and water vapour. The phase diagram of water system is given in Fig. 5.1.

Table 1: Important data for constructing phase diagram of water system

S. No.	Parameters	Temperature	Pressure
1	Boiling point	100°C	1 atm
2	Triple point	0.0075°C	4.58 mm
3	Critical point	374°C	218 atm

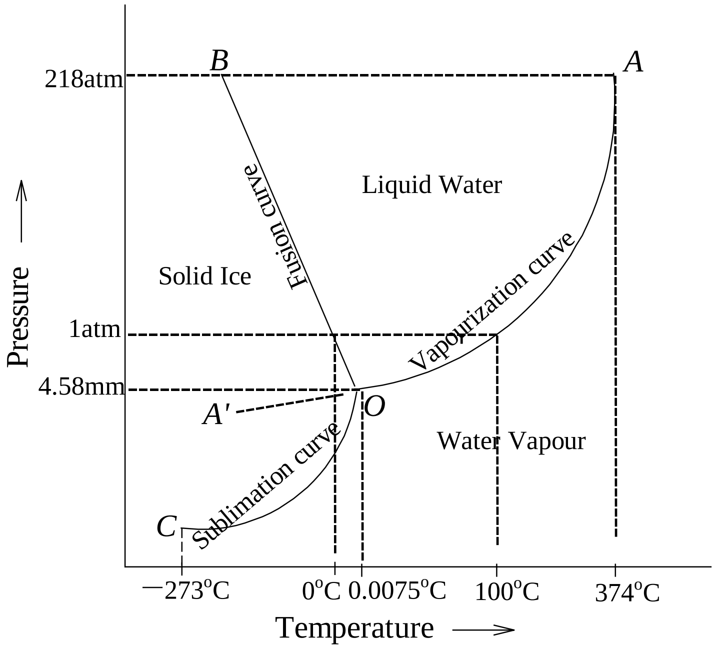


Fig 1: The Phase Diagram of Water System

Salient features of phase diagram of water system

i. Curves: The phase diagram consists of three curves *OA*, *OB* and *OC*. Each curve separates two phases and hence the system is “univariant” along the curve.

$$\begin{aligned} F &= C - P + 2 \\ F &= 1 - 2 + 2 \\ F &= 1 \end{aligned}$$

Curve *OA*: Curve *OA* is the *vaporization curve* because it separates the liquid region from vapour region. Along the curve *OA*, water and water vapour are in equilibrium (water ↔ water vapour). The curve *OA* ends at the point *A*, which corresponds to the critical temperature (374°C) and critical pressure (218.5atm) of water. Beyond the point *A*, the liquid and vapour phases merge into each other to form a single homogeneous phase.

Curve *OB*: Curve *OB* is the *fusion or melting curve* because it separates ice and water phases (ice ↔ water). The curve *OB* is slightly inclined towards pressure axis. This shows that melting point of ice decreases with the application of pressure.

Curve *OC*: Curve *OC* is the *sublimation curve* because it separates ice and water vapour phases (ice ↔ water vapour). At the lower limit, the curve *OC* terminates at absolute zero (−273°C) where no vapour can be present and only ice exists.

ii. Point ‘O’ (Triple point): The three curves *OA*, *OB*, and *OC* meet at a point *O*, at which solid ice, liquid water and water vapour are simultaneously in equilibrium. This is called triple point.

$$\textit{Solid ice} \rightleftharpoons \textit{Liquid water} \rightleftharpoons \textit{Water vapour}$$

At the triple point, the system is ‘invariant’. The triple point of water system corresponds to a temperature of 0.0075°C and a pressure of 4.58 mm mercury.

$$\begin{aligned} F &= C - P + 2 \\ F &= 1 - 3 + 2 \\ F &= 0 \end{aligned}$$

iii. Areas: The curve is divided into three areas *AOB, BOC* and *COA.* Each area represents a single phase and hence the system is ‘bivariant’.

$$F = C - P + 2$$
$$F = 1 - 1 + 2$$
$$F = 2$$

iv. Curve *OA'* (Meta stable equilibrium): The curve *OA’* represents the vapour pressure curve of super cooled water. Super cooling means, cooling of water below its freezing point without the separation of solid. Super cooled water is highly unstable and it can be converted into solid by a slight disturbance. Hence the system along the curve *OA’* is said to be in “meta stable equilibrium”.

4. Application of Phase Rule to Two Component Alloy System

Classification of two component systems

Based on mutual solubility and reactive ability, the two component system is classified into the following three types:

i. Simple eutectic formation: The two solid substances can form a simple eutectic under the following conditions:

- ✓ The two solid metals must be completely miscible in the liquid state but completely immiscible in the solid state.
- ✓ They should not chemically react with each other.

Therefore, *eutectic has the same composition both in liquid and solid states.* Also the eutectic has a sharp melting and freezing point as the pure metals. Hence eutectic composition is a unique mixture of two solids, which has the lowest melting point.

Examples: Lead – Silver system; Bismuth – Cadmium system.

Uses of eutectic system:

- ✓ De-silverisation of lead (Enrichment of silver from argentiferous lead ore) is based on the formation of simple eutectic.
- ✓ The principle of a simple eutectic system is used for preparing solders (Eg: Pb-Sn solder), which are used for joining two metal pieces together.

ii. Formation of compound with congruent melting point: When two solid substances combine in a definite proportion, one or more stable compounds are formed. These compounds melt at constant temperature to give liquid melt of the same composition. The temperature at which a compound melts to give liquid phase of same composition is known as congruent melting point.
Examples: Zinc – Magnesium system; Tin – Magnesium system.

iii. Formation of compound with incongruent melting point: There are solid substances which combine together to form one or more unstable compounds. Further, they decompose into a new solid phase and a liquid melt of different composition. The temperature at which the unstable compound decomposes into a new solid phase and a liquid melt (having different composition from solid phase) is known as incongruent melting point.
Examples**:** Sodium – Potassium system; Gold – Antimony system.

iv. Solid solution formation: When two different metals dissolve each other in liquid and or in solid state, the resulting phase is called solid solution. Solid solution is formed when the solvent and solute atoms have similar sizes and electron structure.
Examples*:* Copper – Nickel system.

Reduced phase rule (or) Condensed system

A solid−liquid alloy system has practically no gaseous phase. Hence the effect of pressure is negligible on this type of equilibrium. Therefore to construct the usual phase diagram with two axes, the vapour phase is neglected. Such a solid-liquid system is called ***"condensed system".*** In condensed system measurements are made at constant pressure. This reduces the degree of freedom of the system by one. Therefore, the phase rule equation for two-component alloy system is written as: $F = C - P + 1$. This equation is known as "***reduced phase rule equation".***

5. Thermal Method of Analysis (or) Experimental Method of Construction of a Simple Eutectic Phase Diagram

Definition: Thermal analysis involves the study of cooling curve of various compositions of two solids during solidification.

1. Cooling curve of a pure metal

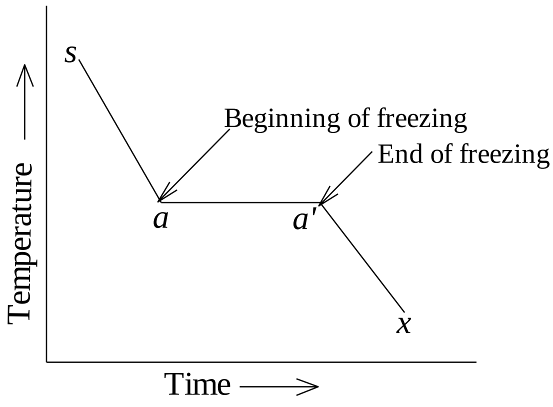


Fig.2a: Cooling Curve of Pure Metal

Definition: Thermal analysis involves the study of cooling curve of various compositions of two solids during solidification.

s : Represents the pure metal is in molten state.

sa : Along s*a*, the temperature of the melt decreases gradually with time.

a : The point '*a'* indicates the temperature at which the molten metal starts freezing at its surface.

aa' : Along *aa',* the liquid melt and solid metal are in equilibrium. Further the temperature remains constant until the liquid melt is completely solidified because the liquid melt and solid metal have same chemical composition.

a' : Indicates the end of freezing.

a'x : Along *a'x*, the temperature of solid metal again decreases with time.

2. Cooling curve of a mixture of solid *A* and solid *B*

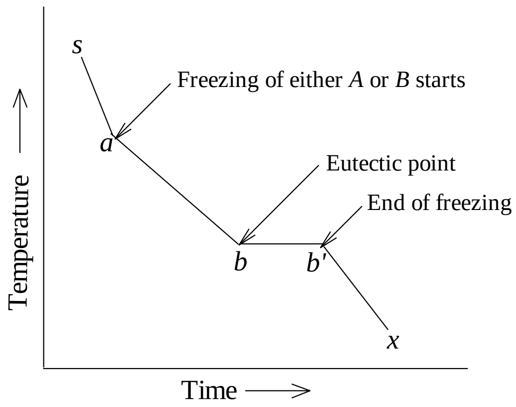


Fig 2b: Cooling Curve of a Mixture of Two Solids A and B

s : Represents a mixture of solid *A* and solid *B* is in fused state.

sa : Along s*a,* the temperature of the mixture containing *A* and *B* decreases with time.

a : The point '*a'* indicates the temperature, at which freezing of base metal (either *A* or *B* depends upon their freezing point) starts from the liquid mixture.

ab : Along *ab*, the liquid melt and solid metal *A* (or solid metal *B*) are in equilibrium. Further, the line *ab* indicates the composition of molten mixture progressively changes due to continuous separation of solid *A* (or solid *B*) with time. Because of two different chemical composition of the liquid mixture (containing *A* and *B*) and solid metal (either *A* or *B*), the temperature of the liquid mixture decreases at a different rate.

b : The point at which the liquid mixture (containing both A and B) starts freezing into solid *A* and solid *B* (eutectic mixture).

bb' : Along *bb',* the liquid mixture and solid *A* and solid *B* are in equilibrium.

b' : Indicates the end of freezing of eutectic mixture.

b'x : Along *b'x,* the temperature of solids again decreases with time.

3. Cooling curve of eutectic mixture and construction of simple eutectic phase diagram

Since eutectic behaves like a pure solid metal, it also has same type of cooling curve as pure solid metal. So, it is possible to construct a complete phase diagram for the two-component system on the basis of large number of cooling curves of various compositions (Fig.5.3c).

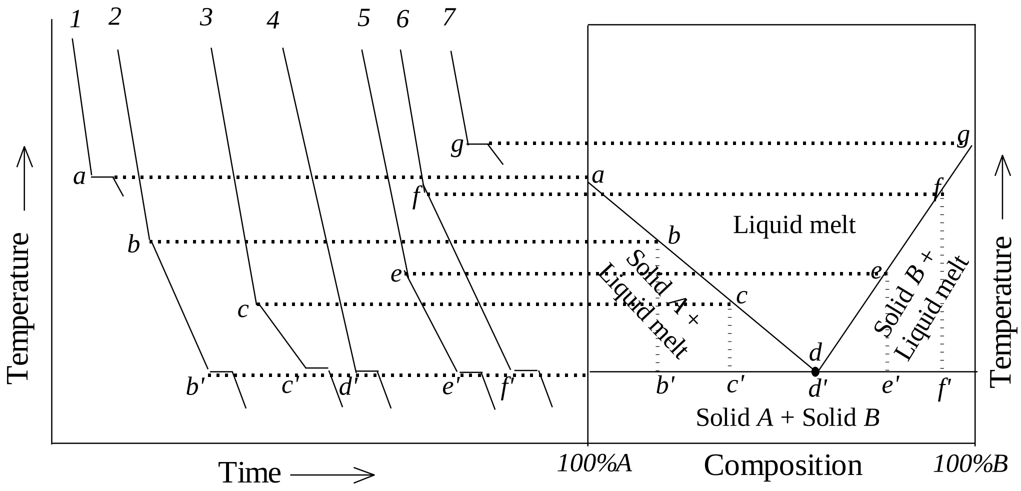


Fig 2c*: *Cooling Curves of Various Compositions of Two Solids (1) 100% A (2) 80%A+20% B (3) 70%A+30%B (4)60%A+ 40% B (5) 45%A+55%B (6) 30%A+70% (7) 100%B

In eutectic phase diagram:

- ✓ Each curve corresponds to a definite composition of *A* and *B.*
- ✓ The break or discontinuity in the graph (*a*, *b, c, d, e, f, g, h*) denotes phase transformation (freezing point of either *A or B*).
- ✓ The cooling curve of eutectic composition (curve *4*) is similar to those of pure substances (curve *1* and *7*).
- ✓ The eutectic phase diagram is obtained by plotting various compositions of two substances against the discontinuity (freezing point), which is nothing but characteristic temperature.

Salient features of simple eutectic phase diagram

i. Curves: The eutectic phase diagram consists of two curves *abcd*, and *gfed.* Along the curve, two phases (Solid $\rightleftharpoons$ Liquid melt) are in equilibrium and hence the system is ‘univariant’ (F = 2–2+1 = 1).

ii. Point *O* (Eutectic Point): The curve *abcd* and *gfed* intersect at *d* which is called eutectic point. At the eutectic point three phases are in equilibrium. Hence the system is non-variant (F = C–P+1 = 2–3+1 = 0).

$$\textit{Liquid melt} \rightleftharpoons \textit{Solid A} + \textit{Solid B}$$

iii. Areas: The eutectic phase diagram consists of four distinct areas (i) Above *abcdefg* has a single phase (molten *A* and *B*) (ii) Below *abcd* (solid *A* + liquid melt) (iii) Below *gfed* (solid *B*+ liquid melt) and (iv) Below the point *d* (solid *A* + solid *B*).

6. Construction of Simple Eutectic System (Lead-Silver System)

The lead-silver system is an example of two component system. It consists of two curves, a point *O* and four areas. The phase diagram of lead-silver system is given in Fig. 5.4.

Table 2: Important Data for Constructing Phase Diagram of Pb-Ag system

S. No.	Parameters	Temperature/Composition
1	Melting point of Lead *(Pb)*	327°C
2	Melting point of Silver *(Ag)*	961°C
3	Eutectic Temperature	303°C
4	Eutectic Composition	97.4%Pb + 2.6%Ag

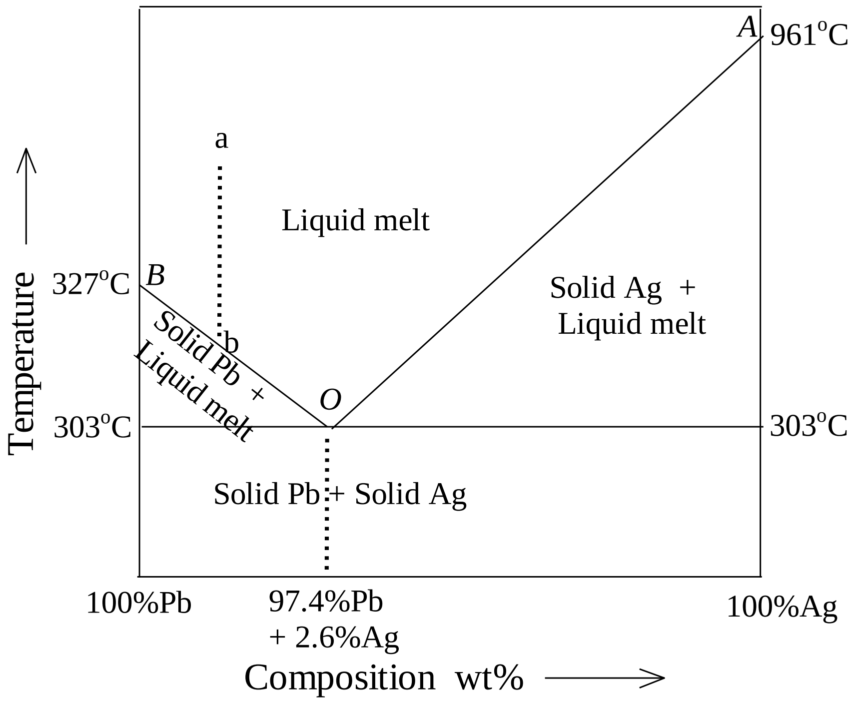


Fig 3: The Lead-Silver System

Salient features of phase diagram of Pb-Ag system

i. Curves

Curve *AO*: Pure *Ag* melts at 961°C. Addition of *Pb* lowers the freezing point of *Ag* along the curve *AO*. Therefore *AO* is the freezing point curve of silver. Along *AO*, ***solid Ag and liquid melt are in equilibrium***. Hence the system along the curve is 'univariant' (F = C–P+1 = 2–2+1 = 1).

Curve *BO**:* Pure *Pb* melts at 327^0C. Addition of *Ag* lowers the freezing point of *Pb* along the curve *BO*. Therefore *BO* is the freezing point curve of *Pb*. Along *BO*, ***solid Pb and liquid melt co-exist*** and hence the system is 'univariant' (F = C–P+1 = 2 – 2 + 1 = 1).

ii. Point *O* (Eutectic point)

The curve *AO* and *BO* intersect at *O* which is called eutectic point. At this point three phases are in equilibrium.

$$\textit{Liquid melt} \rightleftharpoons \textit{Solid Ag} + \textit{Solid Pb}$$

Hence the system is non-variant (F = C–P+1 = 2–3+1 = 0). Below the point *O*, both silver and lead exist in the solid state. Therefore, eutectic point is the lowest temperature at which a mixture of two solids melts (eutectic = easy melting). The corresponding temperature and composition are called ***"eutectic temperature"*** and ***"eutectic composition"*** respectively. The eutectic point of *Pb-Ag* system corresponds to a temperature 303°C and composition 97.4%*Pb*+2.6%*Ag*.

iii. Areas

The area above *AOC* has a single phase (molten *Pb* and *Ag*). Applying the reduced phase rule F = C–P+1 = 2–1+1 = 2, the system is bivariant. The area below *AO* (solid *Ag* + liquid melt), below *BO* (solid *Pb* + liquid melt) and below *O* (solid *Ag* + solid *Pb*) have two phases and hence the system is univariant (F = C–P+1 = 2–2+1 = 1).

Application of Pb-Ag system (Pattinson's Process)

The process of recovery of silver from argentiferous lead is called as desilverisation. Desilverisation of lead is based on the formation of eutectic mixture. Argentiferous lead consists of a very small amount of silver (0.1%). The ore is heated to a temperature well above its melting point, so that it exists as liquid melt (point *a* in Pb-Ag system). When it is allowed to cool, the temperature of the melt falls along the line *ab*. As soon as point *b* is reached, lead is crystallized out. On repeating the process of melting and cooling, more and more lead is separated along the line *BO*. At *O* a eutectic mixture containing 2.6%Ag and 97.4%Pb is obtained. The eutectic alloy is then treated for recovery of silver.

Melting Point, Triple Point and Eutectic Point

a. Melting point: It is the temperature at which, the solid and liquid having the same composition are in equilibrium (Solid $\rightleftharpoons$ Liquid)

b. **Triple Point:** It is the point at which three phases (any types) are in equilibrium.

$$\text{Solid} \rightleftharpoons \text{Liquid} \rightleftharpoons \text{Vapour}$$

$$\text{Solid A} \rightleftharpoons \text{Solid B} \rightleftharpoons \text{Liquid melt}$$

c. Eutectic point: It is the point at which two solids and a liquid are in equilibrium.

$$\text{Solid A} \rightleftharpoons \text{Solid B} \rightleftharpoons \text{Liquid melt}$$

Hence all the eutectic points are triple points but all the triple points are need not be eutectic points.

Problems Based on Phase Rule

1. Is it possible to have a quadruple point in phase diagram of a one-component system?

"No". Quadruple point means 4 phases are simultaneously in equilibrium.

$$F = C - P + 2$$

$$F = 1 - 4 + 2$$

$$F = -1$$

F = – 1 is meaningless. Hence the answer is “No”.

2. How many number of phases, components and degrees of freedom are available in the following systems:

(i) $BaCO_3\,(s) \rightleftharpoons BaO\,(s) + CO_2\,(g)$

(ii) $MgCO_3\,(s) \rightleftharpoons MgO\,(s) + CO_2\,(g)$

(iii) $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$

All the above systems have 2 solid phases and one gaseous phase.

Number of phases, P = 3

Number of components, C = 2

Number of degrees of freedom, F = C – P + 2

F = 2 – 3 + 2

F = 1(univariant)

3. How many phases, components, and degrees of freedom are present in:

(i) **Water at 0.0075°C and 4.58mm Hg**

(ii) **Water $\rightleftharpoons$ Water vapour at 30°C**

(iii) **Pb–Ag alloy system at constant pressure [composition 2.6%Ag and 303°C]**

(i) This indicates triple point of water system,. At the triple point, solid ice, liquid water and water vapour are simultaneously in equilibrium.

Number of phases, P = 3

Number of components, C = 1

Number of degrees of freedom, F = C – P + 2

F = 1 – 3 + 2

F = 0 (invariant)

(ii) Water ↔ Water vapour at 30°C.

Number of phases, P = 2
Number of components, C = 1
Number of degrees of freedom, F = C – P + 2
F = 1 – 2 + 2
F = 1(univariant)

(iii) This indicates eutectic point of Pb-Ag system. At the eutectic point, solid Ag, solid Pb and liquid melt are in equilibrium.

Number of phases, P = 3
Number of components, C = 2
Number of degrees of freedom, F = C – P + 1
F = 2 – 3 + 1
F = 0 (invariant)

4. In the phase diagram of water, point out the phase in equilibrium with (i) One degree of freedom and (ii) No degrees of freedom.

(i)

Number of phases, P = ?
Number of components, C = 1
Number of degrees of freedom, F = 1
F = C – P + 2
P = C + 2 – F
P = 1 + 2 – 1
P = 2 (bivariant)

Any two phases can be in equilibrium.

Water $\rightleftarrows$ Water vapour
Ice $\rightleftarrows$ Water
Ice $\rightleftarrows$ Water vapour

(ii)

Number of phases, P = ?
Number of components, C = 1
Number of degrees of freedom, F = 0
F = C – P + 2
P = C + 2 – F
P = 1 + 2 – 0
P = 3 (trivariant)

All the three phases are simultaneously in equilibrium.

Solid ice $\rightleftarrows$ *Liquid water* $\rightleftarrows$ *Water vapour*

5. $Fe(s) + H_2O\ (g) \leftrightarrow FeO(s) + H_2\ (g)$. Calculate P, C and F for the above system.

Number of phases, P = 3 (2 solids; 1 gaseous)
Number of components, C = 3 (Fe, O_2 and H_2)
Number of degrees of freedom, F = C – P + 2
F = 3 – 3 + 2
F = 2 (bivariant)

6. Determine the number of phases, components, and degrees of freedom available for the following systems:

(i)

Number of phases, P = 3 (2 solids; 1 gaseous)
Number of components, C = 2 (Na_2SO_4 & H_2O)

Number of degrees of freedom, F = C – P + 2
F = 2 – 3 + 2
F = 1 (univariant)

(ii)

Number of phases, P = 1 (all together constitute a single phase)
Number of components, C = 2 (any two)
F = C – P + 2
F = 2 – 1 + 2
F = 3 (trivariant)

(iii)

(a) When $P_{PCl_3(g)} = P_{Cl_2(g)}$, only one constituent is sufficient to express the system.

Number of phases, P = 1
Number of components, C = 1
Number of degrees of freedom, F = C – P + 2
F = 1 – 1 + 2
F = 2 (bivariant)

(b) When $P_{PCl_3(g)} \neq P_{Cl_2(g)}$, minimum of two constituents are needed to express the system.

Number of phases, P = 1
Number of components, C = 2
Number of degrees of freedom, F = C – P + 2
F = 2 – 1 + 2
F = 3 (trivariant)

7. Write the number of phases and components in the following heterogeneous system: $CuSO_4$ (s) + 5 H_2O (l) ↔ $CuSO_4$. 5 H_2O (s).

Number of phases, P = 3 (2 solids; 1 liquid)

Number of components, C = 2 ($CuSO_4$ & H_2O)

Number of degrees of freedom, F = C – P + 2

F = 2 – 3 + 2

F = 1 (univariant)

8. A system consists of benzene and water. What is the number of phases?

Number of phases, P = 2

Number of components, C = 2 (Benzene & water)

Number of degrees of freedom, F = 2 – 2 + 2

F = 2 – 2 + 2

F = 2 (bivariant)

9. Calculate the number of phases present in the following systems:

(i) ***$MgCO_3(s) \rightleftharpoons MgO(s) + CO_2\ (g)$***

(ii) ***Rhombic sulphur (s) $\rightleftharpoons$ Monoclinic sulphur (s)***

(iii) ***Solid ice $\rightleftharpoons$ Liquid water $\rightleftharpoons$ Water vapour***

(iv) ***An emulsion of oil in water***

(i) ***$MgCO_3(s) \rightleftharpoons MgO(s) + CO_2\ (g)$***

Number of phases, P = 3

Number of components, C = 2

Number of degrees of freedom,F = C – P + 2

F = 2 – 3 + 2

F = 1 (univariant)

(ii) ***Rhombic sulphur (s) $\rightleftharpoons$ Monoclinic sulphur (s)***

Number of phases, P = 2

Number of components, C = 1

Number of degrees of freedom,F = C – P + 2

F = 1– 2 + 2

F = 1 (univariant)

(iii) ***Solid ice*** $\rightleftharpoons$ ***Liquid water*** $\rightleftharpoons$ ***Water vapour***

Number of phases, $P = 3$

Number of components, $C = 1$

Number of degrees of freedom, $F = C - P + 2$

$F = 1 - 3 + 2$

$F = 0$ (invariant)

(iv) ***An emulsion of oil in water***

Number of phases, $P = 2$

Number of components, $C = 2$ (Benzene & water)

Number of degrees of freedom, $F = 2 - 2 + 2$

$F = 2 - 2 + 2$

$F = 2$ (bivariant)

10. 100 kg of a sample of argentiferous lead containing 0.5% Ag is melted and then allowed to cool. If eutectic contains 2.6% Ag, (1) what mass of eutectic will be formed and (2) what mass of lead will separate out?

Given: In 1 kg argentiferous lead, silver content is 0.5%; (i.e: 5 gm).

(or) In 100 kg argentiferous lead, silver content = 500 gm = 0.5 kg

In the given eutectic system, 2.6% is silver and hence 97.4% is lead.

Corresponding to 0.5 kg silver, the amount of lead (Pb) present in eutectic = $\frac{0.5 \times 97.4}{2.6} = 18.73\,\text{kg}$

(1) The mass of eutectic formed from 100 kg ore = 0.5 + 18.73

= 19.23 kg

(2) The mass of lead, which is separated out from 100 kg ore = $100 - 18.73$

= 81.27 kg

7. Introduction: Fuels

Fuels are major sources of energy for industries. They are classified mainly into two general classes' namely fossil fuels and nuclear fuels. Fossil fuels are those, which have been derived from fossil remains of plant and animal life. They are found in the earth's crust. All conventional fossil fuels whether solid, liquid or gaseous (coal, petroleum or Natural gas) contain basically carbon and/or hydrogen, which by combustion in presence of oxygen in the air release heat energy. This heat energy can be utilized for domestic and industrial purposes.

$$\text{Fuel} + O_2\ (\text{Air}) \longrightarrow \text{Products} + \text{Heat}$$

Classification of Fuels

Fuel is a substance, which on combustion produces large amount of heat that can be utilized economically for industrial and domestic purposes. Fuels may be divided into: (1) Primary or naturally occurring fuels and (2) Secondary or derived from primary fuels. Primary and secondary fuels may also be divided into three classes' namely solid, liquid and gaseous fuels (Table 3).

Table 3: Classification of fuels

S. No.	Examples	Solid fuels	Liquid fuels	Gaseous fuels
1.	Primary fuel (Natural).	Wood, Peat, Lignite, Anthracite.	Petroleum (or) Crude oil.	Natural Gas.
2.	Secondary fuel (Manufactured).	Semi coke, Coke, Petroleum coke.	Gasoline, Diesel, Kerosene.	Coal gas, Producer gas, Water gas.

Requirements of a good fuel

A good fuel should have the following characteristics:

- ✓ High calorific value.
- ✓ Moderate ignition temperature.
- ✓ Low moisture content.

- ✓ Low contents of non-combustible matters.
- ✓ Free from objectionable and harmful gases.
- ✓ Moderate velocity of combustion.
- ✓ Combustion should be controllable.
- ✓ Easy to transport and readily available at low cost.

Calorific values

Definition: Calorific value may be defined as "the amount of heat liberated by the complete combustion of a unit mass of the fuel".

The quantity of heat can be measured by the following units:

- ✓ Calorie (cal)
- ✓ Kilocalorie (kcal)
- ✓ British thermal units (BTU)
- ✓ Centigrade heat units (CHU)

i. Gross calorific value (GCV) (or) Higher calorific value

Gross calorific value is defined as "the total heat generated when a unit quantity of fuel is completely burnt and the products of combustion are cooled to room temperature".

For example, when a fuel containing hydrogen is burnt, it undergoes combustion and will be converted into steam. If the combustion product is cooled to room temperature, the steam gets condensed into water and the latent heat is evolved. Therefore the latent heat of condensation of steam so liberated is included in Gross calorific value.

ii. Net calorific value (NCV) (or) Lower calorific value

Net calorific value is defined as "the net heat produced when a unit quantity of fuel is completely burnt and the products of combustion are allowed to escape".

NCV = GCV – Latent Heat of Condensation of Steam Produced.

8. Determination of Calorific Values of Solid Fuels by Bomb Calorimeter

Principle: A known weight of the fuel is burnt completely and the quantity of heat liberated is absorbed in water and measured.

Description: A bomb calorimeter consists of the followings:

(i) *A stainless steel bomb:* It can withstand a pressure of about 100 atmospheres. It is provided with two electrodes and an oxygen inlet valve. One of the electrodes acts as support for the crucible. It is placed in copper calorimeter.

(ii) *A copper calorimeter:* The copper calorimeter contains a known weight of water. It has an arrangement for inserting a thermometer and stirrer. The calorimeter is surrounded by air jacket and water jacket to prevent the loss of heat.

(iii)*A stainless steel crucible:* It holds the weighed pellet of fuel sample. The crucible is fixed in such a way that the fuse wire touches the fuel sample.

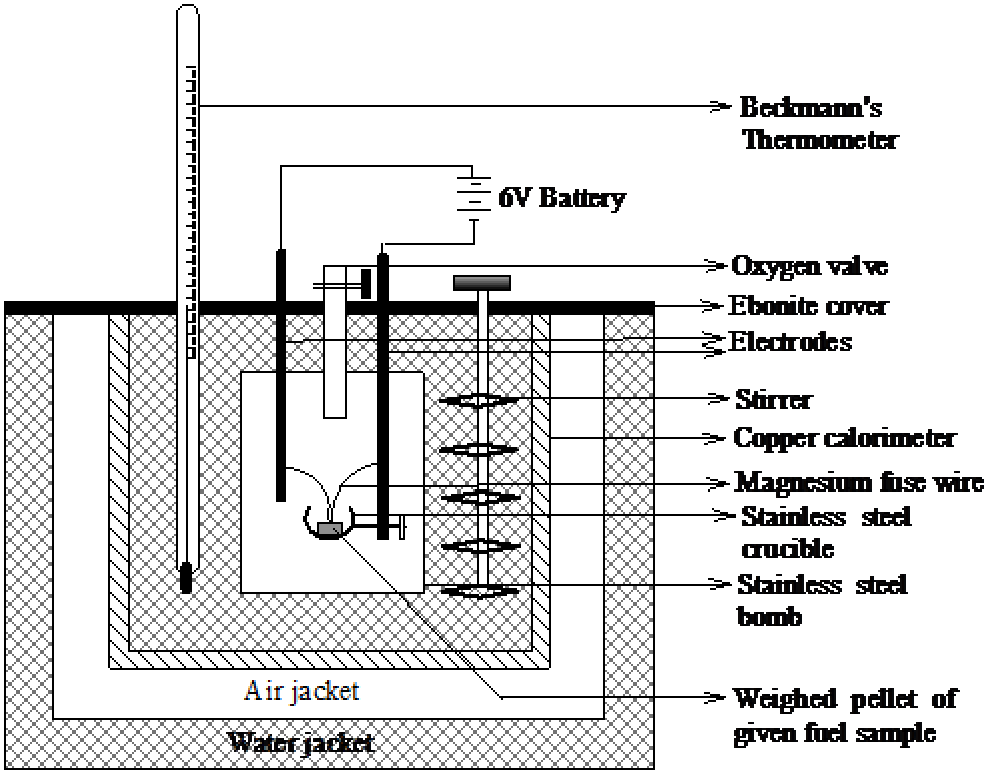


Fig 4: The bomb calorimeter

Working: A known quantity of fuel (m gm)is taken in the crucible. The bomb is charged with oxygen to a pressure of 30 atmospheres and the oxygen charging valve is closed tightly. Then the bomb is placed carefully in a known amount of water (W gm). The water in the calorimeter is stirred throughout the experiment and its initial temperature is noted (T_1ºC). Now the fuel is ignited by passing current through the fuse wire. The heat produced by burning is transferred into the water. The temperature is measured to an accuracy of 0.001°C by a Beckmann's thermometer till the maximum temperature (T_2ºC) is reached.

Calculations:

Mass of fuel = m gm

Mass of water in calorimeter = W g

Water equivalent of calorimeter = w g

Initial temperature of water = T_1°C

Final temperature of water = T_2°C

The water equivalent of the calorimeter is determined by burning a fuel of known calorific value (Example: Benzoic acid, CV = 26565 kcal/kg)

By heat balance, heat produced by the fuel due to combustion = Heat absorbed by water and calorimeter

If x is the calorific value of fuel, heat produced = $(x \times m)$ cal

Heat absorbed by water and calorimeter = $(W + w) \times (T_2 - T_1)$

$(x \times m) \equiv (W + w) \times (T_2 - T_1)$

$$x = \frac{(W + w) \times (T_2 - T_1)}{m} \text{ cal/g}$$

For calculating the more accurate calorific value of a fuel, the following corrections should be considered.

(i) Fuse wire correction (C_1): Since the fuse wire also gives additional heat on heating, it must be subtracted from the heat.

(ii) Cotton/Thread correction (C_2): If fuel is ignited with the help of a cotton or cotton thread, it will give extra heat and that must also be subtracted from the heat.

(iii) Acid correction (C_A): On combustion, the fuels having N and S atoms may produce nitric acid and sulphuric acid respectively. Formation of these acids are exothermic in nature, this additional heat must also be subtracted.

(iv) Cooling correction (T_C): The temperature difference $(T_2 - T_1)$ must be higher than what is actually observed in the calorific value determination. This is because, the process of cooling adds certain temperature differences and it is known as cooling correction. The cooling correction can be obtained by plotting time versus temperature. From the rate of cooling (difference of two temperature per minute, $dT°/min$) and the actual time taken (t), the cooling correction, $dT° \times t$ can be determined. This cooling correction must be added to the measured temperature rise.

By considering all the corrections, the actual calorific value of a fuel is calculated as follows:

$$\text{HCV, } x \equiv \frac{(W + w) \times (T_2 - T_1 + T_C) - (C_1 + C_2 + C_A)}{m} \text{ cal/g}$$

9. Manufacture of Synthetic Petrol By Fischer-Tropsch Method

The raw materials used in this process are hard coke and steam to produce water gas. i.e.: water gas is obtained by passing steam over red hot coke.

$$C + H_2O \xrightarrow{1200^{o}C} \underset{\text{Water Gas}}{CO + H_2}$$

The first step in this process is purification of water gas. To remove H_2S, the gas is passed through Fe_2O_3 and to remove organic sulphur compounds, the gas is again passed through a mixture of Fe_2O_3 and Na_2CO_3.

The purified gas is compressed to 5-25 atmospheres over a catalyst containing oxides of Th, Co and Mg on Kieselguhr at 250^0C (Fig. 5.5). The reaction products mainly contain straight chain paraffins and olefins.

$$nCO + (2n+1)H_2 \longrightarrow \underset{\text{n-Paraffins}}{C_nH_{2n+2}} + nH_2O$$

$$nCO + 2nH_2 \longrightarrow \underset{\text{Olefins}}{C_nH_{2n}} + nH_2O$$

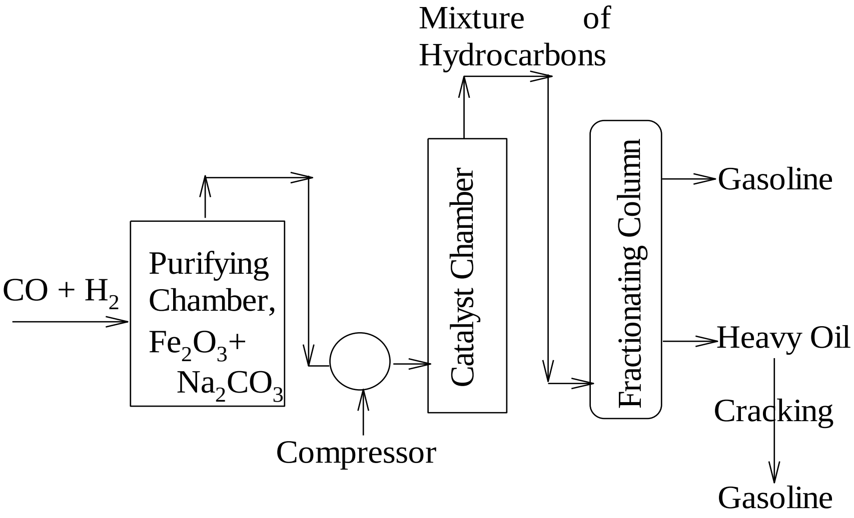


Fig 5: Fischer-Tropsch Process

Since the reactions are exothermic, the vapours leaving the vessel are condensed in the condenser to give petroleum. It is fractionally distilled to yield petrol and heavy oil. Heavy oil is used for cracking to get more amount of gasoline.

10. Knocking in Spark Ignition (SI) Engines

Causes of knocking in SI engines (petrol engines)

Knocking is a kind of mild explosion, which occurs in internal combustion (IC) engines due to sudden increase of pressure developed by spontaneous combustion of fuel–air mixture. Internal combustion engines (IC) are classified into spark ignition (SI) engine and compression ignition

(CI) engine. The spark ignition engine consumes petrol whereas compression ignition engine operates on diesel oil.

Petrol is one of the lightest fractions of petroleum. Chemically, it is a low boiling hydrocarbons in terms of carbon atoms C_5–C_8. Its boiling point range is 40 – 120°C. Its calorific value is 11, 250 *kcals*/*kg*. It is used as fuel for petrol (SI) engines.

⇒ Knocking in SI engine is due to pre-ignition or pre-mature ignition of fuels.

⇒ Knocking causes mechanical damage in cylinder; and reduction in power output.

Chemical structure and knocking in petrol engines

The knocking tendency in SI engines decreases with increase in the compactness of molecules, double bonds and cyclic structure.

⇒ *n*-Paraffins show poor knocking resistance. Their resistance to knock decreases with increase in the length of the hydrocarbon chain.

	n-Butane	→	*n*-Pentane	→	*n*-Hexane	→	*n*-Heptane
Octane Number:	90		60		30		0

⇒ Iso-paraffins have better knocking resistance than *n*-paraffin. Their resistance increase with increasing number of branches.

⇒ Olefins have better knocking resistance than *n*-paraffin and iso-paraffins.

⇒ Aromatic hydrocarbons such as benzene and toluene have highest anti-knock values.

In general, knocking tendency in SI engines decreases in the following order:

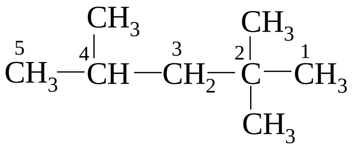
n-Paraffin → Iso-paraffins → Olefins → Naphthenes → Aromatics

⇒ It means that aromatics have highest antiknock value whereas *n*-alkanes have lowest antiknock value.

⇒ So the presence of maximum quantity of aromatics and minimum quantity of *n*-alkanes in petrol is desirable.

Octane rating of fuels (Measurement of knocking in SI engines)

Octane number expresses the knocking characteristics of petrol. *n*-Heptane (a constituent of petrol) knocks very badly, so its antiknock value has been arbitrarily given zero. On the other hand, iso-octane (also a constituent of petrol) gives very little knocking, so its anti-knock value has been arbitrarily given 100.



$CH_3-CH(CH_3)-CH_2-C(CH_3)_2-CH_3$

Iso-octane (2,2,4 trimethyl pentane)
(Octane Number = 100)

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

n-Heptane
(Octane Number = 0)

To measure octane number of a gasoline sample, binary mixtures of the two standard oils (iso-octane + *n*-heptane) are prepared and tested in a test standard engine.

% of iso-octane	**% of *n*-heptane**	**Octane Number**	**Amount of Knocking**
100	0	100	Nil
80	20	80	*A*
60	40	60	*B*
50	50	50	*C*
0	100	0	*D* (maximum)

If a gasoline sample produces same amount of knocking (*A*) as 80% iso-octane and 20% *n*-heptane, then the sample has an octane number of 80.

Definition of octane number: Octane number is defined as "percentage of iso-octane in iso-octane–n- heptane mixture, which matches the same knocking characteristics of gasoline mixture [iso-octane-*n*-heptane mixture of various proportions] when burnt in a standard test engine under standard conditions".

Improvement of antiknock value (or) Leaded petrol (or) Advantages of using tetra ethyl lead (TEL: The octane number of gasoline may be improved by adding about 1-3ml of ethyl fluid (60% Tetra ethyl lead + 29% Ethylene dibromide + 9% Ethylene chloride + 2% Red dye) to 1 gallon of petrol. Petrol containing TEL is known as leaded petrol.

Mechanism (prevention) of knocking (or) Action of TEL: TEL decomposes to form (i) lead metal particles (ii) ethyl free radicals. Lead particles act as oxidation centers and thereby making combustion homogeneous and uniform. Ethyl free radicals convert straight chain paraffins into iso-paraffin. Sometimes ethyl free radical combines with the free radicals of knocking process and terminates the chain growth.

Role of ethylene dibromide: Lead particles produced by TEL may deposit in spark plug of SI engines. To prevent this deposit, ethylene dibromide is added. It reacts with lead particles to form lead dibromide ($PbBr_2$) and goes out with exhaust gases.

Disadvantage of using TEL: TEL causes lead pollution and creates atmospheric pollution.

11. Knocking in Compression Ignition (CI) Engines

Causes of knocking in CI engines (diesel engines)

Diesel is one of the heavier fractions of petroleum. Chemically, it is a mixture of hydrocarbons in terms of carbon atoms C_{15}–C_{18}. Its boiling point range is 250 – 320°C. Its calorific value is 11,000 *kcals*/*kg*. It is used as fuel for diesel engines.

In a CI engine, air is alone compressed. This raises the cylinder temperature as high as 300°C. When the diesel oil is injected or sprayed, it ignites spontaneously and the combustion products expand and power stroke begins.

Sometimes, even after the compression stroke is over and even after the diesel oil is sprayed, burning may not start. So, more and more fuel is injected automatically and sudden ignition may occur and burn the whole of the oil. This delayed ignition results an uncontrolled, excessive combustion known as ‘diesel knock’. So in CI–engines, knocking is due to delayed ignition or ignition lag.

Chemical structure and knocking in diesel engines

In general, knocking tendency in CI engines increases in the following order.

n-Paraffin → Iso-paraffins → Olefins → Naphthenes → Aromatics

It means that n-paraffin have the highest antiknock value whereas aromatics have lowest antiknock value. So the presence of maximum quantity of *n*-paraffin and minimum quantity of aromatics in diesel is desirable. Therefore, an oil of high octane number will have a low cetane number and vice-versa. Consequently, petroleum crude will give petrol of high octane number and diesel of low cetane number

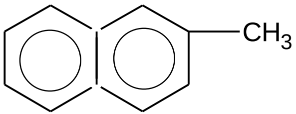
Cetane rating of fuels (Measurement of knocking in CI engines)

The quality of diesel oil is expressed in terms of cetane number. Based on cetane number, diesel oil is classified as (i) high speed diesel (cetane number 45 and above) (ii) medium speed diesel (cetane number 35 – 44) and (iii) low speed diesel (cetane number 25 – 34). Diesel oil having more cetane number will have the highest ignition temperature. It is possible to increase the cetane number (ignition temperature) by using certain additives like acetylene, alkyl nitrates, diethyl ether, nitronaphthalene.

Cetane number expresses the knocking characteristics of diesel. Cetane ($C_{16}H_{34}$) has a very short ignition delay and hence its cetane number is arbitrarily taken as 100. On the other hand, α–methyl naphthalene has very large ignition delay and hence its cetane number is arbitrarily taken as zero. To measure cetane number of a diesel sample, binary mixtures of the two standard oils (*n*-cetane + α-methyl naphthalene) are prepared and tested in a test standard engine.

$CH_3\text{-}(CH_2)_{14}\text{-}CH_3$

n-Cetane
(Cetane Number = 100)



α-Methyl naphthalene
(Cetane Number = 0)

Definition of cetane number: Cetane number is defined as "the percentage of cetane in cetane-α–methyl naphthalene mixture, which has the same ignition delay as the diesel oil when burnt in a standard test engine under standard conditions".

Improvement of antiknock value (or) Cetane number enhancers: Cetane number of diesel oil can be improved by adding additives called dopes. Examples: Ethyl Nitrate, Isoamyl Nitrate.

Table 4: Comparison of petrol and diesel as internal combustion engine fuel

S. No.	**Petrol**	**Diesel**
1.	Low boiling fraction of petroleum. (Boiling point range: 40-120°C)	High boiling fraction of petroleum. (Boiling point range: 320-400°C)
2.	Chemical composition range (C_5-C_8).	Chemical composition range (C_{15}-C_{18}).
3.	Fuel for SI engine.	Fuel for CI engine.
4.	Knocks due to premature ignition.	Knocks due to ignition delay.
5.	Knocking tendency measured in octane rating.	Knocking tendency measured in cetane rating.
6.	Anti-knocking is improved through addition of Tetra Ethyl Lead.	Anti-knocking is improved by doping with isoamyl nitrate.
7.	Lower thermal efficiency.	Higher thermal efficiency.
8.	Less consumption.	More consumption.

12. Introduction: Nanomaterials

Nanochemistry is a branch of nanoscience which deals with synthesis and characterisation of materials at nanoscale. They find applications from nanoelectronics to nanomedicine. Nanometer is so small that if you imagine ten hydrogen atoms placed in a line touching each other, it will measure one nanometer. A bacterial cell measures a few hundred nanometers (200 nm) across and a human hair measures about 50,000nm across. The smallest things seeable with the unaided human eye are 10,000nm across. With only reduction in size and no change in substance, the characteristics such as electrical conductivity, colour, melting point, strength, we usually consider as constant for a given material can all change. Nanotechnology is the manipulation of individual molecules or groups of atoms to make useful materials and devices. Nanotechnology can create a computer laptop screen that has the thickness and weight of a piece of paper, micro devices to make toxic waste inert, nanodevices to perform surgery or to detect cancer cells inside the human blood stream etc.

Nanomaterials Terminology

- **Nano**: The literal meaning of nano is “dwarf” an abnormal short person. In scientific language, nano is “billionth” on some unit scale.

- **Nanometer:** It is a billionth of a meter.

$$1nm = \frac{1}{1{,}000{,}000{,}000}\, m = 10^{-9}\, m$$

- **Nanotechnology:** Nanotechnology refers to the manipulation or self assembly of atoms or molecules to create nanodevices with new and different properties.

- **Nanochemistry:** Nanochemistry is a branch of nanoscience which deals with synthesis and characterization of materials at nanoscale. They find applications from nanoelectronics to nanomedicine.

- **Nanomaterials:** Materials which possess an average size of less than 100 nm at least in one coordinate (dimension) are called nanomaterials or nanostructured materials.

- **Nanoparticles:** Particles or powders with grain size (diameter) less than 100 nm are called nanoparticles.

- **Nanoclusters:** Aggregate of atoms or molecules in nanoscale dimension (1–10 nm) is known as nanoclusters. Individual atoms/molecules can form clusters.

- **Nanorods:** Nanorods are one dimensional cylindrical solid with an aspect ratio (length/diameter) of less than 20 with a diameter ranging from 10 – 100 nm.

- **Nanowires:** Nanowires are one dimensional cylindrical solid with an aspect ratio (length/diameter) of greater than 20 with a diameter ranging from 10 – 100 nm.

- **Nanotube:** When a graphite sheet is folded into a cylinder or tube, it is considered as carbon nanotube.

- **Bucky ball (or) Fullerene, C_{60}:** The Bucky ball (or) Fullerene, C_{60} (short term of buck Minster Fullerene) is a single, stable molecule containing 60 carbon atoms arranged in a soccer ball. It is of about 1nm in diameter. Every Bucky ball surface contains 12 pentagons and 20 hexagons. The pentagon’s permit the sheet of carbon atoms to curve into the shape of a sphere. The Fullerene family is often identified by the letter C followed by the number of carbon atoms. For example, C_{60}, C_{70}, C_{80} *etc.,* out of which C_{60} is more stable and spherical in shape.

- **Dendrimers:** Dendrimers are nanomolecules with regular branching structures. The number of branching determines the size of the dendrimer which can be controlled.

- **Quantum dots:** Quantum dots (QDs) are small devices that contain a tiny droplet of free electrons. QDs are colloidal semiconductor nanocrystals ranging from 2 to 10 nm in diameter.

Examples: The most commonly used QDs are cadmium selenide (CdSe), cadmium telluride (CdTe), indium phosphide (InP), and indium arsenide (InAs).

❖ **Bottom-up nanofabrication:** The process of making nanostructures starting with small components such as atoms or molecules is called bottom-up approach.

Examples: Chemical vapour deposition; Sol-gel process; Chemical reduction.

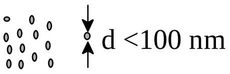
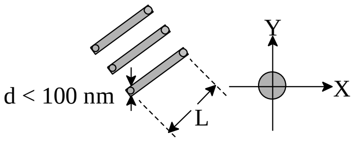
❖ **Top-down nanofabrication:** The process of making nanostructures starting with larger structures and taking parts away is called top-down approach.

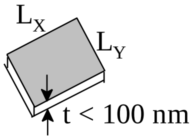
Examples: Lithography; Ball Milling; Epitaxy.

Classification of Nanomaterials on the Basis Dimensions

Nanomaterials can be classified as: zero dimensional (0-D), one dimensional (1-D), and two dimensional (2-D) objects. This classification is based on the number of dimensions, which are not confined to the nanoscale range (1–100 nm).

Table 5: Classification of nanomaterials on the basis of dimensions

S. No.	**Reduction in size in different coordinates**	**Nanoobjects**	**Examples**
1.	0-Dimensional nanomaterials: All dimensions *x*, *y*, *z* are at nanoscale.		Nanoparticles; Quantum dots.
2.	1-Dimensional nanomaterials: Two dimensions *x*, *y* are at nanoscale and other dimension, length (*L*) is not at nanoscale.		Nanotubes; Nanorods; Nanowires.

3.	2-Dimensional nanomaterials: One dimension, thickness, t is at nanoscale and other two dimensions, Lengths along L_X and L_Y are not at nanoscale.		Nanofilms; Nanocoatings.

Classification of Nanoparticles on the Basis Chemical Composition

The currently existing nanoparticles are classified by their chemical composition, namely:

1. Metallic nanoparticles (Au, Ag, Cu, Fe, Zn etc.).
2. Nanoparticles of metal and non-metal oxides (FeO, VO, AlO, ZnO etc.).
3. Semiconductor nanoparticles (ZnS, CdSe, ZnSe, CdS, etc.).
4. Carbon nanoparticles (fullerenes, nanotubes, graphene, diamond).
5. Nanoparticles of organically modified layered silicates and alumosilicates (nanoclays of different compositions).
6. Nanoparticles of organic dendrite polymers (dendrimers of different composition).
7. Quantum dots.

Distinction between Molecules, Nanomaterials and Bulk Materials

Table 6: Differences between Molecules, Nanomaterials and Bulk Materials

S. No.	**Property**	**Molecules**	**Nanomaterials**	**Bulk Materials**
1.	Size	Exhibit few Angstrons (Å)	Exhibit 1 – 100 nm at least in one dimension	Exhibit more than Microns (μ)
2.	Number of constituents	Consist of more than one atom.	Made up of one to several thousand	Consist of infinite number

			depends upon their size.	of atoms and/or molecules.
3.	Electronic structure	Confined.	Confined.	Continuous.
4.	Geometric structure	Well defined and predictable.	Well defined and predictable.	Depends upon crystal structure.
5.	Tools for characterisat-ion	SEM; TEM.	SEM; TEM.	SEM; X-ray diffraction etc. depends upon the properties of bulk.
6.	Examples	O_2; C_2H_2;KCl.	Fullerene; Carbon nanotubes.	Bulk copper; gold.

13. Size Dependent Properties of Nanomaterials

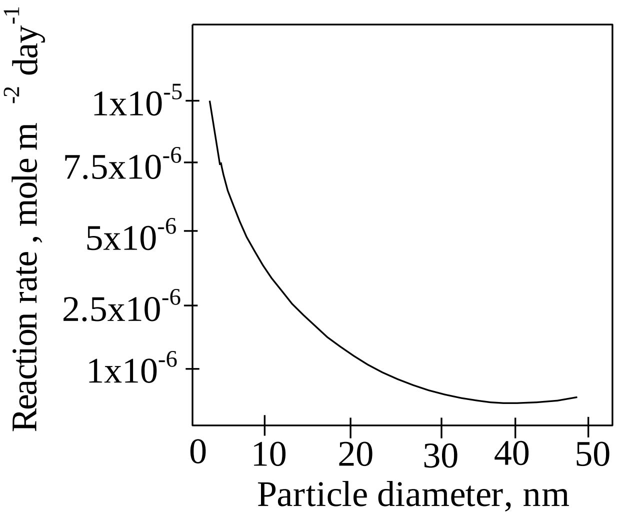
The various properties, which get tremendously altered due to the size reduction in at least one dimension are:

✓ Chemical properties: Reactivity; Catalysis.
✓ Thermal property: Melting point temperature.
✓ Electronic properties: Electrical conduction.
✓ Optical properties: Absorption and scattering of light.
✓ Magnetic properties: Magnetization.

i. Chemical properties

Size reduction in bulk materials leads surface to volume effects. It has been observed that the surface area to volume ratio increases with decrease of particle size diameter. Therefore size reduction in Nanomaterials leads to more number of surface atoms with enhanced surface area. This effect leads more reactivity and catalytic activity of materials in nanoform in turn increases the reaction rate and efficiency of various chemical reactions.

Examples: Au and Ag in bulk form are chemically inert. But they become good catalyst in nanoform.

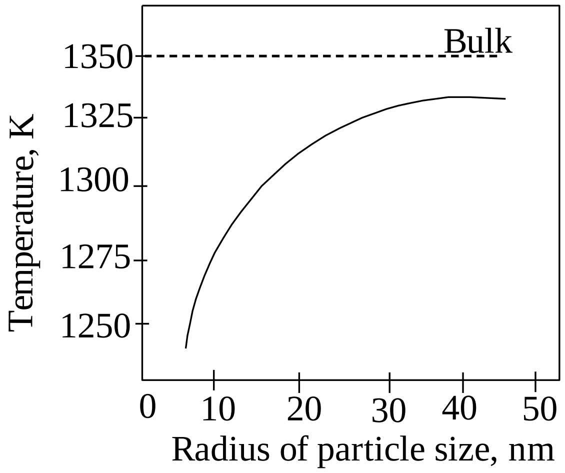


ii. Thermal properties

The melting point of bulk material is directly related with the bond strength. In bulk materials all the atoms are compactly packed and eletrovalently bonded and hence they exhibit higher melting points.

In Nanomaterials, surface atoms are not bonded in direction normal to surface plane and hence surface atoms will have more freedom to move. Hence the melting point of Nanomaterials is size dependent and it decreases with decrease of particle size diameter.

Examples: Bi (in bulk form: 660K): Bi (6nm: 500K); Bi (4nm: 480K) and Bi (2nm: 400K).



iii. Electronic properties

In bulk materials, conduction of electron is delocalized (i.e: the electrons can move freely in all directions). When the scale is reduced to nanoscale, quantum confinement dominates. Due to electron confinement, the energy bands are replaced by discrete energy states of electrons, which make the conducting materials to behave like semiconductors or insulators.

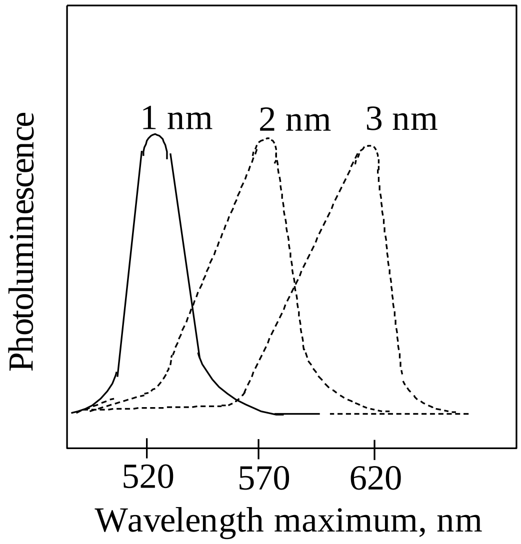
For 0-D nanomaterials, all the dimensions are at nanoscale and hence electrons are confined in 3-D space. Therefore no delocalization occurs. For 1-D nanomaterials, electron confinement occurs in 2-D space and electron delocalization occurs along the axis of Nanowires / Nanotubes / Nanorods.

Examples: Si and Ge are well known semiconductors in single crystal bulk form. But in nanoform, due to electron confinement, they do not show semiconducting properties.

iv. Optical properties

When a beam of visible light falls on certain substances, they absorb light radiations and get excited. In order to come back to their original state, they emit energy in the form of light radiations. This phenomenon is known as photoluminescence.

Because of quantum confinement, size reduction in Nanoparticles shifts the emission of light towards shorter wavelength (Blue shift).



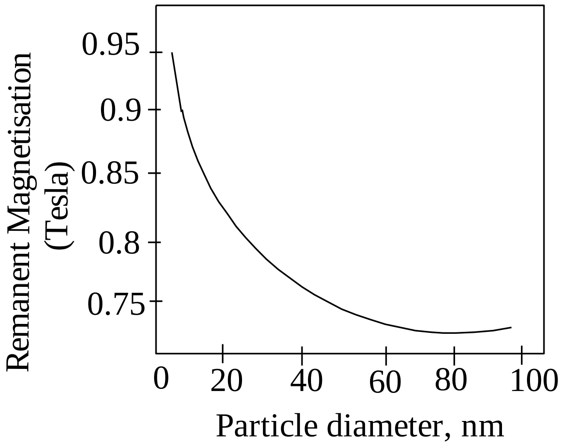
Examples:

CdS (Bulk) + hγ → CdS* (Excited state)
CdS* (Excited) → CdS (Ground state) + Energy as red light
CdS* (6nm) (Excited) → CdS (6nm) (Ground state) + Energy as orange light
CdS* (4nm) (Excited) → CdS (4nm) (Ground state) + Energy as yellow light
CdS* (2nm) (Excited) → CdS (6nm) (Ground state) + Energy as blue/white light

v. Magnetic properties

The size of magnetic nanoparticles influences the value magnetization. The figure 5.4 illustrates the effect of particle size on the saturation magnetization of zinc ferrite.

The magnetization increases significantly below a grain size of 20nm. Hence, by decreasing the particle size of a granular magnetic material it is possible to improve the quality of magnets fabricated from it.



14. Synthesis of Gold Nanoparticles by Chemical Reduction Method

Gold nanoparticles exhibit various sizes ranging from 1 nm to 8 μm. They exhibit different shapes such as spherical, sub-octahedral, octahedral, decahedral, multiple twined, irregular shape, tetrahedral, nanotriangles, nanoprisms, hexagonal platelets and nanorods.

1. Synthesis of gold nanoparticles by citrate reduction process

The reduction of a tetrachloroauric acid ($HAuCl_4$) has been initiated by trisodium citrate ($Na_3C_6H_5O_7$) by injecting specified amount of preheated trisodium citrate solution to a boiled gold solution in a double walled reactor, which is heated by a bath thermostat to control the water bath temperature. The mixture liquid was vigorously stirred by Teflon coated magnetic bars.

The color of the solution changed gradually from transparent light yellow, dark black, and finally to the characteristic wine-red, which indicated the formation of gold nanoparticles.

$$HAuCl_4 + Na_3C_6H_5O_7 \rightarrow Au^o\ (NP) + HCl + [C_6H_5O_7]^{3-} + 3NaCl$$

2. Synthesis of gold nanoparticles by $NaBH_4$ reduction process

In the $NaBH_4$ reduction process, $NaBH_4$ is used as reduction agent, the citrate acts as a stabilizing agent and tetrachloroauric acid ($HAuCl_4$) as the precursor.

When the mixture liquid is vigorously stirred by Teflon coated magnetic bars, the color of the mixture solution immediately changes into pink. Continue stirring the solution for another 15 minutes finally turn the solution wine-red, which indicated the formation of gold nanoparticles.

The reaction rate in this single aqueous system was controlled by the reaction conditions. Different reaction parameters (e.g. reaction temperature, reactant concentration, addition rate for $NaBH_4$) can be optimised to get gold nanoparticles with uniform size distribution.

$$HAuCl_4 + 4\ NaBH_4 \rightarrow Au^o\ (NP) + 5/2\ H_2 + 2B_2H_6 + 4NaCl$$

3. Synthesis of Silver Nanoparticles by Chemical Reduction Method

In chemical reduction method, silver nitrate ($AgNO_3$) is used as a starting material while trisodium citrate ($C_6H_5O_7Na_3$) and ascorbic acid ($C_6H_8O_6$) are used as the reducing agent and surfactant respectively.

During the synthesis process, the reductant ($C_6H_5O_7Na_3$) directly reduced Ag^+ to generate metallic Ag atoms. The coalescence of atoms led to the formation of metal clusters, which are normally stabilized by surfactants.

In this method, it is believed that the ascorbic acid acts as surfactant and adsorbs onto the surface of the Ag atoms, and thus prevented the nanoparticles from agglomerating.

Indication of the formation of silver nanoparticles can be observed by change in the solution colour. During this process, the solution becomes greenish before it stabilised. Later it changes into light yellow colour indicates the growth of the AgNPs.

$$4Ag^+ + C_6H_5O_7Na_3 + 2H_2O \rightarrow 4Ag^o + C_6H_5O_7H_3 + 3Na^+ + H^+ + O_2$$

Applications of Nanomaterials in Medicine

1. Drug discovery and Drug delivery

⇒ CNTs can be widely used as drug carriers for drug delivery, as they can easily adapt themselves and enter the nuclei of the cell. The most important use of CNT in drug delivery is that they can be equipped with miniaturized video cameras, which help in colonscopic and endoscopic procedures.

⇒ Dendrimers carrying different materials on their branches can do several things at one time, such as drug delivery recognizing diseased cells, diagnosing disease states including cell death.

⇒ The pharmaceutical applications of dendrimers include nonsteroidal anti-inflammatory formulations, antimicrobial and antiviral drugs, anticancer agents, pro-drugs, and screening agents for high-throughput drug discovery.

2. Surgery

⇒ Gold coated nanoparticles can be used as flesh welders. In this technique, a greenish liquid containing gold-coated nanoshells is dribbled along the seam. An infrared laser is traced along the seam, causing the two sides to weld together using laser. This could solve the difficulties and blood leaks caused when a surgeon tries to re-stitch the arteries that have been cut during organ transplant.

3. Cancer diagnosis and cancer therapy

⇒ Silver nanoparticles can be used as a promising candidate in chemotherapy, photosensitizers and/or radiosensitizers, biodiagnostics, bioimaging, transfection vectors, and antiviral agents; some of these have been entered into clinic trials.

⇒ Gold nanoparticles have become an interesting research area in cancer diagnosis, imaging and especially treatment. The gold nanoparticles that are located at a site of cancer cells can be irradiated with infrared to heat them up and destroy the nearby cancer cells.

⇒ Cadmium selenide nano particles in the form of quantum dots are used in detection of cancer tumors because when exposed to ultraviolet light, they glow. The surgeon injects these quantum dots into cancer tumors and can see the glowing tumor, thus the tumor can easily be removed.

⇒ In a recent study, antibody-conjugated magnetic poly-(D, L-lactide-co-glycolide) (PLGA) nanoparticles with doxorubicin (DOX) were synthesized for the simultaneous targeted detection and treatment of breast cancer. DOX and magnetic nanoparticles were incorporated into PLGA nanoparticles, with DOX serving as an anticancer drug and Fe_2O_3 nanoparticles used as an imaging agent.

4. Tissue engineering applications.

⇒ Nanoparticles such as graphene, carbon nanotubes, molybdenum disulfide and tungsten disulfide are being used as reinforcing agents to fabricate mechanically strong biodegradable polymeric nanocomposites for bone tissue engineering applications.

5. Dental diagnostics

⇒ The metallic nanoparticles as iron nanoparticles single or conjugated with polysaccarides, and gold nanoparticles single or conjugated with antibodies or peptides for specific cellular biomarkers were used in dental diagnostic. They have recently been investigated as optical or magnetical contrasting agents in medical imaging techniques for early detection of oral cancer, and for identifying and differentiating infectious pathogens.

6. Cell labeling and bio-imaging

⇒ A class of nanoparticles known as ‘quantum dots’, which can emit different types of light depending on their size, have wide applications in biotechnology for cell labelling and bioimaging, including imaging in cancer studies.

⇒ The enhanced magnetic properties of iron (III) oxide nanoparticles make them suitable for use as contrast agents in magnetic resonance imaging (MRI).

⇒ Fluorescent CdSe/ZnS quantum dots could produce a higher contrast image, when used in combination with MRI (magnetic resonance imaging), and are used for tumor targeting, tumor angiogenesis imaging, and metastasis cell tracking.

QUESTIONS

PART-A

1. State phase rule.
2. State mathematical statement of phase rule.
3. Define the term phase.
4. Define the term components.
5. Define the term degrees of freedom.
6. What is meant by phase diagram? State its significance.
7. What are the limitations of phase rule?
8. What are the advantages of phase rule?
9. What is meta-stable equilibrium?
10. What is triple point?
11. State reduced phase rule.
12. State the conditions under which two substances can form a simple eutectic.
13. Eutectic is a mixture and not a compound. Explain.
14. Mention the differences among melting point, triple point and eutectic point.
15. What are fuels? Give one example each for primary and secondary solid, liquid and gaseous fuels.
16. What are the requirements of an ideal fuel?
17. Distinguish between GCV and NCV.
18. Why is net calorific value? Less than gross calorific value? When are they equal?
19. What is synthetic petrol?
20. What is meant by knocking in IC engines?
21. Distinguish between knocking in SI engine and CI engine.
22. Define octane number of petrol. How can it be improved?
23. What is leaded petrol?
24. Define octane number.

25. What are the advantages and disadvantages of leaded petrol?
26. Why is ethylene dibromide added, when TEL is used as antiknock?
27. How does TEL improve the octane number of petrol?
28. Select the compound which possesses highest octane number and cetane number out of n-heptane, n-hexadecane, n-octane and isooctane.
29. Arrange n-octane, naphthalene, isooctane in increasing order of their knocking tendency.
30. Which is having higher octane number, natural gasoline or cracked gasoline?
31. Define cetane number of diesel. How can it be improved?
32. Differentiate petrol and diesel as IC engine fuels.
33. Define nanochemistry.
34. Define nanotechnology.
35. What are nanomaterials?
36. How are nanomaterials classified on the basis of dimensions?
37. How are nanomaterials classified on the basis of chemical composition?
38. Define the terms: top-down nanofabrication and bottom-up nanofabrication.
39. Mention any four methods for the synthesis of nanomaterials.
40. What is Bucky ball?
41. What are dendrimers?
42. Define quantum dots.
43. Differentiate between molecules, nanomaterials and bulk materials.
44. Mention the various properties which get altered by size reduction.
45. What are nanoparticles?
46. Mention some of the applications of nanoparticles.

PART-B

1. State phase rule and explain the terms involved in it with examples.
2. Draw and explain the labeled phase diagram of water system.
3. What is thermal analysis? How is it used for constructing a eutectic phase diagram?
4. Discuss in detail the lead silver system. Explain Pattison’s process.
5. Describe bomb calorimeter with neat diagram for the determination of calorific value of a solid fuel.
6. What is synthetic petrol? Discuss the method of preparation of synthetic petrol by Fischer-Tropsch process.

7. What is meant by knocking in petrol engines? How is knocking prevented?
8. Discuss the size dependent properties of nanomaterials.
9. What are the properties that change from its bulk form to nano size form? Explain with each example.
10. Discuss the synthesis of gold nanoparticlessnanoparticles by chemical reduction method.
11. Discuss the synthesis of silver nanoparticlessnanoparticles by chemical reduction method.
12. Explain any six applications of nanomaterials in medicine.

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